Towards Octupolar Ruthenium Acetylide Complexes for Nonlinear Optical Materials

Synthesis, Characterization, and Linear and Nonlinear Optical Properties

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A Thesis Submitted For The Degree Of Doctor Of Philosophy
Of The Australian National University

Revised Version
Canberra, February 2012
Declaration

The work described in this Thesis is my own unless stated otherwise. I have not submitted this material for any other degree or qualification. Where contributions have been made by others, their efforts have been acknowledged and referenced.

This copy of my Thesis is a modified version of the original version of the Thesis that had been submitted for revision. Suggestions made by the reviewers are listed in the section Reviewers' Comments (page III ff). Where appropriate or required, modifications (including statements addressing suggestions, corrections dealing with spelling or grammar mistakes, and rewriting of unclear or incorrect sections of this Thesis) were implemented in the main body of the text.

Torsten Schwich

Canberra, 19/02/2012
Reviewers' Comments (Erratum)

This section lists the suggestions given by and comments made by the international reviewers, who kindly provided their professional opinion to judge the quality of the present Thesis. Each comment is cited, followed (where required) by a statement from the author of this Thesis, addressing the reviewer's comment. All the changes listed below were implemented in the revised version of this Thesis (page numbers may differ from the ones given below). For the original version, necessary changes and page numbers where they should occur, are given here, and the reader should be aware of the changes while reading the main body of this work.

"Depending on your point of view, possibly a few pages of a more general introduction that covers e.g. the fundamental concepts of nonlinear materials such as the essence of nonlinear optics, response of an optical medium to an intense electromagnetic field, polarization, nonlinear susceptibility, different optical effects between e.g. first and second order nonlinear optical materials and octupolar compounds may have been considered first."

"The introduction is a formidable collection of complexes and results of NLO studies, but does lack an element of overview or insight into the nature of how the chemical variations being presented influence the observed properties."

Author's comment: The introduction is part of a review article that has been written together with Patrick J. West, Marie P. Cifuentes, Marek Samoc and Mark G. Humphrey. The reference list includes citations pointing to excellent reviews and book articles that provide background information on a more general level. In this work, focus was deliberately placed on the latest progress in the area of NLO active complexes and coordination compounds.

"In general, the sections of the Thesis devoted to the synthetic work, structure determinations and descriptions of the NMR assignments are a little less generous in citations of relevant, related work from others. Comparisons of the new work reported here with synthetic strategies, spectroscopic assignments and structural data in the literature therefore somewhat lacking."
"If a small hole was to be picked in the choice of methods and methodologies, one could point to the absence of detailed discussion of the spectroelectrochemical work. A link between the chemical and electronic structure of the molecules studied and the observed NLO response would have been welcomed with a view to establishing structure-property relationships beyond the empirical observations clearly noted in the Thesis, but this may be beyond the state-of-the-art in the area and current computational resources."

"Other aspects that could have merited further discussion include the fluorescence data, with the varying degrees of solvatochromism in the absorption and emission spectra pointing to differences in the polarization of the ground and excited states."

"Perhaps the most notable omission from the discussion relates to the comparison of numerical $\sigma_2$ values. Whilst the graphical material makes it clear that substantial errors can be associated with the values obtained, the text does not carry a matching indication of the precision of the quantity being discussed, or more dangerously, compared."

**Author’s comment:** As referred to below in more detail, the error margins were included in-text in the revised version of this Thesis.

"A final point would be to note that the use of the first person should be avoided in a Thesis or publication document."

**Author’s comment:** There seems to be a trend away from this. Whereas publications in research articles still follow the neutral third-person line, in theses it is acceptable to use the first person where it seems appropriate. In this work, the first person was used where, e.g., responsibility for certain outcomes (positive or negative) was to be indicated. I may not have been able to obtain a certain product, but that does not mean that it was not possible in general. This aspect of the writing style used in the Thesis has been discussed with and used in agreement with my direct supervisor.

"The large difference in the $^{31}\text{P}\{$$^1\text{H}$\} NMR spectra of complex 2-48 in C$_6$D$_6$ and in CDCl$_3$ may suggest a trace of Ru$^\text{III}$ was present in the CDCl$_3$. (Perhaps a small amount of CCl$_2$ generated that oxidizes the Ru?)"
Author's comment: The presence of a paramagnetic species might of course be responsible for the observations described herein, but we have not looked into this aspect in great detail. However, the fact that a sample that does not give a $^{31}$P{$^1$H} NMR signal (or only a signal with poor s/n) in chloroform-D shows a strong and narrow peak after removing the solvent and redissolving the residue in benzene-D6 would mean that the Ru$^{III}$ is reduced back to Ru$^{II}$ after just changing the solvent, which does not seem very reasonable either.

“Apart from the dendrimers, where the quality of the signals decreased drastically, the assignments were competently and unambiguously performed. Could the signal quality of the dendrimers be due to adventitious trace amounts of Ru$^{III}$ or some other metal ion e.g. Cu$^{II}$? Also could the detection of the $^{11}$B NMR resonance in the boron compounds be influenced by the same metal ions or by a fast spin-lattice relaxation time for the quadrupolar $^{11}$B?”

“p XVIII: 3-87”* not *literatur* but *literature”

“page 47: 532 nm (1.39)... (seems to be some formatting issue here)”

Author's comment: Replaced with *532 nm (Figure 1.39).*

“page 49: ...magnitude), but the inverse...”

Author's comment: Comma added after the bracket.

“page 61, line 8 from bottom: are a class of”

“page 87: would the use of Me$_3$SiC≡CC$_6$H$_4$C≡CH (available from sequential coupling of iodo-bromo benzene with HC≡CCMe$_2$OH and HC≡C$i$SiMe$_3$ followed by removal of acetone by treatment with NaOH in toluene) have simplified the synthetic schemes? The cost analysis is critically dependent on the choice of synthetic method, and the use of embedded convergency within an otherwise divergent synthetic route can still be of benefit.”

Author's comment: This question might refer to the section at page 90 (page 88 in the revised version of this Thesis). McDonagh used an approach similar to the one suggested by the reviewer, which did not afford an improvement with regards
to the overall yield. The method suggested by the reviewer here involves the same number of steps as suggested in Scheme 2.1 (5 steps for both synthetic approaches). However, for more extended molecules, using a repeat unit of a certain length would be favourable over the step-by-step extension (i.e. by a strictly divergent method) shown herein.

“Scheme 2.1: Consistency "Bu₄NF vs. NBu₄F vs. TBAF here and throughout the Thesis.”

Author’s comment: Inconsistent expression has been replaced with NBu₄F.

“page 95, first line of paragraph 2: from neopentyl chloride”

“page 104: Isn’t optimization of the reaction conditions a critical element to be factored into the σ₂,C parameter for 2-53 and 2-54? (c.f. Figures 2.63, 2.64)”

Author’s comment: This is true. However, severe time constraints towards the end of this work prevented me from repeating some of the later reactions, which includes the synthesis of the complexes 2-53 and 2-54. The optimization of reaction conditions is a time-consuming process, and in this particular case I had to focus on the characterization of the complexes for the purpose of collecting crucial NLO data. In general, the reviewer’s comment is absolutely justified, and especially towards the end of a synthetic scheme, the improvements of yields by just 10% can result in considerable cost savings (i.e. costs can drop by much more than 10%).

“page 106: Complex 2-14 is not a bis-acetylide”

Author’s comment: The phrase was changed to affording the corresponding mono-acetylide complex 2-14.

“page 107: two equivalent equivalent reactions”

Author’s comment: The second, superfluous equivalent has been removed.

“page 108: the assignment of H and C{H} NMR resonances in dppe containing complexes has been undertaken for a large range of octahedral and pseudooctahedral complexes. See, for example, J. Organomet. Chem. 2009, 694, 2358 and related RuX(dppe)Cp* systems.”
Author's comment: The paragraph was rephrased as follows: "Great effort has been put into the assignment of $^{13}$C{$^{1}$H} and $^{1}$H NMR signals in the complexes synthesized herein. In the present work, the assignment of $^{13}$C{$^{1}$H} NMR signals was accomplished by looking at short (and, in fact, the shortest possible) dppe ligated ruthenium mono- and bis(phenylacetylide) complexes and then extending the systems out in small steps. This was done independent of similar literature reports,[1] leading to a slightly different interpretation of some of the spectra, which was supported by a combination of different techniques. In particular for the longer linear complexes and also for the octupolar species, the determination of signal identities was accomplished by using gradient heteronuclear multiple bond correlation (gHMBC) and gradient heteronuclear single quantum coherence (gHSQC) experiments. The comparison of spectra resulting from different species with only slightly different structural properties also allowed important conclusions. This was particularly important for the assignment of $^{13}$C{$^{1}$H} NMR signals in the aromatic region of the spectra (ca. 125–140 ppm). Attention was also focused on the spectral appearance of carbon atoms from the dppe ligands, including the observed splitting patterns, which will be discussed in the following paragraphs."

"page 143: as a general point, it would have been informative to see comparison of the structural data with those of other related complexes."

Author's comment: The section has been rewritten, and three structurally related complexes were included. The corresponding table with bond lengths and angles has been extended accordingly.

"page 155: take care in expressing energy differences in wavelength (which is inversely related to energy). The energy difference between 1000 and 870 nm (1494 cm$^{-1}$) is considerably lower than between 400 and 270 nm (12 037 cm$^{-1}$)."

Author's comment: In order to enable readers who are used to dealing with nm and those who are more familiar with wavenumbers to read this work equally easily, energies/frequencies were always given both in nm and in cm$^{-1}$. For consistency, this was maintained where energy differences had to be considered, despite the problem that arises from this and which was pointed out by the reviewer.
"Page 160: The values for $\sigma_2$ should be quoted in the text with indications of the errors/precision of the value. The graphical material suggest that the errors in some of these values can be substantial."

**Author’s comment:** For the complexes synthesized and measured herein, the values obtained from Z-scan experiments range between 5 and 15%, although error margins of 20–30% were observed in some cases. In-text error margins were added to the revised version of this Thesis.

"Page 161: $\gamma$-spectrum of 2-52 ($\gamma_{\text{Re}}$ or $\gamma_{\text{Im}}$?). Where is the maximum in Figure 2.51 said to be near 17 300 cm$^{-1}$? The $\gamma_{\text{Im}}$ data look to be a plateau in this region, and $\gamma_{\text{Re}}$ data is too low in precision to draw much of a conclusion."

**Author’s comment:** The corresponding section was changed to the following: "Whereas the high-energy region of the $\gamma_{\text{Im}}$-spectrum of 2-52 does not show a local maximum, the more extended analogue 2-53 shows a local maximum at around 17 300 cm$^{-1}$ (580 nm), although it is subtle, almost appearing as a plateau within the error margins."

"Page 165: What error margins for measurements by UV-Vis spectroscopy might causing issue? 500 M$^{-1}$ cm$^{-1}$ is easily distinguished from 700 M$^{-1}$ cm$^{-1}$ on even the lowest grade teaching instrument. Is this a comment on the difficulty of making samples of known concentration? Seems a little out of place to me."

**Author’s comment:** This note refers to the error that is sometimes observed when working with solutions made from 2–3 mg of material (which is not unusual, particularly at late stages of synthetic schemes, where conservative usage of material is preferred). Repeat measurements carried out by different researchers were seen to deliver values with quite significant error margins. Errors of 20% would give $\epsilon = 700 \pm 140$ M$^{-1}$ cm$^{-1}$, i.e. a range of 560–840 M$^{-1}$ cm$^{-1}$ would be covered. 560 M$^{-1}$ cm$^{-1}$ is quite close to the threshold already, and for $\epsilon = 600 \pm 120$ M$^{-1}$ cm$^{-1}$ the lower-level value would be 480 M$^{-1}$ cm$^{-1}$, the threshold would not be exceeded. Hence, the author simply intended to draw the reader’s attention to difficulties related to a set threshold.

"Page 169: Figure 2.58 should also carry error bars (c.f. Figure 2.57)"

VIII
Author's comment: The error bars have been added in the revised version of this Thesis (see page 170 of the revised version). The corresponding diagram is shown below.

"page 170: Taking the error bars into consideration there is no 'rising trend' in the uncorrected data series $\mathbf{2-52} \rightarrow (\mathbf{2-53}) \rightarrow \mathbf{2-54}$. On the basis of data in Figure 2.59 all that can be said is that there are three identifiable groups: [2-9, 2-10], [2-14, 2-18] and [2-52, 2-53, 2-54]."

"page 170: comparison of $\sigma_{2,M}$ data in Figure 2.58 suggests $\mathbf{2-14}$ (4 GM mol g$^{-1}$) is smaller than $\mathbf{2-54}$ (6 GM mol g$^{-1}$): on what bass are these data said to be 'more or less equal'? (i.e. is there an implicit acknowledgment of the errors in the text without an explicit indication of these in the Figures and numerical data?)"

Author's comment: I absolutely agree with the reviewer here; the statement is clearly not correct. The corresponding section was changed to the following: Considering the molecular weight of the NLO-active material leads to a change in the overall trend. The uncorrected values show a rising trend on increasing the bridge-length $[(\mathbf{2-14} \rightarrow \mathbf{2-52} \rightarrow \mathbf{2-54}; \text{taking error margins into account}, \sigma_2 \text{ of } \mathbf{2-54} \text{ does not exceed that of } \mathbf{2-52})]$. For MW-corrected values this trend is less pronounced, which is particularly clear when $\sigma_{2,M}$ of $\mathbf{2-54}$ is compared to $\sigma_{2,M}$ of $\mathbf{2-52}; \mathbf{2-52}$ dominates over $\mathbf{2-54}$, which demonstrates that the NLO efficiency does not increase with increasing molecular weight.

"page 171: $N_{\alpha,N}$ is a complex concept: the 'extended conjugation' through the N atom depends on the pitch of the three aryl groups relative to the plane
containing the N centre and each other. The degree of overlap has a dependence on the morphology – and triaryl amines are always propeller shaped. It is probably overly simplistic to count all of the $\pi$-electron in the 'active' conjugated portion of N-cored molecules. Lambert has recently published a lovely series of papers dealing with excited state structures of triaryl borane systems with closely related symmetry and inverted electronic structure which is well worth a read and consideration of the effect of symmetry on the excited states of these complexes. See *Chem. Eur. J.* **2006**, *12*, 2358. For discussion on the structure and effect of confirmation on electronic structure and energy of optical transition between the ‘inner’ and ‘outer’ aryl rings in conjugated triaryl amines see *J. Mater. Chem.* **2005**, *15*, 2304; *Chem. Eur. J.* **2004**, *10*, 83; *J. Mater. Chem.* **2004**, *14*, 2516 and references therein.

**Author's comment:** Indeed, this is a difficult topic, which I realized shortly after looking into this type of scaling for NLO values. This problem was the basis of considerable discussion within our research group and beyond. The current approach (which, I agree, is simplistic) is an alternative to more accurate, and hence drastically more complicated, considerations (as indicated above by the reviewer). Such an approach of higher accuracy includes at least modeling of the complexes and compounds and/or requires solid-state structures. This was simply not possible within the scope of this work. Clearly, there is still a lot of room for improvements and refinements of this scaling factor. However, one should keep an eye on the applicability of the scaling factors, which might become a problem when more sophisticated methods are involved to derive the scaling factors. All in all I appreciate the reviewer’s suggestions and comments, which represent a contribution to an ongoing discussion.

“page 172: Table ??”

**Author's comment:** A link had been misplaced here. It should read Table 2.2.

“page 173: Is it really appropriate to list costs, including labor, to the nearest $ (e.g. $1751 vs. 1750 or even $1800)? We are again back to an errors in quantities type argument”

**Author's comment:** Of course, for a discussion, rounding to the nearest $100 would be appropriate. In this table (Table 2.2), the numbers were kept as they
had been obtained from the tables (see Appendix in Chapter 5.4) since they were used in further calculations.

"page 175: Table 2.3 needs re-setting to align first row of data. The errors given here should be included in the text when discussing quantities such as $\sigma_{2,\text{max}}$ in the body of the Thesis."

**Author's comment:** The table has been modified accordingly in the revised version of this Thesis, and error margins were included in in-text discussions.

"page 179: another example of the error issues: absolute value of 35000 (±??) GM"

**Author's comment:** Error margins were included in the revised version of this Thesis.

"page 184: give reference to the DENZO software package"

**Author's comment:** P. T. Beurskens, G. Beurskens, W. P. Bosman, R. S. de Gelder, S. Garcia-Granda, R. O. Gould, J. M. M. Smits, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, 1996. Reference was added to the revised version of this Thesis.

"page 188: provide a reference to all literature compounds and note misplaced parentheses in ($i$-Pr)$_3$SiC≡CC$_6$H$_4$-4-C≡CC$_6$H$_4$-4-Br."

**Author's comment:** Missing reference for the synthesis of the reported compound ($i$-Pr)$_3$SiC≡CC$_6$H$_4$-4-C≡CC$_6$H$_4$-4-Br (T. Weil, E. Reuther, C. Beer, K. Muellen, *Chem.--Eur. J.* **2004**, *10*, 1398) was added to the revised version of this Thesis.

"page 191: specify quantities of iodine and THF for the concentrated solutions"

**Author's comment:** This is not possible. The general method was to make sure that an excess of iodine (i.e. more mmol of iodine than mmol of n-BuLi) was dissolved in a minimum amount of THF. This concentrated solution was then added to the reaction mixture continuously until the indicated irreversible color change to deep-red was observed. Whatever amount of the iodine solution was
left after that was not added to the reaction mixture, but how much was left in any given reaction has never been determined.

"page 216: give ESI MS data for 2-14."

**Author's comment:** ESI MS: 1738 ([M - Cl]^{2+}, 2), 1647.4 (8), 1272.3 (43), 1147.2 ([M - 3 Cl]^{3+}, 95), 897.2 (100). Data were added to the revised version of this Thesis.

"page 259: triple negatives should be avoided: *I was not able ... neither ... nor..."**

**Author's comment:** The sentence was changed to "I was not able to detect a^{11}B NMR resonance for the mono(phenylethynyl)-bridged starting material (Et_{3}SiC≡CC_{6}Me_{4}-4-)_{3}B (3-24^{*}) or the synthesized bis(phenylethynyl)-bridged analogue (Me_{3}SiC≡C-4-C_{6}Me_{4}C≡C-4-C_{6}H_{4})_{3}B (3-27)."

"page 270: 3-3 shows a band at 26500 cm^{-1} not 16500 cm^{-1}.

**Author's comment:** The revised version of this Thesis was modified accordingly.

"page 271: the onset of linear absorption seems to be about the same for both sets of compounds in Figures 3.19 and 3.20."

**Author's comment:** That is correct. The phrase "Apart from that the spectra are similar, and the para-nitrophenylacetylide-capped dendrimer shows the expected additional band at the low-energy end of the spectrum that is accompanied by a red-shift of the onset of linear absorption from 20000 cm^{-1} to just below 16000 cm^{-1}" only refers to the different onsets of the nitro-substituted species *vs.* the complexes without a nitro group. It was not meant to refer to onsets of the first-generation dendrimers being different from those of the zero-generation dendrimers (which they are not).

"p 247: Second last line; not *used to assign of signals* but *used to assign signals*"

"page 283: two ... bands grow in ..."
“page 291: punctuation has gone awry in sentence beginning *What that have in common ...*”

**Author’s comment:** The sentence has been changed to *What they have in common is the presence of a π-delocalized system, and they all have a nitrogen atom as the central atom (‘core’).*

“page 295: ... calculated “by hand” ...”

“page 302: The cost analysis is an interesting approach, but one that is a common issue for the translation between development chemistry and process chemistry in the pharmaceutical industry. The cost of a compound prepared by a development chemistry approach is immaterial. The process chemists job is then to devise a new method to the same target using economically feasible synthetic methods. It is unlikely that the routes and schemes used here (which are essentially the development chemistry route) would be employed in the commercial production of these compounds.”

**Author’s comment:** That is true. And accurate numbers would only be accessible once an industrial plant is set up for the sole purpose of mass-producing any of the complexes or compounds, because then all the costs, including necessary labor, disposal of residues etc. would appear in a business plan (or something similar), which would account for everything that is causing expenses. These numbers, however, are not accessible now, so this naive model was used instead. Importantly, it was consistently applied to all the compounds or complexes that were compared to each other, thus giving a rough idea. Again, this approach still required significant time and effort. Hence, the „number-of-steps-yield combination” would probably deliver comparable results but would be much easier to handle.

“page 319: give literature citations to all compounds. Note the different notation here for i-Pr₃Si vs. that on page 188”

**Author’s comment:** The following literature sources were added: S. Leininger, P. J. Stang, *Organometallics* 1998, 17, 3981 (1,3,5-(HC≡C)₃C₆H₃), T. Weil, E. Reuther, C. Beer, K. Muellen, *Chem.-Eur. J.* 2004, 10, 1398 ((i-Pr)₃SiC≡CC₆H₄-4-C≡CC₆H₄-4-Br), G. T. Dalton, M. P. Cifuentes, L. A. Watson, S. Petrie, R. Stranger,
Acknowledgments

For his guidance and advice, his unlimited support and help, and for the encouragement that I have experienced all the way through my PhD, I would like to thank the chair of my supervisory panel, Prof. Mark Humphrey. I am indebted to an excellent supervisor for allowing me to be part of his group, for being responsible for the progress that I've made, and for bringing me to this current point of my professional career.

I thank the members of my supervisory panel, Dr. Marie Cifuentes, Prof. Marek Samoc, and Prof. Rob Stranger, for their support and professional advice.

The introduction to this Thesis (Chapter 1) is part of a literature review written by Prof. Mark G. Humphrey, Patrick J. West, Torsten Schwich, Prof. Marek Samoc, and Dr. Marie P. Cifuentes.

I acknowledge the administrative support that the Research School of Chemistry has provided, already before I had even started my work at the ANU, and which continues to the present day.

During my time at the ANU, I experienced a wide range of invaluable technical and professional support, so I would like to express my acknowledgments to Mrs. Anitha Jeyasingham, Mr. Gordon Lockhard and Mr. John Allen for providing the large number of mass spectrometry data; to Mrs. Sasha Melnitchenko and Mrs. Vicky Withers for providing all the microanalyses; to Ms. Peta Simmonds and Mr. Chris Blake for their support in all aspects of NMR spectroscopy and for the time they have spent training me on various instruments; to Ms. Elizabeth Owen for training on the fluorescence spectrometer; to Mr. Tony Herlt for providing HPLC training; to Mr. Richard Terrett for his help with the volume calculations; to Dr. Thitima Urathamakulto (University of Wollongong) for running high-molecular weight MS samples; to Mr. Paul Gugger for outstanding technical and synthetic support in the chemical laboratory.

Special thanks to Dr. Anthony Willis for training me on the X-ray diffractometer throughout my PhD, and for crucial support and advice; without his support, a large portion of this work and related projects would not have been possible. It has been a great pleasure.
NLO measurements were carried out by Prof. Marek Samoc (Laser Physics Centre, RSPhysSE, ANU; and Institute of Physical and theoretical Chemistry, Wroclaw University of Technology) and Dr. Timothy Corkery (Laser Physics Centre, RSPhysSE, ANU), and Ms. Malgorzata Wielgus, Ms. Marcin Nyk, Ms. Katarzyna Matczyszyn, Ms. Joanna Olesiak-Banska, Mr. Janusz Szeremeta, Mr. Leszek Mazur, and Ms. Marta Godel (Institute of Physical and theoretical Chemistry, Wroclaw University of Technology). I thank you very much for your efforts, which enabled me to present a great part of the results found in this work.

I was very lucky to have been part of co-operations and joint projects, so I would like to thank the research group of Prof. Masahiko Hara (Flucto-Order Functions Research Team, RIKEN, Tokyo, Japan), in particular Dr. Isoshiba Takashi, for providing extensive training and advice with regards to electroabsorption studies; Prof. Todd Marder (Durham University) for providing crucial starting materials for the boryl-substituted complexes presented herein; Dr. Rachel Roberts (ANU) for the joint work on the nitrogen-cored complexes, for which the organic precursor was kindly provided by Prof. Paul Low (Durham University); Mr. Patrick West (ANU) for the joint work on mixed-metal ruthenium-osmium acetylidy complexes (Section 3.2.4), for the work on our joint review article (Chapter 1), and for all his support, from which I benefited greatly.

I had the great pleasure to conduct teaching activities at ANU, and I would like to thank Assoc. Prof. Geoff Salem, Dr. Mark Ellison, Mr. Vance Lawrence, Mr. Stephan Lee, and Ms. Bozena Belzowski for their help and guidance in the teaching laboratories.

I am very grateful for the input that I received through very interesting and enlightening discussions with members across all research groups in the RSC, and for all the ideas that evolved from this.

There are many people who have provided helping hands, good advice and, most importantly, the feeling of being welcome and part of a team. Therefore, I would like to express my special thanks to past and present group members Dr. Rachel Roberts, Dr. Luca Rigamonti, Dr. Timothy Corkery, Dr. Katy Green, Dr. Mike Randles, Mr. Patrick West, Dr. Nicolas Gauthier, Dr. Peter Simpson, Mr. Paul Gugger, Dr. Sanjay Chavan, Mr. Bandar Babgi, Mr. Adam Barlow, Mr. Vivek Gupta, Mr. Mahbod Morshed, Mr. Mark Jennaway, Mrs. Fazira
Ilyana, Ms. Aisyah Shah, Mr. Guillaume Grelaud, Mr. Jun Hong Fu, Ms. Hua Jian Zhao, Ms. Xin Wei Yang, Ms. Erandi Kulasekera, Mr. Najib Hanuk, Mr. Alan Criddle, Ms. Jennifer Lee, Mr. Samuel Drouet, Ms. Lily Dixon, Ms. Florianne Malvolti, and Mr. Igondjo Ke-Raan. It has been, and continues to be, a great pleasure and a lot of fun to work with each and everyone of you.

Foremost, I thank my wonderful family for the love and support that I've had from them. I am very grateful that I knew you on my side through this. Which leaves me with thanking my extraordinary wife, who has endured all this for so long. Your strength and patience are incredible. Thank you!
Abstract

When nonlinear optical (NLO) effects were first observed experimentally in the early 1960s, the door to a new field of research was opened. Over the last 50 years, this area has expanded rapidly, supported by applications and devices that are based on nonlinear effects. The search for small, and yet fast and highly efficient devices for, e.g., data processing, data storage, or logic gates, is ongoing. Materials with nonlinear optical properties, and in particular organometallic complexes and coordination compounds, have been found to be strong candidates in this area for a number of reasons. An overview of the results that have been published by research groups in this field over the last decade is given in the opening Chapter.

Understanding the highly complex physical processes of nonlinear optics, and maximizing these effects to make practical use of them, is a challenge for theoreticians, physicists and chemists. The overlap of these fields enables us to develop models to derive strategies towards building efficient NLO materials.

The focus of the present work is on two aspects of ruthenium acetylide complexes incorporating π-conjugated systems. The first part considers the effects on NLO properties, resulting from lengthening the π-delocalized system in unbranched octupolar (star-shaped) ruthenium acetylide complexes. Acetylide complexes of bis(bidentate)-ligated RuII have proven to provide desired physical and optical properties; the star-shaped design of the complexes allows access to mono-disperse macromolecular entities that combine large π-conjugated systems, while incorporating the desired metal centers. In this part of the work, a number of systematically varied octupolar ruthenium acetylide complexes were synthesized and characterized. Their optical and physical properties are discussed, and their nonlinear optical properties were explored by frequency-dependent Z-scan measurements. A variety of new NLO scaling factors are suggested and were applied to NLO data, and the applicability of the new NLO scaling factors was explored. Linear, oligo(phenylethynyl)-bridged ruthenium acetylide complex analogues of the star-shaped complexes were also synthesized, in order to establish the different NLO properties of linear (dipolar) vs. star-shaped (octupolar) arrangements.

The second part of this work presents a group of systematically varied mono-disperse, branched ruthenium acetylide complexes (dendrimers). The main in-
terest was the variation of the core unit. Six first-generation organometallic dendrimers with nitrogen, boron, and phenyl cores were synthesized and characterized. The NLO properties of two nitrogen-cored zero-generation dendrimers and an analogous nitrogen-cored first-generation dendrimer were explored; comparison to analogous organic zero-, first- and second-generation dendrimers revealed a drastic enhancement of the NLO properties on incorporation of the metal centers. A number of star-shaped and dendritic mixed-metal osmium-ruthenium acetylide complexes were also synthesized.
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Abbreviations and Symbols

$\alpha$ Linear polarizability

$\alpha^{(2)}$ Nonlinear absorption coefficient

$\beta$ first hyperpolarizability

$\gamma$ Second hyperpolarizability

$\gamma_{im}$ Imaginary part of the second hyperpolarizability

$\gamma_{Re}$ Real part of the second hyperpolarizability

$\kappa$ Ratio of $\sigma_{ex}$ to $\sigma_0$

$\lambda$ Wavelength

$\nu(X-Y)$ X-Y bond stretching frequency

$\phi$ Diameter

$\sigma$ Two-photon absorption cross-section

$\sigma_0$ Ground state two-photon absorption cross-section

$\sigma_{2,CLab}$ Two-photon absorption cross-section divided by the cost to synthesize 1 mmol of the NLO material, including cost for labor.

$\sigma_{2,C}$ Two-photon absorption cross-section divided by the cost to synthesize 1 mmol of the NLO material

$\sigma_{2,NeN}$ Two-photon absorption cross-section divided by the number of effective $\pi$-electrons, considering Ru as disruptor and N as part of the conjugation path
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma_{2,\text{NeRu}}$</td>
<td>Two-photon absorption cross-section divided by the number of effective $\pi$-electrons, considering Ru and N as part of the conjugation path</td>
</tr>
<tr>
<td>$\sigma_{2,\text{Ne}}$</td>
<td>Two-photon absorption cross-section divided by the number of effective $\pi$-electrons, considering N and Ru as disruptors</td>
</tr>
<tr>
<td>$\sigma_{\text{ex}}$</td>
<td>Excited state two-photon absorption cross-section</td>
</tr>
<tr>
<td>$\tilde{\nu}$</td>
<td>Wavenumber</td>
</tr>
<tr>
<td>$\tilde{\nu}_\gamma$</td>
<td>Wavenumber corresponding to a certain $\gamma$-value in a $\gamma$-spectrum</td>
</tr>
<tr>
<td>$\tilde{\nu}_e$</td>
<td>Wavenumber corresponding to a certain extinction coefficient in a linear absorption spectrum</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>Extinction coefficient</td>
</tr>
<tr>
<td>2-EH</td>
<td>2-ethylhexyl</td>
</tr>
<tr>
<td>2PA</td>
<td>Two-photon absorption</td>
</tr>
<tr>
<td>3PA</td>
<td>Three-photon absorption</td>
</tr>
<tr>
<td>$&lt;\text{Ru}&gt;$</td>
<td>$trans$-Ru(dppm)$_2$</td>
</tr>
<tr>
<td>[Ru]</td>
<td>$trans$-Ru(dppe)$_2$</td>
</tr>
<tr>
<td>Ac</td>
<td>Acetyl</td>
</tr>
<tr>
<td>ANU</td>
<td>The Australian National University</td>
</tr>
<tr>
<td>AUD</td>
<td>Australian Dollar</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic voltametry</td>
</tr>
<tr>
<td>d</td>
<td>Doublet</td>
</tr>
<tr>
<td>DASP</td>
<td>4-(4-N,N-dimethylaminostyryl)-1-methylpyridinium</td>
</tr>
<tr>
<td>dba</td>
<td>Dibenzylideneacetone</td>
</tr>
<tr>
<td>DCM</td>
<td>Dichloromethane</td>
</tr>
</tbody>
</table>
dd  Doublet of doublets
DFG  Difference frequency generation
DFT  Density functional theory
DFWM  Degenerate four-wave mixing
DMF  N,N-dimethylformamide
dmso  Dimethylsulfoxide
dppe  1,2-bis(diphenylphosphino)ethane
dppm  bis(diphenylphosphino)methane
dppp  1,3-bis(diphenylphosphino)propane
dt  Doublet of triplets
EA  Electroabsorption
EFISH  Electric field-induced second-harmonic generation
EFISHG  Electric field-induced second-harmonic generation
ESI  Electrospray ionization
esu  Electrostatic standard units
FT  Fourier-transform
gHMBC  Gradient heteronuclear multiple bond correlation
gHSQC  Gradient heteronuclear single quantum coherence
GM  Göppert-Meyer
HOMO  Highest occupied molecular orbital
HRS  Hyper-Rayleigh scattering
ILCT  Intraligand charge transfer
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>LMCT</td>
<td>Ligand-to-metal charge transfer</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>m</td>
<td>medium</td>
</tr>
<tr>
<td>m_c</td>
<td>Centered multiplet</td>
</tr>
<tr>
<td>MeCN</td>
<td>Acetonitrile</td>
</tr>
<tr>
<td>MeOH</td>
<td>Methanol</td>
</tr>
<tr>
<td>mes</td>
<td>Mesitylene</td>
</tr>
<tr>
<td>MHz</td>
<td>Megahertz</td>
</tr>
<tr>
<td>MLCT</td>
<td>Metal-to-ligand charge transfer</td>
</tr>
<tr>
<td>MS</td>
<td>Mass spectrometry</td>
</tr>
<tr>
<td>MW</td>
<td>Molecular weight</td>
</tr>
<tr>
<td>N_{e,N}</td>
<td>Number of effective $\pi$-electrons, calculated using Drobizhev's approach (i.e. N atoms are considered part of the conjugated system)</td>
</tr>
<tr>
<td>N_{e,Ru}</td>
<td>Number of effective $\pi$-electrons, calculated using Drobizhev's approach (i.e. N atoms are considered part of the conjugated system) and also considering Ru atoms as part of the conjugation path</td>
</tr>
<tr>
<td>N_e</td>
<td>Number of effective $\pi$-electrons, calculated using Kuzyk's approach (i.e. N atoms are considered disruptors)</td>
</tr>
<tr>
<td>NIR</td>
<td>Near-infrared</td>
</tr>
<tr>
<td>NLO</td>
<td>Nonlinear optical</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance</td>
</tr>
<tr>
<td>PDB</td>
<td>(Brookhaven) Protein database</td>
</tr>
<tr>
<td>XXX</td>
<td></td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Definition</td>
</tr>
<tr>
<td>--------------</td>
<td>---------------------------------</td>
</tr>
<tr>
<td>PDT</td>
<td>Photodynamic therapy</td>
</tr>
<tr>
<td>pent</td>
<td>Pentet</td>
</tr>
<tr>
<td>ppm</td>
<td>parts per million</td>
</tr>
<tr>
<td>quart</td>
<td>Quartet</td>
</tr>
<tr>
<td>$r_{vdW}$</td>
<td>van der Waals radius</td>
</tr>
<tr>
<td>RT</td>
<td>Room temperature</td>
</tr>
<tr>
<td>s</td>
<td>Singlet</td>
</tr>
<tr>
<td>s/n</td>
<td>Signal-to-noise ratio</td>
</tr>
<tr>
<td>SEC</td>
<td>Size exclusion chromatography</td>
</tr>
<tr>
<td>SES</td>
<td>Solvent excluding surface</td>
</tr>
<tr>
<td>SFG</td>
<td>Sum frequency generation</td>
</tr>
<tr>
<td>SHG</td>
<td>Second-harmonic generation</td>
</tr>
<tr>
<td>t</td>
<td>Triplet</td>
</tr>
<tr>
<td>TBAF</td>
<td>Tetra-$n$-butylammonium fluoride</td>
</tr>
<tr>
<td>TBAPF$_6$</td>
<td>Tetra-$n$-butylammonium hexafluorophosphate</td>
</tr>
<tr>
<td>td</td>
<td>Triplet of doublets</td>
</tr>
<tr>
<td>TD-DFT</td>
<td>Time-dependent density functional theory</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>THG</td>
<td>Third-harmonic generation</td>
</tr>
<tr>
<td>TIPS</td>
<td>Triisopropylsilyl</td>
</tr>
<tr>
<td>TLC</td>
<td>Thin-layer chromatography</td>
</tr>
<tr>
<td>TMS</td>
<td>Trimethylsilyl</td>
</tr>
</tbody>
</table>
TOF          Time-of-flight
TPEF         Two-photon-excited fluorescence
V_m          Molecular volume
V Ses         Molecular volume as defined by the solvent excluding surface
vdW          van der Waals
Vis          Visible
w            weak
WLC          White-light continuum
R_f          Retention factor

3-87         New compound synthesized by the author; compound number 87, first appearing in Chapter 3

3-87^a        Compound number 87, first appearing in Chapter 3; compound or complex has not been synthesized by the author and is published in the literature

3-87^b        Compound number 87, first appearing in Chapter 3; synthesized by the author following published literature procedures.

3-87^b        Compound number 87 of a new compound or complex, first appearing in Chapter 3; compound or complex has been synthesized by the author and a co-operation partner to equal parts.
1 Coordination Compounds and Organometallic Complexes for Nonlinear Optics

This review has been jointly written by Prof. Mark G. Humphrey, Patrick J. West, Torsten Schwich, Prof. Marek Samoc, and Dr. Marie P. Cifuentes.

1.1 Introduction

The technological revolution of the second half of the twentieth century was to a large degree stimulated by progress in semiconductor physics and the resulting advent of solid-state microelectronics. Following these advances, the invention of the laser and developments in fiber optics helped to launch the globally connected information society of the twenty-first century. Both electronics and the science and technology of manipulating photons, termed photonics, depend heavily on the availability of suitable materials for fabricating electronic and photonic devices. Currently, single crystalline silicon is the material of choice for most electronic devices, although the search remains for alternatives needed for further miniaturization of devices or (for example) for very inexpensive (throwaway) devices. There is no single material that can fulfill all or even most of the functions needed for manipulating photons in the form of light beams. This review is concerned with coordination and organometallic molecular materials that may be useful in photonics in specific ways, due to the presence of so-called nonlinear optical (NLO) properties;\(^2,3\) it includes a brief explanation of 'NLO effects' and 'NLO properties', and a summary of the most popular techniques for the determination of such properties. Although computational approaches to
nonlinearities have attracted attention recently (primarily using sum-over-states methods implemented within time-dependent density functional theory, and both finite-field and sum-over-states perturbation calculations within the intermediate neglect of differential overlap framework),\textsuperscript{[4–6]} the results of such calculations necessitate confirmation by comparison to experimental data, and will not be considered further in this review.

The coverage here follows the previous approach and is organized by ligand rather than metal. This review extends earlier reviews in CCC2\textsuperscript{[7]} and COMC3,\textsuperscript{[8]} which surveyed the field to mid-2002 (coordination complexes) and through 2004 (organometallic complexes); there has been a further review of the quadratic and cubic NLO properties of organotransition metal complexes through 2005.\textsuperscript{[9]} More selective surveys of coordination complexes (through 2003)\textsuperscript{[10]}, NLO properties of organometallics and coordination complexes (2002–mid 2005),\textsuperscript{[11]} and quadratic NLO properties of organometallic and coordination complexes\textsuperscript{[12]} and cubic NLO properties of organometallics\textsuperscript{[13]} (through 2008) have also appeared. Where specific complex types have been reviewed in the interim, this is highlighted, and the present coverage continues from these more recent reviews.

1.2 Theory

Light is an electromagnetic wave and the propagation of light and its interaction with matter involve the electrical and magnetic field components of that wave, both of which oscillate at the same frequency $\omega$. In most cases, however, it is sufficient to consider only the electrical component $F(t, \vec{r})$, which, for a monochromatic wave, may be written as shown in Equation 1.1:

$$F(t, \vec{r}) = F_\omega \exp \left[ i \left( \omega t - \vec{k} \cdot \vec{r} \right) \right] + c.c. \quad (1.1)$$

where $\vec{k}$ is the wavevector. As light propagates in a medium, the electric field interacts with matter, forcing the electrons in matter to oscillate at the light frequency. This interaction may lead to various effects including refraction, scattering, and absorption of light beams. At low light intensities, the oscillating electrical polarization induced in matter by a light beam is proportional to the
amplitude of the electrical field $F_\omega$. However, intense laser beams, and especially pulses of light from pulsed lasers, may involve electrical field strengths that approach in magnitude the internal electrical fields corresponding to the interactions of electrons with atomic nuclei. Under such circumstances, the proportionality of the electrical response to $F_\omega$ is no longer assured, and nonlinear optical effects may arise. For optical media composed of molecules, it is useful to consider the response of a molecule to the electrical field as an expansion of the Cartesian components of its electrical dipole moment in a power series (Equation 1.2).

$$\mu_i (F) = \mu_{0,i} + \alpha_{ij} F_j + \beta_{ijk} F_j F_k + \gamma_{ijkl} F_j F_k F_l + \ldots$$  \hspace{1cm} (1.2)

$\alpha$, $\beta$, and $\gamma$ are the linear polarizability and the first and second hyperpolarizabilities, also termed the second-order and third-order polarizabilities, respectively. The field components $F_i$ refer to the local field inside the medium. To appreciate the meaning of the polarizabilities, we note first that they are tensors of consecutively increasing rank (the above equation is written using Einstein’s convention of summing over repeated indices), and thus the effects depend on the direction of the electric field vector in relation to the directions of the molecular axes. In addition to that, however, one needs to account for the fact that the electric field is given by Equation 1.1, or, more generally, by a combination of such terms with various values of $\omega$, $\vec{k}$ and $F_\omega$. By substituting the sums of such terms into Equation 1.2, one can verify that the presence of the quadratic term (the $'\beta$ term') leads to the appearance of dipole oscillations at new frequencies that are sums and differences of the input frequencies (sum and difference frequency generation, SFG and DFG). When there is only a single frequency in the input, the nonlinear response includes a term oscillating at $2\omega$ (second harmonic generation, SHG) as well as a time-independent term. In a similar way, the cubic $'\gamma$ term' is capable of mixing three different components of the input field, or generating the third harmonic of a single input frequency (THG). An important term in the oscillation of the molecular dipole is that having the same frequency as the input field, but arising from the combination of three same-frequency input components. The introduction of time-varying fields into Equation 1.2 necessitates that one accounts for the possible lag between the field oscillation and the response of the electrons in the molecule. Such a lag,
or a phase shift between the two oscillations, is treated by considering Fourier components of the input field and of the response, and defining all polarizabilities as complex quantities exhibiting frequency dispersion. This is relatively simple in the case of $\alpha$ which should be treated as a complex quantity $\alpha(\omega)$, but becomes more complicated for $\beta$ which may depend on two different input frequencies, and $\gamma$ which may depend on three frequencies. The traditional notation for these two quantities is $\beta(-\omega_3; \omega_1, \omega_2)$ and $\gamma(-\omega_4; \omega_1, \omega_2, \omega_3)$, respectively, where the first of the arguments is the output frequency which is equal to the sum of the input frequencies. For example, the quadratic polarizability responsible for SHG is denoted as $\beta(-2\omega; \omega, \omega)$, while the cubic polarizability responsible for a degenerate cubic response is $\gamma(-\omega; \omega, -\omega, \omega)$. The latter quantity is of considerable interest because its real part contributes to the technologically important effect of nonlinear refraction, the dependence of the refractive index of a medium on the light intensity, while its imaginary part contributes to the very useful effect of nonlinear absorption.[14,15] The nonlinear absorption of molecules is usually quantified by presenting it in the form of the nonlinear absorption cross-section. When nonlinear absorption corresponds to the simultaneous absorption of two photons of the same energy, this quantity is called the two-photon absorption cross-section, $\sigma_2$, and is most often given in Göppert-Mayer units where $1\text{GM} = 10^{-50}\text{cm}^4\text{s}$. From a practical point of view, the microscopic properties of molecules forming a photonic material must be summed together to provide the macroscopic NLO properties, while accounting for the differences between the microscopic (local) electric field and the macroscopic (external) field. By analogy to Equation 1.2, the macroscopic effects are described by the power series given in Equation 1.3:

$$P_i(F) = P_{oi} + C \left[ \chi^{(1)}_{ij} F_j + \chi^{(2)}_{ijk} F_j F_k + \chi^{(3)}_{ijkl} F_j F_k F_l + \ldots \right]$$

(1.3)

$C$ is a constant that depends on the choice of the system of units (1 for cgs units, $\varepsilon_0$ for SI units), $P$ is the macroscopic polarization vector, the field $F$ is the external field and $\chi^{(n)}$ are susceptibilities of consecutive orders. As with polarizabilities, the macroscopic susceptibilities are complex quantities with complicated frequency dependences; the calculation of a susceptibility of crystalline media from molecular properties of the constituent molecules requires the knowledge
of the orientations of the molecules as well as the local field factors, and is a particularly tedious task. This is simplified considerably in the case of isotropic media such as solutions or glasses.

1.3 Measurement Techniques

1.3.1 Quadratic NLO Properties of Molecules

The quadratic polarizability $\beta$ is a third-rank tensor, i.e. it can be presented as a $3 \times 3 \times 3$ matrix. As is true for all molecular property tensors, it has to fulfill the Neumann principle (at a minimum, a physical property has to possess the same symmetry as that of the molecule). From this it follows that the existence of a center of symmetry in a molecule causes all the elements of the $\beta$ tensor to vanish. In a similar way, all elements of the $3 \times 3 \times 3 \chi^{(2)}$ tensor are equal to zero for isotropic media, so a perfectly random liquid or a solid solution of second-order NLO-active molecules should not exhibit second-order NLO effects such as coherent second-harmonic generation. Measurements carried out on crystals belonging to noncentrosymmetric symmetry classes afford second-order nonlinear optical properties; however, such measurements are cumbersome because of the necessity to grow large (typically a few millimeters in size) optical quality single crystals of the compound to be studied, coupled to the need to take measurements with different orientations of the crystallographic axes of the sample while varying the polarization of the laser beam, etc. Usually, the SHG signals are collected as so-called Maker fringes,\cite{16} the amplitude and periodicity of the fringes being analyzed. Such measurements are rarely attempted for new materials unless there is the prospect of practical applications in the crystal form. Measurements of the second-harmonic signals from solutions or solid samples in which the NLO chromophores have net noncentrosymmetric alignment are considerably simpler. Various procedures to effect alignment have been employed, the most common being application of a dc electric field. The SHG effect arising under such circumstances is electric field-induced second-harmonic generation (EFISHG or EFISH). In a typical experiment (examples can be found in the literature\cite{17}), a series of solutions of the compound of interest in an organic solvent are prepared, and are then examined in a special cell that permits appli-
cation of intense electric fields (typically of the order of $10^5 \text{ V m}^{-1}$). To minimize
problems with electron and ionic conduction in the samples, the field is usually
applied in the form of a relatively short voltage pulse that is timed to start just
before the laser pulse (which is shorter than the voltage pulse). The molecules
of the solute and the solvent can contribute to the generation of the second
harmonic of the laser frequency in two ways. All molecules, independent of their
symmetry, will contribute through their cubic hyperpolarizabilities. This arises
from a polarization term at the second harmonic that involves the product of
the orientationally-averaged cubic hyperpolarizability and the dc field amplitude
$< \gamma (-2\omega; \omega, \omega, 0) > F_{dc}$. The molecules possessing a static dipole moment
$\mu_0$ provide another (usually larger) contribution: they tend to align with the
dc field direction along their dipole moment direction. Since thermal motions
counteract such alignment, the net alignment can be found from consideration of
the balance between these two tendencies, which leads to the Langevin formula.
In effect, the contribution of dipolar orientation to the nonlinear polarization at
$2\omega$ is found to be proportional to $\frac{\mu_0 \beta}{kT} F_{dc}$. The tensor product $\mu \beta$ appearing here
needs a comment: it can be considered a scalar product of the $\mu$ vector and the
so-called vectorial part of the $\beta$ tensor. Since many molecules of importance for
second-order nonlinear optics are elongated in one direction and possess a dipole
moment in that direction, it is often the case that the value of this product
(the quantity that is determined experimentally in EFISH experiments) can be
treated as the product of the length of the dipole moment of the molecules and
the magnitude of the diagonal component of $\beta$ along the molecular axis (often
denoted $\beta_{333}$, 3 being the molecular axis). It should be noted that the product
$\mu \beta$ may have different signs for different molecules; this explains the need for
measurements on several concentrations of the chromophore in the solvent, so as
to correctly account for the same-sign or opposite-sign contribution of the solvent.
This principle of determining the second-order nonlinearity through electric field
alignment of dipolar molecules can also be applied when the molecules are not in
a liquid, but in a solid solution, e.g. in a polymer or sol-gel glass matrix. The
main difference is that the dipoles must be aligned by electric-field poling when
the system is in a state allowing for reorientation of the dipoles, i.e. above the
glass transition temperature in a polymer, or before crosslinking of a matrix.
1.3. Measurement Techniques

SHG measurements in poled matrices are often used for NLO polymers, but are not common for organometallics.

The EFISH method cannot be applied for determining the NLO properties of second-order NLO molecules possessing trigonal symmetry, which have no net electric dipole but may have an electric octupole moment. The $\beta$ tensor of such molecules is dominated by the octupolar components (examples of a discussion of the dipolar and octupolar components of $\beta$ can be found in the literature\cite{18}). Another deficiency of EFISH is that it is difficult to apply to conducting solutions (i.e. those containing ions). Octupolar and conducting systems can be studied with an alternative technique, namely hyper-Rayleigh scattering (HRS). As mentioned above, solutions of second-order NLO chromophores cannot generate coherent SHG beams because the contributions of individual molecules cancel out through the randomness of their orientations in space. However, such solutions can generate SHG in a non-coherent way: as a signal scattered in all directions. The principle of the effect is similar to that of ordinary Rayleigh scattering, in which light is scattered without the change of its frequency. The experiment to measure this is rather simple. A beam from a pulsed laser (nanosecond, picosecond or femtosecond) is tightly focused inside a cell containing the solution of interest. Light scattered from the vicinity of the focal point is collected with low f-number optics and the component at $2\omega$ is separated with narrow band filters or a monochromator, before being passed to a sensitive detector. The intensity of the HRS signal is proportional to the square of the fundamental light intensity and to the square of a product of a certain combination of the components of the $\beta$ tensor and the concentration of the chromophore. The experiment can be conveniently calibrated by performing measurements on a solution of a well-known NLO chromophore (e.g. $p$-nitroaniline). This technique is currently the most popular way of examining the second-order NLO effects in organometallic molecules. Its main drawback is the fact that the light intensities employed in the experiments are quite high, and can therefore induce effects additional to HRS. The main problem is upconverted emission from multiphoton absorption-induced fluorescence of the solution. Although the fluorescence component can, in principle, be rejected\cite{4} based on the fact that it has a finite lifetime, unlike HRS which is instantaneous, and also because its bandwidth is much broader than the SHG emission\cite{19}, the results obtained for fluorescent
molecules should be treated with care. In both cases (EFISH and HRS), the important factor is the choice of the fundamental wavelength of the experiment. This is significant because of the dispersion of $\beta$ and because of the possibility of artefacts such as multiphoton-excited emission, which can take place if the energies of two photons (or three in the case of three-photon absorption) are sufficient to reach an excited state of the chromophore.

An important second-order NLO effect is the linear electro-optic effect (Pockels effect), where the refractive index of a material changes with the strength of the applied field.\textsuperscript{[20]} This effect can be used for modulators and variable phase retarders. The measurements of this effect can be relatively easily accomplished by several techniques including the ATR technique\textsuperscript{[21]} and the Teng-Man technique.\textsuperscript{[22]} The measured quantity is then the electro-optic coefficient $r$, which involves the $\beta (-\omega; \omega, 0)$ hyperpolarizability.

### 1.3.2 Cubic NLO Properties of Molecules

The cubic hyperpolarizability $\gamma$ is a fourth rank tensor ($3 \times 3 \times 3 \times 3$ matrix). Unlike second-order NLO effects, orientational averaging for a random collection of third-order NLO chromophore molecules always leads to non-zero effects. In most cases, the average hyperpolarizability is given by Equation 1.4:

$$\langle \gamma \rangle = \frac{1}{15} (\gamma_{iiij} + \gamma_{ijij})$$  \hspace{1cm} (1.4)

This expression reduces to $\langle \gamma \rangle = \frac{1}{5} \gamma_{1111}$ when one element of the tensor $\gamma_{1111}$ is dominant. The macroscopic cubic susceptibility $\chi^{(3)}_{ijkl}$ for an isotropic system, such as a solution, has twenty-one non-zero elements, three of which are independent.\textsuperscript{[2]} One usually determines $\chi^{(3)}_{1111}$, which can then be used to calculate $\langle \gamma \rangle$. While polarizabilities of all orders and corresponding to various frequency mixing schemes should be treated as complex, the real and imaginary parts of some have more immediate practical significance than others. There is little interest in the imaginary part of the second-order hyperpolarizability $\beta (-2\omega; \omega, \omega)$, because the second-harmonic generation process is usually carried out at frequencies well removed from the resonance frequencies of the material. On the other hand, both the real and imaginary parts of the above-mentioned degenerate cubic
1.3. Measurement Techniques

hyperpolarizability are of considerable practical interest. The common techniques for the determination of the cubic NLO properties of molecules address different frequency combinations possible for $\gamma (-\omega_4; \omega_1, \omega_2, \omega_3)$. Currently, the most popular techniques are third-harmonic generation (THG), Z-scan, and degenerate four-wave mixing (DFWM). In all cases, solutions in liquid solvents or in solid matrices can be examined.

The third-harmonic generation experiments are performed with a pulsed laser beam impinging on a sample, the intensity of the beam generated at the third harmonic usually being monitored as a function of the angle of inclination of the sample with respect to that of the fundamental beam, which leads to the formation of Maker fringes similar to those from SHG measurements. There is no need to electrically pole the sample; on the contrary, one needs to account for the contributions of THG generated in all components of the system (e.g. glass walls or glass substrate, in addition to the liquid or solid sample). The interference between the signals from components of the system may be helpful in resolving the real and imaginary contributions to the cubic susceptibility $\chi^{(3)} (-3\omega; \omega, \omega, \omega)$ or the corresponding hyperpolarizabilities. A major limitation for organometallics is that $\omega$ needs to be chosen to avoid material resonances at $\omega$, $2\omega$ and $3\omega$, which is difficult for molecules absorbing in the visible region. Z-scan is currently the most widely applied technique for determining the real and imaginary parts of $\gamma (-\omega; \omega, -\omega, \omega)$. This technique measures two technologically relevant NLO parameters of a sample: its nonlinear refractive index and its nonlinear absorption coefficient. The former parameter can be defined by the relation $\Delta n = n_2 I$, while the latter parameter is defined by the analogous expression $\Delta \alpha_n = \alpha^{(2)} I$, where $n$ is the refractive index, $n_2$ is the nonlinear refractive index, $\alpha^{(2)}$ is the nonlinear absorption coefficient, and $\Delta \alpha_n$ represents the change in the linear absorption coefficient induced by the intensity $I$ (the index $a$ is used here to distinguish this absorption coefficient from the linear polarizability).

The principle of Z-scan is as follows: a laser beam is focused by a lens, and the sample travels on a stage from a point before the beam focus ($-z$) through the focus ($z = 0$) to a point beyond the focus ($+z$). As the sample travels, it starts from a location where the light intensity is moderate, crosses the point of the highest intensity at $z = 0$ (because of the smallest beam diameter at that point) to a location where the intensity becomes much smaller again at $+z$. 

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The changes of the intensity cause two effects. The change in the absorbance of the sample will influence the total power transmitted through the sample. The change in the refractive index, on the other hand, causes the sample to act as an induced lens, which contributes to the distortion of the beam in the far field (well after the sample). Both effects can be studied simultaneously: the nonlinear absorption, through monitoring the total power in the transmitted beam as a function of \( z \) (so called open-aperture Z-scan), and the nonlinear refraction, through monitoring the power transmitted through a small pinhole located at the center of the beam in the far-field (closed-aperture Z-scan). The nonlinear refraction and nonlinear absorption coefficients obtained from the Z-scan data can then be used to compute the real and imaginary parts of the hyperpolarizability of the solute, taking into account the contribution to the signal coming from the solvent and the cell walls measured in a separate experiment. The major difficulty with Z-scan measurements is that contributions to absorption and refraction at high light intensities may arise from a number of disparate processes. For example, a common problem is that linear and nonlinear absorption may lead to local heating of the solution, causing thermo-optic phenomena (changes in the refractive index and absorption coefficient due to a change of temperature). To avoid such contributions, it is necessary to use low repetition rate (usually 1 kHz or slower) short (typically 100 fs) laser pulses for Z-scan measurements. Nevertheless, distinguishing between various possible contributions to the Z-scan signals is only possible with additional, time-resolved experiments.

Historically, the most frequently employed time-resolved technique for determining cubic nonlinearities is degenerate four-wave mixing (DFWM). In the so-called BOXCARS geometry of the experiment, suitable for use with short-pulse lasers, a sample is subjected to the simultaneous action of three light beams, which are all derived from a single source by splitting the beam and adjusting the beam paths to ensure all beams arrive at the sample simultaneously. The beams are usually positioned in space in such a way that they arrive at a screen after the sample defining three corners of a rectangle. The interaction of the beams in the sample leads to the formation of volume gratings: periodic structures formed by changes in the refractive index and absorption coefficient of the material. The gratings contribute to the formation of new light beams: in the BOXCARS geometry, there is the possibility of forming a phase-matched beam pointing into
the fourth corner of the above-mentioned rectangle, as well as several (usually weaker) non-phase matched beams.[25] The intensities of the beams created in the DFWM process are proportional to $|\chi^{(3)}|^2$, and so resolving the contributions into those from nonlinear refraction and those from nonlinear absorption requires additional study. This can be accomplished by a separate measurement of nonlinear absorption, or by determination of the phase of the DFWM signal through other means (for example, using concentration dependences for a series of solutions of a chromophore in a solvent,[26] or through coherent detection.[27]) The advantage of DFWM when performed with short laser pulses is the possibility of studying the temporal behavior of the induced changes in the refractive index and the absorption coefficient.

A simpler way of performing time-resolved experiments is by using the pump-probe technique, in which two pulsed laser beams of the same or different wavelengths arrive at the sample with a varied delay. The first beam, the pump, induces a change in the sample and the second, the probe, can sense these changes through the change of transmittance of the sample. This simplest manifestation (using the same wavelength for the pump and probe) affords the nonlinear absorption coefficient related to $\text{Im} \{\gamma (-\omega; \omega, -\omega, \omega)\}$, while the use of two different wavelengths provides $\text{Im} \{\gamma (-\omega_1; \omega_1, -\omega_2, \omega_2)\}$. A useful way of implementing the experiment is with white light supercontinuum as the probe, because this can provide a complete spectrum of the non-degenerate nonlinear absorption coefficient in a single experiment. The use of the pump-probe principle for the determination of nonlinear refraction requires some modification to the experiment. The Kerr gate experiment uses a pump-probe setup in which the transmission of the probe beam, polarized at 45 degrees to the pump beam, is monitored through a crossed analyzer. The intensity of the probe transmitted through the analyzer can then be related to a combination of off-diagonal components of $\chi^{(3)}$. Resolution of the effect into that due to refractive and absorptive NLO properties requires a modification of the technique called heterodyne Kerr gate.[28,29] Nonlinear absorption is often investigated in an indirect way by two-photon excited fluorescence.[30,31] In this technique, a spectrum of the nonlinear absorption coefficient can be obtained by simply recording the dependence of the fluorescence induced by two-photon absorption on the wavelength of the excitation, and then comparing the wavelength dependence of the fluorescence with that of a standard well-known
fluorescent dye. The spectrum obtained is of the product of the two-photon absorption cross-section of a molecule and its fluorescence quantum yield; the quantum yield is usually assumed to be equal to that measured under ordinary one-photon excitation. The cubic NLO properties can also be observed when one of the exciting fields is not derived from a light beam but from a dc source. The refractive behavior observed under these conditions is the quadratic electro-optic effect or Kerr effect, while the absorptive behavior is electroabsorption or the Stark effect. The nonlinear susceptibilities derived from these measurements are the real and imaginary parts of $\chi^{(3)}(-\omega;\omega,0,0)$, respectively.

1.3.3 Units (Conversions, Definitions, Difficulties)

Much confusion may arise when attempts are made to compare results of different authors using various conventions of defining the NLO parameters, different units systems and employing various experimental techniques. These issues have been discussed at length in the literature.$^{[2,3,32]}$ In short, the difficulties arise from three sources.

Definitions of the NLO Parameters. Equations 1.2 (page 3) and 1.3 (page 4) are power series that can be written with or without explicitly including the $\frac{1}{n!}$ factors in the power expansion terms. This in itself may lead to quantities differing by a factor of $2! = 2$ and $3! = 6$ in the cases of second-order and third-order NLO effects, respectively. It should also be noted that the transition from Equations 1.2 and 1.3 to frequency-dependent NLO parameters involves substituting in Equation 1.1 (page 2), which is often written with an additional factor of $\frac{1}{2}$ in front of the field amplitude. This leads to another factor which will be 4 and 8 in the cases of second-order and third-order processes, respectively. An uncertainty is also the question of including so-called degeneracy factors in the definition of the NLO parameters. Since NLO susceptibilities and hyperpolarizabilities are defined for a given combination of the input frequencies, degeneracy factors arise as an effect of summing over the field amplitudes of fields with the same frequency. For example, the $\gamma$ used to describe the process of third-harmonic generation and that used to describe nonlinear refraction may differ by a factor of 3 depending on whether the degeneracy factor is included in the definition of $\gamma$ or not. It is
usually considered prudent to define the hyperpolarizabilities in such a way that they collapse to the same value as the frequencies $\omega_i$ all go to zero.

*Unit System.* Traditionally, the cgs system was used for molecular parameters while the SI system and mixed units systems (e.g. cm$^2$ W$^{-1}$ for the values of the nonlinear refractive index $n_2$) are more common for macroscopic nonlinear parameters. In addition to that, quantum chemists use the atomic units system for the quantities calculated theoretically and care needs to be taken when converting from those units to the experimental ones.

*Comparing Results of Different Experiments.* Even if the degeneracy factors and other contentious issues are dealt with, the remaining problem is always the specificity of the experiment carried out, the frequency dependence of the parameters and the possible dependencies of the parameters on factors such as the laser pulse duration, the repetition rate or other differences such as on-resonant vs. off-resonant measurements.$^{[33]}$ In order to compare complexes or compounds of different chemical families with regards to their NLO efficiencies, intrinsic NLO values have to be considered rather than absolute values. This is achieved through scaling factors that account for the size of systems that are being compared to each other, or the number of electrons that contribute to the observed NLO effects. This aspect of comparing NLO data will be addressed in detail in Chapters 2 and 3.

### 1.4 Second-Order Nonlinearities

Selected second-order nonlinearities of pyridyl, polypyridyl, and porphyrin complexes through 2004 have been summarized, and a review of quadratic NLO properties of square planar d$^8$-metal dithiolene complexes through 2008 has appeared.$^{[34]}$

#### 1.4.1 Pyridyl, Polypyridyl and Related Complexes

Pyridyl complexes were amongst the first inorganic complexes to be assessed for optical nonlinearity$^{[35]}$ and they continue to attract attention with a large number of complexes assayed for second-order properties.$^{[36–75]}$ The N-heterocycle
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![Chemical Structure](image)

**Figure 1.1** Second-order NLO properties of ruthenium chlorobis(diarsine) complexes bearing pyridyl ligands.\(^{50}\)

is typically 4-functionalized with donor or acceptor substituents. The quadratic NLO response in N-ligated pyridyl complexes is dominated by a low-energy transition that is MLCT in nature for acceptor substituents and ILCT in character for donor groups, the metal functioning as an inductive electron acceptor for the latter.\(^{7}\) Coe’s group has explored the effect on quadratic nonlinearity of a variety of structural modifications in this system, and has reviewed his group’s studies through 2005 of pyridyl complexes with pyridinium groups as quadratic NLO switches.\(^{47}\)

Ruthenium complexes bearing a variety of co-ligand sets, namely chlorobis(diarsine),\(^{49,50}\) tetra(amine)pyridine/N-methylpyrazole,\(^{41,43,49,55}\) penta(amine),\(^{38,41,43,55}\) and penta(cyano) co-ligands,\(^{48}\) have been examined. Varying the quaternizing substituent in chlorobis(diarsine) complexes of 4-functionalized pyridines results in an increase in Stark spectroscopy-derived quadratic nonlinearities on proceeding from Me to Ph or pyrimidyl group (1 to 2 or 3).\(^{50}\) Oligo(ethynyl)-connected N-methylpyridinium-functionalized pyridine complexes 1-6 to 1-13 afford Stark- and HRS-derived \(\beta_0\) values that increase on proceeding from \(n = 0\) to 1 and then 2, with lower absolute values than those of the analogous ethynyl-linked complexes.\(^{49}\)

Coe and co-workers have also examined oligo(ethynyl)-connected N-methylpyridinium-functionalized pyridine complexes 1-14 to 1-27 (Figure 1.4) in which the trans-disposed ligand is ammine, N-methylimidazole, or pyridine.\(^{41,43}\) The CT bands in the visible region of these complexes are \(d\rightarrow\pi^*\) metal-to-ligand
1.4. Second-Order Nonlinearities

**Figure 1.2** Second-order NLO properties of two ruthenium chlorobis(diarsine) complexes bearing different pyridyl ligands.\(^{[49]}\)

**Figure 1.3** Second-order NLO properties of ruthenium chlorobis(diarsine) complexes bearing ethynyl-connected pyridinium-functionalized (1-6 to 1-11, 1-13) and pyridine-functionalized (1-12) pyridine ligands.\(^{[49]}\)
Figure 1.4 Second-order NLO properties of ruthenium complexes 1-14 to 1-21\textsuperscript{[41]} and 1-22 to 1-27\textsuperscript{[43]} bearing oligo(ethenyl)-connected N-methylpyridinium-functionalized pyridine ligands.

in character; these CT bands are unusual in that they blue-shift on increasing the number of ethenyl linkages. HRS- and Stark-derived frequency-independent nonlinearities $\beta_0$ are maximized at two ethenyl linkages, unlike related organic compounds for which the nonlinearity increases on $E$-ethenyl chain lengthening.

Coe and co-workers have used similar complexes to demonstrate quadratic NLO “switching”, the earlier solution studies\textsuperscript{[76]} having been extended to the solid-state.\textsuperscript{[38]} The penta(ammine)ruthenium complex 1-28, featuring an aryl-quatierminated 4,4'-bipyridinium ligand (Figure 1.5), was assembled into a non-centrosymmetric multi-layer Langmuir-Blodgett film by alternately depositing the complex and arachidic acid, and the resultant film deposited onto
1.4. Second-Order Nonlinearities

Figure 1.5 a) Reversible redox-switching between 1-28$^{3+}$ and 1-28$^{4+}$. b) Electrochemical switching diagram of the SHG (532 nm) from an alternating Langmuir-Blodgett film of 1-28$^{3+}$ and 1-28$^{4+}$ on ITO coated glass. [38]

ITO-coated glass. Oxidation reduced the SHG intensity by ca. 50%, but continued redox cycling degraded the signal (Figure 1.5 b).

The [Fe(CN)$_5$]$^{3-}$ center is very electron-rich, functioning as a very strong donor when coupled to $N$-methyl/aryl-pyridinium acceptors in donor-bridge-acceptor arrays, and affording complexes with intense and very broad MLCT transitions that are strongly solvatochromic. Stark spectroscopy suggests substantial NLO responses that increase with chromophore length. [52] Not surprisingly, comparison to analogous [Ru(NH$_3$)$_5$]$^{2+}$ complexes reveal an increase in HRS-derived nonlinearity in moving to the iron examples shown in Figure 1.6. Protic switching of nonlinearity was demonstrated in these complexes using both HRS and Stark spectroscopy, with a ca. four-fold decrease in the magnitude of $\beta$ being observed on protonation. [48] The crucial CT interaction in these complexes is along the molecular dipole. Coe’s group has also extended these studies to embrace V-shaped complexes with cis-disposed $N$-pyridyl ligands, [42,55] the resultant com-
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1-29: R = Me, $\lambda_{\text{max}} = 534 \text{ nm (H}_2\text{O)}$, $\beta_0$ (Stark) = $61 \times 10^{-30}$ esu (Glycerol/H$_2$O, 50/50), $\beta_0$ (HRS) = $2 \times 10^{-30}$ esu (H$_2$O)

1-30: R = Ph, $\lambda_{\text{max}} = 566 \text{ nm (H}_2\text{O)}$, $\beta_0$ (Stark) = $88 \times 10^{-30}$ esu (Glycerol/H$_2$O, 50/50), $\beta_0$ (HRS) = $22 \times 10^{-30}$ esu (H$_2$O)

1-31: R = $\text{COMe}$, $\lambda_{\text{max}} = 584 \text{ nm (H}_2\text{O)}$, $\beta_0$ (Stark) = $114 \times 10^{-30}$ esu, (Glycerol/H$_2$O, 50/50), $\beta_0$ (HRS) = $31 \times 10^{-30}$ esu (H$_2$O)

1-32: R = $\text{CN}$, $\lambda_{\text{max}} = 618 \text{ nm (H}_2\text{O)}$, $\beta_0$ (Stark) = $166 \times 10^{-30}$ esu, (Glycerol/H$_2$O, 50/50), $\beta_0$ (HRS) = $50 \times 10^{-30}$ esu (H$_2$O)

1-33: n = 1, R = Me, $\lambda_{\text{max}} = 538 \text{ nm (H}_2\text{O)}$, $\beta_0$ (Stark) = $119 \times 10^{-30}$ esu (Glycerol/H$_2$O, 50/50), $\beta_0$ (HRS) = $4 \times 10^{-30}$ esu (H$_2$O)

1-34: n = 1, R = Ph, $\lambda_{\text{max}} = 562 \text{ nm (H}_2\text{O)}$, $\beta_0$ (Stark) = $174 \times 10^{-30}$ esu (Glycerol/H$_2$O, 50/50), $\beta_0$ (HRS) = $22 \times 10^{-30}$ esu (H$_2$O)

1-35: n = 2, R = Me, $\lambda_{\text{max}} = 520 \text{ nm (H}_2\text{O)}$, $\beta_0$ (Stark) = $54 \times 10^{-30}$ esu (Glycerol/H$_2$O, 50/50), $\beta_0$ (HRS) = $73 \times 10^{-30}$ esu (H$_2$O)

1-36: n = 3, R = Me, $\lambda_{\text{max}} = 502 \text{ nm (H}_2\text{O)}$, $\beta_0$ (Stark) = $59 \times 10^{-30}$ esu (Glycerol/H$_2$O, 50/50), $\beta_0$ (HRS) = $56 \times 10^{-30}$ esu (H$_2$O)

1-37: $\lambda_{\text{max}} = 465 \text{ nm (H}_2\text{O)}$, $\beta_0$ (Stark) = $56 \times 10^{-30}$ esu (Glycerol/H$_2$O, 50/50), $\beta_0$ (HRS) = $228 \times 10^{-30}$ esu (H$_2$O)

1-38: $\lambda_{\text{max}} = 660 \text{ nm (H}_2\text{O)}$, $\beta_0$ (Stark) = $45 \times 10^{-30}$ esu (Glycerol/H$_2$O, 50/50), $\beta_0$ (HRS) = $165 \times 10^{-30}$ esu (H$_2$O)

Figure 1.6 Second-order NLO properties of ligated Fe$^{11}$(CN)$_5$ complexes 1-29 to 1-34$^{[48]}$ and 1-35 to 1-38$^{[52]}$. Each complexes is bearing either a $N$-methylpyridinium- or a $N$-phenylpyridinium-functionalized pyridine ligand.
plexes possessing large NLO responses with 2D character (Figures 1.7 and 1.8). While HRS studies suggest that $\beta_{zzz}$ is the dominant tensor component, Stark measurements and FF calculations are consistent with similar or even greater contribution to the global $\beta$ value from the $\beta_{zyy}$ tensor component.\cite{69}

Coe has also explored an alternative 2D approach, employing pyrazinyl-4,4'-bipyridinium bridges to link multiple ruthenium centers (Figure 1.9).\cite{55} Depolarization ratios from HRS studies at 1064 nm are consistent with dominant off-diagonal $\beta_{zy}$ components contributing strongly to 2D NLO responses in these complexes.

Co-ligand variation in zinc complexes has been examined,\cite{70} the EFISH-derived quadratic nonlinearity at 1.91 $\mu$m increasing on replacing acetate by triflate (proceeding from 1-56 to 1-57 in Figure 1.10); this is accompanied by an increase in dipole moment and a red-shift of the ILCT transition for this structural modification. Dilution of solutions of the triflate complexes results in significant
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Figure 1.8 Second-order NLO properties of Ru\(II\)(NH\(_3\))\(_3\) complexes bearing oligo(ethenyl)-connected N-methylpyridinium- or N-arylpypyridinium-functionalized pyridine ligands.\[63\]
Figure 1.9 Second-order NLO properties of Ru\textsuperscript{II}(NH\textsubscript{3})\textsubscript{5} and pyridyl-ligated Ru\textsuperscript{II}(NH\textsubscript{3})\textsubscript{4} complexes linked by pyrazinyl-4,4'-bipyridinium bridges.\textsuperscript{[53]}

\begin{itemize}
\item \textbf{1-50:} \( R_1 = \text{NH}_3, \lambda_{\text{max}} = 707 \text{nm (MeCN)}, \beta_0 (\text{Stark}) = 252 \times 10^{30} \text{ esu (PrCN)}, \beta_0 (\text{HRS}) = 257 \times 10^{30} \text{ esu (MeCN)} \)
\item \textbf{1-51:} \( R_1 = \text{NH}_3, \lambda_{\text{max}} = 675 \text{ nm (MeCN)}, \beta_0 (\text{Stark}) = 259 \times 10^{30} \text{ esu (PrCN)}, \beta_0 (\text{HRS}) = 200 \times 10^{30} \text{ esu (MeCN)} \)
\item \textbf{1-52:} \( R_2 = \text{NH}_3, \lambda_{\text{max}} = 713 \text{ nm (MeCN)}, \beta_0 (\text{Stark}) = 662 \times 10^{30} \text{ esu (PrCN)}, \beta_0 (\text{HRS}) = 336 \times 10^{30} \text{ esu (MeCN)} \)
\item \textbf{1-53:} \( R_2 = \text{NH}_3, \lambda_{\text{max}} = 674 \text{ nm (MeCN)}, \beta_0 (\text{Stark}) = 816 \times 10^{30} \text{ esu (PrCN)}, \beta_0 (\text{HRS}) = 326 \times 10^{30} \text{ esu (MeCN)} \)
\item \textbf{1-54:} \( R_3 = \text{NH}_3, \lambda_{\text{max}} = 711 \text{ nm (MeCN)}, \beta_0 (\text{HRS}) = 261 \times 10^{30} \text{ esu (MeCN)} \)
\item \textbf{1-55:} \( R_3 = \text{NH}_3, \lambda_{\text{max}} = 665 \text{ nm (MeCN), } \beta_0 (\text{HRS}) = 309 \times 10^{30} \text{ esu (MeCN)} \)
\end{itemize}
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\[ \text{Figure 1.10} \] Second-order NLO properties of Zn\(^{II}\) complexes as a function of the ligand (acetate vs. triflate).\[^{[70]}\]

increases in nonlinearity, an effect explained by solvolysis of the triflate anion and concomitant strong ion-pairing.

Ruthenium polypyridyl complexes have attracted attention for their NLO properties; their quadratic nonlinearities are associated with ILCT bands that are red-shifted on complexation of the free ligand,\[^{[7]}\] and directionally opposed to MLCT transitions. Earlier studies had functionalized the bipy ligands with electron donating groups, so in order for MLCT effects to dominate nonlinearity, Coe \textit{et al.} employed 4,4'-disubstituted bipy ligands with electron-withdrawing pyridinium groups (Figure 1.11), the Ru\(^{II}\) examples revealing larger \(\beta\) coefficients than their Fe\(^{II}\) analogues.\[^{[46,54]}\]

A similar strategy was employed by Mayer and co-workers\[^{[59]}\] – elaboration of bipy and terpy ligands with 4-(4-\(N,\text{N}\)-dimethylaminostyryl)-1-methylpyridinium (DASP) moieties (Figure 1.13) was explored because of the significant bulk susceptibility of this organic cation as its tosylate salt.\[^{[77]}\] The quadratic nonlinearities for the Ru-containing complexes were discussed as a superposition of \(\beta_{\text{DASP}}, \beta_{\text{ICT}},\) and \(\beta_{d\rightarrow \pi^*}\), where the latter two may be either positive or negative compared to \(\beta_{\text{DASP}}\), while the Zn\(^{II}\) complex performance was explained by competing contributions of \(\beta_{\text{DASP}}\) and \(\beta_{\text{ICT}}\).

Le Bozec and co-workers have functionalized 4,4'-bis(dialkyaminostyryl)-[2,2']-bipyridines and incorporated them into the main chain of a polyimiden (Figure 1.14). The resultant assembly was used to construct octupolar tris(bipyridine)ruthenium-containing macromolecules that exhibit intense linear absorption in the visible region, long-lived luminescence, and quadratic
1.4. Second-Order Nonlinearities

1-58: M = Ru, R = Me, $\lambda_{\text{max}}$ = 576 nm (PrCN),
$\beta_0$ (Stark) = $41 \times 10^{-30}$ esu (PrCN),
$\beta_{600}$ (HRS) = $170 \times 10^{-30}$ esu (MeCN)

1-59: M = Ru, R = Ph, $\lambda_{\text{max}}$ = 589 nm (PrCN),
$\beta_0$ (Stark) = $76 \times 10^{-30}$ esu (PrCN),
$\beta_{600}$ (HRS) = $270 \times 10^{-30}$ esu (MeCN)

1-60: M = Ru, R = 4-AcC6H4, $\lambda_{\text{max}}$ = 594 nm (PrCN),
$\beta_0$ (Stark) = $44 \times 10^{-30}$ esu (PrCN),
$\beta_{600}$ (HRS) = $281 \times 10^{-30}$ esu (MeCN)

1-61: M = Fe, R = Me, $\lambda_{\text{max}}$ = 581 nm (PrCN),
$\beta_0$ (Stark) = $56 \times 10^{-30}$ esu (PrCN),
$\beta_{600}$ (HRS) = $78 \times 10^{-30}$ esu (MeCN)

1-62: M = Fe, R = Ph, $\lambda_{\text{max}}$ = 590 nm (PrCN),
$\beta_0$ (Stark) = $82 \times 10^{-30}$ esu (PrCN),
$\beta_{600}$ (HRS) = $80 \times 10^{-30}$ esu (MeCN)

1-63: M = Fe, R = 4-AcC6H4, $\lambda_{\text{max}}$ = 596 nm (PrCN),
$\beta_0$ (Stark) = $112 \times 10^{-30}$ esu (PrCN),
$\beta_{600}$ (HRS) = $290 \times 10^{-30}$ esu (MeCN)

$\lambda_{\text{max}}$ = 593 nm (PrCN), $\beta_0$ (Stark) = $56 \times 10^{-30}$ esu (PrCN),
$\beta_{600}$ (HRS) = $290 \times 10^{-30}$ esu (MeCN)

**Figure 1.11** Second-order NLO properties of Fe$^{II}$ and Ru$^{II}$ complexes with 4,4'-disubstituted bipy ligands with electron-withdrawing pyridinium groups. [46]
Figure 1.12 Second-order NLO properties of Fe\(^{II}\) and Ru\(^{II}\) complexes with 4,4'-disubstituted bipy ligands with electron-withdrawing pyridinium groups.\(^5\)\(^3\)
1.4. Second-Order Nonlinearities

Figure 1.13 Second-order NLO properties of Fe$^{II}$ and Ru$^{II}$ complexes incorporating 4,4'-disubstituted bipy ligands and terpy ligands with electron-withdrawing pyridinium groups.$^{[50]}$
nonlinearities at 1.91 μm, consistent with octupolar ordering in the metalloendrimer.⁶³⁻⁶⁵

Le Bozec and co-workers have used the Zn⁺⁺ center as a template to assemble functionalized bipy ligands in dipolar and octupolar arrangements (the latter both \( D_{2h} \) and \( D_3 \)).⁶⁹ The UV-vis spectra are dominated by ILCT bands that are red-shifted from that of the free ligand. Both octupolar complexes are more quadratic NLO-efficient than the dipolar example, even after scaling for the number of bipy ligands. Similar Zn⁺⁺ complexation of functionalized bipy ligands has been employed to demonstrate photoswitching of quadratic NLO properties.⁶⁻⁶ The continuous π-conjugation of the bridge connecting the donor dialkylamino group to the metal-bound pyridyl acceptor exhibited when the dithienylperfluorocyclopentene unit is in the "closed" state is broken on photoisomerization to the "open" form (Figure 1.15). This structural change is accompanied by dramatic changes in both the linear optical properties (loss of an absorption band centered at 690 nm) and an order of magnitude decrease in the \( \mu_0 \) product evaluated by EFISH at 1.907 μm.

Coordination of 4'-donor or -acceptor functionalized 2,2':6',2''-terpy ligands to Ru⁺⁺⁺, Ir⁺⁺⁺ and Zn⁺⁺ centers (Figure 1.16) significantly increases the absolute value of the quadratic nonlinearity of the terpy.⁶⁸⁻⁷¹ In addition to ILCT bands, which for all complexes are red-shifted from those of the free ligands, crucial charge-transfer transitions are seen that are LMCT (Ru⁺⁺⁺) and MLCT (Ir⁺⁺⁺) in character. Quadratic nonlinearities of these complexes are strongly dependent on the nature of these CT transitions, and can be modified significantly by π-ligand and co-ligand variation.

Iridium complexes of substituted phenanthrolines (Figure 1.17) show significant second-order nonlinearity that is a function of the acceptor strength of the phenanthroline substituent, rather than the nature of the cyclometalated co-ligands.⁵⁷⁻⁵⁸,⁷³ The important CT process that controls the magnitude of the nonlinearity is MLCT in character. Nonlinearities for salts of weakly interacting counter-ions (e.g. PF₆⁻) are dependent on concentration, whereas those for salts of ions that ion-pair (e.g. C₁₂H₂₅SO₃⁻, I⁻) are lower and independent of concentration, an outcome likely to result from perturbation of the LUMO π⁺ levels of the phenanthroline in the former case.
1.4. Second-Order Nonlinearities

Figure 1.14 Second-order NLO properties of octupolar tris(bipyridine)ruthenium-containing macromolecules 1-78 and 1-79, and Zn complexes 1-80, 1-81, 1-82.
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1-84: R = H, $\lambda_{\text{max}} = 357$ nm (CH$_2$Cl$_2$),
$\mu_0$ (EFISH) = $75 \times 10^{-48}$ esu (CH$_2$Cl$_2$)

1-85: R = NMe$_2$, $\lambda_{\text{max}} = 360$ nm (CH$_2$Cl$_2$),
$\mu_0$ (EFISH) = $160 \times 10^{-48}$ esu (CH$_2$Cl$_2$)

1-86: R = H, $\lambda_{\text{max}} = 357$ nm (CH$_2$Cl$_2$),
$\mu_0$ (EFISH) = $1020 \times 10^{-48}$ esu (CH$_2$Cl$_2$)

1-87: R = NMe$_2$, $\lambda_{\text{max}} = 360$ nm (CH$_2$Cl$_2$),
$\mu_0$ (EFISH) = $1800 \times 10^{-48}$ esu (CH$_2$Cl$_2$)

Figure 1.15 Switchable second-order NLO properties of Zn$^{II}$ complexes bearing dithienylperfluorocyclopentene substituted bipy ligands.$^{[66]}$

Quadratic nonlinearities for $\beta$-diketonate-containing analogues 1-105 to 1-107 contain contributions from $\pi \rightarrow \pi^*$ ILCT as well as MLCT processes.$^{[72]}$ Appending an acceptor 2,4-dinitrophenyl unit (proceeding from 1-106 to 1-107) results in a reduction in quadratic nonlinearity, an outcome that is suggested to arise from the unfavorable orientation of the 2-nitro group (which is almost perpendicular to the metal-acac axis).

A major problem in converting significant molecular quadratic nonlinearity into appreciable bulk susceptibility is the proclivity of dipoles to align in an antiparallel fashion. Réau and co-workers exploited the $\text{trans}$-effect at palladium to assemble pyridylphosphole ligands and construct a bis(dipole). The resultant complexes exhibit nonlinearities greater than twice those of the constituent pyridylphospholes.$^{[60]}$

1.4.2 Complexes of Porphyrins and Phthalocyanines

The quadratic nonlinearities of complexes with phthalocyanines (through 2002)$^{[78]}$ and porphyrins and related ligands (through 2005)$^{[79]}$ have been summarized.
1.4. Second-Order Nonlinearities

**Figure 1.16** Second-order NLO properties of Ru$^{III}$, Ir$^{III}$ and Zn$^{II}$ complexes bearing terpy ligands.$^{[68,71]}$
CHAPTER 1. Coordination Compounds and Organometallic Complexes for Nonlinear Optics

**Figure 1.17** Second-order NLO properties of Ir^{III} complexes bearing substituted phenanthroline ligands.\(^{[57,58,73]}\)

![Chemical structure](image)

1-97: \(R_1 = \text{Me}, R_2 = \text{H}, Y = \text{PF}_6, \lambda_{\text{max}} = 377 \text{ nm (CH}_2\text{Cl}_2\), \beta_{1,907} (EFISH) = -1565 \times 10^{-30} \text{ esu (CH}_2\text{Cl}_2\)

1-98: \(R_1 = \text{Me}, R_2 = \text{H}, Y = \text{C}_1\text{H}_2\text{SO}_2, \lambda_{\text{max}} = 376 \text{ nm (CH}_2\text{Cl}_2\), \beta_{1,907} (EFISH) = -1350 \times 10^{-30} \text{ esu (CH}_2\text{Cl}_2\)

1-99: \(R_1 = \text{NO}_2, R_2 = \text{H}, Y = \text{PF}_6, \lambda_{\text{max}} = 378 \text{ nm (CH}_2\text{Cl}_2\), \beta_{1,907} (EFISH) = -2230 \times 10^{-30} \text{ esu (CH}_2\text{Cl}_2\)

1-100: \(R_1 = \text{NO}_2, R_2 = \text{H}, Y = \text{C}_1\text{H}_2\text{SO}_2, \lambda_{\text{max}} = 378 \text{ nm (CH}_2\text{Cl}_2\), \beta_{1,907} (EFISH) = -1430 \times 10^{-30} \text{ esu (CH}_2\text{Cl}_2\)

1-101: \(R_1 = \text{H}, R_2 = \text{H}, Y = \text{PF}_6, \lambda_{\text{max}} = 377 \text{ nm (CH}_2\text{Cl}_2\), \beta_{1,907} (EFISH) = -1270 \times 10^{-30} \text{ esu (CH}_2\text{Cl}_2\)

1-102: \(R_1 = \text{NMe}_2, R_2 = \text{H}, Y = \text{PF}_6, \lambda_{\text{max}} = 334 \text{ nm (CH}_2\text{Cl}_2\), \beta_{1,907} (EFISH) = -1330 \times 10^{-30} \text{ esu (CH}_2\text{Cl}_2\)

1-103: \(R_1 = \text{H}, R_2 = \text{Me}, Y = \text{PF}_6, \lambda_{\text{max}} = 375 \text{ nm (CH}_2\text{Cl}_2\), \beta_{1,907} (EFISH) = -1454 \times 10^{-30} \text{ esu (CH}_2\text{Cl}_2\)

1-104: \(R_1 = \text{H}, R_2 = \text{Ph}, Y = \text{PF}_6, \lambda_{\text{max}} = 385 \text{ nm (CH}_2\text{Cl}_2\), \beta_{1,907} (EFISH) = -1997 \times 10^{-30} \text{ esu (CH}_2\text{Cl}_2\)

**Figure 1.18** Second-order NLO properties of β-diketonate-containing Ir^{III} and Pt^{II} complexes.\(^{[72]}\)

![Chemical structure](image)

1-105: \(R_1 = \text{Me}, R_2 = \text{H}, \lambda_{\text{max}} = 497 \text{ nm (CH}_3\text{Cl}), \beta_{1,91} (EFISH) = -228 \times 10^{-30} \text{ esu (CH}_3\text{Cl}\)

1-106: \(R_1 = \text{Ph}, R_2 = \text{H}, \lambda_{\text{max}} = 468 \text{ nm (CH}_3\text{Cl),} \beta_{1,91} (EFISH) = -268 \times 10^{-30} \text{ esu (CH}_3\text{Cl}\)

1-107: \(R_1 = \text{Me}, R_2 = 2,4-\text{C}_6\text{H}_4\text{NO}_2, \lambda_{\text{max}} = 368 \text{ nm (CH}_3\text{Cl),} \beta_{1,91} (EFISH) = -163 \times 10^{-30} \text{ esu (CH}_3\text{Cl}\)

1-108: \(R = \text{Me,} \lambda_{\text{max}} = 410 \text{ nm (CH}_3\text{Cl),} \beta_{1,5} (EFISH) = -134 \times 10^{-30} \text{ esu (CH}_3\text{Cl}\)

1-109: \(R = \text{Ph,} \lambda_{\text{max}} = 358 \text{ nm (CH}_3\text{Cl),} \beta_{1,5} (EFISH) = -193 \times 10^{-30} \text{ esu (CH}_3\text{Cl}\)

30
1.4. Second-Order Nonlinearities

![Chemical structures](image)

**Figure 1.19** Second-order NLO properties of Pd\(^{11}\) complexes bearing pyridylphosphole ligands.\(^{[60]}\)

Since then, the number of published reports in this area has indicated that the field continues to attract research interest.\(^{[67,80-112]}\)

Therien and co-workers have explored 5-donor-15-acceptor-functionalized porphyrins incorporating solubilizing substituents at the 10- and 20-positions.\(^{[111,112]}\) Varying the chain length of two series of nitro-functionalized oligo(thienyl) groups afforded complexes with essentially identical linear optical properties for each bridge type, but with very different NLO behavior. Nonlinearities of these complexes at the telecommunications wavelength of 1300 nm are exceptionally large.\(^{[111]}\) These studies were extended to include carbazolylthiophenyl-containing donor groups and thiazolyl- or dicyanovinyl-containing acceptor groups. The energies and oscillator strengths of the low-energy Q-bands are very similar across these complexes, but the nonlinearities are not, a result ascribed to transfer of oscillator strength between overlapping \(\pi-\pi^*\) and CT transitions in the low-energy transition manifold. One expected outcome is the increase in nonlinearity observed on decreasing the aromatic stabilization energy of these substituents (proceeding from \(1-112\) to \(1-125\)).\(^{[112]}\) Similar donor-porphyrin-acceptor complexes \(1-117\) and \(1-118\) (Figure 1.20) have been used by Clays and Anderson and their co-workers as dyes for SHG imaging.\(^{[105]}\)

Coupling (terpyridyl)metal centers as donor groups to zinc(porphyrin) bridges affords complexes \(1-126/1-127\) (Figure 1.21) with exceptionally large nonlinearities at 1064 nm, with a further doubling of response on introduction of nitrophenylethenyl acceptor units at the \(meso\) site (proceeding to \(1-128/1-129\)). Replacing the classical organic acceptor with a bis(terpyridyl)metal group (proceeding to \(1-130\)) results in retention of the large quadratic nonlinearity. The
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Figure 1.20 Second-order NLO properties of metallated porphyrins with systematically varied substituents (1-112 to 1-17, 111) 1-118 to 1-123, 112 and 1-124 to 1-125
tt}{10^{30}} \text{esu (THF)}
1-115: M = Zn, R1 = Me, R2 = J, R3 = D (X = NO2, n = 1)
\lambda_{\text{max}} = 640 \text{nm (THF)}, \beta_{(3)} (\text{HRS}) = 2400 \times 10^{-30} \text{esu (THF)}
1-116: M = Zn, R1 = Me, R2 = J, R3 = D (X = NO2, n = 2)
\lambda_{\text{max}} = 641 \text{nm (THF)}, \beta_{(3)} (\text{HRS}) = 2200 \times 10^{-30} \text{esu (THF)}
1-117: M = Zn, R1 = Me, R2 = J, R3 = D (X = NO2, n = 3)
\lambda_{\text{max}} = 641 \text{nm (THF)}, \beta_{(3)} (\text{HRS}) = 4350 \times 10^{-30} \text{esu (THF)}
1-118: M = Zn, R1 = Me, R2 = J, R3 = D (X = CHO, n = 1)
\lambda_{\text{max}} = 676 \text{nm (THF)}, \beta_{(3)} (\text{HRS}) = 1020 \times 10^{-30} \text{esu (THF)}
1-119: M = Zn, R1 = Me, R2 = J, R3 = D (X = CH=CN(CN)2, n = 1)
\lambda_{\text{max}} = 696 \text{nm (THF)}, \beta_{(3)} (\text{HRS}) = 785 \times 10^{-30} \text{esu (THF)}
1-120: M = Zn, R1 = Me, R2 = J, R3 = G
\lambda_{\text{max}} = 686 \text{nm (THF)}, \beta_{(3)} (\text{HRS}) = 1140 \times 10^{-30} \text{esu (THF)}
1-121: M = Zn, R1 = Me, R2 = J, R3 = L
\lambda_{\text{max}} = 694 \text{nm (THF)}, \beta_{(3)} (\text{HRS}) = 1000 \times 10^{-30} \text{esu (THF)}
1-122: M = Zn, R1 = O, R2 = J, R3 = D (X = NPh2, n = 1)
\lambda_{\text{max}} = 674 \text{nm (THF)}, \beta_{(3)} (\text{HRS}) = 810 \times 10^{-30} \text{esu (THF)}
1-123: M = Zn, R1 = O, R2 = J, R3 = D (X = Q, n = 1)
\lambda_{\text{max}} = 665 \text{nm (THF)}, \beta_{(3)} (\text{HRS}) = 1400 \times 10^{-30} \text{esu (THF)}
1-124: M = Cu, R1 = -CH2(CH2)4-Ph, R2 = Ph, R3 = A
\lambda_{\text{max}} = \text{n.a., } \beta_{(3)} (\text{HRS}) = 4000 \times 10^{-30} \text{esu (CH2Cl2)}
1-125: M = Ni, R1 = -CH2(CH2)4-Ph, R2 = Ph, R3 = A
\lambda_{\text{max}} = \text{n.a., } \beta_{(3)} (\text{HRS}) = 612 \times 10^{-30} \text{esu (CH2Cl2)}
(terpyridyl)metal center is a potent donor group, and significantly more stable than the extensively exploited dialkylamino or diarylamino groups in conventional organic chromophores.\(^{[108]}\)

Linked porphyrin dimers have been the subject of earlier studies,\(^{[79]}\) and it is therefore not surprising that meso,meso-linked corrole dimers have also attracted interest.\(^{[106]}\) While the HRS-derived quadratic nonlinearities at 1064 nm for the dimers 1-132 and 1-133 are larger than those of the corresponding monomers 1-130 and 1-131, reflecting the increased size of the \(\pi\)-system, the values are low, consistent with the lack of strongly polarizing donor or acceptor substituents and orthogonality of the rings. Chandrashekar and co-workers have conjugated an
1-131: $M = \text{Cu, } \lambda_{\text{max}} = 750 \text{ nm (CH}_2\text{Cl}_2)$,
$\beta_{1,064} \text{ (HRS) } = 18 \times 10^{-36} \text{ esu (CH}_2\text{Cl}_2)$

1-132: $M = \text{Ni, } \lambda_{\text{max}} = 750 \text{ nm (CH}_2\text{Cl}_2)$,
$\beta_{1,064} \text{ (HRS) } = 13 \times 10^{-36} \text{ esu (CH}_2\text{Cl}_2)$

1-133: $M = \text{Cu, } \lambda_{\text{max}} = 750 \text{ nm (CH}_2\text{Cl}_2)$,
$\beta_{1,064} \text{ (HRS) } = 32 \times 10^{-36} \text{ esu (CH}_2\text{Cl}_2)$

1-134: $M = \text{Ni, } \lambda_{\text{max}} = 750 \text{ nm (CH}_2\text{Cl}_2)$,
$\beta_{1,064} \text{ (HRS) } = 43 \times 10^{-36} \text{ esu (CH}_2\text{Cl}_2)$

**Figure 1.22** Second-order NLO properties of linked Cu(porphyrin) and Ni(porphyrin) dimers (1-133, 1-134) and the corresponding monomeric analogues (1-131, 1-132).\[^{[106]}\]

expanded form of the corrole unit with the ferroceny group, the nonlinearities of the resultant adducts being dependent on the nature of the spacer group; the absolute values are again modest, and again consistent with the orthogonality of the appended group.\[^{[92]}\]

### 1.4.3 Schiff Base Complexes

The quadratic nonlinearities of bis(salicylaldiminato)metal Schiff base complexes have been an active area of research during the last decade,\[^{[113]-[131]}\] and had been reviewed through 1999.\[^{[132]}\] The flexibility of the composition of such complexes (and in particular the facile incorporation of open shell as well as closed shell metals), their enforced planarity with square planar-coordinating metals, and their comparatively robustness, and the ease of derivatization are responsible for the continuing interest in these complexes. Coordination of $N$-diethylaminosalicylidene-$N'$-4-nitrobenzoylhydrazine (to form complexes like 1-135 or 1-136; Figure 1.23) tautomerizes this ligand from the free keto form to the complexed enol form, and thereby completes the conjugation from the dialkylamino donor to the nitro acceptor, the resultant complexes showing appreciable EFISH-derived $\mu\beta_{\text{sec}}$ products at 1.907 $\mu$m; it is therefore an example of complexation “switching on” nonlinearity. The complexes are prepared as dimeric aggregates, but on heating
1.4. Second-Order Nonlinearities

1-135: M = Cu, R = NO₂, λ₀₄ = 460 nm (DMSO),
µβ₁,907 (EFISH) = 460 x 10⁻⁴⁸ esu (DMSO)

1-136: M = Pd, R = NO₂, λ₀₄ = 459 nm (CHCl₃),
µβ₁,907 (EFISH) = 380 x 10⁻⁴⁸ esu (CHCl₃)

1-137: M = Cu, R = A₁, λ₀₄ = 455 nm (DMSO),
µβ₁,907 (EFISH) = 650 x 10⁻⁴⁸ esu (DMSO)

1-138: M = Pd, R = A₁, λ₀₄ = 450 nm (DMSO),
µβ₁,907 (EFISH) = 1500 x 10⁻⁴⁸ esu (DMSO)

1-139: M = Cu, R = A₁, λ₀₄ = n.a.,
µβ₁,907 (EFISH) = 1390 x 10⁻⁴⁸ esu (CHCl₃)

Figure 1.23 Second-order NLO properties of copper and palladium complexes with N-salicylidene-N’-aryldiazide tridentate ligands.[116]

1-137 in refluxing pyridine, the monomer 1-139 is formed, with a concomitant doubling of the µβ_{vec} product.[116]

Ferrocenyl-functionalized Schiff base complexes such as 1-140 or 1-141 (Figure 1.24) potentially combine the advantages of both key inorganic NLO-phores. Related complexes in which the phenoxy aryl is π-complexed to a RuCp* unit (1-142 to 1-144) were also prepared, the arené metallation having no appreciable effect on the HRS-derived nonlinearity at 1.91 μm.[131]

The effect of aryl diazo incorporation and metal variation on the EFISH-derived quadratic nonlinearity of Schiff base complexes has been explored.[123] The former leads (not surprisingly) to a substantial increase (proceeding from 1-145 to 1-149). The CuІІ and ZnІІ complexes 1-147 and 1-148 are considerably more efficient than the NiІІ and VІІ complexes 1-146 and 1-149, the superior performance being ascribed to the differing electronic configurations at the metal centers, and highlighting the potential of open shell species such as 1-147.

Donor-acceptor functionalized Schiff base complexes 1-150 to 1-160 (Figure 1.26) have been examined by EFISH at 1.907 μm.[128] Not surprisingly, the quadratic nonlinearity increases on introduction of strong acceptor and donor groups. De-
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1-140: M = Ni, $\lambda_{\text{max}} = 587$ nm (CH$_2$Cl$_2$), $\beta_{1,91}$ (HRS) = 250 x 10$^{-30}$ esu (CHCl$_3$)

1-141: M = Cu, $\lambda_{\text{max}} = 445$ nm (CH$_2$Cl$_2$), $\beta_{1,91}$ (HRS) = 212 x 10$^{-30}$ esu (CHCl$_3$)

1-142: M = Ni, $\lambda_{\text{max}} = 229$ nm (CH$_2$Cl$_2$), $\beta_{1,91}$ (HRS) = 235 x 10$^{-30}$ esu (DMF)

1-143: M = Cu, $\lambda_{\text{max}} = 474$ nm (CH$_2$Cl$_2$), $\beta_{1,91}$ (HRS) = 237 x 10$^{-30}$ esu (DMF)

1-144: $\lambda_{\text{max}} = 455$ nm (CH$_2$Cl$_2$), $\beta_{1,91}$ (HRS) = 247 x 10$^{-30}$ esu (DMF)

Figure 1.24 Second-order NLO properties of ferroceny-functionalized Schiff base complexes.\textsuperscript{[131]}

1-145: M = Zn, R = H, $\lambda_{\text{max}} = 489$ nm (CHCl$_3$), $\beta_{1,91}$ (EFISH) = -87 x 10$^{-30}$ esu (CHCl$_3$)

1-146: M = Ni, R = N$_2$Ph, $\lambda_{\text{max}} = 495$ nm (CHCl$_3$), $\beta_{1,91}$ (EFISH) = -73 x 10$^{-30}$ esu (CHCl$_3$)

1-147: M = Cu, R = N$_2$Ph, $\lambda_{\text{max}} = 490$ nm (CHCl$_3$), $\beta_{1,91}$ (EFISH) = -234 x 10$^{-30}$ esu (CHCl$_3$)

1-148: M = Zn, R = N$_2$Ph, $\lambda_{\text{max}} = 479$ nm (CHCl$_3$), $\beta_{1,91}$ (EFISH) = -280 x 10$^{-30}$ esu (CHCl$_3$)

1-149: M = VO, R = N$_2$Ph, $\lambda_{\text{max}} = 476$ nm (CHCl$_3$), $\beta_{1,91}$ (EFISH) = -83 x 10$^{-30}$ esu (CHCl$_3$)

Figure 1.25 Second-order NLO properties of Schiff base complexes incorporating aryldiazo units, showing the result of metal variation.\textsuperscript{[123]}

36
Figure 1.26 Second-order NLO properties of Cu\^{II} complexes 1-150 to 1-160 incorporating donor-acceptor functionalized Schiff base ligands\cite{128} and Ni\^{II}-complex 1-161.\cite{117}

The convolution of the electronic spectra and TD-DFT calculations revealed that the NLO response is dominated by charge-transfer transitions from donor to Cu\^{II} and from donor to acceptor in these open-shell complexes. Complexation of a Schiff base to Ni\^{II} to afford 1-161 results in a decrease in EFISH-derived quadratic nonlinearity.\cite{117}

### 1.4.4 Metal Alkynyl Complexes

The quadratic and cubic NLO properties of metal alkynyl complexes through 2002 have been surveyed,\cite{133} and further reports on quadratic NLO properties of such complexes have been published since then.\cite{134-147} Earlier studies by Humphrey and co-workers had defined the impact on quadratic nonlinearity of varying the ligated metal center, co-ligands, $\pi$-bridge, and acceptor group, in donor-bridge-acceptor complexes with short $\pi$-bridge alkynyl ligands. The
bis(bidentate diphosphine)chlororuthenium center proved amongst the most efficient donor groups, so has been used to explore the effect of π-bridge lengthening with phenylenevinylene and/or phenyleneethynylene units.\textsuperscript{134,142} Studies with the series of yne-linked complexes 1-162 to 1-167 (Figure 1.27), E-ene-linked complexes 1-168 to 1-175 (Figure 1.28) and ethoxy-substituted yne-linked complexes 1-176 to 1-181 (Figure 1.29) revealed several trends. The (formally) Ru\textsuperscript{II/III} redox potentials can be tuned in a systematic fashion, as they increase on replacing yne-linkage by ene-linkage at the phenylene adjacent to the metal, and on replacing dppe by dppm co-ligands, and decrease on π-bridge lengthening. The low-energy UV-vis-NIR bands are MLCT in nature, blue-shifting on π-bridge lengthening by addition of phenyleneethynylene units, and replacing E-ene by yne linkages. The β_0 values increase on π-bridge lengthening, replacing yne linkage by E-ene linkage at the phenylene adjacent to the metal center, and replacing dppm by dppe co-ligands, until the tri(phenyleneethynylene) is reached, further lengthening (from 1-177 to 1-178 or 1-180 to 1-181) resulting in a reduction of nonlinearity.

1.4.5 Metalloccenyl Complexes

An article in Nature by Green and co-workers describing the SHG merit of a substituted ferrocene\textsuperscript{148} alerted researchers to the potential of organometallics in nonlinear optics, and ferrocenyl complexes have continued to attract attention.\textsuperscript{149-161} Earlier reports utilized aryl bridges and nitro and other simple organic acceptor groups in conventional donor-bridge-acceptor compositions. Since
1.4. Second-Order Nonlinearities

Figure 1.28 Second-order NLO properties of Ru

Figure 1.29 Second-order NLO properties of ethoxy-substituted phenyleneethynylene-bridged Ru

[142]

[194]
1-182: \( R^1 = R^2 = \text{CH}_3 \),
\[ \beta \text{[Chloroform (HRS)]} = 279 \text{ (MeCN)} \]

1-183: \( R^1 = \text{CF}_3, \ R^2 = \text{Ph} \),
\[ \beta \text{[Chloroform (HRS)]} = 450 \text{ (MeCN)} \]

1-184: \( R^1 = R^2 = \text{CH}_3 \),
\[ \beta \text{[Chloroform (HRS)]} = 2633 \text{ (MeCN)} \]

1-185: \( R^1 = \text{CF}_3, \ R^2 = \text{Ph} \),
\[ \beta \text{[Chloroform (HRS)]} = 3333 \text{ (MeCN)} \]

1-186
\[ \mu \beta \text{ (HRS)} = 92 \times 10^{-48} \text{ esu (MeCN)} \]

1-187
\[ \mu \beta \text{ (HRS)} = 420 \times 10^{-48} \text{ esu (MeCN)} \]

1-188
\[ \mu \beta \text{ (HRS)} = 1120 \times 10^{-48} \text{ esu (MeCN)} \]

**Figure 1.30** Second-order NLO properties of ferrocenyl complexes with 2-dicyanomethylene-3-cyano-4-methyl-2,5-dihydrofuran acceptor substituents.\textsuperscript{[153]}

then, studies in the purely organic sphere by Dalton and co-workers have revealed improvements to this design.\textsuperscript{[162,163]} Coupling analogues of the Dalton 2-dicyanomethylene-3-cyano-4-methyl-2,5-dihydrofuran acceptor to ferrocene afforded 1-182 to 1-185 (Figure 1.30), the quadratic nonlinearities of which increase on replacement of methyl by trifluoromethyl and phenyl groups at the acceptor, and on incorporation of a thiénylvinyylene unit into the bridge. The bond length alternation along the chromophore charge-transfer axis in these molecules fall in the range 0.05–0.10 Å, and correlate closely with the magnitude of the hyperpolarizabilities. Complex 1-185 was doped into amorphous polycarbonate at a loading of 20% w/w, and a solution in cyclopentanone of the resulting composite was spin-coated onto an ITO slide. After poling, the film exhibited an electrooptic \( r_{33} \) coefficient of 25 pm V\(^{-1}\) at 1300 nm, similar in magnitude to efficient organic chromophore-doped films, despite the absence of sterically encumbering groups designed to disfavor aggregation that are usually found with the latter.\textsuperscript{[153]}
1.5. Third-Order Nonlinearities

1.4.6 Powder Measurements

Despite the fact that the need to determine molecular second-order NLO properties in order to gain a reliable idea of structure-property relationships has become more and more obvious over the past 10–20 years, a large number of reports on Kurtz powder measurements has still been published in the literature over the last 10 years.\textsuperscript{[164–317]} One of the main reasons for this is the facile access to bulk susceptibilities, since, experimentally, powder measurements are not very demanding compared to other techniques \textit{(vide supra)}. One obvious drawback, however, is the lack of information on properties at the molecular level. Moreover, the most of the measurements reported in the literature (cited above) were carried out at a single wavelength, which means that spectral dependencies have not been established. This type of measurement is also suffering from the aforementioned problem of potential centrosymmetric crystal packing of noncentrosymmetric molecular units, which, when bulk susceptibilities are evaluated through powder measurements, leads to a distortion of the results thus obtained.

1.5 Third-Order Nonlinearities

1.5.1 Complexes of Pyridyl or Polypyridyl Ligands

The cubic NLO properties of a large number of complexes incorporating pyridyl and polypyridyl have been assessed.\textsuperscript{[54,318–347]} The 2PA properties of polypyridine and alkynyl complexes through 2007 have been summarized.\textsuperscript{[11]}

Single-wavelength fs Z-scan studies on pyridinium-functionalized tris(bipy) complexes \textbf{1-189} to \textbf{1-197} (Figure 1.31) by Coe et al. have revealed a consistent increase in 2PA merit for \( \pi \)-system lengthening, while metal variation affords unclear outcomes.\textsuperscript{[54]}

Whereas the functionalized 1,10-phenthroline ligands in complexes \textbf{1-198} to \textbf{1-200} (Figure 1.32) fluoresce strongly in the free state, complexation to Ni\textsuperscript{II} quenches the fluorescence.\textsuperscript{[346]} A fs white-light continuum (WLC) was used to assess the 2PA cross-sections, the maxima red-shifting on complexation and on increasing the donor strength of the substituents. The maximal values increase on com-
Figure 1.31 Third-order NLO-properties of pyridinium-functionalized tris(bipy) complexes of Ru$^{II}$ and Fe$^{II}$.\textsuperscript{[54]}
1.5. Third-Order Nonlinearities

**Figure 1.32** Third-order NLO-properties of Ni$^{II}$-complexes incorporating functionalized 1,10-phenanthroline ligands\textsuperscript{[346]} (WLC = White-light continuum)

**Figure 1.33** Third-order NLO-properties of an octahedral ruthenium complex incorporating triethylene glycol-functionalized 5-fluorene-1,10-phenanthroline ligands\textsuperscript{[318]}

plexation, but are invariant across the three Ni$^{II}$ complexes. Related Ru$^{II}$ complexes (for photosensitizing) that incorporate triethyleneglycol groups to ensure lipophilicity and fluorenyl substituents to enhance fluorescence (Figure 1.33) have been explored for use in spatially-confined photodynamic therapy.\textsuperscript{[318]} While the maximal value at 740 nm of the example in Figure 1.33 is low (ca. 40 GM), it is much greater than those of common commercial dyes.

The 2PA efficiency of Zn$^{II}$ terpyridine complexes functionalized by aminostilbene units (Figure 1.34) has been examined by fs 2PA-induced photoluminescence.\textsuperscript{[339]} Cross-sections are lower than those of the free terpy ligands. This has been rationalized by (a) the orthogonal terpy ligands acting independently, and (b) coordination to Zn$^{II}$ increasing the acceptor properties of the terpy end of the ligand, which as a consequence has an increasingly cyanine-like behavior, although a significant cyanine-like contribution from a polyaromatic chromophore is unlikely.
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\[
\text{Figure 1.34} \quad \text{Third-order NLO-properties of Zn-complexes incorporating aminostilbene-functionalized terpyridine ligands.}^{[339]}
\]

### 1.5.2 Complexes of Porphyrins and Phthalocyanines

The cubic nonlinearities of complexes with phthalocyanines (through 2002)\(^{[78]}\) and porphyrins and related ligands (through 2005)\(^{[79]}\) have been summarized, and a selected summary of 2PA properties of porphyrins through 2007 has appeared.\(^{[348]}\) The robust nature of the core, established functionalization strategies, biocompatible nature of these molecules, and their strong nonlinear absorption properties serving to maintain considerable interest in this area.\(^{[84,107,349-486]}\)

Kim and co-workers investigated the 2PA behavior of monomeric Zn\(^{II}\) porphyrin complexes with azulenylethynyl substituents at the 5- and 15-\textit{meso}-positions.\(^{[408]}\) The substituents were varied so that D-\(\pi\)-D, D-\(\pi\)-A or A-\(\pi\)-A systems were obtained (Figure 1.35), observing an increase in \(\sigma_2\) compared to the example with phenylethynyl substituents at the 5- and 15-\textit{meso}-positions. The D-\(\pi\)-A system shows the largest value for \(\sigma_2\) (8030 GM), a four-fold increase compared to the phenylethynyl-substituted analogue and ascribed to the enlarged \(\pi\)-electronic interaction (CT character) and an efficient charge separation.

Humphrey and Kuciauskas\(^{[402]}\) employed different transition metal ions (Fe\(^{III}\), Mn\(^{III}\), Co\(^{II}\)) to establish the dependences of the second hyperpolarizability on the nature of the metal (Figure 1.36); compared to the free base porphyrin, an enhancement of an order of magnitude was found and attributed to CT transitions between the \(d\)-orbitals located at the metal and the \(\pi\)-system of the porphyrin. DFWM measurements on electropolymerized thin films of the metallated por-
1.5. Third-Order Nonlinearities

**Figure 1.35** Third-order NLO properties of 5,15-bis(azulenylethynyl) Zn\(^{II}\) porphyrins,\(^{[408]}\) established using the Z-scan technique.

Porphyrins were carried out, the Fe\(^{III}\) and Mn\(^{III}\) complexes showing local maxima in the \(\gamma\)-spectra between 7500–11 500 cm\(^{-1}\), whereas the Co\(^{II}\) porphyrin complex does not exhibit any 2PA. The bands were assigned to two-photon transitions between metal \(d\)-orbitals and macrocycle \(\pi^*\)-orbitals. The \(\sigma_2,\text{max}\)-value of the 2PA active Fe\(^{III}\) is greater than Mn\(^{III}\), an outcome likely to arise from the increased transition dipole moment of the Mn\(^{III}\) complex compared to the Fe\(^{III}\) complex.

**Figure 1.36** Third-order NLO properties of transition metal porphyrin complexes,\(^{[402]}\) established using the DFWM technique.\(^{[402]}\)
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\[ 1-212: R^1 = R^3 = 3,5-(t-Bu)_2C_6H_3, R^2 = R^4 = C=CSi(n-\text{Hex})_3 \]

\[ 1-213: R^1 = R^3 = 3,5-(t-Bu)_2C_6H_3, R^2 = H, X = C=C, M = Zn \]
\[ 1-214: R^1 = R^3 = 3,5-(t-Bu)_2C_6H_3, R^2 = H, X = C=C=CSi(n-\text{Hex})_3, M = Zn \]
\[ 1-215: R^1 = R^3 = 3,5-(t-Bu)_2C_6H_3, R^2 = C=CSi(n-\text{Hex})_3, X = C=C=CSi(n-\text{Hex})_3, M = Zn \]
\[ 1-216: R^1 = R^3 = 3,5-(t-Bu)_2C_6H_3, R^2 = C=CSi(n-\text{Hex})_3, X = C=C=4-C_6H_4C=C, M = Zn \]
\[ 1-217: R^1 = R^3 = 3,5-(t-Bu)_2C_6H_3, R^2 = C=CSi(n-\text{Hex})_3, X = Y, M = Zn \]

**Figure 1.37** Zinc porphyrin dimers with yne or aryl-yne linkages.\(^{[381]}\)

The effect of proceeding from monomeric to dimeric (or oligomeric) porphyrin complexes has been studied by Rebane et al. On-resonant wavelength-dependent NLO studies of Zn\(^{II}\) porphyrin dimers (Figure 1.37)\(^{[381]}\) revealed drastic \(\sigma_2\) enhancements (up to 500-fold) on proceeding from monomers to dimers (Figure 1.38). The increase in \(\sigma_2\) does not correlate with an increase in the conjugation path-length; instead, a combination of transition dipoles, detuning denominator, sharpening of 2PA transitions, and the strength of the second excited-state transition (based on the three-level model) was used to deliver a quantitative explanation for the observed NLO effects. The dimers exhibit singlet oxygen generation upon two-photon (and also one-photon) excitation, which is a requirement for their use in 2PA-induced photodynamic therapy (PDT).

The embedded metal center in phthalocyanine dimers or oligomers with yne-linkages were probed by Torres, Blau and co-workers,\(^{[390, 430]}\) using Z-scan measurements at 532 nm (see Figure 1.39). All examined complexes (1-218 to 1-223)
Figure 1.38 On-resonant wavelength-dependence studies of dimeric Zn$^{II}$ porphyrin complexes. Spectra were recorded using the Z-scan technique.$^{[381]}$
Figure 1.39 Third-order NLO properties of monomeric and ethynyl- and butadiynyl-linked dimeric transition metal phthalocyanines, determined through single-wavelength Z-scans.\cite{390,430}

are reverse saturable absorbers, with the butadiyne-linked dimers 1-222/1-223 showing stronger NLO responses than the corresponding ethynyl-linked analogues, regardless of the metal. For the monomeric complexes, complexation by zinc gives stronger responses (by more than one order of magnitude), but the inverse trend is found for the butadiyne-linked dimers, i.e. the cobalt complex gives a stronger response. The monomeric zinc phthalocyanine 1-218 and the butadiyne-linked dimeric cobalt complex 1-223 are the strongest optical limiters in the series.

The $\sigma_2$-spectra of tetramers 1-224 and 1-225 (Figure 1.40) were evaluated by Kobuke and Ogawa, using off-resonant 150 fs pulse wavelength-dependent Z-scan
measurements (Figure 1.41). The 2PA cross-sections of up to 7600 GM for the butadiyne-linked species represent a significant enhancement compared to the analogous array **1-224** in which the the butadiyne linkages are missing from the linked porphyrins. The stacking of the dimeric units results in an enhancement that scales more than just linearly with the number of porphyrin units. 3PA was found for butadiyne-linked tetramer **1-225**, with $\sigma_3$-values of $7.1 \cdot 10^{-89}$ m$^6$s$^2$ (1188 nm) and $1.8 \cdot 10^{-89}$ m$^6$s$^2$ (1282 nm), respectively.

The octamer **1-229** (Figure 1.42) was shown by Kobuke, Ogawa and coworkers to exhibit an exceptionally large $\sigma_2$-value of 61 000 GM.$^{[385]}$ Tetramer **1-228** (Figure 1.42) is structurally related to tetramer **1-225** (Figure 1.40), but has additional ether linkages, unlike **1-225**. Tetramer **1-228** exhibits an enhanced 2PA cross-section compared to the species without the ether linkages.

The substituent at the 3-position of the 1,4-pentadiynyl bridge in nickel porphyrin dimer carbocations was varied by Perry, Anderson and coworkers.$^{[453]}$ The absorption behavior of the dimers can be tuned,$^{[467]}$ and the carbocation shown in Figure 1.43 can be (reversibly) transformed into a neutral species, which quenches the NLO response from fs Z-scan measurements at 1550 nm.

The squaraines and porphyrins in Figure 1.44a) show large transition dipole moments for some of their 1PA bands, which renders them good candidates for strong two-photon absorbers.$^{[432]}$ Indeed, off-resonant wavelength-dependent 2PA-induced fluorescence measurements by Marder and co-workers showed that dimer **1-233** exhibits a $\sigma_{2,\text{max}}$ of 11 000 GM at 1050 nm (see Figure 1.44b), which is a 200-fold increase compared to that of the zinc porphyrin monomer unit ($\sigma_{2,\text{max}} = 50$ GM at 720 nm). At 1050 nm, the NLO responses of both the monomer and the linker are significantly smaller than that of the dimer. Anderson and co-workers examined the NLO properties of some 5-**meso**-15-**meso** butadiyne-linked porphyrin polymers (Figure 1.45).$^{[446]}$ Introducing aryleneethynylene substituents at the **meso** positions perpendicular to the polymer backbone extends the conjugation of the polymers but does not result in a change of the NLO response at the chosen near-resonant DFWM wavelength of 1064 nm. In the presence of Bipy, polymer **1-234** forms a double-strand ladder (**1-237**). On increasing the concentration of Bipy further, the double-strand cleaves to give the single-strand polymer
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1-224: R = n-Hept, $\lambda_{\text{max}} = 650$ (CHCl$_3$), $\sigma^2_{\text{Z-max}}$ (Z-scan, fs, 964 nm) = 370 GM (CHCl$_3$)

1-225: R = n-Hept, $\lambda_{\text{max}} = 770$ (CHCl$_3$), $\sigma^2_{\text{Z-max}}$ (Z-scan, fs, 887 nm) = 7600 GM (CHCl$_3$)

1-226: R = n-Hept, $\sigma^2_{\text{Z-max}}$ (Z-scan, fs, 873 nm) = 1800 GM (CHCl$_3$)

1-227: R = n-Hept, $\sigma^2_{\text{Z-max}}$ (Z-scan, fs, 873 nm) = 1200 GM (CHCl$_3$)

Figure 1.40 Third-order NLO properties of dimeric (1-226, 1-227) and tetrameric (1-224, 1-225) zinc porphyrins determined using wavelength-dependent Z-scan measurements (pulse length 120–150 fs). [433]
Figure 1.41 $\sigma_2$-spectra of zinc porphyrin tetramers 1-224 and 1-225. The spectra were measured using the Z-scan technique with laser pulses of 120–150 fs at wavelengths remote from one-photon absorption resonance. Triangles: 1-224; circles: 1-225.\textsuperscript{[433]}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure1_41}
\caption{Third-order NLO properties of zinc porphyrin tetramer 1-228 and octamer 1-229, measured by Z-scan using fs laser pulses at off-resonant wavelengths.\textsuperscript{[885]}}
\end{figure}
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![Chemical structures](image)

**Figure 1.43** Third-order NLO properties of 1,4-pentadiynyl linked cationic porphyrin dimer 1-230. Washing with water affords the neutral alcohol 1-231 reversibly, which quenches the NLO-response. NLO measurements were carried out using single-wavelength fs Z-scans.\[453\]

1-236;\[447\] the double-strand polymer is almost one order of magnitude more NLO efficient than the single-strand polymer.

The effect of modulating the dihedral angle between adjacent porphyrin units in the directly meso-linked porphyrin dimers, trimers, tetramers and higher oligomers in Figures 1.46–1.50 on their NLO behavior was studied using the Z-scan technique with fs laser pulses at 800 and 1200 nm.\[349\] The $\sigma_2$ values of the porphyrin dimers shown in Figure 1.46 decrease as the chain length of the dioxyacetone strap lengthens, i.e. as the porphyrin units are subject to increasing flexibility, allowing them to rotate out of coplanarity to reduce steric hindrance between the $\beta$-CH protons of adjacent porphyrin units.

A similar result was obtained for the analogous trimers 1-243 and 1-244 (Figure 1.47). Trimers exhibit larger NLO responses than do dimers with the same length of the dioxy(oligomethylene) strap (e.g. 1-241/1-243 or 1-242/1-244). The Zn centers of adjacent porphyrin units in the porphyrin chain in Figure 1.48 (2– 8 porphyrin units) are linked by 1,7-diaminoheptane linkages. Surprisingly, the NLO response decreases with increasing length of the porphyrin chain, consistent with the $\pi$-conjugation being restricted to the first two porphyrin units (1-245); $\pi$-conjugation into the remaining porphyrins in the trimer (1-246), tetramer (1-247) and octamer (1-248) is disfavored due to the large dihedral angle between adjacent porphyrin units. In contrast, lengthening the porphyrin chain while maintaining a small dihedral angle (close to coplanarity) results in a constant increase in the NLO-response from dimer 1-249 through to pentadecameter 1-253.
Figure 1.44 a) NLO properties of meso-ethynyl-functionalized zinc porphyrin 1-232 and its squaraine-linked dimeric analogue 1-233. b) Wavelength-dependent 2PA-induced fluorescence spectra (red: free squaraine linker; blue: monomer 1-232; green: dimer 1-233). [432]
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1-234: R\textsuperscript{1} = Me, R\textsuperscript{2} = X, R\textsuperscript{3} = H, M = Zn, n = 10-15, 
\(\chi^{(3)}_{\text{Re}}\) (Z-scan, ns, 1064 nm) = -1.9 \times 10^{-16} \text{ m}^2 \text{ V}^{-2} \text{ (pyridine/CHCl}_3)\text{*}

1-235: R\textsuperscript{1} = R\textsuperscript{2} = H, R\textsuperscript{3} = Y, M = Zn, n = 10-15, \(\lambda_{\text{max}} = 1000 \text{ nm (CHCl}_3)\), 
\(\chi^{(3)}_{\text{Re}}\) (DFWM, fs, 1064 nm) = -1.7 \times 10^{-16} \text{ m}^2 \text{ V}^{-2} \text{ (CHCl}_3)\text{*}

1-236: R\textsuperscript{1} = R\textsuperscript{2} = H, R\textsuperscript{3} = Y, M = Zn, Z, n = 10-15, \(\lambda_{\text{max}} = 900 \text{ nm (CHCl}_3)\), 
\(\chi^{(3)}_{\text{Re}}\) (DFWM, fs, 1064 nm) = 0.7 \times 10^{-17} \text{ m}^2 \text{ V}^{-2} \text{ (CHCl}_3)\text{*}

1-237: R\textsuperscript{1} = R\textsuperscript{2} = H, R\textsuperscript{3} = Y, M = Zn, n = 10-15, 
\(\lambda_{\text{max}} = 900 \text{ nm (CHCl}_3)\), 
\(\chi^{(3)}_{\text{Re}}\) (DFWM, fs, 1064 nm) = 6 \times 10^{-17} \text{ m}^2 \text{ V}^{-2} \text{ (CHCl}_3)\text{*}

* Values given per monomeric unit

Figure 1.45 Third-order NLO properties of butadiyne-linked polymers 1-234/1-235\textsuperscript{[446]} and 1-236/1-237\textsuperscript{[447]} determined by near-resonant fs DFWM experiments.
1.5. Third-Order Nonlinearities

![Chemical Structures]

1-238: $n = 1$, $\lambda_{\text{max}} = 650$ (toluene), $\sigma_2$ (Z-scan, fs, 800 nm) = 7500 GM (toluene)
1-239: $n = 2$, $\lambda_{\text{max}} = 650$ (toluene), $\sigma_2$ (Z-scan, fs, 800 nm) = 6330 GM (toluene)
1-240: $n = 3$, $\lambda_{\text{max}} = 650$ (toluene), $\sigma_2$ (Z-scan, fs, 800 nm) = 6120 GM (toluene)
1-241: $n = 4$, $\lambda_{\text{max}} = 650$ (toluene), $\sigma_2$ (Z-scan, fs, 800 nm) = 4830 GM (toluene)
1-242: $n = 5$, $\lambda_{\text{max}} = 650$ (toluene), $\sigma_2$ (Z-scan, fs, 800 nm) = 3920 GM (toluene)

Figure 1.46 Effect on $\sigma_2$ of changing the dihedral angle between adjacent porphyrin units in meso-linked porphyrin dimers.\textsuperscript{[349]}

![Chemical Structures]

1-243: $n = 4$, $\lambda_{\text{max}} = 650$ (toluene), $\sigma_2$ (Z-scan, fs, 800 nm) = 6550 GM (toluene)
1-244: $n = 5$, $\lambda_{\text{max}} = 650$ (toluene), $\sigma_2$ (Z-scan, fs, 800 nm) = 4650 GM (toluene)

Figure 1.47 Effect on $\sigma_2$ of changing the dihedral angle between adjacent porphyrin units in meso-linked porphyrin trimers.\textsuperscript{[349]}
(Figure 1.49). To enforce complete coplanarity of the polymer chains, additional direct linkages were introduced between the $\beta$-carbon atoms of adjacent porphyrin units (Figure 1.50), and the effect on $\sigma_2$ of increasing the chain length was explored, increasing the chain length resulting in an increase in $\sigma_2$. Osaka, Kim and their co-workers found the same trend with coplanar nickel porphyrin polymers, i.e. a monotonic increase in the NLO response with increasing chain length of the polymer backbone while coplanarity is enforced by two direct meso-$\beta$-bonds between adjacent porphyrin units.$^{474}$ The dimer 1-258 shows a $\sigma_2$-value of 8000 GM, which is a 800-fold increase compared to the monomer (1-257), while the largest value of $\sigma_2$ (41 400 GM) was found for the longest species (pentamer 1-261; Figure 1.51).

The optical limiting$^{487}$ properties of complexes of porphyrins or phthalocyanines have also been of considerable interest. Binding a cluster to an indium porphyrin complex to afford the complexes 1-263 and 1-264 (Figure 1.52) was shown by Yang and McEwan$^{426,469}$ to be accompanied by and increase in $\sigma_{\infty}/\sigma_0$, compared to the parent porphyrin 1-262.$^{469}$ Variation of the metal in similar porphyrin complexes did not result in significant changes in the optical limiting behavior, although a slight increase was observed for tin porphyrin 1-269 over the nickel, indium and zinc species.$^{426}$
1.5. Third-Order Nonlinearities

1-249: \( n = 1 \), \( \lambda_{\text{max}} = 620 \) (toluene),
\[ \sigma_2 \text{ (Z-scan, fs, 800 nm) } = 4500 \text{ GM (toluene) } \]

1-250: \( n = 2 \), \( \lambda_{\text{max}} = 680 \) (toluene),
\[ \sigma_2 \text{ (Z-scan, fs, 800 nm) } = 9500 \text{ GM (toluene) } \]

1-251: \( n = 3 \), \( \lambda_{\text{max}} = 680 \) (toluene),
\[ \sigma_2 \text{ (Z-scan, fs, 800 nm) } = 11 \text{ 800 GM (toluene) } \]

1-252: \( n = 7 \), \( \lambda_{\text{max}} = 710 \) (toluene),
\[ \sigma_2 \text{ (Z-scan, fs, 800 nm) } = 12 \text{ 800 GM (toluene) } \]

1-253: \( n = 15 \), \( \lambda_{\text{max}} = 710 \) (toluene),
\[ \sigma_2 \text{ (Z-scan, fs, 800 nm) } = 13 \text{ 200 GM (toluene) } \]

\[ R = \text{O(CH}_2)_n\text{Me} \]

**Figure 1.49** Effect on \( \sigma_2 \) of lengthening the porphyrin chain while keeping the dihedral angle between adjacent porphyrins constant.\(^{[349]}\)

1-254: \( n = 0 \), \( \lambda_{\text{max}} = 1100 \) (toluene), \( \sigma_2 \) (Z-scan, fs, 1200 nm) = 11 900 GM (toluene)

1-255: \( n = 1 \), \( \lambda_{\text{max}} = 900 \) (toluene), \( \sigma_2 \) (Z-scan, fs, 800 nm) = 33 100 GM (toluene)

1-256: \( n = 2 \), \( \lambda_{\text{max}} = 900 \) (toluene), \( \sigma_2 \) (Z-scan, fs, 800 nm) = 93 600 GM (toluene)

**Figure 1.50** Effect on \( \sigma_2 \) of lengthening the porphyrin chain while enforcing coplanarity of adjacent porphyrin units through three direct bonds between any two adjacent porphyrins.\(^{[349]}\)
Figure 1.51 Effect on $\sigma_2$ of lengthening the porphyrin chain in meso-$\beta$-linked porphyrin polymers while enforcing coplanarity of adjacent porphyrin units through three direct bonds between any two adjacent porphyrins.\cite{474}

The nonlinear absorption properties of monomeric main group and transition metal complexes of alkylated phthalocyanines were determined using the Z-scan technique (ns laser pulses at a repetition rate of 10 Hz) by Blau and Cook.\cite{351} The complexes exhibit reverse saturable absorption. Only the lead complex 1-279 and the indium complex 1-281 show a slight increase in the $\sigma_{ex}/\sigma_0$ ratio compared to that exhibited by the free ligand; indeed, complexation with nickel, copper and palladium decreases the ratio by up to 80%. The Pd and Cu species (1-278 and 1-277, respectively) show the lowest fluence threshold. Excluding 1-272, $F_{Th}$ decreases following complexation to the metal, i.e. the limiting behavior occurs at lower input fluences.

The optical limiting properties of Ga$^{III}$ and In$^{III}$ phthalocyanines have also been reported (Figure 1.54).\cite{362-364} Substitution of the metal-bound chloride ligand for arylxy- or aryl ligands and dimerization reduces the limiting threshold fluence and increases the nonlinear absorption. The sulfonyldiphenoxy-linked dimer 1-289 shows the largest nonlinear absorption.
1.5. Third-Order Nonlinearities

1-262: $R^1 = R^2 = R^3 = R^4 = 4$-$C_8$H$_8$Me, $R^5 = H$, $M = InN_3$, linear transmission = 88% (CH$_2$Cl$_2$), $\sigma_{uv}/\sigma_0$ (OPL, ns, 532 nm) = 2.9 (CH$_2$Cl$_2$)

1-263: $R^1 = R^2 = R^3 = R^4 = 4$-$C_8$H$_8$Me, $R^5 = H$, $M = In-E$, linear transmission = 88% (CH$_2$Cl$_2$), $\sigma_{uv}/\sigma_0$ (OPL, ns, 532 nm) = 4.2 (CH$_2$Cl$_2$)

1-264: $R^1 = R^2 = R^3 = R^4 = 4$-$C_8$H$_8$Me, $R^5 = H$, $M = In-G$, linear transmission = 88% (CH$_2$Cl$_2$), $\sigma_{uv}/\sigma_0$ (OPL, ns, 532 nm) = 4.6 (CH$_2$Cl$_2$)

1-265: $R^1 = R^2 = R^3 = R^4 = 4$-$C_8$H$_8$O=CSiMe$_3$, $R^5 = H$, $M = Zn$, linear transmission = 75%, $\sigma_0$ (OPL, ns, 532 nm) = 2 x 10^{-17} cm$^2$ (CH$_2$Cl$_2$), $\sigma_{uv}/\sigma_0 = 3.3$

1-266: $R^1 = R^2 = R^3 = R^4 = 4$-$C_8$H$_8$O=CSiMe$_3$, $R^5 = H$, $M = Ni$, linear transmission = 75%, $\sigma_0$ (OPL, ns, 532 nm) = 7 x 10^{-17} cm$^2$ (CH$_2$Cl$_2$), $\sigma_{uv}/\sigma_0 = n.a.$

1-267: $R^1 = R^2 = R^3 = R^4 = 4$-$C_8$H$_8$O=CSiMe$_3$, $R^5 = H$, $M = GaCl$, linear transmission = 75%, $\sigma_0$ (OPL, ns, 532 nm) = 2 x 10^{-17} cm$^2$ (CH$_2$Cl$_2$), $\sigma_{uv}/\sigma_0 = 3.4$

1-268: $R^1 = R^2 = R^3 = R^4 = 4$-$C_8$H$_8$O=CSiMe$_3$, $R^5 = H$, $M = InCl$, linear transmission = 75%, $\sigma_0$ (OPL, ns, 532 nm) = 2 x 10^{-17} cm$^2$ (CH$_2$Cl$_2$), $\sigma_{uv}/\sigma_0 = 3.0$

1-269: $R^1 = R^2 = R^3 = R^4 = 4$-$C_8$H$_8$O=CSiMe$_3$, $R^5 = H$, $M = SnCl$_2_, linear transmission = 75%, $\sigma_0$ (OPL, ns, 532 nm) = 2 x 10^{-17} cm$^2$ (CH$_2$Cl$_2$), $\sigma_{uv}/\sigma_0 = 4.4$

1-270: $R^1 = R^2 = R^3 = R^4 = Ph$, $R^5 = H$, $M = Zn$, linear transmission = 75%, $\sigma_0$ (OPL, ns, 532 nm) = 2 x 10^{-17} cm$^2$ (CH$_2$Cl$_2$), $\sigma_{uv}/\sigma_0 = 3.0$

**Figure 1.52** Optical limiting properties of In porphyrin complexes 1-263 and 1-264 incorporating Os$_3$ clusters,[46] and porphyrin complexes 1-265 to 1-270, showing the optical limiting behavior as a function of the metal.[426]
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![Chemical Structures]

1-271: R = n-Hex, M = 2H, \( \lambda_{\text{max}} = 733 \text{ nm (toluene)} \), \( \sigma_{\text{av}}/\sigma_0 \) (Z-scan, ns, 532 nm) = 14.5, \( F_{\text{TH}} = 16.8 \text{ J cm}^{-2} \)
1-272: R = n-Hex, M = Ni, \( \lambda_{\text{max}} = 702 \text{ nm (toluene)} \), \( \sigma_{\text{av}}/\sigma_0 \) (Z-scan, ns, 532 nm) = 2.4, \( F_{\text{TH}} = 18.0 \text{ J cm}^{-2} \)
1-273: R = n-Dec, M = Ni, \( \lambda_{\text{max}} = 702 \text{ nm (toluene)} \), \( \sigma_{\text{av}}/\sigma_0 \) (Z-scan, ns, 532 nm) = 2.1, \( F_{\text{TH}} = 13.3 \text{ J cm}^{-2} \)
1-274: R = n-Hex, M = Zn, \( \lambda_{\text{max}} = 705 \text{ nm (toluene)} \), \( \sigma_{\text{av}}/\sigma_0 \) (Z-scan, ns, 532 nm) = 11.4, \( F_{\text{TH}} = 7.1 \text{ J cm}^{-2} \)
1-275: R = n-Dec, M = Zn, \( \lambda_{\text{max}} = 705 \text{ nm (toluene)} \), \( \sigma_{\text{av}}/\sigma_0 \) (Z-scan, ns, 532 nm) = 11.7, \( F_{\text{TH}} = 13.6 \text{ J cm}^{-2} \)
1-276: R = i-Pent, M = Zn, \( \lambda_{\text{max}} = 703 \text{ nm (toluene)} \), \( \sigma_{\text{av}}/\sigma_0 \) (Z-scan, ns, 532 nm) = 12.2, \( F_{\text{TH}} = 6.6 \text{ J cm}^{-2} \)
1-277: R = i-Pent, M = Cu, \( \lambda_{\text{max}} = 705 \text{ nm (toluene)} \), \( \sigma_{\text{av}}/\sigma_0 \) (Z-scan, ns, 532 nm) = 8.6, \( F_{\text{TH}} = 4.6 \text{ J cm}^{-2} \)
1-278: R = n-Hex, M = Pd, \( \lambda_{\text{max}} = 690 \text{ nm (toluene)} \), \( \sigma_{\text{av}}/\sigma_0 \) (Z-scan, ns, 532 nm) = 5.9, \( F_{\text{TH}} = 2.1 \text{ J cm}^{-2} \)
1-279: R = n-Hex, M = Pb, \( \lambda_{\text{max}} = 746 \text{ nm (toluene)} \), \( \sigma_{\text{av}}/\sigma_0 \) (Z-scan, ns, 532 nm) = 16.1, \( F_{\text{TH}} = 9.8 \text{ J cm}^{-2} \)
1-280: R = i-Pent, M = Pb, \( \lambda_{\text{max}} = 744 \text{ nm (toluene)} \), \( \sigma_{\text{av}}/\sigma_0 \) (Z-scan, ns, 532 nm) = 14.2, \( F_{\text{TH}} = 7.1 \text{ J cm}^{-2} \)
1-281: R = n-Hex, M = In(4-C6H4F), \( \lambda_{\text{max}} = 728 \text{ nm (toluene)} \), \( \sigma_{\text{av}}/\sigma_0 \) (Z-scan, ns, 532 nm) = 16.2, \( F_{\text{TH}} = 10.1 \text{ J cm}^{-2} \)
1-282: R = n-Hex, M = Si(OH)2, \( \lambda_{\text{max}} = 704 \text{ nm (toluene)} \), \( \sigma_{\text{av}}/\sigma_0 \) (Z-scan, ns, 532 nm) = 12.4, \( F_{\text{TH}} = 9.2 \text{ J cm}^{-2} \)

Figure 1.53 Optical limiting properties of main group and transition metal phthalocyanine complexes.[531]

1.5.3 Schiff Base Complexes

Schiff base complexes continue to attract interest for both their quadratic (vide supra) and cubic NLO properties.[488–504] The ZnII complexes 1-292 and 1-293 in Figure 1.55 have been shown by Goswami, Bharadwaj and co-workers to possess very large 2PA cross-sections at 890 nm (fs Z-scan), in contrast to the free ligand which is inactive at this wavelength. Complexation enhances the weak acceptor character of the central diimine unit in these ligands possessing a formally D-π-A-π-D composition. Proceeding to the ZnII and CuI complexes 1-294 and 1-295 results in a further six-fold increase, concomitant with the progression to an octupolar structure. The zinc complex is the more efficient, consistent with the greater acceptor character of ZnII compared to CuI.[490]

1.5.4 Metal Alkynyl Complexes

Ruthenium (and to a lesser extent osmium) alkynyl complexes are a class of complexes considered in Chapters 2 and 3 of this work, and for that reason they
1.5. Third-Order Nonlinearities

1-283: R = t-Bu; M = GaCl, $\lambda_{\text{max}} = 400$ nm (toluene),
$\sigma_{\text{UF}}/\sigma_0$ (OPL, ns, 532 nm) = 13.5 (toluene)

1-284: R = t-Bu; M = Ga(4-OC6H4H-CI), $\lambda_{\text{max}} = 356$ nm (toluene),
$\sigma_{\text{UF}}/\sigma_0$ (OPL, ns, 532 nm) = 9.5 (toluene)

1-285: R = t-Bu; M = Ga(4-C6H4CF3),
$\lambda_{\text{max}} = 410$ nm (toluene),
$\sigma_{\text{UF}}/\sigma_0$ (OPL, ns, 532 nm) = 14 (toluene)

1-286: R = t-Bu; M = InCl, $\lambda_{\text{max}} = 358$ nm (toluene),
$\sigma_{\text{UF}}/\sigma_0$ (OPL, ns, 532 nm) = 27.5 (toluene)

1-287: R = t-Bu; M = In(4-C6H4CF3), $\lambda_{\text{max}} = 369$ nm (toluene),
$\sigma_{\text{UF}}/\sigma_0$ (OPL, ns, 532 nm) = 15 (toluene)

1-288: R = t-Bu, M = In, X = no bridge, L = Me2NCH2CH2NMMe2,
$\lambda_{\text{max}} = \text{n.a.}$, $\sigma_{\text{UF}}/\sigma_0$ (OPL, ns, 532 nm) = 13.0 (toluene)

1-289: R = t-Bu; M = Ga, X = O-4-C6H4S(O)2-4-C6H4O, L1 = L2 = no ligand,
$\lambda_{\text{max}} = 357$ nm, $\sigma_{\text{UF}}/\sigma_0$ (OPL, ns, 532 nm) = 4.8 (toluene)

1-290: R = t-Bu; M = Ga, X = O, L1 = L2 = no ligand,
$\lambda_{\text{max}} = 360$ nm, $\sigma_{\text{UF}}/\sigma_0$ (OPL, ns, 532 nm) = 11.3 (toluene)

1-291: R = t-Bu; M = In, X = O, L1 = L2 = no ligand,
$\lambda_{\text{max}} = 360$ nm, $\sigma_{\text{UF}}/\sigma_0$ (OPL, ns, 532 nm) = 12.4 (toluene)

**Figure 1.54** Optical limiting properties of monomeric and dimeric gallium and indium phthalocyanines.[362-364]

1-292: R = CI, M = Zn(ClO4)2, $\lambda_{\text{max}} = 448$ nm (CH2Cl2),
$\sigma_2$ (Z-scan, fs, 890 nm) = 1800 GM (CH2Cl2)

1-293: R = CN, M = Zn(ClO4)2, $\lambda_{\text{max}} = 446$ nm (CH2Cl2),
$\sigma_2$ (Z-scan, fs, 890 nm) = 1700 GM (CH2Cl2)

1-294: M = Zn(ClO4)2, $\lambda_{\text{max}} = 459$ nm (CH2Cl2),
$\sigma_2$ (Z-scan, fs, 890 nm) = 10 700 GM (CH2Cl2)

1-295: M = Cu(BF4), M = Zn(ClO4)2, $\lambda_{\text{max}} = 461$ nm (CH2Cl2),
$\sigma_2$ (Z-scan, fs, 890 nm) = 10 900 GM (CH2Cl2)

**Figure 1.55** Third-order NLO properties of ZnII and CuI Schiff base complexes.[490]
are of particular interest to the author. But beyond the present work, metal alkynyl complexes for third-order NLO materials have been (and still are) an extremely active research area.\cite{134,136,140,141,505-532}

Humphrey and Samoc and their co-workers have examined the third-order NLO behavior of dipolar, quadrupolar, and octupolar ruthenium alkynyl complexes. Z-scan spectral dependence studies of linear Ru\textsuperscript{II} alkynyl complexes 1-162, 1-163, 1-177, 1-178 and 1-181 (Figure 1.56) revealed an approximate correspondence between twice the energy of the one-photon absorption bands and the energy of the major two-photon absorption bands, with evidence of the long wavelength features having a three-photon absorption behavior.\cite{134} As with quadratic nonlinearity, the two-photon absorption cross-section for these complexes is maximized at the tri(phenylenethynylene) complex 1-177; further \(\pi\)-system lengthening results in decreasing importance of the LUMO\textsuperscript{+}–HOMO transition and on-axis rotation-mediated change in the relative intensities of two or more crucial low-lying transitions, both of which serve to reduce the nonlinearity from the continuing increase that may otherwise have been anticipated.

Figure 1.56 Third-order NLO properties of linear ethoxy-substituted ruthenium alkynyl complexes.\cite{134}
1.5. Third-Order Nonlinearities

![Chemical Structure](image)

**Figure 1.57** Third-order NLO properties of linear ruthenium acetylide complexes incorporating oligo(p-phenyleneethynylene) [OPE] linkages.\[^{508}\]

In a similar fashion, Humphrey, Samoc and co-workers investigated the NLO properties of a systematically varied series of linear oligo(p-phenyleneethynylene)-linked ruthenium acetylide complexes with hexyloxy solubilizing units (Figure 1.57), to study the effect of \( \pi \)-bridge lengthening on the NLO response.\[^{508}\] The centrosymmetric complexes have a D-\( \pi \)-D composition; wavelength-dependent Z-scan measurements indicate that \( \sigma_{2,\text{max}} \) generally increases with the chain length, but that the position of the peak does not change when the chain length is altered. The hexyloxy solubilizing groups are not electronically innocent; the linear absorption spectrum is red-shifted on introducing the solubilizing units. The 2PA spectra, however, were found not to be influenced by the presence of these groups. The \( \sigma_2 \) peak position is invariant to all structural variations investigated, including the type of peripheral group and the position of the metal within the OPE chain.

The NLO properties of octupolar complexes have also been of interest. The reader will find that the octupolar (star-shaped and dendritic) complexes presented
CHAPTER 1. Coordination Compounds and Organometallic Complexes for Nonlinear Optics

Figure 1.58 Schematic representation of two ways to depict octupolar complexes. Left: structure drawn fully, i.e. with all arms shown. Right: abbreviated representation. Dark grey (C) = core unit; light-grey = building blocks for linking units; grey (M) = metal center. Wavy lines indicate that the very same arm that is shown (not including the core) propagates from these positions.

in the remainder of this chapter and in Chapters 2 and 3 become very large with increasing number of phenyleneethynylene units incorporated in their arms.\footnote{The expression arm refers to a linear or branched fragment of an octupolar system that is connected to the central unit (whether it be phenyl, nitrogen, boron or other groups). In octupolar systems, three such arms are present in each complex or molecule, and in some quadrupolar systems there are four arms. Branched arms such as found throughout this and the following chapters are sometimes referred to as „dendrons“} Although the author intended to draw complete structures wherever possible or appropriate, in some schemes this was not practical. In those cases, the reader will find an abbreviated representation of star-shaped complexes, as shown on the right-hand side of Figure 1.58. In this sense, the structures for complexes 1-304 to 1-306 (Figure 65) and 1-307/1-308 (Figure 67) represent octupolar complexes with three equivalent arms being connected to the central phenyl ring.

Wavelength-dependence studies of the cubic NLO properties of these octupolar complexes revealed that refractive nonlinearity is maximized at a longer wavelength for the stilbene-linked dendrimers (Figure 1.60) than for the phenyleneethynylene-linked examples (Figure 1.61b), with the maximal values experiencing a nonlinear increase upon increasing dendrimer generation.\cite{516,524} The absorptive nonlinearities are positive through the spectral range for these complexes (i.e. they are two- or three-photon absorbers through this range); 1-308 possesses a record 3PA coefficient under fs conditions (see Figure 1.62), and the stilbene
1.5. Third-Order Nonlinearities

![Chemical structures](image)

**Figure 1.59** Structures of zero-generation (1-304, 1-305) and first-generation (1-306) ruthenium acetylide stilbene-linked dendrimers.\[^{516}\]

examples exhibit appreciable nonlinear absorption at the “telecommunications wavelength” of 1300 nm.

The N-cored analogues 1-277, 1-278 and 1-279 (Figure 1.63 on page 69) have been examined because planarity at the $sp^2$-hybridized nitrogen and involvement in $\pi$-delocalization of the occupied $p_z$ orbital may increase nonlinearity.\[^{521}\] Spectral dependence studies of the cubic nonlinearity revealed 2PA behavior below 1000 nm, with maximal values suggestive of an NLO dendritic effect (a nonlinear increase in nonlinearity upon increasing dendrimer generation; also referred to as cooperative effect). Beyond 1000 nm, data are consistent with 3PA-induced photochemistry. The 2PA cross-sections of these dendrimers are larger than those of comparable N-cored organic dendrimers, an increase in performance that is maintained when the outcomes are scaled by “effective number of electrons”, molecular weight, molecular volume, or even the cost of production.\[^{521,534,535}\] Scaling of NLO data will be discussed in more detail in Chapters 2 and 3.

Cubic nonlinearities of ruthenium alkynyl complexes have been switched under electrochemical control.\[^{536}\] In the resting state, the low-energy transition in these complexes is MLCT in nature. Oxidation, exploiting the Ru$^{II/III}$ couple, results
Figure 1.60 Wavelength-dependent $\gamma$-spectra of stilbene-linked Ru$^\text{II}$ acetylide dendrimers a) 1-304, b) 1-305, and c) 1-306.
Figure 1.61 a) Structures of first-generation phenyleneethynylene-linked ruthenium acetylide dendrimers with (1-307) a phenylacetylide capping group and (1-308) an electron-withdrawing p-nitrophenylacetylide capping group.\footnote{533} b) Wavelength-dependent $\gamma$-spectrum of the nitro-substituted dendrimer 1-308.\footnote{524}
Figure 1.62  a) $\sigma_2$-spectrum of the nitro-substituted first-generation Ru$^{II}$ acetylidyne dendrimer 1-276.  b) $\sigma_3$-spectrum of the same dendrimer. [524]
in the appearance of a low-energy LMCT transition. The cubic nonlinearities are also modified following oxidation, the complexes being two-photon absorbers at 800 nm in the resting state and saturable absorbers at that wavelength following oxidation. This approach to switching nonlinearities has been extended to demonstrate multi-state NLO switching. Coupling the ruthenium alkynyl unit to a more easily oxidizable iron center permits sequential access to Fe$^{II}$Ru$^{II}$, Fe$^{III}$Ru$^{II}$, and Fe$^{III}$Ru$^{III}$ states on stepwise oxidation of 1-312 (Figure 1.65), with the oxidation processes resulting in strong changes to linear and NLO properties; in particular, the Fe$^{II}$Ru$^{II}$ form of 1-312 possesses negligible absorptive nonlinearity at 790 nm, but the Fe$^{III}$Ru$^{II}$ state is a two-photon absorber at this wavelength, and the Fe$^{III}$Ru$^{III}$ form is a saturable absorber (or in other words, the three oxidation states afford successively zero, positive, and negative values of the absorptive nonlinearity at this wavelength).[523]

Three-state cubic NLO switching has also been demonstrated with quadrupolar ruthenium acetylide complex 1-313,[507] but in this case using independent stimuli (Figure 1.66). Oxidation, as above, converts the Ru$^{II}_4$ state to the Ru$^{III}_4$ form, whereas protonation affords a tetra(vinylidene) complex tetracation, in both cases resulting in strong changes to linear and NLO properties. This idea has been extended to include photochemical switching. Ruthenium acetylide complex 1-314 (Figure 1.67) contains a dithienylperfluorocyclopentene unit that
Figure 1.64 $\gamma_{Re}$- and $\gamma_{Im}$-spectra of N-cored zero-generation dendrimers a) 1-309 and b) 1-310 and c) first-generation dendrimer 1-311, recorded from fs Z-scan experiments.\cite{521}
1.5. Third-Order Nonlinearities

![Chemical structure](image)

**Figure 1.65** Multi-state NLO switching in a mixed-metal iron ruthenium acetylide complex.\cite{523}

1-312: $\lambda_{\text{max}} = 400$ nm (CH$_2$Cl$_2$),
$\sigma_2$ (Z-scan, fs, 790 nm) = 0 GM (CH$_2$Cl$_2$)

1-312*: $\lambda_{\text{max}} = 1124$ nm (CH$_2$Cl$_2$),
$\sigma_2$ (Z-scan, fs, 790 nm) = 420 GM (CH$_2$Cl$_2$)

1-312**: $\lambda_{\text{max}} = 706$ nm (CH$_2$Cl$_2$),
$\sigma_2$ (Z-scan, fs, 790 nm) = -250 GM (CH$_2$Cl$_2$)

**Figure 1.66** Protic and electrochemical NLO switching of the quadrupolar ruthenium acetylide complex 1-313.\cite{507}

1-313: $\lambda_{\text{max}} = 470$ nm (CH$_2$Cl$_2$), $\sigma_{2,\text{max}}$ (Z-scan, fs, 750 nm) = 1100 GM (CH$_2$Cl$_2$)

1-313*: $\lambda_{\text{max}} = 925$ nm (CH$_2$Cl$_2$), $\sigma_{2,\text{max}}$ (Z-scan, fs, 750 nm) = -1800 GM (CH$_2$Cl$_2$)

1-313-H$_4$*: $\lambda_{\text{max}} = 410$ nm (CH$_2$Cl$_2$), $\sigma_{2,\text{max}}$ (Z-scan, fs, 750 nm) = 1000 GM (CH$_2$Cl$_2$)
CHAPTER 1. Coordination Compounds and Organometallic Complexes for Nonlinear Optics

![Chemical structures](image)

**Figure 1.67** Ruthenium acetylide complex 1-314 incorporating a dithienylperfluorocyclopentene unit for multi-state NLO switching. The open (1-314-o) and closed (1-314-c) forms of the dithienyl unit add an additional dimension of switchability to the aforementioned protic and electrochemical dimensions.\(^{[513]}\) The switching unit has been highlighted for clarity.

can be reversibly photoisomerized between open (1-314-o) and closed (1-314-c) forms, alkynyl (a) ligands that can be reversibly protonated to the corresponding vinylidene (v) forms, and ruthenium centers that undergo reversible oxidation (II ↔ III). The lack of reversible oxidation of the vinylidene forms, however, restricts the number of switchable states to six. The six switchable states can be interconverted along seven pathways, each of which results in distinct changes to the nonlinear absorption; some of these outcomes have been used to demonstrate NOR and INHIBIT logic gates.\(^{[513]}\) Figure 1.68 shows the results of wavelength-dependent fs Z-scan measurements for three of the aforementioned states.

The effect of \(sp\)-carbon chain lengthening on cubic NLO properties of the platinum-terminated polyacrydyl complexes 1-315 to 1-321 has been examined by broad spectral range Z-scan studies.\(^{[525]}\) The 2PA merit increases markedly on lengthening the carbon chain, affording complexes with extremely high 2PA/MW coefficients. The saturation length was not reached in these studies, despite examples up to \(C_{24}\) being assessed. Extrapolation to the \(C_{\infty}\) case suggested a 2PA maximum for carbyne at ca 1000 nm.

### 1.5.5 Other Complexes and Optical Limiting

Multi-photon absorption is advantageous in applications for which tight spatial control is needed. Ford and co-workers have exploited two-photon absorption at a wavelength at which tissue has strong transparency (800 nm) to demonstrate two-photon excited evolution of NO from the iron sulfide complexes 1-322 and
Figure 1.68 $\sigma_2$-spectra of six distinct states of the multi-state switch 1-314,[313] obtained from wavelength-dependent fs Z-scan measurements. o = open form; c = closed form; a = acetylide form; v = vinylidene form; II = Ru in oxidation state II; III = Ru in oxidation state III. a) $\sigma_2$-spectra of open acetylide form in the oxidation states II and III. b) Open and closed forms of the vinylidene complex in oxidation state II. c) Closed acetylide form in oxidation states II and III.
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Figure 1.69 Third-order NLO properties of platinum-terminated polynediy1 complexes with varying sp-carbon chain lengths.\textsuperscript{525}

1-323 (Figure 1.70), the two-photon excited fluorescence of the latter being four times that of the former.\textsuperscript{537,538}

As is clear from the examples above, employing the classic donor-bridge-acceptor construction for efficient organic NLO molecules in a coordination/organometallic environment gives considerable opportunity to enhance nonlinearity and flexibility to optimize responses. Fullerenes are excellent electron acceptors and tetrathiarevalenes are highly electron rich; coupling these units with a cobaltaldithiolen bridge has afforded 1-324 and 1-325 (Figure 1.71 on the next page), which have been cast onto SiO\textsubscript{2} substrates. The resultant assemblies were studied by THG,

Figure 1.70 Sulfide complexes undergoing 2PA-initiated emission of NO.\textsuperscript{537,538}

1-322: $\lambda_{\text{max}} = 520$ nm (MeCN/phosphate buffer),
\[ \sigma_2 (\text{TPAPL, fs, 800 nm}) = 63 \text{ GM (MeCN/phosphate buffer)} \]

1-323: $\lambda_{\text{max}} = 450$ nm (THF),
\[ \sigma_2 (\text{TPAPL, fs, 800 nm}) = 246 \text{ GM (THF)} \]
1.5. Third-Order Nonlinearities

Figure 1.71 Cobaltadithiolene-substituted fullerene monomer 1-324 and the analogous cobaltadithiolene-bridged dimer 1-325.\textsuperscript{[538]}

with 1-325 being shown to be twice as efficient as 1-324, an outcome ascribed to the importance of the symmetric charge-transfer excitation for the former.\textsuperscript{[538]}

A variety of compounds and complexes have proved efficient at optical limiting, for example complexes with phthalocyanines (summarized through 2002\textsuperscript{[78]}) and porphyrins and related ligands (summarized through 2005\textsuperscript{[79]}). A few examples have already been displayed above (page 59 ff.) Dialkynylbis(phosphine)platinum complexes have also been of long-standing interest as power limiters. Examples in which the alkynyl ligands are functionalized with electron donating or withdrawing substituents (and therefore of the D-\(\pi\)-D or A-\(\pi\)-A compositions, respectively, that have been shown to be efficient 2PA absorbers) were examined by two-photon excited fluorescence under fs conditions, with 2PA efficiency following the trend 1-327 > 1-329 > 1-326 > 1-328 (Figure 76).

\textsuperscript{[522]} In these complexes, one-photon excitation to a singlet state is followed by inter-system crossing to populate a triplet state that is strongly absorbing and very long-lived (\(\tau > 100\) \(\mu\)s). Related diplatinum complexes linked by a 2,5-diphenyl-1,3,4-oxadiazole group (Figure 76), as well as truxene-cored octupolar examples (Figure 77), have also been explored, their two-photon excited fluorescence-derived 2PA coefficients being smaller.\textsuperscript{[605]}
CHAPTER 1. Coordination Compounds and Organometallic Complexes for Nonlinear Optics

1-326: $\lambda_{\text{max}} = 402$ nm ($C_6H_6$), $\sigma_{2,\text{max}}$ (TPEF, fs, 649) = 415 GM ($C_6H_6$)

1-327: $\lambda_{\text{max}} = 383$ nm ($C_6H_6$), $\sigma_{2,\text{max}}$ (TPEF, fs, 612) = 780 GM ($C_6H_6$)

1-328: $\lambda_{\text{max}} = 397$ nm ($C_6H_6$), $\sigma_{2,\text{max}}$ (TPEF, fs, 634) = 290 GM ($C_6H_6$)

1-329: $\lambda_{\text{max}} = 397$ nm ($C_6H_6$), $\sigma_{2,\text{max}}$ (TPEF, fs, 644) = 480 GM ($C_6H_6$)

Figure 1.72 Optical limiting properties of dialkynylbis(phosphine)platinum complexes with functionalized alkynyl ligands.$^{[522]}$

1-330: $\lambda_{\text{max}} = 370$ nm ($C_6H_6$), $\sigma_2$ (TPEF, fs, 720) = 17 GM ($C_6H_6$)

1-331: $\lambda_{\text{max}} = 308$ nm ($C_6H_6$), $\sigma_2$ (TPEF, fs, 720) = 41 GM ($C_6H_6$)

Figure 1.73 Linear 2,5-diphenyl-1,3,4-oxadiazole-substituted diplatinum complexes with optical limiting properties derived from two-photon excited fluorescence (TPEF) studies.$^{[505]}$
Figure 1.74  Truxene-cored octupolar diplatinum complexes with optical limiting properties derived from two-photon excited fluorescence (TPEF) studies. [509]
CHAPTER 1. Coordination Compounds and Organometallic Complexes for Nonlinear Optics

1-336: $R = H$, $n = 2$, linear transmission = 90\% (THF), clamping level (OPL, 532 nm) = 9 $\mu$J (THF)

1-337: Linear transmission = 90\% (THF), clamping level (OPL, 532 nm) = 7.6 $\mu$J (THF), 3.5 $\mu$J (PMMA matrix)

1-338: Linear transmission = 90\% (THF), clamping level (OPL, 532 nm) = 7.1 $\mu$J (THF)

1-339: Linear transmission = 90\% (THF), clamping level (OPL, 532 nm) = 6.3 $\mu$J (THF)

1-340: Linear transmission = 90\% (THF), clamping level (OPL, 532 nm) = 6.6 $\mu$J (THF)

Figure 1.75 Platinum alkynyl complexes with polyester dendrons of varying generations and their Z-scan-derived clamping levels.\cite{529}

One key consideration with such complexes is the lifetimes of relevant excited states, which are frequently affected by intermolecular collisions with quenchers or other chromophores. Malmström and co-workers decorated the periphery of platinum alkynyl complexes with polyester dendrons of varying generations (1-336 to 1-340; Figure 78).\cite{529} The clamping levels for the resulting complexes were assessed by Z-scan at several wavelengths, and shown to decrease as the dendron generation increased, the increased shielding of the chromophore leading to increased excited states' lifetimes and stronger excited state absorption. Related platinum alkynyl complexes were functionalized by "click" chemistry to attach triazole-appended bulky ester groups at various sites (1-342 to 1-345; Figure 79), improving the clamping level significantly.\cite{531} These chromophores were incorporated into poly(methylmethacrylate) matrices, with physically doped
1.5. Third-Order Nonlinearities

Figure 1.76 Triazole-substituted platinum alkynyl complexes with optical limiting properties.\textsuperscript{[530,531]}

1-342: \( n = 1 \), Linear transmission = 90\% (THF),
clamping level (OPL, 532 nm) = 8 \( \mu \)J (THF)

1-343: \( n = 2 \), Linear transmission = 80\% (THF),
clamping level (OPL, 532 nm) = 2.5 \( \mu \)J (THF),
linear transmission = 90\% (PMMA),
clamping level (OPL, 532 nm) = 3.9 \( \mu \)J (PMMA matrix)

1-344: Linear transmission = 90\% (PMMA),
clamping level (OPL, 532 nm) = 8.5 \( \mu \)J (PMMA matrix)

1-345: \( n = 1 \), Linear transmission = 69\% (THF),
clamping level (OPL, 532 nm) = 5.5 \( \mu \)J (THF)
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examples possessing lower clamping levels than those in which the platinum alkynyl units are incorporated by chemical cross-linking.\textsuperscript{530}

Metal clusters belong to a group of intensely reported materials in the field of nonlinear optics.\textsuperscript{539–572} Examples of wavelength-dependent NLO measurements on clusters are rare.\textsuperscript{568} Most commonly, second hyperpolarizabilities or third-order susceptibilities are determined (through single-wavelength Z-scan measurements\textsuperscript{2}; not so much through DFWM\textsuperscript{555}), or the optical limiting behavior is explored.\textsuperscript{3}

\textsuperscript{2} Single-wavelength Z-scan measurements\textsuperscript{541,543–545,551,554,556,557,562,565,567}

\textsuperscript{3} Optical limiting behavior,\textsuperscript{542,550,552,553,563,564,566,573}
2 Stars – Unbranched Octupolar Ruthenium Acetylide Complexes

2.1 Introduction

In 1931, Maria Göppert-Mayer derived the theory for the physical process that is today known as two-photon absorption (2PA). In this process, a light wave of photons with the energy \( h\nu \) interacts with a molecule in which the energy gap between the ground state and the first excited state is \( h(2\nu) \).\(^{[574]}\) To overcome the large energy gap, two photons have to interact with the molecule simultaneously to combine their energies. As Göppert-Mayer described, the probability of the simultaneous interaction with the molecule is low; a high density of photons is required for the process to be detectable. Light/microwave amplification by stimulated emission of light (LASER/MASER) was proposed,\(^{[575,576]}\) and was then successfully used\(^{[577-581]}\) to harvest light of high intensity in the early 1960s. After that, it did not take long until 2PA,\(^{[582,583]}\) and three-photon absorption (3PA)\(^{[584]}\) and other NLO effects such as second-harmonic generation,\(^{[585,586]}\) were first observed experimentally. The first experiments were carried out on inorganic materials, such as quartz,\(^{[585]}\), europium-doped calcium fluoride,\(^{[582]}\) or other inorganic salts\(^{[587-589]}\) (although some organic salts were also investigated\(^{[590,591]}\)). Organic compounds were soon recognized as good candidates for NLO materials for various reasons. Due to the vast number of possible compounds that are synthetically accessible, there is a great diversity of materials, which allows tuning of the NLO properties. Facile processability of organic materials (e.g. films or solutions in common organic solvents, rather than just crystalline samples) is a
great advantage. Another advantage is the fact that organic materials consist of molecular units (except in cases of polymers), since NLO phenomena resulting from electronic polarization on the molecular level take place on a faster time scale than ionic polarization in inorganic solid-state materials. A limiting factor here are selection rules. For example, centrosymmetric molecules or complexes cannot possess second-order (and other even-order) NLO effects, which decreases the number of compounds available for such purposes. The systematic investigation of structure-property relationships in organic materials showing second-order NLO effects began in the late 1960s; strong NLO responses were observed where strong intramolecular charge transfers (provided the material is noncentrosymmetric) accompany the light-matter interaction. This was displayed through a variation of donor-bridge-acceptor systems. Attempts to increase third-order NLO effects of organic materials were also made.

Proceeding from merely organic NLO materials to organometallic materials combines the aforementioned advantages that organic materials have with a further increase of diversity (type of metal center(s), ligand variation), possible switching properties where the incorporated metal center undergoes reversible redox processes, and high chemical and thermal stability (depending on the nature of the metal). The metal centers can adopt the role of either electron donors or electron acceptors, depending on their oxidation state and ligation. Low-lying charge transfers, such as metal-to-ligand charge transfers (MLCT) or ligand-to-metal charge transfers (LMCT), are additional features of organometallic complexes that contribute to facilitate changes in the charge distribution across the complexes. These effects increase the polarizability of the molecule (compared to organic analogues), which in turn enhances NLO effects. Early examples of organometallic complexes have been investigated for their second-order and third-order NLO properties, which can be found in the literature of the late 1980s. Many of those reports involved ferrocene and other metallocene complexes. In these complexes, however, the charge transfer from the metal to the cyclopentadienyl (Cp) ligand is orthogonal to the π-conjugated substituents attached to the Cp ligand, which hinders electron delocalization. Humphrey and co-workers have been investigating the NLO properties of ruthenium vinylidenes and acetylide complexes as these complexes feature a good overlap of orbitals located at the metal center and α-carbon atoms of π-conjugated
substituents attached to the metal center due to the linearity of such systems. At the same time, other groups indicated the potential strength of octupolar structures for NLO materials, suggesting fertile fields of study other than the merely one-dimensional (dipolar) approach. One important advantage of octupolar compounds is that, due to the cancellation of dipole moments, crystal packing in a centrosymmetric fashion is less likely than in dipolar systems.

2.2 Synthesis and Characterization

2.2.1 Synthetic Methods and Pathways

Synthesis of extended organic phenylethynyl-based systems with 2-ethylhexyl solubilizing groups.

The overall synthetic aim of the work described in this Chapter was to extend the π-conjugation pathlength in octupolar ruthenium acetylide complexes where the individual metal centers are linked via oligo(phenylethynyl) bridges. Figure 2.1 depicts a schematic representation of that idea. The abbreviated representation of

![Figure 2.1](image.png)

**Figure 2.1** Schematic representation of ruthenium acetylide complexes with oligo(phenylethynyl) bridges of varying length linking the metal centers. A) Full structure. B) Abbreviated structure, the depicted metal-substituted oligo(phenylethynyl) bridge repeating at the wavy lines.
Figure 2.2 Divergent (top) and convergent (bottom) approach towards octupolar metal complexes. Dark gray (C): core unit. Light gray: building blocks for linking units. Gray (M): metal center. Solid black lines represent C≡C triple bonds, light-gray spheres represent 1,4-substituted phenyl rings.

star-shaped complexes, as shown on the right-hand side of Figure 2.1, has already been introduced in Chapter 1 (see page 64).

There are two major pathways to approach systems as sketched in Figure 2.1, both having advantages and disadvantages. The first is the divergent method, where a small building block is attached to a core unit with three reactive sites. This affords a core unit that is extended by one building block in all three directions. This step is then repeated, giving a core unit that is extended by two building blocks. In that fashion, the arms extending from the initial core unit can be lengthened stepwise. Alternatively, the extended bridge can be synthesized first, up to a desired length, and can then be attached to the non-extended core unit. Figure 2.2 depicts the two options. The problem that arises when the divergent approach is pursued is that, for several steps towards the latter stage of the synthetic scheme, the synthetic chemist has to deal with increasingly large compounds. Some of the larger organic systems that are involved in the synthesis of the aforementioned extended star-shaped complexes are difficult to handle. The problem of self-polymerization is an example of these difficulties and this specific problem is mentioned on various occasions in this and the following Chapter. Moreover, the solubility decreases with increasing size of the
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compounds, and in wet chemistry, this is disadvantageous. An advantage of this method, though, is that small building blocks are used to extend the bridges that are attached to the core unit, and usually the solubility of the small building blocks is significantly better than the solubility of the extended octupolar systems. This facilitates the separation of excess starting material (or small by-products) from the desired octupolar products. The convergent approach,\textsuperscript{[607]} on the other hand, requires chemical modification of smaller molecules before the point at which the assembled bridges can be attached to the core unit, which can make purification procedures along the way to that point more demanding. For core variations, the convergent approach allows more flexibility (see Chapter 2); once a bridge of desired length has been synthesized, attaching it to various core units allows fast access to a variety of extended systems. At this point, the divergent approach would involve more steps, and would thus be more expensive and more time-consuming.

At an early stage of this work, a divergent approach was commenced, starting from the core unit 1,3,5-tribromobenzene. As shown in Scheme 2.1, the core was extended stepwise, employing alternating cross-coupling reactions (Sonogashira protocol\textsuperscript{[608]}) to introduce silyl-protected acetylenes or aryl halides, with desilylation reactions under basic conditions to remove the silyl groups affording the free acetylenes.

One part of the present studies was the introduction of two new scaling factors for NLO materials to allow for a comparison of NLO efficiencies of NLO-responsive materials from various chemical families, which was published earlier this year;\textsuperscript{[535]} a cost-corrected two-photon absorption cross-section (\(\sigma_{2,C}\)) is one of the scaled 2PA cross-sections obtained from the studies. Details on the methodology to determine the individual scaling factors are given at a later section of this Chapter (see page 169\textit{ff.}) and in Chapter 3 (see page 295\textit{ff.}) At this point, it needs to be mentioned that prices to synthesize a certain compound or complex are based on the cost for commercially available chemicals along a synthetic pathway. Therefore, the synthetic pathways shown in Schemes 2.1 (page 86), 2.2 (page 89), 2.3 (page 91), 2.4 (page 94), 2.5 (page 96), 2.6 (page 97), 2.7 (page 98), 2.8 (page 99), 2.9 (page 100) and 2.10 (page 101) include commercially available starting materials and previously-reported products (and corresponding yields). The costing (see page 175\textit{ff.}) was based on these Schemes. This means that,
Scheme 2.1 Synthesis of octupolar triacylenes 2-2° (no phenylethynyl unit attached to the core), 2-5° [mono(phenylethynyl)-bridged] and 2-8° [bis(phenylethynyl)-bridged]. Starred compound numbers indicate previously-reported compounds.
instead of just showing new compounds and complexes, the commercially available starting materials and steps in between are included, even though this is not commonly done. Where available, yields given in the literature were used, all other yields being those obtained by me. Starred compound numbers indicate previously-reported compounds, including published yields. In the Schemes given here, the reaction conditions for previously-reported procedures are given as found in the literature. In some cases these conditions deviate slightly from the conditions I have chosen (e.g. dichloromethane instead of tetrahydrofuran, Pd\textsuperscript{II} instead of Pd\textsuperscript{0}, triethylamine instead of diethylamine). Where the deviations were significant, they are pointed out specifically. Considering the above, the following compounds were prepared following literature procedures (or slight modifications thereof): 2-1\textsuperscript{*,[609,610]} 2-2\textsuperscript{*,[609,610]} 2-3\textsuperscript{*,[611]} 2-8\textsuperscript{*,[612]} starting from 1,3,5-tribromobenzene.\textsuperscript{1} Using the triiodide instead of the bromide has been reported to decrease the reaction time considerably\textsuperscript{[612]}, but was not attempted in this work. The main reason is the easy access to the bromide compared to the iodide, although the iodide can be prepared from the bromide. Despite the fact that the multi-step method suggested by Willgerodt and Arnold\textsuperscript{[613]} was simplified drastically by Schöberl \textit{et al.}\textsuperscript{[614]} I refrained from preparing the triiodide; the coupling reaction was an early step in the synthesis, so the drawback of a prolonged reaction time was considered acceptable, and indeed the extra step to replace the bromine substituents with iodine atoms would not have increased the overall yield significantly. The free acetylene 2-2\textsuperscript{*} has also been described by Trumbo and Marvel\textsuperscript{[615]}, although they used a 2-hydroxybutyl-protected acetylene. The protecting group in their case was removed with KOH in methanol and toluene at 120 °C in a Dean-Stark setup. In my work, the trimethylsilyl protecting group could be removed under milder conditions, as suggested for similar chemical systems by Takahashi and co-workers.\textsuperscript{[616]} Kobayashi and Kijima reported the tribromide 2-3\textsuperscript{*} at the same time I was synthesizing this compound.\textsuperscript{[611]} Under my reaction conditions, the reaction was started at 0 °C, and the reaction mixture was then allowed to warm to room temperature (RT) over roughly 10 hours (not shown in Scheme 2.1). This was done to ensure that the acetylene would selectively react at the iodo-site of para-bromoiiodobenzene, i.e. to avoid double-substitution,

\textsuperscript{1} As mentioned earlier, a star (\textsuperscript{*}) marks previously-reported complexes, and a superscript a (\textsuperscript{a}) marks complexes that I have not synthesized within the scope of this work.
which can potentially result in the formation of polymeric structures. Kobayashi and Kijima worked at room temperature, and they allowed the reaction to proceed over 40 hours, achieving the same results, which indicates that working at low temperature may not be necessary. However, they used a nine-fold excess of para-bromoiodobenzene (i.e. three equivalents of the iodide for each acetylene site), whereas in this work, only three equivalents were used. In the present studies, single crystals suitable for X-ray structure determination were grown by vapor diffusion of diethylether into a chloroform solution (details of the solid-state structure are given in Section 2.3.1), and the resulting X-ray crystal structure adds to the data obtained by Kobayashi and Kijima.

The octupolar, trimethylsilyl-protected acetylene \(2-4^-\) was prepared and characterized by McDonagh et al.\(^{[617]}\) (the same compound was simultaneously reported by Uno and Dixneuf, their report lacking characterization data\(^{[618]}\)). However, McDonagh et al. prepared \(2-4^-\) via a route different from that shown in Scheme 2.1 on page 86. They reacted 1,3,5-triethylnylbenzene \((2-2^-)\) with para-iodotrimethylsilylethynylbenzene \((2-22^-)\) in 71%. The method suggested in this work afforded an improved yield of 90% (over 2 steps from \(2-2^-\) via \(2-3^-\) to \(2-4^-\)). In terms of cost-efficiency, the fact that the synthesis of the iodide \(2-22^-\) is not required when proceeding via the extra step shown in Scheme 2.1 justifies that extra step. The desilylation of the trimethylsilyl-protected acetylene \(2-4^-\), affording the free acetylene \(2-5^-\), was described by the same group,\(^{[617]}\) although they used tetrabutylammonium fluoride \((\text{NBu}^+\text{F})\) in dichloromethane instead of KOH in dichloromethane and methanol. The yields were comparable (89% and 91%), so the literature procedure was stated. Mongin et al. reported the extended organic stars \(2-7^-\) and \(2-8^-\).\(^{[612]}\) They suggested the preparation of the aryl iodide \(2-25^-\) (Scheme 2.5 on page 96), which was then coupled to 1,3,5-triethylnylbenzene \((2-2^-)\). Mongin’s pathway requires 5 steps to get to the linear iodide \(2-25^-\) (5 steps, 58%) and another step to couple this iodide to the acetylene core \(2-2^-\) (70%), i.e. it requires 6 steps in an overall yield of 40%, which deviates from my approach and is inferior. Starting from the same acetylene core \(2-2^-\), the suggested pathway to \(2-8^-\) proceeds via 5 steps in an overall yield of 54%. However, the reaction times in this approach are longer, and intermediate workup procedures and/or recharging the reaction mixture with fresh catalyst is often required.
Scheme 2.2 Synthesis of the octupolar ruthenium mono-acetylide complex 2-9\(^*\) and the bis-acetylide complex 2-10\(^*\) synthesized by McDonagh \textit{et al}. The addition of triethylamine (reaction 2-5\(^*\) → 2-9\(^*\)) was carried out without prior workup of the vinylidene.\[^{617}\] A star (*) marks previously-reported complexes, and a superscript a (\(^a\)) marks complexes that I have not synthesized within the scope of this work.

McDonagh \textit{et al}. reacted acetylene 2-5\(^*\) with \textit{cis}-[RuCl\(_2\)(dppe)]\(_2\) (2-46\(^*\))\[^{513}\] in dichloromethane in the presence of NaPF\(_6\) as a halide extracting agent, a methodology described by Touchard and co-workers.\[^{619,620}\] This afforded the star-shaped ruthenium mono-acetylide complex 2-9\(^*\) (Figure 2.2).\[^{517}\]

The core unit 1,3,5-triethynylbenzene (2-2\(^*\)) does not incorporate phenylethynyl-bridges. As a result, the metallation of all three acetylene sites with \textit{cis}-[RuCl\(_2\)(dppe)]\(_2\) cannot occur. The bulky dppe ligands around the ruthenium center only allow two-fold substitution, with the third acetylene remaining free. In order to achieve three-fold metallation, smaller metal centers with less sterically demanding ligands, such as Au(PPh\(_3\)), have to be used.\[^{621}\] I obtained the first extended analogue of McDonagh’s complex (2-9\(^*\)) by reacting the organic octupolar acetylene 2-8\(^*\) with \textit{cis}-[RuCl\(_2\)(dppe)]\(_2\) in a similar fashion as described by McDonagh \textit{et al}.

The difference, however, is that the vinylidene complex 2-13 (with PF\(_6^-\) being the counter-ion to the charged species) was worked up as an intermediate, which is depicted in Scheme 2.3. The same acetylene core (2-8\(^*\)) was reacted with \textit{cis-}
[RuCl₂(dppe)]²⁺[622] under the same conditions, affording the octupolar vinylidene complex 2-11, which is the dpdm analogue of the dppe complex 2-13.

In the case of 2-14, the isolation of the vinylidene intermediate was carried out to avoid the formation of undesired bis-acetylide complexes. In the case of the dpdm-ligated complex 2-12, this step is not necessary, since the substitution of chloride ligands for acetylide ligands is not easy in Ru(dpdm)₂ mono-acetylide complexes; the risk of obtaining undesired bis-acetylide complexes is not as acute as in reactions involving dppe-ligated ruthenium. Both vinylidene (2-13, 2-11) complexes were then deprotonated, using triethylamine as the base, affording the star-shaped ruthenium mono-acetylide complex 2-14 and the analogous Ru(dpdm)₂ complex 2-12 in 69% and 63% yield. On a few occasions, the formation of cis,cis,cis-[Ru(η²-O₂CMe)(dppe)]PF₆[623] was observed in attempted formations of the mono-acetylide complex 2-14. The characteristic triplets at 59.9 ppm and 58.1 ppm in the $^{31}$P{¹H} NMR spectrum (Figure 2.3) indicated the presence of the acetate adduct. I am not sure of the source of the acetate under the chosen reaction conditions. At no point during the corresponding reactions were acetates used actively or on purpose, and the appearance of the ruthenium acetate complex did not occur consistently. The octupolar ruthenium mono-acetylide complex 2-14 was reacted with para-nitrophenylacetylene[616] in the presence of
Scheme 2.3 Synthesis of the star-shaped ruthenium mono-acetylide complexes 2-14 (dppe) and 2-12 (dpmm) and the bis-acetylide complexes 2-15 (phenylacetylide ligand) and 2-18 (para-nitrophenylacetylide ligand). Starred compound numbers refer to previously-reported compounds. The vinylidene complexes 2-11 and 2-13 were isolated before being deprotonated, but the complexes were not characterized.
NaPF₆ and triethylamine, affording the ruthenium bis-acetylide complex 2-18 (Scheme 2.3).

For ease of description, from this point onwards the number of phenylethynyl units between the core and the metal center will be used to indicate the length of the oligo(phenylethynyl) bridges. Therefore, McDonagh’s complex 2-9⁺ incorporates a mono(phenylethynyl) bridge, i.e. one phenylethynyl unit. Complexes 2-14 and 2-12 incorporate bis(phenylethynyl) bridges; they have a bridge length of 2 phenylethynyl units.

Working with extended phenylethynyl systems can be difficult (vide supra); problems first arose here when the organic octupolar trimethylsilyl-protected acetylene 2-8⁺ was desilylated. After extracting the product with dichloromethane, drying the combined organic layers over MgSO₄ and filtration of the resultant mixture, a clear solution was obtained. Once the solvent had been removed, a clear solution could not be obtained again, even in refluxing chloroform. Dark-brown to black, insoluble material remained undissolved. Filtration of such mixtures afforded clear filtrates again, but the above phenomenon was reproduced when that solution was taken to dryness. Employing such a starting material in reactions would inevitably lead to decreased yields, which was observed for the mono-acetylide complexes 2-12 and 2-14; in particular, the dppe-analogue was synthesized more than half a dozen times, and never did the yield exceed 70%, regardless of the workup procedures.

Due to the last-mentioned problem related to the extended organic acetylene, the plan to extend the octupolar systems out via a divergent approach, i.e. from inside out, could not be sustained. Instead, the synthesis of metallated oligo-(phenylethynyl) bridges, which could then be linked to the organic octupolar acetylenes, was envisaged (Scheme 2.1). However, the problem of poor solubility of the extended systems remained, so solubilizing units were incorporated into the linear building blocks. The choice of the solubilizing unit was not arbitrary. In a recent report by Babgi et al., ethoxy groups were used to enhance the solubility of extended linear systems with donor-bridge-acceptor structures for second-order and third-order NLO studies. There were indications that the ethoxy group is not completely innocent in terms of the optical and electronic properties of ruthenium acetylide complexes incorporating ethoxy groups. These effects were
found to be particularly pronounced in cases where the solubilizing unit was directly adjacent to the metal center. The ethoxy groups act as electron donating moieties, pushing electron density into the system. If close enough to the metal (in this case attached to the phenylethynyl unit adjacent to the ruthenium center), this was found to influence the properties of the complex, such as a drastic increase in the ease of oxidation. A decrease of the first hyperpolarizability at 1064 nm (9400 cm\(^{-1}\)) was also found for complexes with ethoxy groups, in comparison to complexes without them. A solubilizing group with less electron-donating ability was therefore sought, and hence alkyl groups were envisaged. A solubilizing unit had to be found, which would afford sufficiently enhanced solubility of the targeted linear and octupolar systems, without being sterically too demanding for the bridges to fit around the core unit. Branched alkyl groups were of particular interest, since branching typically enhances the solubility in common organic solvents. Based on these criteria, two groups were chosen to be tested, namely the neopentyl group (high degree of branching; sterically not too demanding due to short chain length) and the 2-ethylhexyl group (one branching point; sterically more demanding due to longer chain length).

The formation of Grignard reagents from neopentyl chloride and from 1-bromo-2-ethylhexane were attempted, as indicated in Scheme 2.4. To introduce the neopentyl group, neopentyl chloride was added to a mixture of activated magnesium in diethylether, following a procedure suggested by Beachley and Pazik.\(^{[624]}\) The resulting mixture was heated at reflux for 2 days. No apparent reaction took place, and no apparent decrease in the amount of magnesium (1.3 equivalent) present in the mixture could be observed, indicating that the desired Grignard reagent had not formed. The repetition of this experiment under carefully chosen conditions did not result in a different outcome. Parallel to these attempts, similar trials with 1-bromo-2-ethylhexane were carried out and delivered more promising results in that the Grignard formation seemed to proceed in a more straightforward fashion. I then tried to couple the Grignard reagent to a suitable dihalobenzene. The reaction had to be repeated numerous times to determine conditions that delivered satisfactory results. Egbe et al. have reported a procedure for the synthesis of 1,4-bis(2-ethylhexyl)benzene (2-19').\(^{[625]}\) They used 1,3-bis(diphenylphosphino)propane nickel dichloride [NiCl\(_2\)(dppp)] as a catalyst to support the coupling of 1,4-dibromobenzene to a Grignard reagent formed
Scheme 2.4 Attempted syntheses of 1,4-dialkyl-substituted benzene derivatives 2-19* and 2-20*. Dashed arrows indicate reactions that were not carried out in this work. Starred arrows are yields found in the literature. 2-20* has been described in the literature and synthesized with a yield of 8% (as indicated). I was not able to induce the neopentyl Grignard formation to a significant extend, as indicated by the crossed reaction arrow.
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from the 1-bromo-2-ethylhexane (Kumada coupling\textsuperscript{[626]}). This procedure seemed to result in the formation of the Wurtz-type by-product.\textsuperscript{[627]} Huang \textit{et al.} used 1,4-dichlorobenzene instead of the bromide, under otherwise similar conditions,\textsuperscript{[628]} although they used THF as a solvent instead of diethylether. Eventually, I adapted a combination of both procedures, and in summary, the following points should be paid attention to if the reader intends to repeat the procedure:

- Avoid concentrated solutions (> 2 mol L\textsuperscript{-1}) during the Grignard formation, since this leads to the formation of the Wurtz-coupled byproduct (5,8-diethylidodecane).

- The addition of 1-bromo-2-ethylhexylbenzene should be carried out slowly; addition of a small amount to the activated magnesium under diethylether should initiate the reaction, as indicated by gas formation. Once this is observed, a dilute solution of the bromide in ether should be added at a rate that allows gentle boiling of the mixture without external heating.

- The order of addition seemed to be important. I found it to be favorable to add the Grignard reagent to a solution of dihalobenzene and a catalytic amount of NiCl\textsubscript{2}(dppe) in diethylether, rather than the other way round.

- 1,4-Dichlorobenzene proved to give better results than 1,4-dibromobenzene. The amount of starting material found in the crude product was less when the chloride was used instead of the bromide.

- With no exception across the numerous attempts to synthesize the 2-ethylhexyl substituted benzene, reactions did not go to completion; the dihalobenzene starting material was always found spectroscopically. A convenient way to remove the aryl halide from the product is to sublime the solid off the liquid product.

- Once the Grignard had been added to the dichlorobenzene and the resulting mixture had been refluxing for ca. 16 h, the addition of fresh NiCl\textsubscript{2}(dppe) followed by another period of reflux was found to be highly beneficial for an improved yield.

The 1,4-diethylhexylbenzene solubilizing unit was then functionalized and incorporated into linear metallated phenylethynyl complexes. For the purpose of cost calculations, which requires synthetic routes to start from commercially available
Scheme 2.5 Syntheses of organic linear mono(phenylethynyl)- and bis(phenylethynyl)-bridges. Yields are given as reported in the literature. Starred compound numbers indicate previously-reported compounds.

Starting materials, the synthesis of all precursors is given. Scheme 2.5 shows the synthesis of the linear extending units 2-29*, [629] 2-22*, [630] and 2-25*, [630] and the free acetylenes 2-27*, [631] and 2-26*. These compounds and their precursors 2-21*, [632] 2-28*, [629] 2-23* [630] and 2-24* [630] were prepared following literature procedures or slight modifications thereof; matching spectroscopic data were found for all. For consistency, yields given in the literature were used for the calculation of cost scaling factors. Where more than one possible route to a product or intermediate had been reported in the literature, the one representing conditions closest to those chosen by me were given.

Starting from 1,4-bis(2-ethylhexyl)benzene 2-19*, the free acetylene 2-34 with two linearly arranged phenylethynyl-units (Scheme 2.6) was synthesized via 5 unique steps\(^2\) (plus 4 steps to prepare para-triisopropylsilylphenylacetylene 2-29*; Scheme 2.5). I initially tried to mono-brominate the alkyl-substituted benzene

\(^2\) The term number of unique steps refers to the total number of steps included in a synthetic scheme, not counting repeat reactions; if a material is used twice in a scheme, then the steps required to prepare this material are only counted once.
Scheme 2.6 Synthesis of the acetylene 2-34, with a length of 2 phenylethynyl units, over 5 unique steps (plus 4 steps to acetylene 2-29*). Yields are given as isolated yields.

ring, using molecular bromine in acetic acid at 10 °C, which was not successful. The mono-bromination in carbon tetrachloride in the presence of activated silica\(^{[633]}\) was also tried, with the same result. The next approach was the nitration of the benzene ring using nitric and sulfuric acid, with the intention to then reduce the nitro group to the corresponding amine. The amine would then be susceptible to diazotization, and from there conversion to the iodide could follow. However, the nitration gave a mixture of dinitro compounds (nitro groups in 2,5-, 2,3- or 1,6-positions).

Eventually, I used an iodine-catalyzed dibromination under strict exclusion of light, as described by Rehahn et al.,\(^{[634]}\) giving the desired dibromide 2-30*,\(^{[635]}\) as shown in Figure 2.6 This was followed by mono-lithiation,\(^{[636,637]}\) and the lithiated species was quenched \textit{in situ} with iodine, giving 1-bromo-2,5-bis(2-ethylhexyl)-4-iodobenzene 2-31*.\(^{[638]}\)

All trans-halogenation reactions described in this work were carried out in tetrahydrofuran at -78 °C, which proved to work better than diethylether (at the same temperature). In order to allow carbon-carbon cross coupling reactions between acetylenes and aryl halides, iodide substituents were incorporated, whenever such a coupling reaction was carried out. The yields of all the steps leading to 2-34 were good or very good. This includes the trans-halogenation reactions (2-30* \(\rightarrow\) 2-31* and 2-32 \(\rightarrow\) 2-33), which were carried out on oils. Potentially, this can be
a problem, since oils are harder to dry than solids, in preparation for the highly moisture-sensitive halogen exchange. The high boiling point of the bromides proved to be helpful in that respect; I was able to dry the oils at $10^{-4}$–$10^{-5}$ bar at temperatures between 80–100 °C for several hours to days, in order to remove residual water, without significant loss of starting material due to evaporation. In general, the purification of 1,4-dibromo-2,5-bis(2-ethylhexyl)benzene (2-30⁺) and 1-bromo-2,5-bis(2-ethylhexyl)-4-iodobenzene (2-31⁺) was more demanding than that of longer compounds, because retention times on silica chromatography columns are quite short and similar to byproducts and/or starting materials. Therefore, I used activated silica (160 °C, 24 h) in some cases.

To obtain an analogue of 2-34 [bis(phenylethynyl)-bridged], the iodo-substituted protected acetylene 2-33 was derivatized, affording the tris(phenylethynyl)-bridged compound 2-38, consisting of two phenylethynyl units and a terminal phenylacetylene unit. The synthetic pathway, showing reaction conditions, is presented in Scheme 2.7. The methodology was the same as for the synthesis of 2-35. The strong fluorescence response to UV light found for the
Scheme 2.8 5-step synthesis of the organic linear penta(phenylethynyl)-bridged acetylene 2-44, starting from the bis(phenylethynyl)-bridged acetylene 2-35 (plus 5 unique steps to synthesize the protected acetylene 2-25*). Yields are given as isolated yields.

tris(phenylethynyl)-analogue (2-38) and its precursors (bromide 2-36 and iodide 2-37: page 135 ff.) could be used during column chromatographic purification, since the presence of the product in collected fractions was indicated by the strong fluorescent response to UV light (all chromatography columns were run using silica).

The longest linear iodo substituted acetylene synthesized in this work is compound 2-44; the synthesis is depicted in Scheme 2.8. This compound contains four phenylethynyl units and a terminal phenylacetylene unit, i.e. it is a penta(phenylethynyl)-bridge with linear alignment due to their 1,4-substitution pattern. Again, the general methodology as in the previous Schemes was followed. Overall the yields in Scheme 2.8 improved slightly compared to the previous Schemes, and in particular to Scheme 2.6. Part of the reason for this is that
**Scheme 2.9** Syntheses of the linear ruthenium acetylide complexes 2-45 [bis(phenylethynyl)-bridge], 2-46 [tris(phenylethynyl)-bridge] and 2-47 [penta(phenylethynyl)-bridge]. Yields are given as isolated yields.

The compounds became less oily with increasing chain length, which made it easier to work with them, and the loss during workup procedures decreased.

I tried to avoid the formation of extended organic octupolar compounds whenever possible (in particular those incorporating free acetylene functionalities). Therefore, the linear acetylenes 2-34, 2-38 and 2-44 were reacted with cis-[RuCl₂(dppe)] in the presence of NaPF₆ to form the corresponding vinylidene complexes (in a similar fashion as presented in Scheme 2.3 on page 91). The vinylidene complexes were then deprotonated with triethylamine, giving the three linear mono-acetylide complexes 2-49, 2-50 and 2-51 (Scheme 2.9).

I also synthesized the bromo-substituted complex 2-47 and the iodo-substituted complex 2-48, starting from their acetylene precursors 2-27* and 2-26* (Scheme 2.9). Only the unsubstituted acetylide complexes 2-47 and 2-48 afforded sufficiently good crystals to allow X-ray crystallographic structure determinations.
Scheme 2.10 Syntheses of the star-shaped ruthenium acetylide complexes with tris(phenylethynyl)-bridges (2-52), tetra(phenylethynyl)-bridges (2-53) and hepta(phenylethynyl)-bridges (2-54) linking the core unit to the peripheral metal centers. Yields are given as isolated yields.

The corresponding structures are discussed in Section 2.3.1 (page 139 ff.) All five complexes carry a metal center at one end and an iodo-substituted (2-48 to 2-51) or bromo-substituted (2-47) benzene ring at the remote end. The iodide can be coupled to acetylenes under mild conditions. Permutations of reactions between acetylene cores 2-2*, 2-5*, and 2-8* (Scheme 2.1 on page 86) and the iodo-substituted linear ruthenium acetylide complexes 2-49, 2-50 and 2-51 potentially lead to star-shaped complexes with oligo(phenylethynyl)-bridges, containing 2–7 phenylethynyl units. In this work, I synthesized the complexes with tris(phenylethynyl)-bridges (2-52), tetra(phenylethynyl)-bridges (2-53) and hepta(phenylethynyl)-bridges (2-54), as indicated in Scheme 2.10. Unfortunately, 2-52 and 2-53 were only obtained in moderate and poor yields. The reason for
the poor yields is not certain, although a combination of the excellent solubility of these products (which makes it easier to wash some of the product away with impurities when purifying) and the necessity of multiple purification steps are in part responsible for the low yields. For example, complex 2-52 is completely soluble in a mixture of n-hexane and dichloromethane (12:1), and the solubility effectively disappears at a ratio of around 16:1 (in comparison, the dendrimers presented in Chapter 3 are only poorly soluble when the ratio is 3:1). The separation of the metallated starting material from the product under such conditions is always subject to losses; the complex 2-49 can still be dissolved at a ratio of 15:1. Note, though, that all the yields given in Scheme 2.10 are unoptimized, and the corresponding reactions have only been carried out on small scale once (2-53, 2-54) or twice (2-52); yields are expected to improve on upscaling of the corresponding steps, with focus being on the optimization of reaction conditions. In the case of complex 2-54, the extended reaction period employed may not be necessary. The syntheses of 2-52 and 2-53 proceeded to completion by NMR within the given reaction times, so the formation of 2-54 may occur on the same time scale. However, so far there is no spectroscopic evidence for this, which would have to be acquired once reaction conditions are optimized. Because the primary interest of the present work was the effect of the chain lengthening on the NLO properties and not so much maximizing yields, the optimization of reaction conditions has not been pursued so far.

In an attempt to obtain a non-alkylated ruthenium acetylide complex, analogous to the alkylated octupolar tris(phenylethynyl)-bridged complex 2-52, I reacted the linear ruthenium bis-acetylide complex 2-59 with the bis(phenylethynyl)-bridged octupolar acetylene 2-8, following the Sonogashira protocol (Scheme 2.11). As indicated in this Scheme, the product could not be purified to a satisfying degree; the \(^{31}\text{P}\{^{1}\text{H}\}\) NMR spectrum shows an additional peak close to the peak that was assigned to the desired complex. Therefore, a yield cannot be given; the overall mass of the material recovered from this

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3 A sample of this complex was found during a clean-up and was purified. The identity of the complex was confirmed by means of \(^{1}\text{H}\), \(^{13}\text{C}\{^{1}\text{H}\}\)- and \(^{31}\text{P}\{^{1}\text{H}\}\) NMR spectroscopy as well as matching ESI MS data. Due to the lack of proper labeling on the sample vial, I have not been able to identify the original provider of this complex; Dr. A.M. McDonagh and Dr. C.E. Powell are the two most likely candidates, since they have synthesized this complex through the course of their PhD programs (ANU, unpublished results).
Scheme 2.11 Synthesis of the octupolar ruthenium bis-acetylide complex \( 2-60 \), incorporating tris(phenylethynyl)-bridges between the phenyl core and the metal centers. A yield cannot be given, since the target complex was found to contain an impurity that could not be removed completely. The linear bis-acetylide complex \( 2-58 \) was prepared for the intended synthesis of the octupolar complex \( 2-61 \). The synthesis of \( 2-61 \) has not been attempted thus far.
reaction would correspond to a yield of 38%, if good purity of the product had been assumed, to give the reader an approximate idea. I intended to prepare the analogous complex **2-61**, with a protected acetylene functionality at the periphery of the octupolar complex, because of the possibility of further chemical modifications (e.g. attachment of additional oligo(phenylethynyl)-bridges). For this purpose, the linear bis-acetylide complex **2-58** was prepared, starting from the mono-acetylide complex **2-57**.\(^{[639]}\) This mono-acetylide complex was then reacted with the acetylene **2-29**\(^{[1]}\) under similar conditions as described before, affording the desired bis-acetylide complex in 59% yield. However, so far I have not carried out the next step, i.e. the formation of the octupolar complex **2-61** is yet to be attempted.

A special comment should be made about the reaction times found for some of the reactions described herein. The reaction times for the formation of mono-acetylide and bis-acetylide complexes were found to vary quite drastically, even for repeat reactions under the same conditions; the reaction of the triacetylene core **2-8** with \textit{cis}-[RuCl\(_2\)(dppe)\(_2\)] (**2-46**\(^{[1]}\)), affording the corresponding mono-acetylide complex **2-14**, was carried out several times throughout the present work. In some cases the reaction proceeded to completion within 24 hours, which was indicated by the disappearance of the acetylene signal in the \(^1\)H NMR spectrum and the presence of a single vinylidene signal in the \(^{31}\)P\{\(^1\)H\} NMR spectrum at 37.52 ppm. In other cases, the reaction took 4 days, even at elevated temperature. The reason for this is not known. Increased reaction times were also necessary for the reaction of the linear acetylene **2-38** with \textit{cis}-[RuCl\(_2\)(dppe)\(_2\)]; the reaction went to roughly 60% completion by \(^{31}\)P\{\(^1\)H\} NMR within 2 days. Without changing any reaction conditions, the reaction progressed to completion within a third day. A similar reaction time was required when the reaction was repeated under apparently the same conditions. On a third occasion, however, the reaction proceeded to completion within 24 hours. All three reactions were carried out on a 50–120 mg scale in dichloromethane at ambient temperature. The same was found for desilylation reactions of triisopropylsilyl- or trimethylsilyl-protected acetylenes. In particular, the removal of triisopropylsilyl protecting groups, using NBu\(^n\)\(_4\)F, is generally a fast reaction and usually proceeds within a few hours. However, in some cases, incomplete reactions were found, from which mostly starting material was recovered after reaction times of 4–5 hours. One example
is the desilylation of iodo-substituted triisopropylsilyl-protected acetylene 2-37, giving the corresponding free acetylene 2-38 (Scheme 2.7 on page 98). Under standard conditions (dichloromethane, NBu₄F as 1.0 M solution in tetrahydrofuran at ambient temperature over 4-5 h), only a minor amount of the desired acetylene was recovered. The main component of the reaction mixture was the silyl-protected starting material. Only after a prolonged reaction time (12 h) did the reaction proceed to completion.

The reactions of ruthenium mono-acetylidy complexes with acetylenes under basic conditions, in the presence of a halide extracting agent (typically NaPF₆), affording the corresponding bis-acetylidy complexes, were found to vary greatly, even between two equivalent reactions under the same conditions. More importantly, I encountered a number of unsuccessful reactions, aiming for the formation of bis-acetylidy complexes. The reason for this was not obvious at first, because conditions commonly used in the Group were used at the time. When the attempted formation of bis-acetylidy complexes gave no or hardly any conversion of the mono-acetylidy complex to the corresponding bis-acetylidy complex repeatedly, I sought a reason in a systematic fashion. Eventually, the amount of base was found to be a possible trigger for the lack of progress towards the desired species. Without exception, I used triethylamine as a base in all reactions aiming for the formation of bis-acetylidy complexes. Although the threshold (in vol-% or mol-%) cannot be quantified, reactions did not proceed at all (by NMR), when 0.4-0.5 mL of triethylamine was added to a 60 mL reaction mixture. Once this factor was considered and the amount of base was controlled carefully (ca. 3-10 drops, depending on the volume of the reaction mixture), reactions usually proceeded without the aforementioned problem.

2.2.2 NMR Spectroscopy

Assignment. In all complexes described in this work, the assignment of 31P NMR signals did not require special measures. In most complexes, only one chemical environment was present, even when more than one ligated ruthenium center was incorporated. This holds for all the linear ruthenium mono- and bis-acetylidy complexes and for the star-shaped (i.e. octupolar) complexes. For the dendrimers that will be discussed in Chapter 3, two different chemical environments are
present, but assignment of the corresponding signals in the $^{31}\text{P}$ NMR spectra is unambiguous and could be accomplished based on integration of signal intensities.

Great effort has been put into the assignment of $^{13}\text{C}^{{}\{1\text{H}\}}$ and $^{1}\text{H}$ NMR signals in the complexes synthesized herein. In the present work, the assignment of $^{13}\text{C}^{{}\{1\text{H}\}}$ NMR signals was accomplished by looking at short (and, in fact, the shortest possible) dppe ligated ruthenium mono- and bis(phenylacetylide) complexes and then extending the systems out in small steps. This was done independent of similar literature reports,$^{[1]}$ leading to a slightly different interpretation of some of the spectra, which was supported by a combination of different techniques. In particular for the longer linear complexes and also for the octupolar species, the determination of signal identities was accomplished by using gradient heteronuclear multiple bond correlation (gHMBC) and gradient heteronuclear single quantum coherence (gHSQC) experiments. The comparison of spectra resulting from different species with only slightly different structural properties also allowed important conclusions. This was particularly important for the assignment of $^{13}\text{C}^{{}\{1\text{H}\}}$ NMR signals in the aromatic region of the spectra (ca. 125–140 ppm). Some attention was also put towards the spectral appearance of carbon atoms in the dppe ligands, including observed splitting patterns, which will be discussed in the following paragraphs.

Figure 2.4 shows $^{13}\text{C}^{{}\{1\text{H}\}}$ NMR spectra of unsymmetrically substituted trans-[(PhC≡C)RuCl(dppe)$_2$] (2-55$^\ast$) and symmetrically substituted trans-[Ru(C≡CPh)$_2$(dppe)$_2$] (2-56$^\ast$). These two spectra have been chosen as representative examples of this type of complex, mainly because the spectra are still relatively easy to assign, due to the small size of the two complexes. The assignment of C150/C160 and C153/C163 is unambiguous due to the characteristic splitting pattern of their signals in the $^{13}\text{C}^{{}\{1\text{H}\}}$ NMR spectrum and the lower intensity of the signals (there are only 8 carbon atoms in the para position, but 16 carbons in the ortho and 16 carbons in the meta positions). The assignment of the signals for C151/C161 and C152/C162 was carried out in accordance with literature trends.$^{[640]}$ The situation with the present Ru(dppe)$_2$ complexes with regards to internal coupling (mainly phosphorus-carbon coupling) was considered as being insufficiently clear, so the next few paragraphs are dedicated to this aspect.
Figure 2.4 $^{13}\text{C}^{(1)}\text{H}$ NMR spectra of (bottom) trans-[Ru(C≡CC₆H₅)Cl(dppe)$_2$] (2-55*) and (top) trans-[Ru(C≡CPh)$_2$(dppe)$_2$] (2-56*). Spectra were recorded in CDCl$_3$ at 126 MHz.

Examining the spectra in Figure 2.4 reveals that the mono-acetylide complex with its unsymmetrical substitution at the Ru center gives sets of two signals for each of three of the four magnetically inequivalent phenyl rings in the dppe ligands (bottom part of Figure 2.4; signals 150/160, 152/162 and 153/163). This is not due to coupling of the corresponding carbon atom to its closest phosphorus atom; replacing the chloro ligand with a second phenylacetylide ligand gives only one signal for each of the four carbon atoms (see corresponding signals in the top part of Figure 2.4), inconsistent with the doubling of signals in the mono-acetylide complex resulting from coupling. Figure 2.5 shows the aromatic to acetylenic region of the carbon spectrum of another ruthenium mono-acetylide complex (2-48), showing that the chemical shifts and the pattern in the $^{13}\text{C}^{(1)}\text{H}$ NMR spectrum do not differ significantly from those found for the mono-acetylide complex 2-55* (bottom of Figure 2.4).

Apart from the additional aromatic signals resulting from the extra phenylethynyl unit, the spectrum of 2-48 resembles

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4 The full spectrum of 2-48 can be found in the corresponding NMR Appendix at the end of this work.
Figure 2.5 Low-field $^{13}$C($^1$H) NMR region of the ruthenium mono-acetylide complex 2-48. The two phenyl rings attached to any given phosphorus atom each give a distinct set of four signals, one for ring C150–153 and one for ring C160–C163, the four signals of each set arising from the four carbon atoms in the ipso, ortho, meta, and para positions.
that of 2-55\textsuperscript{+}, although a close inspection of C151/C161 and C153/C163 in both spectra reveals that C151/C161 is a single signal for 2-48, whereas there are two observed resonances for 2-55\textsuperscript{+}, and while C153/C163 gives one signal for 2-48, there are two signals for 2-55. However, the chemical shifts for comparable signals (or sets of signals) are similar, and, importantly, there are more signals for the dppe phenyl rings present than for the completely symmetrically substituted bis-acetylide complex 2-56\textsuperscript{+}. A possible reason for the separate NMR signals in unsymmetrically substituted ruthenium acetylide complexes may be found in the orientation of the dppe phenyl rings relative to the ligands on the Ru center. Figure 2.6 shows a crystal structure of the ruthenium mono-acetylide complex 2-48\textsuperscript{5}, with two dppe ligands coordinating in the equatorial positions of a ruthenium center that has octahedral coordination geometry, i.e. the same as in complexes 2-55\textsuperscript{+} and 2-56\textsuperscript{+}. The ruthenium center shown in Figure 2.6 has a similar coordination geometry to the structures of the mono-acetylide complex

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\textsuperscript{5} I synthesized this complex and carried out an X-ray crystallographic structure determination. Detailed discussion of the structure can be found at a later part of this Chapter. This complex was chosen here as a representative example of ruthenium mono-acetylide complexes.
and the bis-acetylide complex 2-56\textsuperscript* \cite{642} shown in Figure 2.4.\textsuperscript{6} The four equatorial phosphorus atoms roughly define a plane. One set of phenyl rings lies above that plane (red), and the corresponding magnetically inequivalent carbon atoms distinguishable in $^{13}$C{$^{1}$H} NMR spectra are C150–C153. The second set of phenyl rings lies below the plane (blue), and the corresponding inequivalent carbon atoms are C160–C163. This means that carbon atoms C160, C161, C162 and C163 give NMR signals at different chemical shifts, whereas other carbon atoms in the same orientation (i.e. same color) are equivalent to one of these four and therefore resonate at the same corresponding chemical shift. Accordingly, the carbon atoms C150–C153 give signals at different chemical shifts. Also, since the ruthenium center is unsymmetrically substituted (2-55\textsuperscript* carries a chloro ligand and a phenylacetylide ligand), these shifts are different from the chemical shifts of C160–C163 in comparable positions, e.g. C150 gives a signal at a chemical shift that is different from C160. The same then applies to the pairs C151/C161, C152/C152 and C153/C163. However, for a completely symmetrically substituted bis-acetylide complex, such as 2-56\textsuperscript*, the rings would point towards the same environment, regardless of whether they are oriented upwards or downwards. This would render carbon atoms in equivalent positions within the phenyl rings (e.g. the carbon atoms C151 and 161 that are located at ortho positions) magnetically equivalent, and one corresponding signal is seen in the $^{13}$C{$^{1}$H} NMR spectrum.

To further support this idea, another pair of complexes was examined. West et al. have synthesized a series of linear osmium mono- and bis-acetylide complexes where the equatorial coordination sites of octahedrally complexed osmium centers are ligated by dppe ligands,\textsuperscript{643} i.e. analogues of the above ruthenium acetylidy complexes. Figure 2.7 shows a three-dimensional structure and a schematic ChemDraw representation of one of the mono-acetylide complexes. Again, the situation with regards to the orientation of the phenyl rings in the dppe ligands is similar to that described for the ruthenium acetylidy complexes above. West et al. noticed a drastic change in the $^{13}$C{$^{1}$H} NMR chemical shift of one particular set of carbon signals (C160-C163) when the ligand (L)

\textsuperscript{6} The CIFs of the complexes 2-55\textsuperscript* and 2-56\textsuperscript* were not available to me at this time. Because the geometry around dppe-ligated ruthenium acetylidy complexes does not vary significantly, the structure of the mono-acetylide complex 2-48 is given here instead.
Figure 2.7 a) Three-dimensional and (b) schematic representation of the geometric situation around an osmium center ligated by two dppe ligands. The phenyl rings above the plane of the equatorial phosphorus atoms are marked in blue, those below the plane being marked in red. The ligand L is either Cl or NH₃. The counter-ion in the ammine complex is PF₆⁻ (not depicted for clarity).

was changed from chloride to ammine.⁷ Considering the geometry of the ligated metal center, this seems reasonable, since the phenyl rings that are oriented towards the ligand (blue) are affected more by the ligand replacement than the other set (red). As shown in Figure 2.7, the rings above the plane are close to the phenylacetylide ligand, whereas the ones below the plane are closer to the ligand L trans to the phenylacetylide ligand (where L = Cl, NH₃). Hence, changing L should have a stronger influence on the NMR properties of C160–C163 than on C150–C153. Within one set of phenyl rings (e.g. the blue rings), the individual unique carbon atoms are affected by such a change to varying degrees; the carbon atoms closest to the ligand (C160, C161) are affected more than C162 and C163, which are more remote from C160/C161. This is the same situation as in the previous ruthenium example (Figure 2.4 on page 107). This has been observed experimentally, and Figure 2.8 shows the corresponding spectra of the chloro-

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⁷ Both complexes were synthesized and fully characterized by Patrick J. West.
and ammine-substituted osmium mono-acetylidy complexes. The phenyl carbon atoms in the ligands are close to the phosphorus atoms (1, 2, 3 and 4 bonds away for 150/160, 151/161, 152/162 and 153/163). Therefore, the possibility of $^{31}\text{P}-^{13}\text{C}$ coupling exists. In such a case, the signals at 134.2 ppm and 134.3 ppm would not be two singlets resulting from different environments around the corresponding carbon atoms C151 and C161, but instead a doublet, resulting from coupling of the carbon atom to the nearest phosphorus atom. The coupling constants that would result from this option, however, are 6.6 Hz ($^{2}J_{\text{PC}}$), 23.4 Hz ($^{3}J_{\text{PC}}$) and 10.5 Hz ($^{4}J_{\text{PC}}$) for the chloride complex. Common ranges for $^{2}J_{\text{PC}}$, $^{3}J_{\text{PC}}$, and $^{4}J_{\text{PC}}$ in aryl-substituted phosphines are 17–20 Hz, 5–7 Hz and 1–3 Hz (if $^{4}J_{\text{PC}}$ is observed at all). Replacing the chloride ligand with an ammine ligand (i.e. proceeding from spectrum PW364 to PW365 in Figure 2.8) renders

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8 Both osmium acetylidy complexes were synthesized and characterized by Patrick J. West and are described in detail in his PhD Thesis (ANU, 2011). The spectra were recorded by P. J. W. and are displayed here with his kind permission.
Figure 2.9 Insets of the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the ammine-substituted osmium mono-acetylide complex **PW365**, showing the splitting patterns of individual signals. They can be explained by considering them as virtual triplets of triplets. With increasing through-bond distance from the phosphorus atom, the value of $|^{1}J_{\text{PC}} + ^{3}J_{\text{PC}}|$ (depicted above the signals) decreases.

P-C coupling even less likely; the differences between the corresponding signals increase from 6.6 Hz, 23.4 Hz and 10.5 Hz to 486.2 Hz, 139.2 Hz and 19.5 Hz. The reason why the osmium acetylide complexes have been chosen as an example here, rather than the corresponding ruthenium acetylide complexes, is that the osmium acetylide complexes presented in Figure 2.8 show an additional effect that the ruthenium analogues do not reveal. In fact, the ammine adduct of the osmium mono-acetylide complex shows a coupling pattern of C161 and C151 to their nearest phosphorus atoms. The separation between the peaks is 2.3 Hz. This observation is important, since it makes the aforementioned possibility of the different sets of carbon signals to result from P-C coupling appear to be even less likely. C162 and C152 seem to show a coupling as well, with the coupling constant being 1.6 Hz, although this is not well-resolved. Figure 2.9 shows insets of the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum to clarify the situation. The explanation for these splitting patterns is the presence of a phenomenon called virtual coupling, which was first described in the early 1960s.\cite{651} Virtual coupling results in coupling patterns that are not of first-order, and the separation between the
two second-most-intense peaks in each affected signal is important (*vide infra*). Virtual coupling is observed in alkyl- or aryl phosphines where the phosphorus coordinates to a metal center, with a second phosphorus atom being located in a *trans* position with respect to the first one. When phosphorus atoms couple strongly to each other through the metal center, the resonance corresponding to a carbon bonded to either of these two phosphorus atoms can split into a virtual triplet.\[^{652-655}\]

In the case of the dppe ligated ruthenium acetylide complexes, there are two pairs of phosphorus atoms that are in such a *trans*-configuration. The *ipso* carbon atoms of the phenyl rings bonded to the phosphorus atoms can couple to the parent phosphorus atom and to the phosphorus atom in a *cis* position to the parent phosphorus atom, resulting in a virtual triplet of triplets (vtt). The difference $\Delta$ (in Hz) between the two second-most-intense peaks in the resulting signal corresponds to the absolute value of the sum of the $^1J$- and the $^3J$ coupling: $\Delta = |^1J_{PC} + ^3J_{PC}|$. The appearance of the signals depends on the individual coupling constants, i.e. the $J_{PF}(\text{trans})$ and $^1J_{PC}$ and $^3J_{PC}$ values. This is consistent with the coupling pattern that is seen for the bridgehead carbon atoms (C170) in both osmium- and ruthenium acetylide complexes, where the same explanation applies.

As indicated earlier, the assignment of more complex structures throughout this work was carried out by comparing similar structures to each other, in combination with gHSQC and gHMBC spectra. Wherever possible, individual signals were assigned. Where this was not the case, signals were grouped. Complete assignment of signals in $^{13}C\{^1H\}$ NMR spectra is not commonly seen in the literature of this field. Therefore, I have chosen a few examples that will be presented in the following few paragraphs, in order to indicate the methodology and present the arguments that I used in the process of assigning signals. A great part of the work in this Chapter was carried out on compounds and complexes carrying 2-ethylhexyl solubilizing groups. Hence, examples that include such groups seemed most appropriate. Figure 2.10 shows the spectrum of a ruthenium mono-acetylide complex with 2-ethylhexyl solubilizing groups attached to one of the two phenylethynyl units. The structure and the corresponding numbering scheme are given in the spectrum. The aliphatic region (10–44 ppm) shows 17 distinct signals (measured at a frequency of 126 MHz). The virtual triplet at 30.62 ppm is characteristic and could be assigned straight away. The chemical
Figure 2.10 $^{13}$C{${}^1$H} NMR spectrum of the mono-acetylide complex 2-49, which was acquired in CDCl$_3$ at 126 MHz. Labels are displayed above peaks or slightly shifted where necessary for practical use of space.
shift of the signals at 10.78/10.82 ppm and 14.14/14.20 ppm suggests that they correspond to the four methyl groups. Figure 2.11 shows an enlargement of the whole aliphatic region. C1356 and C1386 are in a similar magnetic environment, hence they are expected to give signals at a similar chemical shift. The same applies to C1358/C1388. To make a comparison between the one-dimensional and two-dimensional spectra easier or clearer, the $^1$H NMR spectrum of the same complex is presented in Figure 2.12.

From examination of the structure of **2-49**, C134 is only one C-C bond removed from the iodide, whereas C137 is two C-C bonds removed. This results in H134 appearing at a characteristic chemical shift of 7.65 ppm, and both integration of the signal and the appearance of the signal as a singlet are consistent with the environment of this proton. Direct $^{13}$C-$^1$H coupling is indicated by cross-peaks in gHSQC NMR experiments. Hence, unambiguous assignment of C134 is possible by looking for the cross-peak of 7.65 ppm (H134) in the gHSQC spectrum, which is given in Figure 2.13. The signal at 140.5 ppm must correspond to C134, and the cross-peak that results from this coupling is labeled accordingly. Following
Figure 2.12 $^1$H NMR spectrum of the mono-acetylide complex 2-49, which was acquired in CDCl$_3$ at 500 MHz. Labels are displayed above peaks or slightly shifted where necessary for practical use of space.
Figure 2.13 Part of the gHSQC spectrum of 2-49. The vertical scale gives the $^1$H NMR chemical shift (labels are given next to the linear trace). The horizontal scale gives the $^{13}$C NMR chemical shift (labels are given below the cross-peaks).
Figure 2.14 Part of the gHMBC NMR spectrum of the mono-acetylide complex 2-49. The vertical scale gives the $^1$H NMR chemical shift (labels given are given next to the left-hand-side spectrum). The horizontal scale gives the $^{13}$C($^1$H) NMR chemical shift (labels are given below or above cross-peaks). Typically, $^3 J_{CH}$ give the strongest cross-peaks, although larger or smaller couplings can also be observed.

this, the assignment of C1351 was possible; of all the aliphatic carbon atoms, only C1351 will exhibit a $^3 J_{CH}$ coupling to H134. $^{13}$C-$^1$H correlations can be detected in gHMBC NMR experiments. Typically, the observed coupling constant is set to 8 Hz, which means that 8 Hz couplings give the strongest cross-peaks. In general, this corresponds to a $^3 J_{CH}$ coupling, but it is by no means limited to this. Smaller and larger couplings will also be observed, so care has to be taken when spectra are interpreted. Figure 2.14 shows an enlarged region of the gHMBC spectrum of the complex 2-49. In this spectrum, only one aliphatic signal (38.2 ppm) gives a cross-peak to H134, which must result from coupling to C1351, so C1351 was assigned accordingly. As a result, the signal at 44.3 ppm has to correspond to C1381, being the only aliphatic $^{13}$C NMR signal remaining that gives a cross-peak to an aromatic $^1$H NMR signal. This is consistent with the observation that the
signal at 44.3 ppm (C1381) moves to the same chemical shift as C1351 (38.2 ppm) when the iodide was changed for a \textit{para-}(1-iodo-4-phenylethynyl)phenylethynyl substituent, which made the magnetic environments of the two carbon atoms more similar (for spectra, see $^{13}$C trace in Figure 2.16). H1352 and H1382 give a characteristic multiplet with an integration of 2 (as expected) at a chemical shift of 1.76 ppm (see Figure 2.12). Considering this fact, the gHMBC NMR spectrum then allows differentiation between the two pairs of methyl carbon atoms C1356/C1386 and C1358/C1388, because C1358/C1388 gave a cross-peak to H1352/1382; this cross-peak is not present for C1356/C1386, as would be expected due to the fact that they are five bonds (four C-C bonds and one C-H bond) removed from H1352/H1382. Also, using the same piece of information, resonances at 39.3/40.2 ppm could be assigned to C1352/C1382, based on the observed direct coupling to H1352/H1382 (see Figure 2.15). Again, the two distinct signals become closer together (40.3/40.4 ppm) when the iodide is substituted for a phenylethynyl unit.

The assignment of C1357/C1387, C1354/C1384, C1353/C1383 and C1355/C1385 was accomplished by using the gHMBC spectrum in combination with comparisons to higher-substituted analogues of the complex 2-49. Of those 4 pairs of carbon atoms belonging to CH$_2$ groups, only C1357/C1387 and C1353/C1383 are close enough to H1351/H1381 to give a cross-peak in the gHMBC spectrum, and the cross-peak is observed for 25.6/25.3 ppm and 32.5/32.2 ppm. The other two pairs, i.e. C1354/C1384 and C1355/C1385 are lacking that coupling. However, C1354/C1384 show a cross-peak to H1352/H1382 that C1355/C1385 do not show, from which these two pairs were assigned. The assignment of C1353/C1383 and C1357/C1387 is not trivial and could only be accomplished by comparing 2D NMR spectra of this complex and two of its analogues. In fact, the $^{13}$C-{$^1$H} NMR signals at 32.65/32.59 ppm show cross-peaks to 2.8 ppm, 1.8 ppm and 1.4 ppm. 25.59/25.57 ppm, on the other hand, show cross-peaks to 2.8 ppm and 0.9 ppm (see gHMBC spectrum in Figure 2.16). Based on this observation, C1353/C1383 were assigned to a chemical shift of 32.5/32.2 ppm, whereas C1357/C1387 were assigned to 25.6/25.3 ppm, which was then applied to the analogous complexes with a bridge length of 2 and 3 phenylethynyl units. C1357/C1387 give a cross-peak to the methyl $^1$H NMR signal (see Figure 2.14), which is an example of a $^2J_{\text{CH}}$ coupling appearing strongly
Figure 2.15 Part of the gHSQC spectrum of 2-49, showing the high-field region of both $^{13}C$- and $^1H$ NMR traces. The vertical scale gives the $^1H$ NMR chemical shift (labels given adjacent to linear $^1H$ NMR trace). The horizontal scale gives the $^{13}C\{^1H\}$ NMR chemical shift (relevant labels are given below or above the cross-peaks).
Figure 2.16 Part of the gHMBC spectrum of the linear tetra(phenylethynyl)-bridged ruthenium mono-acetylide complex 2-51. The vertical scale gives the $^1$H NMR chemical shift (labels are given adjacent to left-hand-side linear $^1$H NMR trace). The horizontal scale gives the $^{13}$C{$^1$H} NMR chemical shift (labels are given below the cross-peaks).
Figure 2.17 Aromatic and acetylenic region of the $^{13}$C($^1$H) NMR spectrum of the bis(phenylethynyl)-bridged ruthenium mono-acetylide complex 2-49. The spectrum was acquired in CDCl$_3$ at 126 MHz and referenced to the CDCl$_3$ solvent signal at 77.0 ppm.

In a gHMBC spectrum that is meant to give $^3$J$_{CH}$ couplings, 32.5/32.2 ppm are lacking that cross-peak, which appears reasonable, since C1353/C1383, to which the signals have been assigned, are four bonds removed from both methyl groups.

In order to assign the carbon signals in the aromatic and acetylenic region, a similar approach as described above was pursued. Figure 2.17 shows the corresponding region of the $^{13}$C($^1$H) NMR spectrum of 2-49. The assignment of the signals resulting from the dppe ligand was discussed earlier and was carried out accordingly for complex 2-49. The ipso carbons C150 and C160 give signals with the characteristic splitting pattern from the virtual coupling and are centered around 136.3 and 135.5 ppm. C151/C161 give resonances at 134.4/134.2 ppm, and C162/C152 appear at 127.2/127.0 ppm. The signal assigned to C153 and C163 appears at a chemical shift of 128.8 ppm and is a single signal. C151/C161 give two signals and C153/C163 give only one, in contrast to the situation found in the simple mono-acetylide complex 2-55 (C151/C161 = single signal; C153/C163
two signals; see Figure 2.4). I found that 2-55 is the exception in the series of linear complexes examined herein. All other linear ruthenium mono-acetylide complexes presented in this Chapter (and also analogue Os complexes presented by West et al.) show the pattern that was found for 2-49. By comparing the spectrum to that of 2-55, an idea of the chemical shift of C141–C144 could be gained; C144 as a quaternary carbon atom has a low intensity and appears at 130.3 ppm or 130.4 ppm, respectively, in 2-49 and 2-55. C146 is two bonds removed from four phosphorus atoms and could only just be detected. Due to the coupling, the signal centered at 131.5 ppm has a low peak height, and for some larger systems could not be detected. C134 (140.5 ppm) has been assigned above based on the cross-peak to the characteristic singlet of H134 at 7.65 ppm. The other two signals in that region, centered at 141.5 ppm and 142.8 ppm, do not show any cross-peaks in the gHSQC spectrum (see Figure 2.13 on page 118), so they result from quaternary carbons. Figure 2.18 shows the aromatic and acetylenic region of the gHMBC NMR spectrum. From the indirect coupling experiment, C138 could unambiguously be assigned to a chemical shift of 141.5 ppm based on the cross-peak to H134 (7.65 ppm). 142.8 ppm shows a cross-peak to 7.26 ppm, which corresponds to H137. Both C135 and C138 give additional cross-peaks to H1351 and H1381 (2J). The cross-peaks to H1352 and H1382 were weak. The remaining signals to be assigned in the aromatic region of the 13C{1H} NMR spectrum are 133.4 ppm, 130.7 ppm and 129.9 ppm. Examining Figure 2.17 reveals that the signals at 130.7 ppm and C129.9 ppm have a larger intensity than the ones at 133.4 ppm. C137 is only one carbon atom, whereas C142 corresponds to two (magnetically equivalent) carbon atoms, which also applies to C143. Of C137, C142 and C143, only C137 is expected to give a cross-peak to H1381 in the gHMBC NMR spectrum. A corresponding cross-peak is found for 133.4 ppm, but not for 130.7 ppm or 129.9 ppm (Figure 2.18). Hence, C137 was assigned to a chemical shift of 133.4 ppm. H143 gives a doublet at a characteristic chemical shift of 6.57 ppm (Figure 2.12), far removed from the crowded aromatic region of the dppe ligands and phenylethynyl units. This is informative, since 6.57 ppm shows a cross-peak to 130.4 ppm in the gHSQC NMR spectrum. This allowed unambiguous assignment of C143 as giving rise to the signal at 129.9 ppm.

9 The wedges presented in Chapter 3 show separate signals for all of the aforementioned carbon atoms, i.e. a pattern was found, which is different to the patterns found for 2-55 and 2-49.
Figure 2.18 Aromatic and acetylenic region of the gHMBC NMR spectrum of complex 2-49 in CDCl₃. The observed coupling constant is 8 Hz on a 500 MHz instrument. Methanol (3.5 ppm) and dichloromethane (5.3 ppm) signals were present in the ¹H NMR spectrum.
CHAPTER 2. Stars – Unbranched Octupolar Ruthenium Acetylide Complexes

The region between 75 ppm and 125 ppm shows 6 separate signals. They result from acetylenic and other quaternary carbon atoms. 100.6 ppm can easily be assigned to C133 based on its strong cross-peaks to 7.27 ppm (H137) and 2.62 ppm (H1381), and a somewhat weaker cross-peak to 7.65 ppm (H134; \(^2J\)). The assignment of 94.7 ppm and 88.3 ppm is not clear in 2-49. 88.3 ppm shows a strong cross-peak to 7.26 ppm (H137; close to H142) and a weak correlation to 7.65 ppm (H134). 94.7 ppm, however, shows a cross-peak to 7.27 ppm (H142) only (Figure 2.18). Based on these observations, 88.3 ppm can be assigned to C139, and 94.7 ppm to C140, although the overlapping signals of H137 and H142 in the \(^1\)H NMR spectrum leave some residual ambiguity. The comparison to structurally related complexes is given in Figure 2.19, showing a comparison of the acetylenic region and quaternary region of three \(^{13}\)C{\(^1\)H} NMR spectra. The three complexes shown are 2-49 (iodo-substituted with 2-ethylhexyl groups), 2-48 (iodo-substituted without 2-ethylhexyl groups) and 2-47 (bromo-substituted without 2-ethylhexyl groups). The first observation to be pointed out is that the carbon carrying the halide (C133) gives rise to a signal at 100.6 ppm (2-49) or 93.4 ppm (2-48) in the case of an iodide. For a bromide, a strong downfield shift to 121.3 ppm (2-47) is observed. This supports the assignment of C133. What appears counter-intuitive, however, is the assignment of C139 and C140, when the three complexes are compared to each other. For 2-49, the reason for the assignment was found in its gHMBC NMR spectrum. Comparing its 1D \(^{13}\)C{\(^1\)H} NMR spectrum to that of 2-47 and 2-48, the observed changes in the chemical shifts appear peculiar. The signal for C139 does not vary much across the spectra of the complexes 2-47 and 2-48, although some variation may be expected, considering the fact that it is close to where the structural change occurs (with solubilizing units vs. without). C140, on the other hand, is more remote from this part of the complex, yet the corresponding signal changes from 94.6 ppm (2-49) to 91.8 ppm (2-47) and 92.1 ppm (2-48). A close look at the corresponding region of the gHMBC NMR spectrum of 2-48 seems to support this counter-intuitive assignment (see Figure 2.20). From the earlier discussion, 93.4 ppm could be unambiguously assigned to C133. The additional cross-peak to the doublet at 7.68 ppm (H134) supports this assignment. 93.4 ppm (C133) and 88.6 ppm give cross-peaks to the same proton (7.24 ppm). This is more likely for C139 (3 bonds away) than for C140 (4 bonds away), so 88.6 ppm was assigned to
Figure 2.19 Acetylenic region of the $^{13}$C{H} NMR spectra of complexes 2-49, 2-48 and 2-47, recorded at 126 MHz in CDCl$_3$. 
Figure 2.20 Enlarged acetylenic region of the gHMBC NMR spectrum of complex 2-48, which was acquired in CDCl₃ on a 500 MHz instrument, with an observed coupling constant of 8 Hz.

C139 despite the aforementioned unexpected behavior in terms of the chemical shifts when compared to the 2-ethylhexyl substituted complex 2-49.

The three remaining signals at lower field (114.4 ppm, 116.7 ppm, and 123.5 ppm in 2-49) were assigned. Of these three resonances, only 123.5 ppm cross-couples to 2.7 ppm (H1351), for which reason C136 could be assigned to the peak at 123.5 ppm. Examining the structure of 2-49, H134 is found to be three bonds removed from C136 also, and the gHMBC NMR spectrum shows a corresponding cross-peak (Figure 2.18 on page 125). 144.4 ppm and 116.7 ppm are harder to assign, since they both show only one cross-peak to the same proton at 6.57 ppm (H143). The assignment was therefore accomplished by comparison to the two complexes 2-48 and 2-55⁷. In all three complexes, C145 resonates at 114.0±0.4 ppm. C141, however varies with the variation of the substituent that is attached to C145 (2-55⁷: H; 2-48: 4-iodophenylethynyl; 2-49: 2,5-bis(2-ethylhexyl)-4-iodophenylethynyl; compare Figure 2.4 on page 107 to Figure 2.5 on page 108).
Larger complexes and all organic precursors were treated in a similar fashion. Obviously, the spectra become more complicated with increasing number of phenylethynyl units, to a degree where the resolution of spectra was not sufficient to assign each signal individually. In those cases, signals were grouped. The larger the systems discussed in this work became, i.e. the longer the phenylethynyl-bridges were made, the harder it became to acquire good-quality $^{13}$C{$^1$H} NMR spectra. The main problem is that, specifically in octupolar complexes, the quaternary carbon atoms of C≡C bonds can be difficult to detect due to poor signal-to-noise ratios (s/n). Therefore, high concentrations of the complexes in the appropriate solvent are desirable. This, however, has the disadvantageous side effect of signal-broadening, and shimming becomes difficult for solutions of high concentrations. These two opposing effects had to be considered when $^{13}$C{$^1$H} NMR spectra were acquired. In the case of $^1$H and $^{31}$P NMR spectra, this situation is not a problem, since solutions can be made reasonably dilute and still give a good s/n due to the high abundance of the NMR active isotopes.

In situ NMR. $^{31}$P NMR spectroscopy is a useful and quick technique to follow the progress of reactions in situ; the chemical shift of the signals is highly sensitive to the chemical environment of the corresponding phosphorus atoms. For example, on proceeding from a mono-acetylide complex to a bis-acetylide complex, the chemical shift changes from about 50 ppm to a downfield shift of 55 ppm. Modifications of a mono- or bis-acetylide complex remote from the ruthenium center can result in noticeable yet smaller changes in the $^{31}$P chemical shift so that reactions can be monitored. Where changes in the chemical shift were small, mixing experiments were used to gain further confidence about the desired chemical change having occurred. In these experiments, the $^{31}$P{$^1$H} NMR spectrum of a product is acquired in an appropriate solvent. To the same NMR sample, the starting material is added and a second NMR spectrum is recorded on the same sample. If the chemical changes are different, then the first spectrum gives one signal, whereas the second spectrum shows two. However, with the synthetic pathway that was used to approach the extended octupolar ruthenium acetylide complexes (see Scheme 2.10 on page 101) in the present work, I found

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10 This description is based on the case where both starting material and product are species that show only a single signal in the $^{31}$P{$^1$H} spectrum, i.e. there is only one $^{31}$P chemical environment in each.
Figure 2.21 Comparison of $^1$H NMR spectra of (1) a linear ruthenium acetylide with an aryl iodide substituent, which was reacted with an octupolar triacetylene species, affording (3) the corresponding extended octupolar ruthenium mono-acetylide complex. 2) In the crude reaction mixture, the presence of the two species can be seen. $^{31}$P chemical shifts for both species are too similar to observe a noticeable difference; the same signal is observed for the starting material and the product.

that the change in the chemical shift is too small (if there is any) to detect the change in $^{31}$P NMR spectroscopically, using the techniques described above; no noticeable change in the chemical shift was observed when the octupolar acetylene cores were coupled to the linear ruthenium mono-acetylide complexes. With the $^{31}$P NMR handle being inconclusive in those cases, monitoring reactions was restricted to $^1$H NMR spectroscopy. However, particularly in the aforementioned cross-coupling reactions, changes in the chemical shifts in or the appearance of the aromatic region of $^1$H NMR spectra can be quite subtle. This is the case when proceeding from the extended linear ruthenium acetylide species to the octupolar product via cross-coupling reactions between the metallated complex incorporating an aryl iodide and the octupolar free acetylene. An example is shown in Figure 2.21. Proceeding from the linear starting material to the
octupolar product, the pseudo-doublet centered at 6.55 ppm changes to 6.57 ppm. The crude mixture (spectrum 2 in Figure 2.21) shows the presence of both species. Apart from that, the singlet at 7.64 ppm shifts to 7.69 ppm. The broad signal at 7.53 ppm results from the core moiety. The corresponding $^{31}$P NMR spectra did not reveal a change in the chemical shift. Importantly, using the disappearance of the acetylene proton from the $^1$H NMR spectrum as the only indication for the progress of such a reaction can be misleading; the possibility of free acetylens undergoing homo-coupling is always present under the chosen reaction conditions, which also results in the acetylene signal disappearing.

In order to ensure facile cross-coupling reactions of linear oligo(phenylethynyl)-complexes to octupolar triacetylene cores, affording the corresponding oligo-(phenylethynyl)-bridged octupolar cross-coupling products, aryl iodide moieties were incorporated into the linear species. This concept was followed throughout along the synthetic pathway from shorter (2 and 3 phenylethynyl units) to longer (4 and 5 phenylethynyl units) linear precursors. Hence, bromides were consistently converted into iodides *via* trans-halogenation reactions (see Scheme 2.6, Scheme 2.7 and Scheme 2.8). The retention factors ($R_d$) of two aryl halides are the same in these oligo(phenylethynyl)-bridged linear systems, the only difference being the halide substituent, so thin-layer-chromatography (TLC) is not indicative when monitoring such reactions or checking products against starting materials. However, a significant change in the chemical shifts of the aromatic protons attached to the halogenated phenyl ring occurs on replacing a bromo-substituent with an iodo substituent. An example is given in Figure 2.22. The indicative change occurred in the two doublets centered at 7.40 ppm and 7.50 ppm that change to 7.55 ppm and 7.71 ppm when the bromo-species (bottom species) was converted into the iodo species (top spectrum). Hence, complete conversion of the starting material was indicated by the disappearance of the first set of signals.

**Artifacts.** $^{31}$P and $^1$H NMR spectroscopies are powerful techniques for monitoring the progress of reactions *in situ* and also for characterizing the final product. The high natural abundance of NMR-active $^{31}$P and $^1$H nuclei allows quick data collection, and thus provides crucial information on a short time-scale. However, problems can arise under certain conditions, such as solvent-dependent phenomena. An example is given in Figure 2.23, where two $^{31}$P($^1$H) NMR spectra
Figure 2.22 $^1$H NMR spectra of a halogenated organic linear penta(phenylethynyl) species. A halogen exchange reaction, transforming the bromide (bottom spectrum) into the corresponding iodide (top spectrum), results in a drastic change of the $^1$H NMR chemical shift of the protons directly bonded to the halogenated phenyl ring. The spectrum was taken at 300 MHz in deuterated chloroform and internally referenced to residual chloroform (7.26 ppm).
2.2. Synthesis and Characterization

![Image: NMR spectra of the iodo-substituted ruthenium mono-acetylide complex 2-48 after 250 scans in (left) C₆D₆ and (right) CDCl₃ at room temperature. The width of the signals differs significantly.]

**Figure 2.23** $^{31}\text{P}^{1\text{H}}$ NMR spectra of the iodo-substituted ruthenium mono-acetylide complex 2-48 after 250 scans in (left) C₆D₆ and (right) CDCl₃ at room temperature. The width of the signals differs significantly.

have been acquired, both of the same compound, but in different solvents. The drastic difference in the two spectra is obvious; the signal in the spectrum acquired in CDCl₃ is severely broadened, and the signal-to-noise ratio (s/n) is poor. In other instances, a complete absence of signals was observed. There were also cases where, in a multi-signal NMR spectrum, only certain signals were affected and did not appear whereas others did appear as expected (for examples, see Chapter 3). An obvious reason for these effects cannot be given, and they appeared to occur randomly and were not restricted to a particular type of ruthenium acetylide complexes. Whereas the example in Figure 2.23 resulted from a linear ruthenium acetylide complex, the same effect was observed in the star-shaped ruthenium acetylide complex 2-53 [tetra(phenylethynyl)-bridged]; Figure 2.24. The effects described above have only been observed at ambient temperature; variable-temperature studies have not been conducted within the scope of the present work.
Figure 2.24 $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the octupolar tetra(phenylethynyl)-bridged ruthenium acetylide complex 2-53. In C$_6$D$_6$, the signal-to-noise ratio (s/n) is good, and the signal appears as a sharp peak. Switching to CDCl$_3$ decreases the s/n drastically, and the signal broadens significantly. Both spectra were recorded using the same instrument and a comparable number of scans.
Figure 2.25 Fluorescence behavior of an organic linear oligo(phenylethynyl) compound, incorporating 2-ethylhexyl solubilizing groups. a) Fluorescence observed in solution as the material is eluted from a silica column. b) Fluorescence observed in the solid-state after adsorbing the material onto silica.

2.3 Physical and Linear Optical Properties

Fluorescence. The extended linear phenylethynyl species were found to exhibit strong fluorescence under irradiation with UV light. This fluorescence could be observed in both solution and the solid-state, e.g. when the material was adsorbed onto silica, which is shown in Figure 2.25. The fluorescence properties could also be determined using fluorescence spectroscopy. The concentration-dependent fluorescence spectra of the linear organic species 2-40, 2-41, 2-44, and 2-42 are shown in Figures 2.26, 2.27, 2.28, and 2.29. As expected, the removal of the trimethylsilyl protecting group from 2-40, affording the free acetylene 2-41, did not change the fluorescence behavior significantly (see Figure 2.27). The spectra were acquired in dichloromethane. The concentration of the mother liquor (c₀) was 6.0 mg in 100 mL dichloromethane, which corresponds to c₀ = 7.04 · 10⁻⁵ mol L⁻¹. The emission was measured with an excitation frequency of 27 800 cm⁻¹ (360 nm) and then scanning in the range between 26 300 cm⁻¹ and 16 700 cm⁻¹ (380–600 nm). Since the scaling of fluorescence spectra is not as straightforward as the scaling of UV-Vis spectra, the response is given in arbitrary units. Hence, the results allow one to read a concentration-dependent trend for an individual compound, but the absolute comparison of one compound to another
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Figure 2.26 Concentration-dependent fluorescence spectra of the linear organic tetra(phenylethynyl) species 2-40. The initial concentration of the solution \( c_0 \) was \( 7.96 \times 10^{-5} \text{ mol/L} \). \( c_x \) indicates the concentration obtained by x-fold dilution. A zero-intensity baseline for neat dichloromethane was confirmed prior to measuring solutions containing the compound. Colored traces show the fluorescence response at various concentrations, the black trace shows the excitation frequency.

Figure 2.27 Concentration-dependent fluorescence spectra of organic mono(silyl-protected) tetra(phenylethyneylene) species 2-41 with a free acetylene functionality. The initial concentration of the solution \( c_0 \) was \( 8.12 \times 10^{-5} \text{ mol/L} \). \( c_x \) indicates the concentration obtained by x-fold dilution. A zero-intensity baseline for neat dichloromethane was confirmed prior to measuring solutions containing the compound. Colored traces show the fluorescence response at various concentrations, the black trace shows the excitation frequency.
Figure 2.28 Concentration-dependent fluorescence spectra of the linear organic penta(phenylethynyl) compound 2-44. The initial concentration of the solution \( c_0 \) was 7.035 \( \times 10^{-5} \) mol L\(^{-1} \). \( c_x \) indicates the concentration obtained by x-fold dilution. A zero-intensity baseline for neat dichloromethane was confirmed prior to measuring solutions containing the compound. Colored traces show the fluorescence response at various concentrations, the black trace shows the excitation frequency.

should not be attempted. Figure 2.28 shows that the fluorescence response decreases linearly with decreasing concentration, i.e. diluting the solution two-fold from 1.76 \( \times 10^{-7} \) mol L\(^{-1} \) to 8.79 \( \times 10^{-8} \) mol L\(^{-1} \) decreases the fluorescence response to 50\% of the initial value. For different chain lengths and/or terminal substituents, the fluorescence spectra differ only slightly.

The effect of changing the polarity of the solvent on the fluorescence properties was explored for the penta(phenylethynyl)-species 2-42 (Figure 2.30). Diethyl ether and \( n \)-hexane give almost identical traces, with a main band being centered at 24700 cm\(^{-1} \). The peak position for the toluene solution and the dichloromethane solution are the same, but at the low-energy end of the spectrum, the trace for the dichloromethane solution tending towards zero slower than the toluene solution. The main band of the tetrahydrofuran solution lies between the peaks resulting from the \( n \)-hexane, the toluene and the dichloromethane solution (i.e. around 25 2000 cm\(^{-1} \)). The effects are not as pronounced as in the dimesitylboryl-substituted linear analogues, which will be discussed in Chapter 3 (see page 280 ff).
Figure 2.29 Fluorescence spectra of the linear organic bromo-substituted penta(phenylethynyl) compound 2-42. The concentration of the mother liquor was $4.62 \cdot 10^{-5}$ mol L$^{-1}$ (4.45 mg in 100 mL dichloromethane). The excitation wavelength was set to $27,800$ cm$^{-1}$ (360 nm). For measuring the excitation wavelength, the emission was set to $25,000$ cm$^{-1}$ (400 nm). A zero-intensity baseline for neat dichloromethane was confirmed prior to measuring solutions containing the compound. Colored traces show the fluorescence response at various concentrations, the black trace shows the excitation frequency.

Figure 2.30 Solvent-dependent fluorescence spectra of the triisopropylsilyl-protected acetylene 2-42, incorporating a linear, bis(2-ethylhexyl)-substituted penta(phenylethynyl) unit. The intensities were normalized to allow for an easy comparison of the traces.
2.3.1 X-ray crystallographic structure determinations\textsuperscript{11}

Single crystals of complexes 2-48, 2-47, and the organic bromide 2-3\textsuperscript{+} suitable for X-ray crystallographic structure determinations were grown by slow liquid-liquid diffusion of n-hexane into a dichloromethane solution (2-48, 2-47) and diethyl-ether into a chloroform solution (2-3\textsuperscript{+}) at ambient temperature. The crystal and refinement data for compound 2-3\textsuperscript{+} and for complexes 2-47 and 2-48 are summarized in Table 5.1 on page 465.

2.3.1.1 Discussion of X-ray structures

Figure 2.31 shows an ORTEP plot of the crystal structure of 2-3\textsuperscript{+}. The C-Br bond lengths are the same within the error margin (1.894(5)–1.900(5) Å), and the same applies to the C≡C bonds (1.182(7)–1.196(7) Å). The phenyl rings are not coplanar. Compared to the plane of the central phenyl ring, the deviations for the three peripheral rings are ca. 3° for C(13)-C(18), 24° for C(33)-C(38) and -47° for C(53)-C(58). Figure 2.32 shows a view along the plane of the central phenyl ring C(1)-C(6). This orientation highlights (a) the different torsion angles and (b) the phenyl rings C(33)-C(38) and C(53)-C(58) (partly obstructed by the central phenyl ring in Figure 2.32) being rotated in opposite directions (hence the opposite signs of their torsion angles of 24° and -47°). For a compound like this, where no substituents project perpendicular to the plane of the aromatic rings, a sheet-like packing behavior can be expected, due to π-π stacking. This was found in the present case; Figure 2.33 shows a packing diagram with a viewing direction along the b-axis of the unit cell (slightly tilted to display the stacking of the molecules). The main contacts between adjacent molecules are around 3.5 Å. Figure 2.34 shows the unit cell with a view along the a-axis (again, with a slight tilt), contacts of 3.4–3.6 Å being indicated by dashed lines. The distances fall into the typical range for π-π stacking.\textsuperscript{656,657}

ORTEP diagrams of the solid-state structures of the linear ruthenium mono-acetylide complexes 2-47 and 2-48 are shown in Figures 2.35 and 2.36. In

\textsuperscript{11} All crystal structures discussed in this section have been synthesized and crystallized by the author. The collection of crystallographic data sets, solving and refining the structures, as well as the preparation of publishable material was also carried out by me, with some support in the form of professional advice provided by Dr. Anthony Willis (ANU).
Figure 2.31 ORTEP plot of 1,3,5-(BrC₆H₄-4-C≡C)₃C₆H₃ (2-3⁺). Temperature ellipsoids were drawn on a 40% probability level. Hydrogen atoms were omitted for clarity. White: carbon; gray: bromine. Selected bond lengths (Å): Br(1)-C(16) = 1.900(5), Br(3)-C(36) = 1.894(5), Br(5)-C(56) = 1.899(5), C(11)-C(12) = 1.182(7), C(31)-C(32) = 1.188(7), C(51)-C(52) = 1.196(7). Selected torsion angles (°): C(2)-C(1)-C(13)-C(14) = 3.1, C(4)-C(3)-C(33)-C(34) = 23.7, C(6)-C(5)-C(53)-C(58) = -47.0.

Figure 2.32 ORTEP plot of 1,3,5-(BrC₆H₄-4-C≡C)₃C₆H₃ (2-3⁺) to show rotation of the peripheral phenyl rings out of the plane of the central ring. The central phenyl ring is oriented perpendicular to the plane [(C1), C(2), C(3) pointing towards the reader and obstructing C(4)-C(6)]. Temperature ellipsoids were drawn on a 40% probability level. Hydrogen atoms were omitted for clarity.
Figure 2.33 Packing diagram of the octupolar organic bromide 2-3°. The unit cell is displayed so that the view is along the b-axis. Carbon atoms are displayed in gray and Br atoms are displayed in dark gray. H atoms have been omitted for clarity.

Figure 2.34 Packing diagram of the octupolar organic bromide 2-3°. The unit cell is viewed along the a-axis. Carbon atoms are displayed in gray and Br atoms are displayed in dark gray. H atoms have been omitted for clarity. Dashed lines indicate C-C contacts of 3.4–3.6 Å.
Figure 2.35 ORTEP diagram of the linear ruthenium mono-acetylide complex 2-47. Thermal ellipsoids are drawn at a 40% probability level. Hydrogen atoms were omitted for clarity. The dichloromethane solvent molecule is not displayed.

Figure 2.36 ORTEP diagram of the linear ruthenium mono-acetylide complex 2-48. Thermal ellipsoids are drawn at a 40% probability level. Hydrogen atoms were omitted for clarity. The dichloromethane solvent molecule is not displayed.
both complexes, the two phenyl rings C(3)–C(8) and C(11)–C(16) linked by the
C(9)≡C(10) bond are twisted out of coplanarity by roughly 85 °. The structures
are almost identical; a comparison of relevant bond lengths and angles can be
found in Table 2.1, which reveals that the geometry of the structure, including
the coordination spheres around the ruthenium centers, are almost identical. The
angle Cl(1)-Ru(1)-P(1) is the only exception, where values deviate by 5 °. The
Ru(1)-C(1) bond lengths in both structures are the same within the standard
deviations, and the same applies for the C(1)≡C(2) bonds. There is no difference
in the C≡C bond length of C(1)≡C(2) (adjacent to the ruthenium center) and
C(9)≡C(1) (between the two phenyl rings) in both structures. In Table 2.1 the
two complexes synthesized herein are compared to the two structurally related
complexes 2-55* (previously-reported[641]) and 2-63*a (previously-reported[141])
shown in Figure 2.37. The comparison shows that the geometry and bond lengths
of the new complexes are similar to those of the previously-reported structures,
with slight variations being found in the Cl-Ru-P and P(X)-Ru-P(Y) bond angles.
The twisting of phenyl rings away from coplanarity in the two complexes 2-47 and
2-48 was also found in the structurally related osmium mono-acetylide complex
2-64*a described by West et al.[658] (Figure 2.38, bond lengths and angles are
given in Table 2.1). In this case, the phenyl rings are rotated against each other
by ca. 44 °, i.e. the twisting as not as pronounced as in the Ru-complexes 2-47
and 2-48.

Figure 2.37 Structure representation of the two previously-reported[141,641] complexes
2-55* and 2-63*a.
<table>
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<td>2.54 (6)</td>
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<td>2.54 (6)</td>
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</tr>
<tr>
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<td>2.57 (6)</td>
<td>2.57 (6)</td>
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<td>2.57 (6)</td>
<td>2.57 (6)</td>
<td>2.57 (6)</td>
<td>2.57 (6)</td>
</tr>
</tbody>
</table>

Note: \( \chi = 0.8 \), \( \beta = 0 \), unless otherwise stated. \( \theta = \text{not given} \). \( \delta = 50 \), \( \epsilon = \text{Ga} \).
2.4 Nonlinear Optical Properties

The NLO properties of the star-shaped ruthenium mono-acetylide complexes 2-9, 2-10, 2-18, 2-14, 2-52, 2-53 and 2-54 were explored. The corresponding measurements were carried out using the Z-scan technique with simultaneous recording of the open-aperture and closed-aperture signals. A schematic representation of the experimental setup is given in Figure 2.39. For each complex, the real and imaginary parts of the second hyperpolarizability $\gamma$ ($\gamma_{Re}$ and $\gamma_{Im}$) were determined at various off-resonant energies to obtain the spectra of NLO data. Such wavelength-dependence studies are time consuming, but are necessary in order to derive reliable trends from measurements. Recognizing this importance, and accompanied by the increased accessibility of tunable laser systems, such studies have been reported more often since the mid-1990s and early 2000s. However, the majority of those reports were on organic materials.

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12 As mentioned earlier, a star (*) marks previously-reported complexes, and a superscript a (a) marks complexes that I have not synthesized within the scope of this work.

13 Complexes 2-9* and 2-10* were synthesized by McDonagh et al. and are presented here for comparison.

14 Z-scan measurements and curve-fittings were carried out by Prof. Marek Samoc, Ms. Malgorzata Wielgus, Ms. Marcin Nyk, Ms. Katarzyna Matczyszyn, Ms. Joanna Olesiak-Banska, Mr. Janusz Szeremeta, Mr. Leszek Mazur, and Ms. Marta Gordel at the Institute of Physical and Theoretical Chemistry of the Wroclaw University of Technology (Wroclaw, Poland).

15 Figure drawn after a figure provided by Samoc and co-workers. Technical details are given in the experimental section.
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![Diagram of optical setup](image)

**Figure 2.39** Schematic representation of the Z-scan experimental setup. M = Mirror; OPA = Optical parametric amplifier; F = filter; A = aperture (pinhole); BS = beam splitter; D = detector; L = lens; S = sample. Sample translates along +z and -z direction. Sample as a solution in dichloromethane. Pulse length 130 fs with a 1 kHz repetition rate.

compounds. One of the early examples of wavelength-dependence measurements on organometallic complexes, exploring spectral dependencies of both real and imaginary components of the third-order nonlinearity, was conducted by Powell et al.\[668]\n
Figures 2.40–2.56 show plots of $\gamma_{\text{Re}}$ and $\gamma_{\text{Im}}$ or uncorrected $\sigma_2$, for complexes 2-9*, 2-10*\[a\], 2-18, 2-14, 2-52, 2-53 and 2-54 as a function of the incident photon frequency (in cm\(^{-1}\); 1 cm\(^{-1}\) = 1.24 x 10\(^{-4}\) eV). The two octupolar complexes 2-9* and 2-10*\[a\] [mono(phenylethynyl)-bridged] were synthesized and have been published by McDonagh et al.,\[617\] and their NLO spectra are shown here for comparison with the octupolar systems that I have synthesized and that are analyzed and presented in this work.

The two complexes 2-9* and 2-10*\[a\] show a similar behavior in terms of $\gamma_{\text{Im}}$, and their nonlinear refractive properties ($\gamma_{\text{Re}}$) are also comparable. At low energy (ca. 6000–8500 cm\(^{-1}\); 1670-1180 nm), $\gamma_{\text{Re}}$ is positive, i.e. the complexes show a self-focusing effect. The sign changes at around 9000 cm\(^{-1}\) (1110 nm; complex 2-9*) and 10,000 cm\(^{-1}\) (1000 nm; complex 2-10*\[a\]), so both complexes become self-defocusing at higher energy. The imaginary part of $\gamma$ shows two main bands in both cases. For 2-10*\[a\], they occur at 12,100 cm\(^{-1}\) (825 nm) and 15,500 cm\(^{-1}\) (645 nm). The two bands are in reasonable agreement with the linear absorption...
Figure 2.40 a) Energy-dependent plot of $\gamma_{\text{Re}}$ and $\gamma_{\text{Im}}$ for the octupolar mono-acetylide complex 2-9*. Empty circles: imaginary (absorptive) part of $\gamma$. Full diamonds: real (refractive) part of $\gamma$. Solid line: linear absorption spectrum displayed at half energy. b) Structure of 2-9*.
Figure 2.41 a) Energy-dependent plot of $\sigma_2$ for the octupolar mono-acetylide complex 2-9$^\circ$. $\sigma_2$ derived from $\gamma_{\text{imag}}$ and given in units of Göppert-Mayer (GM). b) Structure of 2-9$^\circ$. 
Figure 2.42 a) Energy-dependent plot of $\gamma_{Re}$ and $\gamma_{Im}$ for the octupolar ruthenium bis-acetylide complex 2-10$^a$. Empty circles: imaginary (absorptive) part of $\gamma$. Full diamonds: real (refractive) part of $\gamma$. Solid line: linear absorption spectrum displayed at half energy. b) Structure of 2-10$^a$. 
Figure 2.43 a) Energy-dependent plot of $\sigma_2$ for the octupolar ruthenium mono-acetylide complex 2-$10^{\text{a}}$. $\sigma_2$ was derived from $\gamma_{\text{im}}$ and is given in units of Göppert-Mayer (GM). b) Structure of 2-$10^{\text{a}}$. 
spectrum (projected into the same graph at half energy for comparison). In the case of 2-9\textsuperscript{+}, the situation is similar. However, the two \(\gamma_{Im}\) bands are slightly red-shifted against the linear absorption trace. They appear at 11 600 cm\textsuperscript{-1} (860 nm) and 15 100 (660 nm), whereas the linear spectrum shows two bands at 24 200 cm\textsuperscript{-1} (420 nm) and 33 000 cm\textsuperscript{-1} (300 nm), which corresponds to 2PA energies of 12 100 cm\textsuperscript{-1} (830 nm) and 16 500 cm\textsuperscript{-1} (610 nm). In absolute terms, the mono-acetylide complex 2-9\textsuperscript{+} exhibits stronger nonlinear absorption at around 12 000 cm\textsuperscript{-1} (0.5 \cdot 10\textsuperscript{-32} esu) than the bis-acetylide complex 2-10\textsuperscript{a} (0.2 \cdot 10\textsuperscript{-32} esu). The maximal value at \(ca.\ 15 500\ cm\textsuperscript{-1}\) is the same within the given error margins for both complexes (0.4 \cdot 10\textsuperscript{-32} esu). The real part of \(\gamma\) shows the opposite trend. The bis-acetylide complex 2-10\textsuperscript{a} shows a response of -0.6 \cdot 10\textsuperscript{-32} esu (12 500 cm\textsuperscript{-1}), whereas the mono-acetylide complex is only -0.2 \cdot 10\textsuperscript{-32} esu (12 000 cm\textsuperscript{-1}). The \(\sigma_2\) spectra (Figures 2.41 and 2.43) that were extracted from the corresponding \(\gamma_{Im}\) spectra show a band at around 8000 cm\textsuperscript{-1} (1250 nm). If 2PA is assumed, the linear absorption spectra should show absorption bands at \(ca.\ 16 000\ cm\textsuperscript{-1}\) (625 nm). However, the corresponding linear spectra are transparent in that region, and the resonance onset does not occur until \(ca.\ 20 200\ cm\textsuperscript{-1}\) (525-500 nm), which means that the onset is too remote to be responsible for the observed NLO response at 8000 cm\textsuperscript{-1} (1250 nm). Therefore, multiphoton processes have to be considered here. 3PA at that wavenumber would necessitate a band at around 24 000 cm\textsuperscript{-1} (417 nm), which is indeed observed for both complexes. The absolute \(\sigma_2\) maxima of 1350±430 GM (2-9\textsuperscript{+}) and 1460±195 GM (2-10\textsuperscript{a}) are located at 15 100 cm\textsuperscript{-1} (660 nm) and 15 500 cm\textsuperscript{-1} (650 nm). Proceeding from octupolar ruthenium mono-acetylide complexes incorporating mono(phenylethynyl)-bridges to complexes with a bridge-length of 2 phenylethynyl units results in a drastic increase in the nonlinear response, as can be seen in Figure 2.44. The first obvious difference between this spectrum and the spectrum of 2-9\textsuperscript{+} (Figure 2.40) is that \(\gamma_{Re}\) is negative at all wavenumbers, i.e. in this case the complex does not show self-focusing behavior at all. On bridge lengthening, the modulus of the negative nonlinear refractive response increases from 0.2 \cdot 10\textsuperscript{-32} esu (12 200 cm\textsuperscript{-1}, 820 nm) to 12 \cdot 10\textsuperscript{-32} esu, i.e. by more than one order of magnitude. A similar trend was found for the imaginary part of \(\gamma\), which is about one order of magnitude larger than that of 2-9\textsuperscript{+}. As was found for 2-9\textsuperscript{+}, the bis(phenylethynyl)-bridged analogue 2-14 shows
Figure 2.44 a) Energy-dependent plot of $\gamma_{Re}$ and $\gamma_{Im}$ for the octupolar ruthenium mono-acetylide complex 2-14. Empty circles: imaginary (absorptive) part of $\gamma$. Full diamonds: real (refractive) part of $\gamma$. Solid line: linear absorption spectrum displayed at half energy. b) Structure of 2-14.
two main bands that are slightly red-shifted against the corresponding bands at half energy in the linear absorption spectrum: \( \tilde{\nu}_\gamma = 11500 \text{ cm}^{-1} \) (870 nm) and 14500 cm\(^{-1}\) (690 nm); \( \tilde{\nu}_\epsilon = 23500 \text{ cm}^{-1} \) (425 nm) and 30500 cm\(^{-1}\) (330 nm). Again, the shift is larger for the band at higher energy. Although the onset of the linear absorption occurs at slightly lower energy (19800 cm\(^{-1}\), 510 nm) than for the complex with the shorter bridge (20200 cm\(^{-1}\), 495 nm), the open-aperture data between 6500 cm\(^{-1}\) and 9000 cm\(^{-1}\) (1538–1110 nm) fall into a transparent window if the energy is doubled, and yet the corresponding \( \gamma_{lm} \) values in that region are non-zero. Hence, multiphoton absorption processes are likely to be present. Due to the experimental conditions under which the measurements have been conducted (pulse length in the order of 130 fs, low repetition rate of 1 kHz), the possibility of contribution from excited state absorption (ESA) can be excluded. Hence, instantaneous 3PA (or possibly even higher multiphoton absorption) can be used to explain the non-zero \( \gamma_{lm} \) in the low-energy region. The \( \sigma_2 \) spectrum that was extracted from the \( \gamma_{lm} \) trace is shown in Figure 2.45. The largest \( \sigma_2 \)
value of just over 20,000±3400 GM was observed at roughly 18 100 cm\(^{-1}\) (550 nm). Although this is not a local maximum, measurements at higher energy would encroach into the on-resonant region of the linear absorption spectrum, which artificially increases the NLO response and should, in principal, be avoided. The band at 8000 cm\(^{-1}\) (1250 nm) falls in the region of 3PA (or higher MPA) as mentioned earlier. Values tend to return to a zero response for the two data points at lowest energy, marking the onset of that band.

Before effects on the NLO response obtained by further bridge lengthening will be discussed, a brief section will be devoted to changes that occurred when the chloro ligand was replaced by a second alkyne. From previously-reported NLO measurements, an enhancement of the NLO response on introducing a \(p\)-nitrophenylacetylide ligand into complexes, which were similar to the complexes discussed in the present work, was derived. The price to pay for this NLO enhancement is the loss of optical transparency in the visible region. Figure 2.46 shows a comparison of linear absorption spectra for the chloro-capped (2-14), phenylacetylide-capped (2-15) and \(p\)-nitrophenylacetylide-capped (2-18) octupolar ruthenium acetylide complexes, all of which have bis(phenylethynyl)-bridges, linking the central phenyl ring to the peripheral metal centers; whereas the chloro-capped complex and the phenylacetylide-capped complex show similar frequencies at which 1PA occurs, the \(p\)-nitrophenylacetylide-capped complex shows an additional band at low energy. The band appears in the form of a broad shoulder that stretches from ca. 16 000 cm\(^{-1}\) (630 nm) through to the main band that peaks at 23 500 cm\(^{-1}\) (430 nm). Compared to the former two complexes, this means that the transparent region is decreased by almost 4000 cm\(^{-1}\) (130 nm). With regards to NLO measurements, this means that the available off-resonant frequency range is decreased significantly; wavenumbers larger than 16 000 cm\(^{-1}\) would be on-resonant. From examination of the \(\sigma_2\) spectrum of the chloro-capped complex 2-14 (Figure 2.45), this means that the region in which the largest \(\sigma_2\) values are found, could not be measured without contributions from linear absorption. The smaller data range for the nitro-capped complex reflects the same problem; the corresponding spectrum is given in Figure 2.47. A striking difference between this spectrum and the three previous \(\gamma\) spectra is that in the spectrum for the nitro-capped complex 2-18, both \(\gamma_{Re}\) and \(\gamma_{Im}\) do not reach near-zero values at the low-energy end of the spectrum. At ca. 6500 cm\(^{-1}\) (1538 nm), \(\gamma_{Re}\) is
Figure 2.46 a) Linear absorption spectra of three bis(phenylethylnyl)-bridged octupolar ruthenium acetylide complexes, the ruthenium centers coordinating to different capping groups; red solid line: \( X = \text{Cl} \) (2-14), purple solid line: \( X = \text{C} \equiv \text{CPh} \) (2-15), dashed black line: \( X = \text{C} \equiv \text{CC}_6\text{H}_4\text{-4-NO}_2 \) (2-18). b) Generic structure of the three complexes.
Figure 2.47 a) Energy-dependent plot of $\gamma_{\text{Re}}$ and $\gamma_{\text{Im}}$ for the nitro-substituted octupolar ruthenium bis-acetylide complex 2-18. Empty circles: imaginary (absorptive) part of $\gamma$. Full diamonds: real (refractive) part of $\gamma$. Solid line: linear absorption spectrum displayed at half energy. b) Structure of 2-18.
-5 \cdot 10^{-32} \text{ esu}, and \gamma_{lm} is roughly 2.5 \times 10^{-32} \text{ esu}. This interesting outcome indicates that strong multiphoton absorption processes are present and extend past the lower measurable energy limit. Further experiments to elucidate the present phenomena are currently in progress. It is also important to note that non-zero \gamma values at ca. 7000 \text{ cm}^{-1} combined with optical transparency at that frequency in the linear spectrum are of interest, since this is the telecommunications range of the spectrum. At the high-energy end of the spectrum, data were not collected beyond 16700 \text{ cm}^{-1} (600 \text{ nm}) for the reason mentioned above. Even this last data point has to be treated with care, being at the onset of linear absorption. There seems to be a good correlation between the linear absorption band centered at 31000 \text{ cm}^{-1} (323 \text{ nm}) and the 2PA band at ca. 15500 \text{ cm}^{-1} (645 \text{ nm}). Figure 2.48 shows the \sigma_2 spectrum that was derived from the \gamma_{lm} trace. There is a remote resemblance between the 1PA spectrum and the \sigma_2 spectrum; \sigma_2 shows a local minimum at around 13000 \text{ cm}^{-1} (769 \text{ nm}), and the linear spectrum shows a minimum at ca. 27500 \text{ cm}^{-1} (364 \text{ nm}), i.e. at slightly higher energy than half
the energy of the $\sigma_2$ band. The linear absorption spectrum shows a sharp band (12000 cm$^{-1}$) to lower energy, which can be assigned to a charge transfer from the metal to the $p$-nitrophenylacetylidy ligand. The 2PA spectrum, however, shows a plateau at ca. 5000–6000±800 GM instead of defined bands. The $\sigma_2$ values do not return to zero at low energy. Single-wavelength NLO measurements used to be common (and are often found in the literature today). Trends that are drawn from such measurements can be misleading, and an example can be found when comparing Figures 2.45 and 2.48; had measurements been carried out only at 15 000 cm$^{-1}$ (670 nm), then the nitro-substituted bis-acetylidy complex 2-18 (15 000–16 000±3500 GM) would have been considered as being a stronger nonlinear absorber than the mono-acetylidy complex 2-14 (9400±2600 GM). This could potentially lead to the assumption that the nitro-substituent enhances the NLO behavior of the complex. However, examining the complete spectrum reveals that the largest $\sigma_2$ values for the mono-acetylidy complex are simply appearing at a higher energy. In absolute terms, the chloro complex even outperforms the nitro complex by almost 2000 GM (20 100±1800 GM vs 18 900±3900 GM).

Due to the clear indications of the nitro-substituted complex 2-18 exhibiting 3PA at low energy, its 3PA cross-section, $\sigma_3$, was determined from the absorptive nonlinear spectrum in the range 6700–9100 cm$^{-1}$ (1500–1100 nm). The result is presented graphically in Figure 2.49. Although the number of data points is limited, a maximum somewhere between 8500 and 8800 cm$^{-1}$ is present. The graph also shows that this maximum is blue-shifted from the expected position (8000 cm$^{-1}$, i.e. the corresponding maximum in the linear spectrum at a third of the original energy) by less than 800 cm$^{-1}$. Based on the experimental conditions under which the measurements were carried out, the 3PA process that causes the observed nonlinear absorption behavior can be considered instantaneous with significant contribution from excited state absorption (ESA). The maximum value ($\sigma_{3,\text{max}} = 5.0 \cdot 10^{-77} \text{ cm}^6 \text{s}^2$) exceeds the reported $\sigma_{3,\text{max}}$ value of the nitro-substituted first-generation dendrimer 2-62 at (see Figure 2.50) more than two-fold. After examining the substitution effects at the periphery, the focus is now back on lengthening the oligo(phenylethyny1)-bridges of the unbranched octupolar complexes. The $\gamma$ spectrum and the $\sigma_2$ spectrum of the ruthenium mono-acetylidy complex 2-52, incorporating tris(phenylethyny1)-bridges, are given in Figures 2.51 and 2.51.
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Figure 2.49 a) $\sigma_3$ spectrum of the nitro-capped octupolar complex 2-18. Full diamonds: $\sigma_3$. Solid line: Linear absorption spectrum at a third of its original energy. b) Structure of 2-18.

Figure 2.50 The nitro-substituted first-generation dendrimer 2-62$^a$, which was found to exhibit instantaneous 3PA; the corresponding $\sigma_{3,max}$ value of $1.5 \times 10^{-77}$ cm$^6$ s$^2$ is among the largest reported.
Figure 2.51  a) Structure of 2-52.  b) Energy-dependent plot of $\gamma_{\Re}$ and $\gamma_{\Im}$ for the octupolar ruthenium acetylide complex 2-52. Empty circles: imaginary (absorptive) part of $\gamma$. Full diamonds: real (refractive) part of $\gamma$. Solid line: linear absorption spectrum displayed at half energy.
\begin{figure}[h]
  \centering
  \includegraphics[width=0.8\textwidth]{figure.png}
  \caption{a) Structure of the complex ruthenium mono-acetylide complex 2-52. b) Frequency-dependent $\sigma_2$ spectrum of 2-52. $\sigma_2$-values were derived from $\gamma_{im}$ and are given in units of G"oppert-Mayer (GM).}
\end{figure}

$\gamma_{Re}$ is negative at all energies, which means that solutions of 2-52 are self-defocusing in the observed energy range. The imaginary part of $\gamma$ is positive throughout, with a maximum of $5.9 \cdot 10^{-32}$ esu at 18200 cm$^{-1}$ (550 nm). Compared to complex 2-14, i.e. a species with one less phenylethynyl unit in each bridge, this is an increase of ca. 50%. The agreement with the linear spectrum at half energy is not as good as for 2-14. The trisv(phenylethynyl)-bridged complex 2-52 has a more pronounced local maximum (ca. 8000 cm$^{-1}$) in the $\gamma_{im}$ spectrum than the bis(phenylethynyl)-bridged complex 2-14. The band at lowest energy potentially originates from instantaneous 3PA. The increase in the nonlinear absorptive response with increasing the number of phenylethynyl units in each bridge from 2 to 3 is reflected by the larger $\sigma_2$ maximum of 31300±3000 GM (3 phenylethynyl
Figure 2.53  a) Structure of 2-53.  b) Energy-dependent plot of $\gamma_{\text{Re}}$ and $\gamma_{\text{Im}}$ for the octupolar ruthenium acetylide complex 2-53. Empty circles: imaginary (absorptive) part of $\gamma$. Full diamonds: real (refractive) part of $\gamma$. Solid line: linear absorption spectrum displayed at half energy.

units) compared to 20100±1800 GM found for 2-14 (2 phenylethynyl units). The high energy maximum of $\sigma_2$ value has not been found; there is no local maximum (see Figure 2.52).

Proceeding from bis- and tris(phenylethynyl)-bridges to tetra(phenylethynyl)-bridges (complex 2-53), and from there to hepta(phenylethynyl)-bridges (2-54), does not result in a drastic increase of the NLO response, as can be seen in Figures 2.53 and 2.54. The energies, at which local maxima of $\gamma_{\text{Im}}$ appear are very similar. A band at 8000 cm$^{-1}$ (1250 nm) was observed in both, which results from 3PA (see page 168). The band at ca. 11200 cm$^{-1}$ (890 nm; 2-53) is shifted to slightly higher energy for the most extended octupolar complex 2-54

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Figure 2.54 a) Structure of 2-54. b) Energy-dependent plot of $\gamma_{R \epsilon}$ and $\gamma_{I \epsilon}$ for the octupolar ruthenium acetylide complex 2-54. Empty circles: imaginary (absorptive) part of $\gamma$. Full diamonds: real (refractive) part of $\gamma$. Solid line: linear absorption spectrum displayed at half energy.
Figure 2.55 a) Structure of 2-53. b) Frequency-dependent \( \sigma_2 \) spectrum of the octupolar ruthenium acetylide complex 2-53. \( \sigma_2 \)-values were derived from \( \gamma_{1m} \) and are given in units of Göffpert-Mayer (GM).

(11 500 cm\(^{-1}\); 870 nm). Whereas the high-energy region of the \( \gamma_{1m} \)-spectrum of 2-52 does not show a local maximum, the more extended analogue 2-53 shows a local maximum at around 17 300 cm\(^{-1}\) (580 nm), although it is subtle, almost appearing as a plateau within the error margins. 2-54 plateaus in that region, i.e. it does not show a maximum, but the slope of the curve at the high-energy-end of the spectrum tends towards zero. The corresponding two \( \sigma_2 \) spectra of 2-53 and 2-54 are given in Figures 2.55 and 2.56. In absolute terms, there are no sizable differences between 2-52 and 2-53. Complex 2-53 has a \( \sigma_{\text{max}} \) value of 28 400±3700 GM, whereas the largest value for 2-52 was measured to be slightly higher (31 300±3000 GM). Lengthening the phenylethynyl bridges from 4 (complex 2-53) to 7 phenylethynyl units in each bridge (2-54), \( \sigma_{2,\text{max}} \) increases
Figure 2.56  a) Structure of 2-54.  b) Frequency-dependent $\sigma_2$-spectrum of the octupolar ruthenium acetylide complex 2-54. $\sigma_2$-values were derived from $\gamma_{1m}$ and are given in units of Göppert-Mayer (GM).

by 15% to an absolute value of $35\,800 \pm 3100\,\text{GM}$ (at 18 200 cm$^{-1}$ or 550 nm). All the chloro-capped stars, including the previously-reported complex 2-9*, show a defined band in the region between 11 200 and 11 600 cm$^{-1}$ (890–860 nm). For the phenylacetylide-capped complex 2-10*, this band is blue-shifted (ca. 12 300 cm$^{-1}$; 810 nm), and in the case of the nitro-substituted complex 2-18, the band is obscured by additional adjacent bands, so that this part of the spectrum appears more like a plateau. Interestingly, the intensity of the band is higher for the bis(phenylethynyl)-bridged complex 2-14 than it is for the tris(phenylethynyl)-bridged complex 2-52. For the 2-ethylhexyl substituted complexes 2-52, 2-53 and 2-54, the intensity of the band increases with increasing bridge-length. In order to make a qualitative comparison easier to follow for the reader, the $\sigma_2$
traces of all 5 octupolar ruthenium mono-acetylide complexes discussed above were combined in one graph in Figure 2.57. The comparison emphasizes the drastic increase in $\sigma_2$ on increasing the bridge-length from one phenylethynyl unit (2-9°) to two units (2-14). Increasing the bridge length further, even when (more than) doubled again (from 3 phenylethynyl units in 2-52, to 7 phenylethynyl units in 2-54), does not result in a comparable enhancement. The diagram also shows that the four complexes 2-14, 2-52, 2-53 and 2-54 show nonlinear absorption around 8000 cm$^{-1}$, which is likely to be the result of 3PA. Therefore, the 3PA cross-section ($\sigma_3$) was calculated from experimental data in the same way as had been done for the nitro-substituted complex 2-18 (see Figure 2.49 on page 159). Figure 2.58 shows the 3PA spectra of the four mono-acetylide complexes. All four complexes show a $\sigma_{3,\text{max}}$ between 8000 and 8300 cm$^{-1}$ (1250–1200 nm). The absolute values of $\sigma_{3,\text{max}}$ are $2 \cdot 10^{-77}$ cm$^6$ s$^2$ for the complex with a bridge-length of 2 (2-14) and 3 (2-52) phenylethynyl units. A slight increase to just above $3 \cdot 10^{-77}$ cm$^6$ s$^2$ was observed for the complexes with bridge-length of 4 (2-53) and 7 (2-54) phenylethynyl units. In comparison to the nitro-substituted complex 2-18 ($\sigma_{3,\text{max}} = 5 \cdot 10^{-77}$ cm$^6$ s$^2$), all four chloro-substituted complexes, even the hepta(phenylethynyl)-bridged complex 2-54 exhibits a smaller 3PA cross-section.

Figure 2.59 shows the $\sigma_{2,\text{max}}$-values of the 7 ruthenium mono- and bis-acetylide complexes, taking into account the „1PA threshold” of 500 M$^{-1}$ cm$^{-1}$. For the complex 2-14 this means that the largest $\sigma_2$-value measured at 18 200 cm$^{-1}$ (550 nm) cannot be included (20 600±1800 GM at a linear extinction coefficient of $\varepsilon = 700$ M$^{-1}$ cm$^{-1}$). Although this value is not exceeding the threshold significantly, in particular when error margins in UV-Vis measurements are considered, the data point should certainly be treated with care and should probably be considered at the onset of linear absorption. For consistency, I decided to exclude this data point in this discussion. The error margins vary between 10–20% (see Table 2.3 on page 176), and 15% error margin are depicted in Figure 2.59.

Comparing uncorrected $\sigma_2$-values gives an idea about absolute differences, but does not reflect on the NLO efficiencies of materials that are being compared.

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16 To obtain the graphs, experimental data were computationally interpolated from a curve fit, using the KaleidaGraph program (v. 4.1.0). Interpolated $\sigma_2$ values were exported to a data sheet to permit plotting all five traces in one diagram. Because error margins have been neglected in this procedure, the represented comparison should only be considered qualitative.
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Figure 2.57 a) Structures of complexes 2-9', 2-14, 2-52, 2-53, and 2-54. b) Frequency-dependent $\sigma_2$ spectra of the chloro-capped octupolar ruthenium mono-acetylide complexes. The legend shows compound numbers, followed by the number of phenylethynyl units in the oligo(phenylethynyl)-bridges. Error bars were omitted for clarity, and lines were included to guide the eye.
Figure 2.58 $\sigma_3$ spectra of octupolar ruthenium mono-acetylide complexes. a) 2-14; b) 2-52; c) 2-53; d) 2-54. Data points with error bars: $\sigma_3$ calculated from $\gamma_{1}\text{Im}$. Solid black line: Linear absorption spectra projected into the wavenumber region at $1/3$ of the initial photon energy. e) Structures of the above complexes.
to each other. Kuzyk addressed this matter and suggested normalized 2PA cross-sections.\textsuperscript{[669]} His approach was to work with a ratio of the measured NLO response to the highest theoretically achievable NLO response of a given NLO-active material, rather than with absolute (i.e. uncorrected) values.\textsuperscript{[670]} Kuzyk calls this the intrinsic NLO value, and he specifically writes about the intrinsic first and second hyperpolarizabilities, $\beta^\text{int}$ and $\gamma^\text{int}$. They can be obtained by dividing measured values ($\beta_0$, $\gamma_0$) by the theoretically derived maxima $\beta_0^\text{max}$ or $\gamma_0^\text{max}$, which are referred to as the \textit{fundamental limits} (Equations 2.1 and 2.2).

\begin{align*}
\beta_0^\text{int} &= \frac{\beta_0}{\beta_0^\text{max}} \quad (2.1) \\
\gamma_0^\text{int} &= \frac{\gamma_0}{\gamma_0^\text{max}} \quad (2.2)
\end{align*}

What this means is that values obtained from the two given equations can be compared across different compounds, independent of the size of the molecules. The larger the value for a given molecule, the more efficiently that molecule uses its electronic and structural features to yield the NLO response. This sort of scaling is of interest, in order to explore the structure-property relationships within families of compounds, i.e. to determine the origin of NLO effects. In
Figure 2.60 a) Structures of the seven octupolar ruthenium mono- and bis-acetylide complexes 2-9\textsuperscript{*}, 2-10\textsuperscript{*a}, 2-14, 2-18, 2-52, 2-53, and 2-54. b) Comparison of uncorrected 2PA cross-section maxima ($\sigma_{2,\text{max}}$: blue) with values that have been scaled by the molecular weight ($\sigma_{2,M}$: red).

terms of the applicability of materials for optical devices, the intrinsic values are not too important. The determination of fundamental limits for complexes synthesized throughout the present work is not trivial. Moreover, other (more easily accessible) scaling factors have to be chosen when the NLO efficiency of materials for devices is to be established. A common approach is to scale NLO data by the molecular weight. Figure 2.60 shows a comparison between the uncorrected $\sigma_{2,\text{max}}$ and the corresponding molecular weight-corrected values ($\sigma_{2,M}$) of the 7 ruthenium acetylide complexes discussed above. Considering the molecular weight of the NLO-active material leads to a change in the overall trend.
The uncorrected values show a rising trend on increasing the bridge-length [(2-14 → 2-52 (→ 2-54; taking error margins into account, $\sigma_2$ of 2-54 does not exceed that of 2-52)]. For MW-corrected values this trend is less pronounced, which is particularly clear when $\sigma_{2,M}$ of 2-54 is compared to $\sigma_{2,M}$ of 2-52; 2-52 dominates over 2-54, which demonstrates that the NLO efficiency does not increase with increasing molecular weight.

Another scaling factor is the number of effective $\pi$-electrons ($N_e$) in the compound.\textsuperscript{[671]} Recently, $N_e^2$ (instead of $N_e$) was suggested as the appropriate scaling factor for third-order NLO effects.\textsuperscript{[534]} Scaling by the molecular weight accounts for the weight (and thus approximately for the size) of the molecule. Scaling by $N_e$ or $N_e^2$ considers the conjugation pathlength. The calculation of $N_e$ for fully conjugated (organic) systems was described by Kuhn.\textsuperscript{[672,673]} If a molecule consists of conjugated fragments that are separated by moieties that disrupt the full conjugation across the whole molecule, then $N_e$ can be calculated using Equation 2.3.\textsuperscript{[670]}

\[
N_e = \sqrt{\sum_{i}^{n} N_i^2}
\]  

(2.3)

$N_e$ is the total number of effective $\pi$-electrons in the molecule and $N_i$ the number of effective $\pi$-electrons in the $i$\textsuperscript{th} conjugated fragment separated from all other conjugated fragments. An example found in the literature\textsuperscript{[674]} is given in Figure 2.61. Importantly, Perez-Moreno’s and Kuzyk’s approach to calculate $N_e$ is different from what has been suggested by Drobizhev et al.\textsuperscript{[675]} According to Drobizhev, the nitrogen nodes are considered as part of a fully conjugated system, and each N atom contributes two electrons to the $\pi$-system, which increases $N_e$. Kuzyk and Perez-Moreno, however, describe the nitrogen atoms as moieties that disrupt the conjugation (because the series of alternating single- and double bonds is broken at the nitrogen atoms), which results in the aforementioned compounds consisting of $\pi$-conjugated fragments. Drobizhev’s approach is supported by crystallographic data, for which all three N-C bonds in the solid-state structure of triphenylamine\textsuperscript{[676]} and a related stilbene derivative\textsuperscript{[677]} are lying in one plane. Calculations also support an extended $\pi$-conjugation across the central nitrogen atom.\textsuperscript{[678]} Lupton et al. provided a combination of experimental data and calcu-
lations that emphasized the stark difference between N-cored and phenyl cored dendrimers in terms of the delocalization of \( \pi \)-electrons across the central unit.\cite{679} Lupton's result points towards a disruption of the conjugation in dendrimers with a 1,3,5-substituted phenyl core, whereas N-cored dendrimers show conjugation through the nitrogen atom. Yang et al. describe this as the *amino conjugation effect*.\cite{680} Based on these results, I saw the need to suggest a different approach to calculate \( N_e \), where nitrogen contributes to the conjugation across the system.

In order to be able to distinguish between the two different methods, the effective \( \pi \)-electrons that are calculated from the approach that includes the nitrogen atoms will be abbreviated as \( N_{e,N} \) from this point onwards. Applying this method to the two sample structures in Figure 2.61 results in an increase of the number of effective \( \pi \)-electrons from \( N_e \) to \( N_{e,N} \). This aspect of calculating the effective number of \( \pi \)-electrons will become important for the complexes in Chapter 3. For the octupolar complexes presented in this Chapter, the situation is different, since 1,3,5-substituted phenyl rings replace the nitrogen atoms. As indicated above, phenyl rings with such a substitution pattern behave like disrupting or insulating moieties. Therefore, each bridge was considered as a conjugated moiety, being separated from all remaining bridges by the central phenyl ring. Because some of the \( \pi \)-electrons of the central phenyl ring are delocalized into each bridge, two of the six electrons were assigned to each bridge. The ruthenium centers also have to be considered in these systems. If Kuzyk's approach is followed, where nitrogen atoms are seen as disruptors, then the ruthenium centers should be treated similarly, giving \( N_e \). However, if an attempt was made to distinguish between non-carbon moieties that are insulating and those that are not (fully) disrupting the conjugated system, then the ruthenium centers should not be treated as disruptors. Unlike other metal centers, such as platinum, ruthenium

Figure 2.61 Counting of effective \( \pi \)-electrons when nitrogen atoms are considered as nodes that disrupt the \( \pi \)-conjugation (\( N_e \)) or when they are considered part of the conjugation pathway (\( N_{e,N} \)).
centers facilitate electron transfer across the metal. Therefore, two ways to count the effective electrons in the presence of ruthenium centers are possible again. This means that for complexes containing both nitrogen and ruthenium, three different values for the effective \( \pi \)-electrons can be envisaged:

- **\( N_e \)**: Both nitrogen and ruthenium are considered as disrupting units that separate conjugated moieties from each other.

- **\( N_{e,N} \)**: Nitrogen atoms are part of the conjugated system and contribute 2 electrons to it. Ruthenium centers are considered as disrupting units that separate conjugated moieties from each other.

- **\( N_{e,Ru} \)**: Both nitrogen and ruthenium are considered as part of the conjugated system; each nitrogen and ruthenium atom contributes 2 electrons to the conjugated system.

Two examples are given in Figure 2.62, where all three methods of counting the effective number of \( \pi \)-electrons were applied to complexes; Table ?? gives values for \( N_e \), \( N_{e,N} \) and \( N_{e,Ru} \) for the octupolar complexes discussed so far. Table 2.3 shows the scaling factors obtained from employing different methods of counting the effective number of \( \pi \)-electrons in the octupolar ruthenium-acetylide complexes (besides other scaling factors that are discussed in the next few paragraphs). Using
The table below lists the number of unique configurations for the octupole of ruthenium complexes. The table includes columns for the number of unique configurations, the number of electrons, and the angular momentum quantum number (l). The complexes are labeled as 2.5, 2.10, 2.14, 2.18, 2.22, and 2.24. The number of unique configurations increases with decreasing angular momentum quantum number, indicating that the complexes with lower angular momentum have more unique configurations.
the electron-scaling factor, the octupolar ruthenium mono-acetylide complex 2-52 dominates over all other larger and smaller complexes by more than 20%, and it has twice the NLO efficiency of the hepta(phenylethynyl)-bridged ruthenium mono-acetylide complex 2-54. The bis-acetylide complexes show a loss of NLO efficiency compared to their analogous mono-acetylide complexes. There is a constant loss of NLO efficiency on increasing the bridge-length from 2 phenylethynyl units via 3 (2-52) units to 7 units (2-54), the tetra(phenylethynyl)-bridged complex 2-53 not following this trend due to the aforementioned low yield. This renders 2-53 a poorer NLO material than both 2-52 (3 phenylethynyl units) and 2-54 (7 phenylethynyl units).

The NLO results discussed above, including corrected and uncorrected $\sigma_{2,\text{max}}$, are summarized in Table 2.3. Using the number of effective $\pi$-electrons as a scaling factor for the NLO properties of the octupolar complexes discussed so far, Figure 2.63 was obtained, showing the maximum two-photon absorption cross-section divided by $N_e$ ($\sigma_{2,N_e}$) and $N_{e,Ru}$ ($\sigma_{2,NeRu}$). Because none of these complexes bears nitrogen atoms linking conjugated fragments to each other, the values obtained for $N_{e,N}$ and $N_e$ are the same. Recently, Perez-Moreno has pointed out that using the squared number of effective $\pi$-electrons ($N_e^2$) as a scaling factor for third-order NLO effects is more appropriate, rather than using $N_e$.\textsuperscript{[534]} If this suggestion is included in the current work, the appearance of Figure 2.63 adjusts to the diagram that is given in Figure 2.64; comparing the two diagrams, the considerable impact of the applied scaling scheme on the NLO efficiency is revealed. In particular, the bis-acetylide complexes 2-10$^*$ and 2-18 show sharp drops in the scaled 2PA cross-sections when the ruthenium centers are included as part of the conjugated system. For the mono-acetylide complexes, the difference between $\sigma_{2,Ne}$ and $\sigma_{2,NeRu}$ becomes smaller with increasing bridge-length, which is intuitively clear. Regardless of the chosen method to calculate the number of effective $\pi$-electrons, the NLO efficiency peaks for a bridge-length of 2 or 3 phenylethynyl units, and drops after that. This drop is even more pronounced when the square of $N_e$ or $N_{e,Ru}$ is used (see Figure 2.64).

Besides molecular weight and effective $\pi$-electrons, we have suggested scaling NLO data by the cost of production that occurs when a specific NLO material is synthesized.\textsuperscript{[535]} In order to calculate the overall cost that occurs with the preparation of 1 mmol of a final complex, the synthetic route was traced back

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Figure 2.63 $\sigma_{2,\text{max}}$ of complexes 2-9*, 2-10*, 2-14, 2-18, 2-52, 2-53 and 2-54 divided by $N_{e,N}$ (blue, left) and $N_{e,Ru}$ (red, right), giving the corresponding scaled two-photon absorption cross-sections $\sigma_{2,NeN}$ and $\sigma_{2,Ru}$. 
Figure 2.64 $\sigma_{2,\text{max}}$ of complexes $2-9^*$, $2-10^{\text{n}}$, 2-14, 2-18, 2-52, 2-53 and 2-54 divided by $N_e^2$ and $N_{e,Ru}^2$, giving the corresponding scaled two-photon absorption cross-sections $\sigma_{2,Ne^2}$ (blue, left) and $\sigma_{2,Ne\text{Ru}^2}$ (red, right).
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to commercially available starting materials. This was accomplished based on Schemes 2.1, 2.2, 2.3, 2.4, 2.5, 2.6, 2.7, 2.8, 2.9 and 2.10. For each step, the required amount of starting materials/reagents was calculated based on the yield (in %) of the reaction and the desired amount of the product (in mol). Because solvents can contribute significantly to the overall cost of such a scheme, the average volume of solvent used in a reaction per mol of starting material in that reaction was calculated based on the reactions described in the experimental section of this Chapter. This revealed that roughly 1000 equivalents of solvent were used in the reactions described herein. Where mixtures of two solvents were used, 500 equivalents were included in the calculations for each solvent – only a rough approach as an alternative to excluding solvents completely, which would throw numbers off further. Sigma-Aldrich was chosen as the supplier for the commercially available starting materials, offering all required chemicals.[681]

I am aware that in some (if not most) cases, this is not the cheapest option, but this ensures a consistent approach. Prices were chosen, which keep costs to a minimum; the largest available (and therefore cheapest) quantities were selected when more than one option was given, extra pure reagents were not selected. Solvents that were recognizable as such were included in the calculations using an average amount of 1000 equivalents. The required amount of starting materials was calculated based on the number of steps and yields throughout the synthetic scheme so that 1 mmol of each of the seven octupolar complexes discussed herein would be obtained. For this purpose, each Scheme was followed back from the last step through to the very first one. The required amount of starting materials were adjusted so that at each step, a reaction would give just enough material as necessary to run the next reaction. The spreadsheets giving prices used for the calculations, chemicals involved and yields are provided in the attached Tables (see Appendix). The digital spreadsheets, which allow facile adjustment of prices, yields and desired amounts of the final product, to give instantaneous overall costs, are available and can be provided. Calculating the costs for the synthesis of a given amount of material over a certain number of individual steps involves a variety of starting materials, work-up procedures, reaction times and conditions, reproducibility and many other factors. The numbers given here should therefore be considered as trends only. By keeping criteria for the determination of costs constant (single-provider, cheapest option, same methodology for the calculation,
Figure 2.65 Comparison of syntheses of 1 mmol of the octupolar ruthenium-acetylide complexes 2-9*, 2-10**, 2-14, 2-18, 2-52, 2-53 and 2-54. a) Number of steps for each complex. b) Absolute costs associated with the syntheses.

etc.), the ratios should represent reasonably reliable trends even though significant errors may be involved in absolute terms. The number of steps and overall costs associated with the synthesis of 1 mmol of complexes 2-9*, 2-10**, 2-14, 2-18, 2-52, 2-53 and 2-54 are depicted in Figure 2.65. A rising trend of the cost with increasing size of the conjugated system is seen, as expected, since the number of steps required to synthesize the complexes increases. The cost of the tetra(phenylethynyl)-bridged complex 2-53 incurs higher costs than the hepta(phenylethynyl)-bridged complex 2-54. The reason for this is the aforementioned low yield in the final step of the synthesis of 2-53. The number of steps are not influenced by the yield and therefore do not follow this trend. The cost-scaled 2PA cross-sections (σ_{2,σ}), are displayed in Figure 2.66.

In conclusion, increasing the number of linearly arranged phenylethynyl units in each bridge of the phenyl cored octupolar ruthenium acetylide complexes discussed herein from 1 via 2 and 3 to 7, was found to result in an increase in the absolute NLO response. The tetra(phenylethynyl)-bridged complex did not follow the trend, giving a slightly decreased response in comparison to the tris(phenylethynyl)-bridged complex 2-52. The largest observed 2PA cross-section was exhibited by the hepta(phenylethynyl)-bridged complex 2-54, the absolute value being 35 000±3100 GM. The two most common scaling factors, namely
the molecular weight (MW) and the number of effective π-electrons, were applied to maximum 2PA cross-sections of all 7 complexes, to account for the size of the complexes and the length of the conjugated system across the complexes. In the case of scaling by MW, the rising trend of $\sigma_2$ is not maintained; a bridge-length of 2 phenylethynyl units (2-14) is almost as efficient as a bridge-length of seven phenylethynyl units (2-54), and the complex incorporating the tris(phenylethynyl)-bridge was found to exhibit the largest NLO efficiency. The two complexes with mono(phenylethynyl) bridges, 2-9* and 2-10*, show significantly lower NLO values than all other complexes, regardless of the applied scaling scheme. Scaling by the number of effective π-electrons renders the complex with tris(phenylethynyl)-bridges the most NLO efficient species, whereas 2-54 (7 phenylethynyl units) shows the smallest NLO efficiency. The decrease in NLO efficiency on extending the bridge-length beyond 3 phenylethynyl units is even more pronounced when the square of the number of effective π-electrons is used. The cost that is associated with the synthesis of 1 mmol of any of the given octupolar complexes was introduced as a new scaling factor, which depends on the cost of commercially available starting materials, the number of steps in a given reaction scheme and the corresponding yields. This scheme rendered complex 2-14 [bis(phenylethynyl bridges] the most NLO efficient by at least 100%. Replacing the chloro ligand in mono-acetylide complexes with a
second alkyne, affording the corresponding bis-acetylide complexes, increases the cost of production significantly. This is the case even if simple acetylenes, such as phenylacetylene, are used for the ligand replacement, which means that bis-acetylide complexes show significantly decreased cost-corrected NLO efficiencies compared to their parent mono-acetylide complexes. Overall, a bridge-length of 2 or 3 phenylethynyl units was found to deliver NLO responses that lead to good NLO efficiencies, although the absolute values have not reached a plateau at a bridge-length of 7 phenylethynyl units. However, regardless of the scaling scheme that is applied to the NLO values, anything beyond 4 phenylethynyl units does not afford an increase in the intrinsic NLO properties.

2.5 Experimental

2.5.1 Instrumentation

Electrospray ionization (ESI) mass spectra were recorded using a LCT-ZMD single quadrupole liquid chromatograph-MS (Waters-Micromass). High resolution ESI mass spectra were carried out utilizing a LCT Premier XE ESI-TOF instrument (Waters-Micromass). Organometallic complexes were usually measured in acetonitrile or methanol, using minimal amounts of dichloromethane when lack of solubility necessitated, under the following conditions: 12000 RP, w+ mode, capillary potential = +3500 V, cone potential = +150 V. Some linear organic molecules required similarly forcing conditions, such as capillary potentials of +3000 V and cone potential of +180 V with added formic acid. EI mass spectra were recorded using a quadrupole VG Autospec EI-MS instrument (Fisons Instruments); all mass spectrometry peaks are reported as m/z ([assignment], relative intensity).

Microanalyses were carried out by the Microanalysis Service Unit at the Research School of Chemistry, Australian National University. Standard CHN analyses were carried out on an EA3000 instrument (EuroVector) with U-shaped quartz oxidation tube or on a CE1106 instrument (Carlo Erba) with a straight quartz oxidation tube; Co²⁺/Co³⁺ or chromium dioxide were used as oxidation catalysts,
and Cu(0) was used as reduction catalyst; for all organometallic complexes, V\textsubscript{2}O\textsubscript{5} combustion agent was added to the samples.

Infrared (IR) spectra were recorded using a Perkin-Elmer System 2000 FT-IR spectrometer as dichloromethane solutions using CaF\textsubscript{2} cells; peaks are reported as frequencies in wavenumbers (cm\textsuperscript{-1}) [Relative Transmission, Assignment].

UV-Vis spectra were recorded on a Cary 5 spectrophotometer as dichloromethane solutions in 1 cm quartz cells; bands are reported as frequencies in wavenumbers (cm\textsuperscript{-1}) [extinction coefficient (10\textsuperscript{3} M\textsuperscript{-1} cm\textsuperscript{-1})].

\textsuperscript{1}H (300 MHz, 500 MHz), \textsuperscript{13}C (75 MHz, 126 MHz) and \textsuperscript{31}P (121 MHz, 202 MHz) NMR spectra were recorded using a Mercury 300 FT NMR spectrometer (Varian) or an Innova 500 FT NMR spectrometer (Varian), and were referenced to residual chloroform (7.26 ppm), solvent CDCl\textsubscript{3} (77.0 ppm) and external H\textsubscript{3}PO\textsubscript{4} (0.0 ppm); \textsuperscript{11}B (96 MHz) NMR spectra were recorded on an Innova 300 FT NMR spectrometer (Varian) and were referenced to BF\textsubscript{3}·Et\textsubscript{2}O. Atom labeling follows the schemes displayed on the individual spectra that are attached to the Appendix.

Cyclic voltammetry measurements were recorded using an EA161 potentiostat (eDAQ Pty Ltd.) and an e-corder 401 (eDAQ Pty Ltd.) on Echem 2.5.4 software; measurements were carried out at room temperature (RT) using Pt disk working-, Pt wire auxiliary-, and Ag/AgCl reference electrodes, such that the ferrocene/ferrocenium redox couple was located at 0.56 V (peak separation ca. 0.09 V). Scan rates were typically 100 mV s\textsuperscript{-1}. Electrochemical solutions contained 0.1 M NBu\textsubscript{n}\textsubscript{4}PF\textsubscript{6} and about 10\textsuperscript{-3} M complex in freshly distilled and deoxygenated tetrahydrofuran (unless stated otherwise). Solutions were purged and maintained under a nitrogen or argon atmosphere.

Concentration dependent fluorescence spectrometry was carried out using a Cary Eclipse fluorescence spectrophotometer (Varian) on Cary Eclipse Scan Application software (v. 1.1.; Galactic Industries). Solutions were prepared in concentrations of ca. 10\textsuperscript{-4} mol L\textsuperscript{-1} and then diluted using the same solvent. Unless stated otherwise, glass-distilled dichloromethane dried over calcium hydride was used as solvent.

Spectroelectrochemical studies were carried out in solutions of 0.3 M NBu\textsubscript{n}\textsubscript{4}PF\textsubscript{6} in freshly distilled and deoxygenated tetrahydrofuran at room temperature unless
stated otherwise; oxidized species were electrogenerated in an optically transparent thin-layer electrochemical (OTTLE) cell with potentials ca 50–200 mV beyond $E_{1/2}$ for each couple, to ensure complete electrolysis. UV-Vis spectra during the oxidation/reduction processes were recorded on a Cary 5 spectrophotometer.

The real and imaginary parts of the second hyperpolarizability $\gamma (\gamma_{Re}$ and $\gamma_{Im})$ were determined using the Z-scan technique. An amplified femtosecond laser system consisting of an Integra-C regenerative amplifier (Quantronix) operating as a 800 nm (12500 cm$^{-1}$)pump and a Palitra-FS BIBO crystal-based optical parametric amplifier (Quantronix) was used. Measurements were carried out for 23 different energies between 18 180 cm$^{-1}$ (550 nm) and 6250 cm$^{-1}$ (1600 nm) with 400–700 cm$^{-1}$ between each step (ca. 20–50 nm gaps), where the pulse duration was approximately 130 fs and the repetition rate was 1 kHz. The pulse energy was adjusted to keep the nonlinear phase shifts from the samples in the range 0.5–1.5 rad, which typically corresponded to light intensities on the order of 100 GW/cm$^2$. This was achieved by attenuating the beam power with neutral density filters. In some cases, color glass filters were used, in order to remove unwanted spectral components of the Palitra output. The source beam was focused to provide a focal spot in the range $w_0 \approx 25-50 \mu$m, resulting in a Rayleigh range being kept well in excess of the total light path in the sample (ca. 3 mm, including the solution and the walls of the glass cell). The solutions of the measured compounds and the reference solvent were placed in Starna glass cuvettes with a 1mm path length to satisfy the thin sample condition. The cuvettes were moved along the source beam (z-axis) through its focus point over a travel distance of 40 mm (-20 mm to +20 mm). The data were collected by three InGaAs photodiodes that were measuring signals proportional to the intensities of the reference, closed-aperture and open-aperture beams. Signals from the photodiodes were fed into a digital oscilloscope, transferred to a personal computer and collected by custom software written in LabVIEW. All measurements were calibrated by referencing to signals obtained from a 4.66 mm thick fused silica plate. Analysis of the data was performed using custom software that computed theoretical Z-scans according to equations introduced by Sheik-Bahae et al.\textsuperscript{[24]} Fitting the theoretical curves to the measured traces afforded parameters (nonlinear phase shift, T parameter and beam radius at the focal spot) that were then used in the calculation of the real and imaginary parts of the second
hyperpolarizability $\gamma$ ($\gamma_{Re}$ and $\gamma_{Im}$). The effective two-photon absorption (2PA) cross-section, $\sigma_2$, was derived from $\gamma_{Im}$.\cite{32,682} The aforementioned calculations were made assuming the additivity of solvent and solution nonlinearities and using the Lorentz local field approximation. Measurements were carried out at multiple photon energies, in order to obtain a spectral range of NLO data.

### 2.5.2 X-Ray Crystallography

#### 2.5.2.1 Instrumentation

A suitable single crystal of the complexes 2-48, 2-47 and of the organic bromide 2-3\* was coated with a thin layer of the viscous cryoprotectant Paratone-N (Hampton Research) and attached to a glass fiber. Crystallographic data were collected on a Nonius Kappa CCD diffractometer\cite{683} using graphite monochromated Mo-K$_\alpha$ radiation ($\lambda = 0.71073$ Å). During data collection, the crystal was kept at 200 K in a cold stream of an Oxford Cryosystems open-flow nitrogen cryostat,\cite{684} with a nominal stability of ±0.1 K. The unit cell parameters were obtained by least-squares refinement of the reflections, using the DENZO package.\cite{685} After complete data collection and reduction,\cite{686} the crystal faces were measured to allow for absorption correction using numerical methods,\cite{687} implemented from within maXus.\cite{688} Equivalent reflections were merged. The structures were solved by direct methods using the SIR92 software,\cite{689,690} peaks of electron density were located by difference techniques,\cite{691} and the structures refined with the use of the CRYSTALS software package.\cite{692–696} Graphical representations of compound 2-3\* and complexes 2-47 and 2-48 were generated in ORTEP,\cite{697,698} and pictures were graphically refined using the POV-Ray program.\cite{699}.

#### 2.5.2.2 Refinement Details

1,3,5-(BrC$_6$H$_4$-4-C≡C)$_3$C$_6$H$_3$ (2-3\*). Colorless crystals suitable for X-ray crystallographic structure determination were grown by slow diffusion of diethyl-ether into a chloroform solution. The crystallographically asymmetric unit of the monoclinic space group P2$_1$/n contains one molecular unit, and four molecules were found to occupy the unit cell. The Fourier map indicated the presence of
additional electron density away from the main molecule. Attempts to model
the solvent moieties did not withstand anisotropic refinement, so the PLATON
SQUEEZE function\textsuperscript{[695,700,701]} was used, in order to remove excess electron density
and account for the resulting holes in the structure. On applying the SQUEEZE
function, the R-value dropped from 4.03% to 3.96%, so the change was subtle.
The contribution of the electron density to the overall structure were therefore
considered minor.

\textit{trans-}[Ru(C≡C₆H₄-4-C≡CC₆H₄-4-X)Cl(dppe)₂] (2-47: X = Br, 2-48:
X = I). Suitable single crystals were grown by slow diffusion of n-hexane into
a dichloromethane solution, affording orange blocks (2-47). The complex crys-
tallized in the monoclinic space group \textit{P}2\textsubscript{1}/\textit{c}. The crystallographic asymmetric
unit contains one molecular unit and one dichloromethane molecule of solvation.
Four of these units occupy the unit cell. All non-hydrogen atoms were refined
anisotropically with no restraints or constraints being implemented. H atoms
were placed in calculated positions. Restraints on their bond lengths and angles
were applied to regularize their geometry. C-H bonds were set to be 0.950 Å,
and \textit{U}_{\text{iso}}(H) was kept at values corresponding to 1.2 \textit{x} \textit{U}_{\text{eq}} of the parent atom
throughout the refinement. The positions of the hydrogen atoms were refined
with riding constraints and recalculated frequently. Since the shift in the thermal
displacement parameters of the atoms in the dichloromethane molecule did not
stabilize during the anisotropic refinement, soft vibrational restraints were im-
posed on the two chlorine atoms and the carbon atom (2-47 only). The ten largest
peaks in the final difference Fourier map were located within the dichloromethane
moiety and near the halogen atom (2-47, 2-48). The final R-values were 4.44% (2-48)
and 3.84% (2-47).

2.5.3 General Synthetic Conditions and Purification
Procedures

All reactions were carried out in flame-dried glassware and under a nitrogen
atmosphere using standard Schlenk techniques unless stated otherwise. Dichloro-
methane (DCM) was distilled over calcium hydride, and tetrahydrofuran (THF)
was distilled over sodium/benzophenone prior to use. Triethylamine (NE\textsubscript{t}₃),
dimethylsulfoxide (dmoso), toluene, acetone, methanol (MeOH), \textit{n}-pentane and
n-hexane were used as received. Petrol refers to a fraction of petroleum with a boiling range of 60–80 °C; where applicable, the use of petroleum with a boiling range of 40–60 °C is specifically stated.

Trans-halogenation reactions were carried out in tetrahydrofuran. The corresponding workup procedure is the following: \( \text{Na}_2\text{S}_2\text{O}_3 \) (aq.) was added to the reaction mixture at ambient temperature to remove excess iodine. The tetrahydrofuran was removed under reduced pressure, and dichloromethane was added. The organic layer was removed, and the aqueous layer was extracted with dichloromethane twice. The combined organic layers were washed with water twice and dried over anhydrous \( \text{MgSO}_4 \). Filtration through filter paper gave the filtrate that was taken to dryness under reduced pressure.

All organic materials were purified using column chromatography (silica gel, 230–400 mesh ASTM). Products were eluted using appropriate solvent mixtures, where polarity gradients were usually used. Small organic by-products or other impurities were usually removed by washing the column with a non-polar solvent, in most cases \( n \)-hexane, \( n \)-pentane or petroleum spirit (boiling range 40–60 °C). Mixtures of one of these solvents with ethylacetate (or in some cases dichloromethane) was used to increase the polarity and elute the product. In the majority of purifications, flash column chromatography was used, i.e. pressure was applied wherever the separation of products and by-products (or starting materials) allowed this. Where required, activated silica was prepared by heating silica gel to 120 °C for 4–5 days. To generate deactivated silica gel in a controlled fashion 5–10 weight-% of water was added to activated silica; the resulting mixture was placed into a round-bottom flask that was rotated until a homogeneous powder was obtained.

In the case of the ruthenium mono-acetylide complexes and bis-acetylide complexes, purifications were attempted based on differing solubilities of products, starting materials and undesired by-products). For this purpose, concentrated solutions of the material to be purified in an appropriate solvent (in most cases dichloromethane with a small amount of added triethylamine) were dropped into a different solvent or a mixture of solvents. In most cases, smaller components, such as linear mono-acetylide complexes or wedges, would then remain in solution whereas the larger (and less soluble) product would precipitate out and be
collected by filtration. In almost all cases, several such washings or precipitations were necessary to achieve satisfactory purity of the complexes. Where this point could not be reached, chromatographic purification of organometallic complexes was carried out using ungraded basic alumina. Negative results have been obtained in some cases where the alumina was not basic or insufficiently basic. To ensure a basic environment of the complex during workup at all times, a small amount of triethylamine was added to all eluants or eluant mixtures, and the alumina was washed with such a basic eluant (or mixture) before the column was loaded with the complex. Eluants were typically mixtures of \( n \)-hexane or petroleum spirit (boiling range 40–60°C) and dichloromethane in ratios between 8:1 to 1:2. Precipitating products thus obtained from methanol again proved to be convenient, since the precipitate can be isolated by a simple filtration, which is easier than mechanically removing products from the wall of reaction flasks.

### 2.5.4 Starting materials

#### 2.5.4.1 Commercially Available and Previously-Reported Materials

The following starting materials, substrates and catalysts were commercially available, purchased from common chemical suppliers and used as received: 1-bromo-4-iodobenzene, \([\text{PdCl}_2(\text{PPh}_3)_2]\), \([\text{Pd}(\text{PPh}_3)_4]\), \(\text{CuI}\), \(\text{KOH}\), iodine, bromine, \(\text{Me}_3\text{SiC}==\text{CH}\), \((\text{i-Pr})_3\text{SiC}==\text{CH}\), \(\text{PhC}==\text{CH}\), 1-bromo-2-ethylhexane, \(\text{NBu}^n\text{F}\) (1.0 M in \(\text{THF}\)), \(n\)-\(\text{BuLi}\) (1.6 M in \(n\)-hexane), \(\text{RuCl}_3.3\text{H}_2\text{O}\), 1,3,5-tribromobenzene, 1-bromo-4-nitrobenzene, 1,2-bis(diphenylphosphino)ethane, magnesium.

Commercially available \(\text{NaPF}_6\) was recrystallized from acetonitrile prior to use and kept under an argon or nitrogen atmosphere.

The following materials were synthesized using published literature procedures or slight modifications thereof:

- 1,3,5-(\(\text{HC}==\text{C}\))\(_3\)\(\text{C}_6\text{H}_3\) (procedure\(^{[609]}\), characterization\(^{[610]}\))
- 1,3,5-(\(\text{Me}_3\text{SiC}==\text{C}\))\(_3\)\(\text{C}_6\text{H}_3\) (procedure\(^{[609]}\), characterization\(^{[610]}\))
- 1,3,5-(\(\text{BrC}_6\text{H}_4-4\)-\(\text{C}==\text{C}\))\(_3\)\(\text{C}_6\text{H}_3\)\(^{[611]}\)
- 1,3,5-(\(\text{HC}==\text{CC}_6\text{H}_4-4\)-\(\text{C}==\text{C}\))\(_3\)\(\text{C}_6\text{H}_3\)\(^{[617]}\)
• 1,3,5-(HC≡C₆H₄-4-C≡C₆H₄-4-C≡C)₃C₆H₃ \[^{612}\]
• 1,4-bis(2-ethylhexyl)benzene \[^{625}\]
• 1,4-dibromo-2,5-bis(2-ethylhexyl)benzene \[^{635}\]
• 1-bromo-2,5-bis(2-ethylhexyl)-4-iodobenzene \[^{638}\]
• (i-Pr)₃SiC≡C₆H₄-4-C≡CSiMe₃ \[^{629}\]
• (i-Pr)₃SiC≡C₆H₄-4-C≡CH \[^{629}\]
• Me₃SiC≡C₆H₄-4-Br \[^{630}\]
• Me₃SiC≡C₆H₄-4-I \[^{632}\]
• HC≡C₆H₄-4-Br \[^{630}\]
• (i-Pr)₃SiC≡C₆H₄-4-C≡C₆H₄-4-Br \[^{702}\]
• Me₃SiC≡C₆H₄-4-C≡C₆H₄-4-Br \[^{630}\]
• HC≡C₆H₄-4-C≡C₆H₄-4-Br \[^{631}\]
• RuCl₂(dmsol)₂ \[^{703}\]
• cis-[RuCl₂(dppe)₂] \[^{513}\]
• cis-[RuCl₂(dppm)₂] \[^{704}\]
• trans-[Ru(C≡C₆H₄-4-I)Cl(dppe)₂] \[^{639}\]

The following starting material was kindly supplied by Prof. P. J. Low and co-workers (Durham University, UK):

• N(C₆H₄-4-C≡CSiMe₃)₃

The following materials were locally synthesized by Patrick J. West and used in a joint project, resulting in the mixed-metal star-shaped Ru/Os-complexes:

• trans-\([HC≡C₆H₄-4-C≡C]Os(C≡C₆H₄-4-C≡CSi(i-Pr)₃)(dppe)₂\]
• trans-\([IC₆H₄-4-C≡C]Os(C≡C₆H₄-4-C≡CH)(dppe)₂\]
• trans-\([IC₆H₄-4-C≡C₆H₄-4-C≡C]Os(C≡C₆H₄-4-C≡CH)(dppe)₂\]
• 1,3-\{trans-[OsCl(dppe)₂(C≡C)]\}_2-5-(HC≡C)C₆H₃

\[^{17}\] cis-[RuCl₂(dppm)₂] was provided by Dr. M. P. Cifuentes, so I did not prepare this complex.
2.5.4.2 Modified literature procedures

\( 1,3,5-(\text{Me}_3\text{SiC}≡\text{CC}_6\text{H}_4·4·\text{C}≡\text{CC}_6\text{H}_4·4·\text{C}≡\text{C})_2\text{C}_6\text{H}_3 \) (2-7*)

2-6 (0.60 g, 0.66 mmol, 1.0 eq.), [PdCl₂(PPh₃)₂] (0.023 g, 0.023 mmol, 0.03 eq) and CuI (0.024 g, 0.13 mmol, 0.19 eq) were dissolved in a mixture of triethylamine and dichloromethane (30 mL/35 mL). The mixture was deoxygenated, and \( \text{Me}_3\text{SiC}≡\text{CH} \) (0.32 g, 3.28 mmol, 5.0 eq.) was added. An instantaneous color change to brown-green was observed. The mixture was stirred at room temperature for 30 min, before being heated at reflux for 12 h. The solution was allowed to cool to room temperature, after which [PdCl₂(PPh₃)₂] and CuI (catalytic amount) were added. The resultant mixture was deoxygenated, and \( \text{Me}_3\text{SiC}≡\text{CH} \) (0.10 g, 1.1 mmol, 1.6 eq.) was added. The solution was stirred at room temperature for 40 min and was then heated at reflux for 20 h, over which time the addition of \( \text{Me}_3\text{SiC}≡\text{CH} \) (0.06 g, 0.61 mmol, 0.9 eq) was repeated twice. The salt was removed from the solution by filtration through a sintered glass filter funnel. The solvent was removed from the filtrate in vacuo, affording a solid, which was purified, using silica column chromatography (l = 10 cm, \( \phi = 4.5 \) cm). A mixture of petrol and ethylacetate (6:1 to 3:1) and then petrol and dichloromethane (1:1) was used to elute the product from the silica column. All fractions containing the product were combined, affording a deep red solution. The solvent was removed in vacuo, and the flask containing the residue was cooled on liquid nitrogen. Cold dichloromethane was added, and the solid was separated from the solution by filtration through a sintered glass filter funnel. The beige, solid residue was washed with cold dichloromethane several times. The combined washing solutions were taken to dryness under reduced pressure, affording 0.518 g (0.54 mmol, 82%) of the product as a beige, amorphous solid. Spectroscopic properties matched previously-reported data.\(^{[612]}\)

\( 1,3,5-(\text{Me}_3\text{SiC}≡\text{CC}_6\text{H}_4·4·\text{C}≡\text{C})_2\text{C}_6\text{H}_3 \) (2-4*)

In a flame-dried 250 mL two-neck round-bottom flask fitted with a condenser, 1,3,5-(\( \text{BrC}_6\text{H}_4·4·\text{C}≡\text{C} \))_3\text{C}_6\text{H}_3 (6.0 g, 9.75 mmol, 1.0 eq.), [PdCl₂(PPh₃)₂] (0.48 g, 0.68 mmol, 0.07 eq) and CuI (0.11 g, 0.59 mmol, 0.06 eq.) were suspended in
2.5. Experimental

triethylamine (140 mL). The mixture was deoxygenated, and to the highly cloudy, yellow solution was added dichloromethane (70 mL). Me$_3$SiC≡CH (4.79 g, 6.84 mL, 49.8 mmol, 5.1 eq.) was added at room temperature, and the mixture was then heated at reflux for 14 h. The solution was allowed to cool to room temperature, and the addition of Me$_3$SiC≡CH (1.0 g, 10.2 mmol, 2.1 eq.), [PdCl$_2$(PPh$_3$)$_2$] (0.10 g, 0.14 mmol, 0.01 eq) and CuI (0.05 g, 0.28 mmol, 0.02 eq.) was repeated. The mixture was heated at reflux for 6 days, over which period the solution was charged with fresh catalyst four times. The salt was removed from the solution by filtration through a sintered glass filter funnel. To the filtrate was added silica, and the solvent was removed in vacuo, affording a gray, smooth powder. A silica column (l = 8 cm; Ø = 4.5 cm) was charged with the powder, and the product was eluted with a mixture of petrol and ethylacetate (15:1 to 2:1). Removal of the solvent under reduced pressure afforded 5.88 g (8.81 mmol, 90%) of a pale beige solid that was identified as the product by comparison of spectroscopic properties with previously-reported data.[617]

2.5.5 Synthesis and characterization of new compounds

\((i$-$Pr)$_3$SiC≡CC$_6$H$_4$-4-C≡CC$_6$H$_2$-2,5-\{CH$_2$CHEt(CH$_2$)$_3$Me\}$_2$-4-Br (2-32)\)

In a flame-dried 250 mL two-neck round-bottom flask, 1-bromo-2,5-bis(2-ethylhexyl)-4-iiodobenzene \((2-31^*)\) (3.90 g, 7.69 mmol, 1.02 eq.) was dissolved in triethylamine (120 mL). The clear, colorless solution was deoxygenated by bubbling argon through it for 10 min. \((i$-$Pr)$_3$SiC≡CC$_6$H$_4$-4-C≡CH (2-29^*)\) (2.10 g, 7.60 mmol, 1.0 eq.) was added, giving a clear, orange solution. The solution was cooled to 0°C, and [PdCl$_2$(PPh$_3$)$_2$] (0.080 g, 0.11 mmol, 0.02 eq.) and CuI (0.030 g, 0.16 mmol, 0.02 eq.) were added, after which the solution became slightly cloudy. The formation of a light precipitate occurred within 5 min after the addition. The yellow mixture was stirred at 0°C for 1.5 h before the addition of the catalyst pair was repeated. The cooling bath was removed, and the reaction mixture was allowed to warm to ambient temperature over 3 h. The mixture was filtered through a sintered glass filter funnel, affording a beige-brown solid residue. The solvent was removed from the dark-brown to black filtrate in vacuo, giving
a black, cloudy oil, which was dissolved in \( n \)-pentane (10 mL). The resultant solution was pipetted onto a silica column (\( l = 12 \text{ cm}, \varnothing = 7.5 \text{ cm} \)), and the product was eluted with \( n \)-pentane. The combined fractions were dried over MgSO\(_4\), and the solution was filtered. The solvent of the clear filtrate was removed under reduced pressure, affording a clear, colorless oil. The residual solvent was removed under vacuum at 60–70°C over 8 h, affording 3.59 g (5.42 mmol, 71%) of the product as a clear, colorless oil.

**EI MS:** 662.3 ([M]+, 85), 619.3 ([M - C\(_3\)H\(_7\)]+, 100), 549.2 ([M - C\(_6\)H\(_{10}\) + H]+, 35).

**HR EI MS:** Calcld. for C\(_{41}\)H\(_{61}\)\(^{81}\)BrSi: 662.3705. Found: 662.3705. **IR** (CH\(_2\)Cl\(_2\)) [Rel. Transm., Assignn.]: 910 [95.1], 997 [91.2], 1018 [93.3], 1103 [96.1], 1114 [94.3], 1221 [93.7], 1379 [89.9], 1463 [80.2], 1500 [84.2], 1508 [86.0], 2153 [88.9], 2865 [62.5, broad], 2965 [69.9 cm\(^{-1}\)]. UV–Vis (\( \lambda_{\text{max}}, \text{cm}^{-1}\) [\( \varepsilon, 10^3 M^{-1} \text{ cm}^{-1}\)]): 29800 [42.2], 31900 [44.3], 37300 [33.4, sh]. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) 7.45 (s, 4H, H\(_{142}, H_{143}\)), 7.36 (s, 1H, H\(_{134}\)), 7.29 (s, 1H, H\(_{137}\)), 2.75–2.65 (m, 2H, H\(_{1351}\)), 2.65–2.55 (m, 2H, H\(_{1381}\)), 1.78–1.65 (m, 2H, H\(_{1351}, H_{1381}\)), 1.40–1.19 (m, 16H, H\(_{1353}, H_{1354}, H_{1355}, H_{1357}, H_{1383}, H_{1384}, H_{1385}, H_{1387}\)), 1.14 (s, 21H, H\(_{111}\)), 0.94–0.79 (m, 12H, H\(_{1355}, H_{1358}, H_{1386}, H_{1388}\)) ppm. \(^{13}\)C\(^{\text{(1H)}}\) NMR (126 MHz, CDCl\(_3\)): \( \delta \) 143.2 (C\(_{135}\)), 138.5 (C\(_{138}\)), 134.6 (C\(_{137}\)), 133.9 (C\(_{134}\)), 132.0, 131.1 (C\(_{142}, C_{143}\)), 125.1 (C\(_{133}\)), 123.3, 123.2 (C\(_{141}, C_{144}\)), 121.7 (C\(_{136}\)), 106.6 (C\(_{145}\)), 92.8 (C\(_{146}, C_{140}\)), 89.9 (C\(_{139}\)), 40.3 (C\(_{1352}\)), 39.9 (C\(_{1381}\)), 39.2 (C\(_{1382}\)), 38.4 (C\(_{1351}\)), 32.4, 32.3 (C\(_{1353}, C_{1383}\)), 28.8, 28.7 (C\(_{1354}, C_{1384}\)), 25.5, 25.4 (C\(_{1357}, C_{1387}\)), 23.06, 23.03 (C\(_{1355}, C_{1385}\)), 18.7 (C\(_{111}\)), 14.1 (C\(_{1356}, C_{1386}\)), 11.3 (C\(_{110}\)), 10.8 (C\(_{1358}, C_{1388}\)) ppm.

\[ (\text{i-Pr})_3\text{SiC}=\text{CC}_6\text{H}_4-4-\text{C}=\text{CC}_6\text{H}_2-2,5-\{\text{CH}_2\text{CHEt}(\text{CH}_2)_3\text{Me}\}_2-4-\text{I} \ (2-33) \]

In a flame-dried 250 mL two-neck round-bottom flask, 2-32 (3.59 g, 5.42 mmol, 1.0 eq.) was dissolved in freshly distilled tetrahydrofuran (120 mL). The clear, colorless solution was cooled to -78°C (dry ice/acetone). \( n \)-BuLi (2.5 M in \( n \)-hexane; 8.0 mL, 20.0 mmol, 3.69 eq.) was added dropwise over 10 min. Over the course of the addition, the colorless solution became yellow and then green and eventually dark green. The solution was stirred at -78°C for 1 h before a concentrated solution of iodine in dry tetrahydrofuran was added slowly over 20 min. Following the addition, the reaction mixture gradually became dark
yellow to orange. Further iodine solution was added until ensure the presence of excess iodine, which was indicated by the deep, red color of the reaction mixture. The formation of a significant amount of salt was observed shortly after the addition was finished. The reaction mixture was allowed to warm to ambient temperature over 1.5 h. The standard workup procedure for trans-halogenation reactions (see page 2.5.3) was carried out. A crude orange oil was obtained, which was purified by silica column chromatography (l = 17 cm, Ø = 4.5 cm) with n-pentane as eluant. The solvent of the combined fractions was removed under reduced pressure, giving a pale pink, viscous oil. The residual solvent was removed under vacuum at -60°C, affording 3.51 g (4.95 mmol, 91%) of the product.

EI MS: 708.9 ([M]+, 76), 665.6 ([M - C₅H₇]⁺, 100), 637.5 ([M - C₅H₁₁]⁺, 28), 623.4 ([M - C₆H₁₃]⁺, 48), 609.4 ([M - C₇H₁₅]⁺, 42), 595.3 ([M - C₈H₁₇]⁺, 50). 
HR EI MS: Calcd. for C₄₁H₆₁I: 708.3587. Found: 708.3586. IR (CH₂Cl₂) [Rel. Transm., Assignm.]: 997 [95.1], 997 [91.2], 1073 [92.9], 1103 [93.1], 1113 [91.4], 1221 [90.4], 1237 [93.8], 1378 [85.6], 1463 [70.4], 1498 [76.4], 1507 [80.5], 2152 [83.0], 2866 [48.3], 2968 [62.5] cm⁻¹. UV-Vis (vmax, cm⁻¹ [ε, 10³ M⁻¹ cm⁻¹]): 29700 [37.0], 31100 [34.3, sh], 31500 [38.3], 32300 [31.2, sh]. ¹H NMR (500 MHz, CDCl₃): δ 7.65 (s, 1H, H134), 7.45 (s, 4H, H142, H143), 7.25 (s, 1H, H137), 2.66 (d, 3JHH = 7.3 Hz, 2H, H1351), 2.60 (d, 3JHH = 6.6 Hz, 2H, H1381), 1.79–1.64 (m, 2H, H1352, H1382), 1.40–1.19 (m, 16H, H1353, H1354, H1355, H1357, H1383, H1384, H1385, H1387), 1.14 (s, 21H), 0.96–0.79 (m, 12H, H1356, H1358, H1386, H1388) ppm. ¹³C{¹H} NMR (126 MHz, CDCl₃): δ 143.2 (C135), 141.7 (C138), 140.7 (C134), 133.5 (C137), 132.0, 131.1 (C142, C143), 123.3, 123.2 (C141, C144), 122.5 (C136), 106.6 (C145), 101.6 (C133), 93.1 (C140), 92.8 (C146), 90.0 (C139), 44.2 (C1381), 40.3 (C1352), 39.3 (C1382), 38.2 (C1351), 32.4, 32.2 (C1353, C1383), 28.8, 28.7 (C1354, C1384), 25.5, 25.3 (C1357, C1387), 23.1 (C1355, C1385), 18.7 (C11), 14.1 (C1356, C1386), 11.3 (C10), 10.8 (C1358, C1388) ppm.

\[ HC≡CC₆H₄-4-C≡CC₆H₂-2,5-\{CH₂CHEt(CH₂)₃Me\}₂-4-I \] (2-34)

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¹⁸ Despite chromatographic purification, the pale color of the product remained. In other reactions affording the same compound, a similar situation was observed.
In a flame-dried 100 mL two-neck round-bottom flask, 2-33 (0.839 g, 1.16 mmol, 1.0 eq.) was dissolved in dry dichloromethane (70 mL). To the clear, colorless solution was added NBu₄F (1.0 M in tetrahydrofuran, 3.0 mL, 3.0 mmol, 2.5 eq.), after which the solution turned pale yellow. The solution was stirred at ambient temperature under a nitrogen atmosphere for 16 h. The solvent was removed, affording a dark red resin, which was redissolved in dichloromethane. Silica was added to the homogeneous, deep-red solution, and the solvent was removed under reduced pressure. A pale rosé powder was obtained,¹⁹ which was placed on a silica column (l = 14 cm, Ø = 2.5 cm). The column was washed with n-pentane (100 mL), and the product was then eluted with a mixture of n-pentane and ethylacetate (20:1, 60 mL). The combined fractions were dried over MgSO₄ and were then filtered, affording a pale yellow, clear solution. The solvent was removed under reduced pressure, giving a yellow, slightly cloudy oil (0.55 g, 1.00 mmol, 84%).

EI MS: 552.2 ([M]⁺, 100), 453.1 ([M - C₇H₁₅]⁺, 25), 355.0 ([M - 2C₇H₁₅]⁺, 46).
HR EI MS: Calcd. for C₃₂H₄₁⁻²⁻I⁻: 552.2253. Found: 552.2256. IR (CH₂Cl₂)
[Rel. Transm., Assignm.]: 1104 [92.6], 1112 [92.1], 1192 [94.8], 1378 [81.9], 1444 [86.8], 1463 [70.1], 1497 [76.3], 1509 [72.5], 2859 [55.4, ν(C-Hالتهافحة)], 2873 [57.0, ν(C-Hالتهافحة)], 2968 [57.0, ν(C-Hالتهافحة)], 3297 [85.0, ν(C≡C-H)] cm⁻¹. UV-
Vis (λ_max, cm⁻¹ [ε, 10⁵ M⁻¹ cm⁻¹]): 30100 [40.5], 31800 [38.7, sh], 32100 [40.5].
¹H NMR (500 MHz, CDCl₃): δ 7.65 (s, 1H, H134), 7.47 (s, 4H, H142, H143), 7.24 (s, 1H, H137), 3.18 (s, 1H, H146), 2.71-2.63 (m, 2H, H1351), 2.62-2.57 (m, 2H, H1381), 1.76-1.67 (m, 2H, H1352, H1382), 1.38-1.20 (m, 16H, H1353, H1354, H1355, H1357, H1383, H1384, H1385, H1387), 0.93-0.80 (m, 12H, H1356, H1358, H1386, H1388) ppm. ¹³C{¹H} NMR (126 MHz, CDCl₃): δ 143.2 (C135), 141.7 (C138), 140.7 (C134), 133.6 (C137), 132.1, 131.3 (C142, C143), 122.5 (C136), 123.8, 121.8 (C141, C144), 101.7 (C133), 92.8 (C140), 90.2 (C139), 83.2 (C145), 78.9 (C146), 44.2 (C1381), 40.3 (C1352), 39.2 (C1382), 38.2 (C1351), 32.4, 32.2 (C1353, C1383), 28.8, 28.7 (C1354, C1384), 25.5, 25.3 (C1357, C1387), 23.1 (C1355, C1385), 14.1 (C1356, C1386), 10.8 (C1358, C1388) ppm.

¹⁹ The compound was expected to be fairly soluble in n-pentane. After the solvent of the crude reaction mixture had been removed, I found that this was not the case. Therefore, the product could not be placed on the chromatography column as a solution in n-pentane as desired. Instead, the crude product was adsorbed onto silica and the chromatography column was charged with the corresponding powder instead.
(t-Pr)₃SiC≡CC₆H₄-4'·C≡CC₆H₂-2,5-·{CH₂CHEt(CH₂)₃Me}₂·4'·C≡CSiMe₃
(2-63)

In a flame-dried 100 mL two-neck round-bottom flask, 2-33 (0.98 g, 1.39 mmol, 1.0 eq.) was dissolved in deoxygenated triethylamine (90 mL). The clear, colorless solution was deoxygenated, and [PdCl₂(PPh₃)₂] (0.040 g, 0.06 mmol, 0.04 eq.) and Cul (0.020 g, 0.11 mmol, 0.08 eq.) were added. The cloudy, pale yellow mixture was deoxygenated, and Me₂SiC≡CH (1.1 mL, 0.75 g, 7.64 mmol, 5.5 eq.) was added at ambient temperature, after which a color change to a pale gray occurred, and an off-white precipitate was formed within 20 min. The mixture was stirred for another 16 h. Silica was added and the solvent of the black mixture was removed under reduced pressure, giving a grayish-brown powder that was loaded onto a silica column (l = 10 cm, Φ = 2.5 cm). The column was washed with a mixture of n-pentane and ethylacetate (20:1, 180 mL) and the product was then eluted with the same solvent mixture. Removal of the solvent under reduced pressure, and drying under vacuum at 30–40°C afforded the product (0.83 g, 1.22 mmol, 88%) as a pale yellow, viscous oil.

EI MS: 678.5 ([M]⁺, 100), 635.5 ([M - C₅H₇]⁺, 85), 607.4 ([M - C₆H₁₁]⁺, 30), 593.4 ([M - C₆H₁₃]⁺, 65), 579.4 ([M - C₇H₁₅]⁺, 45), 565.3 ([M - 2C₄H₆]⁺, 60). HR EI MS: Caled. for C₄₆H₇₀Si₂: 678.5016. Found: 678.5016. IR (CH₂Cl₂) [Rel. Transm., Assignm.]: 1000 [82.2], 1018 [83.6], 1072 [87.8], 1112 [91.8], 1220 [85.6], 1379 [82.6], 1463 [64.4], 1500 [68.8], 1508 [68.2], 2150 [59.9, ν(Si-C≡C)], 2867 [38.2, ν(C-H aliphatic)], 2967 [44.9, ν(C-H aliphatic)] cm⁻¹. UV-Vis (νmax, cm⁻¹ [ε, 10³ M⁻¹ cm⁻¹]): 28 600 [46.3], 30 000 [42.7, sh], 30 500 [45.6], 32 200 [38.6, sh].

¹H NMR (500 MHz, CDCl₃): δ 7.45, 7.44 (2s, H142, H143), 7.27 (s, 1H, H137), 7.25 (s, 1H, H134), 2.74–2.68 (m, 2H, H1351), 2.68–2.64 (m, 2H, H1381), 1.78–1.69 (m, 2H, H1352, H1382), 1.37–1.20 (m, 16H, H1353, H1354, H1355, H1357, H1383, H1384, H1385, H1387), 1.14 (s, 21H, H10, H11), 0.92–0.81 (m, 12H, H1356, H1358, H1386, H1388), 0.26 (s, 9H, H12) ppm. ¹³C{¹H} NMR (126 MHz, CDCl₃): δ 141.7 (C138), 141.2 (C135), 133.8 (C134), 133.4 (C137), 132.0, 131.2 (C142, C143), 123.31, 123.26 (C141, C144), 122.9 (C133), 122.7 (C136), 106.7 (C145), 104.3 (C132), 98.9 (C131), 93.5 (C140), 92.8 (C146), 90.7 (C139), 40.3, 40.1 (C1352, C1382), 38.46, 38.42 (C1351, C1381), 32.5, 32.4 (C1353, C1383), 28.8, 28.7 (C1354, C1384), 25.5, 25.4 (C1357, C1387), 23.12, 23.09 (C1355, C1385),
18.7 (C11), 14.1 (C1356, C1386), 11.3 (C10), 10.8, 10.6 (C1358, C1388), 0.0 (C12) ppm.

\((i-Pr)_3SiC≡CC_8H_4-4-C≡CC_8H_2-2,5-{\{CH_2CHEt(CH_3)_3Me\}_2-4-C≡CH\) (2-35)

In a flame-dried 250 mL two-neck round-bottom flask, 2-34 (1.896 g, 2.79 mmol, 1.0 eq.) was dissolved in freshly distilled dichloromethane (90 mL). KOH (1.70 g, 30.3 mmol, 10.9 eq.) and methanol (80 mL) were added. The clear, pale yellow solution was stirred under a nitrogen atmosphere for 12 h. The solvent was removed, affording a cloudy, orange oil. Water and dichloromethane were added and the organic layer was isolated and washed with water twice, dried over MgSO₄ and filtered. A clear, yellow solution was obtained, which was reduced in vacuo, affording the crude product as a yellow cloudy oil. The oil was dissolved in n-pentane and pipetted onto a silica column (1 = 14 cm, \(\bar{\Omega} = 2.5\) cm). The column was initially washed with n-pentane (100 mL) and a mixture of n-pentane and ethylacetate (40:1, 80 mL), before the product was eluted with a mixture of the same solvents (30:1). Removal of the solvent afforded 1.69 g (2.79 mmol, 99%) of a pale yellow, viscous oil, which was identified as the product.

EI MS: 606.5 ([M]+, 90), 563.4 ([M - C₃H₇]+, 100), 549.4 ([M - C₅H₉]+, 5), 535.4 ([M - C₆H₁₁]+, 25), 521.4 ([M - C₆H₁₃]+, 45), 507.4 ([M - C₆H₁₅]+, 45), 493.3 ([M - C₈H₁₇]+, 50). HR EI MS: Calcd. for C₄₃H₆₂Si: 606.4621. Found 606.4628. IR (CH₂Cl₂) [Rel. Transm., Assignmn.]: 996 [96.7], 1016 [97.8], 1072 [99.6], 1102 [100.5], 1220 [97.4], 1237 [98.2], 1379 [96.6], 1461 [89.9], 1501 [92.4], 2152 [94.5, \(\nu(Si-C≡C)\)], 2867 [77.1, \(\nu(C-H_{aliphatic})\)], 2967 [83.7, \(\nu(C-H_{aliphatic})\)], 3300 [91.0, \(\nu(C≡C-C-H)\)] cm⁻¹. UV-Vis (\(\nu_{max}, \) cm⁻¹ [\(\varepsilon, 10^3 M^{-1} cm^{-1}\)]): 29 000 [51.3], 30 600 [46.5, sh], 31 000 [50.4], 31 500 [45.0, sh]. ¹H NMR (500 MHz, CDCl₃): δ 7.45 (s, 4H, H142, H143), 7.30 (s, 1H, H134), 7.29 (s, 1H, H137), 3.30 (s, 1H, H131), 2.74–2.63 (m, 4H, H1351, H1381), 1.78–1.67 (m, 2H, H1352, H1382), 1.37–1.22 (m, 16H, H1353, H1354, H1355, H1357, H1383, H1384, H1385, H1387), 1.14 (s, 21H, H10, H11), 0.93–0.81 (m, 12H, H1356, H1358, H1386, H1388) ppm. ¹³C{¹H} NMR (126 MHz, CDCl₃): δ 141.9 (C138), 141.2 (C135), 134.2 (C134),

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20 The movement of the band containing the product could be followed using UV-light, to which the compound responds with fluoresence on the chromatography column. Hence, the start of the band from the column can be detected.
133.4 (C137), 132.0, 131.2 (C142, C143), 123.3, 123.2 (C141, C144), 123.0 (C136), 121.9 (C133), 106.6 (C145), 93.6, 92.8 (C140, C146), 90.5 (C139), 82.8, 81.6 (C131, C132), 40.3, 40.1 (C1352, C1382), 38.4, 38.2 (C1351, C181), 32.5 (C1353, C1383), 28.84, 28.76 (C1354, C1384), 25.56, 25.54 (C1357, C1387), 23.07, 23.03 (C1355, C1385), 18.7 (C11), 14.10, 14.09 (C1356, C1386), 11.3 (C10), 10.78, 10.76 (C1358, C1388) ppm.

$$(i-Pr)_3SiC≡CC_6H_{14-4′-C≡CC_6H_2-2,5′-{CH_2CHEt(CH_2)_3Me}_2-4′-C≡CC_6H_{14-4′-Br \ (2-36)}}$$

In a flame-dried 100 mL two-neck round-bottom flask, 2-35 (0.570 g, 0.94 mmol, 1.0 eq.) was dissolved in triethylamine (50 mL), affording a clear, pale green solution, which was deoxygenated by bubbling argon through it for ca. 15 min. 1-Bromo-4-iodobenzene (0.270 g, 0.95 mmol, 1.02 eq.) was added. The clear solution was cooled to 0°C, before it was deoxygenated again. [PdCl$_2$(PPPh$_3$)$_2$] (0.030 g, 0.04 mmol, 0.05 eq.) and CuI (0.010 g, 0.05 mmol, 0.06 eq.) were added. The resultant mixture was stirred at ambient temperature for 6 h, over which period the mixture became a more intense yellow color and contained a large amount of precipitate. To the mixture was added silica, and the solvent was removed under reduced pressure. A pale yellow powder was obtained, which was loaded onto a silica column. The column was washed with n-pentane (100 mL) and a mixture of n-pentane and ethylacetate (40:1, 250 mL) before the product was eluted with a mixture of n-pentane and ethylacetate (40:1, and later 20:1). The corresponding fractions were combined, dried over MgSO$_4$ and filtered. Removal of the solvent from the clear solution afforded 0.690 g (0.91 mmol, 96%) of the product as a clear, pale orange oil.

EI MS: 762.3 ([M]$^+$, 100), 719.5 ([M - C$_2$H$_7$]$^+$, 40), 691.5 ([M - C$_6$H$_{11}$]$^+$, 25), 677.5 ([M - C$_6$H$_{13}$]$^+$, 40), 661.5 ([M - C$_7$H$_{15}$]$^+$, 45), 647.4 ([M - C$_8$H$_{17}$]$^+$, 50). HR EI MS: Calcd. for C$_{49}$H$_{63}$Si$^{79}$Br: 760.4039. Found: 760.4039. IR (CH$_2$Cl$_2$) [Rel. Transm., Assignm.]: 997 [98.3], 1008 [96.4], 1069 [97.5], 1222 [99.6], 1377 [99.1], 1464 [95.9], 1500 [94.8], 2153 [98.0, $\nu$(Si-C≡C)], 2866 [89.0, $\nu$(C-H$_{aliphatic}$)], 2899

21 The fluorescence properties of the compound were used to follow its movement on the silica column, allowing for accurate collection of the desired fractions.
[94.2, \(\nu(C-H)_{alliphatic}\)], 2963 [91.7, \(\nu(C-H)_{alliphatic}\)] cm\(^{-1}\). UV-Vis (\(\tilde{\nu}_{\text{max}}, \text{ cm}^{-1}\) [\(\varepsilon, \text{ 10}^3 \text{ M}^{-1} \text{ cm}^{-1}\)]: 27 400 [47.2], 28 700 [60.8], 29 400 [64.8, sh], 40 200 [25.1], 42 700 [27.7, sh]). \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.49 (d, \(\text{ }^3J_{\text{HH}} = 8.5\) Hz, 2H, H128), 7.48 (s, 4H, H142, H143), 7.38 (d, \(\text{ }^3J_{\text{HH}} = 8.5\) Hz, 2H, H129), 7.32, 7.38 (2s, H134, H137), 2.77–2.66 (m, 4H, H1351, H1381), 1.80–1.70 (m, 2H, H1352, H1382), 1.39–1.21 (m, 16H, H1353, H1354, H1355, H1357, H1383, H1384, H1385, H1387), 1.14 (s, 21H, H10, H11), 0.92–0.87 (t, \(\text{ }^3J_{\text{HH}} = 7.4\) Hz, 6H, H1358, H1388), 0.85, 0.84 (t, \(\text{ }^3J_{\text{HH}} = 7.0\) Hz, \(\text{ }^3J_{\text{HH}} = 7.0\) Hz, 6H, H1356, H1386) ppm. \(^{13}\)C\({}^{1}\)H NMR (126 MHz, CDCl\(_3\)): \(\delta\) 141.4, 141.3 (C135, C138), 133.6, 133.5 (C134, C137), 132.8 (C129), 132.0, 131.2 (C142, C143), 131.6 (C128), 123.3, 123.2 (C141, C144), 122.8, 122.5 9C133, C136), 122.43, 122.38 (C127, C130), 106.6 (C145), 93.7 (C140), 92.81, 92.78 (C146, C131), 90.6 (C139), 89.9 (C132), 40.34, 40.31 (C1352, C1382), 38.49 (C1351, C1381), 32.50, 32.46 (C1353, C1383), 28.90, 28.85 (C1354, C1384), 25.5 (C1357, C1387), 23.1 (C1355, C1385), 18.7 (C11), 14.1 (C1356, C1386), 11.3 (C10), 10.78, 10.77 (C1358, C1388) ppm.

(i-Pr)_3SiC≡CC_6H_4-4-C≡CC_6H_2-2,5-{CH_2CH_2CH(CH_3)_3Me}_2-4-C≡CC_6H_4-4-I

(2-37)

In a flame-dried 100 mL two-neck round-bottom flask, 2-36 (0.68 g, 0.89 mmol, 1.0 eq.) was dried with occasional warming under vacuum for 2 d. The cloudy, highly viscous orange oil was dissolved in freshly distilled tetrahydrofuran (60 mL). The clear, orange solution was cooled to -78 °C (dry ice/acetone), and n-BuLi (2.5 M in n-hexane; 1.5 mL, 3.8 mmol, 4.2 eq.) was added dropwise, after which the solution became very dark green. The reaction mixture was stirred at low temperature for 1 h before a concentrated solution of I\(_2\) in tetrahydrofuran was added dropwise over 10 min. A color change from dark-green via orange to dark-red occurred, indicating the desired presence of excess iodine. The cooling bath was removed, and the reaction mixture was allowed to warm to ambient temperature over 1 h. The standard workup procedure for trans-halogenation reactions (vide supra) was followed, affording a clear, yellow solution. Removal of the solvent from this solution under reduced pressure gave a yellow, highly viscous resin, which was dissolved in n-pentane (10 mL). The resultant solution was pipetted onto a silica column (l = 14 cm, \(\Phi = 4.5\) cm). The column was
washed with a mixture of n-pentane and ethylacetate (30:1), before the product was eluted with the same solvent system. The presence of product in the desired fractions was indicated by strong fluorescence under radiation with UV-light. Removal of the solvent from the corresponding fractions under reduced pressure gave 0.53 g (0.66 mmol, 74%) of the product in the form of a yellow resin.

ESI MS: 808.4 ([M]+, 100), 765.3 ([M - C₃H₇]+, 40), 737.3 ([M - C₅H₁₁]+, 18), 723.3 ([M - C₆H₁₃]+, 38), 709.3 ([M - C₇H₁₉]+, 35), 695.2 ([M - C₈H₁₇]+, 40).

HR EI MS: Calcd. for C₄₉H₆₅Si: 808.3900. Found: 808.3900. IR (CH₂Cl₂) [Rel. Transm., Assignm.]: 994 [94.3], 1006 [89.8], 1014 [95.3], 1058 [96.2], 1072 [97.2], 1103 [98.4], 1219 [95.8], 1378 [94.1], 1461 [84.7], 1500 [84.3], 1508 [84.5], 2151 [91.2], ν(Si-C≡C) [2342 [97.8], 2360 [96.8], 2865 [70.4], ν(C-H_alkyl)], 2895 [81.5], ν(C-H_alkyl) cm⁻¹. UV-Vis (ν_max, cm⁻¹ [ε, 10^3 M⁻¹ cm⁻¹]): 27 400 [43.9], 29 200 [62.9].

¹H NMR (500 MHz, CDCl₃): δ 7.70 (d, J_HH = 8.4 Hz, 2H, H128), 7.46 (s, 4H, H142, H143), 7.32, 7.31 (2s, H134, H137), 7.25 (d, J_HH = 8.4 Hz, 2H, H129), 2.76–2.66 (m, 4H, H1351, H1381), 1.80–1.70 (m, 2H, H1351, H1381), 1.39–1.22 (m, 16H, H1353, H1354, H1355, H1357, H1383, H1384, H1385, H1387), 1.14 (s, 21H, H10, H11), 0.89 (t, J_HH = 7.4 Hz, 6H, H1358, H1388), 0.85, 0.84 (t, J_HH = 6.9 Hz, J_HH = 7.0 Hz, 6H, H1356, H1386) ppm. ¹³C¹H NMR (126 MHz, CDCl₃): δ 141.4, 141.3 (C135, C138), 137.5 (C128), 133.56, 133.53 (C134, C137), 132.9 (C129), 132.0, 131.2 (C142, C143), 123.28, 123.24 (C141, C144), 122.9 (C130), 122.8, 122.5 (C133, C136), 106.6 (C145), 94.1 (C127), 93.7 (C140), 92.9 (C131), 92.8 (C146), 90.6 (C139), 90.2 (C132), 40.34, 40.31 (C1352, C1382), 38.5 (C1351, C1381), 32.50, 32.46 (C1353, C1383), 28.90, 28.85 (C1354, C1384), 25.5 (C1357, C1387), 23.1 (C1355, C1385), 18.7 (C111), 14.10 (C1356, C1386), 11.3 (C110), 10.79 (C1356, C1386) ppm.

HC≡CC₆H₄·4·5·C≡CC₆H₂·2,5·{(CH₂CH₂Et)(CH₂)₃Me}·2·4≠C≡CC₆H₄·4·5·C (2-38)

To a pale yellow solution of 2-37 (0.53 g, 0.66 mmol, 1.0 eq.) in freshly distilled dichloromethane (50 mL) was added NBu₄F (1.0 M in tetrahydrofuran, 1.5 mL, 1.50 mmol, 2.3 eq.), after which the solution became green, green and then very dark green within 2 min. The reaction mixture was deoxygenated and stirred at ambient temperature for 16 h, over which time the solution turned back to yellow and then orange. Water was added and the mixture was stirred
vigorously for 3 min. The layers were separated, and the aqueous layer was washed with dichloromethane twice. The combined organic layer were washed with water twice, dried over MgSO\textsubscript{4} and filtered. A clear, pale yellow solution was obtained, from which the solvent was removed under reduced pressure. The orange, inhomogeneous resin with a characteristic acetylene smell was adsorbed onto silica. The resultant powder was placed on a silica column (l = 16 cm, \( \varnothing = 2.5 \text{ cm} \)). The column was washed with a mixture of n-pentane and ethylacetate (30:1, 140 mL) before the product was eluted using the same solvent system. Removal of the solvent from the combined fractions afforded 0.34 g (0.52 mmol, 79%) of a yellow to light-orange, crystalline solid.

Anal. Calcd. for C\textsubscript{40}H\textsubscript{45}: C 73.61, H 6.95%. Found: C 73.50, H 7.07%. EI MS: 652.2 ([M]+, 100), 553.1 ([M - C\textsubscript{7}H\textsubscript{15}]+, 13), 526.4 ([M - I]+, 10), 455.0 ([M - 2C\textsubscript{7}H\textsubscript{15}]+, 23). HR EI MS: Calcd. for C\textsubscript{40}H\textsubscript{45}: 652.2566. Found: 652.2563. IR (CH\textsubscript{2}Cl\textsubscript{2}) [Rel. Transm., Assignm.]: 1007 [84.1], 1060 [97.7], 1464 [86.0], 1500 [82.9], 1509 [80.5], 2860 [77.2, \( \nu \text{(C-H} \text{aliphatic}) \)], 2873 [78.4, \( \nu \text{(C-H} \text{aliphatic}) \)], 2950 [50.5, \( \nu \text{(C-H} \text{aliphatic}) \)], 2960 [50.5, \( \nu \text{(C-H} \text{aliphatic}) \)], 3297 [82.4, \( \nu \text{(C\equivC-H}) \)] cm\textsuperscript{-1}. UV-Vis (\( \nu \text{max, cm}^{-1} \)): 28.000 [43.9], 29.400 [61.9], 30.700 [48.4]. \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): \( \delta \) 7.70 (d, \( ^3J_{HH} = 8.2 \text{ Hz}, 2\text{H}, \text{H}128 \)), 7.48 (s, 4H, H142, H143), 7.31, 7.32 (2s, H134, H137), 7.25 (d, \( ^3J_{HH} = 8.2 \text{ Hz}, 2\text{H}, \text{H}129 \)), 3.18 (s, 1H, H146), 2.79–2.64 (m, 4H, H1351, H1381), 1.81–1.69 (m, 2H, H1351, H1381), 1.41–1.19 (m, 16H, H1353, H1354, H1355, H1357, H1383, H1384, H1385, H1387), 0.89 (t, \( ^3J_{HH} = 7.4 \text{ Hz}, 6\text{H}, \text{H}1358, \text{H}1388 \)), 0.84 (t, \( ^3J_{HH} = 6.8 \text{ Hz}, 6\text{H}, \text{H}1356, \text{H}1386 \)) ppm. \textsuperscript{13}C\{\textsuperscript{1}H\} NMR (126 MHz, CDCl\textsubscript{3}): \( \delta \) 141.4, 141.3 (C135, C138), 137.6 (C128), 133.6, 133.5 (C134, C137), 132.9 (C129), 132.1, 131.3 (C142, C143), 123.9 (C141), 123.0 (C130), 122.7 (C133), 121.8 (C144), 94.1 (C127), 93.4 (C140), 93.0 (C131), 90.8 (C139), 90.2 (C132), 83.3 (C145), 78.9 (C146), 40.4 (C1352, C1382), 38.5 (C1351, C1381), 32.5 (C1353, C1383), 28.9 (C1354, C1384), 25.6 (C1357, C1387), 23.1 (C1355, C1385), 14.10 (C1356, C1386), 10.79 (C1356, C1386) ppm.

\((\text{i-Pr})_3\text{SiC≡C}_8\text{H}_4-4\text{-C≡C}_8\text{H}_2-2,5-\{\text{CH}_2\text{CH}E\text{t}(\text{CH}_3)_3\text{Me}\}_2-4\text{-C≡C}_8\text{H}_4-4\text{-C≡C}_8\text{H}_4-4\text{-C≡C}_8\text{H}_4-4\text{-C≡C}_8\text{H}_1\) \(\text{SiMe}_3\) \((2-40)\)

In a flame-dried 250 mL two-neck round-bottom flask, \(2-35\) (0.54 g, 0.89 mmol,
was dissolved in deoxygenated triethylamine (120 mL). The clear, near-colorless solution with a slight green tinge was deoxygenated further for 5 min before 2-25 (0.42 g, 1.05 mmol, 1.18 eq.) was added. The clear, pale yellow solution was deoxygenated again, and [PdCl₂(PPh₃)₂] (0.02 g, 0.03 mmol, 0.03 eq.) and Cul (0.01 g, 0.05 mmol, 0.06 eq.) were added. Within 10 min, the mixture became cloudy and a yellow color, and the formation of a light precipitate was observed. The solution was stirred at ambient temperature for 14 h. The reaction was monitored by TLC and ¹H NMR spectroscopy, and small portions of 2-35 were added repeatedly over 12 h. This was continued until only a trace amount of the iodide could be detected spectroscopically; i.e. the required stoichiometric amount of acetylene was adjusted throughout the course of the reaction (total of extra acetylene added: 0.10 g, 0.16 mmol, 0.18 eq.). To the intense yellow, cloudy mixture was added silica, and the solvent was removed under reduced pressure. A yellow powder was obtained, which was loaded onto a silica column (l = 15 cm, Ø = 4.5 cm). The column was washed with a mixture of n-pentane and ethylacetate (40:1), before the product was eluted using the same solvent system. The solvent was removed in vacuo, and the residual oil was dissolved in dichloromethane (10 mL). The solution was dried over MgSO₄ and was then filtered through cotton wool. Removal of the solvent and drying under vacuum afforded 0.84 g (0.95 mmol, 90%) of the product as a greenish-yellow, viscous oil.

ESI MS: 901.6 ([M + Na]⁺, 1), 879.6 ([M + H]⁺, 2), 803.5 ([M - C==CSiMe₃ + Na]⁺, 25). HR ESI TOF MS: Calcd. for C₆₂H₇₆Si₂: 879.5720. Found: 879.5723. Calcd. for C₆₂H₇₆NaSi₂: 901.5540. Found: 901.5545. IR (CH₂Cl₂) [Rel. Transm., Assignmn.]: 995 [87.1], 1015 [84.8], 1073 [93.0], 1104 [91.6], 1221 [85.7], 1256 [78.8], 1380 [87.8], 1403 [91.1], 1462 [73.0], 1516 [50.8], 1600 [94.1], 1671 [97.3], 1798 [98.0], 1917 [97.2], 2156 [68.8, ν(Si=C≡C)], 2867 [49.0, ν(C-Haliphatic)] cm⁻¹. UV-Vis (νₘₐₓ cm⁻¹ [ε, 10⁴ M⁻¹ cm⁻¹]): 27200 [68.0], 28200 [75.7], 35600 [28.0]. ¹H NMR (500 MHz, CDCl₃): δ 7.51 (s, 4H, H128, H129), 7.46 (s, 8H, H122, H123, H142, H143), 7.33 (s, 2H, H134, H137), 2.81-2.67 (m, 4H, H1351, H1381), 1.82-1.73 (m, 2H, H1352, H1382), 1.42-1.22 (m, 16H, H1353, H1354, H1355, H1357, H1383, H1384, H1385, H1387), 1.14 (s, 21H, H10, H11), 0.90-0.89 (t, 3JHH = 7.4 Hz, 3JHH = 7.4 Hz, 6H, H1358, H1388), 0.85 (2 overlapping triplets, 3JHH = 6.6 Hz, 6H, H1356, H1386), 0.26 (s, 9H, H12) ppm. ¹³C{¹H} NMR (126 MHz,
CDCl₃): δ 141.4 (C135, C138), 133.60, 133.57 (C134, C137), 132.0, 131.6 (C122, C123), 131.9, 131.2 (C142, C143), 131.4 (C128, C129), 123.5 (C130), 123.3 (C141, C144), 123.12, 123.06 (C121, C124), 122.78, 122.75, 122.68 (C127, C133, C136), 106.7 (C145), 104.6 (C120), 96.5 (C119), 93.7 (C140), 93.6 (C131), 92.8 (C146), 91.0, 90.9, 90.7 (C125, C126, C132), 40.38, 40.34 (C3152, C3182), 38.5 (C1351, C1381), 32.56, 32.50 (C1353, C1383), 28.94, 28.88 (C1354, C1384), 25.6 (C1357, C1387), 23.11, 23.09 (C1355, C1385), 18.7 (C11), 14.1 (C1356, C1386), 11.3 (C10), 10.81, 10.79 (C1358, C1388), -0.1 (C12) ppm.

\((t-Pr)_2SiC≡CC₆H₄-4·C≡CC₆H₂-2,5·\{CH₂CH₂Et(CH₂)₃Me\}₂-4·C≡CC₆H₄-4·C≡CH\) (2-41)

In a flame-dried 100 mL two-neck round-bottom flask, 2-40 (0.84 g, 0.96 mmol, 1.0 eq.) was dissolved in freshly distilled and deoxygenated dichloromethane (50 mL). To the clear, orange solution were added KOH pellets (0.30 g, 5.35 mmol, 5.6 eq.) and methanol (20 mL). After the mixture became cloudy, dichloromethane (10 mL) was added, following which the solution became clear again. The reaction mixture was stirred at room temperature for 16 h. A cloudy, yellow solution was obtained, from which the solvent was removed under reduced pressure. This afforded a pale yellow, highly viscous resin, which was redissolved in dichloromethane (20 mL). Water was added to the solution, and the product was extracted by washing the aqueous phase with dichloromethane three times. The combined organic layers were washed with water three times and were dried over MgSO₄. Filtration afforded a clear, yellow solution, to which silica was added. The solvent was removed in vacuo, affording an off-white powder that was loaded onto a silica column (l = 12 cm, Ø = 4.5 cm). The product was eluted with a mixture of n-pentane and ethylacetate (30:1). The fractions containing the product were combined, and the solvent was removed to afford 0.71 g (0.88 mmol, 92%) of the off-white, solid product.

Anal. Calcd. for C₅₉H₇₀Si: C 87.78, H 8.74%. Found: C 87.60, H 8.60%. ESI MS: 807.5 ([M + H]⁺, 100). HR ESI TOF MS⁺: Calcd. for C₅₉H₇₀Si: 806.5247. Found: 806.5248. IR (CH₂Cl₂) [Rel. Transm., Assignm.]: 996 [99.1], 1017 [99.1], 1073 [99.9], 1104 [99.6], 1219 [99.5], 1244 [99.4], 1379 [99.5], 1462 [98.2], 1516 [95.4], 2150 [99.0, ν(Si-C≡C)], 3300 [98.8, ν(C≡C-H)] cm⁻¹. UV-Vis (νmax, cm⁻¹

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2.5. Experimental

\([\varepsilon, 10^3 \text{M}^{-1} \text{cm}^{-1}])\): 27 400 [87.6, sh], 28 200 [96.4], 35 900 [32.2]. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.51 (s, 4H, H128, H129), 7.48 (s, 4H, H122, H123), 7.46 (4H, H142, H143), 7.33 (s, 2H, H134, H137), 3.19 (s, 1H, H119), 2.80–2.67 (m, 4H, H1351, H1381), 1.81–1.72 (m, 2H, H1352, H1382), 1.41–1.22 (m, 16H, H1353, H1354, H1355, H1357, H1383, H1384, H1385, H1387), 1.14 (s, 21H, H10, H11), 0.90, 0.89 (t, \(3J_{HH} = 7.4\) Hz, 6H, H1358, H1388), 0.85 (t, \(3J_{HH} = 6.9\) Hz, 6H, H1356, H1386) ppm. \(^{13}\)C\{\(^1\)H\} NMR (126 MHz, CDCl\(_3\)): \(\delta\) 141.4 (C135, C138), 133.59, 133.56 (C134, C137), 132.1, 131.6 (C122, C123), 132.0, 131.2 (C142, C143), 131.5, 131.4 (C128, C129), 123.55 (C130), 123.48 (C124), 123.28, 123.25 (C141, C144), 122.8, 122.7 (C127, C133, C136), 122.0 (C121), 106.6 (C145), 93.7 (C131), 93.6 (C140), 92.8 (C146), 91.1, 90.9 (C126, C132), 90.68, 90.64 (C139, C125), 83.2 (C120), 79.0 (C119), 40.36, 40.32 (C3152, C3182), 38.5 (C1351, C1381), 32.53, 32.47 (C1353, C1383), 28.94, 28.86 (C1354, C1384), 25.5 (C1357, C1387), 23.1 (C1355, C1385), 18.7 (C11), 14.1 (C1356, C1386), 11.3 (C10), 10.8 (C1358, C1388) ppm.

\((i\text{-Pr})_3\text{SiC}≡\text{CC}_6\text{H}_4\text{-Br}\) (2-42)

In a flame-dried 100 mL two-neck round-bottom flask, 2-41 (0.52 g, 0.64 mmol, 1.0 eq.) was dissolved in a mixture of deoxygenated triethylamine (50 mL) and freshly distilled and deoxygenated dichloromethane (15 mL). To the resultant clear solution was added para-bromiodobenzene (0.19 g, 0.67 mmol, 1.04 eq.), before the mixture was cooled to 0 °C. The solution was stirred at low temperature for 20 min before [PdCl\(_2\)(PPh\(_3\))\(_2\)] (0.030 g, 0.04 mmol, 0.07 eq.) and CuI (0.010 g, 0.05 mmol, 0.08 eq.) were added, after which the solution became significantly darker instantaneously and turned a dark-brown color. The solution was allowed to stir on the melting ice bath for 4 h and was then stirred at ambient temperature for another 6 h. An inhomogeneous, orange-brown reaction mixture containing a light precipitate was obtained, to which silica was added. The solvent was removed under reduced pressure, affording a brown powder. This solid was loaded onto a silica column (l = 10 cm, \(\varnothing = 4.5\) cm), and the product was eluted with a mixture of n-pentane and ethylacetate (20:1). The solvent of fractions containing the product was removed under reduced pressure.

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CHAPTER 2. Stars – Unbranched Octupolar Ruthenium Acetylide Complexes

For facile collection of the product, a concentrated solution of the product in dichloromethane was dropped into stirring methanol. A grainy, pale rosé precipitate was formed, which was isolated by filtration and dried at 30–40 °C under vacuum for 10 h. 0.56 g (0.58 mmol, 90%) of the product was isolated.

Anal. Calcd. for C_{65}H_{73}BrSi: C 81.13, H 7.65%. Found: C 81.47, H 7.75%. ESI MS: 961.5 ([M + H]^+, <2). HR ESI TOF MS: Calcd. for C_{65}H_{73}Si^{79}Br: 961.4743. Found: 961.4747 ([M + H]^+). Calcd. for C_{65}H_{73}Si^{79}Br: 960.4665. Found: 960.4652 ([M]^+). IR (CH_{2}Cl_{2}) [Rel. Transm., Assignm.]: 1012 [99.4], 1070 [99.5], 1517 [95.6], 2153 [99.4, ν(Si-C≡C)], 2865 [97.2, ν(C-H)_{aliphatic}], 2915 [92.7, ν(C-H)_{aliphatic}], 3056 [98.2, ν(C-H)_{aromatic}] cm\(^{-1}\). UV-Vis (ε_{max}, cm\(^{-1}\) [ε, 10\(^3\) M\(^{-1}\) cm\(^{-1}\)]): 27 600 [123.8], 34 300 [38.2]. \(^1\)H NMR (500 MHz, CDCl\(_3\)): δ 7.53, 7.52 (s, s, 8H, H122, H123, H128, H129), 7.50 (d, 3\(^3\)J_{HH} = 8.5 Hz, 2H, H116), 7.46 (s, 4H, H142, H143), 7.40 (d, 3\(^3\)J_{HH} = 8.5 Hz, 2H, H117), 7.33 (s, 2H, H134, H137), 2.80–2.68 (m, 4H, H1351, H1381), 1.82–1.73 (m, 2H, H1351, H1381), 1.41–1.23 (m, 16H, H1353, H1354, H1355, H1357, H1358, H1384, H1385, H1387), 1.14 (s, 21H, H10, H11), 0.91, 0.90 (t, 3\(^3\)J_{HH} = 7.4 Hz, 3\(^3\)J_{HH} = 7.4 Hz, 6H, H1358, H1388), 0.89 (t, 3\(^3\)J_{HH} = 7.4 Hz, 6H, H1356, H1386) ppm. \(^13\)C\(^{1}\)H NMR (126 MHz, CDCl\(_3\)): δ 141.4 (C135, C138), 133.60, 133.57 (C134, C137), 133.0 (C117), 132.0, 131.2 (C142, C143), 131.7 (C116), 131.6, 131.5, 131.4 (C122, C123, C128, C129), 123.6 (C130), 123.30, 123.28 (C141, C144), 123.1, 122.9 (C124, C122), 122.78, 122.75, 122.72, 122.66 (C133, C136, C127, C115), 122.0 (C118), 106.7 (C145), 93.7 (C140), 93.6 (C131), 92.8 (C146), 91.2, 91.0, 90.9 (C120, C125, C126), 90.7 (C139), 90.3, 90.2 (C119, C132), 40.38, 40.34 (C3152, C1382), 38.53 (C1351, C1381), 32.56, 32.50 (C1353, C1383), 28.94, 28.88 (C1354, C1384), 25.6 (C1357, C1387), 23.1 (C1355, C1385), 18.7 (C11), 14.1 (C1356, C1386), 11.3 (C10), 10.8 (C1358, C1388) ppm.

(i-Pr)\(_3\)SiC≡CC\(_6\)H\(_4\)-4-C≡CC\(_6\)H\(_2\)-2,5- \{CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)\}_5Me \}_2-4-C≡CC\(_6\)H\(_4\)-4-C≡CC\(_6\)H\(_4\)-4-I (2-43)

In a flame-dried 250 mL two-neck round-bottom flask, 2-42 (0.42 g, 0.44 mmol, 1.0 eq.) was dissolved in freshly distilled tetrahydrofuran (80 mL). The clear, yellow solution was cooled to -78 °C (acetone/dry ice), and n-BuLi (2.5 M in n-hexane; 0.5 mL, 1.25 mmol, 2.9 eq.) was added dropwise at low temperature,
after which the solution became an intense dark green instantaneously. The mixture was stirred at low temperature for 90 min. A solution of iodine (0.40 g, 1.58 mmol, 3.6 eq.) in freshly distilled tetrahydrofuran (20 mL) was added dropwise, and the resultant mixture was stirred at low temperature for 5 min before the cooling bath was removed. The dark red mixture was allowed to warm to room temperature over 2.5 h. The standard workup procedure for trans-halogenation reactions (see page 2.5.3) was followed. The crude material was adsorbed onto silica, affording a yellow powder that was placed on a silica column (l = 12 cm, Ø = 4.5 cm). The product was eluted with a mixture of n-pentane and ethylacetate (10:1). The fractions containing the product were combined and taken to dryness under reduced pressure. A yellow solid was obtained, which was dissolved in a minimal amount of dichloromethane. The resultant solution was dropped into stirring methanol (80 mL). A pale yellow precipitate was formed that was isolated by filtration and taken to dryness. The residual solvent was removed under vacuum at 40 °C, affording 0.40 g (0.40 mmol, 91%) of the product as an amorphous off-white solid.

ESI MS: 1009.5 ([M]+, < 2). HR ESI TOF MS: Calcd. for C_{65}H_{74}Si: 1009.4605. Found: 1009.4606. IR (CH_{2}Cl_{2}) [Rel. Transm., Assignm.]: 997 [92.7], 1007 [88.5], 1017 [92.5], 1058 [96.8], 1073 [97.6], 1103 [97.0], 1222 [96.5], 1380 [95.6], 1463 [87.8], 2152 [93.1, ν(Si−C≡C)], 2855 [73.9, ν(C−H_{aliphatic})], 2954 [66.6, ν(C−H_{aliphatic})], 2964 [72.8, ν(C−H_{aliphatic})], 3057 [97.2, ν(C−H_{aromatic})] cm\(^{-1}\). UV-Vis (ν_{max}, cm\(^{-1}\) [ε, 10\(^3\) M\(^{-1}\) cm\(^{-1}\)]): 78 000 [124.3, with diffuse shoulder to lower energy], 34 100 [38.1]. \(^1\)H NMR (500 MHz, CDCl\(_3\)): δ 7.70 (d, ^3^J_{HH} = 8.4 Hz, 2H, H116), 7.52, 7.51 (s, 8H, H122, H123, H128, H129), 7.46 (s, 4H, H142, H143), 7.33 (s, 2H, H134, H137), 7.26 (d, J = 8.4 Hz, 2H, H117), 2.82–2.67 (m, 4H, H1351, H1381), 1.83–1.71 (m, 2H, H1352, H1382), 1.44–1.22 (m, 16H, H1353, H1354, H1355, H1357, H1383, H1384, H1385, H1387), 1.14 (s, 21H, H10, H11), 0.91, 0.90 (2t, ^3^J_{HH} = 7.4 Hz, ^3^J_{HH} = 7.4 Hz, 6H, H1358, H1388), 0.85 (t, ^3^J_{HH} = 6.9 Hz, 6H, H1356, H1386) ppm. \(^13\)C\(^{1}\)H NMR (126 MHz, CDCl\(_3\)): δ 141.4 (C135, C138), 137.6 (C116), 133.60, 133.57 (C134, C137), 133.1 (C117), 132.0, 131.2, (C142, C143), 131.58, 131.55, 131.40 (C122, C123, C128, C129), 123.6 (C130), 123.3, 123.2 (C141, C144), 123.1, 122.9 (C121, C124), 122.79, 122.72, 122.66 (C127, C133, C136), 122.5 (C118), 106.6 (C145), 94.4 (C115), 93.7 (C140), 93.6 (C131), 92.8 (C146), 91.2, 90.95, 90.92 (C120, C125, C126), 90.7 (C139),
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90.45, 90.43 (C119, C132), 40.38, 40.34 (C3152, C1382), 38.5 (C1351, C1381), 32.55, 32.50 (C1353, C1383), 28.94, 28.88 (C1354, C1384), 25.6 (C1357, C1387), 23.10 (C1355, C1385), 18.7 (C11), 14.1 (C1356, C1386), 11.3 (C10), 10.81, 10.79 (C1358, C1388) ppm.

\[
HC\equiv CC_6H_4\cdot 4\cdot C\equiv CC_6H_2\cdot 2\cdot 5\cdot CH_2CH(\text{CH}_3)_3Me\cdot 4\cdot C\equiv CC_6H_4\cdot 4\cdot C\equiv CC_6H_4\cdot 4\cdot I \quad (2-44)
\]

In a flame-dried 100 mL two-neck round-bottom flask, 2-43 (0.29 g, 0.29 mmol, 1.0 eq.) was dissolved in freshly distilled dichloromethane (80 mL). To the clear, pale yellow solution was added NBu\textsuperscript{n}_{4}F (1.0 M solution in tetrahydrofuran; 1.20 mL, 1.20 mmol, 4.2 eq.), after which the solution became significantly darker, turning ruby-red instantaneously. The mixture was stirred at ambient temperature for 18 h, over which time the solution remained clear, but turned back to yellow. Water was added, and the resulting mixture was stirred vigorously under nitrogen for 10 min. The layers were separated, and the aqueous layer was washed with dichloromethane twice. The combined organic layers were washed with water twice and dried over MgSO\textsubscript{4}. Filtration afforded a clear, yellow solution that gave a yellow solid after removal of the solvent. The solid was purified by column chromatography (silica column, l = 12 cm, \( \varnothing = 4.5 \) cm). The product was eluted, using a mixture of \textit{n}-pentane and ethylacetate (5:1). After removal of the solvent, a solid was obtained, which was dissolved in a minimal amount of dichloromethane. The resultant solution was dropped into methanol. A pale yellow, fluffy precipitate was formed that was recovered by filtration through a sintered glass filter funnel (pore size G4). The solid residue was dried under vacuum, affording 0.22 g (0.26 mmol, 90%) of the pale apricot-colored solid product.

Anal. Calcd. for C\textsubscript{56}H\textsubscript{53}I: C 78.86, H 6.26%. Found: C 79.10, H 6.15%. ESI MS: 852.3 ([M]\textsuperscript{+}, 80). HR ESI TOF MS: Calcd. for C\textsubscript{56}H\textsubscript{53}I: 852.3192. Found: 852.3171. IR (CH\textsubscript{2}Cl\textsubscript{2}) [Rel. Transm., Assignmn.]: 1006 [91.7], 1017 [96.3] 1057 [96.8], 1103 [96.0], 1307 [97.0], 1379 [96.0], 1393 [97.0], 1406 [96.3], 1461 [93.8], 1482 [94.9], 1516 [76.7], 1601 [94.8, \( \nu(C=\text{C}_{\text{aromatic}}) \)], 1917 [98.9], 2107 [99.1], 2208 [98.2, \( \nu(C=\text{C}=\text{C}) \)], 2860 [89.2, \( \nu(C-\text{H}_{\text{aliphatic}}) \)], 2873 [89.5, \( \nu(C-\text{H}_{\text{aliphatic}}) \)], 3044 [98.3, \( \nu(C-\text{H}_{\text{aromatic}}) \)], 3297 [92.3, \( \nu(C=\text{C}-\text{H}) \)] cm\textsuperscript{-1}. UV-Vis (\( \bar{\nu}_{\text{max}} \), cm\textsuperscript{-1})
2.5. Experimental

$[\varepsilon, \ 10^3 \text{M}^{-1} \text{cm}^{-1}] = 27800 \ [105.7], \ 34\ 400 \ [29.1]$.  
$^{1}H$ NMR (500 MHz, CDCl$_3$):  
$\delta$ 7.70 (d, $J_{HH} = 8.4$ Hz, 2H, H116), 7.52, 7.51 (s, 3H, H122, H123, H128, H129), 7.48 (s, 4H, H142, H143), 7.339, 7.340 (s, 2H, H134, H137), 7.26 (d, $J = 8.4$ Hz, 2H, H117), 3.18 (s, 1H, H146), 2.81–2.67 (m, 4H, H1351, H1381), 1.83–1.74 (m, 2H, H1352, H1382), 1.42–1.21 (m, 16H, H1353, H1354, H1355, H1357, H1383, H1384, H1385, H1387), 0.91, 0.90 (2t, $J_{HH} = 7.4$ Hz, $J_{HH} = 7.4$ Hz, 6H, 1H358, H1388), 0.86, 0.86 (2t, $J_{HH} = 6.9$ Hz, $J_{HH} = 6.9$ Hz, 6H, H1356, H1386) ppm.  
$^{13}C$-$^1$H NMR (126 MHz, CDCl$_3$):  
$\delta$ 141.4 (C135, C138), 137.6 (C116), 133.6 (C134, C137), 133.1 (C117), 132.1, 131.3 (C142, C143), 131.6, 131.4 (C122, C123, C128, C129), 123.9 (C141), 123.5 (C130), 123.1, 122.9 (C124, C121), 122.8, 122.7 (C133, C136, C127), 122.5 (C118), 121.8 (C144), 94.4 (C115), 93.7 (C131), 93.4 (C140), 91.15, 90.93, 90.91 (C120, C125, C126), 90.84 (C139), 90.4 (C119, C132), 83.3 (C145), 78.9 (C146), 40.4 (C3152, C1382), 38.5 (C3151, C3131), 32.5 (C1353, C1383), 28.9 (C1354, C1384), 25.6 (C1357, C1387), 23.1 (C1355, C1385), 14.1 (C1356, C1386), 10.8 (C1358, C1388) ppm.

$trans$-[(IC$_6$H$_4$-$4^-$-C≡C)Ru(C≡CC$_6$H$_4$-$4^-$-C≡CSi(i-Pr)$_3$)(dppe)$_2$] (2-60)

In a flame-dried 100 mL two-neck round bottom flask fitted with a condenser, 2-59$^\dagger$ (0.128 g, 0.11 mmol, 1.0 eq.) and 2-29$^*$ (0.070 g, 0.25 mmol, 2.25 eq.) were dissolved in distilled dichloromethane (70 mL), and triethylamine (8 drops) was added. To the clear, pale orange solution was added NaPF$_6$ (0.060 g, 0.36 mmol, 3.25 eq.), after which the solution became yellow. The resultant reaction mixture was heated at reflux for 12 h. The volume of solvent was reduced to 2 ml under reduced pressure. The residual suspension was dropped into chilled methanol, while stirring vigorously. An off-white precipitate was formed that was separated from the solution by filtration through a sintered glass filter funnel. The solid residue was washed with $n$-hexane and was then redissolved in a minimal amount of dichloromethane. The resultant solution was filtered through cotton wool and was dropped into chilled methanol. The filtration/washing procedure was repeated, and the solid was taken to dryness under vacuum, giving a pale yellow, microcrystalline solid (0.092 g, 0.07 mmol, 59%).

Anal. Calcd. for C$_{76}$H$_{77}$IP$_4$RuSi: C 67.46, H 5.52%. Found: C 67.42, H 5.58%. ESI MS: 1407.3 ([M + H]$^+$, 100). HR ESI TOF MS: Calcd. for C$_{79}$H$_{78}$IP$_4$RuSi$^{102}$.
1407.2912; Found: 1407.2936. IR (CH₂Cl₂) [Rel. Transm., Assignm.]: [s, ν(Ru–C≡C)], [m, ν(C=H aliphatic)], [m, ν(C=H aromatic)] cm⁻¹. UV-Vis (λₘₐₓ, cm⁻¹ [ε, 10³ M⁻¹ cm⁻¹]): 14500 [57.5]. ¹H NMR (500 MHz, CDCl₃): δ 7.54–7.49 (m, 16H, H151, H161), 7.43 (d, J_HH = 8.4 Hz, 2H, H142), 7.28 (d, J_HH = 8.3 Hz, 2H, H205), 7.21–7.15 (m, 16H, H152, H162), 6.65 (d, J_HH = 8.3 Hz, 2H, H204), 6.46 (d, J_HH = 8.4 Hz, 2H, H143), 2.67–2.57 (m, 8H, H170), 1.15 (s, 21H, H10, H11) ppm. ³¹P [¹H] NMR (121 MHz, CDCl₃): δ 54.27 ppm. ¹³C [¹H] NMR (126 MHz, CDCl₃): δ 136.8 (m, C150, C160), 136.4 (C142), 135.4 (m, C146, C201), 134.2, 134.1 (C151, C161), 131.9 (C143), 131.4 (C205), 130.6 (C203), 129.8 (C144), 129.7 (C204), 128.7 (C153, C163), 127.1 (C152, C162), 117.3, 117.2 (C202, C206), 116.0 (C145), 108.4 (C207), 89.7 (C208), 87.0 (C141), 31.4 (vtt, |¹J_FC + ³J_FC| = 23.9 Hz, C170), 18.8 (C11), 11.4 (C10) ppm.

trans-[(dppe)₂ClRu(C≡CC₆H₄-4-C≡CC₆H₄-4-Br)] (2-47)

In a 100 mL two-neck round bottom flask fitted with a rubber septum, 2–27⁺ (0.050 g, 0.18 mmol, 1.0 eq.) and cis-[RuCl₂(dppe)₂] (0.18 g, 0.19 mmol, 1.04 eq.) were dissolved in freshly distilled dichloromethane (50 mL). The orange, clear, solution was deoxygenated, and NaPF₆ (0.060 g, 0.36 mmol, 2.0 eq.) was added, after which the mixture became red instantly. The mixture was stirred at 25–30°C for 36 h, after which the mixture became reddish-brown and slightly cloudy. The amount of solvent was reduced in vacuo, and the residual solution was dropped into stirring diethylether. The vinylidene complex precipitated out as a pale brown, fluffy solid, which was isolated by filtration. The solid was redissolved in a minimal amount of dichloromethane (4 mL). On dropwise addition of triethylamine (0.5 mL), the solution became yellow instantaneously and was stirred for 3 min before it was filtered through cotton wool into stirring methanol. A yellow precipitate was formed, which was separated from the yellow solution by filtration. The solid residue was suspended in dichloromethane and the resulting mixture dropped into n-pentane. A grainy, dark-yellow precipitate was formed that was isolated by filtration, taken to dryness under suction and further dried under vacuum. The product (0.138 g, 0.11 mmol, 64%) was obtained as a microcrystalline, yellow powder. Crystals
suitable for X-ray structural analysis were obtained from slow diffusion of n-hexane into a dichloromethane solution over two days.

Anal. Calcd. for C_{65}H_{59}BrClP_{4}Ru: C 67.30, H 4.65%. Found: C 67.05, H 4.99%.  
ESI MS: 1220.2 [(M - Cl + MeCN)^+], 1051.2 (15), 727.5 (25), 651.5 (35).  
HR ESI TOF MS: Calcd. for C_{70}H_{69}N_{1}P_{4}BrRu^{102}: 1218.1825. Found: 1218.1842.  
IR (CH_{2}Cl_{2}) [Rel. Transm., Assignm.]: 1001 [96.9], 1010 [94.7], 1028 [96.6], 1097 [95.0], 1134 [94.6], 1435 [85.2], 1486 [91.8], 1504 [89.2], 1583 [93.9], 1595 [91.8], 2061 [78.0, \nu([Ru]-C\equivC)], 2211 [96.2], 3055 [92.7, \nu(C-H_{aromatic})] cm^{-1}.  
UV-Vis (\bar{v}_{max}, cm^{-1} [\%], 10^{3} M^{-1} cm^{-1}): 25300 [38.1].  
{^1}H NMR (500 MHz, CDCl_{3}): \delta 7.49 (d, J_{HH} = 8.4 Hz, 2H, H134), 7.49-7.44 (m, 8H, H161), 7.39 (d, J_{HH} = 8.4 Hz, 2H, H135), 7.36-7.31 (m, 8H, H151), 7.27 (d, J_{HH} = 8.3 Hz, 2H, H142), 7.24-7.16 (m, 8H, H153, H163), 7.05-7.00 (m, 8H, H162), 7.00-6.93 (m, 8H, H152), 6.57 (d, J_{HH} = 8.3 Hz, 2H, H143), 2.80-2.61 (m, 8H, H170) ppm.  
{^31}P{^1}H NMR (121 MHz, CDCl_{3}): \delta 49.84 ppm.  
{^{13}}C{^1}H NMR (126 MHz, CDCl_{3}): \delta 136.3 (vtt, 1{^1}J_{P-C} + 3{^3}J_{P-C} = 19.2 Hz, C150), 135.5 (vtt, 1{^1}J_{P-C} + 3{^3}J_{P-C} = 18.0 Hz, C160), 134.4 (C161), 134.1 (C151), 132.8 (C135), 132.1 (m, C146), 131.5 (C134), 130.8 (C143), 130.7 (C144), 129.9 (C142), 128.8 (C153, C153), 127.2 (C163), 127.0 (C153), 122.9 (C136), 121.8 (C133), 116.1 (C141), 114.4 (C145), 91.8 (C139), 88.4 (C140), 30.6 (vtt, 1{^1}J_{P-C} + 3{^3}J_{P-C} = 23.0 Hz, C170) ppm.

trans-[(dppe)_2ClRu(C\equivCC_6H_4-4-C\equivCC_6H_4-4-I)] (2-48)

In a flame-dried 250 mL two-neck round-bottom flask, 2-26* (0.180 g, 0.55 mmol, 1.0 eq.) and cis-[RuCl_2(dppe)_2] (0.550 g, 0.57 mmol, 1.03 eq.) were dissolved in freshly distilled dichloromethane (150 mL). The yellow, clear solution was deoxygenated, and NaPF_6 (0.130 g, 0.77 mmol, 1.4 eq.) was added, after which the solution became orange gradually and turned to deep-orange within 10 min. The mixture was stirred at ambient temperature for 18 h, over which period the solution turned dark red. The volume of solvent was reduced to 4 mL in vacuo. A deep red-brown, cloudy mixture was obtained that was dropped into stirring diethylether, affording a plum-colored precipitate with a gray tinge. The solid was isolated by filtration and redissolved in dichloromethane (5 mL). To this solution was added triethylamine (1 mL), after which a large amount of a grainy precipitate was formed and the solution turned orange. The cloudy
mixture was stirred for 3 min and was then dropped into stirring methanol. A yellow precipitate was formed, which was isolated by filtration and suspended in dichloromethane. The resultant mixture was dropped into stirring n-pentane with a small amount of added triethylamine. A grainy precipitate was formed that was isolated by filtration. The residual solvent was removed from the solid under reduced pressure, affording 0.530 g (0.42 mmol, 77%) of the product.

Anal. Calcd. for C_{68}H_{56}ClIP_{4}: C 64.79, H 4.48%. Found: C 64.66, H 4.77%. ESI MS: 1266.7 ([M - Cl + MeCN]^+ + 2), 1225.6 ([M - Cl]^+, 100), 897.6 ([Ru(dppe)_{2}]^+, 15). HR ESI TOF MS: Calcd. for C_{70}H_{59}NP_{4}^{102}RuI: [M - Cl + MeCN]^+: 1266.1686. Found: 1266.1694. IR (CH_{2}Cl_{2}) [Rel. Transm., Assignmnt.]: 1003 [88.3], 1028 [94.3], 1097 [81.7], 1135 [91.9], 1314 [96.6], 1390 [95.6], 1434 [74.9], 1487 [83.8], 1504 [81.1], 1578 [91.2], 1596 [82.7], 2061 [60.9], (ν(Ru-C≡C)), 2211 [94.2], 2952 [13.7], 3055 [92.1, (ν(C-H_{aromatic})), 3063 [92.4, (ν(C-H_{aromatic}))] cm^{-1}. UV-Vis (ν_{max}, cm^{-1} [ε, 10^3 M^{-1} cm^{-1}]): 25200 [34.5], 34400 [30.4, sh], 39700 [40.4]. ^{1}H NMR (300 MHz, C_{6}D_{6}): δ 7.68 (m, 2H, H134), 7.53–7.42 (m, 8H, H161), 7.39–7.29 (m, 8H, H151), 7.27–7.25 (m, 2H, H142), 7.25–7.22 (m, 2H, H135), 7.22–7.15 (m, 8H, H153, H163), 7.05–6.98 (m, 8H, H162), 6.98–6.92 (m, 8H, H152), 6.57–6.53 (m, 2H, H143), 2.79–2.56 (m, 8H, H170) ppm. ^{31}P^{[1}H{]} NMR (121 MHz, C_{6}D_{6}): δ 49.81 ppm. ^{13}C^{[1}H{]} NMR (126 MHz, CDCl_{3}): δ 137.4 (C134), 136.3 (vtt, |J_{PC} + 3J_{PC}| = 20.5 Hz, C150), 135.5 (vtt, |J_{PC} + 3J_{PC}| = 18.5 Hz, C160), 134.4 (C151), 134.1 (C161), 132.9 (C142), 130.8 (C135), 130.7 (C144), 129.9 (C143), 128.8 (C153, C163), 127.2 (C152), 127.0 (C126), 123.4 (C136), 116.1 (C141), 114.5 (C145), 93.4 (C133), 92.1 (C139), 88.6 (C140), 30.6 (vtt, |J_{PC} + 3J_{PC}| = 23.2 Hz, C170) ppm.

\[ \text{trans-[(dppe)_{2}ClRu(C≡CCH_{2}-4-C≡CC≡CH_{2}-2.5-(CH_{2}CH=CHCH_{2}Me)_{2}-4-I)]} \]
\[ (2-49) \]

In a flame-dried 250 mL two-neck round-bottom flask, \[ \text{2-34} \] (0.38 g, 0.68 mmol, 1.08 eq.) was dissolved in freshly distilled and deoxygenated dichloromethane (240 mL). \[ \text{cis-[RuCl}_{2}(dppe)_{2}] \] (0.611 g, 0.62 mmol, 1.0 eq.) was added, and the clear, yellow solution was deoxygenated again. NaPF_{6} (0.30 g, 1.79 mmol, 2.8 eq.) was added, after which the solution became slightly cloudy and turned orange instantaneously and then wine-red within 2 h. The mixture was stirred
at ambient temperature for 30 h. The mixture was concentrated under reduced pressure, affording 3 mL of a deep plum-red mixture, to which was added triethylamine (0.5 mL) dropwise until the color changed to dark yellow.\textsuperscript{[22]} The mixture was filtered through tightly packed cotton wool and was then dropped into stirring methanol (100 mL), after which a yellow precipitate was formed that was removed from the solution by filtration. The solid was adsorbed onto basic alumina, giving a yellow powder. A short chromatography column over basic alumina (l = 7 cm; \( \Phi = 3.5 \) cm) was charged with the powder and initially washed with a mixture of n-pentane and dichloromethane (10:1). The product was eluted with a mixture of the same solvents (1:1). The solvent was removed, giving a yellow, solid residue that was suspended in a mixture of n-pentane and dichloromethane (10:1). Dichloromethane was added dropwise until just enough of this solvent was present to dissolve the majority of the solid. The solution was filtered through cotton wool and was dropped into warm methanol. A solid was formed, which was removed from the solution by filtration through a sintered glass filter funnel. The residual solution was removed from the solid under vacuum, affording the product (0.71 g, 0.48 mmol, 75%) as a yellow, amorphous powder.

Anal. Calcd. for C\(_{84}\)H\(_{86}\)Cl\(_2\)IP\(_4\)Ru: C 67.94, H 5.97%. Found: C 68.08, H 5.84%. ESI MS: 1490.2 ([M - Cl + MeCN]\(^+\), 2), 1449.9 ([M - Cl]\(^+\), 100). HR ESI TOF MS: Calcd. for C\(_{86}\)H\(_{91}\)INP\(_4\)Ru\(^{102}\) [M - Cl + MeCN]: 1490.4190. Found: 1490.4191. IR (CH\(_2\)Cl\(_2\)) [Transm., Assignm.]: 1000 [98.8], 1029 [98.2], 1096 [91.7], 1110 [95.5], 1173 [97.9], 1192 [98.2], 1315 [98.7 (broad)], 1379 [97.8], 1420 [97.3], 1435 [86.5], 1466 [95.7 (broad)], 1488 [92.7], 1501 [92.8], 1573 [97.9], 1593 [92.6], 2066 [81.2, \( \nu(Ru\text{-}C\equivC)\)], 2200 [98.6], 2859 [94.6], 2873 [94.6, \( \nu(C\text{-}H_{aliphatic})\)], 3051 [94.0, \( \nu(C\text{-}H_{aromatic})\)], 3058 [93.5, \( \nu(C\text{-}H_{aromatic})\)] cm\(^{-1}\). UV-Vis (\( \nu_{max}\), cm\(^{-1}\) [\( \epsilon\), 10\(^3\) M\(^{-1}\) cm\(^{-1}\)]): 25 500 [38.0], 34 500 [28.7, sh], 39 900 [51.4]. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \( \delta\) 7.66 (s, 1H, H134), 7.50–7.45 (m, 8H, H161), 7.36–7.30 (m, 8H, H151), 7.28 (s, 1H, H137), 7.27 (d, \( J_{HH} = 8.1 \) Hz, 2H, H142), 7.23–7.16 (m, 8H, H153, H163), 7.05–6.99 (m, 8H, H162), 6.99–6.93 (m, 8H, H152), 6.57 (d, \( J_{HH} = 8.1 \) Hz, 2H, H143), 2.79–2.58 (m, 12H, H170, H1351, H1381), 1.83–1.69 (m, 2H, H1352, H1382).

\textsuperscript{[22]} In a later attempt, the vinylidene complex was worked up as an intermediate by precipitation from cold diethyl ether before the base was added; trans-RuCl\(_2\)(dppe)\(_2\) seems less likely to be found in the product as a contaminant under such conditions, which makes the workup procedure less tedious.
1.44–1.26 (m, 16H, H1353, H1354, H1355, H1357, H1383, H1384, H1385, H1387),
0.97–0.88 (m, 12H, H1356, H1358, H1386, H1388) ppm. $^{31}$P-$^1$H NMR (121 MHz,
CDCl$_3$): $\delta$ 49.86 ppm. $^{13}$C-$^1$H NMR (126 MHz, CDCl$_3$): $\delta$ 142.8 (C135), 141.5
(C138), 140.5 (134), 136.3 (vtt, $|J_{PC} + 3J_{PC}| = 19.4$ Hz, C150), 135.5 (vtt,
$|J_{PC} + 3J_{PC}| = 17.9$ Hz, C160), 134.4, 134.2 (C151, C161), 133.4 (C137), 131.5
(pent., $3J_{PC} = 15.2$ Hz, C146), 130.7 (C142), 130.4 (C144), 129.9 (C143), 128.8
(C153, C163), 127.2 (C162), 127.0 (C152), 123.5 (C136), 116.7 (C141), 114.4
(C145), 100.6 (C133), 94.7 (C139), 88.3 (C140), 44.3 (C1381), 40.2 (C1382), 39.3
(C1352), 38.2 (C1351), 32.5, 32.2 (C1357, C1387), 30.6 (vtt, $|J_{PC} + 3J_{PC}| =
23.6$ Hz, C170), 28.9, 28.7 (C1354, C1384), 25.6, 25.3 (C1353, C1383), 23.2, 23.1
(C1355, C1385), 14.2, 14.1 (C1356, C1386), 10.82, 10.78 (C1358, C1388) ppm.

trans-[{(dppe)$_2$}ClRu(C≡CC$_6$H$_4$-4'-C≡CC$_6$H$_2$-2,5-CH$_2$CH$\equiv$TH$_2$)$_2$Me}$_2$-4-
C≡CC$_6$H$_4$-4'-I)] (2-50)

In a flame-dried 100 mL two-neck round-bottom flask, cis-[RuCl$_2$(dppe)$_2$]
(0.120 g, 0.12 mmol, 0.99 eq.) was dissolved in freshly distilled and deoxygenated
dichloromethane (60 mL). The clear, yellow solution was deoxygenated, and
NaPF$_6$ (0.045 g, 0.27 mmol, 2.10 eq.) was added, after which the solution turned
ruby-red within 14 h. To this solution was added a solution of 2-38 (0.050 g,
0.08 mmol, 1.0 eq.) in freshly distilled and deoxygenated dichloromethane
(30 mL), and the resultant mixture was stirred at ambient temperature for
2.5 d. The amount of solvent was reduced to 2 mL in vacuo. A deep-red, cloudy
solution was obtained, which was filtered through tightly packed cotton wool
into cold diethylether. A plum-colored, flocculent precipitate was formed that
was isolated by filtration. The resultant solid was dissolved in dichloromethane
(1.5 mL). To the deep-red solution was added triethylamine (0.5 mL), after
which the solution turned orange instantaneously. The solution was dropped
into cold methanol, affording a yellow, fluffy precipitate that was isolated by
filtration. The solid was washed with methanol three times and with n-pentane
once quickly. The resultant solid was dried under vacuum at 40–50 °C for 12 h.
0.126 g (0.079 mmol, 63%) of a yellow solid was isolated, which was identified to be
the product.

23 The solubility of the complex is poor, but it still dissolves to some degree.
2.5. Experimental

ESI MS: 1590.5 ([M - Cl + MeCN]+, 65). HR ESI TOF MS: Calcd. for C₉₄H₈₅INP₁₁₀²Ru: 1590.4503. Found: 1590.4509. IR (CH₂Cl₂) [Rel. Transm., Assignmn.]: 1006 [93.4], 1029 [97.2], 1097 [89.4], 1173 [95.3], 1435 [83.2], 1465 [95.4 (broad)], 1486 [90.6], 1505 [86.5], 1590 [88.7], 2064 [75.0, ν(Ru-C≡C)], 2859 [93.0], 2873 [93.2, ν(C-H_{aliphatic})], 3047 [95.5, ν(C-H_{aromatic})], 3062 [95.7, ν(C-H_{aromatic})] cm⁻¹. UV-Vis (ν_{max}, cm⁻¹ | ε, 10³ M⁻¹ cm⁻¹): 24 200 [44.2], 29 800 [42.4], 31 500 [43.4]. ¹H NMR (500 MHz, CDCl₃): δ 7.72 (d, 3_j_{HH} = 8.3 Hz, 2H, H₁₂₈), 7.53–7.45 (m, 8H, H₁₆₁), 7.37–7.31 (m, 10H, H₁₃₃, H₁₃₇, H₁₅₁), 7.29, 7.27 (d, 3_j_{HH} = 8.3 Hz, 3_j_{HH} = 8.3 Hz, 6H, H₁₂₉, H₁₄₂), 7.25–7.16 (m, 8H, H₁₅₃, H₁₆₃), 7.08–6.93 (m, 16H, H₁₆₂, H₁₅₂), 6.59 (d, 3_j_{HH} = 8.3 Hz, 2H, H₁₄₃), 2.86–2.78 (m, 2H, H₁₃₅₁), 2.77–2.62 (m, 12H, H₁₇₀, H₁₃₈₁), 1.88–1.74 (m, 2H, H₁₃₅₂, H₁₃₈₂), 1.47–1.24 (m, 16H, H₁₃₅₃, H₁₃₅₄, H₁₃₅₅, H₁₃₅₇, H₁₃₈₃, H₁₃₈₄, H₁₃₈₅, H₁₃₈₇), 0.99–0.83 (m, 1H₃₅₆, H₁₃₅₈, H₁₃₈₆, H₁₃₈₈) ppm. ³¹P{¹H} NMR (121 MHz, CDCl₃): δ 49.87 ppm. ¹³C{¹H} NMR (126 MHz, CDCl₃): δ 141.2, 140.9 (C₁₃₅, C₁₃₈), 137.5 (C₁₂₈), 136.3 (vtt, 3j = 17.8 Hz, C₁₅₀), 135.5 (vtt, 3j = 17.6 Hz, C₁₆₀), 134.4 (C₁₆₁), 134.2 (C₁₅₁), 133.4, 133.37 (C₁₃₄, C₁₃₇), 132.9 (C₁₂₉), 131.4 (m, C₁₄₆), 130.7 (C₁₄₂), 130.4 (C₁₄₄), 129.9 (C₁₄₃), 128.8 (C₁₅₃, C₁₆₃), 127.2, 127.0 (C₁₆₂, C₁₅₂), 123.7 (C₁₃₆), 123.1 (C₁₃₀), 121.7 (C₁₃₃), 116.7 (C₁₄₁), 114.5 (C₁₄₅), 95.4 (C₁₄₀), 93.9 (C₁₂₇), 92.6 (C₁₃₂), 90.5 (C₁₃₁), 88.9 (C₁₃₂), 40.4, 40.2 (C₁₃₅₂, C₁₃₈₂), 38.5 (C₁₃₅₁, C₁₃₈₁), 32.64, 32.55 (C₁₃₅₃, C₁₃₈₃), 30.6 (vtt, 3j = 23.1 Hz, C₁₇₀), 29.0, 28.9 (C₁₃₅₄, C₁₃₈₄), 25.6 (C₁₃₅₇, C₁₃₈₇), 23.2, 23.1 (C₁₃₅₅, C₁₃₈₅), 14.2, 14.1 (C₁₃₅₆, C₁₃₈₆), 10.8 (C₁₃₅₈, C₁₃₈₈) ppm.

trans-[(dppe)₂ClRu(C≡CC₆H₄-4-C≡CC₆H₂-2,5-{CH₂CHEMEt(CH₂)}₃Me)₂-4-C≡CC₆H₄-4-C≡CC₆H₄-4-I] (2-51)

In a flame-dried 100 mL two-neck round-bottom flask, 2-44 (0.190 g, 0.22 mmol, 1.0 eq.) was dissolved in freshly distilled and deoxygenated dichloromethane (90 mL). To the clear, yellow solution was added cis-[RuCl₂(dppe)₂] (0.240 g, 0.25 mmol, 1.1 eq.). The yellow, clear solution was deoxygenated, and NaPF₆ (0.070 g, 0.42 mmol, 1.9 eq.) was added. The slightly cloudy, yellow solution was deoxygenated once more and allowed to stir at ambient temperature for 18 h. The mixture was warmed to ca. 40 °C and stirred at that temperature for another
12 h. The amount of solvent was reduced to 3 mL \textit{in vacuo}. The residual, dark plum-colored, cloudy solution was dropped into stirring diethylether, affording a flocculent, reddish-brown precipitate, which was separated from the clear, red filtrate by filtration through a sintered glass filter funnel (pore size G3). The solid residue was redissolved in dichloromethane (3 mL). To this dark-red solution was added triethylamine (1 mL), after which the solution changed to orange. After stirring for 3 min, the mixture was dropped into stirring methanol (80 mL), affording a yellow, grainy precipitate. The solvent was removed from the solid by filtration, and the solid was redissolved in dichloromethane (10 mL). The resultant cloudy, orange solution was filtered through a sintered glass filter funnel (pore size G4) and the clear, orange filtrate dropped into n-pentane (150 mL). A yellow precipitate was formed, which was isolated by filtration. A yellow solid was obtained, which was dried under vacuum, affording 0.287 g (0.16 mmol, 72%) of the product as a yellow amorphous solid.

Anal. Calcd. for C_{108}H_{100}ClIP_{4}Ru: C 72.66, H 5.65%. Found: C 72.18, H 5.95%.
HR ESI-TOF MS: Calcd. for C_{110}H_{103}P_{4}Ru: 1790.5129. Found: 1790.5128 ([M - Cl + MeCN]^+) . IR (CH_{2}Cl_{2}) [Rel. Transm., Assignm.]: 1006 [95.3], 1096 [89.9], 1172 [95.2], 1193 [97.3], 1435 [84.3], 1463 [92.8], 1486 [89.4], 1504 [88.6], 1515 [83.1], 1592 [83.0], 1604 [79.6], 2065 [77.1, \nu(Ru-C≡C)], 2859 [88.6, \nu(C-H_{aliphatic})], 2873 [88.1, \nu(C-H_{aliphatic})], 3056 [93.3, \nu(C-H_{aromatic})] cm\(^{-1}\).

UV-Vis (\nu_{max}, cm^{-1} [\epsilon, 10^3 M^{-1} cm^{-1}]): 24000 [45.5], 28100 [84.8]. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.71 (d, \(^3\)J\(_{HH}\) = 8.2 Hz, 2H, H116), 7.53 (s, 4H, H122, H123), 7.52 (m, 2H, H128), 7.50–7.45 (m, 8H, H161), 7.35–7.30 (m, 10H, H151, H137, H134), 7.30–7.27 (m, 2H, H142), 7.27–7.25 (m, 4H, H117, H129), 7.23–7.16 (8H, H153, H163), 7.04–6.99 (m, 8H, H162), 6.99–6.93 (m, 8H, H152), 6.58 (d, \(^3\)J\(_{HH}\) = 8.1 Hz, 2H, H143), 2.85–2.62 (m, 12H, H170, H1351, H1381), 1.87–1.76 (m, 2H, H1352, H1382), 1.46–1.24 (m, 16H, H1353, H1354, H1355, H1357, H1383, H1384, H1385, H1387), 0.97–0.84 (m, 12H, H1356, H1358, H1386, H1388) ppm.

\(^{31}\)P\(^{1}\)H NMR (121 MHz, CDCl\(_3\)): \(\delta\) 49.88 (s, 4P) ppm. \(^{13}\)C\(^{1}\)H NMR (126 MHz, CDCl\(_3\)): \(\delta\) 141.3, 140.9 (C135, C138), 137.6 (C115), 136.3 (vtt, \(|J_{PC} + 3J_{FC}| = 19.7\) Hz, C150), 135.5 (vtt, \(|J_{PC} + 3J_{FC}| = 19.7\) Hz, C150), 134.4, 134.2 (C161, C151), 133.5, 133.4 (C134, C137), 133.1 (C117), 131.7 (C122, C123, C128), 131.4 (C129), 130.7 (C142), 130.4 (C144), 129.9 (C143), 128.8 (C153, C163), 127.2, 127.0 (C162, C152), 123.7 (C136), 123.2 (C130), 122.9–122.6 (C127, C124, C121),

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122.5 (C118), 121.8 (C133), 116.7 (C141), 114.5 (C145), 95.4 (C140), 94.4 (C115), 93.3 (C120), 91.2 (C139), 91.1-90.3 (C125, C126, C131), 90.4 (C119), 89.0 (C132), 40.4, 40.2 (C1352, C1383), 38.6 (C1351, C1381), 32.7, 32.6 (C1353, C1383), 30.6 (vtt, $|J_{PC} + 3J_{PC}| = 22.8$ Hz, C170), 29.02, 28.98 (C1354, C1384), 25.6 (1357, C1387), 23.2, 23.1 (C1355, C1385), 14.20, 14.13 (C1356, C1386), 10.8 (C1358, C1388) ppm.

$1,3,5-\text{-(Br}C_6H_4\text{-4-}C\equiv C\text{C}_6H_4\text{-4-}C\equiv C\text{)}_3C_6H_5 \ (2-6)$

In a flame-dried 100 mL two-neck round-bottom flask, $para$-bromiodobenzene (4.0 g, 14.14 mmol, 3.19 eq.) was dissolved in triethylamine (170 mL). The resultant solution was deoxygenated, and [PdCl$_2$(PPh$_3$)$_2$] (0.060 g, 0.08 mmol, 0.02 eq.) and CuI (0.025 g, 0.12 mmol, 0.03 eq.) were added. The solution was cooled to 0°C, and a chilled solution of 2-5 ($2.0$ g, 4.44 mmol, 1.0 eq.) in dry dichloromethane (100 mL) was added slowly, after which the reaction mixture turned dark-brown within 5 min. The reaction mixture was allowed to warm to room temperature over 16 h. The solvent was removed from the solution in vacuo, affording an amorphous, light-beige, solid residue, which was washed with hot methanol several times until the washing solutions were clear and colorless. The solid was washed with $n$-hexane a few times before the residual solvent was removed under reduced pressure. A beige solid (3.65 g, 3.99 mmol, 90%) was obtained, which was identified to be the product.

Anal. Calcd. for C$_{54}$H$_{27}$Br$_3$: C 70.84, H 2.97%. Found: C 70.91, H 3.04%. UV-Vis ($\lambda_{max}$, cm$^{-1}$, $[\varepsilon, 10^3$ M$^{-1}$ cm$^{-1}$]): 28 500 [158.4], 30 300 [210.6]. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.66 (s, 3H, H10), 7.51 (s, 12H, H134, H135), 7.50 (d, $^3J_{HH} = 8.5$ Hz, 6H, H142), 7.39 (d, $^3J_{HH} = 8.5$ Hz, H143) ppm. $^{13}$C($^1$H) NMR (126 MHz, CDCl$_3$): $\delta$ 134.2 (C10), 133.0 (C143), 131.68, 131.66, 131.57 (C134, C135, C142), 123.9 (C11), 123.2, 122.8, 122.7 (C133, C136, C144), 121.9 (C141), 90.4, 90.3 (C132, C139), 90.1 (C140), 89.6 (C131) ppm.\textsuperscript{24}

$1,3,5-\text{trans-}[(dppm)_2ClRu(C\equiv C\text{C}_6H_4\text{-4-}C\equiv C\text{C}_6H_4\text{-4-}C\equiv C\text{)}_3C_6H_5 \ (2-12)$

\textsuperscript{24} Despite several attempts, a molecular ion could not be detected under EI or ESI MS conditions.
In a flame-dried 250 mL two-neck round-bottom flask, 2-8\(^*\) (0.040 g, 0.05 mmol, 1.0 eq.) was dissolved in freshly distilled and deoxygenated dichloromethane (130 mL). The resulting brown, inhomogeneous mixture was warmed gently for a few min.\(^{25}\) cis-[RuCl\(_2\)(dpdm)\(_2\)] (0.130 g, 0.14 mmol, 2.6 eq.) was added, followed by addition of NaPF\(_6\) (0.040 g, 0.24 mmol, 4.5 eq.). The resulting mixture was stirred at ambient temperature for 36 h. cis-[RuCl\(_2\)(dpdm)\(_2\)] (0.010 g, 0.01 mmol, 0.6 eq.) and NaPF\(_6\) (0.010 g, 0.06 mmol, 1.1 eq.) were added, and the reaction mixture stirred at 30 °C for 10 h and then at ambient temperature for another 12 h. The amount of solvent was reduced in vacuo, affording 3 mL of a deep-red residual solution, which was dropped into stirring diethylether. A pale brown precipitate was formed that was isolated by filtration. The solid thus obtained was redissolved in dichloromethane (4 mL). To the resultant solution was added triethylamine (1 mL), after which the dark mixture turned slightly orange, but remained dark brown. The solution was dropped into stirring methanol, affording an orange-brown precipitate, which was collected by filtration and dissolved in dichloromethane (20 mL). The inhomogeneous solution was filtered through a sintered glass filter funnel (pore size G4). A clear, dark-orange to red filtrate was obtained, which was concentrated in vacuo. The clear residual solution was dropped into stirring n-pentane. An orange precipitate was formed that was isolated by filtration through a sintered glass filter funnel (pore size G4). The orange solid was then dried under vacuum, giving 0.116 g (0.033 mmol, 63%) of the product.

Anal. Calcd. for C\(_{210}\)H\(_{159}\)Cl\(_3\)P\(_{12}\)Ru\(_3\): C 72.82, H 4.63%. Found: C 72.73, H 4.77%.
ESI MS: 1733.8 ([M - Cl + MeCN + H]\(^{2+}\), < 2), 933.1 (100). IR (CH\(_2\)Cl\(_2\)) [Rel. Transm., Assignm.]: 999 [99.7], 1027 [99.9], 1099 [96.0], 1136 [99.8], 1176 [99.9], 1435 [92.6], 1487 [97.6], 1515 [96.1], 1579 [96.2], 1589 [95.8], 2071 [90.4, \(\nu\)(Ru-C≡C), br] 2205 [99.6, br], 2919 [77.4], 2952 [66.2], 2959 [80.6] cm\(^{-1}\). UV-Vis

\(^{25}\) Several group members, including myself, have found that in some reactions extended π-conjugated systems consisting of phenylethynyl units show the tendency to undergo what is believed to be a self-polymerization. Although there is no spectroscopic proof for this, the result is the formation of dark-brown to black material when the solvent of a clear solution of the initial π-extended compound is removed under reduced pressure; the residual solid containing the „polymerized“ material does not give a clear solution in common organic solvents anymore. This circumstance is particularly prevalent wherever the oligo(phenylethynyl) compound bears one or two free acetylene functionalities. In order to maximize the amount of dissolved material before the reaction was started, the inhomogeneous solution of the acetylene was warmed prior to addition of the remaining reagents.
2.5. Experimental

(ν\textsubscript{max}, cm\textsuperscript{-1} [ε, 10\textsuperscript{3} M\textsuperscript{-1} cm\textsuperscript{-1}]): 24 300 [100.6], 30 900 [141.3], 30 200 [151.3], 37 600 [126.3]. \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}): 6.76 (s, 3H, H10), 7.54–7.48 (m, 32H, H134, H135, H151), 7.48–7.41 (m, 24H, H161), 7.34–7.23 (m, 24H, H153, H163), 7.22–7.15 (m, 24H, H152), 7.12–7.04 (m, 32H, H162, H142), 6.02 (d, J\textsubscript{HH} = 8.1 Hz, 6H, H143), 4.99–4.90 (m, 12H, H170) ppm. \textsuperscript{31}P\{\textsuperscript{1}H\} NMR (121 MHz, CDCl\textsubscript{3}): δ-5.75 ppm. \textsuperscript{13}C\{\textsuperscript{1}H\} NMR (126 MHz, CDCl\textsubscript{3}): δ 134.9 (vtt, |J\textsubscript{PC} + 3J\textsubscript{FC}| = 22.5 Hz, C150), 134.1 (vtt, |J\textsubscript{PC} + 3J\textsubscript{FC}| = 20.5 Hz, C160), 133.7, 133.3 (C151, C161), 131.6 (C135), 131.3 (C134), 131.1 (C144), 130.4 (C142), 130.0 (C143), 129.3, 129.1 (C153, C163), 127.5 (C152, C162), 124.3, 124.0 (C11, C133), 121.8 (C136), 115.6 (C141), 113.4 (C145), 93.2 (C93.2), 90.6 (C139), 89.3 (C131), 88.9 (C132), 50.3 (vtt, |J\textsubscript{PC} + 3J\textsubscript{FC}| = 23.3 Hz, C170) ppm.

1,3,5-{\textit{trans}-[(dppe)\textsubscript{2}ClRu(C≡CC\textsubscript{6}H\textsubscript{4}-4-C≡CC\textsubscript{6}H\textsubscript{4}-4-C≡C})\textsubscript{3}C\textsubscript{6}H\textsubscript{3}} (2-14)

In a flame-dried 100 mL two-neck round-bottom flask, finely ground 2-8 (0.100 g, 0.13 mmol, 1.0 eq.) was suspended in freshly distilled dichloromethane (90 mL). The inhomogeneous mixture was warmed gently to increase the solubility of the starting material. To the clear, red-brown solution was added \textit{cis}-[RuCl\textsubscript{2}(dppe)\textsubscript{2}] (0.38 g, 0.39 mmol, 2.95 eq.), affording an orange-brown solution, to which NaPF\textsubscript{6} (0.15 g, 0.89 mmol, 6.7 eq.) was added. The resultant reaction mixture was stirred at ambient temperature for 36 h, over which course the mixture became dark red. The volume of solvent was reduced to 4 mL \textit{in vacuo}, and the residual solution was filtered through cotton wool into stirring, cold diethyl ether. The formation of a flocculent, brown precipitate was observed. The precipitate was isolated by filtration and redissolved in a minimal amount of dichloromethane. Triethylamine (3 mL) was added to the near-black solution dropwise. The resultant solution was dropped into warm and vigorously stirring methanol. An orange-yellow precipitate was formed, which was isolated by filtration through a sintered glass filter funnel and reprecipitated from n-pentane. The precipitate was isolated by filtration and was then dried under vacuum, affording 0.319 g (0.090 mmol, 69%) of a dark-yellow amorphous solid that was identified as the product.

Anal. Calcd. for C\textsubscript{216}H\textsubscript{171}Cl\textsubscript{3}P\textsubscript{12}Ru\textsubscript{3}: C 73.12, H 4.86%. Found: C 73.37, H 4.79%. ESI MS: 1738 ([M Cl]\textsuperscript{2+}, 2), 1647.4 (8), 1272.3 (43), 1147.2 ([M - 3 Cl]\textsuperscript{3+}, 95),
CHAPTER 2. Stars – Unbranched Octupolar Ruthenium Acetylide Complexes

897.17 (100). IR (CH2Cl2) [Rel. Transm., Assignm.]: 1000 [92.8], 1017 [95.7], 1027 [93.2], 1072 [94.6], 1097 [70.6], 1137 [92.2], 1177 [89.8], 1193 [93.6], 1313 [95.1 (broad)], 1417 [91.4], 1433 [54.8], 1487 [76.1], 1513 [67.2], 1578 [68.8], 1588 [64.5], 2061 [39.7, \( \nu(\text{Ru-C} \equiv \text{C}) \)], 2205 [88.7], 3056 [82.9, \( \nu(\text{C-H}_{\text{aromatic}}) \)] cm\(^{-1}\). UV-Vis (\( \tilde{\nu}_{\text{max}}, \text{cm}^{-1} [\varepsilon, 10^3 \text{M}^{-1} \text{cm}^{-1}] \)): 23600 [135.4], 30500 [159.8], 31100 [155.5, sh], 40000 [168.3].

\(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) 7.69 (s, 3H, H10), 7.53 (s, 12H, H134, H135), 7.50–7.42 (m, 24H, H161), 7.38–7.30 (m, 24H, H151), 7.30 (d, \( 3J_{HH} = 8.3 \text{Hz} \), 6H, H142), 7.23–7.16 (m, 24H, H153, H163), 7.06–6.99 (m, 24H, H162), 6.99–6.92 (m, 24H, H152), 6.58 (d, \( 3J_{HH} = 8.3 \text{Hz} \), 6H, H143), 2.81–2.61 (m, 24H, H170) ppm. \(^{31}\)P\{\(^1\)H\} NMR (121 MHz, CDCl\(_3\)): \( \delta \) 49.84 ppm. \(^{13}\)C\{\(^1\)H\} NMR (75 MHz, CDCl\(_3\)): \( \delta \) 136.2 (vtt, \( |1J_{PC} + 3J_{PC}| = 20.6 \text{Hz} \)), 135.5 (vtt, \( |1J_{PC} + 3J_{PC}| = 19.2 \text{Hz} \)), 134.4, 134.1 (C161, C151), 131.6, 131.3 (C134, C135), 130.9 (C142), 130.7 (C144), 129.9 (C143), 128.8 (C163, C153), 127.2, 127.0 (C162, C152), 124.2 (C133), 124.0 (C11), 121.89 (C136), 116.1 (C141), 114.5 (C145), 93.0 (C140), 90.5 (C132), 89.4 (C131), 89.3 (C139), 30.6 (vtt, \( |1J_{PC} + 3J_{PC}| = 23.3 \text{Hz} \), C170) ppm.

1,3,5-{trans-[(PhC≡C)Ru(C≡CC\(_6\)H\(_4\)-4-C≡CC\(_6\)H\(_4\)-4-C≡C)(dppe)\(_2\)]_5C\(_6\)H\(_8\)} (2-15)

In a flame-dried 100 mL two-neck round-bottom flask fitted with a condenser, 2-14 (0.070 g, 0.020 mmol, 1.0 eq.) was dissolved in freshly distilled and deoxygenated dichloromethane (70 mL). To the resultant solution were added triethylamine (3 drops) and NaPF\(_6\) (0.030 g, 0.18 mmol, 9.0 eq.). A slightly cloudy, orange solution was obtained, which was deoxygenated before phenylacetylene (0.05 mL, 0.05 mmol, 25 eq.) was added. The reaction mixture was heated at reflux for 18 h. NaPF\(_6\) (0.015 g, 0.09 mmol, 4.5 eq.) and triethylamine (2 drops) were added, and the temperature was increased to ca. 80 °C for 5 h. The volume of solvent was reduced to 2 mL in vacuo, affording a cloudy, orange residual solution, which was dropped into stirring methanol. A fine, orange precipitate was formed that was isolated by filtration through a sintered glass filter funnel (pore size G4). An orange, solid residue was obtained, which was washed off the sintered glass filter funnel with dichloromethane. The washing solution was concentrated to 3 mL under reduced pressure, and the
precipitation into methanol and filtration were repeated. The resultant solid was dissolved in dichloromethane (2 mL). This solution was filtered through tightly packed cotton wool into a stirring mixture of n-pentane and dichloromethane (9:1). A yellow, homogeneous suspension was obtained. Filtration through a sintered glass filter funnel (pore size G4) gave a clear, yellow filtrate and an orange, solid residue. The solid was dried under vacuum, affording 0.056 g (0.015 mmol, 76%) of the desired orange, solid product.

Anal. Calcd. for C_{240}H_{186}P_{12}Ru_3: C 76.97, H 5.01%. Found: C 76.85, H 5.22%. IR (CH_2Cl_2) [Rel. Transm., Assignm.]: 1100 [94.1], 1175 [97.6], 1208 [98.2], 1421 [93.7], 1434 [88.6], 1484 [91.6], 1512 [92.2], 1580 [92.1], 1590 [88.8], 2056 [73.1, \nu(Ru=C\equivC)], 2206 [97.1], 3055 [83.7, \nu(C-H_{aromatic})] cm^{-1}. UV-Vis (\tilde{\nu}_{max}, cm^{-1} [\epsilon, 10^{3} M^{-1} cm^{-1}]): 23700 [126.3], 30300 [197.8]. 1H NMR (500 MHz, CDCl_3): \delta 7.69 (s, 3H, H10), 7.65-7.56 (m, 24H, H161), 7.53 (s, H134, H135), 7.46-7.36 (m, 24H, H151), 7.32 (d, \nu_J_{HH} = 7.9 Hz, 6H, H142), 7.23-7.10 (m, 30H, H153, H163, H205), 7.05-6.87 (m, 51H, H152, H162, H206), 6.82 (d, \nu_J_{HH} = 7.4 Hz, H204), 6.65 (d, \nu_J_{HH} = 8.0 Hz, H143), 2.69-2.54 (m, 24H, H170) ppm. 31P {1H} NMR (121 MHz, CDCl_3): \delta 54.34 ppm. 13C {1H} NMR (121 MHz, CDCl_3): \delta 137.3-136.5 (m, C160, C150), 134.3 (C161), 134.1 (C151), 131.6, 131.3 (C134, C135), 131.0 (C144), 130.9 (C142), 130.5 (C203), 129.9 (C204, C143), 128.7, 128.6 (C163, C153), 127.5 (C205), 127.0 (C162, C152), 124.2, 124.0 (C133, C11), 122.9 (C206), 121.9 (C136), 117.2 (C141), 116.2 (C145, C202), 93.0 (C140), 90.6 (C139), 89.4, 89.2 (C131, C132), 31.4 (vtt, \nu_J_{PC} + 3 \nu_J_{PC} = 23.5 Hz, C170) ppm.

1,3,5-{trans-[Ru(C≡CC_6H_4-4-NO_2)\langle C≡CC_6H_4-4-C≡CC_6H_4-4-C≡C\rangle (dppe)_2]}_2C_6H_6 (2-18)

In a flame-dried 50 mL three-neck round-bottom flask fitted with a condenser, 2-14 (0.060 g, 0.017 mmol, 1.0 eq.) and para-nitropheny lacetylene (0.020 g, 0.136 mmol, 8.0 eq.) were dissolved in dry dichloromethane (40 mL). To the clear, golden-yellow solution were added NaPF_6 (0.030 g, 0.179 mmol, 10.6 eq.) and triethylamine (2 drops). The inhomogeneous mixture was heated at reflux for 45 min. Triethylamine (4 drops) was added, and the resultant mixture was heated at reflux for 5 h. The addition of triethylamine (3 drops) was repeated, and the reaction mixture heated at reflux for 11 h. Para-nitropheny lacetylene
(0.005 g, 0.045 mmol, 2.0 eq.) and NaPF₆ (0.005 g, 0.060 mmol, 1.3 eq.) were added and the solution was heated at reflux for 5 h. The solvent was removed under reduced pressure, and the residue was redissolved in dichloromethane (2 mL). The mixture was filtered through tightly packed cotton wool into stirring methanol. A red precipitate was formed, which was isolated by filtration through a sintered glass filter funnel. The solid residue was redissolved in dichloromethane (2 mL), and the resulting solution was dropped into stirring methanol. A solid was obtained after filtration. The solid was washed with n-hexane (4 x 15 mL) and was then dried in vacuo, affording 0.038 g (0.010 mmol, 58%) of the dark brick-red product.

Anal. Calcd. for C₂₄₀H₁₈₃N₉O₆P₁₂Ru: C 74.29, H 4.75, N 1.08%. Found: C 74.10, H 4.54, N 0.80%. . IR (CH₂Cl₂) [Ref. Transm., Assignm.]: 1108 [81.1], 1176 [91.9], 1324 [55.5], 1436 [84.9], 1464 [92.0], 1487 [88.6], 1499 [87.0], 1512 [86.2], 1580 [65.8], 1604 [80.3], 2046 [53.2], ν(Ru-C≡C)], 2206 [95.6], 2911 [93.1], 2920 [91.7], 3057 [92.4], ν(C-H aromatic)] cm⁻¹. UV-Vis (νmax, cm⁻¹ [ε, 10^3 M⁻¹ cm⁻¹]): 21 800 [87.6, sh], 23 900 [115.9], 30 200 [159.0]. ¹H NMR (300 MHz, CDCl₃): δ 7.99 (d, 3 JHH = 8.9 Hz, 6H, H205), 7.69 (s, 3H, H10), 7.62–7.45 (m, 24H, H161), 7.54 (s, 12H, H134, H135), 7.42–7.31 (m, 30H, H142, H151), 7.24–7.13 (m, 24H, H153, H163), 7.03–6.89 (m, 48H, H152, H162), 6.81 (d, 3 JHH = 8.2 Hz, 6H, H143), 6.59 (d, 3 JHH = 8.9 Hz, 6H, H204), 2.73–2.52 (m, 24H, H170) ppm. ³¹P {¹H} NMR (121 MHz, CDCl₃): δ 54.23 ppm. ¹³C {¹H} NMR (126 MHz, CDCl₃): δ 142.6 (C206), 137.2 (C203), 136.8–136.0 (m, C150, C160), 134.1, 133.9 (C151, C161), 131.6, 131.4 (C134, C135), 131.1 (C142), 129.8 (C143, C204), 128.93, 128.90 (C153, C163), 127.2 (C152, C163), 124.1, 124.0 (C11, C133), 123.4 (C205), 122.0 (C136), 119.2, 118.7 (C145, C202), 116.9 (C141), 92.8 (C140), 90.5 (C139), 89.3 (C131, C132), 31.3 (vtt, 1 JPC + 3 JPC) = 22.3 Hz, C170) ppm.

1,3,5-{trans-[{(dppe)₂ClRu(C≡CC₆H₄-4-C≡CC₆H₄-4-C≡CC₆H₄-4-C≡C)]}₃C₆H₉ (2-60)

In a flame-dried 100 mL two-neck round-bottom flask, 2-8* (0.018 g, 0.024 mmol, 1.0 eq.) and trans-[Ru(C≡CC₆H₄-4-I(C≡CPh)(dppe)₂] (2-59*) (0.090 g, 0.073 mmol, 3.06 eq.) were suspended in triethylamine (30 mL). The highly cloudy, pale yellow mixture was deoxygenated, and freshly distilled
dichloromethane (30 mL) was added, after which the mixture became orange and clear. The resultant solution was warmed gently to increase the solubility further, and [PdCl$_2$(PPh$_3$)$_2$] and CuI were added in catalytic amounts, after which the reaction mixture became significantly darker instantaneously and changed to a brown color. The solution was stirred at ambient temperature for 14 h and was then filtered through filter paper. The solvent of the filtrate was removed under reduced pressure. The solid residue was redissolved in a minimal amount of dichloromethane, and the resultant solution was filtered through tightly packed cotton wool and was dropped into stirring methanol. A yellow, flocculent precipitate was formed, which was removed from the solution by filtration through a sintered glass filter funnel (pore size G4). The yellow, solid residue was redissolved in a minimal amount of dichloromethane, and precipitations were repeated from a mixture of n-pentane and dichloromethane (6:1) and then from n-pentane. The solid was collected on a sintered glass filter funnel and was dried under vacuum, affording 0.035 g (0.009 mmol, 36%$^{26}$) of an orange solid.

Anal. Calcd. for C$_{264}$H$_{198}$P$_{12}$Ru$_{5}$: C 78.38, H 4.93%. Found: C 78.49, H 4.97%.
UV-Vis ($\lambda_{\text{max}}$, cm$^{-1}$ [ε, 10$^3$ M$^{-1}$ cm$^{-1}$]): 24400 [101.0], 28300 [351.8]. $^1$H NMR (300 MHz, CDCl$_3$): δ 7.68 (s, 3H, H10), 7.65–7.36 (m, 78H, H128, H129, H134, H135, H142, H151, H161), 6.85–6.86 (m, 81H, H152, H153, H162, H163, H205, H206), 6.82–6.76 (m, 6H, H204), 6.40 (d, $J_{HH} = 8.5$ Hz, 6H, H143), 2.70–2.52 (m, 24H, H170) ppm. $^{31}$P{$_1^1$H} NMR (121 MHz, CDCl$_3$): δ 54.46 ppm.

1,3,5-{(trans-[(dppe)$_2$ClRu(C≡CC$_6$H$_4$-4'-C≡CC$_6$H$_8$-2,5-{CH$_2$CH$_2$Et(CH$_2$)$_3$Me}$z$-4-C≡CC$_6$H$_4$-4'-C≡C])/}$3$C$_6$H$_9$ (2-52)

In a flame-dried 100 mL two-neck round-bottom flask, 2-49 (0.120 g, 0.08 mmol,

$^{26}$ The product contained an impurity that could not be removed to a satisfying degree; the given yield of 36% includes this impurity, so the yield for the product would be even lower.
2.4 eq.\textsuperscript{27} and 2-5\textsuperscript{o} (0.015 g, 0.03 mmol, 1.0 eq.) were added to deoxygenated triethylamine (30 mL). A cloudy, yellow suspension was obtained, to which just enough distilled and deoxygenated dichloromethane (15 mL) was added, to give a clear, yellow solution. The solution was deoxygenated twice, and [PdCl\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2}] and CuI were added in catalytic amounts at ambient temperature, after which the reaction mixture changed from clear and yellow to cloudy and brown instantaneously. After 10 h, a brown, flocculent precipitate had formed that was removed from the reaction mixture by filtration through a sintered glass filter funnel. The clear, orange filtrate was collected and concentrated \textit{in vacuo}, affording 4 mL of a clear, orange solution. This solution was filtered through tightly packed cotton wool into stirring methanol. An intense yellow, flocculent precipitate was formed. The mixture was filtered through a sintered glass filter funnel. A yellow, solid residue was obtained, which was redissolved in dichloromethane (2 mL) with a small amount of added triethylamine. The resultant solution was dropped into a mixture of \textit{n}-pentane and methanol (20:1). An orange precipitate was formed, which was isolated by filtration and was then dried \textit{in vacuo}, affording 0.063 g (0.014 mmol, 42\%) of the product as an orange solid.

Anal. Calcd. for C\textsubscript{288}H\textsubscript{279}Cl\textsubscript{3}P\textsubscript{12}Ru\textsubscript{3}: C 76.50, H 6.22%. Found: C 76.82, H 6.08%.

IR (CH\textsubscript{2}Cl\textsubscript{2}) [Rel. Transm., Assignm.]: 1098 [88.8], 1172 [93.5], 1435 [82.9], 1464 [94.8], 1487 [89.9], 1508 [86.3], 1580 [88.7], 1590 [87.5], 2064 [77.3, \nu(Ru-C≡C)], 2198 [96.2], 2860 [92.0, \nu(C-H\textsubscript{aliphatic})], 2872 [92.0, \nu(C-H\textsubscript{aliphatic})], 3054 [89.9, \nu(C-H\textsubscript{aromatic})] cm\textsuperscript{-1}. UV-Vis (\nu_{max}, cm\textsuperscript{-1} [c, 10\textsuperscript{3} M\textsuperscript{-1} cm\textsuperscript{-1}]): 28 000 [208.2], 28 900 [134.1], 41 000 [180.8]. \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): \delta 7.70 (s, 3H, H10), 7.55 (s, 12H, H128, H129), 7.50–7.23 (m, 24H, H161), 7.36–7.29 (m, 30H, H151, H134, H137), 7.28 (d, \textsuperscript{3}J\textsubscript{HH} = 8.1 Hz, 6H, H142), 7.23–7.14 (m, 24H, H153, H163), 7.05–6.98 (m, 24H, H162), 6.98–6.92 (m, 24H, H152), 6.58 (d, \textsuperscript{3}J\textsubscript{HH} = 8.1 Hz, 6H, H143), 2.90–2.50 (m, 36H, H170, H1351, H1381), 1.85–1.69 (m, 2H, H1352).

\textsuperscript{27} From preceding reactions, I had found that problems are acquainted with extended octupolar phenylethynyl systems bearing free acetylene functionalities. As a result, I had to assume that the actual molar amount of acetylene core available in the reaction mixture for the reaction with the iodide coupling partner was always less than what was calculated from the weighed amount. For that reason, 2.4 equiv. equivalent were employed initially, rather than the required 3.0 equivalent. Later during the reaction, the \textsuperscript{1}H NMR spectrum indicated the absence of any free acetylene, i.e. all the core material had reacted and yet some excess iodide starting material was recovered during workup, suggesting that the above assumption was justified.
H1382), 1.46–1.18 (m, 48H, H1353, H1354, H1355, H1357, H1383, H1384, H1385, H1387), 1.01–0.71 (m, 36H, H1356, H1358, H1386, H1388) ppm. $^{31}$P{$^{1}$H} NMR (121 MHz, CDCl$_3$): $\delta$ 49.88 ppm. $^{13}$C{$^{1}$H} NMR (126 MHz, CDCl$_3$): $\delta$ 141.3, 140.9 (C135, C138), 136.3 (vtt, $|J_{PC} + 3J_{PC}|$ = 19.2 Hz, C170), 135.5 (vtt, $|J_{PC} + 3J_{PC}|$ = 18.2 Hz, C170), 134.4, 134.1 (C10, C151, C161), 133.5, 133.4 (C134, C137), 131.7, 131.4 (C128, C129), 130.7 (C142), 130.4 (C144), 129.9 (C143), 128.8 (C153, C163), 127.2, 127.0 (C152, C162), 123.9 (C136, C11), 123.7 (C130), 122.3 (C127), 121.8 (C133), 116.7 (C141), 114.5 (C145), 95.4 (C140), 93.2 (C131), 91.3 (C139), 90.4 (C126), 89.5 (C132), 88.9 (C132), 40.4, 40.2 (C1352, C1382), 38.5 (C1351, C1381), 32.6, 32.6 (C1353, C1383), 30.6 (vtt, $|J_{PC} + 3J_{PC}|$ = 22.5 Hz, C170), 29.0 (C1354, C1384), 25.5 (C1357, C1387), 23.2, 23.1 (C1355, C1385), 14.2, 14.2 (C1356, C1386), 10.8 (C1358, C1388) ppm.

1,3,5-{$\text{trans-}[\text{dppe}]_2\text{RuCl}(\text{C}≡\text{CC}_6\text{H}_4\text{-}4\text{-}\text{C}≡\text{CC}_6\text{H}_2\text{-}2\text{-}5\text{-}\{\text{CH}_2\text{CHEt(CH}_3\text{)}_3\text{Me}\}_2\text{C}-\text{C}_6\text{H}_2\text{-}4\text{-}\{\text{C}≡\text{CC}_6\text{H}_4\text{-}4\text{-}\text{C}≡\text{C}\})_2\}_2\text{C}_6\text{H}_3$ (2-53)

In a flame-dried 250 mL two-neck round-bottom flask, 2-8* (0.022 g, 0.029 mmol, 1.0 eq.) was dissolved in freshly distilled and deoxygenated dichloromethane (100 mL). The resultant cloudy, brown solution was warmed gently for 5 min. Triethylamine (40 mL) was added, and the resulting solution was deoxygenated. 2-49 (0.13 g, 0.09 mmol, 3.0 eq.), [PdCl$_2$(PPPh)$_3$] (cat.) and Cul (cat.) were added. On addition of the catalyst pair, the solution became darker and cloudy and turned from yellow-orange to brown within 45 min. The reaction mixture was allowed to stir at ambient temperature for 14 h before the amount of solvent was reduced to 2 mL in vacuo. A highly cloudy, brown suspension was obtained, which was dropped into stirring methanol (200 mL). An orange-brown precipitate was formed. Filtration of the mixture afforded a brown slurry that was suspended in dichloromethane (10 mL). The resultant mixture was filtered through a sintered glass filter funnel, and the clear, orange filtrate was taken to dryness under reduced pressure. The residual solid was dissolved in dichloromethane (3 mL), and the resulting solution was dropped into stirring
n-hexane. A fluffy, yellow precipitate was formed.\textsuperscript{28} Filtration afforded 0.038 g (0.008 mmol, 27\%) of an orange powder.\textsuperscript{29}

Anal. Calcd. for C\textsubscript{31}H\textsubscript{29}Cl\textsubscript{3}P\textsubscript{12}Ru\textsubscript{3}: C 77.72, H 6.08\%. Found: C 77.67, H 5.95\%.

IR (CH\textsubscript{2}Cl\textsubscript{2}) [Rel. Transm., Assignmn.]: 1097 [80.7], 1169 [89.8], 1434 [71.3], 1486 [81.9], 1503 [80.0], 1517 [72.5], 1586 [76.3], 1600 [85.1 (sh)], 2063 [61.8, ν(Ru-C=\textit{C})], 2197 [95.4], 2856 [85.8, ν(\textit{C}-H\textsubscript{aliphatic})], 2875 [86.3, ν(\textit{C}-H\textsubscript{aromatic})], 3050 [85.7, ν(\textit{C}-H\textsubscript{aromatic})], 3062 [87.0, ν(\textit{C}-H\textsubscript{aromatic})] cm\textsuperscript{-1}. UV-Vis (ν\textsubscript{max}, cm\textsuperscript{-1} [ε, 10\textsuperscript{3} M\textsuperscript{-1} cm\textsuperscript{-1}]): 23 800 [147.6], 27 400 [295.7], 40 700 [195.0]. \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): δ 7.69 (s, 3 H, H10), 7.54 (s, 24 H, H122, H123, H128, H129), 7.52–7.42 (m, H161), 7.38–7.27 (m, 36 H, H134, H137, H142, H151), 7.23–7.13 (m, 24 H, H152, H162), 7.09–6.88 (m, 48 H, H152, H162), 6.58 (d, 3\textit{J}_{HH} = 8.4 Hz, 6 H, H143), 2.88–2.56 (m, 36 H, H170, H1351, H1381), 1.89–1.74 (m, 6 H, H1352, H1382), 1.50–1.22 (m, 48 H, H1353, H1354, H1355, H1357, H1383, H1384, H1385, H1387), 1.04–0.81 (m 36 H, H1356, H1358, H1386, H1388) ppm. \textsuperscript{31}P{\textsuperscript{1}H} NMR (121 MHz, C\textsubscript{6}D\textsubscript{6}): δ 49.86 ppm. \textsuperscript{13}C{\textsuperscript{1}H} NMR (126 MHz, CDCl\textsubscript{3}): δ 141.3, 140.9 (C135, C138), 136.3 (vtt, |\textit{J}_{PC} + 3\textit{J}_{PC}| = 16.2 Hz, C150), 135.5 (vtt, |\textit{J}_{PC} + 3\textit{J}_{PC}| = 17.3 Hz, C160), 134.4 (C161), 134.2 (C151), 133.5, 133.4 (C134, C137), 131.7 (C128, C129), 131.6 (C123), 131.4 (C122), 130.7 (C142), 130.4 (C144), 129.9 (C143), 128.8 (C153, C163), 127.2 (C162), 127.0 (C152), 123.9 (C124), 123.7 (C11, C136), 123.4 (C127), 122.7, 122.6 (C121, C130), 121.8 (C133), 116.7 (C141), 114.5 (C145), 95.4 (C140), 93.3 (C131), 91.3 (C139), 91.2, 90.8 (C125, C126), 90.4 (C120), 89.6 (C119), 89.0 (C132), 40.4, 40.2 (C1352, C1382), 38.6, 32.7 (C1351, C1381), 32.6 (C1353, C1383), 30.6 (vtt, |\textit{J}_{PC} + 3\textit{J}_{PC}| = 23.7 Hz, C170), 29.02, 29.98 (C1354, C1384), 25.6 (C1357, C1387), 23.2, 23.1 (C1355, C1385), 14.22, 14.16 (C1356, C1386), 10.8 (C1358, C1388) ppm.

\textsuperscript{28} The solubility of the material seemed reasonably good in the solvent mixture; the material started to redissolve slowly. Therefore, for subsequent preparations I would recommend a precipitation at low temperature.

\textsuperscript{29} The fact that a considerable amount of the starting material, i.e. the ruthenium acetylide complex, was recovered, combined with the fact that the crude reaction mixture \textsuperscript{1}H NMR spectrum had not shown any residual acetylene, lead to the assumption that the reason for the low yield could be found in the triacetylene core starting material. Despite numerous purification steps and clean \textsuperscript{1}H- and \textsuperscript{13}C{\textsuperscript{1}H} NMR spectra, these types of acetylenes afforded problems. The excellent solubility of the product, i.e. the octupolar acetylide complex, is also a contributing factor to the low yield.
1,3,5-\{trans-[(dppe)2ClRu(C≡C6H4-4-C≡C6H2-2,5-\{CH2CHEt(CH2)3Me\}2-4-(C≡C6H4-4-)}5C≡C]}5C6H3 (2-54)

In a flame-dried 100 mL two-neck round-bottom flask fitted with a condenser, 2-8\* (0.016 g, 0.021 mmol, 1.0 eq.) was dissolved in freshly distilled and deoxygenated dichloromethane (70 mL). The inhomogeneous solution was warmed gently for 5 min before 2-51 (0.120 g, 0.067 mmol, 3.2 eq.) was added. The orange, slightly cloudy solution was deoxygenated, and [Pd(PPh3)4] and Cul were added in catalytic amounts. The resultant mixture was deoxygenated once more and then warmed to ca. 30°C for 10 min. On addition of deoxygenated triethylamine (15 mL), a color change occurred from dark-yellow to dark-orange (2 min) and then to brown (15 min). The reaction mixture was heated at reflux for 2.5 d, over which time the color changed back to orange, and significant formation of a light precipitate was observed. The volume of solvent was reduced to 40 mL \textit{in vacuo}, and the residual mixture was filtered through a sintered glass filter funnel (pore size G3). The filtrate was taken to dryness under reduced pressure, and the yellow solid residue was added to dichloromethane (5 mL). The resultant solution was dropped into stirring methanol, after which a yellow, flocculent precipitate was formed. The solid was isolated by filtration and suspended in dichloromethane (5 mL). The suspension was dropped into methanol again. A fine, grainy precipitate was formed, which was isolated by filtration. This solid was added to dichloromethane again, and the resultant mixture was filtered through cotton wool into a stirring mixture of n-pentane and dichloromethane (6:1) with a small amount of added triethylamine. An orange, flocculent precipitate was formed that was isolated by filtration, affording a dark-orange to brown solid. The residual solvent was removed from the solid under vacuum at 40–50°C, giving 0.083 g (0.015 mmol, 68%) of the product.

Anal. Calcd. for C_{384}H_{327}Cl_{13}P_{12}Ru_{3}: C 80.59, H 5.76%. Found: C 80.73, H 5.84%.

IR (CH2Cl2) [Rel. Transm., Assignm.]: 1000 [80.2], 1017 [95.5], 1028 [97.7], 1072 [97.9], 1097 [89.6], 1173 [95.2], 1192 [97.5], 1436 [83.8], 1486 [90.6], 1503 [87.8], 1520 [77.1], 1580 [91.1 (sh)], 1590 [88.0 (sh)], 2064 [77.2, ν(Ru-C≡C)], 2200 [97.0], 2858 [93.0, ν(C-H\text{aliphatic})], 2873 [93.4, ν(C-H\text{aliphatic})], 3053 [89.9, ν(C-H\text{aromatic})] cm\(^{-1}\). UV-Vis (ν\text{max}, cm\(^{-1}\) [ε, 10\(^3\) M\(^{-1}\) cm\(^{-1}\)]: 24300 [sh, 195.8], 27100 [526.5]. \(^1\)HNMR (300 MHz, CDCl\(_3\)): δ 7.68 (s, 3H, H10), 7.53 (s, 6H, H104,
H105, H110, H111, H116, H117, H122, H123, H128, H129), 7.50–7.42 (m, 24H, H151), 7.33 (s, 6H, H134, H137), 7.33–7.27 (m, 30H, H161, H142), 7.24–7.14 (m, 24H, H153, H163), 7.07–6.09 (m, 48H, H152, H162), 6.57 (d, JHH = 8.0 Hz, 6H, H143), 2.85–2.58 (m, 36H, H170, H1351, H1381), 1.87–1.73 (m, 6H, H1352, H1382), 1.47–1.22 (m, 48H, H1353, H1354, H1355, H1357, H1383, H1384, H1385, H1387), 1.01–0.80 (m, 36H, H1356, H1386, H1358, H1388) ppm. 31P{1H} NMR (121 MHz, CDCl3): δ 49.86 ppm. $^{13}$C{1H} NMR (126 MHz, CDCl3): δ 141.2, 140.9 (C135, C138), 136.3 (vtt, $|J_{FC} + J_{PC}| = 17.7$ Hz, C150), 135.5 (vtt, $|J_{FC} + J_{PC}| = 17.7$ Hz, C160), 134.4 (C161), 134.2 (C151, C10), 133.5, 133.4 (C134, C137), 131.6 (C105, C110, C111, C116, C117, C122, C123, C128, C129), 131.4 (C104), 130.7 (C142), 130.4 (C144), 129.9 (C143), 128.8 (C153, C163), 127.2 (C162), 127.0 (C152), 123.9 (C106), 123.7 (C11, C136), 123.0 (C109, C114, C115, C118, C121, C124, C127), 122.8, 122.6 (C103, C130), 121.8 (C133), 116.8 (C141), 114.5 (C145), 95.5 (C140), 93.3 (C131), 91.1 (C107, C108, C113, C114, C119, C120, C125, C126, C139), 90.4 (C102), 89.7 (C101), 89.0 (C132), 40.4, 40.2 (C1352, C1382), 38.6 (C1351, C1361), 32.7, 32.6 (C1353, C1383), 30.6 (vtt, $|J_{FC} + J_{PC}| = 22.8$ Hz, C170), 29.02, 28.92 (C1354, C1384), 25.6 (C1357, C1387), 23.2, 23.1 (C1355, C1385), 14.22, 14.15 (C1356, C1386), 10.8 (C1358, C1388) ppm.
2.6 Chemical Structure Sheet (Fold-Out)
2-36: n = 1, X = Br, \( R^1 = Si(i-Pr)_3 \)
2-37: n = 1, X = I, \( R^1 = Si(i-Pr)_3 \)
2-38: n = 1, X = I, \( R^1 = H \)
2-40: n = 2, X = C\( \equiv \)CSiMe\(_3\), \( R^1 = (i-Pr)_3Si \)
2-41: n = 2, X = C\( \equiv \)CH, \( R^1 = (i-Pr)_3Si \)
2-42: n = 3, X = Br, \( R^1 = (i-Pr)_3Si \)
2-43: n = 3, X = I, \( R^1 = (i-Pr)_3Si \)
2-44: n = 3, X = I, \( R^1 = H \)

2-52: \( R = A \), n = 1, X = Cl
2-53: \( R = A \), n = 2, X = Cl
2-54: \( R = A \), n = 5, X = Cl
2-60: R = H, n = 1, X = C\( \equiv \)CPh
2-61: R = H, n = 1, 
X = C\( \equiv \)CC\(_6\)H\(_4\)-4-C\( \equiv \)CSi(i-Pr)_3

2-9*: X = Cl
2-10*: X = C\( \equiv \)CPh
2-62*: X = E

2-55*: R = Cl, X = H
2-56*: R = C\( \equiv \)CPh, X = H
2-57*: R = Cl, X = I
2-58: R = C\( \equiv \)CC\(_6\)H\(_4\)-4-C\( \equiv \)CSi(i-Pr)_3, X = I
2-59*: R = C\( \equiv \)CPh, X = I
3 Dendrimers – Branched
Octupolar Ruthenium Acetylide
and Mixed-Metal
Ruthenium-Osmium Acetylide
Complexes

3.1 Introduction

The term dendrimer originates from the Greek word dendron (tree) and refers to a branched monodisperse unit. Early examples have been reported by Vögtle[705,706] and Tomalia.[707,708] Dendrimers typically consist of a core unit, branching units, and bridging units that connect the core and the first branching unit or branching units to each other. The number of branching points increases from the core unit to the periphery, which gives dendrimers their tree-shaped appearance (Figure 3.1).

The potential of organic dendritic structures as nonlinear optical materials has been recognized; proceeding from a single dendron to the dendrimer may lead to nonlinear increase of certain optical and other physical properties, an effect today called dendritic or cooperative. For example, Abbotto et al. found found a strong cooperative effect in pyridinium-cored zero-generation dendrimers with pyrrole substituents at the periphery.[709] Drobizhev and co-workers reported dendritic structures incorporating 4,4'-bis(diphenylamino)stilbene repeat units and also detected a dendritic effect, i.e. they noticed that the NLO response increases by more than would be expected on increasing the number of repeat units.[710] The
CHAPTER 3. Dendrimers – Branched Octupolar Ruthenium Acetylide and Mixed-Metal Ruthenium-Osmium Acetylide Complexes

Figure 3.1 a) The branched tree-like structure gave dendrimers their name. b) Schematic representation of a first-generation dendrimer. Yellow circle: core. Orange triangles: branching units. Green squares: incorporated functionalities, e.g. metal centers. Blue line: bridges connecting the core to branching units and embedded functionalities.

concept of dendrimers for NLO materials was widened to include organometallic dendrimers. Dendrimers, and in particular organometallic dendrimers, offer a range of opportunities for the tuning of physical properties: the bridge length can be varied, functional groups can be attached to the periphery of the dendrimer, or such groups can be embedded into the dendrons, generations can be increased, and the type of metal or their ligands can be modified.

McDonagh’s first-generation ruthenium acetylide dendrimer had a phenyl core. As indicated in the previous Chapter, the $\pi$-conjugation of the system is interrupted by such a 1,3,5-substituted benzene ring. Triaryl-substituted amines have been found to allow $\pi$-conjugation across the core N-atom, which is beneficial for NLO properties. In this Chapter, six organometallic first-generation dendrimers are presented, where the three different core units were employed. The nitrogen-, boron- and phenyl-cored dendrimers were capped with phenylacetylilide ligands or para-nitrophenylacetylile ligands. Linear analogues of the boron-cored dendrimers were also synthesized, permitting to explore the effect that branching of these complexes has on their NLO properties. A number of octupolar mixed-metal osmium-ruthenium acetylide complexes were synthesized jointly with Patrick J. West (ANU). The presence of two different metal cen-
ters offers possible electrochemical switchability of linear and nonlinear optical properties.

3.2 Synthesis and Characterization

3.2.1 N-CORED DENDRIMERS

As in Chapter 2, previously-reported compounds and complexes are marked with a star. Again, reaction schemes start at commercially available starting materials for the purpose of calculating the overall costs associated with the synthesis of the final complexes. The costing tables that can be found in the Appendix (only available for the N-CORED dendrimers) are based on the schemes given in this chapter. Compounds and complexes I did not synthesize as part of the present work are (a) marked with a superscript a throughout the text (e.g. 3-3\(^a\)), and (b) not listed or described in the experimental section and not listed under compounds provided by other research groups.

The synthesis of the N-CORED zero-generation dendrimers 3-3\(^a\) and 3-4\(^a\),\(^1\) and the first-generation-dendrimers 3-19\(^b\) and 3-20 can be achieved by starting with commercially available N,N,N-tris(p-bromophenyl)amine, which affords the trimethylsilyl-protected acetylene 3-1\(^a\) via a Pd-catalyzed Sonogashira cross-coupling reaction in 80% yield (Scheme 234).\(^3\) The removal of the trimethylsilyl protecting group under mild basic conditions afforded the free acetylene 3-2\(^a\) in 97% yield. This acetylene could then be reacted with cis-[RuCl\(_2\)(dppe)]\(_2\) (2-46\(^a\); see Chapter 2, page 100) in the presence of KPF\(_6\) as a halide extracting agent. In the absence of a base, this reaction afforded a ruthenium vinylidene complex in the fashion that has been described earlier. I isolated the vinylidene complex, although it was incompletely characterized, and the following deprotonation using triethylamine was subsequently carried out without any delay. The deprotonation

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\(^1\) I did not synthesize this complex. Linear and nonlinear optical data were obtained from the complex that was synthesized by Dr. Rachel Roberts (ANU).

\(^2\) The work on this dendrimer was started by Dr. Rachel Roberts (ANU), and I continued with it after she had left the group at an early stage of this work.

\(^3\) The protected N-CORED acetylene 3-1\(^a\) was kindly provided by Prof. Paul Low and co-workers (Durham University); I did not synthesize it myself.
Scheme 3.1 Synthesis of N-cored zero-generation dendrimers 3-3* and 3-4** via 5 and 6 unique steps, starting from $N,N,N$-tris(para-bromophenyl)amine. Stars mark previously-reported compounds; asterisk mark compounds that I did not synthesize.

afforded the tris(ruthenium mono-acetylidy) complex 3-3* in 74% yield. The reaction of the mono-acetylidy complex with phenylacetylene in the presence of KPF$_6$ and triethylamine gave the ruthenium bis-acetylidy complex 3-4** in 94% yield, as described in the literature.

As in Chapter 2, a convergent approach was used to convert the N-cored mono-acetylidy complex 3-3* to the corresponding first-generation dendrimers 3-19b and 3-20. For this purpose, the two wedges$^4$ 3-17 and 3-18 were synthesized via the route shown in Schemes 3.3 and 3.4. The synthesis of the lin-

$^4$ The term wedge refers to a branched part of a dendron attached to a dendrimer, where dendron refers to one complete branched unit that is directly attached to the core unit of the dendrimer.
3.2. Synthesis and Characterization

**Scheme 3.2** Synthesis of bis(phenyleneethynylene) unit 3-8* over 4 unique steps.

ear bis(phenyleneethynylene) unit 2-25* over 4 unique steps was displayed in Chapter 2 (Scheme 2.5 on page 96). The analogue triisopropylsilyl-protected acetylene with a bromo-substituent remote from the protecting group (3-8*) was synthesized in a comparable fashion, which is shown in Scheme 3.2. With the two bis(phenyleneethynylene) units at hand, the wedges 3-11, 3-12, 3-13*,[712] 3-14, 3-15*,[712] and 3-16 were synthesized by coupling the linear bis(phenylethynyl) units to 3-9* and 3-10* (Scheme 3.3), following the Sonogashira protocol. Initially, the bromide was used in the coupling reaction, and no CuI was used, to avoid homocoupling. Under those conditions, the reaction took significantly longer and required harsh conditions compared to when the iodide was used. The increased temperature that is needed to drive the reactions to completion also increases the chance of homocoupling. However, the highest yields found for the reaction with the bromide exceed the yields found in reactions with the iodide (which might be a reflection of the fact that the reaction with the bromide was carried out more often than the reaction with the iodide, and not so much a reflection of one or the other being beneficial). Scheme 3.3 depicts the synthetic pathway to extended π-conjugated systems incorporating ruthenium acetylide complexes; the Sonogashira protocol[608,616,713,714] (or slightly modified variations thereof) appears frequently in the synthetic Schemes throughout this and the preceding Chapter, mainly because it is a reliable and well-established method to approach the targeted species. Under conditions involving aryl bromides as cross-coupling partners, reaction times can be very long, or the reactions may

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5 The term **unique number of steps** is equivalent to the number of different compounds and complexes, i.e. if a compound or complex is required twice throughout a reaction scheme, the steps required to prepare the compound or complex are only counted once.
Scheme 3.3 Synthesis of organometallic wedges, incorporating various capping groups at the ruthenium centers, as well as trialkylsilyl-protected acetylene functionalities remote from the metal centers.
Figure 3.2 $^{31}$P$\{^1$H$\}$ NMR spectrum of (left) the crude mixture containing the homocoupled by-product vs. (right) the product after workup.

require harsh conditions. Iodides, on the other hand, allow facile coupling of the aryl substituent to the terminal carbon atom of the C≡C bond. This has obvious advantages, one of which is a shorter reaction time, another reason being that the reactions can be carried out under mild conditions. This is an important fact, since a common side reaction is the coupling of the acetylene to itself, i.e. the formation of undesired homocoupled by-products. This occurs predominantly under forcing reaction conditions, so mild reaction conditions and strict exclusion of oxygen are desirable. Using catalytic amounts of CuI decreases reaction times, but at the same time, the rate of the competing formation of the undesired homocoupled by-product is increased. In many cases, CuI was necessary to afford the desired reaction, although there are some examples where reactions proceeded without addition of CuI. A few reactions shown in Schemes above involve non-extended wedges with free acetylene functionalities. On several occasions I found that, under Sonogashira conditions and despite taking account of the aspects mentioned above, homocoupled by-products were formed to a significant extent. Hence, even with thorough deoxygenation of the solvent and repeated deoxygenation of the reaction mixture, employing aryl iodide coupling agents and working under mild reaction conditions, the undesired homocoupled species were formed. The $^{31}$P$\{^1$H$\}$ NMR spectra in Figure 3.2 shows an example.
Unfortunately, undesired homocoupling could not be avoided and obviously leads to the loss of valuable starting materials, and therefore decreased yields. However, the removal of the by-product from the desired cross-coupled species proved to be straightforward in all observed cases and did not represent any problems from the synthetic point of view. For example, the contaminated material shown in Figure 3.2 could be purified by making use of differences in solubilities in diethylether. The solubility of the product (with two ruthenium centers) in diethylether is slightly better than that of the homocoupled by-product (possessing four ruthenium centers). Thus, suspending the mixture in diethylether afforded, over time, a solution of the desired species, whereas the tetraruthenium complex remained undissolved, allowing for separation by a simple filtration. Depending on the amount of the tetraruthenium species present in the mixture, the washing sometimes had to be repeated a few times, since the solubility of the diruthenium wedge is limited, and yet noticeably better than the homocoupled by-product (for details, see the corresponding experimental part of this Chapter).

The three protected wedges \(3\text{-}13^*\), \(3\text{-}15^*\), and \(3\text{-}16\) were then desilylated under conditions shown in Scheme 3.4, which afforded the two desilylated wedges \(3\text{-}17^*\) and \(3\text{-}18\).\(^6\)

The N-cored zero-generation dendrimer \(3\text{-}3^*\) was reacted with the two wedges \(3\text{-}17^*\) and \(3\text{-}18\), affording the corresponding N-cored first-generation dendrimers \(3\text{-}19^b\) (phenylacetylide-capped) and \(3\text{-}20\) (p-nitrophenylacetylide-capped), which is shown in Scheme 3.5.\(^8\) This procedure for assembling the dendrimers has two advantages over the divergent approach. (1) Because the last step is the formation of a bis-acetylide complex (rather than a Pd-catalyzed cross-coupling reaction), there is no risk of losing (some of) the wedge starting material due to the formation of homocoupled by-products. (2) There are two unambiguous NMR handles that indicate the progress of the reaction, namely the disappearance of the acetylene

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\(^6\) The complexes \(3\text{-}13^*\), \(3\text{-}15^*\), and \(3\text{-}17^*\) have been synthesized by Dr. Katy Green as part of her Honours Thesis (ANU, 2005). Since the characterization data therein was lacking crucial elements, I present the data along with the reaction conditions that I have chosen herein to add to Dr. Green's data, i.e. these are not new compounds, although literature reports have not been published.

\(^7\) Due to time constraints, the boron-capped wedge was not pursued further.

\(^8\) The abbreviated way to depict large dendrimers (see Figure 1.58 on page 64) was used in Scheme 3.5 and will be used throughout this Chapter.
3.2. Synthesis and Characterization

Scheme 3.4 desilylation of trialkylsilyl-protected wedges, affording the phenyl-acetylide-capped wedge 3-17\* and the p-nitrophenylacetylide-capped wedge 3-18.

proton in the $^1H$ NMR spectrum (which can only occur due to the progress of the desired reaction and not due to the formation of the undesired homocoupled by-product), and the disappearance of the $^{31}P\{^1H\}$ NMR signal in the region for mono-acetylide complexes (ca. 50 ppm), while a second signal at ca. 55 ppm, which is characteristic for bis-acetylide complexes, grows in as the reaction proceeds.

My intention was to synthesize an organometallic N-cored second-generation (G2) dendrimer, analogous to the N-cored first-generation dendrimer, via the same synthetic approach, i.e. using the convergent method. The required G2 wedge was prepared by a reaction of the acetylene wedge 3-17\* with the mono-acetylide wedge 3-11 or 3-12, under conditions similar to those described before. In this particular case, the trimethylsilyl-protected acetylene wedge 3-11 was used, and the desired reaction proceeded in the desired fashion for 14 h at reflux in the presence of a minimal amount of triethylamine (Scheme 3.6). The disappearance of the signal in the $^{31}P\{^1H\}$ NMR spectrum, which corresponds to the mono-acetylide complex, and simultaneous growth of a second signal in the region characteristic of bis-acetylide complexes indicated the successful formation of the desired second-generation wedge 3-21. This was supported by the disappearance of the signal corresponding to the free acetylene in the $^1H$ NMR spectrum.
Scheme 3.5 Formation of the N-cored first generation dendrimers 3-19\textsuperscript{b} and 3-20 (abbreviated structures) through the replacement of the chloro ligands in the N-cored mono-acetylide complex 3-3\textsuperscript{*}, following reaction with the two wedges 3-17\textsuperscript{*} and 3-18.
Scheme 3.6 Reaction of two first-generation wedges to afford the corresponding second-generation wedge 3-21, followed by removal of the trimethylsilyl protecting group, giving the free acetylene 3-22*.
Figure 3.3 $^{31}\text{P}^{1}\text{H}$ NMR spectra of (left) a successful attempt and (right) an unsuccessful attempt to synthesize the second-generation organometallic wedge 3-21. The mixture of materials is indicated by the presence of an additional set of signals in the right-hand-side spectrum. The two spectra on the top show enlarged regions of the spectra below them.

(3.2 ppm). This was followed by the removal of the silyl-protecting group with NBu$_3$F at room temperature, the yield over the two steps being 61%. The desilylation did not result in a significant shift of the signals in the $^{31}\text{P}^{1}\text{H}$ NMR spectrum. The appearance of the expected signal in the $^1\text{H}$ NMR spectrum at 3.2 ppm, however, was detected, while the signals originating from the methyl protons of the trimethylsilyl group vanished. The formation of the ruthenium bis-acetylide complex was attempted several times, before it afforded the desired G2-wedge with sufficient purity. The early attempts showed more than the two expected $^{31}\text{P}^{1}\text{H}$ NMR signals, which is shown in Figure 3.3. The desilylated wedge (3-22)$^9$ was reacted with the N-cored zero-generation dendrimer 3-3$^+$ in an attempt to obtain the corresponding organometallic N-cored second-generation dendrimer 3-23 (Scheme 3.7), but the reaction could only be carried out on a small scale once, and NMR spectra after workup indicated the presence of residual

$^9$ This wedge has previously been synthesized by Dr. Katy Green as part of her Honours Thesis (ANU, 2005)
free acetylene that could not be removed. The $^{31}$P\{¹H\} NMR spectrum showed two singlets (54.58 ppm and 54.31 ppm) that integrated to a ratio of 2.8:1.0. Because the analogous organometallic N-cored G1-dendrimer 3-19$^b$ gave two distinct signals in the $^{31}$P\{¹H\} NMR spectrum, three signals in a ration of 1:2:4 would be expected for the G2-dendrimer. After this point the loss of material due to repeated workup steps had become so substantial that this approach was abandoned.

3.2.2 Boron-cored Dendrimers and Linear Analogues

3.2.2.1 Synthesis

The silyl-protected acetylene (Et$_3$SiC≡CC$_6$Me$_4$-4-)$_3$B$^{10}$ (3-24$^{8a}$) was desilylated using NBu$_4$F in diethyl ether at ambient temperature over 3 h, which afforded the corresponding free acetylene (HC≡CC$_6$Me$_4$-4-)$_3$B (3-25$^*$).$^{[715]}$ The reaction of cis-[RuCl$_2$(dppe)$_2$]$^{[513]}$ with this boron-cored acetylene did not give the desired tris-metallated product cleanly (see Scheme 3.8). $^{31}$P\{¹H\} NMR spectra indicated the presence of several P-containing species (at least 8 distinct signals). Steric hindrance between the bulky ligands around the metal center and the methyl groups of the tetramethylated phenyl rings adjacent to the boron atom may be a contributing reason for this outcome, while steric repulsion of the metal centers may also play a role; three trans-[RuCl(dppe)$_2$] centers can be accommodated around the structurally related phenyl cored acetylene 1,3,5-(HC≡CC$_6$H$_4$-4-C≡C)C$_6$H$_3$ (2-5$^*$; see Scheme 2.2 on page 89). Since replacing the central 1,3,5-triethynylbenzene moiety with a boron atom reduces the diameter of the resultant core acetylene, steric hindrance between the metal centers may increase when trying to fit three metal centers around the boron-cored acetylene 3-25$^*$. Because the available amount of 3-25$^*$ was limited, only two attempts were undertaken to obtain the metallated species before this approach was abandoned. Instead, the acetylene was extended by one phenyleneethynylene unit, affording trimethylsilyl-protected acetylene (Me$_3$SiC≡C-4-C$_6$H$_4$C≡C-4-C$_6$Me$_4$)$_3$B (3-267). The trimethylsilyl group was removed under basic conditions, giving the

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10 The silyl-protected acetylene (Et$_3$SiC≡C-4-C$_6$Me$_4$)$_3$B was kindly provided by Prof. Todd Marder and co-workers (Durham University).
Scheme 3.7 Reaction of the N-cored zero-generation dendrimer 3-3* with the second-generation wedge 3-22*, in an attempt to obtain the N-cored second-generation dendrimer 3-23.
Scheme 3.8 Synthesis of the organometallic B-cored zero-generation dendrimers. 3-26 could not be obtained cleanly, as indicated by a multitude of signals in the $^{31}$P($^1$H)NMR spectrum. The same reaction on the bis(phenylethynyl)-bridged core afforded the product 3-29.
Scheme 3.9 Reaction of the B-cored zero-generation dendrimer 3-29 with the two wedges 3-17* (phenylacetylide-capped) and 3-18 (p-nitrophenyl-acetylide-capped), affording the two B-cored first-generation dendrimers 3-30 and 3-31.

corresponding free acetylene (HC≡C-4-C₆H₄-4-C≡CC₆Me₄-4-)₃B (3-28) in 62% over two steps. The reaction of this acetylene with cis-[RuCl₂(dppe)₂] proceeded smoothly in the desired fashion, with a yield of 64%.

The resultant core was reacted with the phenylacetylide-capped wedge 3-17* and its p-nitrophenylacetylide-capped analogue 3-18 (Scheme 3.4 on page 239), which afforded the two B-cored first-generation dendrimers 3-30 and 3-31 (Scheme 3.9). The conditions are similar to the conditions that were previously described in similar reactions. The reaction of the core unit with the p-nitrophenylacetylide-capped wedge was found to be significantly slower than the reaction with the
3.2. Synthesis and Characterization

nitro-free wedge; a near four-fold reaction time was required in the case of the nitro-containing example, compared to the phenylacetylide-capped compound.

The current approach also highlights the strength of the convergent method; core variations using the divergent method involve significantly more steps than the convergent method, which renders the convergent method preferred over the divergent method in such studies. Another positive side effect of the chosen approach is that the last step, in which the full dendrimer is assembled, is the formation of a bis-acetylide complex. This avoids the risk of the undesired formation of homocoupled by-products (*vide supra*), in contrast to the situation in Chapter 1, where the stars were also prepared in a convergent fashion, but in which the final assembly occurred *via* Sonogashira cross-coupling reactions.

In order to be able to assess the effect that branching has on the NLO properties of the complexes described above, it is important to compare properties of linear and branched analogues. In Chapter 1, the linear ruthenium acetylide complexes were attached to core units; a comparison is then easy to effect by simply measuring the linear moiety before its attachment to the core unit, together with the resultant star-shaped complex. In the case of the B-cored zero- and first-generation dendrimers, this is not possible due to the presence of the boron atom. As a result, some linear model complexes were synthesized, and in which the boron center carries two mesitylene moieties, and the third substituent is a phenyleneethynylene bridge of varying length that links the boron atom to the ruthenium center. The following paragraphs describe the synthetic approach. A detailed discussion of the NMR spectroscopic characterization of the building blocks follows in the next section.

Scheme 3.10 shows the syntheses of linear oligo(phenylethynyl) compounds incorporating a bis(mesitylene)borane unit. The organic bis(phenylethynyl)-bridged acetylene 3-34 has been synthesized by Prof. Todd Marder and co-workers (Durham University, UK) in the past. Although a literature report has not been published, Marder and co-workers provided Dr. Nicolas Gauthier (Université de Rennes, France) with a sample, which can be found in Dr. Gauthier’s PhD Thesis. Since no characterization data was provided, I fully characterized this compound for reasons of comparison to analogous compounds synthesized
Scheme 3.10 Syntheses of the linear boron-containing oligo(phenyleneethynylene) compounds as precursors for the analogous ruthenium acetylide complexes.
herein and for data completeness; the corresponding data can be found in the experimental section, despite the fact that it is not a new compound.

The methodology presented in Figure 3.10 is the same as or similar to that employed for the synthesis of the linear phenyleneethynylene compounds described in Chapter 2; alternating Sonogashira cross-coupling reactions and desilylation reactions under basic conditions were used to build up the compounds of varying length. Iodo-substituted linear phenyleneethynylene units were used to extend the boron-cored species. All organic compounds were purified by silica column chromatography, typically eluting with n-pentane or mixtures of n-pentane and ethylacetate. During the reactions, complete reaction of the long-chain starting material was ensured by monitoring reactions by $^1$H NMR, and if necessary, more of the shorter component was added, because the presence of excess shorter building blocks facilitates purification; the short building blocks (a) can be eluted from chromatography columns with low-polarity solvent mixtures and (b) do not give a response to UV-light in the visible range. The long-chain products can then be eluted with more polar solvent mixtures once the short fragments have been eluted, and a convenient way to follow the movement of the compound on the columns is irradiation with UV-light, which gives a fluorescence response.

The organic B(mes)$_2$-substituted phenylethynyl-bridged compounds show increased solubility compared to their unsubstituted analogues. The tris(phenylethynyl)-bridged compound 3-35 is soluble in n-pentane, and even the analogous compound with four phenylethynyl units 3-37 possesses reasonable solubility in the same solvent. For unsubstituted linear phenylethynyl compounds, the solubility drops drastically when the $\pi$-bridge contains more than two phenylethynyl units.

The organic precursors were then metallated, reacting the organic acetylenes with cis-[RuCl$_2$(dppe)$_2$] under conditions described before, which is shown in Scheme 3.11. Incorporating the ruthenium center was achieved by reaction of the boron-containing acetylenes with cis-[RuCl$_2$(dppe)$_2$]. In the case of the penta(phenylethynyl) complex 3-42, the reaction was not started with the free acetylene, but with the trimethylsilyl-protected analogue instead, which was desilylated and incompletely purified before the resultant acetylene was then
Scheme 3.11 Metallation of linear boron-containing oligo(phenylethynyl) compounds.
metallated. A sample of the intermediate acetylene was isolated to confirm the presence of the expected signal at 3.2 ppm in the $^1$H NMR spectrum.

The analogous complex with 2-ethylhexyl solubilizing groups (3-43) is an exception in the series given in Scheme 3.11; the complex was not prepared by reaction of an acetylene with cis-[RuCl$_2$(dppe)$_2$]. Instead, the boron-containing acetylene was cross-coupled to an iodo-substituted linear bis(phenylethynyl)-unit incorporating the metal center remote from the iodo substituent, following the Sonogashira protocol. The yield (43%) was lower than the yields obtained in the ligand replacement reactions, which afforded the mono-acetylide complexes 3-39–3-42 in 51–66%.

The reaction times required for the formation of complexes 3-39, 3-40 and 3-41 increase in that order. In fact, in situ $^{31}$P{$^1$H} NMR spectra of 3-40 indicated that the reaction had not proceeded to completion within 24 hours. After 36 hours, the ratio of the integrals of the vinylidene signal and the precursor five-coordinate complex signal did not change further, at which point the reaction was considered as having proceeded to completion. The reaction giving 3-41 was monitored by $^1$H and $^{31}$P NMR and seemed to proceed even slower.

The boron-containing ruthenium acetylide complex 3-39 and its organic precursor 3-32$^a$ were used to synthesize the boron-containing star-shaped complexes 3-44 and 3-45, where the boron-containing moiety is attached to the periphery of the octupolar phenyl cored complexes. In a sense, these two complexes are related to the topic of bridge-length variation (i.e. Chapter 2), rather than core variation. In order to be able to group all B-containing compounds and complexes, however, the two complexes are discussed here. Moreover, these complexes are zero-generation analogues of the first-generation dendrimers with boron-containing moieties at the periphery that can be obtained by reacting the wedge 3-13 (Scheme 3.3 on page 236) with an appropriate core unit. The corresponding synthetic conditions that afforded the complexes 3-44 and 3-45 are given in Scheme 3.12.

3.2.2.2 NMR spectroscopy

Assignment of $^1$H and $^{13}$C NMR signals. As in Chapter 2, multidimensional NMR was used to assign signals in the 1D $^1$H and $^{13}$C NMR spectra. Because of the high sensitivity of 2D spectra, in some cases this was also helpful in detecting
Scheme 3.12 Synthesis of octupolar phenyl cored zero-generation ruthenium acetylide dendrimers with dimesitylboryl substituents at the periphery.
3.2. Synthesis and Characterization

**Figure 3.4** Inset of the gHMBC NMR spectrum of the phenylacetylide-capped ruthenium acetylide wedge 3-13'. The acetylenic region of the $^{13}$C($^{1}$H) NMR spectrum is displayed vs. the full $^{1}$H NMR range. The information gained from the 1D trace does not reveal all signals unambiguously. The 2D NMR resonances, however, indicate where poorly resolved signals can be found.

poorly resolved signals in the 1D spectra. In HMBC and HSQC experiments, the magnetic response from protons is probed, and through the cross-peaks, information on the carbon signals is also obtained. This significantly reduces the acquisition time that is required to resolve weak signals. Examples are given in Figures 3.4 and 3.5. In Figure 3.5, insets of the gHMBC spectra of 3-32' and 3-34' are depicted. The cross-peaks of interest have been labeled; the signals resulting from the ipso carbon atoms C10 and C115, which are directly bonded to the boron atom, are weak – which is consistent with literature reports.\cite{717,718}

In the case of 3-36, these signals are not resolved, despite 1D $^{13}$C NMR spectra having been recorded over 14 hours with a relaxation delay of 2 seconds. However, the 2D spectra of the same samples, which were acquired over ca. 3 hours, show clear and strong cross-peaks for the corresponding atoms. What this comparison also shows, is (a) that the $^{13}$C($^{1}$H) NMR chemical shift of the signals corresponding to C10 and C115 do not change significantly on lengthening the phenylethynyl-bridge from one (3-32"s) to two phenylethynyl-units (3-34"),
Figure 3.5 Insets of the gHMBC NMR spectra of (a) 3-32 and (b) 3-34. Both spectra were acquired on a 500 MHz NMR instrument in CDCl₃ over a period of ca. 3 hours. The cross-peaks corresponding to the ipso carbon atoms C10 and C115 in both species are labeled.
(b) that the observed signals are not artefacts. A coupling pattern as one may expect from the direct bonding of a spin-3/2 species $^{11}$B to carbon$^{719-722}$ was not observed.

The assignment of acetylenic signals in the $^{13}$C$^{1H}$ NMR spectrum was also significantly facilitated by 2D NMR spectroscopy. Figure 3.6 shows part of the gHMBC NMR spectrum of the trimethylsilyl-protected acetylene 3-33. C125 has a characteristic $^{13}$C$^{1H}$ NMR chemical shift, which is comparable to that found for other species incorporating a trimethylsilyl ethynyl moiety. The cross-peak to H123 is consistent with this assignment. C126 is lacking a cross-peak with any proton in the depicted region (it shows a cross-peak to H16, which is not included in Figure 3.6). C119 and C120 could be assigned based on their cross-peaks to protons on different phenyl rings: C119 cross-couples to H117 (phenyl ring adjacent to the boron atom), whereas C120 cross-couples to H122 (phenyl ring adjacent to the trimethylsilyl ethynyl moiety).

On proceeding from the protected acetylene 3-34 to the free acetylene 3-36, the $^1$H NMR signal for H122/H123 splits, giving two separate signals (although the individual signals are close enough to overlap significantly; see Figure 3.7).
Examining the one-dimensional spectra only, this change would suggest the assignment of H128/H129 to this signal, due to the fact that those two protons are closest to where the chemical change occurs. However, the 2D NMR spectra showing indirect C-H coupling (gHMBC; Figure 3.8), show the presence of a cross-peak of C131 (with its characteristic $^{13}$C{1H} NMR chemical shift for tertiary aryl-carbon atoms in aryl rings adjacent to an acetylene functionality) and H128/H129. The same cross-peak is present in the corresponding gHMBC NMR spectrum of the silyl-protected precursor (spectrum not shown). Despite this fact, the present assignment of H122/H123 remains counter-intuitive.

The same strategy was pursued for the B-cored octupolar compounds. Despite the octupolar compounds being bigger, the number of observed signals does not increase, due to the symmetry of such compounds. For the extended trimethylsilyl-protected octupolar species 3-27, the assignment of the signals in the $^{13}$C{1H} NMR spectrum was unambiguous. The *ips* carbon atom of the phenyl ring attached to the boron center resonates at lower field than the related carbon in the linear species described above (150 ppm vs. 146 ppm). The gHMBCNMR cross-peak of this carbon signal to the proton signal at 1.98 ppm makes the assignment of this proton signal as H1341 (see Figure 3.9) unambiguous, and therefore 2.42 ppm can also be assigned without doubt. From here, the gHSQC NMR spectrum (direct C-H coupling) allows the assignment of the $^{13}$C{1H} signal at 20.2 ppm to C1341. The signal at 18.6 ppm must therefore correspond to C1351, and the expected cross-peak in the gHSQC NMR spectrum was indeed observed (see Figure 3.10). Only one acetylenic $^{13}$C{1H} signal (96.3 ppm) shows a cross-peak to the SiMe₃ protons (0.26 ppm) and can therefore be assigned as C144, which is the only carbon atom close enough to the protons to result in a strong cross-peak. From several other spectra that have been presented in this Chapter and in Chapter 2 (and many more in the corresponding appendices), it is known that the β-carbon atom of a trimethylsilyl-protected acetylene resonates at a characteristic $^{13}$C{1H} NMR chemical shift of ca. 104.5 ppm. Such a signal was also found in the carbon NMR spectrum of 3-27 and was assigned based on these observations. The gHMBC NMR cross-peak of this signal to the proton signal at 7.44 ppm then allows differentiation between H141 (7.44 ppm) and H140 (7.47 ppm). With this information, the reader can return to the gHSQC NMR spectrum to find that the cross-peak of these two
Figure 3.7 $^1$H NMR spectra of (a) the triisopropylsilyl-protected acetylene 3-35 and (b) the corresponding free acetylene 3-36.
Figure 3.8 Part of the gHMBC NMR spectrum of free acetylene 3-36. The cross-peak of interest between C131 and H128/129 is present.

Figure 3.9 gHMBC NMR spectrum of the octupolar B-cored trimethylysilyl-protected acetylene 3-27. The spectrum was recorded on a 500 MHz instrument in CDCl₃.
Figure 3.10 gHSQC NMR spectrum of octupolar B-cored trimethylsilyl-protected acetylene 3-27. The spectrum was recorded on a 500 MHz instrument in CDCl₃.

proton signals to the corresponding carbon NMR signals does not allow differentiation between the two signals at 131.0 and 131.9 ppm (see Figure 3.11). This means that the two signals can be assigned as C140 and C141, but it is not possible to say, which particular signal corresponds to which of the two carbon atoms based on the gHSQC NMR spectrum. However, the gHMBC NMR spectrum indicates a cross-peak between 131.9 ppm and 7.44 ppm (H141), which suggests that 131.9 ppm corresponds to C141, and accordingly 131.0 ppm would correspond to C140 (see Figure 3.12). Due to the presence of a cross-peak between 124.1 ppm and 2.42 ppm (H1351) in the gHMBC NMR spectrum, 124.1 ppm can be assigned as C136. The same carbon NMR signal shows a second cross-peak to 7.44 ppm, which had been assigned as H141 earlier. This indicates that C139 coincidentally resonates at the same ¹³C{¹H} NMR chemical shift, because it would not be likely for any carbon atom in this structure to couple to both H1351 and H141 and give comparably strong cross-peaks for both. The increased intensity of the signal at 124.1 ppm in comparison to its neighboring signal at 122.6 ppm supports the indicated coincidental ¹³C{¹H} NMR chemical shift (in
Figure 3.11 Inset of the gHSQC NMR spectrum of the octupolar B-cored trimethylsilyl-protected acetylene 3-27. The spectrum was recorded on a 500 MHz instrument in CDCl₃.

Figure 3.12 Inset of the gHSQC NMR spectrum of the octupolar B-cored trimethylsilyl-protected acetylene 3-27. The spectrum was recorded on a 500 MHz instrument in CDCl₃.
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Figure 3.13 Inset of the gHMBC NMR spectrum of the octupolar B-cored acetylene 3-28. The spectrum was recorded on a 500 MHz instrument in CDCl₃.

fact, the two signals separate when the trimethylsilyl protecting group is removed, which results in the appearance of an extra signal in the corresponding region of the spectrum, and all three signals are of comparable intensity: see Figure 3.13 and compare to Figure 3.9 on page 258). The signal at 122.6 ppm shows a gHMBC NMR cross-peak to 7.47 ppm, which was formerly assigned as H140. Assigning 122.6 ppm to C142 is consistent with (a) the observed cross-peak and (b) the $^{13}$C{$^1$H} NMR chemical shift of ipso carbon atoms in other (structurally related) trimethylsilylethynyl-substituted aryls. Often, the two signals (C139, C142) are found at very similar $^{13}$C{$^1$H} NMR chemical shift. In this case, however, they are separated by ca. 1.5 ppm. The two remaining quaternary carbon atoms C134 and C135 give rise to signals at similar $^{13}$C{$^1$H} NMR chemical shifts (135.8 and 135.7 ppm), and the two gHMBC NMR cross-peaks to H1341 and H1351 for such a situation are observed. The two remaining acetylenic carbon atoms, after assigning C144 and C143 unambiguously, are C137 and C138. Again, the gHMBC NMR spectrum permits assignment; only one of the remaining signals in the acetylenic region of the spectrum (78–106 ppm) shows a cross-peak to H140 (7.47 ppm), which is the signal at 97.3 ppm. Only C138 is close enough to H140 to give such a strong observed cross-peak. The last signal (91.2 ppm) is four bonds
away from the nearest protons (H1351 and H140), so it would not be expected
to give a strong cross-peak; indeed, only a weak contact to H1351 is observed.

Describing the assignment of NMR signals of additional species in such detail here
is beyond the scope of the present work. The above is to illustrate the reader
the approach that I have used, and to indicate that assignments were undertaken
carefully. The same methodology was applied to the spectra that can be found in
the Appendix. The full process is time-consuming and involves comparing various
spectra of structurally related species simultaneously. Often, it is insufficient to
work on one compound only at a time (which leaves residual ambiguity). Despite
this, there were cases, in which complete assignments were not possible. These
have been indicated by grouped signals or marked in some way.

NMR Spectroscopy and Dendrimers. The $^{13}$C{$^{1}$}H NMR spectra of linear or-
ganic compounds and organometallic complexes as well as unbranched octupolar
complexes and wedges (i.e. branched, but not symmetrical octupolar complexes)
could in general be obtained with a good s/n that permitted the observation of
most expected signals (a few exceptions have been described earlier throughout
this work). The quality of the spectra decreases quite drastically on proceeding to
branched octupolar complexes (first-generation dendrimers). In typical attempts
to obtain spectra of reasonable quality, deuterated chloroform or deuterated ben-
zene were tried, relaxation delays were increased, relaxation agents ([Cr(acac)$_3$])
were used in some early attempts, concentrations were maximized (up to the
point of saturated solutions), acquisition times were increased, and experiments
of higher sensitivity (gHMBC NMR; *vide supra*) were carried out. Maximizing
the concentration of the solutions results in the broadening of the signals, in
some cases beyond 10 Hz, the loss of spectral information, such as coupling
patterns. The shimming on concentrated samples is also more difficult than on
dilute samples. Again, poor shimming results in the broadening of the signals
in the spectrum. Relaxation agents did not show any beneficial effects and also
seemed to render shimming more difficult. Due to the quadratic dependence of the
s/n of a spectrum on acquisition time used in the experiment, and availability of
instrumentation, increasing the acquisition time beyond 18 hours is unreasonable.
In most spectra of dendritic complexes in this work, some signals do not even

11 Usually, I aimed for a width of 1.5-2.0 Hz
begin to appear after 18 hours (e.g. those of quaternary carbon atoms, and in particular acetylenic carbon atoms). The assignment of signals in spectra of such low quality would have suffered from large inaccuracies and was therefore not attempted.

Heteroatom NMR Spectroscopy is a useful technique to identify structural properties of dendrimers.\cite{645,723} In the syntheses described in this work, one of the most useful handles for monitoring the progress of reactions are the phosphorus atoms in the dppe ligands. $^{31}\text{P}\{^1\text{H}\}$ NMR chemical shifts are highly sensitive to the chemical environment of the phosphorus atoms, which extends to the environment of the ruthenium centers. Combined with a 100% natural abundance of $^{31}\text{P}$, this is a quick yet powerful technique to observe in situ changes in reaction mixtures as well as ensuring the purity of a complex (to some extent). The indicative $^{31}\text{P}\{^1\text{H}\}$ NMR chemical shift of signals in the range 50–55 ppm permit facile monitoring of reactions of mono-acetylide complexes with alkynes, affording the corresponding bis-acetylide complexes. However, significantly smaller differences in the chemical environment of the ligated metal center can also be resolved. As such, the phosphorus atoms at the periphery of a dendrimer experience a different magnetic influence from the external field than the phosphorus atoms located near the core of the dendrimer. As a result, their magnetic resonances are different, resulting in separate signals in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of such dendritic species. An example is given in Figure 3.14. Although accurate integration of signals in $^{31}\text{P}\{^1\text{H}\}$ NMR spectra requires a drastically increased relaxation delay (in combination with inverse gated decoupling), the integration of signals in complexes presented in this work was found to be a good indicator with regards to the presence of only partly substituted sites and the presence of by-products. Because $^{11}\text{B}$ is a NMR-active nucleus (natural abundance of about 80%, spin $\frac{3}{2}$), I tried to obtain the corresponding NMR spectra of the B-containing star-shaped organic compounds and organometallic complexes on a few occasions. Unfortunately, these attempts remained unsuccessful for no obvious reason. I was not able to detect a $^{11}\text{B}$ NMR resonance for the mono(phenylethynyl)-bridged starting material ($\text{Et}_3\text{SiC}=\text{CC}_6\text{Me}_4=4-$)$\text{B}$ (3-24$^a$) or the synthesized bis(phenylethynyl)-bridged analogue ($\text{Me}_3\text{SiC}=\text{C}-4-\text{C}_6\text{Me}_4\text{C}=\text{C}-4-\text{C}_6\text{H}_4)$)$\text{B}$ (3-27). Variation of parameters, such as the acquisition time or the relaxation delay, did not change this outcome. Under the chosen conditions, the reference material $\text{BF}_3 \cdot \text{Et}_2\text{O}$ gave a
Figure 3.14 $^{31}$P{H} NMR spectrum of the boron-cored first-generation dendrimer 3-31 with p-nitrophenylacetylide ligands at its periphery. The spectrum was measured in CDCl$_3$ over ca 60 scans and with a relaxation delay of 1 second at a frequency of 121 MHz.

sharp and strong signal after only a few scans, which indicated the functionality of the experimental setup (examples are given in Figure 3.15). The series of spectra shown in Figure 3.15 indicates that the broad signal seen in the spectra of compounds 3-24$^{a}$ and 3-28 results from the borosilicate glass of the NMR tube; the spectrum of the blank solvent shows the same signal. Mass spectrometry was used to confirm the presence of the protected acetylene (Et$_3$SiC≡C-4-C$_6$Me$_4$)$_3$B. With the NMR setup functioning correctly and the mass spectrum confirming the presence of the boron-containing star-shaped species, the absence of the expected signal in the $^{11}$B NMR spectrum cannot be explained at this point. The same outcome was observed for 3-29, the metallated analogue of 3-28.

**Artefacts in NMR Spectra.** Although $^{31}$P{H} NMR spectroscopy was extensively used in this work and is amongst the most powerful techniques with regards to the given complexes, there are artefacts that the synthetic chemist should be aware of, in order not to be confused or even led into false conclusions. An example of this is shown in Figure 3.16. Figure 3.16a shows the spectrum, taken from an aliquot from the reaction mixture of a ruthenium mono-acetylide core with a free acetylene incorporating a ruthenium bis-acetylide complex. The
Figure 3.15 $^{11}$B NMR spectra of samples containing (a) the blank solvent (CDCl$_3$), (b) the triethylsilylethynyl compound 3-24$^{1a}$, (c) the synthesized extended and desilylated analogue 3-28, and (d) reference material BF$_3$·Et$_2$O. The spectra were recorded on the same spectrometer under the same conditions.
starting material, a mono-acetylide complex with a $^{31}\text{P}^1\text{H}$ NMR chemical shift of ca. 50 ppm, is not present anymore, i.e. the starting complex has fully reacted. However, the region around 55 ppm (characteristic for ruthenium bis-acetylide complexes incorporating a trans-[Ru(dppe)$_2$] center) shows only one signal where two are expected due to the different magnetic environments of the phosphorus atoms (see previous paragraph). Spectrum 3.16b shows the same species following workup. No extra material was added, and the time between the acquisition of spectra a) and b) was less than 5 hours. Effects like this can lead to the complete absence of expected signals and often depend on peripheral conditions such as solvents used to run the spectrum or the acidity of the solution.

### 3.2.3 Phenyl-Cored Dendrimers

The synthesis of the core unit of the phenyl-cored octupolar ruthenium acetylide dendrimer (2-14) and its organic precursors has already been discussed in Chapter 2 (see page 86 ff). The convergent method was again chosen to assemble the dendrimers, and the preparation of the required wedges was described above (see page 235 ff).
The two octupolar phenyl cored first-generation dendrimers 3-46 and 3-47 were obtained through reactions involving the phenyl cored star-shaped ruthenium mono-acetylilide complex 2-14 and the two wedges 3-17* (phenylacetylilide-capped) and 3-18 (p-nitrophenylacetylilide-capped). (Scheme 3.13). In the case of the phenylacetylilide-capped dendrimer (3-46), many workup steps were required to achieve satisfactory purity of the complex.

For both dendrimers, the expected two signals at a $^{31}$P-$^1$H NMR chemical shift of around 54.0–54.5 ppm in the $^{31}$P-$^1$H NMR spectrum were observed, whereas the mono-acetylilide complex (ca. 50 ppm) could not be detected anymore, indicating the complete replacement of the chloro ligands with phenylacetylilide or p-nitro-
phenylacetylide ligands, respectively (Figure 3.17). Interestingly, in the case of the p-nitropheny lacetylide-substituted dendrimer, the two signals are only ca. 0.1 ppm apart, whereas the phenylacetylide-capped species shows a gap of almost 0.5 ppm between both signals. The nitro-substituted dendrimer was one example that showed severely broadened signals in CDCl₃, so the spectrum had to be acquired in C₆D₆ instead, which improved the situation significantly.

### 3.2.4 Ruthenium- and Osmium-Containing Mixed-Metal Zero- and First-Generation Dendrimers

In a joint project with Patrick J. West¹², a number of mixed-metal zero- and first-generation dendrimers were synthesized, using the methodologies established and described in previous sections of this Chapter and also in Chapter 2. Mixed-

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¹² PhD candidate at ANU in the research group of Prof. Mark G. Humphrey (2011)
metal complexes are attractive, since the different metals may give rise to distinct redox-processes that can be targeted independently, which leads into the area of electrochemical switching of linear and, more importantly, nonlinear optical properties. Complexes that were synthesized jointly by P. J. West and me are marked with a superscript b. Complexes that I did not synthesized are marked with a superscript „a. Previously-reported compounds and complexes are marked with a *.

West synthesized the monometallated osmium-acetylide wedge 3-49b (structure given in Scheme 3.14) by reacting cis-[OsCl2(dppe)2] with 1,3,5-(HC≡C)3C6H3 in a stepwise fashion, which enabled him, by stoichiometric control and careful monitoring of the reaction mixture, to isolate the osmium-acetylide wedge 3-49a, in accordance with observations reported previously[724] When West carried the same reaction out in the presence of excess osmium precursor and over a prolonged period of time, the bimetallic wedge 3-50a was formed, i.e. this wedge was prepared by West making use of the same steric effect that is used to synthesize its ruthenium analogue; the trimetallic species cannot be formed for steric reasons. For more detail on these and related reactions involving osmium acetylide complexes, the reader may refer to West’s PhD Thesis[643]

Using these two osmium acetylide wedges, the first-generation dendrimers 3-51b and 3-52b were prepared via Sonogashira cross-coupling reactions with the extended octupolar ruthenium bis-acetylide complex 3-48, as indicated in Scheme 3.14.

As indicated earlier, homocoupling is a problem that arises when metallated wedges bearing a free acetylene are coupled to halogenated aryl moieties. This was also observed in the above reactions; the homometallic tetraosmium by-product resulting from homocoupling of the acetylene functionalities was observed reproducibly, even under mild and strictly anaerobic conditions. Initially, the reaction mixtures were stirred at ambient temperature to reduce the chance of homocoupling. However, NMR spectra indicated that no chemical changes occurred under these conditions. Gentle reflux in dichloromethane was therefore necessary to drive the reaction to completion over 24 hours, where completion refers to the complete substitution of the iodo-substituted linear precursor. To determine this, the integration of the phosphorus signals in the $^{31}$P{¹H} NMR
Scheme 3.14 Synthesis of the mixed-metal ruthenium-osmium acetylide dendrimers 3-51\(^b\) and 3-52\(^b\)
3.2. Synthesis and Characterization

![Figure 3.18](image)

Figure 3.18 $^{31}\text{P}^{(1\text{H})}$ NMR spectra from the synthesis of the first-generation mixed-metal ruthenium-osmium dendrimer 3-52C. The two $^{31}\text{P}^{(1\text{H})}$ NMR spectra indicate the (left) presence and (right) absence of homocoupled by-product (peak at 16.64 ppm). The product signal is centered at 16.51 ppm. Spectra were taken in C$_6$D$_6$ at 121 MHz.

In the two dendrimers 3-51$^b$ and 3-52$^b$, the metal centers in each dendron are separated by branching units (i.e. phenyl rings with a 1,3,5-substitution pattern). West and I also synthesized two mixed-metal ruthenium-osmium phenyl cored complexes with two metal centers in each arm, the metal centers being linked through linear mono(phenylethynyl)- or bis(phenylethynyl)-bridging units. Scheme 3.15 shows the synthetic approach. In complex 3-55$^b$, the ruthenium center and the osmium center in each arm are separated by one phenyleneethynylene unit, whereas in 3-56$^b$ the bridge consists of two linear phenyleneethynylene units, with the remainder of the complex being of the same composition as that
Scheme 3.15 Synthesis of the octupolar phenyl cored bimetallic ruthenium-osmium acetylide complexes 3-55\textsuperscript{b} and 3-56\textsuperscript{b}. 
Scheme 3.16 Synthesis of the symmetrically substituted N-cored mixed-metal ruthenium-osmium acetylide complex 3-58b.

of 3-55b. The yields obtained in both reactions (56% and 53%) and the required reaction times are comparable.

The final mixed-metal ruthenium-osmium acetylide complex, which was jointly synthesized by West and myself, is the symmetrically substituted N-cored acetylide complex 3-58b shown in Scheme 3.16. This reaction was found to be incomplete after 20 hours in refluxing dichloromethane. A crude workup was carried out before the reaction was reinitiated with the same reaction mixture, which was allowed to react at reflux for an additional 20 hours. The low yield (26%) is, to some extent, a result of the unintended workup partway through the reaction.

3.3 Linear Optical and Physical Properties

3.3.1 Monometallic Ruthenium Acetylide Complexes

3.3.1.1 UV-Vis and Fluorescence Spectroscopy

On proceeding from the N-cored zero-generation dendrimer 3-3* to the two first-generation dendrimers 3-19b (phenylacetylide-capped) and 3-20 (para-nitrophenyldacetylide-capped), the linear absorption spectra change in a fashion that
Figure 3.19 Linear absorption spectra of the N-cored first-generation dendrimers 3-19\textsuperscript{b} (phenylacetylide-capped) and 3-20 (\textit{p}-nitrophenylacetylide-capped), and their precursors, wedges 3-17\textsuperscript{a} and 3-18 and the core unit 3-3\textsuperscript{*}.

is depicted in Figure 3.19. The wedges show a band at 29 500 cm\textsuperscript{-1}, which is also found in the first-generation dendrimers with close to no frequency-shift. The core unit (i.e. the zero-generation dendrimer 3-3\textsuperscript{*}), however, shows a band at 26 500 cm\textsuperscript{-1}, which is shifted to 25 000 cm\textsuperscript{-1} and 23 500 cm\textsuperscript{-1} for the phenylacetylide-capped dendrimer 3-19\textsuperscript{b} and the \textit{para}-nitrophenylacetylide-capped dendrimer 3-20. The most striking difference between the two first-generation dendrimers is the additional absorption band that accompanies the substitution of the proton in the \textit{para} position of the peripheral phenylacetylide ligands for nitro-groups. This band is found in both the dendrimer and its precursor wedge, and in both complexes, the band peaks at 20 500 cm\textsuperscript{-1} (in the dendrimer, this band severely overlaps with the adjacent band from the core unit, which makes it difficult to determine the exact peak position). In terms of NLO-properties, this additional band reduces the available off-resonant frequency-range that is available for NLO-measurements. The question whether or not this loss of transparency is worthwhile to be pursued based on a potential increase in the NLO-response has already been addressed in Chapter 2.

Changing the core from nitrogen to boron is accompanied by changes that are depicted in Figure 3.20. An obvious difference to the N-cored species described above it that the core unit of the boron-containing complex incorporates a
3.3. Linear Optical and Physical Properties

![Graph showing absorption spectra](image)

**Figure 3.20** Linear absorption spectra of the B-cored first-generation dendrimers 3-30 (phenylacetylide-capped) and 3-31 (p-nitrophynylacetylide-capped), and their precursors, wedges 3-17* and 3-18 and the core unit 3-29.

bis(phenylethynyl)-bridge between the core atom and the first metal center, resulting in an extra linear absorption band at 23000 cm\(^{-1}\). The second band is found at slightly higher energy compared to the N-cored species (27500 cm\(^{-1}\) vs. 26500 cm\(^{-1}\)). Apart from that the spectra are similar, and the para-nitrophenylacetylide-capped dendrimer shows the expected additional band at the low-energy end of the spectrum that is accompanied by a red-shift of the onset of linear absorption from 20000 cm\(^{-1}\) to just below 16000 cm\(^{-1}\).

The linear oligo(phenylethynyl)-bridged compounds presented in Chapter 2 show strong fluorescence under the influence of UV-light. The same effect was observed for the linear boron-containing tris- and penta(phenylethynyl)-bridged compounds, which was spectroscopically confirmed using fluorescence spectroscopy. Figure 3.21 shows solutions of three linear dimesitylboryl-substituted oligo(phenylethynyl)-bridged compounds in comparison to linear compounds without the boryl-substituent under UV-irradiation.

Figure 3.22 shows the fluorescence spectrum of the triisopropylsilyl ethynyl substituted tris(phenylethynyl)-bridged dimesitylborane 3-35. The linear desilylated tetra(phenylethynyl)-bridged compound 3-36 units was also spectroscopically examined Figure 3.23). *Enroute* to the way to the ruthenium
Figure 3.21 Solutions of linear oligo(phenylethynyl)-bridged organic compounds (right) with and (left) without dimesitylboryl substituents. From left to right: neat dichloromethane; 2-34 (bis(phenylethynyl)-bridged, no boron); 2-41 (tetra(phenylethynyl)-bridged, no boron); 2-44 (penta(phenylethynyl)- bridged, no boron); 3-32\(^a\) (mono(phenylethynyl)-bridged, dimesitylboryl-substituted); 3-36 (tris(phenylethynyl)-bridge, dimesitylboryl-substituted); intermediate acetylene precursor for 3-42 (penta(phenylethynyl)-bridge, dimesitylboryl-substituted). a) No UV-light. b) Solutions under UV-irradiation.

Figure 3.22 Concentration-dependent fluorescence spectra of the organic boryl-substituted tris(phenylethynyl)-bridged compound 3-35.
Figure 3.23 Concentration-dependent fluorescence spectra of dimesitylboryl-containing tetra(phenylethynyl) compound 3-36. The emission was measured between 16700 and 26700 cm\(^{-1}\) (600–375 nm) with an excitation frequency of 25300 cm\(^{-1}\) (400 nm). The excitation trace was acquired by setting the emission to 25000 cm\(^{-1}\) (400 nm) and scanning the region between 26000 and 34500 cm\(^{-1}\) (390–290 nm).

Acetylide complex 3-42, which incorporates a penta(phenylethynyl)-bridged dimesitylboryl-substituted acetylide ligand, the trimethylsilyl-protected acetylene 3-38 was prepared. The corresponding fluorescence spectrum is given in Figure 3.24.

The ruthenium acetylide complex 3-42 was prepared by deprotecting the trimethylsilyl-ethynyl-substituted compound 3-38 in situ, followed by the reaction of the intermediate free acetylene (3-46) with cis-[RuCl\(_2\)(dppe)\(_2\)] (see Scheme 3.11 on page 250). Although the acetylene was not isolated, a sample was removed from the reaction mixture of the desilylated acetylene for characterization. The concentration-dependent fluorescence spectra of this sample were acquired and are shown in Figure 3.25.

A noticeable change in the spectra given in Figures 3.22–3.25 is the occurrence of a shoulder to the main peak on lengthening the phenylethynyl-bridge. This may be the result of two overlapping bands in the spectra of the tris(phenylethynyl) compound separating on bridge lengthening. The above spectra were collected in dichloromethane. The fluorescence behavior of the boron-containing linear
Figure 3.24 Concentration-dependent fluorescence spectra of the boron-containing penta(phenylethynyl)-bridged compound 3-38. The concentration of the mother solution was 5700 μg in 100 mL dichloromethane and diluted down until the spectra fell in the appropriate intensity range. The emission was measured between 16 667 and 26 316 cm⁻¹ (600-380 nm) with an excitation wavenumber of 27 778 cm⁻¹ (360 nm). The excitation trace was acquired by setting the emission to 25 316 cm⁻¹ (395 nm) and scanning the region between 25 974 and 40 000 cm⁻¹ (385-250 nm).
3.3. Linear Optical and Physical Properties

![Figure 3.25](image)

**Figure 3.25** Concentration-dependent fluorescence spectra of the dimesitylboryl-containing penta(phenylethynyl) compound 3-46. The emission was measured between 16,700 and 26,300 cm\(^{-1}\) (600-380 nm) with an excitation wavenumber of 27,800 cm\(^{-1}\) (360 nm). The excitation trace was acquired by setting the emission to 25,000 cm\(^{-1}\) (400 nm) and scanning the region between 26,000 and 40,000 cm\(^{-1}\) (390-250 nm).

species in different solvents was also explored, which is shown in Figure 3.26. The spectra show the change of the fluorescence properties when the polarity of the solvent is change. Whereas the position of the absorption bands in the linear absorption spectra did not show a solvent-dependence, the fluorescence spectra changed significantly on varying the solvent. Whereas the spectrum in dichloromethane shows only one broad band, probably resulting from two or more overlapping bands, varying degrees of separation of defined bands occurs for the spectra in diethylether, tetrahydrofuran, toluene and n-hexane; toluene and diethylether incur the largest separation. The position of individual bands also changes with the solvent.

### 3.3.1.2 Cyclic Voltammetry and Spectroelectrochemistry

During spectroelectrochemical measurements on the nitrogen-cored first-generation dendrimer 3-19\(^b\), the solution of the electrolyte (NBu\(^n\)\(_4\))(PF\(_6\)) and the solute in deoxygenated THF was divided into two portions. To the first portion were
applied different potentials, and the linear optical response to these was monitored by UV-Vis spectroscopy. The second portion of the deoxygenated solution was kept in a glass syringe for the duration of the measurements, which was roughly 4 hours. The UV-Vis spectrum of this second portion was then acquired again and compared to the UV-Vis spectrum of the fresh solution. The result is presented in Figure 3.27. A band at ca. 20 000 cm\(^{-1}\) grows in, and the intensity of the band at 21 500 cm\(^{-1}\) decreases, which shows that the complex changes quite rapidly in solution, even in the absence of an applied voltage. The band at 29 500 cm\(^{-1}\) also loses intensity, although the loss is not as significant as in the case of the band at 21 500 cm\(^{-1}\).

The phenyl cored first-generation dendrimer with \(p\)-nitrophenylacetylide ligands coordinated to the peripheral ruthenium centers shows reversible redox properties under both localized electrolysis conditions (cyclic voltammetry measurements) and bulk electrolysis conditions (spectroelectrochemical measurements). Figure 3.28 shows the outcome of spectroelectrochemical measurements in THF solution.

The boron cored first-generation dendrimer with phenylacetylide capping groups (3-30) shows reversible redox properties in cyclic voltammetry experiments (lo-
Figure 3.27 Comparison of UV-Vis spectra of a fresh solution of the N-cored first-generation dendrimer with phenylacetylide ligands attached to the peripheral metal centers (3-19b) and the same solution after ca. 4 hours under air.

Figure 3.28 Changes of the linear optical properties of the phenyl cored first-generation dendrimer 3-47 under the influence of applied electric potentials. The number in brackets is the absolute number of cycles. Changes on oxidation (0 mV to 900 mV over 10 cycles: blue traces) and changes on reduction of the oxidized species (900 mV to -500 mV over 6 cycles: red traces) are displayed.
calized redox processes), as can be seen in Figure 3.29. However, under spectro-electrochemical conditions (bulk redox processes) at room temperature in both tetrahydrofuran and dichloromethane, the oxidation of the metal center is not reversible, as shown in Figure 3.30.

### 3.3.1.3 Solid-State Structures

The solid-state structure of the boron-containing ruthenium mono-acetylide complex 3-39 was investigated by means of X-ray structural analysis. Details on the data collection and the data refinement are given in the experimental section (page 353 ff.). Figure 3.31 shows an ORTEP diagram of the complex, where hydrogen atoms and the dichloromethane molecule were omitted (a list of bond angles and bond lengths is given in Table 3.1). The coordination geometry around the ruthenium center is distorted octahedral. The Cl(1)-Ru(1)-C(1) bond angle and the Ru(1)-C(1)-C(2) bond angle are 174° and 180°, so the deviation from linearity is small. The three carbon atoms directly attached to the boron atom define a plane, and the boron-atom lies exactly in that plane, i.e. all three boron-carbon bonds are perfectly co-planar. The three benzene rings attached to the boron atom are all rotated from that plane in the same direction, resulting in a propeller-type arrangement. The rotation from the plane
Figure 3.30 A spectroelectrochemical experiment to probe the bulk redox properties of the boron-cored first-generation dendrimer 3-30. Measurements were carried out in a 0.03 M (NBu₄)⁺(PF₆⁻) solution in tetrahydrofuran. The concentration of the complex in that solution was ca. 2 · 10⁻⁵ mol L⁻¹.

Figure 3.31 ORTEP plot of the dimesitylboryl-substituted ruthenium acetylido complex 3-39. Temperature ellipsoids were drawn at a 40% probability level. Hydrogen atoms and the dichloromethane solvent molecule were omitted for clarity. White: carbon; grey: chlorine, boron, phosphorus; dark grey: ruthenium.
Table 3.1 Relevant solid-state bond lengths and angles found for complex 3-39 from the X-ray crystallography studies.

<table>
<thead>
<tr>
<th>Bond</th>
<th>[Å]</th>
<th>Angle [°]</th>
<th>Angle [°]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru(1)-Cl(1)</td>
<td>2.5316(6)</td>
<td>Cl(1)-Ru(1)-P(1)</td>
<td>83.12(2)</td>
</tr>
<tr>
<td>Ru(1)-P(1)</td>
<td>2.3546(6)</td>
<td>Cl(1)-Ru(1)-P(2)</td>
<td>83.33(2)</td>
</tr>
<tr>
<td>Ru(1)-P(2)</td>
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<td>P(1)-Ru(1)-P(2)</td>
<td>82.29(2)</td>
</tr>
<tr>
<td>Ru(1)-P(3)</td>
<td>2.3860(6)</td>
<td>P(1)-Ru(1)-P(3)</td>
<td>176.26(2)</td>
</tr>
<tr>
<td>Ru(1)-P(4)</td>
<td>2.3620(6)</td>
<td>P(2)-Ru(1)-P(3)</td>
<td>99.15(2)</td>
</tr>
<tr>
<td>Ru(1)-C(1)</td>
<td>2.014(2)</td>
<td>Cl(1)-Ru(1)-P(4)</td>
<td>100.42(2)</td>
</tr>
<tr>
<td>C(1)-C(2)</td>
<td>1.185(3)</td>
<td>P(1)-Ru(1)-P(4)</td>
<td>96.18(2)</td>
</tr>
<tr>
<td>C(6)-B(6)</td>
<td>1.556(3)</td>
<td>P(2)-Ru(1)-P(4)</td>
<td>175.79(2)</td>
</tr>
<tr>
<td>C(611)-B(6)</td>
<td>1.587(4)</td>
<td>P(3)-Ru(1)-P(4)</td>
<td>82.15(2)</td>
</tr>
<tr>
<td>C(621)-B(6)</td>
<td>1.586(4)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(2)-C(3)</td>
<td>1.437(3)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

is 23° for plane C(3)–C(8), 55° for C(611)–C(616) and 57° for C(621)–C(626). The boron–carbon bonds of the methylated benzene rings are only slightly longer than the boron–carbon bond of the phenylacetylide ligand.

3.3.2 Mixed-Metal Ruthenium-Osmium Acetylide Complexes

3.3.2.1 Cyclic Voltammetry and Spectroelectrochemistry

Cyclic voltammetry measurements revealed that the first-generation mixed-metal ruthenium–osmium dendrimer 3-52b shows three reversible redox-processes. Figure 3.32 shows the corresponding trace, where peaks were corrected against the ferrocene/ferrocenium couple (0.56 V in THF).

The processes occur at 0.38 V, 0.53 V and 0.63 V. The first two processes are assigned to the osmium centers at the periphery. Because the two Os-centers in each branch are only separated by one phenyl ring, the oxidation state of one metal center influences the redox behavior of the second one. Hence, on oxidation of the first osmium from OsII to OsIII, the remaining OsII becomes harder to oxidize. The increased charge of the OsIII is located in close proximity to the OsII center, which makes it harder to oxidize the second OsII to OsIII; a higher potential (0.53 V) is required. The ruthenium center, however, is remote from both osmium atoms and is therefore not or at least not noticeably influenced by the oxidation state of the osmium atoms. The potential of 0.63 V, at which the RuII is oxidized to RuIII is only slightly higher than values that
Figure 3.32 Cyclic voltammogram of the mixed-metal ruthenium-osmium first-generation dendrimer 3-52\textsuperscript{b}. The voltammogram was recorded in THF, with (NBu\textsubscript{4})\textsubscript{2}(PF\textsubscript{6}) as the electrolyte. Values were corrected against the ferrocene/ferrocenium couple (0.56 V in THF).

can be found for monometallic ruthenium acetylide complexes with comparable structural features.\textsuperscript{[134,533,725–727]} For ruthenium bis-acetylide complexes with no acceptor groups in close proximity to the metal center, potentials of 0.54 V to 0.67 V can be found. If electron-acceptor groups are present, such as in ruthenium centers that are bound to p-nitrophenylacetylide ligands, the potential lies at ca. 0.68 V to 0.75 V, i.e. slightly higher. Examining these values, it seems that the ruthenium center in the mixed metal ruthenium-osmium dendrimer 3-52\textsuperscript{b} is not strongly influenced by the presence of the Os\textsuperscript{III} centers and that the oxidation potential falls in the normal range of bis-acetylide complexes without electron accepting groups.

Changing the oxidation state of one or several metal centers in the dendrimer 3-52\textsuperscript{b} is accompanied by changes in the linear absorption spectrum. This was examined by spectroelectrochemical experiments. Figure 3.33 shows the traces of corresponding measurements.

By applying increasing potentials stepwise it was tried to address each oxidation process separately. As can be seen, a new band grows in on applying the first potential (0.48 V), the two existing main bands losing intensity. Applying a voltage
Figure 3.33 Spectroelectrochemical traces for the mixed-metal ruthenium-osmium acetylide dendrimer 3-52\textsuperscript{b}. Figures a) to e) show the linear optical behavior of the complex in THF/(NBu\textsubscript{4})\textsubscript{4}(PF\textsubscript{6}) solution at different applied voltages at room temperature.
of 0.59 V leads to the appearance of a new band at \textit{ca.} 7000 cm$^{-1}$ (Figure 3.33b), whereas the initial band at 23 500 cm$^{-1}$ loses intensity. With osmium generally showing lower oxidation potentials than ruthenium (providing a similar ligand environment of both metal centers), the two observed oxidation processes are likely to be the result of oxidizing the osmium centers. Increasing the voltage to 0.79 V and then 0.90 V, in order to address the oxidation of Ru$^{II}$ to Ru$^{III}$, drives the aforementioned changes in the linear absorption spectrum into the same direction, leading to a complete disappearance of the band at 23 500 cm$^{-1}$ (Figure 3.33d). Taking the sample back to zero-voltage does not return the complex to its initial state. Applying negative potentials, the band at 23 500 cm$^{-1}$ reappears, but this process ceases far from reaching the initial intensity of the band. Whereas the low-energy band at 7500 cm$^{-1}$ disappears completely under these conditions, the weak band at 13 000 cm$^{-1}$ remains (Figure 3.33e).

Since the dendritic mixed-metal complex 3-52$^b$ had been found not to have reversible redox properties under the chosen conditions spectroelectrochemical measurements, the unbranched (octupolar) mixed-metallic ruthenium-osmium acetylide complex 3-55$^b$ was also examined. The result is shown in Figure 3.34. In this case, the two different processes can be addressed separately (first process occurs at 0.30 V, second process occurs at 0.65 V). Comparing the initial trace of the resting state (solid black trace) to the trace after oxidizing the metal centers and then applying zero-potential (dashed black trace) suggests redox reversibility under the chosen conditions.

Proceeding to from the octupolar mixed-metal complex with one phenylethynyl-unit separating the metal centers (3-55$^b$) to the analogous bis(phenylethynyl)-bridged complex 3-56$^b$ results in the loss of redox-reversibility under bulk electrolysis conditions (Figure 3.35). Again, two overlapping bands grow in, which occurs almost simultaneously, independent of the applied voltage, whereas the band at 23 500 cm$^{-1}$ almost completely disappears at a voltage of 0.70 mV. The black dashed trace shows the final state after applying positive voltages and then returning to zero-voltage; the band does not fully recover.
Figure 3.34 Spectroelectrochemistry of the octupolar mixed-metal acetylide complex 3-55\textsuperscript{b}. The linear optical behavior of the complex in THF/(NBu\textsubscript{4})\textsubscript{a}/(PF\textsubscript{6}) solution at different applied voltages at room temperature is displayed. Numbers in brackets (n) indicate the n\textsuperscript{th} cycle of the experiment.

Figure 3.35 Spectroelectrochemistry of the octupolar mixed-metal acetylide complex 3-56\textsuperscript{b}. The linear optical behavior of the complex in THF/(NBu\textsubscript{4})\textsubscript{a}/(PF\textsubscript{6}) solution at different applied voltages at room temperature is displayed. Numbers in brackets (n) indicate the n\textsuperscript{th} cycle of the experiment.
3.4 Nonlinear Optical Properties

3.4.1 N-cored Dendrimers

3.4.1.1 Uncorrected NLO

The NLO properties of the N-cored zero- and first-generation dendrimers 3-3*, 3-4*a and 3-19b were explored using wavelength-dependent Z-scan measurements[728] with laser pulse lengths on the fs time scale (for a general introduction about the Z-scan technique, see page 9 ff.). The corresponding γ- and σ₂-spectra are given in Figures 290-294.

The γ-spectrum of the zero-generation N-cored dendrimer with a chloride ligand as the capping group (3-3C*) is given in Figure 3.36. The σ₂-diagram shown in Figure 3.37 was extracted from the corresponding γm values of complex 3-3*. There are several bands at frequencies between 7500 cm⁻¹ and 14000 cm⁻¹ (1330–720 nm). Beyond 14 000 cm⁻¹, towards higher energies, γm and σ₂ increase steadily until the high-energy end of the spectrum is reached at ca. 19 000 cm⁻¹ (525 nm). As the onset of linear absorption (i.e. IPA) is approached, a variety of saturation effects can occur, which overlaps with genuine third-order NLO effects; such data should be discarded, if the interest lies in exploring mere third-order NLO effects. Under the condition that measurements were carried out in the present work (cuvette thickness of 1 mm, concentration of around 10⁻³ mol L⁻¹), saturation effects are likely to occur at linear absorption coefficients of 1000 M⁻¹ cm⁻¹ and higher. In order to be able to reduce the chance of having saturation effects mixing into the desired third-order NLO effects, values were not considered once the linear absorption at a given frequency exceeds 500 M⁻¹ cm⁻¹.

In the case of the zero-generation ruthenium mono-acetylido dendrimer 3-3*, this point is reached at 18 000 cm⁻¹ (555 nm). Considering this, a σ₂,max of around 1700 ±270 GM at 16 500 cm⁻¹ (605 nm) is suggested.

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13 Z-scan measurements were carried out by Prof. Marek Samoc and Timothy Corkery of RSPhysSE at ANU.
14 As in Chapter 2, the linear UV-Vis traces are projected into this and the following γ-spectra. The reader may be reminded that the traces are drawn at half frequency, which means that the frequency shown in the spectrum has to be doubled to get the actual frequency of a particular band in the linear UV-Vis spectrum. As an example, the lowest energy band in Figure 3.36 is located at 25 200 cm⁻¹ (and not at 12 600 cm⁻¹)
Figure 3.36 Frequency-dependent spectrum of the second hyperpolarizabilities (in esu) of the N-cored zero-generation dendrimer 3-3. Circles: $\gamma_{\text{Im}}$; solid diamonds: $\gamma_{\text{Re}}$; solid line: frequency-dependent extinction coefficient (in M$^{-1}$ cm$^{-1}$), plotted at half energy.

Figure 3.37 Frequency-dependent $\sigma_2$-plot of the N-cored zero-generation dendrimer 3-3.
Replacing the chloride ligands with phenylacetylide ligands (i.e. proceeding from a ruthenium mono-acetylide complex to a bis-acetylide complex), affording the complex 3-4$^{a}$ results in the $\gamma$-spectrum shown in Figure 3.38. The phenylacetylide-capped zero-generation dendrimer reaches the linear absorption threshold at 17 800 cm$^{-1}$ (560 nm). Despite the fact that this is basically the same frequency as in the mono-acetylide complex 3-3$^{*}$, the NLO-behavior of 3-4$^{a}$ contrasts that of 3-3$^{*}$. $\gamma_{im}$ of the bis-acetylide complex 3-4$^{a}$ has a local maximum centered around 16 100 cm$^{-1}$, beyond which values drop, whereas the chloro-capped analogue shows the aforementioned rising trend of $\gamma_{im}$ values beyond 16 500 cm$^{-1}$. Both zero-generation complexes show all-negative $\gamma_{Re}$ values with an extremal negative value at ca. 17 500 cm$^{-1}$ (3-4$^{a}$) and ca. 17 000 cm$^{-1}$ (3-3$^{*}$). Whereas $\gamma_{Re}$ and $\gamma_{im}$ values of the phenylacetylide-capped species 3-4$^{a}$ tend to near-zero values at low frequencies (10 000–11 000 cm$^{-1}$, 1000–910 nm), both $\gamma_{Re}$ and $\gamma_{im}$ of the chloro-capped dendrimer 3-3$^{*}$ show non-zero values in that region. The chloro-capped species seem to undergo higher-order NLO processes (e.g. 3PA), which is quenched on ligand replacement. Figure 3.39 shows
Figure 3.39 Frequency-dependent $\sigma_2$-plot of the N-cored zero-generation dendrimer 3-4C$^a$.

the $\sigma_2$-plot for the phenylacetylide-capped zero-generation dendrimer 3-4$^a$ that was obtained from the corresponding $\gamma_m$ values.

Exchanging the chloride ligand with the wedge 3-17$^a$ (see page 239) afforded a sharp increase of the NLO response, as shown in Figure 3.40. The linear absorption threshold (500 M$^{-1}$ cm$^{-1}$) is reached at 18 000 cm$^{-1}$, i.e. at the same frequency as in the two zero-generation dendrimers. The highest energy band in the $\gamma_m$-spectrum of 3-19$^b$ is shifted to higher energy compared to the spectrum of 3-4$^a$ (from 16 100 cm$^{-1}$ to 16 800 cm$^{-1}$). Apart from that, the appearance of the $\gamma_m$-spectrum is similar to that of the phenylacetylide-capped complex. As was found for the zero-generation dendrimers, the first-generation dendrimer shows negative $\gamma_m$ values at all measured frequencies. An extremal negative value of $-3.5 \cdot 10^{-32}$ esu was found at 17 400 cm$^{-1}$ (570 nm). Near the low-energy end of the spectrum, values for both $\gamma_m$ and $\gamma_R$ tend away from zero, as was observed for the chloro-capped species. Therefore, the frequency range of the incident laser beam was extended to cover the range 10 000–6250 cm$^{-1}$ (1000–1600 nm). From that extension it can be qualitatively said that nonlinear absorption occurs. However, it appears that more than just one nonlinear effect is responsible for the observed
Figure 3.40 Frequency-dependent spectrum of the second hyperpolarizabilities (in esu) of the N-cored first-generation dendrimer 3-19\textsuperscript{b}. Circles: $\gamma_{\text{Re}}$; solid diamonds: $\gamma_{\text{Im}}$; solid line: frequency-dependent extinction coefficient (in $10^3$ M\textsuperscript{-1} cm\textsuperscript{-1}), plotted at half energy.

absorption\textsuperscript{[521]} Because Z-scan measurements do not allow temporal resolution of simultaneously occurring effects, the origin of the observed response cannot be determined without additional multi-beam experiments, such as DFWM (or other pump-probe techniques). A severe deviation of the Z-scan traces from the theoretically calculated curves was observed, and at present it is suggested that they result from 3PA-initiated photochemical changes that occur near the focal point of the laser beam (i.e. at $z = 0$). Figure 3.41 shows a Z-scan trace taken at a frequency of 8060 cm\textsuperscript{-1} (1024 nm) as an example. At negative $z$ values, i.e. before reaching the focal point, nonlinear absorption that is of at least fifth-order in nature (i.e. 3PA) occurs, which can be seen by the steep slope of the trace. At positive $z$ values, beyond $z = 0$, there is a clear deviation from a symmetric trace, away from both calculated 3PA and calculated 2PA. The $\sigma_{2}$-spectrum of the N-cored first-generation dendrimer 3-19\textsuperscript{b} is given in Figure 3.42.
CHAPTER 3. Dendrimers – Branched Octupolar Ruthenium Acetylide and Mixed-Metal Ruthenium-Osmium Acetylide Complexes

Figure 3.41 Z-scan trace of the N-cored first-generation dendrimer 3-19b at an incident laser frequency of 8060 cm⁻¹ (1024 nm). Solid black line: calculated trace for 2PA; broken black line: calculated trace for 3PA; grey circles: experimental data. z = 0 corresponds to the sample being positioned at the focal point of the laser, with the sample running from negative to positive z.

Figure 3.42 Frequency-dependent $\sigma_2$-plot of the N-cored first-generation dendrimer 3-19b.
3.4. Nonlinear Optical Properties

3.4.1.2 NLO-Scaling Factors

Despite the fact that a vast number of reported NLO data are accessible today (see Chapter 1, page 13 ff), it remains difficult to compare NLO data. Several reasons are responsible for this circumstance; firstly, the conditions, under which the data are obtained, are important (technique, type of laser, pulse length, repetition rate, wavelength, just to name a few). Secondly, the diversity of data analyses and data processing techniques, along with varying unit systems and conversions also plays a role. However, even if a set of structurally different materials was measured under the same experimental conditions and the data were then analyzed in a consistent fashion, the determination of the NLO efficiency of one compound compared to the others is not straightforward. The molecules may be of different size, their conjugation pathlengths may differ from each other or they may contain different functional groups, and the effective number of \( \pi \)-electrons \( N_e \) or the square of it \( N_e^2 \), as well as the molecular weight and the cost to synthesize a material may differ (mentioned in Chapter 2 and used to calculate corrected NLO values). The same methodology was applied to the three organometallic dendrimers 3-3\(^*\), 3-4\(^*\(a\) and 3-19\(^b\).

An interesting aspect of this work is the effect that the incorporation of metal centers has on the NLO response of the resulting organometallic complexes. For that reason, the three N-cored organometallic dendrimers were compared to the three structurally related organic analogues 3-59\(^*\(a\), 3-60\(^*\(a\) and 3-61\(^*\(a\) shown in Figure 3.43. All six species have been reported to show NLO responses. What they have in common is the presence of a \( \pi \)-delocalized system, and they all have a nitrogen atom as the central atom ("core"). The structural differences between them are also obvious; different conjugation path lengths, presence or absence of metal centers, and different degree of branching. The question is, how these three structurally related dendrimers can be compared to each other fairly with regards to their NLO properties, i.e. how can structural or electronic differences be accounted for and intrinsic NLO-properties (see Chapter 2, page 166 ff) be calculated. The following section presents the methodology to calculate or determine various scaling factors for NLO data and compares their effects on NLO trends when being applied to uncorrected NLO data. In addition to the
Figure 3.43 Structure representations of three N-cored organic dendrimers 3-59a, 3-60a and 3-61a that show NLO effects.
3.4. Nonlinear Optical Properties

aforementioned scaling factors, another aspect was examined, namely the volume of the six species. The motivation for the new scaling factors is apparent:

Molecular volume: The smaller the volume that a single molecule of a species with a given NLO response takes up, the more molecules can fit into a volume element of an optical device. This maximizes the macroscopic NLO response of the device per unit volume. Alternatively, if a manufacturer aims for a certain level of NLO response in its device, then the device can be made smaller to achieve this by using molecules with strong NLO properties that take up a small volume.

Cost of production: The cheaper it is to produce a material with a given NLO response, the more attractive it becomes for using it in manufactured optical devices (see Chapter 2).

The following paragraphs will explain the procedure, by which the two parameters were determined.

**MOLECULAR VOLUMES** can be calculated by a variety of procedures. Employing van der Waals radii \( r_{vdW} \) derived from bond lengths in crystal structures is straightforward and reliable for small molecules consisting of light main group elements,\(^{[729,730]} \) but less practical for larger molecules, such as those explored in the present work. Abraham and co-workers introduced an alternative method that does not necessitate generation of 3D models, and so more rapidly affords volumes of organic and organometallic compounds that are consistent with values obtained by computational methods and the crystal structure-derived \( r_{vdW} \) approach.\(^{[731]} \)

The molecular structures of the six compounds discussed herein were generated using Spartan '08\(^{[732]} \) on a MacPro 2 x 2.66 GHz Dual Core, running on MacOSX v.10.4.11. The MMFF molecular mechanics method was applied to the models to obtain equilibrium geometries of the structures in the ground state, although this was just a rough approach considering the size of the compounds and complexes. Molecular volumes (\( \text{Å}^3 \)) of 3-3\(^*\), 3-4\(^*\), 3-59\(^*\), and 3-60\(^*\) were provided by the program as part of the output. The \( r_{vdW} \) used in Spartan '08 are given in Table 3.2.

Alternatively, for large structures, such as proteins, it is common to calculate solvent-excluding surfaces (SES) and the volume that they enclose \( (V_{SES}) \), in order to estimate a molecular volume. The software MSMS\(^{[733,734]} \) uses a fast algorithm
and produces reliable values (the calculated values of known compounds are comparable to those obtained with similar programs). The program employs a spherical probe of a certain radius ($r_{\text{probe}}$) simulating a solvent, that is "rolled" across the whole molecule. The spherical probe cannot access every point on the surface of a molecule because of geometric constraints. The contact area corresponds to all points on the surface of the molecule that the sphere is able to touch. When the probe touches more than one atom simultaneously, the areas that are spanned between the atoms form the so-called reentrant surface (Figure 3.44). Combining the reentrant surface and the contact surface gives a closed surface that can be considered as the molecular surface or solvent excluding surface, SES (in Å²). The volume that the SES encloses is the $V_{\text{SES}}$ (in Å³). In other words, the SES volume is the volume impenetrable by a defined solvent. This resembles the definition of the molecular volume (or van der Waals volume) of a molecule as expressed by Bondi: "[...] the volume impenetrable for other molecules with thermal energies at ordinary temperatures." The $V_{\text{SES}}$ calculated with MSMS are referred to as molecular volume ($V_m$) from this point onwards. For the calculation of $V$ using the MSMS software, Brookhaven Protein Database (PDB) files were generated in Spartan '08 from the same modeled structures as described above and were converted into xyzr-files using the MSMS software. This software was then used to calculate $V_{\text{SES}}$ from the xyzr-files, using $r_{\text{vdw}}$ given in Table 3.2. In all calculations, a probe radius ($r_{\text{probe}}$) of 1.50 Å was used. $V_m$ values of 3-3,
3.4. Nonlinear Optical Properties

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<th>N</th>
<th>P</th>
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Table 3.2 Van der Waals radii ($r_{vdW}$) used for the calculation of four sets of $V_m$ values using MSMS software ($V_{m,\text{min}}$, $V_{m,\text{init}}$, $V_{m,\text{max}}$, $V_{m,\text{uni}}$) and the SPARTAN '08 software ($V_{m,\text{Spartan}}$).

3-4\textsuperscript{a}, 3-59\textsuperscript{a}, and 3-60\textsuperscript{a} were calculated using MSMS and compared to $V_m$ values obtained from Spartan '08. For the larger compounds 3-19\textsuperscript{b} and 3-61\textsuperscript{a}, Spartan did not deliver any $V_m$ values, so the corresponding values could not be included in the comparison. For each of the six dendrimers, four different $V_m$ values were calculated with MSMS, where the $r_{vdW}$ values were varied, in order to obtain an estimate of the variation in $V_m$ as a function of $r_{vdW}$. The upper and lower limits of $r_{vdW}$ were chosen in accordance with values suggested by Bondi.\textsuperscript{[729,730]} The $r_{vdW}$ values that were chosen for the different sets of $V_m$ calculated in MSMS are given in Table 3.2. Radii suggested by Bondi are widely used for the calculation of molecular volumes of organic molecules,\textsuperscript{[737]} but $r_{vdW}$ values for metals (in particular, transition metals) were not investigated in detail by Bondi. The default $r_{vdW}$ value of 1.7 Å used by MSMS for transition metals was therefore used as a maximum value in the present complexes. In clusters with Ru-Ru contacts, bond lengths of 2.75–2.88 Å are commonly found,\textsuperscript{[738]} indicating that $r_{vdW}(\text{Ru})$ is much smaller than 1.7 Å, possibly ca 1.4 Å (and the formal Ru\textsuperscript{II} oxidation state in the organometallic dendrimers should correspond to a smaller radius). Therefore, a min/max range 1.35–1.70 Å was chosen for Ru centers (see Table 3.2).

An alternative approach towards molecular volumes (at least in a relative fashion) commonly used in the area of X-ray crystallography is Hofmann\textsuperscript{\textquotesingle}s method; it has been suggested that, to good approximation, the volume that a molecule occupies in a crystal lattice can be estimated by multiplying the number of atoms in the molecule (N) by 18 Å\textsuperscript{3}, as shown by Kempster and Lipson.\textsuperscript{[739]} The accuracy of this model was improved by Mighell \textit{et al.}\textsuperscript{[740]} and then D. W. F. Hofmann,\textsuperscript{[741]}
CHAPTER 3. Dendrimers – Branched Octupolar Ruthenium Acetylide and Mixed-Metal Ruthenium-Osmium Acetylide Complexes

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Table 3.3 Average atomic volumes [Å³] derived from results of X-ray structure determinations.⁷⁴⁰,⁷⁴¹

who gave average atomic volumes for many elements across the periodic table, based on the investigation of a vast number of crystal structures. The values that are relevant for this work and that were taken from Hofmann’s results are presented in Table 3.3. Whereas the values for molecular volumes obtained by Hofmann’s method and Mighell’s method gave similar results, their methods appeared to deliver more accurate results than the 18 Å³ rule. For comparison of the trends obtained by computational methods described above, volumes of the six dendrimers were therefore also calculated “by hand” using Hofmann’s method.

A preliminary comparison of molecular volumes of some model compounds calculated using Spartan ‘08 and MSMS to those given in the literature⁷⁴² revealed that there are deviations (results not presented here). This trend has been described in the literature before,⁷³⁷,⁷⁴² and confirms the difficulties that are related to such calculations. However, a comprehensive study to determine exact Figures was not within the scope of the current work. For the present calculations, only the two programs MSMS and Spartan were used, giving V_m values that deviate from each other by up to 15%. Similar observations have been noted by other groups carrying out calculations employing Spartan, MSMS, Molecular Modelling Pro or Insight II.⁷³¹,⁷⁴³ The preliminary comparisons suggested that V_m values calculated with MSMS approximate those calculated with Spartan ‘08 within a 15% margin, but that differing values are sometimes obtained when using programs other than the two used herein.

The results that were obtained for the six dendrimers using the three methods described above are given in Figure 3.45a. Because r_vdw values are subject to variance, calculations may give significantly different values when different r_vdw values are used. The variation in V_SES as a function of different r_vdw can be extracted from Figure 3.45a. For the variation of r_vdw, the largest and
smallest values given by Bondi were used (see Table 3.2), and the corresponding volumes were labeled $V_{m,\text{max}}$ and $V_{m,\text{min}}$. $V_{m,\text{init}}$ values were obtained when the $r_{\text{vdW}}$ values suggested by the authors of the MSMS software were used in the calculations, and $V_{m,\text{uni}}$ values were obtained when the same $r_{\text{vdW}}$ values that were used in Spartan calculations were used in MSMS. Comparing volumes obtained from Spartan '08 ($V_{m,\text{Spartan}}$) to the values retrieved from MSMS, it can be seen that values obtained from MSMS are consistently larger than $V_{m,\text{Spartan}}$ by a maximum of 14% ($V_{m,\text{Spartan}}$ values were obtained for compounds 3-3*, 3-4*, 3-59*, and 3-60* only). The deviations of $V_{m,\text{uni}}$ from $V_{m,\text{min}}$ and $V_{m,\text{max}}$ are within a 10% margin to lower values and ca. 5% to higher values, while $V_{m,\text{uni}}$ and $V_{m,\text{init}}$ values are almost identical. The absolute values for $V_{m}$ obtained via Hofmann's method ($V_{m,\text{Hof}}$) cannot be compared to the computationally derived methods. The reason is that Hofmann extracted average atomic volumes from a large number of X-ray crystal structures. Because molecules in a crystal lattice are subject to packing effects, $V_{m}$ values calculated from these atomic volumes will always be larger than $V_{\text{SES}}$, since packing effects are not considered in $V_{\text{SES}}$. The problem of varying atomic volumes when the oxidation state of atoms in a molecule is changed remains. Hofmann accounted for these effects only indirectly, by taking the average over a vast number of crystal structures, which included compounds with metals in different oxidation states.

The important aspect of the approach towards the volume scaling factor, however, is not so much the absolute values of $V_{m}$; relative volumes of the investigated molecules in comparison to each other are more important. The calculated $V_{m,x}$ values (where x is the employed method or model) were therefore put in relation to each other, giving relative molecular volumes ($V_{m,\text{rel}}$). The results are depicted in Figure 3.45b.

What can be seen from this graph is that the relative molecular volumes for the organic dendrimers are almost the same for all employed models. In the case of the organometallic dendrimers, there are differences of up to 20%, comparing relative $V_{m,\text{Hof}}$ and relative $V_{m,\text{min}}$. The relative values obtained from $V_{m,\text{uni}}$ (and $V_{m,\text{init}}$) are in between these two extremes. The absolute $V_{m,\text{uni}}$ values are within 10% of $V_{m,\text{Spartan}}$, and it appeared reasonable to use $V_{m,\text{uni}}$ for all the following calculations and bear a 10% deviation in either direction in mind. Hence, of the volumes calculated using the MSMS program ($V_{m,\text{min}}, V_{m,\text{init}},$
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Figure 3.45 Calculated \( V_m \) values for the organometallic dendrimers 3-3\(^*\), 3-4\(^*\)\(^a\), and 3-19\(^b\) and the organic dendrimers 3-59\(^a\), 3-60\(^a\), and 3-61\(^a\), using different methods. 

(a) Absolute \( V_m \) obtained using the MSMS software (\( V_{m,\text{min}} \), \( V_{m,\text{init}} \), \( V_{m,\text{max}} \), \( V_{m,\text{uni}} \), the Spartan '08 software (\( V_{m,\text{Spartan}} \)) and Hofmann's method (\( V_{m,\text{Hof}} \)). 14% error bars were applied to \( V_{m,\text{uni}} \) values. 

(b) Relative \( V_{m,m} \), where the smallest absolute \( V_{m,x} \) values (3-59\(^a\)) were used as a reference and assigned to an arbitrary value of 1. 10% error bars were applied to \( V_{m,\text{uni}} \).
3.4. Nonlinear Optical Properties

\( V_{m,\text{max}}, V_{m,\text{uni}} \), \( V_{m,\text{uni}} \) was used to normalize the uncorrected \( \sigma_2 \) values of the dendrimers, affording the corresponding volume-corrected values, \( \sigma_{2,V,\text{uni}} \) (see Figure 3.47). However, since molecular volumes are accessible more easily via Hofmann's method (i.e. without generating the structure computationally first and then calculating \( V_m \) using MSMS), it is favorable to use \( V_{m,\text{Hof}} \) for the scaling. Both \( V_{m,\text{Hof}} \) and \( V_{m,\text{uni}} \) were therefore used for the scaling, in order to show the difference in the results, bearing in mind that \( V_{m,\text{Hof}} \) is more practical for general use.

**COST OF PRODUCTION.** The cost for producing one of the presented compounds or complexes was calculated the same way as described in more detail in Chapter 2. The same rules were applied. The results presented in this section have been published by us in 2010.\(^{[53]}\) A few changes have been made since then, giving rise to differences between the results herein and the published results. These changes are listed below.

- Prices for chemicals were updated to numbers found in the online Aldrich catalogue 2011 for consistency with the results presented in Chapter 2.

- Because solvents contribute significantly to the overall cost, they were included in the costing schemes.

- The synthesis of the triacetylene core 2-2\( ^+ \) was changed to match the synthetic procedure that I chose. The literature yield (73\% over 2 steps) is slightly higher than for the the procedure presented herein (68\% over 2 steps).

- Whereas an alternative provider for chemical supplies (Strem) besides Aldrich had still been considered formerly,\(^{[536]}\) only Aldrich was used in the present work for consistency; Strem offers a range of organometallic components that are significantly cheaper than from Aldrich, which favors the organometallic complexes.

- The yield for the reaction of the wedge 3-17\( ^+ \) with the N-cored zero-generation dendrimer 3-3\( ^+ \), affording the organometallic first-generation dendrimer 3-19\( ^b \), was improved from 19\%\(^{[521]}\) to 55\%.

The calculations for the organometallic complexes were carried out based on Schemes 3.1 (page 234), 3.2 (page 235), 3.3 (page 236), 3.4 (page 239), and 3.5
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Scheme 3.17 Synthesis of the organic zero-generation dendrimer 3-59\textsuperscript{a} in 4 unique steps. Ac = acetyl, DMF = N,N-dimethylformamide, dba = dibenzylideneacetone.

(page 240). The organic analogues 3-59\textsuperscript{a}, 3-60\textsuperscript{a}, and 3-61\textsuperscript{a} were not prepared by the author (which is indicated by the superscript a), so Schemes 3.17, 3.18 and 3.19 were drawn based on reported literature procedures in accordance with aforementioned methodology. The Schemes were costed for the synthesis of 1 mmol of each of the six compounds. Tables showing amounts, yields, individual costs for each chemical at each step, and overall costs for each final product can be found in the Appendix.

Yields for the compounds 3-3\textsuperscript{a} and 3-4\textsuperscript{a}, \textsuperscript{[744]} 3-19\textsuperscript{b}, \textsuperscript{[521]} 2-45\textsuperscript{a}, \textsuperscript{[703]} 2-46\textsuperscript{a}, \textsuperscript{[613]} 3-1\textsuperscript{a} and 3-2\textsuperscript{a}, \textsuperscript{[744]} 2-21\textsuperscript{a}, 2-28\textsuperscript{b}, 2-29\textsuperscript{b}, 3-8\textsuperscript{[702]} 2-1\textsuperscript{a} (procedure \textsuperscript{[609]}, characterization \textsuperscript{[610]}), 2-2\textsuperscript{b}, \textsuperscript{[615]} 3-9\textsuperscript{a} and 3-10\textsuperscript{a}, \textsuperscript{[745]} 3-17 and 3-18, \textsuperscript{[521]} 3-62\textsuperscript{a}, \textsuperscript{[746,747]} 3-63\textsuperscript{a}, \textsuperscript{[747]} 3-64\textsuperscript{a}, \textsuperscript{[748]} 3-66\textsuperscript{a}, \textsuperscript{[748]} 3-67\textsuperscript{a}-3-69\textsuperscript{a}, \textsuperscript{[671]} 3-59\textsuperscript{a}, \textsuperscript{[747]} 3-60\textsuperscript{a}, \textsuperscript{[671]} and 3-61\textsuperscript{a} \textsuperscript{[671]} were as reported in the literature. Where more than one method for an individual step was reported, the higher yielding step was chosen.

In the same way that the first-generation organometallic dendrimer 3-19\textsuperscript{b} exceeds the other five compounds in terms of absolute $\sigma_2$ value, it is also significantly
Scheme 3.18 Synthesis of the organic first-generation dendrimer 3-60\textsuperscript{a} in 7 unique steps. THF = tetrahydrofuran, DMF = N,N-dimethylformamide, Ac = acetyl.
Scheme 3.19 Synthesis of the organic second-generation dendrimer 3-61$^a$ in 9 unique steps (6 steps to compound 3-70$^a$, which involves synthesis of 3-67$^a$ and 3-69$^a$: see Scheme 3.18).
more expensive to synthesize. The differences in cost are not as drastic between
the organic zero-generation dendrimer 3-59\textsuperscript{a} and organometallic zero-generation
dendrimers 3-3\textsuperscript{*} and 3-4\textsuperscript{b} but the trend is still the same. It is certainly possible
to locate chemical providers that offer the required chemicals cheaper than found
at Sigma-Aldrich; however, it is beyond the scope of these preliminary studies to
investigate this in any more detail. The above approach has merit, being mindful
of the fact that it is not straightforward to compare prices for each chemical
involved across all possible providers, that some research groups may be provided
with free chemicals due to internal arrangements or cooperations, that some
research institutes may provide chemicals for a fraction of the commercial price
due to large bulk orders, and so forth. The author is aware of all these aspects
that surely leave room for discussion, but the single-provider approach (defining,
for example, an Aldrich-coefficient) seems a reasonably accessible starting point.

Besides costs related to labor, varying shipping costs, electricity, consumables,
general wear and tear of equipment, peripheral equipment (stirrer hotplates,
glassware, stirrers etc.), extensive workup or purification procedures (e.g. column
chromatography) requiring additional chemicals (e.g. solvents, adsorbents) were
not directly included in the calculations, despite the fact that they may contribute
quite significantly to the overall costs. However, these additional factors are
difficult to track (and in some instances require information not supplied in the
original articles, such as quantities of solvents used for chromatography or other
workup procedures).

The one cost in this list that is likely to be a substantial component of the
overall cost of the target chemical is that of labor. The author has estimated the
labor costs from the number of steps involved. Assuming a purification step by
silica flash column chromatography after each reaction may lead to an average
time of 5 hours of labor for each reaction. At an hourly wage of AUD$30 for
a lab technician, plus AUD$10 for adsorbents and AUD$20 for solvents, such
as petroleum spirits (ca. AUD$L\textsuperscript{-1}), this adds AUD$180 for each step to the
overall cost.\textsuperscript{15} The effect that considering labor costs has on the overall cost of
synthesizing these compounds is compared in Figure 3.46.

\textsuperscript{15} Only unique synthetic steps are counted into the overall number of steps, i.e. repeat reactions
are merged to just one unique reaction.
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![Graph showing cost comparison between syntheses excluding and including labor](image)

**Figure 3.46** Total cost [AUD$] for syntheses considering the costs of precursor chemicals only (blue) and costs for syntheses when including costs for labor and purification (red).

**NUMBER OF EFFECTIVE \( \pi \)-ELECTRONS.** The three different approaches to calculate this scaling factor have been described in Chapter 2 already (see page 171 ff) but are repeated here for the reader's convenience:

- \( N_e \): Both nitrogen and ruthenium are considered as disrupting units that separate conjugated moieties from each other.

- \( N_{e,N} \): Nitrogen atoms are part of the conjugated system and contribute 2 electrons to it. Ruthenium centers are considered as disrupting units that separate conjugated moieties from each other.

- \( N_{e,Ru} \): Both nitrogen and ruthenium are considered as part of the conjugated system, where each nitrogen and ruthenium atom contributes 2 electrons to the conjugated system.

Considering these three approaches, three different values for the effective number of \( \pi \)-electrons were obtained for each of the six species to be compared. The scaling factors are displayed in Table 3.4.

**3.4.1.3 Corrected NLO**

The scaling factors presented in the previous section were used to calculate scaled (intrinsic) NLO data. Depending on the type of scaling factor that is used for the
Table 3.4 Summary of scaling factors that have been discussed throughout this

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<td>10000000.0</td>
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<td>100000000000.0</td>
<td>1000000000000.0</td>
<td>335.2</td>
<td>118.3</td>
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</tr>
</tbody>
</table>

3.4. Nonlinear Optical Properties
### Table 3.5 Uncorrected maxima of $\sigma_2$ and corrected 2PA cross-sections $\sigma_{2,x}$, where $x$ is the scaling factor. $x = \text{uni}$: volume-corrected $\sigma_2$ ($V_{\text{m,uni}}$); $x = \text{Hof}$: volume-corrected $\sigma_2$ ($V_{\text{m,Hof}}$); $x = \text{C}$: cost-corrected $\sigma_2$; $x = \text{CLab}$: cost-corrected $\sigma_2$ including labor cost; $x = \text{M}$: molecular weight-corrected $\sigma_2$; $x = N_e$: $\sigma_2$ scaled by effective number of $\pi$-electrons (N and Ru considered as disruptors); $x = N_{e,N}$: $\sigma_2$ scaled by effective number of $\pi$-electrons (each nitrogen atom contributes 2 electrons, and ruthenium is considered as a disruptor); $x = N_{e,Ru}$: $\sigma_2$ scaled by effective number of $\pi$-electrons (each nitrogen and each ruthenium contributes 2 electrons).

<table>
<thead>
<tr>
<th>$3\text{-}3^\ast$</th>
<th>$3\text{-}4^\ast a$</th>
<th>$3\text{-}18$</th>
<th>$3\text{-}59^\ast a$</th>
<th>$3\text{-}60^\ast a$</th>
<th>$3\text{-}61^\ast a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma_{2,\text{max}}$ [GM]</td>
<td>1720±270 1250±300</td>
<td>10600±300</td>
<td>32±n.a.</td>
<td>370±n.a.</td>
<td>840±n.a.</td>
</tr>
<tr>
<td>$\sigma_{2,\text{uni}}$ [GM Å$^{-3}$]</td>
<td>0.57</td>
<td>0.37</td>
<td>1.04</td>
<td>0.03</td>
<td>0.13</td>
</tr>
<tr>
<td>$\sigma_{2,\text{Hof}}$ [GM Å$^{-3}$]</td>
<td>0.45</td>
<td>0.30</td>
<td>0.84</td>
<td>0.02</td>
<td>0.09</td>
</tr>
<tr>
<td>$\sigma_{2,C}$ [GM mol AUD$^{-1}$]</td>
<td>15.4</td>
<td>10.0</td>
<td>5.1</td>
<td>0.7</td>
<td>0.4</td>
</tr>
<tr>
<td>$\sigma_{2,\text{CLab}}$ [GM mol AUD$^{-1}$]</td>
<td>1.70</td>
<td>1.04</td>
<td>2.14</td>
<td>0.04</td>
<td>0.17</td>
</tr>
<tr>
<td>$\sigma_{2,\text{M}}$ [GM mol g$^{-3}$]</td>
<td>0.55</td>
<td>0.38</td>
<td>1.06</td>
<td>0.03</td>
<td>0.13</td>
</tr>
<tr>
<td>$\sigma_{2,\text{Ne}}$</td>
<td>123.7</td>
<td>63.8</td>
<td>244.8</td>
<td>1.3</td>
<td>8.8</td>
</tr>
<tr>
<td>$\sigma_{2,\text{NeN}}$</td>
<td>8.9</td>
<td>3.3</td>
<td>5.7</td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>$\sigma_{2,\text{NeRu}}$</td>
<td>66.2</td>
<td>35.3</td>
<td>218.6</td>
<td>0.6</td>
<td>2.6</td>
</tr>
<tr>
<td>$\sigma_{2,\text{NeN}^2}$</td>
<td>2.5</td>
<td>1.0</td>
<td>4.5</td>
<td>0.01</td>
<td>0.02</td>
</tr>
<tr>
<td>$\sigma_{2,\text{NeRu}^2}$</td>
<td>53.8</td>
<td>23.1</td>
<td>107.9</td>
<td>0.6</td>
<td>2.6</td>
</tr>
</tbody>
</table>

$^d$Given in GM electron$^{-1}$ $^e$Given in GM electronelectron$^{-2}$

Calculations, emphasis is placed on different aspects of NLO efficiency. Table 3.5 summarizes the uncorrected and the range of corrected $\sigma_{2,\text{max}}$ values for the organometallic dendrimers $3\text{-}3^\ast$, $3\text{-}3^\ast a$ and $3\text{-}19^b$ and their organic analogues $3\text{-}59^\ast a$–$3\text{-}61^\ast a$. Figure 3.47 shows volume-corrected 2PA cross-sections ($\sigma_{2,V}$) and molecular weight-corrected 2PA cross-sections ($\sigma_{2,M}$). In the case of $\sigma_{2,V}$, three differently calculated molecular volumes ($V_{\text{m,uni}}$, $V_{\text{m,Spartan}}$, $V_{\text{m,Hof}}$) were used, which resulted in three different values of $\sigma_{2,V}$, namely $\sigma_{2,\text{Spartan}}$ and $\sigma_{2,\text{uni}}$ and $\sigma_{2,\text{Hof}}$. Because trends, i.e. relative values, are of greater interest than absolute values, the corrected $\sigma_2$ values in Figure 3.47a were normalized, where the smallest of all absolute corrected $\sigma_2$ values was used as the normalization.
factor. The result is shown in Figure 3.47b. Because some of these scaling factors have not been used before, the different approaches should briefly be looked at in terms of their practicality and the trends they deliver. Examining the second diagram in Figure 3.47 it seems as if Spartan '08 underestimates the volume of the organometallic species, leading to increased $\sigma_{2,V}$ compared to the remaining corrected 2PA cross-sections. The normalization overcompensates the large absolute values of molecular volumes that leads to comparably small $\sigma_{2,Hof}$ values (see Figure 3.47a) and brings them level with trends gained from Spartan '08. The trends with respect to molecular weight-corrected 2PA cross-sections gained after the normalization shows that $\sigma_{2,M}$ lies at the lower end of the range for relative 2PA cross-sections across all six species, although the difference with the $\sigma_{2,V}$ values is larger for the organometallic species than it is for the organic compounds, where the trends obtained through MW as the scaling factor and the different molecular volumes as scaling factors are basically the same. Two important conclusions can be drawn from the above results; firstly, it does not make a significant difference whether molecular volumes calculated from Spartan '08 or molecular volumes calculated via Hofmann's rule are used for comparisons. Therefore, it is probably sufficient to use the atomic volumes given in Table 3.3 (page 300) to calculate the molecular volume based on the molecular composition of the complex or compound. Secondly, the absolute values of molecular volumes, regardless how they are calculated, do not differ greatly from the molecular weights, so volume-corrected 2PA cross-sections and MW-corrected 2PA cross-sections are similar. This is a reflection of the fact that the organometallic complexes are so carbon rich that the metal centers do not influence the molecular volume greatly. However, their presence is noticeable through the $\sigma_{2,M}$ values, which are slightly smaller than the relative $\sigma_{2,V}$ values (Figure 3.47b).

Examining the trends that the volume- and weight-corrected 2PA cross-sections deliver for the organometallic complexes in comparison with their organic analogues, it is obvious that the organometallic complexes dominate significantly on both zero- and first-generation levels. Both the organic and organometallic species show a dendritic effect on proceeding from zero-generation species to first-generation dendrimers. The reader may be reminded here that, in the absence of any such effect, the corrected 2PA cross-sections should be the same
Figure 3.47  a) Volume-corrected $\sigma_2$ values ($\sigma_{2,\text{Spa}}$ and $\sigma_{2,\text{uni}}$ and $\sigma_{2,\text{Hof}}$ in $\text{GM} \cdot \text{Å}^2$) and molecular weight-corrected $\sigma_2$ values ($\sigma_{2,M}$ in $\text{GM} \cdot \text{mol} \cdot \text{g}^{-1}$) in comparison.  b) Relative volume-corrected and molecular weight-corrected $\sigma_2$ values, where the values for the organic zero-generation dendrimer ($3-59^\text{ta}$) were arbitrarily set to 1.
for zero- and first-generation dendrimers, because their size has been taken care of by the scaling factor already. This can be seen for the organic first- and second-generation dendrimers, where corrected 2PA cross-sections are the same for both. In absolute terms, the second-generation dendrimer $3-61^a$ still dominates over the first-generation dendrimer $3-60^a$ (see Table 3.5 on page 310).

Using $N_e$ and $N_e^2$ as scaling factors, the difference between the organic compounds and the organometallic complexes becomes even more pronounced. Figure 3.48a shows absolute electron-corrected $\sigma_{2,\text{max}}$ values. In order to permit facile comparison, the relative numbers are given in Figure 3.48b, where absolute $\sigma_{N}$- and $\sigma_{N^2}$ values of the organic zero-generation dendrimer $3-59^a$ were arbitrarily set to 1. Figure 3.48b shows that the NLO efficiency of the organometallic zero-generation dendrimers exceeds that of the analogous organic species ($3-59^a$) up to 200-fold, and the same applies to the first-generation level. These extremal ratios are obtained when $N_{e,N}$ is used as the scaling factor, which neglects contributions from the ruthenium centers. Because there are significantly more nitrogen nodes in the organic species than there are in the organometallic dendrimers, the organic dendrimers suffer severely when $N_{e,N}$ is used as the scaling factor. However, the electrons in the d-orbitals of the ruthenium centers are not tightly bound to the metal, therefore it is suggested that $N_{e,Ru}$ should be used instead of $N_e$ or $N_{e,N}$. Examining the corresponding $\sigma_{2,NeRu}$ values, the ratios drop in favor of the organic species. Under such circumstances, the NLO efficiency of the organometallic zero-generation dendrimer $3-3^*$ is still 80 times that of the organic zero-generation dendrimer $3-59^a$, i.e. close to two orders of magnitude. This ratio drops to ca. 60 for the phenylacetylide-capped zero-generation dendrimer $3-4^a$, which means that the NLO efficiency decreases on replacing the chloro ligand with a phenylacetylide ligand; the extension of the $\pi$-conjugated system does not result in an increase in the NLO-response, and in this case, which applies to both uncorrected and intrinsic 2PA cross-sections. Using $N_{e,Ru}$ as a scaling factor leads to the result that there is no longer a dendritic effect on proceeding from the ruthenium mono-acetylide zero-generation dendrimer $3-3^*$ to the first-generation dendrimer $3-19^b$. For the organic dendrimers, there is a dendritic effect under all applied electron-scaling factors on proceeding from the zero- to the first-generation level, although it becomes almost negligible in the case of $N_{e,N}$ (which is the same as $N_{e,Ru}$, since there are no Ru centers embedded.
Figure 3.48 a) Absolute values of electron-corrected 2PA cross-sections $\sigma_{2,Nx}$, where $x$ depends on the applied model for calculating the number of effective $\pi$-electrons in the compound or complex; $x = e$: N and Ru are considered as disrupting units; $x = eN$: N is part of the conjugated system and donates 2 electrons, while Ru is considered as a disruptor; $x = eRu$: both N and Ru are part of the conjugated system, each donating 2 electrons. b) Relative values, where $\sigma_{2,Nx}$ values of 3-60$^a$ were used as normalization factors. c) Inset of b) to show the ratios of the organic dendrimers 3-59$^a$–3-61$^a$. 
in the organic compounds). There is no dendritic effect on proceeding from the organic first-generation dendrimer to its second-generation analogue, unless $N_e$ is used as the scaling factor (which is the least realistic).

Lastly, the cost-scaling was applied to $\sigma_{3,\text{max}}$ values. Figure 3.49a shows the costs that occur on preparation of 1 mmol of any of the six N-cored dendrimers with and without labor costs. The number of steps that are involved across each synthetic Scheme are also depicted. The obtained results are graphically displayed in Figure 3.49b. The results vary greatly, depending on whether or not labor costs are included or not, up to the point where trends are inverted; whereas the organometallic zero-generation dendrimer 3-3* shows a higher NLO efficiency than the first-generation dendrimer 3-19\textsuperscript{b} when labor costs are not considered, the NLO efficiency of 3-19\textsuperscript{b} exceeds that of 3-3* when labor costs are considered. The same is observed for the organic zero- and first-generation dendrimers. This is based on the aforementioned fact that species, which can be produced comparably cheaply (high yields and/or small number of steps), suffer relatively more from the addition of a fixed per-step-rate for workup and labor than do the (larger) species that involve more steps, which is related to a higher chance encountering one or two low-yielding steps along a synthetic scheme, increasing the overall cost. And there are more factors that need to be included, if the cost-scaling was to be pursued on a more accurate level; reaction times (related to labor cost, electricity and other resources, wear and tear of equipment, use of facilities), accurate amount of solvents (also related to the disposal of chemical waste, which is not included in the present studies at all, despite the fact that waste disposal contributes significantly to the cost involved in chemical synthesis), types of starting materials, intermediates, and by-products (e.g. special storage and/or waste disposal of hazardous materials) and many more. Examining the Tables in the Appendix and the reaction Schemes that need to be followed back to commercially starting materials to calculate overall costs, it is obvious that the calculation of the cost-scaling factors is tedious and time-consuming, and such calculations also bear a high degree of inaccuracy. Hence, although the idea of scaling by cost of production is reasonable, the applicability of such a scaling system, particularly at a high turnover rate of acquired NLO data and/or long syntheses, is too low and renders the scaling factor less attractive than other scaling factors. However, a combination of the number of steps and the overall
Figure 3.49 a) Costs that occur on producing 1 mmol of the organometallic dendrimers 3-3, 3-4, and 3-19, and the organic dendrimers 3-59, 3-60, and 3-61, and the number of unique steps required along each synthetic pathway. b) Cost-corrected $\sigma_{2,max}$ values with ($\sigma_{2,CLab}$: red) and without ($\sigma_{2,C}$: blue) labor costs.

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yield in a synthetic scheme may result in an easy-to-access scaling factor, which would target the same type of NLO efficiency as described above. Such a scaling factor would also be independent of prices for chemicals, which change regularly over time and from provider to provider.

In summary, the NLO-properties of the N-cored organometallic zero-generation dendrimers 3-3\(^a\) and 3-4\(^a\) and their first-generation analogue 3-19\(^b\) were explored and compared to the structurally related organic N-cored dendrimers 3-59\(^a\)–3-61\(^a\). A variety of scaling factors was applied to \(\sigma_{2,\text{max}}\) values of all six species, which allowed to target specific intrinsic 2PA cross-sections, highlighting the size/molecular weight of the investigated species, their \(\pi\)-conjugation path length or the cost of production. Independent of the chosen scaling factor, the organometallic complexes showed NLO-efficiencies that exceeded those of the organic analogues by 1–2 orders of magnitude, and in some cases by even more than 2 orders of magnitude. When scaled by the size or the molecular weight, both organometallic and organic dendrimers show a dendritic effect on proceeding from the zero- to the first-generation level. This effect is less pronounced or even vanishes when the conjugation path length is used as the scaling factor, particularly when both nitrogen and ruthenium are counted as part of the \(\pi\)-conjugated system, an approach that differs from previously-reported scaling methods, but which I consider more appropriate.

### 3.4.2 Mixed-Metal Dendrimers

Frequency-dependent Z-scan measurements were carried out on the mixed-metal ruthenium-osmium acetylide complexes 3-52\(^b\), 3-55\(^b\), 3-56\(^b\), and 3-58\(^b\).\(^{16}\) The conditions were similar to those described above; the repetition rate at light-intensities of 100 GW cm\(^{-2}\) was 1 kHz, at a pulse length of 130 fs, to avoid contributions from excited state absorption. Measurements were carried out in glass cuvettes of 1 mm thickness as solutions in dichloromethane with a small amount of added triethylamine to avoid decomposition of the complexes in solution. Five frequencies (18,900, 18,000, 12,500, 8300, 6700 cm\(^{-1}\); 530, 555, 800, 1200, 16 Measurements were carried out by Marek Samoc, Malgorzata Wielgus and Joanna Olesiak-Banska at the Wroclaw University of Technology – Institute of Physical and Theoretical Chemistry.
1500 nm) were probed, and it was found that the compounds show photochemical instability at all frequencies except 18900 cm⁻¹ when exposed to the femtosecond laser beam. The effects were particularly pronounced at 18000 cm⁻¹ and 8300 cm⁻¹. What lead to the conclusion that photochemical changes of the examined organometallic complexes must occur under the influence of the focused laser beam was (a) the occurrence of a colored spot in the sample under laser irradiation and (b) a significant asymmetry of the experimental curves during data analysis, which leads to deviations of the experimental curves from the theoretical curves, typically after the focal point (i.e. at \( z \geq 0 \)). Two curve fitting diagrams are given in Figure 3.50, showing the difference between (a) a smooth fit of the experimental data to the theoretical curve and (b) experimental data, showing an asymmetry of detected light-intensities across the full z-range, which leads to a flattening of the experimental curve beyond the focal point. For the reasons given above, measured data at frequencies other than 18900 cm⁻¹ have to be interpreted as resulting from a combination of processes; nonlinear absorption of the complex, followed by absorption and reflection processes, involving the products formed from the complex undergoing photochemical changes may be part of the complex mixture of phenomena. At 18900 cm⁻¹ (530 nm), only the first-generation dendrimer 3-52b showed such effects, whereas the remaining three complexes appeared to behave normal, which means that the NLO data obtained at this frequency were considered as being reliable. The following

**Figure 3.50** Z-scan traces obtained from Z-scans at 18 900 cm⁻¹, shown during the curve fitting process. **(a)** The experimental trace of complex 3-55b (dots) fits the theoretical curve (single-extremum solid trace) before and after the the focal point. **(b)** The experimental trace of first-generation dendrimer 3-52b fits the theoretical curve before the focal point. After the focal point, the experimental curve flattens faster than the theoretical trace, leading to a deviation from each other.
### Table 3.6 Uncorrected and corrected NLO data of the mixed-metal osmium-ruthenium acetylide complexes 3-55\(^b\) 3-56\(^b\) and 3-58\(^b\) in comparison to the nitrogen zero- and first-generation ruthenium acetylide complexes 3-3\(^a\), 3-4\(^a\) and 3-19\(^b\).

<table>
<thead>
<tr>
<th></th>
<th>3-3(^a)</th>
<th>3-4(^a)</th>
<th>3-19(^b)</th>
<th>3-55(^b)</th>
<th>3-56(^b)</th>
<th>3-58(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\tilde{\nu}_{\text{fundamental}}) [cm(^{-1})]</td>
<td>17500</td>
<td>16100</td>
<td>16800</td>
<td>18900</td>
<td>18900</td>
<td>18900</td>
</tr>
<tr>
<td>(\epsilon_{\text{fundamental}}) [M(^{-1}) cm(^{-1})]</td>
<td>500</td>
<td>400</td>
<td>200</td>
<td>4200</td>
<td>2300</td>
<td>4000</td>
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<td>(\sigma_2) [10(^3) GM]</td>
<td>1.7±0.3</td>
<td>1.3±0.3</td>
<td>10.6±0.3</td>
<td>74.5±10.7(^#)</td>
<td>117.9±10.8(^#)</td>
<td>92.3±22.5(^#)</td>
</tr>
<tr>
<td>(\gamma_{\text{Im}}) [10(^{-32}) esu]</td>
<td>0.5±0.05</td>
<td>0.34±0.07</td>
<td>3.05±1.25</td>
<td>13.5±1.92</td>
<td>21.3±1.92</td>
<td>16.7±4.08</td>
</tr>
<tr>
<td>(\gamma_{\text{Re}}) [10(^{-32}) esu]</td>
<td>-1.0±0.3</td>
<td>0.3±0.1</td>
<td>-3.7±0.8</td>
<td>-22.3±1.9</td>
<td>-27.4±0.9</td>
<td>-23.8±4.0</td>
</tr>
<tr>
<td>(MW) [g mol(^{-1})]</td>
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<td>3311.4</td>
<td>10044.0</td>
<td>7455.8</td>
<td>7756.1</td>
<td>7185.7</td>
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<tr>
<td>(N'_{[n,Ru]}) [electrons]</td>
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<td>98.2</td>
<td>72.7</td>
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<td>(N''_{[n,Ru]}) [electrons(^\dagger)]</td>
<td>1024</td>
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<td>9643</td>
<td>5285</td>
<td>7499.6</td>
<td>9604</td>
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<tr>
<td>(\sigma_{2,M}) [GM mol(^{-1}) g(^{-1})]</td>
<td>0.55</td>
<td>0.38</td>
<td>1.06</td>
<td>10.0</td>
<td>15.2</td>
<td>12.8</td>
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<tr>
<td>(\sigma^d_{2,NeRu}) (^d) [GM electron(^{-1})]</td>
<td>53.8</td>
<td>23.1</td>
<td>107.9</td>
<td>1024.8</td>
<td>1361.4</td>
<td>941.8</td>
</tr>
<tr>
<td>(\sigma^d_{2,NeRu}) (^\ast) [GM electron(^{-2})]</td>
<td>1.7</td>
<td>0.4</td>
<td>1.1</td>
<td>14.1</td>
<td>15.7</td>
<td>9.6</td>
</tr>
</tbody>
</table>

\(^#\) \(e > 2000 M^{-1} cm^{-1}\)

\(^d\) in GM electron\(^{-1}\)

\(^\ast\) in GM electron\(^{-2}\)

Discussion is therefore limited to values obtained at 18900 cm\(^{-1}\). Table 3.6 shows the corresponding \(\gamma_{\text{Im}}, \gamma_{\text{Re}}\) and \(\sigma_2\) values in comparison to \(\gamma_{\text{Im,max}}, \gamma_{\text{Re,max}}\) and \(\sigma_{2,max}\) values of the N-cored dendrimers discussed in Section 3.4.1 (page 289 ff). As the reader will find, the aforementioned IPA threshold of 500 M\(^{-1}\) cm\(^{-1}\) is exceeded at the frequency of the fundamental in all mixed-metal Ru-Os complexes, for which reason the data should be treated with care; contributions from IPA may artificially be enhancing the NLO response in those cases. Of the three mixed-metal complexes, the phenyl cored species with two phenyleneethynylene units in the bridge between the ruthenium and the osmium centers gives the strongest response, which is also one order of magnitude larger than the response measured for the all-Ru N-cored first-generation dendrimer 3-19\(^b\) (again, such comparisons of on-resonant values to off-resonant values should be treated with care and a highly critical eye).

In order to draw reliable trends and allow for a fair comparison between homometallic ruthenium acetylide complexes and heterometallic ruthenium-osmium complexes, conditions have to be found that permit (a) the determination of NLO data at off-resonant frequencies without the occurrence of the aforementioned photochemical changes and (b) the evaluation of spectral dependencies of the NLO properties of such mixed-metal complexes.
3.5 Experimental

3.5.1 General part

3.5.1.1 Instrumentation

Electrospray ionization (ESI) mass spectra were recorded using a LCT-ZMD single quadrupole liquid chromatograph-MS (Waters-Micromass). High resolution ESI mass spectra were carried out utilizing a LCT Premier XE ESI-TOF instrument (Waters-Micromass). Organometallic complexes were usually measured in acetonitrile or methanol, using minimal amounts of dichloromethane when lack of solubility necessitated under the following conditions: 12000RP, w+ mode, capillary potential = +3500 V, cone potential = +150 V. Some linear organic molecules required similarly forcing conditions, such as capillary potentials of +3000 V and cone potential of +180 V with added formic acid. EI mass spectra were recorded using a quadrupole VG Autospec EI-MS instrument (Fisons Instruments); all mass spectrometry peaks are reported as m/z ([assignment], relative intensity).

Microanalyses were carried out by the Microanalysis Service Unit at the Research School of Chemistry, Australian National University; standard CHN analyses were carried out on an EA3000 instrument (EuroVector) with U-shaped quartz oxidation tube or on a CE1106 instrument (Carlo Erba) with a straight quartz oxidation tube; standard CHN analyses were carried out on an EA3000 instrument (EuroVector) with U-shaped quartz oxidation tube or on a CE1106 instrument (Carlo Erba) with a straight quartz oxidation tube; Co²⁺/Co³⁺ or chromium dioxide were used as oxidation catalysts, and Cu(0) was used as reduction catalyst; for all organometallic complexes, V₂O₅ combustion agent was added to the samples.

Infrared (IR) spectra were recorded using a Perkin-Elmer System 2000 FT-IR spectrometer as dichloromethane solutions using CaF₂ cells; peaks are reported as frequencies in wavenumbers (cm⁻¹) [Rel. Transm., Assignment].

UV-Vis spectra were recorded on a Cary 5 spectrophotometer as dichloromethane solutions in 1 cm quartz cells; bands are reported as frequencies in wavenumbers (cm⁻¹) [extinction coefficient (10³ M⁻¹ cm⁻¹)].
$^1$H (300 MHz, 500 MHz), $^{13}$C (75 MHz, 126 MHz) and $^{31}$P (121 MHz, 202 MHz) NMR spectra were recorded using a Mercury 300 FT NMR spectrometer or an Innova 500 FT NMR spectrometer, and spectra were referenced to residual chloroform (7.26 ppm), solvent CDCl$_3$ (77.0 ppm) and external H$_3$PO$_4$ (0.0 ppm); $^{11}$B (96 MHz) NMR spectra were recorded on an Innova 300 FT NMR spectrometer and referenced to BF$_3$·Et$_2$O.

Cyclic voltammetry measurements were recorded using an EA161 potentiostat (eDAQ Pty Ltd.) and an e-corder 401 (eDAQ Pty Ltd.) on Echem 2.5.4 software; measurements were carried out at room temperature (RT) using Pt disk working-, Pt wire auxiliary-, and Ag/AgCl reference electrodes, such that the ferrocene/ferrocenium redox couple was located at 0.56 V (peak separation ca. 0.09 V); scan rates were typically 100 mV s$^{-1}$; electrochemical solutions contained 0.1 M NBut$_4$PF$_6$ and about 10$^{-3}$ M complex in freshly distilled and deoxygenated tetrahydrofuran unless stated otherwise; solutions were purged and maintained under a nitrogen or argon atmosphere.

Concentration dependent fluorescence spectrometry was carried out using a Cary Eclipse fluorescence spectrophotometer (Varian) on Cary Eclipse Scan Application software (v. 1.1.; Galactic Industries); solutions were prepared in concentrations of ca. 10$^{-4}$ mol L$^{-1}$ and then diluted down using the same solvent; unless stated otherwise, glass-distilled dichloromethane dried over calcium hydride was used as solvent.

Spectroelectrochemical studies were carried out in solutions of 0.3 M NBut$_4$PF$_6$ in freshly distilled and deoxygenated tetrahydrofuran at room temperature unless stated otherwise; oxidized species were electrogenerated in an optically transparent thin-layer electrochemical (OTTLE) cell with potentials ca 50–200 mV beyond $E_{1/2}$ for each couple, to ensure complete electrolysis. UV-Vis spectra during the oxidation/reduction processes were recorded on a Cary 5 spectrophotometer.

### 3.5.1.2 General synthetic procedures

All reactions were carried out in flame-dried glassware and under a nitrogen atmosphere using standard Schlenk techniques unless stated otherwise. Dichloromethane (DCM) was distilled over calcium hydride, and tetrahydrofuran (THF)
was distilled over sodium/benzophenone prior to use. Triethylamine (NEt₃),
dimethylsulfoxide (dmso), toluene, acetone, methanol (MeOH), n-pentane and
n-hexane were used as received. Petrol refers to a fraction of petroleum with
a boiling range 60–80°C; where applicable, the use of petroleum with a boiling
range 40–60°C is specifically stated.

Trans-halogenation reactions were carried out in tetrahydrofuran. The corre-
sponding workup procedure is the following: Na₂S₂O₃ (aq.) was added to the re-
action mixture at ambient temperature to remove excess iodine. The tetrahydro-
furan was removed under reduced pressure, and dichloromethane was added. The
organic layer was removed, and the aqueous layer was extracted with dichloro-
methane twice. The combined organic layers were washed with water twice and
dried over anhydrous MgSO₄. Filtration through filter paper gave the filtrate
that was taken to dryness under reduced pressure.

All organic materials were purified using column chromatography (silica gel,
230–400 mesh ASTM). Products were eluted using appropriate solvent mixtures,
where polarity gradients were usually used. Small organic by-products and greasy
impurities were usually removed by washing the column with a non-polar solvent,
in most cases n-hexane, n-pentane or petroleum spirit (boiling range 40–60°C).
Mixtures of one of these solvents with ethylacetate (and in some cases dichloro-
methane) was used to increase the polarity and elute the product. In the majority
of purifications, flash column chromatography was used, i.e. pressure was applied
wherever the separation of products and by-products (or starting materials)
allowed this. Where required, activated silica was prepared by heating silica gel
to 120°C for 4–5 days. To generate deactivated silica gel in a controlled fashion
5–10 weight-% of water was added to activated silica; the resultant mixture was
placed into a round-bottom flask that was rotated until a homogeneous powder
was obtained.

In the case of the ruthenium mono-acetylide complexes and bis-acetylide com-
plexes, purifications were attempted based on differing solubilities of products,
starting materials and undesired by-products). For this purpose, concentrated
solutions of the material to be purified in an appropriate solvent (in most cases
dichloromethane with a small amount of added triethylamine) were dropped into
a different solvent or a mixture of solvents. In most cases, smaller components,
such as linear mono-acetylde complexes or wedges, would then remain in solution, whereas the bigger (and less soluble) product would precipitate and be collected by filtration. In almost all cases, several such washings or precipitations were necessary to achieve satisfactory purity of the complexes. Where this point could not be reached, chromatographic purification of organometallic complexes was carried out using ungraded basic alumina. Importantly, negative results have been obtained in some cases, where the alumina was not basic or not sufficiently basic. To ensure a basic environment of the complex during workup at all times, a small amount of triethylamine was added to all eluants or eluant mixtures, and the alumina was washed with a basic eluant, before the column was loaded with the complex. Typically, eluants were mixtures of n-hexane or petroleum spirit (boiling range 40–60 °C) and dichloromethane in ratios between 8:1 to 1:2. A final precipitation of the products from methanol proved to be convenient; the precipitate that forms can easily be isolated by filtration, which is considerably easier than removing products from the walls of reaction flasks.

3.5.1.3 Starting materials

The following starting materials, substrates and catalysts were commercially available, purchased from common chemical suppliers and used as received: 1-bromo-4-iodobenzene, [PdCl₂(PPh₃)₂], [Pd(PPh₃)₄], CuI, KOH, iodine, bromine, Me₃SiC≡CH, i-Pr₃SiC≡CH, PhC≡CH, 1-bromo-2-ethylhexane, NBu₄⁺F (1.0 M in THF), n-BuLi (1.6 M in n-hexane), RuCl₃·3H₂O, 1,3,5-tribromobenzene, 1-bromo-4-nitrobenzene, 1,2-bis(diphenylphosphino)ethane, magnesium.

Commercially available NaPF₆ was recrystallized from acetonitrile prior to use and kept under an argon or nitrogen atmosphere.

The following materials were synthesized using published literature procedures or slight modifications thereof:

- 1,3,5-(Me₃SiC≡C)₃C₆H₃ (procedure⁶⁰⁹, characterization⁶¹⁰)
- 1,3,5-(HC≡C)₃C₆H₃ (procedure⁶⁰⁹, characterization⁶¹⁰)
- 1,3,5-(BrC₆H₄-4-C≡C)₃C₆H₃⁶¹¹
- 1,3,5-(HC≡CC₆H₄-4-C≡C)₃C₆H₃⁶¹⁷
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- 1,3,5-(HC≡CC₆H₄-4-C≡CC₆H₄-4-C≡C)₃C₆H₃[^612]
- (i-Pr)₃SiC≡CC₆H₄-4-C≡CSiMe₃[^629]
- (i-Pr)₃SiC≡CC₆H₄-4-C≡CH[^629]
- Me₉SiC≡CC₆H₄-4-Br[^630]
- Me₉SiC≡CC₆H₄-4-I[^632]
- HC≡CC₆H₄-4-Br[^630]
- (i-Pr)₃SiC≡CC₆H₄-4-C≡CC₆H₄-4-Br[^702]
- (i-Pr)₃SiC≡CC₆H₄-4-C≡CC₆H₄-4-I[^749]
- Me₉SiC≡CC₆H₄-4-C≡CC₆H₄-4-Br[^630]
- Me₉SiC≡CC₆H₄-4-C≡CC₆H₄-4-I[^630]
- HC≡CC₆H₄-4-C≡CC₆H₄-4-I[^750]
- HC≡CC₆H₄-4-C≡CC₆H₄-4-Br[^631]
- [RuCl₂(dmoso)₄][^703]
- cis-[RuCl₂(dppe)₂][^513]
- (HC≡C-4-C₆H₄)₃N[^744]
- {trans-[(dppe)₂ClRu(≡C-4-C₆H₄)]}₃N[^744]
- 1,3-{trans-[(dppe)₂ClRu(≡C)Ru]₂-5-(HC≡C)C₆H₃}[^745]
- 1,3-{trans-[(PhC≡C)Ru(dppe)₂(C≡C)]₂-5-(HC≡C)C₆H₃}[^745]
- (HC≡C-4-C₆Me₄)₃B[^715]

The following new precursors were discussed in Chapter 2:

- 1,3,5-(Me₉SiC≡CC₆H₄-4-C≡CC₆H₄-4-C≡C)₃C₆H₃ (page 190)
- 1,3,5-(Me₉SiC≡CC₆H₄-4-C≡C)₃C₆H₃ (page 190)
- 1,3,5-(BrC₆H₄-4-C≡CC₆H₄-4-C≡C)₃C₆H₃ (page 215)
- 1,3,5-{trans-[(dppe)₂ClRu(≡CC₆H₄-4-C≡CC₆H₄-4-C≡C)]}₃C₆H₃ (page 217)

The following starting materials were kindly supplied by external research groups:
• HC≡C-4-C₆H₄B(mes)₂ (Prof. T. Marder and co-workers, Durham University)

• (Et₃SiC≡C-4-C₆H₄)₃B (Prof. T. Marder and co-workers, Durham University)

• (Me₃SiC≡C-4-C₆H₄)₃N (Prof. P. Low, Durham University)

3.5.2 Syntheses and Characterization of New Compounds

\[1,3-\{\text{trans-}\{\text{dppe}\}_2\text{ClRu(C≡C)}\}\}_2-5-\{\text{Me₃SiC≡CC₆H₄-4-C≡CC₆H₄-4-C≡C}\}_2\text{C₆H₃}\ (3-11)\]

In a flame-dried 250 mL two-neck round-bottom flask, Me₃SiC≡CC₆H₄-4-C≡CC₆H₄-4-I (0.28 g, 0.70 mmol, 1.08 eq.) and 1,3-\{\text{trans-}\{\text{dppe}\}_2\text{ClRu(C≡C)}\}_2-5-\{\text{HC≡C}\}_2\text{C₆H₃}\ (1.30 g, 0.65 mmol, 1.00 eq.) were suspended in deoxygenated triethylamine (60 mL). To the highly cloudy, yellow suspension was added dry, deoxygenated dichloromethane (60 mL) until the mixture turned into a clear solution. The solution was deoxygenated, and [PdCl₂(PPH₃)₂] (0.030 g, 0.04 mmol, 0.07 eq.) and CuI (0.010 g, 0.05 mmol, 0.08 eq.) were added. The mixture was deoxygenated, before being stirred at ambient temperature for 16 h. Alumina was added to the mixture, and the solvent was removed under reduced pressure. A dark yellow powder was obtained, which was loaded onto a short chromatography column over basic alumina (l = 8 cm, Ø = 3.5 cm). The column was washed with a mixture of n-pentane and dichloromethane (10:1). The product was then eluted with a mixture of the same solvents (1:2). The amount of solvent was reduced to 4 mL \textit{in vacuo}. The residual solution was dropped into stirring methanol. A yellow, grainy precipitate was formed, which was removed from the mixture by filtration. The solid residue was washed with small portions of methanol three times and then with n-pentane once.¹⁷ The resultant solid was suspended in diethylether, affording a yellow mixture with undissolved yellow-orange solid. The mixture was filtered, and the residual solid was washed with diethylether five times.

¹⁷ The $^{31}$P{$^{1}$H} NMR spectrum at this point indicated the presence of homocoupled by-product, so further purification steps were necessary.
until the washing solution was a pale yellow color. The solvent of the combined
washing solutions was removed under reduced pressure. A yellow solid was
obtained, which was washed with mixtures of n-pentane and dichloromethane in
ratios of 15:1 (3 times) and 8:1 (once, quickly\textsuperscript{18}) and lastly with neat n-pentane.
The residual solvent was removed under reduced pressure at 30–40 °C, affording
0.91 g (0.40 mmol, 61%) of the product.

Anal. Calcd. for $\text{C}_{135}\text{H}_{116}\text{Cl}_{2}\text{P}_{8}\text{Ru}_{2}\text{Si}$: C 70.89, H 5.11%. Found: C 71.17, H
5.26%. ESI MS: 2292.5 ([M-Cl+MeCN]$^+$, 4), 1360.4 (8), 1149.3 (100), 1145.3
(6), 897.2 (8). HR ESI TOF MS: Calcd. for $\text{C}_{137}\text{H}_{119}\text{NSiP}_{8}^{37}\text{Cl}_{102}\text{Ru}$: 2292.4788.
Found: 2292.4780. IR (CH$_2$Cl$_2$) [Rel. Transm., Assignmnt.]: 1029 [99.5], 1097
[95.3], 1157 [99.3, br], 1192 [99.3, br], 1421 [96.7], 1434 [90.9], 1486 [96.5], 1514
[97.5], 1560 [94.3, br], 2059 [91.2, $\nu$(RuC≡C), br], 2155 [98.4, $\nu$(SiC≡C) br],
2908 [95.7], 3056 [91.7], 3688 [98.9] cm$^{-1}$. UV-Vis ($\bar{\nu}_{\text{max}}$, cm$^{-1}$; $[\varepsilon$, 10$^4$ M$^{-1}$ cm$^{-1}$]):
29400 [192.8], 28200 [151.3, sh]. $^1$H NMR (500 MHz, CDCl$_3$): 7.65–7.59 (m, 16H,
H261), 7.58 (s, 4H, H210, H211), 7.51–7.45 (m, 4H, H204, H205), 7.22–7.14 (m,
24H, H251, H263), 7.14–7.09 (m, 8H, H253), 6.61 (s, 1H, H23), 6.45 (s, 2H, H21),
2.86–2.55 (16H, H270), 0.27 (s, 9H, H10) ppm. $^{31}$P($^1$H) NMR (121 MHz, CDCl$_3$):
$\delta$ 50.57 ppm. $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 136.8 (vtt, $|J_{PC} + 3J_{PC} = 20.0$ Hz,
C250), 135.3 (vtt, $|J_{PC} + 3J_{PC} = 18.7$ Hz, C260), 134.3, 134.2 (C251, C261),
131.9, 131.6 (C204, C205), 131.4 (C210, C211), 129.7, 129.6 (C23, C21), 129.5
(C22) 128.9, 128.7 (C253, C263), 127.2, 126.9 (C252, C262), 124.4, 122.2 (C209,
C212), 124.1 (C216), 123.12, 123.06 (C206, C203), 121.0 (C20), 113.8 (C215),
104.6 (C202), 96.4 (C201), 93.3 (C214), 91.2, 90.7 (C207, C208), 873.3 (C213),
30.8 (C270, vtt, $|J_{PC} + 3J_{PC} = 22.9$ Hz, C260), -0.08 (C10) ppm.

$^\circ -\{(\text{trans-}[\text{dppe}]_2\text{ClRu}(\text{C≡C})\}_2 - 5-\{(\text{i-Pr}_3\text{SiC≡CC}\text{H}_4 -4\text{-C≡CC}\text{H}_4 -4\text{-Br (0.75 g, 1.71 mmol, 4.6 eq.) was dissolved in triethylamine (50 mL). The clear, colorless solution was deoxygenated thoroughly.\\

\textsuperscript{18} The solubility of the product in a mixture of n-pentane and dichloromethane (8:1) is significant, so the product should not be left in such a solvent mixture for too long to avoid substantial losses of the desired material.
1,3-{trans-[(dppe)$_2$ClRu(C≡C)]}$_2$-5-(HC≡C)C$_6$H$_3$ (3-9$^*$) (0.75 g, 0.37 mmol, 1.0 eq.) and [Pd(PPh$_3$)$_4$] (0.040 g, 0.03 mmol, 0.09 eq.) were added. The cloudy, yellow mixture was deoxygenated again, before dichloromethane (50 mL) was added until all material had dissolved. The resultant solution was deoxygenated once more and was then stirred at 45 °C for 16 h. The addition of [Pd(PPh$_3$)$_4$] (0.020 g, 0.02 mmol, 0.05 eq.) and i-Pr$_3$SiC≡CC$_6$H$_4$-4-C≡CC$_6$H$_4$-4-Br (2-32$^*$) (0.12 g, 0.27 mmol, 0.74) was repeated, and the resultant reaction mixture was heated at reflux for 16 h. The amount of solvent was reduced in vacuo, and the residual suspension was filtered through cotton wool. The clear filtrate was dropped into stirring methanol, after which a yellow precipitate was formed. The solid was separated from the solution by filtration through a sintered glass filter funnel. The solid was adsorbed onto basic alumina, and a short chromatography column over basic alumina was charged with the yellow powder. The product was eluted with a basic mixture of n-hexane and dichloromethane (4:1). The solvent was removed in vacuo, affording 0.71 g (0.30 mmol, 80%) of the product.

Anal. Calcd. for C$_{141}$H$_{226}$Cl$_2$P$_8$Ru$_2$Si: C 71.41, H 5.44%. Found: C 71.26, H 5.49%. ESI MS: 2376.4 ([M - Cl + MeCN]$^+$, 10), 1444.4 ([M - Cl - RuCl(dppe)$_2$ + MeCN]$^+$, 25), 1150.3 ([M - 2 Cl]$^{2+}$, 100). IR (CH$_2$Cl$_2$) [Rel. Transm., Assignm.]: 1000 [95.6], 1028 [96.3], 1074 [96.9], 1097 [79.0], 1192 [97.4, br], 1434 [64.3], 1486 [84.7], 1515 [88.4], 1561 [77.3, br], 2059 [65.2, $\nu$(RuC≡C)], br, 2153 [96.5, $\nu$(SiC≡C)], 2867 [90.8], 2919 [53.0], 3056 [83.5, br] cm$^{-1}$. UV-Vis (\(\bar{\epsilon}_{\text{max}}\), cm$^{-1}$ [\(\epsilon\)], 10$^3$ M$^{-1}$ cm$^{-1}$): 28300 [154.1], 29400 [192.6]. $^1$H NMR (500 MHz, CDCl$_3$): \(\delta\) 7.64–7.60 (m, 16H, H261), 7.59 (s, 6H, H210, H211), 7.49 (d, \(J_{HH} = 2.3\) Hz, 6H, H204, H205), 7.21–7.15 (m, 24H, H251, H253), 7.15–7.09 (m, 32H, H252, H262), 6.61 (s, 1H, H23), 6.45 (s, 2H, H21), 2.84–2.60 (m, 16H, H270), 1.15 (s, 21H, H10, H11) ppm. $^{31}$P{$^1$H} NMR (121 MHz, CDCl$_3$): $\delta$ 50.5 ppm. $^{13}$C{$^1$H} NMR (126 MHz, CDCl$_3$): $\delta$ 138.6 (vtt, $|J_{PC} + 3|J_{FC}| = 20.0$ Hz, C250), 135.3 (vtt, $|J_{PC} + 3|J_{FC}| = 20.0$ Hz, C260), 134.3, 134.4 (C251, C261), 133.0, 131.6 (C204, C205), 131.4 (C210, C211), 129.7, 129.6 (C21, C23), 129.4 (C22), 128.9, 128.7 (C252, C262), 124.4, 122.3 (C209, C212), 124.1 (C216), 121.3, 122.9 (C204, C205), 121.0 (C20), 93.3 (C214), 92.9 (C201), 91.1 (C207), 90.8 (C208), 87.4 (C213), 30.8 (vtt, $|J_{PC} + 3|J_{FC}| = 23.0$ Hz, C270), 18.9 (C11), 11.3 (C10) ppm.
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1,3-\{trans-[(PhC≡C)Ru(dppe)₂(C≡C)]\}_2-5-(Me₃SiC≡CC₆H₄-4-C≡CC₆H₄-4-C≡C)C₆H₃ (3-13⁺)¹⁹

**Method a:** In a flame-dried 100 mL two-neck round-bottom flask fitted with a condenser, 1,3-\{trans-[(dppe)₂ClRu(C≡C)]\}_2-5-(Me₃SiC≡CC₆H₄-4-C≡CC₆H₄-4-C≡C)C₆H₃ (3-11) (0.28 g, 0.12 mmol, 1.0 eq.) was dissolved in freshly distilled and deoxygenated dichloromethane (70 mL). To the clear, yellow solution were added NaPF₆ (0.20 g, 1.19 mmol, 9.7 eq.) and triethylamine (5 drops). The resultant, slightly cloudy, dark yellow mixture was deoxygenated, and phenylacetylene (0.32 mL, 0.30 g, 2.94 mmol, 24 eq.) was added. The reaction mixture was heated at reflux for 2 h, giving an orange, cloudy mixture. The amount of solvent was reduced to 3 mL in vacuo. A highly cloudy, orange-brown residue was obtained that was dropped into stirring methanol (50 mL). A thick, yellow precipitate was formed that was removed from the solution by filtration through a sintered glass filter funnel (pore size G3). The solid, dark yellow residue was suspended in dichloromethane (4 mL) with a small amount of added triethylamine. An orange suspension was obtained that was filtered through tightly packed cotton wool. A clear, orange solution was obtained that was dropped into stirring n-pentane (60 mL). A yellow precipitate was formed. The solution was removed from the solid by filtration through a sintered glass filter funnel (pore size G3). The yellow, solid residue was dried under vacuum at 30–40 °C for 12 h, giving 0.21 g (0.086 mmol, 70%) of the product.

**Method b:** In a flame-dried 100 mL two-neck round-bottom flask, 1,3-\{trans-[(PhC≡C)Ru(dppe)₂(C≡C)]\}_2-5-(HC≡C≡C)C₆H₃ (3-10⁺) (0.18 g, 0.084 mmol, 1.0 eq.) was suspended in deoxygenated triethylamine (40 mL). The inhomogeneous mixture was deoxygenated, and dry, deoxygenated dichloromethane (15 mL) was added until a clear, yellow solution was obtained, which was deoxygenated, before Me₃SiC≡CC₆H₄-4-C≡CC₆H₄-4-I (2-25⁺) (0.080 g, 0.20 mmol, 2.4 eq.) was added. The solution was deoxygenated, and [Pd(PPh₃)₄] and CuI were added in catalytic amounts. The resultant clear, yellow solution was stirred at room temperature for 26 h. The solvent was removed under reduced

¹⁹ This compound has been synthesized by Dr. Katy Green as part of her Honours Thesis (ANU, 2007). Since the characterization data therein was lacking crucial elements, I present the data along with the reaction conditions that I have chosen here to add to Dr. Green’s data. The same applies to the complexes 3-15⁺ and 3-17⁺.
pressure, and the dark orange, solid residue was suspended in a mixture of 
$n$-pentane and dichloromethane (5:2). The resultant mixture was stirred for 
5 min and was then filtered through a sintered glass filter funnel. The clear, 
yellow filtrate was taken to dryness under reduced pressure, giving a solid residue, 
which was suspended in dichloromethane (4 mL). The cloudy, orange mixture was 
filtered through cotton wool. The resultant orange solution was dropped into 
stirring $n$-pentane. A yellow, flocculent precipitate was formed that was isolated 
by filtration. The solid was suspended in diethylether (80 mL) with a small 
amount of added triethylamine, and the resultant mixture was stirred vigorously 
for 30 min before being filtered through a sintered glass filter funnel (pore size 
G3). A beige-brown, solid residue and a yellow, clear filtrate were obtained. 
The filtrate was taken to dryness under reduced pressure, giving an orange-brown 
residue, which was dissolved in dichloromethane (2 mL). The resultant solution 
was dropped into stirring $n$-pentane. A pale yellow, flocculent precipitate was 
formed that was removed from the clear, yellow filtrate. The pale yellow solid 
was dried under vacuum, giving 0.14 g (0.058 mmol, 69%) of the product.

Anal. Calcd. for $C_{151}H_{126}P_8Ru_2Si$: C 74.99, H 5.25%. Found: C 74.83, H 5.26%. 
ESI MS: 2419.6 ([M + H]$^+$, 6), 2063.5 (3), 1790.5 (3), 1051.2 (100), 859.2 
(30), 727.5 (40), 651.5 (45). HR ESI TOF MS: Calcd. for $C_{151}H_{127}P_8^{102}Ru_2$: 
2419.5695. Found: 2419.5754. IR (CH$_2$Cl$_2$): 1000 [97.5], 1027 [97.2], 1097 
[89.3], 1434 [82.5], 1484 [87.5], 1514 [95.3], 1560 [88.1], 1592 [92.5], 2055 [69.8, 
$\nu$(Ru-$\equiv$C)], br], 2156 [97.6, $\nu$(Si-$\equiv$C)], 2910 [85.1], 2920 [88.2], 2924 [86.0, 
2954 [66.0], 2962 [68.0], 3054 [90.6] cm$^{-1}$. UV-Vis ($\bar{\nu}_{\text{max}}$, cm$^{-1}$ [$\varepsilon$, 10$^3$ M$^{-1}$ cm$^{-1}$]): 
29 500 [128.9], 27 900 [98.6]. $^1$H NMR (500 MHz, CDCl$_3$): 7.64–7.54 (m, 20H, 
H210, H211, H261), 7.52–7.44 (m, 4H, H204, H205), 7.49–7.40 (m, 16H, H251), 
7.19–7.13 (m, 8H, H253), 7.13–7.06 (m, 12H, H263, H305), 7.03–6.97 (m, 4H, 
H306), 6.99–6.89 (m, 32H, H252, H262), 6.76, 6.75 (s, 5H, H23, H304), 6.52 
(s, 2H, H21), 2.76–2.61 (m, 16H, H270), 0.27 (s, 9H, H10) ppm. $^{31}$P{$^1$H} NMR 
(121 MHz, CDCl$_3$): $\delta$ 50.58 ppm. $^{13}$C{$^1$H} NMR (126 MHz, CDCl$_3$): $\delta$ 137.2 (vtt, 
$^1J_{\text{PC}} + ^3J_{\text{PC}} = 18.3$ Hz, C250), 136.9 (vtt, $^1J_{\text{PC}} + ^3J_{\text{PC}} = 19.1$ Hz, C260), 
134.3, 134.1 (C251, C262), 131.9, 131.6 (C204, C205), 131.4 (C210, C211), 130.6

20 The solubility of the homocoupled byproduct, which can be formed under Sonogashira cross- 
coupling conditions, is poor, whereas the solubility of the product is considerably better. Thus, 
suspending a mixture of the two products in diethylether permits separation.

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(C303), 130.0 (C304), 129.6 (C22), 128.7, 128.5 (C253, C263), 127.3 (C305), 127.1, 127.0 (C252, C253), 124.5, 122.2 (C209, C211), 123.2, 123.0 (C203, C206), 122.7 (C306), 120.9 (C20), 116.8 (C215), 116.1 (C302), 104.7 (C202), 96.4 (C201), 93.4 (C214), 91.2 (C208), 90.7 (C207), 87.3 (C213), 31.6 (vtt, $^3J_{PC} = 23.4$ Hz, C270), -0.1 (C10) ppm.

$1,3-\{\text{trans-}[(\text{PhC}≡\text{C})\text{Ru(dppe)}_2(\text{C≡C})]\}_2\text{5-}(\text{i-Pr}_3\text{SiC≡CC}_6\text{H}_4·4·\text{C≡CC}_6\text{H}_4·4·\text{C≡C})\text{C}_6\text{H}_3$

In a flame-dried 250 mL two-neck round bottom flask fitted with a condenser, 1,3-{trans-}[(dppe)$_2$ClRu(≡C≡C)]$_2$5-(i-Pr$_3$SiC≡CC$_6$H$_4$·4·C≡CC$_6$H$_4$·4·C≡C)C$_6$H$_3$

(0.62 g, 0.26 mmol, 1.0 eq.) was dissolved in dry dichloromethane (130 mL). To the clear, yellow solution were added NaPF$_6$ (1.46 mmol, 7.5 eq.) and phenylacetylene (0.44 mL, 0.40 g, 3.92 mmol, 15.0 eq.), after which the mixture became slightly cloudy and changed to an orange color. Triethylamine (12 drops) was added, after which the mixture changed back to yellow, still being slightly cloudy. The reaction mixture was heated at reflux for 24 h. The volume of the mixture was reduced in vacuo, and triethylamine (0.5 mL) and alumina were added. The residual solvent was removed under reduced pressure, affording a yellow powder that was loaded onto a chromatography column over basic alumina. The product was eluted with a mixture of petrol and dichloromethane (2:1). The solvent was removed from the yellow filtrate in vacuo, giving a yellow solid that was dissolved in a minimal amount of dichloromethane. The resultant solution was pipetted into stirring methanol (100 mL), affording a flocculent, yellow precipitate. The solid was isolated by filtration through a sintered glass filter funnel and washed with n-hexane. The product was dried under vacuum to afford 0.52 g (0.21 mmol, 80%) of the desired complex.

Anal. Calcd. for C$_{157}$H$_{138}$P$_8$Ru$_2$Si: C 75.34, H 5.56%. Found: C 75.16, H 5.20%. ESI MS (CH$_2$Cl$_2$/MeOH): 2503.7 ([M + H]$^+$), 33. HR TOF ESI MS: Calcd. for C$_{157}$H$_{139}$SiP$_8$Ru$_2$: 2503.6634. Found: 2503.6677. IR (CH$_2$Cl$_2$) [Rel. Transm., Assignm.]: 998 [97.8], 1017 [99.1], 1029 [98.5], 1070 [98.8], 1098 [92.2], 1434 [86.6], 1490 [90.2], 1516 [96.2], 1560 [91.0], 1592 [94.8], 2056 [73.0, $\nu$(Ru=C≡C), br], 2153 [99.6, $\nu$(SiC≡C)], 2867 [97.2], 3049 [96.4], 3063 [97.4] cm$^{-1}$. UV-Vis ($\nu_{\text{max}}$, cm$^{-1}$ [ε,
10³ M⁻¹ cm⁻¹]): 29 400 [112.1], 28 100 [87.9]. ¹H NMR (500 MHz, CDCl₃): δ 7.65–7.57 (m, 16H, H₂61), 7.61 (s, 4H, H₂10, H₂11), 7.51, 7.50 (s, 4H, H₂04, H₂05), 7.49–7.40 (m, 16H, H₂51), 7.20–7.14, 7.14–7.09 (m, 16H, H₂53, H₂63), 7.16–7.12 (m, 4H, H₃05), 7.04–7.01 (m, 2H, H₃06), 7.00–6.93 (m, 32H, H₂25, H₂26), 6.79–6.75 (m, 5H, H₃04, H₂3), 6.54 (m, 2H, H₂1), 2.76–2.66 (m, 16H, H₂70), 1.16 (s, 21H, H₁0, H₁1) ppm. ³¹P{¹H} NMR (121 MHz, CDCl₃): δ 54.47 ppm. ¹³C{¹H} NMR (126 MHz, CDCl₃): δ 137.2 (vtt, |¹J₉C + ³J₉C| = 19.0 Hz, C₂50), 136.9 (vtt, |¹J₉C + ³J₉C| = 19.4 Hz, C₂60), 134.3, 134.1 (C₂51, C₂61), 132.0, 131.6 (C₂04, C₂05), 131.40, 131.36 (C₂10, C₂11), 130.6 (C₃03), 130.0 (C₃04), 129.6 (C₂2), 128.7, 128.5 (C₂53, C₂63), 127.3 (C₃05), 127.1, 127.0 (C₂52, C₂62), 124.5, 122.19 (C₂09, C₂12), 123.5, 122.9 (C₂03, C₂06), 122.7 (C₃06), 120.9 (C₂0), 116.8, 116.1 (C₃02, C₂15), 106.60 (C₂02), 93.4 (C₂14), 92.9 (C₂01), 91.1 (C₂07), 90.8 (C₂08), 87.3 (C₂13), 31.6 (vtt, |¹J₉C + ³J₉C| = 23.7 Hz, C₁70), 18.7 (C₁1), 11.3 (C₁0) ppm.

1,3-{trans-[(PhC≡C)Ru(dppe)₂(C≡C)]}₂-5-(HC≡CC₆H₄-4-C≡CC₆H₄-4-C≡C)C₆H₃ (3-17*)

**Method a:** In a flame-dried 100 mL two-neck round-bottom flask, 1,3-{trans-[(dppe)₂ClRu(C≡C)]}₂-5-(i-Pr₃SiC≡CC₆H₄-4-C≡CC₆H₄-4-C≡C)C₆H₃ (3-15) (0.49 g, 0.195 mmol, 1.0 eq) was dissolved in freshly distilled dichloromethane (90 mL). The clear, yellow solution was deoxygenated, and NBu₄F (1.0 M solution in THF; 1.53 mL, 1.53 mmol, 7.8 eq.) was added, after which the reaction mixture became a deep orange color. The solution was stirred at ambient temperature for 7 h, affording a clear, red solution. Triethylamine (0.5 mL) and alumina were added. The solvent was removed under reduced pressure, giving an orange powder that was loaded onto a short chromatography column over basic alumina. The product was eluted with a mixture of petrol and dichloromethane (1:1). Removal of the solvent under reduced pressure afforded an orange, amorphous solid, which was dissolved in dichloromethane with a small amount of added triethylamine. The resultant solution was pipetted into stirring methanol, giving an orange precipitate. The mixture was filtered

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through a sintered glass filter funnel, and the solid residue was washed with n-hexane. The residual solvent was removed \textit{in vacuo}, giving 0.39 g (0.17 mmol, 87\%) of the desired solid as a pale orange solid.

**Method b:** In a flame-dried 100 mL two-neck round-bottom flask, 1,3-\{trans-[(dppe)$_2$ClRu(C≡C)]\}$_2$-5-(Me$_2$SiC≡CC$_6$H$_4$-4-C≡CC$_6$H$_4$-4-C≡C)C$_6$H$_3$ (3-13$^\star$) (0.18 g, 0.074 mmol, 1.0 eq) was dissolved in freshly dissolved and deoxygenated dichloromethane (70 mL). NBu$_4$F (1.0 M solution in THF; 0.80 mL, 0.80 mmol, 10.8 eq.) was added, which was accompanied by no apparent macroscopic change. The clear, yellow solution was stirred at ambient temperature for 12 h, after which the solution became slightly darker. The volume of the solution was reduced to 2 mL \textit{in vacuo}, and the residue was dropped into stirring methanol (60 mL). A yellow, flocculent precipitate was formed, which was removed from the solution by filtration. The solid thus obtained was redissolved in dichloromethane (4 mL). The orange, clear solution was dropped into stirring n-pentane, after which a flocculent, pale yellow precipitate was formed that was isolated by filtration through a sintered glass filter funnel (pore size G4). Drying under vacuum at 30–40 °C afforded 0.13 mg (0.055 mmol, 74\%) of the product.

**Analytical data:**

Anal. Calcd. for C$_{148}$H$_{118}$P$_8$Ru$_2$: C 75.76, H 5.07%. Found: C 75.68, H 5.12%.

**IR (CH$_2$Cl$_2$):** [Rel. Transm., Assignm.]: 998 [98.0], 1027 [97.9], 1103 [93.5], 1435 [89.6], 1485 [92.2], 1515 [97.3], 1561 [92.4], 1593 [95.3], 2056 [79.5, $\nu$(RuC≡C)], 2919 [77.6], 2953 [80.0], 2963 [72.2], 3052 [94.6, br], 3297 [98.6, $\nu$(C≡C-H)] cm$^{-1}$.

**ESI MS:** 2369.5 ([M - H + Na$^+$], 5), 2347.5 ([M + H$^+$], 20), 2146.4 ([M - 2 C$_6$H$_5$ + 2 H$^+$], 15), 898.2 ([Ru(dppe)$_2$]$^+$, 100).

**HR-ESI MS:** Calcd. for C$_{148}$H$_{118}$P$_8$Ru$_2$: 2347.5300; Found: 2347.5339.

**UV-Vis:** ($\nu_{\text{max}}$, cm$^{-1}$ [ε, 10$^3$ M$^{-1}$ cm$^{-1}$]): 29 600 [128.9], 28 000 [101.6, sh].

**$^1$H NMR (500 MHz, CDCl$_3$):** δ 7.65–7.58 (m, 16H, H261), 7.61 (s, 4H, H210, H211), 7.55–7.49 (m, 4H, H204, H205), 7.49–7.44 (m, 16H, H251), 7.20–7.15, 7.13–7.09 (m, 16H, H253, H263), 7.16–7.12 (m, 4H, H305), 7.05–6.99 (m, 2H, H306), 7.00–6.93 (m, 32H, H252, H262), 6.79–6.75 (m, 5H, H304, H23), 6.55–6.53 (m, 2H, H21), 3.20 (s, 1H, H201), 2.77–2.67 (m, 16H, H270) ppm. $^{31}$P($^1$H) NMR. (121.5 ppm, CDCl$_3$): δ 54.55 (8P, Ru(Ph$_2$P(CH$_2$)$_2$PPh$_2$)$_2$ ppm).

**$^{13}$C($^1$H) NMR (126 MHz, CDCl$_3$):** δ 137.2, 136.9 (vtt, $^1$J$_{PC}$ + $^3$J$_{PC}$ = 19.1 Hz, vtt, $^1$J$_{PC}$ + $^3$J$_{PC}$ = 19.6 Hz, C250, C260), 134.3, 134.1 (C251, C261), 132.1, 131.6 (C204, C205), 131.80 (C216, C301), 131.47, 131.41 (C210, C211), 130.6 (C303), 130.0 (C304), 129.6 (C21, C22, C23), 128.7,
128.5 (C253, C263), 127.3 (C305), 127.1, 127.0 (C252, C253), 124.6, 122.1 (C209, C212), 123.6 (C206), 122.7 (C305), 122.0 (C203), 120.9 (C20), 116.8, 116.1 (C302, C215), 93.5 (C214), 91.3, 90.5 (C208, C207), 87.3 (C213), 83.2 (C202), 79.0 (C201), 31.57 (vtt, $|1J_{PC} + 3J_{PC}| = 23.8$ Hz, C170) ppm.

1,3-\{trans-[(O$_2$NC$_6$H$_4$-4-C≡C)Ru(dppe)$_2$(C≡C)]\}$_2$-5-(Me$_3$SiC≡CC$_6$H$_4$-4-C≡C)C$_6$H$_5$ (3-16)

In a flame-dried 100 mL round-bottom flask fitted with a condenser, 1,3-\{trans-[(dppe)$_2$ClRu(C≡C)]\}$_2$-5-(Me$_3$SiC≡CC$_6$H$_4$-4-C≡CC$_6$H$_4$-4-C≡C)C$_6$H$_5$ (3-11) (0.30 g, 0.13 mmol, 1.0 eq.) was dissolved in freshly distilled and deoxygenated dichloromethane (80 mL). The clear, yellow solution was deoxygenated twice, and para-nitrophenylacetylene (0.045 g, 0.31 mmol, 2.3 eq.) was added. After deoxygenating again, NaPF$_6$ (0.060 g, 0.36 mmol, 2.7 eq.) was added, after which the yellow solution became orange. Triethylamine (3 drops) was added, and the resultant reaction mixture was deoxygenated, before being heated at reflux for 2 h. Triethylamine (3 drops)$^{22}$ was added, and the deep-red mixture was further heated at reflux for 18 h. The amount of solvent was reduced to 2 mL in vacuo, and the residual suspension was filtered through tightly packed cotton wool. The clear, dark red solution was dropped into stirring methanol, affording a dark red precipitate. After filtration, a red solid was obtained, which was redissolved in dichloromethane (2 mL). The resultant solution was filtered through cotton wool into a mixture of n-pentane and dichloromethane (20:1). Filtration and drying of the solid residue under vacuum afforded 0.28 g (0.11 mmol, 84%) of the brick-red product.

Anal. Calcd. for C$_{151}$H$_{124}$N$_2$O$_4$P$_8$Ru$_2$Si: C 72.29, H 4.98, N 1.12%. Found: C 72.36, H 5.14, N 1.01%. ESI MS: 2508.6 ([M]$^+$, 65), 1944.3 (100), 1661.2 (10), 1190.2 (35), 1085 (82). HR ESI TOF MS: Calcd. for C$_{151}$H$_{124}$N$_2$O$_4$P$_8$Ru$_2$Si: 2509.5397. Found: 2509.5479. IR (CH$_2$Cl$_2$) [Rel. Transm., Assignm.]: 999

$^{22}$ Before this reaction, unsuccessful attempts to form bis-acetylide complexes had been encountered, and the amount of triethylamine used in the reactions seemed to be crucial. Therefore, care was taken in this respect thereafter, which is the reason for repeated addition of small portions (a few drops each time) of triethylamine, rather than using one larger portion at the beginning.
CHAPTER 3. Dendrimers - Branched Octupolar Ruthenium Acetylide and Mixed-Metal Ruthenium-Osmium Acetylide Complexes

[83.5,sh], 1107 [68.0], 1174 [91.6], 1323 [27.8], 1435 [79.3], 1487 [85.8], 1500 [81.7], 1563 [83.4,sh], 1582 [54.4], 2049 [ν(RuC≡C)], 31.0, 2156 [96.0, ν(SiC≡C)], 2918 [82.2], 2959 [80.1], 3050 [92.6,sh], 3059 [89.5] cm⁻¹. UV-Vis (νmax, cm⁻¹ [ε, 10³ M⁻¹ cm⁻¹]): 20 600 [36.3], 28 500 [7.12, sh], 29 500 [8.61]. ¹H NMR (300 MHz, CDCl₃): δ 7.99 (d, JHH = 8.8 Hz, 4H, H305), 7.78–7.69 (m, 16H, H261), 7.61 (s, 4H, H210, H211), 7.56–7.46 (m, 4H, H204, H205), 7.32–7.23 (m, 18H, H251), 7.23–7.10 (m, 18H, H253, H263), 7.06–6.90 (m, H252, H262), 6.85 (s, 1H, H23), 6.72 (s, 2H, H21), 6.55 (d, JHH = 8.8 Hz, 4H, H304), 2.78–2.65 (m, 18H, H270), 0.29 (s, 9H, H10) ppm. ³¹P [¹H] NMR (121 MHz, C₆D₆): δ 54.07 ppm. ¹³C [¹H] NMR (126 MHz, CDCl₃): δ 142.5 (C306), 137.4 (C303), 136.9 (vtt, JPC + ³JPC = 19.0 Hz, C250), 136.20 (vtt, JPC + ³JPC = 17.7 Hz, C260), 134.3 (C261), 133.7 (C251), 131.9, 131.6 (C204, C205), 131.42, 131.38 (C210, C211), 129.9 (C304), 129.8 (C22), 129.0, 128.75 (C263, C253), 127.3, 127.1 (C252, C263), 124.3, 122.37 (C209, C212), 123.3 (C203), 123.1 (C203, C206), 121.4 (C20), 118.5, 118.3 (C302, C215), 104.6 (C203), 96.5 (C201), 93.0 (C214), 93.0 (C214), 91.1, 90.81 (C207, C208), 87.6 (C213), 31.43 (vtt, JPC + ³JPC = 23.2 Hz, C270), -0.1 (C10) ppm.

1,3-{trans-[(O₂NC₆H₄-4-C≡C)Ru(dppe)₂(C≡C)]}₂-5-(HC≡CC₆H₄-4-C≡CC₆H₄-4-C≡C)C₆H₉ (3-18)

In a flame-dried 100 mL two-neck round-bottom flask, 1,3-{trans-[(O₂NC₆H₄-4-C≡C)Ru(dppe)₂(C≡C)]}₂-5-(C≡CC₆H₄-4-C≡CC₆H₄-4-C≡C)C₆H₉ (3-16) (0.213 g, 0.08 mmol, 1.0 eq.) was dissolved and dry and deoxygenated dichloromethane (80 mL). The dark red solution was deoxygenated, and NBu₄F (1.0 M solution in THF; 0.30 mL, 0.30 mmol, 3.5 eq.) was added. The resultant solution was stirred at ambient temperature for 28 h. The volume of the solution was reduced to 2 mL in vacuo, and the residual mixture was dropped into stirring methanol. A dark red precipitate was formed, which was separated from the clear, orange-red solution by filtration through a sintered glass filter funnel. The solid thus obtained was redissolved in a minimal amount of dichloromethane. The resultant, dark red solution was filtered through tightly packed cotton wool. The clear filtrate was dropped into stirring n-pentane, giving a flocculent, brick-red precipitate, which was separated from the clear.
orange solution by filtration through a sintered glass filter funnel. A red solid was obtained that was dried under vacuum, affording 0.18 g (0.075 mmol, 88%) of the product.

Anal. Calcd. for $\text{C}_{148}\text{H}_{116}\text{N}_2\text{O}_4\text{P}_8\text{Ru}_2$: C 72.96, H 4.80, N 1.15%. Found: C 73.09, H 4.61, N 0.90%. ESI MS: 2437.5 ([M + H]$^+$, 4), 1790.5 (2), 1688.5 (2), 1072.2 (58), 1051.2 (100). HR TOF ESI MS: Calcd. for $\text{C}_{148}\text{H}_{117}\text{N}_2\text{O}_4\text{P}_8$$^{102}$Ru$_2$: 2437.5001. Found: 2437.5039. IR (CH$_2$Cl$_2$) [Rel. Transm., Assignm.]: 1099 [93.8, sh], 1107 [88.5], 1175 [97.2], 1324 [67.0], 1435 [91.3], 1486 [94.4], 1499 [94.0], 1515 [96.9], 1560 [92.1], 1581 [82.8], 2046 [67.7, $\nu$(RuC≡C)], 2064 [93.4], 3057 [94.9], 3296 [99.3, C≡C-H] cm$^{-1}$. UV-Vis ($\nu_{\text{max}}$, cm$^{-1}$ [$\epsilon$, $10^3$ M$^{-1}$ cm$^{-1}$]): 20600 [49.0], 28500 [93.7], 29700 [114.7]. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.98 (d, $J_{\text{HH}}$ = 9.0 Hz, 4H, H305), 7.75–7.68 (m, 16H, H251), 7.60 (s, 4H, H210, H211), 7.54–7.47 (m, 4H, H204, H205), 7.26–7.20 (m, 16H, H261), 7.20–7.15, 7.15–7.08 (m, 16H, H261, H251), 7.02–6.95, 6.95–6.88 (m, 32H, H252, H262), 6.83 (s, 1H, H23), 6.69 (s, 2H, H21), 6.52 (d, $J_{\text{HH}}$ = 8.9 Hz, 4H, H304), 3.20 (s, 1H, H201), 2.75–2.63 (m, 16H, H270) ppm. $^{31}$P($^1$H) NMR (121 MHz, CDCl$_3$): $\delta$ 54.01 ppm. $^{13}$C($^1$H) NMR (126 MHz, CDCl$_3$): $\delta$ 142.4 (C306), 137.4 (C303), 136.8 (vtt, $^1$J$_{\text{PC}}$ + $^3$J$_{\text{PC}}$ = 19.7 Hz, C250), 136.2 (vtt, $^1$J$_{\text{PC}}$ + $^3$J$_{\text{PC}}$ = 19.4 Hz, C260), 134.3, 133.7 (C251, C261), 132.1 (C204), 131.7 (C205), 131.5, 131.4 (C210, C211), 129.9 (C304), 129.8 (C23), 129.6 (C21), 129.0, 128.7 (C253, C263), 127.2, 127.1 (C252, C262), 124.3, 122.3 (C209, C212), 123.5 (C206), 123.3 (C305), 122.0 (C203), 121.3 (C20), 118.5 (C302), 118.3 (C215), 93.0 (C214), 91.2 (C208), 90.6 (C207), 87.6 (C213), 83.2 (C202), 79.1 (C201), 31.4 (vtt, $^1$J$_{\text{PC}}$ + $^3$J$_{\text{PC}}$ = 23.8 Hz, C270) ppm.

In a flame-dried 100 mL two-neck round-bottom flask fitted with a condenser, HC≡C$_6$H$_4$-4-B(mes)$_2$ (3-32$^a$) (0.060 g, 0.17 mmol, 2.2 eq.)$^{23}$ was dissolved in freshly distilled and deoxygenated dichloromethane (90 mL). To the clear, colorless solution were added 1,3-$\{\text{trans-}[(\text{dppe})_{2}\text{ClRu(C≡C)}]_{2}$-$^5$-$(\text{Mes}_3\text{SiC}=\text{CC}_6\text{H}_4$-4-C≡C$=\text{CC}_6\text{H}_4$-4-C≡C$=\text{C}_6\text{H}_3$ (3-14)

$^{23}$The material was kindly provided by Prof. Todd B. Marder and co-workers (Durham University).
and NaPF₆ (0.060 g, 0.36 mmol, 4.5 eq.). The clear, yellow solution was deoxygenated, and triethylamine (2 drops) was added. The resultant solution was stirred in refluxing dichloromethane for 8 h. HC≡CC₆H₄-4-B(mes)₂ (0.015 g, 0.06 mmol, 0.6 eq.) was added, and the solution was further heated at reflux for 24 h. Over this time, a color change occurred from yellow to orange. The volume of the solution was reduced to 2 mL in vacuo. The residual solution was filtered through cotton wool and was dropped into stirring methanol. A fine, yellow precipitate was formed, resulting in the formation of a yellow suspension. Filtration through a sintered glass filter funnel (pore size G4) allowed the separation of a yellow solid from the orange, slightly cloudy filtrate. The solid was dissolved in dichloromethane (1 mL), and the orange solution was filtered through cotton wool. The clear filtrate was dropped into stirring n-pentane. A yellow, flocculent precipitate was formed, which was removed from the solution by filtration. A solid residue was obtained, which was dried under vacuum to afford 0.173 g (0.059 mmol, 75%) of the product as a yellow powder.

Anal. Calcd. for C₁₈₇H₁₆₈B₂P₈Ru₂Si: C 77.05, H 5.81%. Found: C 76.98, H 5.70%. ESI MS: 2915.84 [(M + H)⁺, 7], 1708.50 (7), 1354.16 (22), 1275.32 (25), 1146.19 (56), 972.14 (55), 666.26 (62), 517.16 (75). IR (CH₂Cl₂) [Rel. Transm., Assignm.]: 894 [78.6%, 1097 [92.8], 1401 [97.3], 1434 [90.0], 1487 [95.4, ν(C=Ĉaromatic)], 1501 [96.6], 1592 [95.7, ν(C=Ĉaromatic)], 2066 [86.3, ν(RuC≡C)], 2156 [98.4, ν(SiC≡C)], 3048 [98.0], 3064 [98.4] cm⁻¹. UV-Vis (νₑ,max, cm⁻¹ [ε], 10³ M⁻¹ cm⁻¹): 23200 [86.1], 30100 [111.8].¹H NMR (300 MHz, CDCl₃): δ 7.67–7.57 (m, 16H, H261), 7.58 (s, 4H, H210, H211), 7.52–7.43 (m, 4H, H204, H205), 7.41–7.33 (m, 16H, H251), (d, JHH = 7.9 Hz, 4H, H305), 7.20–7.04 (m, 16H, H253, H263), 7.01–6.86 (m, 32H, H253, H263), 6.86 (s, 8H, H12), 6.67 (d, JHH = 7.9 Hz, 4H, H304), 6.73 (s, 1H, H23), 6.53 (s, 2H, H21), 2.77–2.57 (m, 16H, H270), 2.34 (s, 12H, H15), 2.10 (s, 24H, H14) ppm. ³¹P{¹H} NMR (121 MHz, CDCl₃): δ 54.28 ppm. ¹³C{¹H} NMR (75 MHz, CDCl₃): δ 142.1 (C10), 140.8 (C11), 139.4 (C306), 137.9 (C13), 137.1 (C305), 137.4–136.2 (m, C150, C160), 134.9 (C303), 134.3, 134.0 (C251, C261), 131.9, 131.6 (C204, C205), 131.4 (C210, C211), 129.9, 129.6 (C22, C303), 129.4 (C304), 128.7, 128.5 (C253, C263), 128.0 (C12), 127.1 (C252, C262), 124.4, 122.2 (C209, C212), 123.1, 123.0 (C203, C206), 121.0 (C20), 118.4, 117.4 (C302, C215), 104.6 (C203), 96.4 (C201), 93.3 (C214), 91.2, 90.7
3.5. Experimental

(C207, C208), 87.3 (C213), 31.6 (vtt, $|^{1}J_{PC} + ^{3}J_{PC}| = 23.5$ Hz, C170), 23.5 (C14), 21.2 (C15), -0.1 (C16) ppm.

$$1,3,5-\{\text{trans-}[\{3,5-\{\text{trans-}[(\text{PhC≡C})\text{Ru(dppe)}]_{2}(\text{C≡C})]\}_{2}C_{6}H_{5}-1-(\text{C≡CC}_{6}H_{4}-4-C≡CC_{6}H_{4}-4-C≡C)\}Ru(dppe)_{2}(\text{C≡CC}_{6}H_{4}-4-C≡CC_{6}H_{4}-4-C≡C)\}_{3}C_{6}H_{3} \quad (3-46)$$

In a flame-dried 100 mL two-neck round-bottom flask fitted with a condenser, 1,3,5-{$\text{trans-}[\text{dppe}]_{2}\text{ClRu(C≡CC}_{6}H_{4}-4-C≡CC_{6}H_{4}-4-C≡C)\}_{3}C_{6}H_{3} \quad (2-14)$

(0.050 g, 0.014 mmol, 1.0 eq.) and 1,3-{$\text{trans-}[(\text{PhC≡C})\text{Ru(dppe)}]_{2}(\text{C≡C})]\}_{2}$-$\text{5-(HC≡CC}_{6}H_{4}-4-C≡CC_{6}H_{4}-4-C≡C)\}C_{6}H_{3} \quad 3-17 \quad (0.100 g, 0.043 mmol, 3.02 eq.)$

were dissolved in freshly distilled dichloromethane (50 mL). To the solution were added triethylamine (5 drops) and NaPF$_{6}$ (0.040 g, 0.18 mmol, 12.7 eq.). The orange, clear solution was heated at reflux for 18 h. The volume of solvent was reduced to 2 mL in vacuo. The residual solution was dropped into stirring methanol, resulting in the formation of a fine, orange-yellow, flocculent precipitate. The mixture was filtered through a sintered glass filter funnel, and the solid residue was washed with methanol several times. The solid was redissolved in a minimal amount of dichloromethane, and the resultant solution was filtered through cotton wool. The clear filtrate was dropped into a mixture of n-pentane and dichloromethane (3:1). An emulsion was formed that was filtered through a sintered glass filter funnel. The solid residue was redissolved in a minimal amount of dichloromethane, and the precipitation was repeated from n-pentane/dichloromethane (10:1). Filtration afforded a yellow solid that was dried under vacuum at 30–40°C, giving 0.062 g (0.0058 mmol, 41%) of the product as a yellow-orange, amorphous solid.

Anal. Calcd. for C$_{666}$H$_{522}$P$_{36}$Ru$_{9}$: C 75.65, H 5.02%. Found: C 75.95, H 5.12%. IR (CH$_{2}$Cl$_{2}$) [Rel. Transm., Assignm.]: 1101 [90.6], 1436 [84.3], 1485 [90.1], 1513 [90.7], 1562 [92.5], 1591 [88.2], 2054 [63.4, ν(RuC=C)], 2208 [98.6], 3048 [96.4], 3066 [98.0] cm$^{-1}$. UV-Vis ($\tilde{\nu}_{\text{max}}$, cm$^{-1}$ [ε, 10$^{4}$ M$^{-1}$ cm$^{-1}$]): 29900 [451.1], 23400 [282.6]. $^{1}$H NMR (500 MHz, CDCl$_{3}$): δ 7.70 (s, 3H, H10), 7.63–7.28 (m, 180H, H151, H161, H251, H261, H134, H135, H210, H211, H142, H205), 7.23–7.05 (m, 90H, H153, H163, H253, H263, H305, H306), 7.04–6.87 (m, 144H, H, H152, H162, H252, H262), 6.79–6.66 (m, 21H, H23, H143, H204, H304), 6.53 (m, 6H, H21), 2.77–2.56 (m, 72H, H170, H270) ppm. $^{31}$P($^{1}$H) NMR (121 MHz, CDCl$_{3}$):
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δ 54.48 (24P), 54.01 (12P) ppm. $^{13}$C\{1H\} NMR (126 MHz, CDCl$_3$): δ 137.4–136.3 (m, C150, 160, 250, 260), 134.2, 134.1 (C151, C161, C251, C261), 133.0, 132.1, 131.61, 131.4, 131.0, 130.0, 129.9, 129.6, 128.9, 128.7 (C134, C135, C142, C143, C204, C205, C210, C211, C304), 130.6, 128.5 (C22, C303), 127.3 (C305), 127.1, 127.0 (C153, C163, C253, C263), 123.2, 122.7 (C306), 116.8, 116.1 (C215, C302, C202, C145), 31.6 (m, C170, C270) ppm.$^{24}$

1,3,5-\{trans-\{3,5-\{trans-[(O$_2$NC$_6$H$_4$-4-C≡C)Ru(dppe)$_2$(C≡C)]\}$_2$C$_6$H$_3$-1-(C≡CC$_6$H$_4$-4-C≡CC$_6$H$_4$-4-C≡C)]\}Ru(dppe)$_2$(C≡CC$_6$H$_4$-4-C≡CC$_6$H$_4$-4-C≡C)]\}_3C$_6$H$_3$ (3-47)

In a flame-dried 250 mL two-neck round-bottom flask fitted with a condenser, 1,3-\{trans-[(O$_2$NC$_6$H$_4$-4-C≡C)Ru(dppe)$_2$(C≡C)]\}$_2$-5-(HC≡CC$_6$H$_4$-4-C≡CC$_6$H$_4$-4-C≡C)C$_6$H$_3$ (3-18) (0.066 g, 0.027 mmol, 3.4 eq.) and 1,3,5-\{trans-\{dppe\}$_2$ClRu(C≡CC$_6$H$_4$-4-C≡CC$_6$H$_4$-4-C≡C)]\}_3C$_6$H$_3$ (2-14) (0.028 g, 0.008 mmol, 1.0 eq.) were dissolved in freshly distilled dichloromethane (70 mL). The solution was deoxygenated, and NaPF$_6$ (0.020 g, 0.119 mmol, 15.1 eq.) was added. The resultant dark red solution was stirred at ambient temperature for 2 min. Triethylamine (2 drops) was added, and the solution was deoxygenated again before being heated at reflux for 24 h. The volume of the solution was reduced to 2 mL in vacuo, and the residual solution was pipetted into stirring methanol. A red precipitate was formed, which was removed from the mixture by filtration through a sintered glass filter funnel. The solid residue was redissolved in dichloromethane (3 mL). The resultant solution was filtered through tightly packed cotton wool, giving a clear filtrate, which was dropped into a stirring mixture of n-pentane and dichloromethane (4:1) with a small amount of added triethylamine. A red precipitate was formed, which was isolated by filtration through a sintered glass filter funnel. The residual solvent was removed under vacuum at 30–40 °C, affording 0.062 g (0.058 mmol, 73%) of the dark orange solid product after filtration.

Anal. Calcd. for C$_{666}$H$_{116}$N$_6$O$_{12}$P$_{36}$Ru$_9$: C 73.76, H 4.84, N 0.78%. Found: C 73.93, H 5.07, N 0.94%. IR (CH$_2$Cl$_2$) [Rel. Transm., Assignm.]: [s, ν(RuC≡C)]:

$^{24}$ Only observed peaks are reported.
3.5. Experimental

894 [39.5], 1098 [92.9], 1108 [90.4], 1323 [75.2], 1434 [90.8], 1487 [94.2], 1499 [94.5], 1512 [94.2], 1561 [93.3], 1581 [85.2], 2047 [68.2, \( \nu(C\equivC) \)], 3045 [95.3] cm\(^{-1}\). UV-Vis (\( \tilde{\nu}_{\text{max}}, \text{cm}^{-1} [\varepsilon, 10^3 \text{M}^{-1} \text{cm}^{-1}] \)): 20600 [150.3, sh], 23200 [369.7], 30100 [438.6]. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \( \delta \) 8.12 (d, \( J_{HH} = 8.9 \text{Hz}, 12\text{H}, H305\)), 7.99–6.75 (m, 420H, H151, H161, H152, H162, H153, H163, H134, H135, H142, H143, H204, H205, H210, H211, H21, H23, H251, H261, H252, H262, H253, H263), 6.62 (d, \( J_{HH} = 8.9 \text{Hz}, 12\text{H}, H304\)), 2.77–2.66 (m, 48H, H270), 2.61–2.44 (m, 24H, H170) ppm. \(^{31}\)P\(^{(1)}\) NMR (121 MHz, CDCl\(_3\)): \( \delta \) 54.08 (s, 24P, peripheral Ru[Ph\(_2\)PCH\(_2\)CH\(_2\)PPh\(_2\)]\(_2\)), 53.98 (s, 12P, core Ru[Ph\(_2\)PCH\(_2\)CH\(_2\)PPh\(_2\)]\(_2\)) ppm.

\[ \{\text{trans-}[\{3,5-\{\text{trans-}[(\text{PhC} \equiv \text{C}) \text{Ru(dppe)}_2(C \equiv \text{C})]\}]_2 \text{C}_6 \text{H}_3 \equiv \text{C} \equiv \text{C}_6 \text{H}_4 \equiv \text{C} \equiv \text{C}_6 \text{H}_4 \equiv \text{C} \equiv \text{C}_6 \text{H}_4 \equiv \text{C} \equiv \text{C}\} \} \text{Ru(dppe)}_2(C \equiv \text{C}_4 \equiv \text{C}_6 \text{H}_4)\}_3 \text{N} \quad (3-19) \]

In a flame-dried 100 mL two-neck round-bottom flask fitted with a condenser, \( \textbf{3-3}^* \) (0.020 g, 0.006 mmol, 1.0 eq.) and \( \textbf{3-17} \) (0.045 g, 0.019 mmol, 3.0 eq.) were dissolved in freshly distilled dichloromethane (30 mL). To the solution were added triethylamine (5 drops) and NaPF\(_6\) (0.016 g, 0.089 mmol, 13.9 eq.) The orange solution was stirred in refluxing dichloromethane for 12 h. The volume of the resultant mixture was reduced to 2 mL \textit{in vacuo}. The residual mixture was dropped into stirring methanol, after which an orange-yellow, fine precipitate was formed. The mixture was filtered through a sintered glass filter funnel, and the obtained solid was washed with methanol and \( n \)-hexane several times. The solid was taken to dryness under reduced pressure, and the residual solvent was removed under vacuum at 30–40°C for 16 h, giving 0.035 g (0.004 mmol, 55%) of a yellow-orange, amorphous solid, which was identified to be the product.

Anal. Calcd. for C\(_{624}\)H\(_{507}\)NP\(_{36}\)Ru\(_9\): C 74.62, H 5.09, N 0.14%. Found: C 74.24, H 5.29, N 0.29%. IR (CH\(_2\)Cl\(_2\)) [Rel. Transm., Assignm.]: 1097 [96.4], 1434 [92.9], 1485 [95.1], 1495 [95.5], 1513 [98.3], 1562 [97.0], 1591 [96.4], 2055 [83.2, \( \nu(C\equivC) \)] cm\(^{-1}\). UV-Vis (\( \tilde{\nu}_{\text{max}}, \text{cm}^{-1} [\varepsilon, 10^3 \text{M}^{-1} \text{cm}^{-1}] \)): 24900 [213.5], 29400 [397.4]. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) 7.96–6.36 (m, 435H, Ar-H), 2.85–2.47 (m, 72H, H170, H270) ppm. \(^{31}\)P\(^{(1)}\) NMR (121 MHz, CDCl\(_3\)): \( \delta \) 54.58 (24P), 54.22 (12P) ppm. \(^{13}\)C\(^{(1)}\) NMR (126 MHz, CDCl\(_3\)): \( \delta \) 137.0, 134.4, 134.3, 134.1, 131.4, 130.8, 130.7, 130.4, 130.0, 129.6, 128.7, 128.5, 127.3, 127.1, 127.0, 124.4, 123.2,
122.7, 121.1, 118.9, 117.1, 116.8, 116.1, 93.0, 89.4, 89.3, 87.5, 81.2, 31.6 (C170, C270) ppm.\(^{25}\)

\[
\{\text{trans-}\{\text{trans-}\{O_2NC_6H_4-4-C\equiv C\}Ru(dppe)_2(C\equiv C)\}_2C_6H_5-1-(C\equiv CC_6H_4-
4-C\equiv CC_6H_4-4-C\equiv C)\}Ru(dppe)_2(C\equiv C-4-C_6H_4)\}_3N \ (3-20)
\]

In a flame-dried 100 mL three-neck round-bottom flask fitted with a condenser, \{\text{trans-}\{ \text{dppe} \}_2ClRu(C\equiv C-4-C_6H_4)\}_3N \ (3-3') \ (0.028 \text{ g}, 0.009 \text{ mmol, 3.2 eq.}) and 1.3-\{\text{trans-}\{O_2NC_6H_4-4-C\equiv C\}Ru(dppe)_2(C\equiv C)\}_2-5-(HC\equiv CC_6H_4-4-C\equiv CC_6H_4-
4-C\equiv C)C_6H_5 \ (3-18) \ (0.070 \text{ g}, 0.029 \text{ mmol, 3.2 eq.}) were dissolved in freshly distilled and deoxygenated dichloromethane (60 mL). To the dark red solution were added triethylamine (3 drops) and NaPF\(_6\) (0.015 g, 0.089 mmol, 9.9 eq.). The solution was deoxygenated and then heated at reflux for 12 h. The solvent was removed in vacuo, and the solid residue was redissolved in a minimal amount of dichloromethane. The resultant mixture was dropped into methanol, giving a fine, flocculent, dark red precipitate, which was removed from the solution by filtration through a sintered glass filter funnel (pore size G4). A semi-solid, dark red residue and a dark orange, slightly cloudy filtrate were obtained. The residue was redissolved in dichloromethane (2 mL). The resultant solution was dropped into methanol, after which a fine precipitate was formed. The solid was collected by filtration through a sintered glass filter funnel. The solid residue was reprecipitated four times from the following solvents or solvent mixtures: methanol, \text{n-pentane/dichloromethane (4:1)}, \text{n-pentane/dichloromethane (3:1)}, and \text{n-pentane}. After filtration and drying under vacuum at 30–40 °C, 0.054 g (0.0052 mmol, 58%) of a brick-red solid was obtained, which was characterized as the desired complex.

Anal. Calcd. for C\(_{524}H_{501}N_7O_{12}P_{36}Ru_9\): C 72.66, H 4.90, N 0.95%. Found: C 72.99, H 5.02, N 0.77%. IR (CH\(_2\)Cl\(_2\)) [Rel. Transm., Assignm.]: 1000 [99.8], 1028 [99.8], 1099 [98.2], 1107 [96.4], 1175 [99.7], 1323 [83.9], 1422 [97.3], 1434 [94.8], 1496 [95.7], 1563 [97.3], 1583 [92.2], 2046 [\(\nu(RuC\equiv C)\), 81.5], 2922 [91.3], 2952 [69.2], 2958 [84.6], 2965 [96.9], 3055 [92.2] cm\(^{-1}\). UV-Vis (\(\epsilon_{\text{max}}\), cm\(^{-1}\) [\(\epsilon\), 10\(^{3}\) M\(^{-1}\) cm\(^{-1}\)]): 21600 [159.5, sh], 23600 [230.1], 29800

\(^{25}\) Only observed peaks are reported.
3.5. Experimental

[316.4]. $^1$H NMR (300 MHz, CDCl$_3$): 7.99 (d, $J_{HH} = 8.5$ Hz, 4H, H305), 7.83–7.65 (m, 72H, H151, H251), 7.61 (s, 12H, H210, H211), 7.48–7.39 (m, 24H, H161), 7.34 (d, $J_{HH} = 8.0$ Hz, 6H, H142), 7.30–7.23 (m, 48H, H261), 7.24–6.90 (m, 222H, H153, H163, H253, H263, H152, H162, H252, H262, H205), 6.86–6.78 (m, 9H, H23, H143), 6.72 (s, 6H, H21), 6.68–6.61 (6H, H204), 6.54 (d, $J_{HH} = 8.5$ Hz, 4H, H304) ppm. $^{31}$P$^1$H NMR (121 MHz, CDCl$_3$): $\delta$ 54.23 (s, 12P, core Ru[Ph$_2$PCH$_2$CH$_2$PPPh$_2$]), 54.03 (s, 24P, peripheral Ru[Ph$_2$PCH$_2$CH$_2$PPPh$_2$]) ppm. $^{13}$C$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 142.5 (C306), 137.4 (C303), 136.9, 136.2 (vtt, $|^{1}J_{PC} + ^{3}J_{PC}|_1 = 18.7$ Hz, $|^{1}J_{PC} + ^{3}J_{PC}|_2 = 19.2$ Hz, C150, C160, C250, C260), 134.4, 134.3, 134.1, 133.8 (C151, C161, C251, C261, C10), 131.4, 130.8, 130.6, 130.4, 130.0, 129.7, 129.8, 129.0, 128.6 (C22, C134, C135, C142, C143, C144, C203, C204, C205, C210, C211, C304), 127.3, 127.1 (C152, C162, C252, C262), 123.2, 123.3 (C133, C11, C305), 124.4, 121.5, 118.6, 118.3 (203, C302, C215, C145, C211, C206), 94.0–87.8 (C212, C140, C208, C132, C139, C131, C207, C214), C87.8 (C213), 31.4, 31.9–31.0 (m, C170, C270) ppm.

$(Me_3SiC≡C-4-C_6H_4C≡C-4-C_6Me_4)_3B$ (3-27)

In a flame-dried 100 mL two-neck round-bottom flask, (HC≡C-4-C$_6$Me$_4$)$_3$B (3-25*) (0.098 g, 0.20 mmol, 1.0 eq.) and $Me_3SiC≡CC_6H_4-4-I$ (2-22*) (0.200 g, 0.67 mmol, 3.2 eq.) were dissolved in deoxygenated triethylamine (40 mL). To the clear, pale yellow solution were added [PdCl$_2$(PPPh$_3$)$_2$] (0.009 g, 0.01 mmol, 0.06 eq.) and CuI (0.005 g, 0.03 mmol, 0.13 eq.). The pale yellow, slightly cloudy solution was deoxygenated again, before being stirred at ambient temperature for 20 h. Silica was added to the reaction mixture, and the solvent was removed under reduced pressure. An off-white powder was obtained, which was loaded onto a silica column. The product was eluted from the column, using a mixture of $n$-pentane and ethylacetate (20:1). The solvent was removed under reduced pressure, and the resultant solid was dried under vacuum at 50–60°C for 24 h, affording 0.148 g (0.148 mmol, 71%) of the product as a beige, semi-crystalline solid.

Anal. Calcd. for C$_{69}$H$_{72}$BSi$_3$: C 82.92, H 7.56%. Found: C 82.97, H 7.65%. IR (CH$_2$Cl$_2$) [Rel. Transm., Assignm.]: 1100 [85], 1727 [33], 1402 [78], 1509 [95],

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2156 [78, ν(SiC≡C)], 2920 [56, ν(CHaliphatic)], 2951 [70] cm⁻¹. UV-Vis (νmax, cm⁻¹ [ε, 10³ M⁻¹ cm⁻¹]): 31 200 [79.1], 26 700 [92.0]. ¹H NMR (500 MHz, CDCl₃): δ 7.48–7.45 (m, 6H, H140), 7.45–7.43 (m, 6H, H141), 2.42 (s, 18H, H1351), 1.98 (s, 18H, H1341), 0.26 (s, 21H, H16) ppm. ¹³C(¹H) NMR (126 MHz, CDCl₃): δ 149.8 (C133), 135.8, 135.7 (C134, C135), 131.9 (C141), 131.0 (C140), 124.1 (C136, C139), 122.6 (C142), 104.7 (C143), 97.3 (C138), 96.1 (C144), 91.2 (C137), 20.2 (C1341), 18.4 (C1351), -0.1 (C16) ppm.

\( (HC≡C₆H₄)₂C≡C₆Me₄)₉B \) (3-28)

In a flame-dried 100 mL two-neck round-bottom flask (Me₃SiC≡C₆H₄C≡C₆Me₄)₉B (3-27) (0.140 g, 0.140 mmol, 1.0 eq.) was dissolved in freshly distilled dichloromethane (70 mL). To the clear, pale yellow solution was added NBn₄F (1.0 M solution in THF; 1.20 mL, 1.20 mmol, 8.6 eq.), after which the solution became significantly darker, and a color change to yellow occurred, the solution remaining clear at all times. The resultant reaction mixture was stirred for 2.5 h at ambient temperature under a nitrogen atmosphere. Water was added and the product was extracted with dichloromethane. The combined organic layers were washed with water, dried over MgSO₄ and filtered, giving a clear, pale orange solution, to which silica was added. The solvent was removed under reduced pressure, and the resultant powder was loaded onto a silica column. The product was eluted with a mixture of n-pentane and ethylacetate (5:1). The solvent was removed under reduced pressure, affording a solid that was further dried under vacuum. 0.096 g (0.12 mmol, 88%) of the product was isolated.

Anal. Calcd. for C₆₀H₃₁B: C 92.05, H 6.57%. Found: C 91.73, H 6.82%. UV-Vis (νmax, cm⁻¹ [ε, 10³ M⁻¹ cm⁻¹]): 27 000 [63.3], 31 600 [54.7], 33 600 [51.7]. ¹H NMR (500 MHz, CDCl₃): δ 5.41–5.48 (m, 6H, H140), 7.48–7.46 (m, 6H, H141), 3.17 (s, 3H, H144), 2.42 (s, 18H, H1351), 1.98 (s, 18H, H1341) ppm. ¹³C(¹H) NMR (126 MHz, CDCl₃): δ 149.8 (C133), 135.8, 135.7 (C134, C135), 132.1 (C141), 131.1 (C140), 124.5 (C139), 124.0 (C136), 121.5 (C142), 97.1 (C138), 91.3 (C137), 83.4 (C143), 78.8 (C144), 20.2 (C1341), 18.4 (C1351) ppm.

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\[\text{trans-}[(\text{dppe})_2\text{ClRu}(\text{C}=\text{C}-\text{C}_6\text{H}_4\text{C}=\text{C}-\text{C}_6\text{Me}_4))]_3\text{B (3-29)}\]

In a flame-dried 100 mL two-neck round bottom flask fitted with a condenser, \((\text{HC}=\text{C}-\text{C}_6\text{H}_4\text{C}=\text{C}-\text{C}_6\text{Me}_4)_3\text{B (0.028 g, 0.036 mmol, 1.0 eq.) and cis-}[\text{RuCl}_2(\text{dppe})_2]\) (0.140 g, 0.14 mmol, 4.04 eq.) were dissolved in freshly distilled and deoxygenated dichloromethane (50 mL). The clear, yellow solution was deoxygenated twice, and \(\text{NaPF}_6\) (0.030 g, 0.18 mmol, 5 eq) was added, after which it gradually changed from yellow and orange to ruby-red over 20 min. The solution was stirred at 25 °C for 18 h and then at 30 °C for another 12 h. The solution was concentrated to 1 mL under reduced pressure. The dark red residual mixture was pipetted into cold, stirring diethylether. A red-brown, flocculent precipitate was formed, which was removed from the mixture by filtration. The solid residue was dissolved in deoxygenated dichloromethane, and triethylamine (1 mL) was added with stirring, after which the deep red mixture turned orange and became almost clear. The mixture was filtered through tightly packed cotton wool and dropped into stirring methanol (50 mL). A yellow precipitate was formed that was isolated by filtration, affording a yellow, amorphous solid, which was suspended in dichloromethane (2 mL). The cloudy, orange mixture was filtered through tightly packed cotton wool, affording a clear filtrate, which was dropped into stirring n-pentane. A yellow precipitate was formed, which was separated from the solvent by filtration. A solid was obtained, which was dried under vacuum at 30–40 °C, giving 0.082 g (0.023 mmol, 64%) of the product.

Anal. Calcd. for \(\text{C}_{216}\text{H}_{192}\text{BCl}_3\text{P}_{12}\text{Ru}_3\): C 72.47, H 5.41%. Found: C 72.53, H 5.51%. ESI MS: 3585.84 \([\text{M} - \text{Cl} - \text{H} + \text{MeCN]}^+, 2\) 1795.47 \([\text{M} - 2\text{Cl} + 2\text{MeCN}]^{2+}, 20\). HR ESI TOF MS: Calcd. for \(\text{C}_{218}\text{H}_{195}\text{[11BNP}_{12}\text{Cl}_2^{102}\text{Ru}_3\): 3588.8683 Found: 3588.8677. IR (\(\text{CH}_2\text{Cl}_2\) [Rel. Transm., Assignm.]: 1001 [97.9], 1029 [97.9], 1097 [92.9], 1107 [90.2], 1174 [96.6] 1326 [75.1], 1433 [90.8], 1486 [94.2], 1501 [94.6], 1511 [94.2] 1561 [93.4], 1581 [85.2], 2046 [68.1, \(\nu(\text{RuC}≡\text{C})\)] cm\(^{-1}\). UV-Vis (\(\bar{\nu}_{\text{max}}, \text{cm}^{-1} [\varepsilon, 10^3 \text{M}^{-1} \cdot \text{cm}^{-1}]\)): 23 400 [102.8], 27 800 [97.2], 39 800 [160.5].

\(^1\text{H} \text{NMR (500 MHz, CDC}_{13}\)): \(\delta 7.65–7.44\) (m, 24H, H161), 7.43–7.28 (m, 30H, H151, H142), 7.29–7.15 (m, 24H, H153, H163), 7.14–6.92 (m, 48H, H152, H162), 6.63 (d, \(J_{\text{HH}} = 7.5\) Hz, 6H, H143) ppm. \(^{31}\text{P}{^1\text{H}} \text{NMR (121 MHz, CDC}_{13}\)): \(\delta 50.03\) ppm. \(^{13}\text{C}{^1\text{H}} \text{NMR (126 MHz, CDC}_{13}\)): \(\delta 149.4\) (C161), 136.3 (vtt, \(|J_{\text{FC}} + |J_{\text{PC}} = 19.7\) Hz, C150), 135.5 (vtt, \(|J_{\text{FC}} + |J_{\text{PC}} = 17.9\) Hz, C160), 135.8,
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135.2 (C134, C135), 134.4, 134.2 (C151, C161), 130.5 (C142), 130.1 (C144), 129.9 (C143), 128.8 (C153, C163), 127.2, 126.9 (C152, C162), 124.8 C136), 117.5 (C141), 114.4 (C145), 98.9 (C140), 89.4 (C139), 30.6 (vtt, $|\text{J}_{\text{FC}} + 3\text{J}_{\text{FC}}| = 22.8 \text{ Hz, C170}$), 20.2 (C1341), 18.5 (C1351) ppm.

\{\text{trans-}[(\text{O}_2\text{NC}_6\text{H}_4\text{H}_4\text{-}4\text{-C}:=\text{C})\text{Ru(dppe)}_2(\text{C}:=\text{C})]\}_2\text{C}_6\text{H}_{12-1\text{-}(\text{C}:=\text{C})\text{CC}_6\text{H}_4\text{-}4\text{-C}:=\text{C}}\text{C}_6\text{H}_4\text{-}4\text{-C}:=\text{C})\text{Ru(dppe)}_2(\text{C}:=\text{C4}\text{-C}_6\text{H}_4\text{C}:=\text{C4}\text{-C}_6\text{Me}_4)\}_3\text{B} \ (3-31)

In a flame-dried 100 mL two-neck round-bottom flask fitted with a condenser, 1,3-\{\text{trans-}[(\text{O}_2\text{NC}_6\text{H}_4\text{-}4\text{-C}:=\text{C})\text{Ru(dppe)}_2(\text{C}:=\text{C})]\}_2-5\text{-}(\text{HC}:=\text{C})\text{CC}_6\text{H}_4\text{-}4\text{-C}:=\text{C}}\text{C}_6\text{H}_3 \ (3-18) \ (0.060 \text{ g}, 0.025 \text{ mmol, 4.0 eq.}) and \{\text{trans-}[\text{RuCl(dppe)}_2(\text{C}:=\text{C4}-\text{C}_6\text{H}_4\text{C}:=\text{C4}-\text{C}_6\text{Me}_4)]\}_3\text{B} \ (3-29) \ (0.022 \text{ g, 0.006 mmol, 1.0 eq.}) were dissolved in freshly distilled and deoxygenated dichloromethane. To the clear, dark red solution were added triethylamine (3 drops) and NaPF_6 (0.015 g, 0.089 mmol, 14.5 eq.). The resultant reaction mixture was deoxygenated, before being heated to reflux for 12 h. Triethylamine (3 drops) was added and the reaction mixture heated at reflux further for 8 h. NaPF_6 (0.008 g, 0.045 mmol, 7.3 eq.) was added and the reaction mixture heated at reflux for 18 h. The amount of solvent was reduced to 2 mL \text{in vacuo}. The residual red solution was dropped into stirring methanol, giving a brick-red, flocculent precipitate, which was isolated by filtration through a sintered glass filter funnel (pore size G4). The solid product was redissolved in dichloromethane (2 mL), and the resultant solution was filtered through tightly packed cotton wool. The clear, dark red filtrate was dropped into a mixture of n-pentane and dichloromethane (3.5:1.0). A red, flocculent precipitate was formed, which was isolated by filtration through a sintered glass filter funnel (pore size G4). The solid residue was reprecipitated from the same solvent mixture, and the solvent was removed from the resultant mixture by filtration. The solid residue was dried \text{in vacuo}, affording 0.052 g (0.005 mmol, 78%) of the brick-red, amorphous solid product.

Anal. Calcd. for C_{660}H_{587}BN_{6}O_{12}P_{36}Ru_{9}: C 73.54, H 5.02, N 0.78%. Found: C 73.42, H 5.17, N 0.72%. IR (CH_2Cl_2) [Rel. Transm., Assignm.]: 896 [14.5], 1098 [92.2], 1104 [89.8], 1174 [97.4], 1323 [71.2], 1434 [88.8], 1487 [93.4], 1500 [93.7], 1560 [93.1], 1582 [84.3], 2046 [65.4, $\nu(\text{RuC}:=\text{C})], 3049 [98.0],

344
3.5. Experimental

3062 [98.0] cm\(^{-1}\). UV-Vis \((\tilde{\nu}_{\text{max}}, \text{ cm}^{-1} [\varepsilon, 10^3 \text{ M}^{-1} \text{ cm}^{-1}])\): 20 200 [119.0, sh], 23 100 [249.3], 29 500 [272.2]. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\tilde{\nu} \approx 8.00 \text{ (d, } J_{\text{HH}} = \text{8.9 Hz, } 12\text{H, H305)}\), 7.79–7.68 (m, 48H, H251), 7.61 (s, 18H, H210, H211), 7.58–7.45 (m 72H, H151, H161), 7.40–7.29 (m, 12H, H142, H205), 7.28–7.22 (m, 48H, H261), 7.22–7.09 (m, 72H, H153, H163, H253, H263), 7.06–6.90 (m, 144H, H152, H162, H252, H262), 6.84 (s, 6H, H23), 6.78–6.69 (m, 18H, H21, H143, 204), 6.54 (d, \(J_{\text{HH}} = \text{8.9 Hz, } 12\text{H, H304)}\), 2.81–2.58 (m, 72H, H170, H270), 2.49 (s, 18H, H1351), 2.05 (s, 18H, H1341) ppm. \(^{31}\)P\(^{\{1\}H}\) NMR (121 MHz, CDCl\(_3\)): \(\tilde{\nu} \approx 54.19 \text{ (s, 12P, core Ru(Ph}_2\text{PCH}_2\text{CH}_2\text{PPP}_2\text{)}_2\text{), 54.02 (s, 24P, peripheral Ru(Ph}_2\text{PCH}_2\text{CH}_2\text{PPP}_2\text{)}_2\text{) ppm.} \(^{13}\)C\(^{\{1\}H}\) NMR (126 MHz, CDCl\(_3\)): \(\tilde{\nu} \approx 149.0 \text{ (C133), 142.4, 137.4, 136.8, 136.3, 136.3, 135.8, 134.3, 134.3, 133.7, 132.1, 131.6, 131.4, 130.9, 130.6, 129.9, 129.0, 128.7, 127.2, 127.1, 123.3, 118.5, 118.3, 98.9, 92.6, 89.3, 31.4 \text{ (vtt, } ^1J_{\text{FC}} + ^3J_{\text{FC}} = 21.4 \text{ Hz, C170), 20.2 (C1341), 18.5 \text{ (C1351) ppm.}} \)

\(\text{trans-} [\{3,5-\{\text{trans-} \{(\text{PhC} ≡ C)\text{Ru(dppe)}_2\text{C} ≡ C\} \}_2\text{C}_6\text{H}_5\text{-}1\text{-}(\text{C} ≡ \text{CC} = \text{H}_4\text{-}4\text{-}\text{Me})\} \}_2\text{Ru(dppe)}_2\text{C} ≡ \text{C} = \text{C} \text{ terrifying!}} \)

\(\text{trans-} [\{(\text{dppe})_2\text{ClRu(C} ≡ \text{C} = \text{H}_4\text{-}4\text{-C} ≡ \text{C} = \text{H}_4\text{-}4\text{-C} ≡ \text{C} = \text{H}_4\text{-}4\text{-Me})\}_2\text{B (3-29)} \)

In a flame-dried two-neck round-bottom flask fitted with a condenser, \(\{(\text{dppe})_2\text{ClRu(C} ≡ \text{C} = \text{H}_4\text{-}4\text{-C} ≡ \text{C} = \text{H}_4\text{-}4\text{-C} ≡ \text{C} = \text{H}_4\text{-}4\text{-Me})\}_2\text{B (3-29)} \) (0.015 g, 0.004 mmol, 1.0 eq.) was dissolved in freshly distilled and deoxygenated dichloromethane (70 mL). To the yellow, clear solution were added triethylamine (5 drops), \(\text{trans-} [\{(\text{O}_2\text{NC}_6\text{H}_4\text{-}4\text{-C} ≡ \text{C})\text{Ru(dppe)}_2\text{C} ≡ \text{C} = \text{Me})\}_2\text{B (3-17)} \) (0.045 g, 0.019 mmol, 4.6 eq.) and NaPF\(_6\) (0.015 g, 0.09 mmol, 21.3 eq.). The resultant solution was yellow-orange slightly cloudy mixture was deoxygenated, before being heated at reflux for 15 h, after which the mixture had reverted to yellow color. The amount of solvent was reduced to 2 mL \textit{in vacuo}. The cloudy, orange-brown residue was pipetted into stirring methanol, affording a yellow precipitate. Filtration of the mixture through a sintered glass filter funnel (pore size G4) gave a clear, pale yellow filtrate and a yellow, solid residue. The solid was suspended in dichloromethane. A cloudy, orange-brown suspension was obtained, which was filtered through tightly packed

\(\text{26 Only observed in gHMBC NMR spectrum; not detected in 1D } ^{13}\text{C}\{1\}H\) NMR spectrum.
cotton wool. The resultant, clear filtrate was dropped into a stirring mixture of n-pentane and dichloromethane (4:1). A yellow, homogeneous suspension was obtained. Filtration through a sintered glass filter funnel (pore size G4) gave a yellow, solid residue. A second precipitation from n-pentane/dichloromethane (6:1) was carried out. After filtration, a yellow solid was obtained, which was dried in vacuo at 30–40 °C for 16 h, affording 0.036 g (0.0034 mmol, 82%) of the product.

Anal. calcd. for C_{660}H_{543}BP_{36}Ru_{9}: C 75.43, H 5.21%. Found: C 75.30; H 5.11%. IR (CH_{2}Cl_{2}) [Rel. Transm., Assignm.]: 999 [99.5], 1028 [99.4], 1097 [92.1], 1434 [87.3], 1485 [92.3], 1512 [96.8], 1561 [93.4], 1592 [92.5], 2054 [71.3, ν(RuC≡C)], 3049 [96.3], 3061 [96.7 cm⁻¹]. UV-Vis (ν_{max}, cm⁻¹ [ε, 10^{3} M⁻¹ cm⁻¹]): 23500 [256.0], 29200 [380.0]. ^{1}H NMR (300 MHz, CDCl₃): δ 7.89–6.81 (m, 435H, Ar-H). 2.86–2.40 (m, 108H, H₂70, H₃70, H₁341, H₁351) ppm. ^{31}P{^{1}H} NMR (121 MHz, CDCl₃): δ 53.92 (24P, peripheral Ph₂PCH₂CH₂PPh₂), 53.37 (s, 12P, core Ph₂PCH₂CH₂PPh₂) ppm.

\( Me_{3}SiC≡C-4-C₆H₄C≡C-4-C₆H₄B(2,4,6-C₆H₃Me₃)₂ \) (3-33)

In a flame-dried 100 mL two-neck round-bottom flask, HC≡C-4-C₆H₄B(2,4,6-C₆H₃Me₃)₂ (3-32*) (0.100 g, 0.29 mmol, 1.0 eq.) and \( Me_{3}SiC≡CC₆H₄-4-I \) (0.100 g, 0.33 mmol, 1.17 eq.) were dissolved in deoxygenated triethylamine (40 mL). The resultant mixture was stirred at ambient temperature until all the solid had dissolved. [PdCl₂(PPh₃)₂] (0.006 g, 0.009 mmol, 0.03 eq.) and CuI (0.003 g, 0.016 mmol, 0.06 eq.) were added. A pale yellow, slightly cloudy mixture was obtained, which was warmed gently to 30–35 °C for less than 1 min to initiate the reaction, after which time the reaction mixture turned a pale orange color. The reaction mixture was stirred at ambient temperature for 2 h. Catalytic amounts of [PdCl₂(PPh₃)₂] and CuI were added. The reaction mixture was warmed again, before being stirred at ambient temperature 4 h. The solvent was removed under reduced pressure. The brown residue was adsorbed onto silica, and the resultant powder was loaded on a short silica column (l = 10 cm, Ø = 2.5 cm). The product was eluted with a mixture of petrol and ethylacetate (10:1). A second silica column (l = 8 cm, Ø = 2.5 cm) was run for further purification, using n-pentane to elute the product. The solvent was removed,
and the residual solid was dried under vacuum, affording 0.10 g (0.19 mmol, 67%) of the microcrystalline, white product.

**Anal. Calcd. for C_{37}H_{39}BSi:** C 85.03, H 7.52%. Found: C 85.08, H 7.44%. **EI MS:** 522.3 ([M]^+, 50), 507.3 (18), 402.2 (100), 387.2 (83), 248.2 (25), 193.7 (57). **HR EI MS:** Calcd. for C_{37}H_{39}^{11}BSi: 522.2914. Found: 522.2918. IR (CH_{2}Cl_{2}) [Rel. Transm., Assignm.]: 1219 [81], 1424 [92, br], 1501 [93], 1540 [94], 1593 [83], 1607 [81], 2157 [93, ν(SiC≡C)], 3679 [95] cm^{-1}. UV-Vis (ν_{max}, cm^{-1} [ε, 10^3 M^{-1} cm^{-1}]): 28 200 [45.6], 29 400 [45.4]. **{^1}H NMR** (500 MHz, CDCl_{3}): δ 7.50 (s, 4H, H116, H117, 7.48 (d, J_{HH} = 8.8 Hz, 2H, H123), 7.45 (d, J_{HH} = 8.8 Hz, 2H, H122), 6.84 (s, 4H, H12), 2.32 (s, 6H, H15), 2.00 (s, 12H, H14), 0.26 (s, 9H, H16) ppm. **{^{13}}C{^{1}}H NMR** (126 MHz, CDCl_{3}): δ 146.1 (C115), 141.5 (C10), 140.8 (C11), 138.9 (C13), 136.1 (C116), 131.9, 131.5 (C122, C123), 131.0 (C117), 128.2 (C12), 126.2 (C118), 123.11, 123.08 (C121, C124), 104.6 (C125), 96.4 (C126), 91.6 (C119), 91.0 (C120), 23.4 (C14), 21.2 (C15), -0.08 (C16) ppm.

\[ HC≡C-4-C_6H_4C≡C-4-C_6H_4B(2,4,6-C_6H_2Me_3)_2 \ (3-34^*) \]

In a flame-dried 100 mL two-neck round-bottom flask, Me_{3}SiC≡CC_{6}H_{4}-4-C≡CC_{6}H_{4}-4-B(2,4,6-C_{6}H_{2}Me_{3})_{2} (3-33) (0.075 g, 0.14 mmol, 1.0 eq.) was dissolved in freshly distilled dichloromethane (40 mL). To the clear, colorless solution was added NBu^n_{4}F (1.0 M in THF: 0.80 mL, 0.80 mmol, 5.6 eq.). The clear, colorless solution was stirred at ambient temperature for 4.5 h. Water was added to the reaction mixture, and the product was extracted with dichloromethane. The combined organic layers were dried over MgSO_{4}. Filtration afforded a clear, colorless solution. The solvent was removed under reduced pressure, affording an off-white solid that was dissolved in n-pentane. A silica column was charged with this solution, and the product was eluted with a mixture of n-pentane and ethylacetate (20:1). The solvent was removed, and the residue was transferred to a sample vial as a solution in n-pentane. The solvent was evaporated under a constant stream of gaseous nitrogen. A solid was

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27 This is not a new compound. It has originally been synthesized by Prof. Todd Marder (Durham University, UK). A literature report has not been published, so I characterized this compound, in order to be able to compare the data to those of other compounds in this Thesis.
obtained, which was further dried under vacuum. An off-white solid (0.062 g, 0.10 mmol, 96%) was recovered, which was characterized as the product.

Anal. Calcd. for C₃₄H₃₁B: C 90.66, H 6.94%. Found: C 90.69, H 7.07%. EI MS: 450.3 ([M]⁺, 10), 330.1 ([M - C₆H₃Me₃]⁺, 100), 315.1 (10). HR EI MS: Calcd. for C₃₄H₃₁¹¹B: 450.2519. Found: 450.2520. IR (CH₂Cl₂) [Rel. Transm., Assignm.]: 1017 [96, br], 1103 [96, br], 1153 [96], 1173 [94], 1220 [85], 1240 [86], 1343 [97, br], 1377 [96, br], 1450 [95, br], 1510 [96], 1543 [97, br], 1597 [89], 1603 [87], 3296 [93, ν(C≡C-H), br] cm⁻¹. UV-Vis (νmax, cm⁻¹ [ε, 10³ M⁻¹ cm⁻¹]): 29600 [40.7], 28600 [41.8]. ¹H NMR (500 MHz, CDCl₃): 7.51 (s, 4H, H116, H117), 7.50–7.48 (m, 4H, H122, H123), 6.84 (s, 4H, H12), 3.19 (s, 1H, H126), 2.32 (s, 6H, H15), 2.01 (s, 12H, H14) ppm. ¹³C¹H NMR (126 MHz, CDCl₃): δ 146.1 (C115), 141.4 (C10), 140.8 (C11), 138.9 (C13), 136.1 (C116), 132.1, 131.52, 131.0 (C117, C122, C123), 128.2 (C12), 126.1 (C118), 123.5 (C121), 122.1 (C124), 91.6 (C119), 90.8 (C120), 83.2 (C125), 79.0 (C126), 23.4 (C14), 21.2 (C15) ppm.

\[ i-\text{Pr}_3\text{SiC}≡C-4·C₆H₄\text{C}≡C-4·C₆H₄\text{C}≡C-4·C₆H₄B(2,4,6-C₆H₃Me₃)_2 \] (3-35)

In a flame-dried 100 mL two-neck round-bottom flask, triethylamine (90 mL) was deoxygenated by bubbling argon through it for 20 min. \[ i-\text{Pr}_3\text{SiC}≡\text{CC}_6\text{H}_4·4·\text{C}≡\text{CC}_6\text{H}_4·4·\text{I} \] (0.33 g, 0.68 mmol, 1.08 eq.) was added, and the clear, pale yellow solution was further deoxygenated for 15 min. \[ \text{HC}≡\text{CC}_6\text{H}_4·4·\text{B}(2,4,6·\text{C}_6\text{H}_3\text{Me}_3)_2 \] (0.22 g, 0.63 mmol, 1.0 eq.) was added. The clear solution was deoxygenated as before, and \[ \text{[PdCl}_2\text{(PPPh}_3\text{)}_2] \] (0.015 g, 0.02 mmol, 0.03 eq.) and CuI (0.010 g, 0.05 mmol, 0.08 eq.) were added. The pale yellow, slightly cloudy mixture became significantly darker and turned a brown color within 10 min after the addition, and the formation of a precipitate was observed. The mixture was stirred at ambient temperature for 20 h. \[ i-\text{Pr}_3\text{SiC}≡\text{CC}_6\text{H}_4·4·\text{C}≡\text{CC}_6\text{H}_4·4·\text{I} \] (0.03 g, 0.07 mmol, 0.11 eq.) and \[ \text{[PdCl}_2\text{(PPPh}_3\text{)}_2] \] (cat.) and CuI (cat.) were added,28 and the reaction mixture was warmed gently to 30–40 ºC for 30 s before being stirred at ambient temperature for 1.5 h. Silica was added to the reaction mixture, and the solvent was removed.

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28 Both TLC and ¹H NMR spectra indicated that all acetylene initially present in the reaction mixture had reacted, which suggested that the stoichiometric ratio needed this later adjustment.
under reduced pressure. A pale yellow powder was obtained, which was loaded onto a chromatographic silica column. The product was eluted with a mixture of n-pentane and ethylacetate in a (60:1). The solvent was removed under reduced pressure, affording an orange resin that turned into a pale yellow solid (0.33 g, 0.47 mmol, 74%), which was identified as the product after drying under vacuum.

Anal. Calcd. for C\textsubscript{51}H\textsubscript{53}BSi: C 86.65, H 7.84%. Found: C 86.33, H 8.18%. EI MS: 706.4 ([M]+, 90), 663.3 (60), 635.3 (25), 621.3 (60), 607.3 (83), 593.2 (94), 543.2 (35). HR EI MS: Calcd. for C\textsubscript{51}H\textsubscript{53}\textsuperscript{11}BSi: 706.4166. Found: 706.4166. IR (CH\textsubscript{2}Cl\textsubscript{2}) [Rel. Transm., Assignm.]: 1018 [95.4], 1073 [97.0], 1103 [96.4], 1153 [95.8], 1174 [94.4] 1219 [87.2] 1241 [89.9], 1421 [91.7], 1464 [93.4], 1516 [90.1], 1594 [87.8], 1606 [88.4], 2153 [95.0, \nu(SiC≡C)], 2866 [88.8], 2962 [81.4], 3050 [95.7], 3057 [93.5] cm\textsuperscript{-1}. UV-Vis (\nu_{max}, cm\textsuperscript{-1} [\epsilon, 10\textsuperscript{3} M\textsuperscript{-1} cm\textsuperscript{-1}]): 27 000 [42.9, sh], 28 700 [54.6], 37 600 [10.4]. \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): 7.51 (s, 4H, H116, H117), 7.50 (s, 4H, H122, H123), 7.46 (s, 4H, H128, H129), 6.83 (s, 4H, H12), 2.32 (s, 6H, H15), 2.01 (s, 12H, H14), 1.14 (21H, H17, H16) ppm. \textsuperscript{13}C\textsuperscript{[1]}H NMR (126 MHz, CDCl\textsubscript{3}): \delta 146.1 (C115), 141.5 (C115), 140.8 (C111), 138.9 (C13), 136.1 (C116), 132.0, 131.61, 131.55, 131.4 (C122, C123, C128, C129), 131.1 (C117), 128.2 (C12), 126.2 (C118), 123.6, 122.8 (C121, C124), 123.1 (C130, C127), 106.6 (C131), 93.0 (C132), 91.7 (C125), 91.1 (C119, C120), 90.8 (C126), 23.4 (C14), 21.2 (C15), 18.7 (C17), 11.3 (C16) ppm.

HC≡C-\textsubscript{4-C\textsubscript{6}H\textsubscript{4}}C≡C-\textsubscript{4-C\textsubscript{6}H\textsubscript{4}}C≡C-\textsubscript{4-C\textsubscript{6}H\textsubscript{4}}B(2,4,6-C\textsubscript{6}H\textsubscript{3}Me\textsubscript{3})\textsubscript{2} (3-36)

In a flame-dried 100 mL two-neck round-bottom flask, i-Pr\textsubscript{3}SiC≡C-\textsubscript{4-C\textsubscript{6}H\textsubscript{4}}C≡C-\textsubscript{4-C\textsubscript{6}H\textsubscript{4}}C≡C-\textsubscript{4-C\textsubscript{6}H\textsubscript{4}}B(2,4,6-C\textsubscript{6}H\textsubscript{3}Me\textsubscript{3})\textsubscript{2} (3-35) (0.30 g, 0.42 mmol, 1.0 eq.) was dissolved in freshly distilled dichloromethane (90 mL). To the clear, pale yellow solution was added NBu\textsuperscript{n-4}F (1.0 M solution in THF, 1.5 mL, 1.5 mmol, 3.5 eq.) at ambient temperature, after which the solution turned a stronger yellow, yet remaining clear. The solution was stirred at ambient temperature for 20 h. The solvent was removed under reduced pressure, affording a dark red and highly viscous oil. The oil was adsorbed onto silica, giving a pale red powder, which was loaded onto a silica column. The product was eluted with a mixture of n-pentane and ethylacetate (30:1). The solvent was removed under reduced pressure, affording a pale yellow solid, which was
dissolved in a minimal amount of dichloromethane. The resultant solution was
dropped into methanol, after which an off-white, flocculent precipitate was
formed. The solid was removed from the mixture by filtration, and the residual
solvent was removed in vacuo, giving 0.148 g (0.27 mmol, 63%) of the desired
product as a white powder.

Anal. Calcd. for C_{42}H_{35}B: C 91.63, H 6.41%. Found: C 91.64, H 6.58%. El MS:
550.3 ([M]+, 28), 446.1 (5), 430.2 ([M - C_{6}H_{3}Me_{3}]^+, 100), 451.1 (12), 399.1 (5),
302.2 (15). HR El MS: Calcd. for C_{42}H_{35}B: 550.2832. Found: 550.2840. UV-Vis
(ν max, cm⁻¹ [ε, 10^3 M⁻¹ cm⁻¹]): 27300 [47.7], 28700 [56.7], 37900 [10.4]. ¹H NMR
(500 MHz, CDCl₃): δ 7.52, 7.51 (s, 4H, H₁₁₆, H₁₁₇), 7.50 (s, 4H, H₁₁₆, H₁₁₇),
7.48 (s, 4H, H₁₂₂, H₁₂₃), 6.83 (s, 4H, H₁₂), 3.18 (s, 1H, H₁₃₂), 2.32 (s, 6H,
H₁₅), 2.01 (s, 12H, H₁₄) ppm. ¹³C[¹H] NMR (126 MHz, CDCl₃): δ 146.1 (C₁₁₅),
141.5 (C₁₀), 140.8 (C₁₁), 138.9 (C₁₃), 136.1 (C₁₁₆), 132.1, 131.6, 131.6, 131.5,
131.1 (C₁₁₇, C₁₂₂, C₁₂₃, C₁₂₈, C₁₂₉), 128.2 (C₁₂), 126.2 (C₁₁₈), 123.5, 123.12,
122.9, 122.1 (C₁₁₂, C₁₂₄, C₁₂₇, C₁₃₀), 91.7, 91.1. 91.0. 90.8 (C₁₁₉, C₁₂₀, C₁₂₅,
C₁₂₆), 83.2 (C₁₃₁), 79.0 (C₁₃₂), 23.4 (C₁₄), 21.2 (C₁₅) ppm.

\[i-Pr_3SiC≡C(-C_{6}H_{4}C≡C)_{3-4}C_{6}H_{4}B(2,4,6-C_{6}H_{2}Me_{3})_2\] (3-37)

In a flame-dried 100 mL two-neck round-bottom flask,
HC≡C–C₄H₄C≡C–C₄H₄B(2,4,6-C₆H₂Me₃)₂ (3-34) (0.059 g, 0.131 mmol,
1.0 eq.) and \[i-Pr_3SiC≡CC₆H₄–4-C≡CC₆H₄–4—I\] (2-33) (0.070 g, 0.144 mmol,
1.10 eq.) were dissolved in deoxygenated triethylamine (60 mL). To the clear,
white yellow solution were added [PdCl₂(PPh₃)₂] (0.008 g, 0.01 mmol, 0.09 eq.)
and CuI (0.004 g, 0.02 mmol, 0.15 eq.). The pale yellow and slightly cloudy mixture
was deoxygenated again. Within 15 min after the addition of the catalyst,
the reaction mixture became significantly more cloudy, and the color changed to
orange-brown. The mixture was stirred at ambient temperature for 18 h. Silica
was added to the mixture, and the solvent was removed under reduced pressure.
A pale orange powder was obtained, which was loaded onto a silica column (l =
12 cm, Ø = 2.5 cm). The product was eluted from the column with a mixture of
n-pentane and ethylacetate (30:1). The solvent was removed in vacuo, affording
a cloudy, pale green, viscous oil, which solidified after warming the material to
30–40 °C under vacuum, affording 0.083 g (0.103 mmol, 79%) of the product.
Anal. Calcd. for C_{59}H_{99}B_{2}Si: C 87.81%, H 7.37%. Found: C 88.05, H 7.10%. EI MS: 807.0 ([M]^+, 100), 763.8 ([M - i-Pr]^+, 40), 735.7 (25), 721.7 (50), 707.6 (58), 693.6 (70), 643.4 (35), 500.2 (25), 370.2 (48), 286.5 (85). IR (CH2Cl2) [Rel. Transm., Assignm.]: 1017 [95.2], 1220 [90.1], 1240 [91.3], 1456 [95.3], 1519 [87.4], 1593 [93.4], 1604 [96.1], 2152 [97.2, v(SiC≡C)], 2867 [91.8], 2921 [84.9] cm⁻¹. UV-Vis (ν_max, cm⁻¹ [ε, 10^3 M⁻¹ cm⁻¹]): 27 800 [82.7, with shoulders to both sides]. ¹H NMR (500 MHz, CDCl₃): δ 7.52, 7.51 (s, 8H, H122, H123, H128, H129), 7.50 (s, 4H, H116, H117), 7.46 (s, 4H, H134, H135), 2.32 (s, 6H, H15), 2.01 (s, 12H, H14), 1.14 (s, 21H, H16, H17) ppm. ¹³C{¹H} NMR (126 MHz, CDCl₃): δ 146.1 (C115), 141.5 (C10), 140.8 (C11), 138.9 (C13), 136.1 (C116), 132.0, 131.7, 131.4, 131.1, (C122, C123, C134, C135, C117), 131.6 (C128, C129), 128.2 (C12), 126.2 (C118), 123.6, 123.1, 123.1, 123.0, 122.8 (C121, C124, C127, C130, C133, C136), 106.6 (C139), 93.0 (C119), 91.7, 91.1, 91.1, 90.8 (C120, C125, C126, C131, C132), 23.4 (C14), 21.2 (C15), 18.7 (C17), 11.3 (C16) ppm.

Me₉SiC≡C-4-C₆H₄C≡C-4-C₆H₄C≡C-4-C₆H₄C≡C-4-C₆H₄C≡C-4-C₆H₄B(2,4,6-C₆H₃Me₉)₂ (3-38)

In a flame-dried 100 mL two-neck round-bottom flask, HC≡C-4-C₆H₄C≡C-4-C₆H₄C≡C-4-C₆H₄C≡C-4-C₆H₄B(2,4,6-C₆H₃Me₉)₂ (3-36) (0.060 g, 0.11 mmol, 1.0 eq.) was dissolved in deoxygenated triethylamine (40 mL), giving a clear, colorless solution. Me₉SiC≡CC≡C₆H₄-4≡C≡C₆H₄≡I (2-25ₚ) (0.060 g, 0.15 mmol, 1.4 eq.) was added. [PdCl₂(PPh₃)₂] and CuI were added in catalytic amounts, and the resultant pale yellow solution was deoxygenated, before being stirred at ambient temperature for 10 h, over which period a color change to yellow occurred, and a significant amount of a precipitate was formed. Silica was added to the reaction mixture, and the solvent was removed in vacuo. A silica column (l = 12 cm, Ø = 2.5 cm) was loaded with the resultant yellow powder. The product was eluted with a mixture of n-pentane and ethylacetate (10:1, and then 5:1). The fractions containing the product were combined, and the solvent was removed in vacuo. The resultant residue was dissolved in a minimal amount of dichloromethane, affording a clear solution, which was dropped into a mixture of n-pentane and methanol. A flocculent, off-white precipitate was formed, which was removed from the the orange mixture by filtration. The resultant
solid was dried under vacuum at 30–40°C for 12 h, affording 0.047 g (0.06 mmol, 52%) of the product.

EI MS: 822.2 ([M]⁺, 1), 702.4 (2), 600.2 (42), 529.9 (100), 514.9 (25), 486.8 (34), 236.0 (48). HR EI MS: Calcd. for C₆₁H₅₁¹¹BSi: 822.3853. Found: 822.3539. IR (CH₂Cl₂): 1018 [99.3], 1103 [98.9], 1155 [98.4], 1175 [98.1], 1220 [94.8], 1420 [94.3], 1519 [90.5], 1594 [93.9], 1606 [93.6], 2156 [97.6, ν(SiC≡C)], 2305 [98.3], 2924 [94.0], 2960 [92.1], 2965 [92.8], 3056 [93.1, br], 3688 [97.6] cm⁻¹. UV-Vis (νmax, cm⁻¹ [ε, 10³ M⁻¹ cm⁻¹]): 27500 [114.6]. ¹H NMR (300 MHz, CDCl₃): δ 7.52, 7.51 (s, 18H, H141, H140, H135, H134, H129, H128, H123, H122, H117), 7.46 (s, 4H, H116), 6.83 (s, 4H, H12), 2.31 (s, 6H, H15), 2.00 (s, 12H, H14), 0.26 (s, 9H, H16) ppm. ¹³C{¹H} NMR (75 MHz, CDCl₃): δ 146.1 (C115), 141.5 (C10), 140.8 (C11), 138.9 (C13), 136.1 (C116), 131.9, 131.6, 131.4, 131.1 (C122, C123, C128, C129, C134, C135, C140, C141), 128.2 (C12), 126.2 (C118), 123.1, 123.0, (C121, C124, C127, C130, C133, C136, C139, C142, 104.5 (C144), 96.5 (C143), 91.7, 91.1, 90.9 (C121, C124, C127, C130, C133, C136, C139, C142), 23.4 (C14), 21.2 (C15), -0.1 (C16) ppm.

trans-[(dppe)₂ClRu{C≡C-C₆H₄B(2,4,6-C₆H₃Me₃)}₂] (3-39)

In a flame-dried 250 mL two-neck round-bottom flask, HC≡CC₆H₄-4-B(2,4,6-C₆H₃Me₃)₂ (3-32ᵃ) (0.050 g, 0.14 mmol, 1.15 eq.) and cis-[RuCl₂(dppe)₂] (0.120 g, 0.12 mmol, 1.0 eq.) were dissolved in distilled dichloromethane (80 mL). To the clear, yellow solution was added NaPF₆ (0.045 g, 0.27 mmol, 2.2 eq.). After stirring the slightly cloudy mixture for 20 h, the color changed from yellow through orange and red to brown. The volume of the solvent was reduced to 2 mL in vacuo. Triethylamine (1 mL) was added, after which the mixture turned yellow within 1 min. The mixture was dropped into stirring methanol, resulting in the formation of a fine, yellow precipitate. The mixture was filtered through a sintered glass filter funnel, and the solid residue was washed with n-hexane a few times. The residual yellow solid was redissovled in a minimal amount of dichloromethane. The resultant mixture was filtered through cotton wool and dropped into chilled methanol. A precipitate

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²⁹ The acetylene was kindly provided by Prof. Todd Marder and co-workers (Durham University).
was formed, which was removed from the solution by filtration. The solid residue was washed with cold \( n \)-hexane and then dried under vacuum, affording 0.081 g (0.06 mmol, 51\%) of the product.

Crystals suitable for X-ray structural analysis were grown by slow diffusion of \( n \)-hexane into a dichloromethane solution at room temperature. Diffraction data were collected under conditions similar to those described in Chapter 2 (see page 139ff), allowing for solving and refining the structure. The data were collected for a theta-range 2.6–27.5° over 42 hours. The complex was found to crystallize in the triclinic space group P-1. One complex molecule and one solvated dichloromethane molecule are present in the asymmetric unit, two of which occupy the unit cell. All non-hydrogen atoms were refined anisotropically with no restraints or constraints being implemented. H atoms were placed in calculated positions. C-H bonds were restrained to 0.950 Å, and \( U_{iso}(H) \) was kept at values corresponding to 1.2 \( x \) \( U_{eq} \) of the parent atom throughout the refinement to regularize the geometry of the hydrogen atoms. The positions of the hydrogen atoms were refined with riding constraints and recalculated frequently. The largest peaks of residual electron density were located in a difference Fourier map and found to be near the ruthenium center and to the dichloromethane solvent molecule. The dichloromethane molecule shows elongated ellipsoids, indicating the possibility of it being split and the whole molecule being slightly disordered. However, this was not investigated further and no other models were tried, since the overall structure was not affected.

Anal. Calcd. for C\(_{78}\)H\(_{74}\)BCl\(_4\)P\(_4\)Ru : C 73.04, H 5.82%. Found: C 73.16, H 5.85%. ESI MS: 1288.4 ([M - Cl + MeCN]+, 100). HR ESI TOF MS: Calcd. for C\(_{80}\)H\(_{77}\)BNP\(_4\)Ru [M - Cl + MeCN]: 1288.4143. Found: 1288.4171. IR (CH\(_2\)Cl\(_2\)) [Rel. Transm., Assignm.]: 1097 [70], 1171 [53], 1435 [50], 1583 [27], 2058 [40, \( \nu(\text{RuC=Cl}) \)], 2964 [68, \( \nu(\text{C-H}_{\text{aliphatic}}) \)], 3050 [82, \( \nu(\text{C-H}_{\text{aromatic}}) \)] cm\(^{-1}\). UV-Vis (\( \bar{\nu}_{\text{max}} \), cm\(^{-1}\) [\( \epsilon, 10^3 \text{M}^{-1} \text{cm}^{-1} \)]): 23300 [33.1], 31800 [12.9]. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) 7.52–7.50 (m, 8H, H151), 7.30 (d, \( J_{HH} = 8.0 \text{ Hz}, 2H, H116 \)), 7.30–7.24 (m, 8H, H161), 7.22–7.13 (m, 8H, H153, 163), 7.04–6.97, 6.97–6.90 (m, 16H, H152, 162), 6.86 (s, 4H, H12), 6.23 (d, \( J_{HH} = 8.0 \text{ Hz}, 2H, H117 \)), 2.77–2.56 (m, 8H, H170), 2.34 (s, 6H, H15), 2.09 (s, 12H, H14) ppm. \(^31\)P{\(^1\)H} NMR (121 MHz, CDCl\(_3\)): \( \delta \) 50.02 ppm. \(^{13}\)C{\(^1\)H} NMR (126 MHz, CDCl\(_3\)): \( \delta \) 142.1 (C10), 140.8 (C11), 139.3 (C115), 137.9 (C13), 136.7 (C116), 136.3 (vtt, \( |J_{PC} + 3J_{PC}| = \)
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20.6 Hz, C150), 135.4 (vtt, $^1J_{PC} + ^3J_{PC} = 19.4$ Hz, C160), 134.6 (C118), 134.4 (C151), 134.2 (C161), 129.4 (C117), 128.82, 128.79 (C153, C163), 128.0 (C12), 127.2 (C152), 126.9 (C162), 30.7 (vtt, $^1J_{PC} + ^3J_{PC} = 23.1$ Hz, C170), 23.5 (C14), 21.2 (C15) ppm.

$trans-$[(dppe)$_2$ClRu{C≡C-4-C$_6$H$_4$C≡C-4-C$_6$H$_4$B(2,4,6-C$_6$H$_2$Me$_3$)$_2$}] (3-40)

In a flame-dried 100 mL two-neck round-bottom flask, HC≡C-4-C$_6$H$_4$C≡C-4-C$_6$H$_4$B(2,4,6-C$_6$H$_2$Me$_3$)$_2$ (3-34*) (0.055 g, 0.12 mmol, 1 eq.) and $cis-$[RuCl$_2$(dppe)$_2$] (0.110 g, 0.11 mmol, 0.93 eq.) were dissolved in freshly distilled dichloromethane (80 mL). The yellow, clear solution was deoxygenated again, before NaPF$_6$ (0.050 g, 0.30 mmol, 3.0 eq.) was added, after which the solution turned pale orange. The resultant reaction mixture was stirred at ambient temperature for 42 h. The volume of solvent was reduced to 2 mL under reduced pressure, giving a solid, which was suspended in dichloromethane (3 mL). To the dark red mixture was added triethylamine (0.5 mL), after which the solution turned from dark red to orange. The mixture was dropped into stirring methanol, and the resultant mixture was cooled close to the freezing point. The cold mixture was poured into a sintered glass filter funnel and was carefully overlayed with a mixture of n-hexane and a few drops of triethylamine. Suction was applied to remove the solvent, affording a yellow solid, which was redissolved in a minimal amount of dichloromethane. The resultant solution was filtered through tightly packed cotton wool, affording a clear, yellow filtrate, which was dropped into cold n-pentane. A fine precipitate was formed, which was removed from the solution by filtration. A yellow, microcrystalline solid (0.089 g, 0.064 mmol, 66%), identified as the product, was obtained.

Anal. Calcd. for C$_{86}$H$_{78}$BCl$_2$Ru: C 74.70, 5.69%. Found: C 74.62, H 5.77%. ESI MS: 1388.4 ([M - Cl + MeCN]$,^+$, 100), 1051.2 (22), 727.5 (22), 651.5 (20). HR ESI TOF MS: Calcd. for C$_{88}$H$_{81}$BNP$_4^{102}$Ru: 1388.4456. Found: 1388.4464. IR (CH$_2$Cl$_2$) [Rel. Transm., Assignm.]: 1000 [94.9], 1018 [96.2], 1029 [93.0], 1097 [76.9], 1132 [82.4], 1155 [93.1], 1177 [88.2], 1221 [75.7], 1242 [79.0], 1434 [61.9], 1488 [78.7], 1507 [89.9], 1588 [49.9], 1606 [80.7], 2060 [53.6, $\nu$(RuC≡C), br], 2207 [91.1, br], 3027 [29.1], 3050 [87.3], 3062 [89.2] cm$^{-1}$. UV-Vis ($\tilde{\nu}_{max}$, cm$^{-1}$ [ε, 10$^3$ M$^{-1}$ cm$^{-1}$]): 23 000 [23.7], 29 900 [29.1]. $^1$H NMR (500 MHz, CDCl$_3$): δ 7.49
(s, 4H, H16, H17), 7.49–7.40 (m, 8H, H161), 7.36–7.27 (m, 10H, H151, H122), 7.23–7.14 (m, 8H, H153, H163), 7.06–6.90 (m, 16H, H152, H162), 6.84 (s, 4H, H12), 6.55 (d, JHH = 8.3 Hz, 2H, H123), 2.79–2.58 (m, 8H, H170), 2.32 (s, 6H, H15), 2.02 (s, 12H, H14) ppm. 31P{1H} NMR (121 MHz, CDCl₃): δ 49.82 ppm. 13C{1H} NMR (126 MHz, CDCl₃): δ 145.3 (C115), 141.6 (C10), 140.8 (C11), 138.7 (C13), 136.2 (C116, C160), 135.5 (C150), 134.1, 134.4 (C151, C161), 130.9, 130.8, 129.9 (C117, C12, C123), 130.7 (C124), 128.8 (C153, C163), 128.2 (C12), 127.2, 127.0 (C152, C162), 116.3 (C121), 114.5 (C125), 93.0, 89.9 (C119, C120), 30.6 (vtt, 1JPC + 3JPC = 21.9 Hz, C170), 23.4 (C14), 21.2 (C15) ppm.

\[
\text{trans-}/(\text{dppe})₂\text{ClRu}\{C≡C}C₆H₄=CH₂C₆H₄=CH₂B(2,4,6-C₆H₄Me₃)₂\} \quad (3-41)
\]

In a flame-dried 100 mL two-neck round-bottom flask, HC≡CC₆H₄=CH₂=CC₆H₄=CH₂=B(2,4,6-C₆H₄Me₃)₂ (3-36) (0.050 g, 0.091 mmol, 1.0 eq.) and cis-[RuCl₂(dppe)₂] (0.095 g, 0.098 mmol, 1.1 eq.) were dissolved in freshly distilled and deoxygenated dichloromethane (70 mL). To the clear, yellow solution was added NaPF₆ (0.040 g, 0.24 mmol, 2.6 eq.), and the resultant mixture was deoxygenated again. The solution gradually turned orange and then red over a period of 6 h at room temperature and was further stirred with occasional warming for 3.5 d. The amount of solvent was reduced to 2 mL in vacuo. The residual solution was filtered through cotton wool and was dropped into cold n-pentane. A fine, orange precipitate was formed that was removed from the solution by filtration through a sintered glass filter funnel. The orange-brown, solid residue was redissolved in dichloromethane (6 mL). The deep-red mixture was deoxygenated, and triethylamine (1 mL) was added, after which the solution turned slightly lighter and was then of dark yellow to orange color. The mixture was stirred at room temperature for 15 min before the amount of solvent was reduced to 1 mL in vacuo. The residual mixture was

\[\text{30} \quad \text{The reaction appeared to proceed at a particularly slowl rate, which was indicated by} 31P \text{NMR spectra that were taken while the reaction was running. The spectra showed two triplets at 56.7 ppm and 84.7 ppm, corresponding to} [\text{RuCl(dppe)}₂]^{7+}, \text{that were continuously losing intensity compared to the vinylidene signal at 37.3 ppm.}
\]

\[\text{31} \quad \text{Diethylether is usually used for the precipitation of the vinylidene complex. This was attempted here, resulting in the complex to dissolve. The solubility in cold n-pentane seemed lower, so I used this solvent instead.}
\]
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filtered through tightly packed cotton wool and dropped into cold methanol. A fine, yellow precipitate was formed. The mixture was poured into a sintered glass filter funnel and was carefully overlayed with n-pentane before suction was applied to remove the solvent by filtration. A yellow solid was obtained that was dried under vacuum to afford 0.080 g (0.054 mmol, 59%) of the product.

Anal. Calcd. for C_{94}H_{82}BCIP_{4}Ru: C 76.14, H 5.57%. Found: C 76.36, H 5.25%. ESI MS: 1488.4755 ([M - Cl + MeCN]^+, 100). HR ESI TOF MS: Calcd. for C_{96}H_{85}^{11}BNP_{4}^{102}Ru: 1488.4767. Found: 1488.4755. IR (CH_2Cl_2) [Rel. Transm., Assignm.]: 1001 [99.5], 1018 [99.5], 1030 [99.2], 1097 [96.1], 1126 [99.2], 1155 [99.7], 1175 [97.5], 1220 [95.6], 1240 [96.6], 1345 [91.3], 1488 [96.7], 1515 [95.1], 1591 [89.1], 1606 [95.5], 2063 [87.7, ν(RuC≡C), br], 2207 [9951, br], 3049 [97.8], 3061 [98.7] cm^{-1}. UV-Vis (ν_{max}, cm^{-1} [ε, 10^3 M^{-1} cm^{-1}]): 23600 [39.1], 28100 [56.7], 29100 [54.8]. ^1H NMR (500 MHz, CDCl3): δ 7.51 (s, 8H, H116, H117, H122, H123), 7.48–7.43 (m, 8H, H161), 7.35–7.29 (m, 8H, H151), 7.28 (s, 2H, H128), 7.20–7.15 (m, 8H, H153, H163), 7.04–6.98, 6.98–6.92 (m, 16H, H152, H162), 6.83 (s, 4H, H12), 6.56 (d, δ_{HH} = 8.2 Hz, 2H, H129), 2.78–2.63 (m, 8H, H170), 2.32 (s, 6H, H15), 2.02 (s, 12H, H14) ppm. ^31P{^1H} NMR (121 MHz, CDCl3): δ 49.83 ppm. ^13C{^1H} NMR (126 MHz, CDCl3): δ 146.0 (C115), 141.5 (C10), 140.8 (C11), 138.8 (C13), 136.3 (vtt, 1^4J_{PC} + 3^3J_{PC} = 20.2 Hz, C150), 136.1 (C116), 135.6 (vtt, 1^4J_{PC} + 3^3J_{PC} = 19.3 Hz, C160), 134.4, 134.1 (C151, C161), 131.6, 131.3, 130.9 (C117, C122, C123), 131.0 (C128), 130.7 (C130), 129.9 (C129), 128.8 (C153, C163), 128.2 (C12), 127.2, 127.0 (C152, C163), 126.4 (C118), 124.0, 122.3 (C121, C124), 116.2 (C131), 114.5 (C127), 92.9 (C126), 91.4 (C119, C120), 89.3 (C125), 30.6 (vtt, 1^4J_{PC} + 3^3J_{PC} = 23.2 Hz, C170), 23.4 (C14), 21.2 (C15) ppm.

trans-[(dppe)_2ClRu{C≡C-4-C_6H_4C≡C-2,5-{CH_2CHEt(CH_2)_3Me}_2}_4-C_6H_4C≡C-C-4-(C_6H_4C≡C-4-)_2C_6H_4B{(2,4,6-C_6H_3Me)_2}_2] (3-43)

In a flame-dried 100 mL two-neck round-bottom flask, HC≡CC_6H_4-4-C≡CC_6H_4-4-C≡CC_6H_4-4-B{(2,4,6-C_6H_3Me)_2}_2 (3-36) (0.050 g, 0.091 mmol, 1.0 eq.) and trans-[(dppe)_2ClRu{C≡CC_6H_4-4-C≡CC_6H_4-2,5-{CH_2CHEt(CH_2)_3Me}_2}_4-1] (2-50) (0.135 g, 0.091 mmol, 1.0 eq.) were dissolved in a deoxygenated mixture
of triethylamine and freshly distilled dichloromethane (40 mL/30 mL). To the resultant, clear, yellow solution were added [PdCl₂(PPh₃)₂] (0.011 g, 0.15 mmol, 0.18 eq.) and CuI (0.005 g, 0.026 mmol, 0.29 eq.), after which the solution turned orange, then red and finally brown within 1 min after the addition of the catalyst. The reaction mixture was stirred at ambient temperature for 24 h, over which period it reverted to dark orange, and the formation of a precipitate was observed. The solvent was removed under reduced pressure. The brown residue was dissolved in dichloromethane (2 mL). The resultant mixture was filtered through tightly packed cotton wool and was dropped into a stirring mixture of methanol and n-pentane (15:1). An orange, flocculent precipitate was formed that was removed from the mixture by filtration through a sintered glass filter funnel. The precipitation was repeated with a mixture of n-pentane and dichloromethane (10:1), and the solvent was removed from the precipitate by filtration. The solvent was removed from the filtrate under reduced pressure, affording an orange, solid, transparent film on the inside of the flask. The film was dissolved in a minimal amount of dichloromethane, and the resultant clear, orange solution was dropped into stirring cold n-pentane. An orange, flocculent precipitate was formed, which was removed from the mixture by filtration. The solid residue was dried under vacuum at 30–40 °C, affording a yellow-orange solid (0.075 g, 0.039 mmol, 43%) that was identified to be the product.

Anal. Calcd. for C₁₂₈H₁₃₂BCl₂P₄Ru: C 79.33, H 6.45%. Found: C 79.00, H 6.76%. ESI MS: 1912.79 ([M - Cl + MeCN]⁺, 28), 1810.70 (28), 1680.55 (75), 1490.37 (80), 1364.49 (80), 1322.48 (68), 899.15 ([Ru(dppe)₂]⁺, 100). HR ESI TOF MS: Calcd. for C₁₂₈H₁₃₂BCl₂P₄Ru: 1912.7899. Found: 1912.7899. IR (CH₂Cl₂) [Rel. Transm., Assignm.]: 1000 [94.1], 1017 [93.6], 1028 [93.2], 1097 [83.2], 1173 [88.5], 1220 [87.6], 1379 [93.3], 1435 [74.6], 1458 [90.7], 1487 [85.5], 1505 [84.1], 1519 [78.8], 1592 [76.6], 1605 [85.7], 2065 [67.8, ν(RuC≡C), br], 2200 [94.9, br], 2859 [88.6], 2873 [88.9], 2923 [67.8], 2963 [74.6] cm⁻¹. UV-Vis (ν_max, cm⁻¹ [ε, 10³ M⁻¹ cm⁻¹]): 27 400 [109.5], 24 300 [52.1, sh]. ¹H NMR (500 MHz, CDCl₃): δ 7.56–7.41 (m, 18H, H116, H117, H128, H122, H123, H161), 7.34–7.24 (m, 12H, H151, H133, H137), 7.23–7.13 (m, 14H, H153, H163, H129, H142), 7.07–6.89 (m, 16H, H152, H162), 6.83 (s, 4H, H12), 6.56 (d, J_HH = 7.6 Hz, 2H, H143), 2.86–2.78 (m, 2H, H1351), 2.77–2.62 (m, 12H, H170, H1381), 1.88–1.74 (m, 2H, H1352, H1382), 1.47–1.24 (m, 16H, H1353, H1354, H1355, H1357, H1383, H1384,
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H1385, H1387), 0.99–0.83 (m, H1356, H1358, H1386, H1388) ppm. $^{31}$P{$^1$H} NMR (121 MHz, CDCl$_3$): $\delta$ 49.88 ppm.

trans-[(dppe)$_2$ClRu{C≡C-4-[(C$_6$H$_4$C≡C-4-)$_4$C$_6$H$_4$B(2,4,6-9C$_6$H$_2$Me$_3$)$_2$}] (3-42)

In a flame-dried 100 mL two-neck round-bottom flask, i-Pr$_3$SiC≡C(C$_6$H$_4$-4-C≡C)$_4$C$_6$H$_4$-4-B(2,4,6-C$_6$H$_2$Me$_3$)$_2$ (0.030 g, 0.036 mmol, 1.0 eq.) was suspended in freshly distilled and deoxygenated dichloromethane (90 mL). The clear, pale yellow solution was stirred at 20–30°C for 40 min to dissolve as much starting material as possible. NBu$_n$$_4$F (1.0 M solution in THF; 0.10 mL, 0.10 mmol, 2.7 eq.) was added at room temperature, after which the solution became a slightly darker yellow but remained clear. The reaction mixture was stirred at ambient temperature for 17 h, over which time the color became less intense. Water was added, and the resultant mixture was stirred vigorously for 3 min. The layers were separated, and the aqueous layer was washed with dichloromethane twice. The combined organic layers were washed with water twice and then with a dilute aqueous HCl solution. The organic layer was dried over MgSO$_4$. Filtration through filter paper into a flame-dried 100 mL two-neck round-bottom flask gave a clear, golden-yellow solution$^{32}$ that was deoxygenated by bubbling argon through it for 20 min. cis-[RuCl$_2$(dppe)$_2$] (0.050 g, 0.52 mmol, 1.4 eq.) was added. The clear, yellow solution was deoxygenated, and NaPF$_6$ (0.025 g, 0.15 mmol, 4.0 eq.) was added. The resultant solution was deoxygenated again and was then stirred at 25–30°C for 17 h. The majority of solvent of the slightly cloudy, red solution was removed in vacuo, giving 2 mL of the residual mixture. Triethylamine (1 mL) was added to the mixture, after which the mixture turned from dark red to yellow instantaneously. The mixture was immediately dropped into stirring methanol, giving a yellow, flocculent precipitate that was removed from the mixture by filtration through a sintered glass filter funnel (pore size G4). A yellow, amorphous solid was obtained that was redissolved in a minimal amount of dichloromethane (2 mL). The mixture was filtered through tightly packed cotton wool into a mixture of n-pentane and dichloromethane (6:1), giving a yellow solution with a small

$^{32}$ A minimal amount of this intermediate acetylene solution was isolated for characterization.
amount of a yellow, floculent precipitate. Filtration through a sintered glass filter funnel (pore size G4) gave an orange, microcrystalline residue and a clear, yellow filtrate. To the filtrate was added n-hexane, and the volume of the resultant clear, yellow solution was reduced in vacuo, until it became cloudy. A grainy, yellow precipitate was formed, which was removed from the solution by filtration. The yellow, solid residue was washed with n-pentane and was then taken to dryness under reduced pressure. The filtrate was taken to dryness and the solid thus obtained subjected to a second, careful washing to afford a second portion of the product. The solvents were combined, and the residual solvent was removed under vacuum at 30–40 °C, giving 0.056 g (0.021 mmol, 57%; over two steps) of the product as a yellow solid.

Data for the intermediate acetylene (HCC=CH2C≡C=CH2H4C≡C=CH2H4C≡C=CH2):

1H NMR (300 MHz, CDCl3): δ 7.52, 7.50, 7.50 (s, 2OH, H116, H117, H122, H123, H128, H129, H134, H135, H142, H143), 6.83 (s, 4H, H13), 3.19 (s, 1H, H146), 2.31 (s, 6H, H15), 2.00 (s, 12H, H12) ppm.

Data for trans-[(dppe)2ClRu{C≡C=CH2H4C≡C=CH2H4C≡C=CH2H4C≡C=CH2}]


Calcd. for C94H72NP4102Ru: 1440.3659. Found 1440.3652 ([M - Cl - B(mes)]2 + MeCN)^+.

IR (CH2Cl2) [Rel. Transm., Assignm.]: [s, ν(RuC≡C)]: 1096 [99.5], 1436 [97.5], 1519 [96.1], 1605 [86.2], 2062 [97.4, ν(RuC≡C)], 2956 [80.4], 3600 [95.2], 3687 [86.2] cm⁻¹. UV-Vis (νmax, cm⁻¹ [ε, 10^4 M⁻¹ cm⁻¹]): 23 600 [39.4], 27 800 [91.9]. 1H NMR (500 MHz, CDCl3): δ 7.52 (s, 16H, 116, H117, H122, H123, H128, H129, H134, H135), 7.49–7.43 (m, 12H, H161), 7.35–7.29 (m, 12H, H151), 7.24–7.15 (m, 8H, H153, H163), 7.06 (d, JHH = 7.5 Hz, 2H, H140), 7.04–6.98, 6.98–6.92 (m, 16H, H152, H162), 6.83 (s, 4H, H12), 6.62–6.47 (m, 2H, H141), 2.79–2.60 (m, 8H, H170), 2.32 (s, 6H, H15), 2.01 (s, 12H, H14) ppm. 31P{1H} NMR (121 MHz, CDCl3): δ 49.84 ppm. 13C{1H} NMR (126 MHz, CDCl3): δ 145.8 (C115), 141.1 (C10), 140.8 (C11), 138.9 (C13), 136.3 (C150), 136.1 (C116), 135.5 (C160), 134.4, 134.2 (C151, C161), 133.6, 133.4,
(C117, C122, C123, C128, C129, C134, C135, C140), 131.1 (C141), 128.9 (C153, C163), 128.2 (C12), 127.2, 127.0 (C152, C162), 126.2 (C118), 123.4–121.9 (C121, C124, C127, C130, C133, C136), 91.7–88.5 (C119, C120, C125, C126, C131, C132, C137, C138), 30.6 (m, C170), 23.4 (C14), 21.2 (C15) ppm.33

3,5-\{trans-\{trans-\{(PhC≡C)Ru(dppe)2(C≡C)\}]\}C6H4-1-(C≡CC6H4-4-C≡CC6H4-4-C≡CC6H4-4-C≡C)C6H3 \(3.21\)

In a flame-dried 100 mL two-neck round-bottom flask fitted with a condenser, 1.3-\{trans-RuCl(dppe)2(C≡C)\}2-5-(Me3SiC≡CC6H4-4-C≡CC6H4-4-C≡C)C6H3 \(3.11\) (0.030 g, 0.013 mmol, 2.0 eq.) and 1.3-\{trans-\{(PhC≡C)Ru(dppe)2(C≡C)\}]2-5-(HC≡CC6H4-4-C≡CC6H4-4-C≡C)C6H3 \(3.17^*\)34 (0.070 g, 0.030 mmol, 2.3 eq.) were dissolved in freshly distilled and deoxygenated dichloromethane. To the clear, yellow solution were added triethylamine (4 drops) and NaPF6 (0.015 g, 0.090 mmol, 6.8 eq.). The resultant reaction mixture was deoxygenated and was then heated at reflux for 14 h. The amount of solvent was reduced to 2 mL in vacuo. The residual mixture was dropped into stirring methanol. A flocculent, yellow precipitate was formed, which was isolated by filtration through a sintered glass filter funnel (pore size G4). The solid residue was redissolved in dichloromethane (2 mL), and the resultant mixture was dropped into methanol. A homogeneous, yellow suspension was obtained that was filtered through a sintered glass filter funnel (G4). An orange, glossy, solid residue was obtained that was precipitated from a mixture of n-pentane and dichloromethane (6:1) in the same fashion as described above, which gave a homogeneous, yellow suspension. Filtration afforded 0.066 g (0.010 mmol, 73%) of the orange, solid product.

Anal. Calcd. for C431H359P24Ru6Si: C 74.94, H 5.11%. Found: C 74.75, H 5.16%.
IR (CH2Cl2) [Rel. Transm., Assignm.]: [s, ν(RuC≡C)]: 999 [99.8], 1029 [99.8], 1099 [91.1], 1420 [96.6], 1434 [82.8], 1484 [90.0], 1512 [94.3], 1560 [87.5], 1591 [92.3], 2054 [65.9, ν(RuC≡C)], 2909 [93.1], 2963 [84.7], 3054 [88.5, br] cm⁻¹.

33 Not all expected peaks could be observed; only observed peaks are reported.
34 Unpublished results, Honours Thesis Katy A. Green, ANU.
3.5. Experimental

UV-Vis (ν_{max}, cm⁻¹ [ε, 10^3 M⁻¹ cm⁻¹]): 24100 [126.0], 29400 [326.3]. ¹H NMR (300 MHz, CDCl₃): δ 7.80–6.50 (m, 293H, Ar-H), 2.70 (m, 48H, PCH₂), 0.27 (s, 9H, Si(CH₃)₃) ppm. ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 54.58 (s, 16P), 54.32 (s, 8P) ppm. ¹³C{¹H} NMR (126 MHz, CDCl₃): δ 138.2–135.9 (m, C250, C260, C250, C360), 134.3, 134.1, 134.0 (C251, C261, C351, C361), 131.9, 131.6 (C204, C205, C304, C305), 131.4 (C210, C211, C310, C311), 130.6 (C203, C303), 130.0 (C304), 129.6 (C22, C32), 128.8, 128.7, 128.6, 128.5 (C253, C263, C353, C363), 127.3 (C305, C405), 127.1, 127.0 (C252, C262, C352, C362), 124.4, 123.7, 123.2, 123.1, 122.3, 121.1 (C203, C206, C209, C212, C303, C306, C309, C312), 122.7 (C406), 116.8, 116.4, 116.1 (C215, C302, C315, C402), 104.7 (C202, C302), 96.5 (C201, C301), 93.0 (C214, C314), 92.5, 91.2, 90.7, 89.4 (C207, C208, C307, C308), 87.5, 87.4 (C213, C313), 31.6 (vtt, ¹¹J_{PC} + ³³J_{PC} = 22.2 Hz, C270, C370), -0.1 (C10) ppm.

\[ 3,5-(\text{trans}-[\{3,5-(\text{trans}-[(\text{PhC}≡\text{C})\text{Ru(dpppe)}_2(\text{C}≡\text{C})])\text{C}_6\text{H}_3-I-(\text{C}≡\text{CC}_6\text{H}_4-4-\text{C}≡\text{C})\text{Ru(dpppe)}_2(\text{C}≡\text{C})]\}_2-1-(\text{HC}≡\text{CC}_6\text{H}_4-4-\text{C}≡\text{CC}_6\text{H}_4-4-\text{C}≡\text{C})\text{C}_6\text{H}_3 \] (3-22)

In a flame-dried 100 mL one-neck round-bottom flask, 3,5-(trans-\{3,5-(trans-[(PhC≡C)Ru(dpppe)_2(C≡C)])C_6H_3-I-(C≡CC_6H_4-4-C≡CC_6H_4-4-C≡C)\}Ru(dpppe)_2(C≡C)]_2-1-(Me_3SiC≡CC_6H_4-4-C≡CC_6H_4-4-C≡C)C_6H_3

(0.035 g, 0.005 mmol, 1.0 eq.) was dissolved in freshly distilled and deoxygenated dichloromethane (60 mL). To the clear, yellow solution was added NBu^4F (1.0 M solution in THF; 0.2 mL, 0.2 mmol, 40 eq.), after which a color change to slightly darker orange occurred. The clear, yellow solution was deoxygenated, and within ca. 5–10 min, the solution became slightly cloudy. The mixture was stirred at ambient temperature for 10 h. The clear, yellow solution was reduced to 2 mL in vacuo, and the orange residual mixture was pipetted into stirring methanol. A fine, grainy precipitate was formed, which was removed from the mixture by filtration through a sintered glass filter funnel (pore size G4). The orange, solid residue was redissolved in dichloromethane (2 mL), and the resultant, orange mixture was filtered through tightly packed cotton wool into a stirring mixture of n-pentane and dichloromethane (7:1). A yellow, flocculent precipitate was formed that was isolated by filtration. A yellow-orange solid was obtained, which
was dried under vacuum at 30–40 °C, affording 0.028 g (0.0041 mmol, 81%) of the product.

Anal. Calcd. for C_{428}H_{342}P_{24}Ru_{6}: C 75.21; H 5.04%. Found: C 75.46; H 4.94%.

^1^H NMR (500 MHz, CDCl₃): δ 7.72–7.29 (m, 120H, H204, H205, H210, H211, H251, H261, H304, H305, H310, H311, H351, H361), 7.22–7.04 (m, 56H, H253, H263, H353, H363, H405), 7.03–6.83 (m, 100H, H252, H262, H352, H362, H406), 6.79–6.56 (m, 15H, H23, H31, H33, H404), 6.52 (s, 2H, H21), 3.19 (s, 1H, H201) 2.79–2.62 (m, 48H, H270, H370) ppm. ^13^C{^1^H} NMR: δ 137.6–136.4 (m, C250, C260, C350, C360), 134.3, 134.1, 134.0 (C251, C261, C351, C361), 132.1, 131.7, 131.5 (C204, C205), 131.4 (C210, C211), 130.8, 130.7 (C403), 130.0 (C404), 129.6 (C21, C22, C23, C32, C33), 128.8, 128.7, 128.5 (C253, C263, C353, C363), 127.3 (C405), 127.1, 127.0 (C252, C262, C352, C362), 123.7, 123.6 (C206, C209, C306, C309), 122.7 (C406), 122.0 (C203, C212, C312), 121.0 (C20, C30), 116.8, 116.1 (C215, C302, C315, C402), 93.0, 92.5 (C214, C314), 91.3, 89.4 (C208, C207, C308, C307), 87.5 (C213, C313), 83.2 (C202), 79.0 (C201), 31.6 (vtt, ^3^J_{PC} = 24.0 Hz, C270, C370) ppm. ^31^P{^1^H} NMR (162 MHz, CDCl₃): δ 54.58 [16P, peripheral Ru(P_{2}PCH_{2}CH_{2}P_{2}Ph_{2})_{2}], 54.31 [8P, core Ru(P_{2}PCH_{2}CH_{2}P_{2}Ph_{2})_{2}] ppm.

\[1,3,5-\{\text{trans-}[\text{IC}_{6}H_{4-4}-\text{C}≡\text{CC}_{6}H_{4-4}-\text{C}≡\text{C}]\text{Ru(dppe)_{2}}(\text{C}≡\text{CC}_{6}H_{4-4}-\text{C}≡\text{CC}_{6}H_{4-4}-\text{C}≡\text{C})\}\}_{3}\text{C}_{6}H_{3} \ (3-48)\]

In a flame-dried 100 mL two-neck round-bottom flask fitted with a condenser, 1,3,5-(HC≡CC_{6}H_{4-4}-\text{C}≡CC_{6}H_{4-4}-\text{C}≡\text{C})_{3}C_{6}H_{3} \ (2-8') \ (0.080 g, 0.11 mmol, 1.0 eq.) was suspended in freshly distilled and deoxygenated dichloromethane (160 mL). The inhomogeneous mixture was warmed gently while stirring for 10 min to maximize the amount of dissolved material.\(^ {35}\) To the reddish-brown, inhomogeneous mixture was added

\(^ {35}\) Large π-conjugated systems, such as this starting material consisting of phenylethynyl units, show the tendency to undergo what is believed to be a self-polymerization process. This occurs particularly when free acetylene functionalities are present in the molecule. The undesired material is of dark brown to black color and shows poor solubility in most common organic solvents. The formation of such materials has been observed independently by several group members and is a common problem when it comes to the extension of phenylethynyl-bridged compounds.
trans-[Ru(C≡CC₆H₄-4-C≡CC₆H₄-4-I)Cl(dppe)₂] (2-48) (0.41 g, 0.33 mmol, 3.1 eq.). The resultant mixture was deoxygenated, and triethylamine (3 drops) was added, followed by addition of NaPF₆ (0.10 g, 0.60 mmol, 5.6 eq.). The mixture was heated at reflux for 30 min before a second portion of triethylamine (2 drops) was added. The mixture was heated at reflux for 8 h, over which period the mixture turned orange with a brown tinge. The solvent was reduced to 2 mL in vacuo. A brown-orange, highly cloudy mixture was obtained that was dropped into stirring methanol. A thick, orange precipitate was formed, which was removed from the mixture by filtration. The dark yellow solid was redissolved in dichloromethane (10 mL), and the resultant mixture was filtered through a sintered glass filter funnel (pore size G3). A clear, dark orange filtrate was obtained, with a dark brown, solid residue remaining on the funnel, which did not dissolve in dichloromethane. The volume of the filtrate was reduced in vacuo, and the concentrated mixture was dropped into a mixture of n-pentane and dichloromethane (20:1). A thick, orange precipitate was formed that was isolated by filtration through a sintered glass filter funnel (pore size G3). The orange, solid residue was dried under vacuum at 30–40°C, affording 0.33 g (0.080 mmol, 75%) of the product.

Anal. Calcd. for C₂₆₄H₁₉₅I₃P₁₂Ru₃: C 71.69, H 4.44%. Found: C 71.91, H 4.51%.
IR (CH₂Cl₂) [Rel. Transm., Assignm.]: [s, ν(RuC≡C)]: 1006 [97.8], 1098 [93.5], 1134 [95.9], 1175 [97.5], 1213 [99.0], 1421 [94.7], 1434 [87.0], 1487 [92.2], 1504 [87.6], 1512 [89.7], 1579 [88.6], 1592 [85.7], 2051 [58.2, ν(RuC≡C)], 2209 [95.6], 2909 [91.2], 2920 [59.8], 2953 [77.5], 2959 [82.9], 3055 [86.2, br] cm⁻¹. UV-Vis (ν_max, cm⁻¹ [ε, 10³ M⁻¹ cm⁻¹]): 24 000 [209.3], 29 600 [171.7, sh], 31 600 [194.4].
¹H NMR (500 MHz, CDCl₃): δ 7.73–7.67 (m, 9H, H10, H211), 7.55 (s, 12H, H134, H135), 7.54–7.46 (m, 48H, H151, H161), 7.38–7.29 (m, 12H, H142, H210), 7.29 (m, 6H, H205), 7.23–7.15 (m, 24H, H153, H163), 7.04–6.93 (m, 48H, H152, H162), 6.75–6.64 (m, 12H, H143, H204), 2.71–2.59 (m, 24H, H170) ppm. ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 54.04 ppm. ¹²C{¹H} NMR (126 MHz, CDCl₃): δ 138.5 (m, C201, C146), 137.4 (C211), 136.7 (vtt, |J_PC + 3J_PC| = 19.7 Hz, C150, C160), 134.2 (C10), 134.1 (C151, C161), 132.9 (C205), 131.6, 131.3 (C134, C135, C144), 131.0, 130.9 (C20, C142, C203), 129.9 (C204, C143), 128.7 (C153, C163), 127.1 (C152, C162), 124.2, 124.0 (C11, C133), 123.4 (C209), 121.9 (C136), 117.8, 117.7 (C206, C141), 116.4, 116.3 (C145, C202), 93.4 (C212), 92.9 (C140), 92.1 (C208),
1,3,5-{(trans-{[(2,4,6-C_{6}H_{5}Me_{3})B=4-C_{6}H_{4}C≡C]Ru(dppe)}_{2}[C≡CC_{6}H_{4}-4- C≡C])})_{3}C_{6}H_{3}} (3-44)

In a flame-dried 100 mL two-neck round-bottom flask, 
1,3,5-(HC≡CC_{6}H_{4}-4-C≡C)_{3}C_{6}H_{3} (2-5\textsuperscript{*}) (0.009 g, 0.020 mmol, 1.0 eq.) and trans-[(dppe)_{2}ClRu(C≡CC_{6}H_{4}-4-B(2,4,6-C_{6}H_{5}Me_{3})_{2})] (3-38) (0.078 g, 0.061 mmol, 3.04 eq.) were dissolved in freshly distilled and deoxygenated dichloromethane (60 mL). Triethylamine (5 drops) and NaPF_{6} (0.025 g, 0.15 mmol, 7.45 eq.) were added. The reaction mixture was deoxygenated again and then heated at reflux for 12 h. The amount of solvent was reduced to 2 mL in vacuo, and the residual mixture was filtered through cotton wool into stirring methanol. A fine, yellow precipitate was formed, which was isolated by filtration through a sintered glass funnel (pore size 4). The yellow, solid residue was redissolved in dichloromethane (2 mL), and the precipitation repeated from n-pentane. After filtration, a yellow solid was obtained that was dried under vacuum at 40–50 °, affording 0.056 g (0.013 mmol, 67%) of the product.

Anal. Calcd. for C_{276}H_{427}B_{3}P_{12}Ru_{3}: C 77.41, H 5.70%. Found: C 77.02, H 5.58%. IR (CH_{2}Cl_{2}) [Rel. Transm., Assignm.]: 1097 [90.7], 1170 [82.8], 1214 [92.0], 1241 [90.1], 1434 [85.9], 1487 [92.5], 1502 [1498], 1584 [70.6], 1606 [94.4], 2050 [64.4, ν(RuC≡C)], 2910 [90.1], 2919 [69.9], 3053 [95.3,br] cm\textsuperscript{-1}. UV-Vis (ν_{max}, cm\textsuperscript{-1} [ε, 10\textsuperscript{3} M\textsuperscript{-1} cm\textsuperscript{-1}]): 23200 [197.6], 31900 [101.4]. \textsuperscript{1}H NMR (500 MHz, CDCl_{3}): δ 7.63 (s, 3H, H10), 7.57–7.51 (m, 24H, H152), 7.51–7.45 (m, 24H, H162), 7.38–7.32 (m, 12H, H142, H205), 7.24–7.18, 7.18–7.13 (m, 24H, H153, H163), 7.02–6.92 (m, 48H, H152, H162), 6.87 (s, 12H, H22), 6.76 (d, J_{HH} = 8.0 Hz, 6H, H204), 6.68 (d, J_{HH} = 8.2 Hz, 6H, H143), 2.67–2.58 (m, 24H, H170), 2.35 (s, 18H, H25), 2.11 (s, 36H, H24) ppm. \textsuperscript{31}P{\textsuperscript{1}H} NMR (121 MHz, CDCl_{3}): δ 54.09 ppm. \textsuperscript{13}C{\textsuperscript{1}H} NMR (126 MHz, CDCl_{3}): δ 142.2 (C20), 140.8 (C21), 139.6 (C206), 137.9 (C23), 137.0–136.4 (m, C150, C160), 136.8 (C205), 134.7 (C203), 134.1 (C151, C161), 133.2 (C10), 131.0 (C142), 130.9 (C144), 129.9 (C143), 129.3 (C204), 128.7 (C153, C163), 128.0 (C22), 127.1 (C152, C162), 124.4 (C11), 119.3 (C202), 117.8 (C145), 364
3.5. Experimental

116.4 (C141), 91.6 (C140), 88.3 (C139), 31.4 \( (\text{vtt, } |^1 J_{PC} + ^3 J_{PC}| = 24.1 \text{ Hz, C170})\), 23.5 (C24), 21.2 (C25) ppm.

\[ 1,3,5-\{\text{trans-}[{(2,4,6-C_6H_5Me_3)B-4-C_6H_4C≡C}]Ru(dppe)_2\{[C≡CC_6H_4-4-C≡CC_6H_4-4-C≡C]}_3C_6H_3 \] (3-45)

In a flame-dried 100 mL two-neck round-bottom flask fitted with a condenser, 1,3,5-\{\text{trans-}[{\text{dppe}}]_2\text{ClRu(C≡C_6H_4-4-C≡CC_6H_4-4-C≡C]}}_3\text{C}_6\text{H}_3 \] (2-14)
(0.090 g, 0.025 mmol, 1.0 eq.) was dissolved in freshly distilled and deoxygenated dichloromethane (60 mL). To the orange, clear solution was added HC≡CC_6H_4-4-B(mes)_2 (3-32^a) (0.050 g, 0.143 mmol, 5.6 eq.).^36 The resultant solution was deoxygenated, and NaPF_6 (0.030 g, 0.18 mmol, 7.0 eq.) and triethylamine (5 drops) were added. The reaction mixture was then heated at reflux for 48 h. The slightly cloudy, orange reaction mixture was reduced to 2 mL in vacuo. The cloudy residual mixture was filtered through cotton wool into stirring methanol. A fine, yellow precipitate was formed that was isolated by filtration. The solid residue was redissolved in dichloromethane (2 mL). The resultant, slightly cloudy mixture was filtered through cotton wool and dropped into stirring n-pentane. A yellow precipitate was formed that was separated from the mixture by filtration through a sintered glass filter funnel. An orange solid was obtained, which was dried under vacuum at 30–40°C, affording 0.075 g (0.017 mmol, 66%) of the product.

Anal. Calcd. for C_{294}H_{249}B_3P_{12}Ru_3: C 78.65, H 5.59%. Found: C 78.61, H 5.34%.
IR (CH_2Cl_2) [Rel. Transm., Assignm.]: [s, \( \nu(\text{RuC≡C}) \): 1098 [96.3], 1170 [91.9], 1214 [96.5], 1241 [96.9], 1421 [93.2], 1435 [92.4], 1487 [96.5] 1513 [94.8], 1578 [82.3], 1605 [96.8], 2049 [79.8, \( \nu(\text{RuC≡C}) \)], 2908 [93.2], 2920 [84.8], 2950 [93.6], 2958 [86.0], 2965 [93.4], 3055 [88.6] cm\(^{-1}\). UV-Vis (\( \tilde{\nu}_{\text{max}} \), cm\(^{-1}\) [\( \varepsilon, \times 10^3 \text{ M}^{-1}\text{cm}^{-1}\)]): 22900 [224.1], 30700 [180.0]. ^1H NMR (500 MHz, CDCl_3): \( \delta 7.70 \) (s, 3H, H10), 7.54 (s, 12H, H134, H135), 7.58–7.51 (m, 24H, H161), 7.51–7.44 (m, 24H, H152), 7.35 (d, \( J_{HH} = 7.9 \) Hz, 6H, H205), 7.33 (d, \( J_{HH} = 8.2 \) Hz, 6H, H142), 7.22–7.12 (m, 24H, H153, H163), 7.03–6.91 (m, 48H, H152, H162), 6.87 (s, 12H, H22),

^36 The boron-containing starting material was kindly provided by Prof. Todd Marder and co-workers (Durham University).
CHAPTER 3. Dendrimers – Branched Octupolar Ruthenium Acetylide and Mixed-Metal Ruthenium-Osmium Acetylide Complexes

6.79 (d, $J_{HH} = 7.9$ Hz, 6H, H204), 6.67 (d, $J_{HH} = 8.2$ Hz, 6H, H143) ppm. $^{31}$P{$^1$H} NMR (121 MHz, C$_6$D$_6$): δ 54.03 ppm. $^{13}$C{$^1$H} NMR (126 MHz, CDCl$_3$): δ 142.2 (C20), 140.8 (C21), 139.7 (C206), 137.9 (C23), 137.0–136.4 (m, C150, C160), 136.8 (C205), 134.7 (C203), 134.4 (C10), 134.2 (C151, C161), 131.6, 131.4 (C134, C135), 130.9 (C142), 129.9 (C143), 129.4 (C204), 128.7 (C153, C163), 128.0 (C122), 127.1 (C152, C162), 124.2 (C11), 124.0 (C133), 121.9 (C136), 119.3 (C202), 117.8 (C145), 116.4 (C141), 93.0 (C140), 90.5 (C139), 89.4 (C132), 89.2 (C131), 31.4 (vtt, $^1J_{PC} + 3^3J_{PC} = 23.9$ Hz, C170), 23.5 (C24), 21.2 (C25) ppm.

$^{1,3,5}$-{($trans$-{[(IC$_6$H$_4$-4-C≡C)](dppe)$_2$O$_3$(C≡CC$_6$H$_4$-4-C≡C)})Ru(dppe)$_2$(C≡CC$_6$H$_4$-4-C≡CC$_6$H$_4$-4-C≡C)}$_3$C$_6$H$_3$ (3-55$^b$)

In a flame-dried 100 mL two-neck round-bottom flask, $^{1,3,5}$-{($trans$-[RuCl(dppe)$_2$(C≡CC$_6$H$_4$-4-C≡CC$_6$H$_4$-4-C≡C)])$_3$C$_6$H$_3$ (2-14) (0.034 g, 0.010 mmol, 1.0 eq.) and $trans$-{[(IC$_6$H$_4$-4-C≡C)]Os(C≡CC$_6$H$_4$-4-C≡CH)(dppe)$_2$]} (3-53$^a$) (0.040 g, 0.030 mmol, 3.1 eq.) were dissolved in freshly distilled anddeoxygenated dichloromethane (60 mL). The orange, clear solution wasdeoxygenated, and NaPF$_6$ (0.018 g, 0.011 mmol, 11 eq.) was added. The resultant solution wasdeoxygenated again, and triethylamine (10 drops) was added. The reaction mixture was heated at reflux for 36 h. The amount of solvent of the red, slightly cloudy mixture was reduced to 2 mL under reduced pressure, and the residual mixture was filtered through tightly packed cotton wool into stirring methanol, after which a flocculent, orange-brown precipitate was formed. The solid was removed from the mixture by filtration through a sintered glass filter funnel. The residual solid was redissolved in a minimal amount of dichloromethane. The resultant solution was dropped into stirring n-pentane, affording a flocculent precipitate, which was isolated by filtration. The residual solvent was removed under reduced pressure at 30–40°C, affording 0.040 g (0.006 mmol, 56%) of the product.

Anal. Calcd. for C$_{428}$H$_{339}$I$_3$Os$_3$P$_{24}$Ru$_3$: C 68.62, H 4.58%. Found: C 68.11, H 4.49%. ESI MS: 3573.8 (<1), 2276.4 ([$trans$-{($trans$-[(IC$_6$H$_4$-4-C≡C)](dppe)$_2$O$_3$)]C≡CC$_6$H$_4$-4-C≡C})Ru(dppe)$_2$(NCMe) - 2H$^+$, 1), 1787.3 (2), 1466.50 (34), 1243.2 (100), 1117.3 (22). IR (CH$_2$Cl$_2$) [Rel. Transm.,
Assignm.: 1000 [92.9], 1028 [94.6], 1097 [84.6], 1176 [94.8], 1211 [94.7], 1434 [78.6], 1477 [89.5, sh], 1487 [86.1], 1412 [91.0], 1574 [90.2, sh], 1590 [86.5], 1966 [94.0], 2055 [57.6, $\nu$(RuC≡C), $\nu$(OsC≡C), br], 2205 [97.2], 2912 [91.0], 2955 [84.3], 2961 [82.7], 3046 [95.0], 3067 [95.8] cm$^{-1}$. UV-Vis ($\bar{\nu}_{\text{max}}, \text{cm}^{-1} [\epsilon, 10^3 \text{M}^{-1} \text{cm}^{-1}]$): 23800 [149.1], 25900 [222.3], 29000 [219.7]. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.13–6.38 (m, 291H, Ar-H), 2.84–2.27 (m, 48H, H170, H270) ppm. $^{31}$P{$^1$H} NMR (121 MHz, CDCl$_3$): $\delta$ 54.22 [12P, Ru(Pb$_2$PCH$_2$CH$_2$PPh$_2$)$_2$], 16.55 [12P, Os(Pb$_2$PCH$_2$CH$_2$PPh$_2$)$_2$] ppm.

$1,3,5$-$\{\text{trans-$\{(IC_6H_4-4-C≡C)\}(dppe)\}_2Os(C≡CC_6H_4-4-C≡CC_6H_4-4-C≡C)\}}$Ru(dppe)$_2${$C≡CC_6H_4-4-C≡CC_6H_4-4-C≡C$)}$_3$C$_6$H$_3$ (2-14) (0.043 g, 0.012 mmol, 1.0 eq.) and $\text{trans-$\{(IC_6H_4-4-C≡C)\}Os(dppe)\}_2$}{$C≡CC_6H_4-4-C≡CC_6H_4-4-C≡C$)} (3-54a) (0.055 g, 0.038 mmol, 3.3 eq.) were dissolved in freshly distilled and deoxygenated dichloromethane (60 mL). To the orange, clear solution was added NaPF$_6$ (0.012 g, 0.073 mmol, 6.0 eq.). The resultant solution was deoxygenated again, and triethylamine (10 drops) was added. The solution was heated at reflux for 12 h, after which the mixture became significantly darker, and a color change to dark orange occurred. NaPF$_6$ (0.012 g, 0.073 mmol, 6.0 eq.) was added.$^{37}$ The reaction mixture was heated at reflux for 6 h, before more $\text{trans-$\{(IC_6H_4-4-C≡C)\}Os(dppe)\}_2$}{$C≡CC_6H_4-4-C≡CC_6H_4-4-C≡C$)} (3-54a) (0.015 g, 0.010 mmol, 1.0 eq.) was added. The resulting mixture was heated at reflux for 12 h. The amount of solvent was reduced to 2 mL under reduced pressure. The residual mixture was filtered through tightly packed cotton wool. The clear filtrate was dropped into stirring methanol, after which a flocculent, orange-brown precipitate was formed that was collected by filtration through a sintered glass filter funnel. The residual solid was redissolved in a minimal amount of dichloromethane. The resultant mixture was dropped into stirring n-hexane. A flocculent, orange-brown precipitate was formed, which was

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$^{37}$ The crude $^{31}$P NMR spectrum indicated the presence of both starting materials, for which reason more NaPF$_6$ was added.
removed from the mixture by filtration. A solid was obtained, which was dried under vacuum at 30–40 °C, affording 0.050 g (0.006 mmol, 53%) of the product.

**Anal. Calcd.** for C_{450}H_{351}I_{3}O_{38}P_{24}Ru_{3}:  C 69.68,  H 4.56%.  Found:  C 69.04,  H 5.11%.  ESI MS:  2465 (< 1), 2378.5 ([(trans-){(trans-][(IC_6H_4-4-C≡C)](dppe)_{2}Os]}C≡CC_6H_4-4-C≡CC_6H_4-4-C≡C)Ru(dppe)_{2}(NCMe)]^{+},  1), 2365.4 ([(trans-){(trans-][(IC_6H_4-4-C≡C)](dppe)_{2}Os]}C≡CC_6H_4-4-C≡CC_6H_4-4-C≡C)Ru(dppe)_{2}(N_{2})^{+},  1),  1460.2 (4), 1316.2 (4), 1256.2 (12),  1243.2 (100),  1117.3 (15),  1033.2 (12).  IR (CH$_2$Cl$_2$) [Rel. Transm., Assignm.]:  2052 [73.5, ν(RuC≡C), ν(RuC≡C)] cm$^{-1}$.  UV-Vis (ν$_{max}$, cm$^{-1}$ [ε, 10$^3$ M$^{-1}$ cm$^{-1}$]):  23 300 [269.1], 29 800 [218.6], 31 400 [213.5].  $^{1}$H NMR (500 MHz, CDCl$_3$):  δ 7.70 (s, 3H, H10), 7.33 (d, δ$_{HH}$ = 6.55 Hz, 6H, H142), 7.63–7.36 (m, 122H, H151, H161, H251, H261, H134, H135, H304, H305, H205), 7.24–7.10 (m, 48H, H153, H163, H253, H263), 7.05–6.86 (m, 96H, H152, H162, H252, H262), 6.78–6.64 (m, 8H, H143, H203) 2.72–2.60, 2.62–2.50 (m, 48H, H170, H270) ppm.  $^{31}$P($^{1}$H) NMR (121 MHz, CDCl$_3$):  δ 54.12 [12P, Ru(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$], 16.60 [12P, Os(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$] ppm.

$^{1,3,5}$-{trans-}{[(3,5-{trans-][(dppe)$_2$ClOs(C≡C)]}$_2$C$_6$H$_3$-1-(C≡CC$_6$H$_4$-4-C≡CC$_6$H$_4$-4-C≡C)Ru(dppe)$_2$(C≡CC$_6$H$_4$-4-C≡CC$_6$H$_4$-4-C≡C)]}$_3$C$_6$H$_3$  

(3-52$^{b}$)

In an oven-dried 150 mL two-neck round-bottom flask, 1.35-{trans-}{[(I$_6$H$_4$-4-C≡CC$_6$H$_4$-4-C≡C)Ru(dppe)$_2$(C≡CC$_6$H$_4$-4-C≡CC$_6$H$_4$-4-C≡C)]}$_3$C$_6$H$_3$  

(3-48)  (0.040 g, 0.0090 mmol, 1.0 eq.), 1-(HC≡C)-3.5-{trans-}{[(dppe)$_2$ClOs(C≡C)]}$_2$C$_6$H$_3$  

(3-50$^{a}$)  (0.080 g, 0.037 mmol, 4.0 eq.) and catalytic amounts of [Pd(PPh$_3$)$_4$] and Cul were dissolved in a deoxygenated mixture of triethylamine (30 mL) and freshly distilled and deoxygenated dichloromethane (40 mL). The clear, orange-yellow reaction mixture was heated at reflux for 20 h, over which time the solution became increasingly cloudy with the formation of an off-white precipitate. The solvent of the mixture was removed by filtration through a sintered glass filter funnel (pore size G3), which afforded a clear, orange filtrate. The solvent was removed under reduced pressure, and the orange solid residue was suspended in dichloromethane (10 mL) with a small amount of added triethylamine. The
highly cloudy suspension was dropped into stirring methanol (60 mL), resulting in the formation of a fine, flocculent, yellow precipitate. The solid was removed from the pale yellow, clear solution by filtration through a sintered glass filter funnel (pore size G4). The yellow, solid residue was dissolved in dichloromethane (4 mL), and the resultant cloudy, brown mixture was filtered through tightly packed cotton wool. The clear filtrate was dropped into stirring methanol (50 mL). A yellow suspension was obtained, which was filtered through a sintered glass funnel (pore size G4), affording a pale yellow, clear filtrate and a yellow, solid residue. The solid was redissolved in dichloromethane (4 mL), with a small amount of triethylamine being added to the mixture. The resultant solution was filtered through tightly packed cotton wool, and the clear filtrate was dropped into a stirring mixture of \( n \)-pentane and dichloromethane (60 mL/25 mL), with a small amount of triethylamine being added. An orange suspension was obtained, which was filtered through a sintered glass filter funnel (pore size G4). The solid residue was redissolved in dichloromethane (4 mL + 4 drops of triethylamine). Filtration through cotton wool and precipitation was repeated twice from (1) \( n \)-pentane/dichloromethane (60 mL/18 mL) and (2) \( n \)-pentane, affording a flocculent, yellow precipitate, which was isolated by filtration through a sintered glass filter funnel (G4). The solid residue was washed with \( n \)-pentane once, and the residual solvent was removed under reduced pressure at 30–40 °C, giving 0.033 g (0.0031 mmol, 34%) of an orange solid that was identified as the product.

Anal. Calcd. for C_{612}H_{492}Cl_{6}Os_{6}P_{36}Ru_{3}: C 69.22, H 4.67%. Found: C 68.78, H 4.93%. IR (CH_{2}Cl_{2}) [Rel. Transm., Assignm.]: 894 [63.6], 1098 [91.5], 1434 [89.3], 1487 [94.3], 1513 [94.1], 1555 [93.8], 1590 [93.7], 1954 [97.3, br], 2053 [83.5, \( \nu \)(RuC≡C), \( \nu \)(RuC≡C), br], 2207 [97.5, br], 2923 [82.9], 2953 [80.1], 2966 [76.0] cm\(^{-1}\). UV-Vis (\( \bar{\nu}_{\text{max}} \), cm\(^{-1}\) [\( \varepsilon \), 10\(^3\) M\(^{-1}\) cm\(^{-1}\)]): 23600 [241.2], 29800 [348.9], 36000 [256.9]. \(^{1}\)H NMR (300 MHz, CDCl\(_3\)): \( \delta \) 7.89–6.79 (m, 420H, H10, H134, H135, H142, H143, H204, H205, H210, H211, H21, H23), 2.80–2.60 (m, 48H, H270), 2.60–2.43 (m, 24H, H17) ppm. \(^{31}\)P{\(^{1}\)H} NMR (121 MHz, CDCl\(_3\)): \( \delta \) 53.97 [s, 12P, Ru(Ph\(_2\)PCH\(_2\)CH\(_2\)PPh\(_2\))\(_2\)], 16.51 [s, 24P, Os(Ph\(_2\)PCH\(_2\)CH\(_2\)PPh\(_2\))\(_2\)] ppm. \(^{13}\)C{\(^{1}\)H} NMR (126 MHz, CDCl\(_3\)): \( \delta \) 137.4, 136.7, 135.9, 135.0, 134.8, 134.6, 132.1, 131.9, 131.7, 131.3, 130.9, 130.6, 130.6, 129.3, 129.1, 129.1, 127.7, 127.5, 127.2, 124.7, 124.3, 123.9, 122.5, 122.1, 118.4, 109.8, 103.0, 102.9, 102.8, 94.3, 93.8, 93.3, 90.4, 90.1, 89.9, 88.2, 32.1, 31.8 ppm.
In an oven-dried 100 mL two-neck round-bottom flask, 1,3,5-\{trans-\{3-(HC≡C)-5-\{trans-\{OsCl(dppe)\(\_\)C≡C\}\}\(\_\)C≡C\(\_\)C\}\}\(\_\)C≡C\(\_\)H\(\_\)4\(\_\)4-C≡C\(\_\)C\}\}\(\_\)C≡C\(\_\)H\(\_\)4\(\_\)4-C≡C\(\_\)C\}\}\(\_\)C≡C\(\_\)H\(\_\)4\(\_\)4-C≡C\(\_\)C\}\}\(\_\)C≡C\(\_\)H\(\_\)4\(\_\)4-C≡C\(\_\)C\}\}\(\_\)C≡C\(\_\)H\(\_\)4\(\_\)4-C≡C\(\_\)C\}\}\(\_\)C≡C\(\_\)H\(\_\)4\(\_\)4-C≡C\(\_\)C\}\}\(\_\)C≡C\(\_\)H\(\_\)4\(\_\)4-C≡C\(\_\)C\}\}\(\_\)C≡C\(\_\)H\(\_\)4\(\_\)4-C≡C\(\_\)C\}\}\(\_\)C≡C\(\_\)H\(\_\)4\(\_\)4-C≡C\(\_\)C\}\}\(\_\)C≡C\(\_\)H\(\_\)4\(\_\)4-C≡C\(\_\)C\}\}\(\_\)C≡C\(\_\)H\(\_\)4\(\_\)4-C≡C\(\_\)C\}\}\(\_\)C≡C\(\_\)H\(\_\)4\(\_\)4-C≡C\(\_\)C\}\]\(\_\)3C≡C\(\_\)H\(\_\)3 (3-51b)

Material synthesized by Patrick J. West as described in his PhD Thesis, ANU, 2011.
In an oven-dried 100 mL two-neck round-bottom flask fitted with a reflux condenser, \( \text{trans-}[\text{dppe}]_2\text{ClRu(C≡C-4-\text{C}_8\text{H}_4)]}_3\text{N} \) (0.041 g, 0.013 mmol, 1.0 eq.) and \( \text{trans-}[\text{i-Pr}_3\text{SiC}≡\text{CC}_6\text{H}_4-4-\text{C≡C}≡\text{C}]\text{Os(dppe)}_2(\text{C≡CC}_6\text{H}_4-4-\text{C≡CH}) \) (0.055 g, 0.039 mmol, 3.1 eq.) were dissolved in freshly distilled and deoxygenated dichloromethane (70 mL). To the orange, clear solution were added triethylamine (10 drops) and NaPF\(_6\) (0.026 g, 0.15 mmol, 11.9 eq.). The resultant mixture was deoxygenated and heated at reflux for 20 h. The volume of the reaction mixture was reduced in vacuo. The residual mixture (3 mL) was dropped into stirring methanol. A precipitate was formed that was isolated by filtration through a glass-sintered filter funnel (pore size G4). A brown solid was obtained, which was redissolved in dichloromethane (2 mL) with a small amount of added triethylamine, and the resultant mixture was filtered through tightly packed cotton wool into stirring \( n \)-pentane. A flocculent, pale brown precipitate was formed that was isolated by filtration, giving a brown, amorphous solid\(^{40}\), which was dissolved in freshly distilled and deoxygenated dichloromethane (50 mL). \( \text{trans-}[\text{i-Pr}_3\text{SiC}≡\text{CC}_6\text{H}_4-4-\text{C≡C}]\text{Os(dppe)}_2(\text{C≡CC}_6\text{H}_4-4-\text{C≡CH}) \) (0.030 g, 0.022 mmol, 1.7 eq.), NaPF\(_6\) (0.020 g, 0.12 mmol, 9.1 eq.) and triethylamine (6 drops) were added, and the resultant mixture was heated at reflux for 22 h. The same workup procedure as described above was followed, and an additional precipitation from a concentrated dichloromethane solution into a mixture of \( n \)-pentane and dichloromethane (5:1) was carried out. Filtration through a sintered glass filter funnel (pore size G4) afforded the product (0.024 g, 0.003 mol, 26%) as a dark brown, amorphous solid.

Anal. Calcd. for C\(_{42}\)H\(_{38}\)NO\(_3\)S\(_3\)Ru\(_3\)Si\(_3\): C 70.70, H 5.43, N 0.19%. Found: C 70.38, H 5.16, N 0.25%. UV-Vis (\( \nu_{\text{max}} \), cm\(^{-1} \), [\( \varepsilon \), M\(^{-1}\) cm\(^{-1}\)]): 25 600 [340.7]. IR (CH\(_2\)Cl\(_2\) [Rel. Transm., Assignm.]): 2055 [72, \( \nu(\text{RuC≡C}) \)], 2146 [98, \( \nu(\text{SiC≡C}) \)], 3687 [93] cm\(^{-1}\). \(^1\)H NMR (CDCl\(_3\), 300.1 MHz): \( \delta \) 7.97–6.68 (m, 276H, Ar-H), 2.68–2.31 (m, 48H, H170, H270), 1.23 (s, 63H, H10, H11) ppm. \(^{31}\)P\(^{\text{1H}}\) NMR (121.5 MHz, CDC\(_3\)): \( \delta \) 54.37 [s, 12P, Ru(\( \text{PCH}_2\text{CH}_2\text{PCH}_2\text{PPh}_2\text{)}_2\), 16.43 [s, 12P, Os(\( \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2\text{)}_2\)] ppm.

\(^{39}\) Synthesized by Patrick J. West according to procedure given in his PhD Thesis, ANU, 2011

\(^{40}\) The reaction was found not to have proceeded to completion only after the workup, for which reason the reaction was restarted.
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3.6 Chemical Structure Sheet (Fold-out)
4 Summary

In this work, octupolar ruthenium mono- and bis-acetylide complexes were successfully synthesized via a convergent approach. The design of the linear oligo(phenylethynyl)-bridged building blocks for theses complexes were carefully chosen to (a) avoid working with extended organic octupolar oligo-(phenylethynyl)-compounds, (b) ensure the attachment of the metallated bridges to the organic cores under mild conditions, and (c) obtain octupolar complexes with sufficient solubility in common organic solvents to permit measurements and further chemical modifications. The incorporation of iodo aryl moieties into the linear building blocks permitted the coupling of the metallated units to the acetylene cores at ambient temperature, although reaction times of up to 2–3 days were found in necessary in isolated cases. The incorporation of 2-ethylhexyl solubilizing groups into the linear oligo(phenylethynyl)-bridges resulted in excellent solubility of both the linear and the octupolar ruthenium acetylide complexes. Moreover, due to the convergent approach, the availability of the linear complexes will enable us to carry out facile core-variations.

The linear organic oligo(phenylethynyl)-compounds were found to exhibit strong fluorescence, which was explored by concentration-dependent fluorescence spectroscopy. Solvatochromism was found based on the fluorescence spectra. The linear absorption spectra (UV-Vis), however, did not show any such behavior.

Through coupling of the linear ruthenium acetylide complexes to the cores, octupolar ruthenium complexes with a bridge length of up to seven phenylethynyl units in each bridge was accomplished. Due to the incorporated solubilizing groups, all complexes showed excellent solubility in common organic solvents.

The NLO properties of these complexes were explored using frequency-dependent Z-scan measurements. Large NLO responses exceeding those of previously-reported organic and organometallic dendrimers were detected. The complexes show large
transparent windows in the UV-Vis spectra, which is beneficial with regards to exploiting off-resonant NLO responses. The NLO values obtained herein were scaled, using both common scaling factors (e.g. molecular weight) and scaling factors that we suggested recently, namely the cost of production and the number of effective π-electrons that were calculated three different ways, where nitrogen and/or ruthenium were treated either as insulators or nodes that contribute to the π-conjugation in the complexes. Besides two-photon absorption, instantaneous three-photon absorption was found for the phenyl-core ruthenium acetylide complexes, large 3PA cross-sections in the order of $3 \cdot 10^{-77}$ cm$^6$ s$^2$ having been measured.

In the second part of this work, six organometallic dendrimers were successfully synthesized, where the core units were systematically varied; dendrimers with boron-, nitrogen-, and phenyl-cores were prepared and characterized. Two different capping groups were employed, namely phenylacetylide ligands, and electron-withdrawing $p$-nitrophenylacetylide ligands.

The NLO properties of the organometallic nitrogen-cored zero- and first-generation dendrimers were explored through frequency-dependent Z-scan measurements and compared to previously-reported analogous organic N-cored dendrimers. It was found that the organometallic dendrimers dominate significantly (up to 2 orders of magnitude). Different scaling schemes were applied, including the aforementioned cost-scaling. The molecular volume was suggested as a fairer alternative to the molecular weight as scaling factor, and calculations for both the organometallic and the organic dendrimers were carried out. It was found that the absolute numbers do not differ significantly from the molecular weights, which also applies to the organometallic species due to their carbon-richness.

A number of boron-containing linear analogues of the B-cored organometallic dendrimers were synthesized. Comparing the NLO properties of the linear and the dendritic complexes will allow us to look further into the effect that branching has on the NLO response of such organometallic complexes.

In-depth analysis of NMR spectra, including multi-dimensional correlation experiments, was carried out for organic compounds and organometallic complexes in both parts of this work, with particular focus on $^{13}$C NMR spectroscopy.
Incorporating branching points into the octupolar complexes reduces the quality of the spectra significantly.

Lastly, a number of octupolar mixed-metal ruthenium-osmium acetylide complexes were synthesized in a joint project with Patrick West (ANU). Their electrochemical behavior was probed through spectroelectrochemistry studies, showing a dependence of the reversibility from the distance between the two metal centers within the oligo(phenylethynyl)-bridged systems. Attempts were made to investigate their NLO properties; due to photochemical processes occurring under the intense laser light, measurements were restricted to a single wavelength. Since linear absorption is interfering with the NLO effects, the obtained data has to be treated with care.
5 Appendices

5.1 NMR Spectra – Linear and Star-Shaped Complexes and Their Organic Precursors (Chapter 2)

Figure 5.1 $^1$H NMR spectrum of 2-6 recorded in CDCl$_3$ at 500 MHz.
Figure 5.2 $^{13}$C{$^1$H} NMR spectrum of 2-6 recorded in CDCl$_3$ at 500 MHz.

Figure 5.3 $^1$H NMR spectrum of 2-12 recorded in CDCl$_3$ at 500 MHz.
Figure 5.4 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 2-12 recorded in CDCl$_3$ at 126 MHz.

Figure 5.5 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of 2-12 recorded in C$_6$D$_6$ at 121 MHz.
Figure 5.6 $^1$H NMR spectrum of 2-14 recorded in CDCl$_3$ at 500 MHz.
Figure 5.7 $^{13}\text{C}^1\text{H}$ NMR spectrum of 2-14 recorded in CDCl$_3$ at 126 MHz.

Figure 5.8 $^{31}\text{P}^1\text{H}$ NMR spectrum of 2-14 recorded in CDCl$_3$ at 121 MHz.
**Figure 5.9** $^1$H NMR spectrum of 2-15 recorded in CDCl$_3$ at 500 MHz.

**Figure 5.10** $^{13}$C($^1$H) NMR spectrum of 2-15 recorded in CDCl$_3$ at 126 MHz.
5.1. NMR Spectra – Linear and Star-Shaped Complexes and Their Organic Precursors (Chapter 2)

Figure 5.11 $^{31}\text{P}^1\text{H}$ NMR spectrum of 2-15 recorded in CDCl$_3$ at 121 MHz.

Figure 5.12 $^1\text{H}$ NMR spectrum of 2-18 recorded in CDCl$_3$ at 300 MHz.
Figure 5.13 ¹³C{¹H} NMR spectrum of 2-18 recorded in CDCl₃ at 126 MHz.

Figure 5.14 ³¹P{¹H} NMR spectrum of 2-18 recorded in CDCl₃ at 121 MHz.
5.1. NMR Spectra – Linear and Star-Shaped Complexes and Their Organic Precursors (Chapter 2)

**Figure 5.15** $^1$H NMR spectrum of 2-32 recorded in CDCl$_3$ at 500 MHz.

**Figure 5.16** $^{13}$C($^1$H) NMR spectrum of 2-32 recorded in CDCl$_3$ at 126 MHz.
Figure 5.17 $^1$H NMR spectrum of 2-33 recorded in CDCl$_3$ at 500 MHz.

Figure 5.18 $^{13}$C\{H\} NMR spectrum of 2-33 recorded in CDCl$_3$ at 126 MHz.
5.1. NMR Spectra – Linear and Star-Shaped Complexes and Their Organic Precursors (Chapter 2)

Figure 5.19 $^1$H NMR spectrum of 2-34 recorded in CDCl$_3$ at 500 MHz.

Figure 5.20 $^{13}$C{$^1$H} NMR spectrum of 2-34 recorded in CDCl$_3$ at 126 MHz.
Figure 5.21 $^1$H NMR spectrum of 2-35 recorded in CDCl$_3$ at 500 MHz.

Figure 5.22 $^{13}$C{$^1$H} NMR spectrum of 2-35 recorded in CDCl$_3$ at 126 MHz.
5.1. NMR Spectra – Linear and Star-Shaped Complexes and Their Organic Precursors (Chapter 2)

Figure 5.23 $^1$H NMR spectrum of 2-36 recorded in CDCl$_3$ at 500 MHz.

Figure 5.24 $^{13}$C($^1$H) NMR spectrum of 2-36 recorded in CDCl$_3$ at 126 MHz.
Figure 5.25 $^1$H NMR spectrum of 2-37 recorded in CDCl$_3$ at 500 MHz.

Figure 5.26 $^{13}$C($^1$H) NMR spectrum of 2-37 recorded in CDCl$_3$ at 126 MHz.
Figure 5.27 $^1$H NMR spectrum of 2-38 recorded in CDCl$_3$ at 500 MHz.

Figure 5.28 $^{13}$C-$^1$H NMR spectrum of 2-38 recorded in CDCl$_3$ at 126 MHz.
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Figure 5.29 $^1\text{H}$ NMR spectrum of 2-40 recorded in CDCl$_3$ at 500 MHz.

Figure 5.30 $^{13}\text{C}^\{^1\text{H}\}$ NMR spectrum of 2-40 recorded in CDCl$_3$ at 126 MHz.
5.1. NMR Spectra – Linear and Star-Shaped Complexes and Their Organic Precursors (Chapter 2)

Figure 5.31 $^1$H NMR spectrum of 2-41 recorded in CDCl$_3$ at 500 MHz.

Figure 5.32 $^{13}$C($^1$H) NMR spectrum of 2-41 recorded in CDCl$_3$ at 126 MHz.
Figure 5.33 $^{13}$C-$^1$H NMR spectrum of $2-42$ recorded in CDCl$_3$ at 126 MHz.

Figure 5.34 $^{13}$C-$^1$H NMR spectrum of $2-42$ recorded in CDCl$_3$ at 126 MHz.
5.1. NMR Spectra – Linear and Star-Shaped Complexes and Their Organic Precursors (Chapter 2)

Figure 5.35 \(^1\)H NMR spectrum of 2-43 recorded in CDCl\(_3\) at 500 MHz.

Figure 5.36 \(^{13}\)C\((^1\)H\)) NMR spectrum of 2-43 recorded in CDCl\(_3\) at 126 MHz.
Figure 5.37 $^1$H NMR spectrum of 2-44 recorded in CDCl$_3$ at 500 MHz.

Figure 5.38 $^{13}$C($^1$H) NMR spectrum of 2-44 recorded in CDCl$_3$ at 126 MHz.
5.1. NMR Spectra – Linear and Star-Shaped Complexes and Their Organic Precursors (Chapter 2)

Figure 5.39 $^1$H NMR spectrum of 2-47 recorded in CDCl$_3$ at 500MHz.

Figure 5.40 $^{13}$C\{$^1$H} NMR spectrum of 2-47 recorded in CDCl$_3$ at 126 MHz.

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Figure 5.41 $^{31}$P$^{1}{\text{H}}$ NMR spectrum of 2-47 recorded in CDCl$_3$ at 121 MHz.

Figure 5.42 $^1$H NMR spectrum of 2-48 recorded in CDCl$_3$ at 500 MHz.
Figure 5.43 $^{13}$C{¹H} NMR spectrum of 2-48 recorded in CDCl₃ at 126 MHz.

Figure 5.44 $^{31}$P{¹H} NMR spectrum of 2-48 recorded in C₆D₆ at 121 MHz.
Figure 5.45 $^1\text{H}$ NMR spectrum of 2-49 recorded in CDCl$_3$ at 500 MHz.

Figure 5.46 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 2-49 recorded in CDCl$_3$ at 126 MHz.
5.1. NMR Spectra – Linear and Star-Shaped Complexes and Their Organic Precursors (Chapter 2)

**Figure 5.47** $^{31}$P($^1$H) NMR spectrum of 2-49 recorded in CDCl$_3$ at 121 MHz.

**Figure 5.48** $^1$H NMR spectrum of 2-50 recorded in CDCl$_3$ at 500 MHz.
Figure 5.49 $^{13}$C\{$^{1}$H\} NMR spectrum of 2-50 recorded in CDCl$_3$ at 126 MHz.

Figure 5.50 $^{31}$P\{$^{1}$H\} NMR spectrum of 2-50 recorded in CDCl$_3$ at 121 MHz.
5.1. NMR Spectra – Linear and Star-Shaped Complexes and Their Organic Precursors (Chapter 2)

**Figure 5.51** $^1$H NMR spectrum of 2-51 recorded in CDCl$_3$ at 500 MHz.

**Figure 5.52** $^{13}$C($^1$H) NMR spectrum of 2-51 recorded in CDCl$_3$ at 126 MHz.
Figure 5.53 $^{31}P\{^1\text{H}\}$ NMR spectrum of 2-51 recorded in CDCl$_3$ at 121 MHz.

Figure 5.54 $^1\text{H}$ NMR spectrum of 2-52 recorded in CDCl$_3$ at 500 MHz.
Figure 5.55 $^{13}\text{C}\{^{1}\text{H}\}\}$ NMR spectrum of 2-52 recorded in CDCl$_3$ at 126 MHz.

Figure 5.56 $^{31}\text{P}\{^{1}\text{H}\}$ NMR spectrum of 2-52 recorded in CDCl$_3$ at 121 MHz.
Figure 5.57 $^1$H NMR spectrum of 2-53 recorded in CDCl$_3$ at 500 MHz.

Figure 5.58 $^{13}$C($^1$H) NMR spectrum of 2-53 recorded in CDCl$_3$ at 126 MHz.
5.1. NMR Spectra – Linear and Star-Shaped Complexes and Their Organic Precursors (Chapter 2)

Figure 5.59 $^{31}P\{^1H\}$ NMR spectrum of 2-53 recorded in C$_6$D$_6$ at 121 MHz.

Figure 5.60 $^1H$ NMR spectrum of 2-58 recorded in CDCl$_3$ at 500 MHz.
Figure 5.61 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 2-58 recorded in CDCl$_3$ at 126 MHz.

Figure 5.62 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of 2-58 recorded in CDCl$_3$ at 121 MHz.
Figure 5.63 $^1$H NMR spectrum of 2-60 recorded in CDCl$_3$ at 300 MHz.

Figure 5.64 $^{31}$P{$^1$}H NMR spectrum of 2-60 recorded in CDCl$_3$ at 121 MHz.
Figure 5.65 $^1$H NMR spectrum of 2-63 recorded in CDCl$_3$ at 500 MHz.

Figure 5.66 $^{13}$C($^1$H) NMR spectrum of 2-63 recorded in CDCl$_3$ at 126 MHz.
5.2 NMR Spectra – Branched Complexes and Their Organic Precursors (Chapter 3)

Figure 5.67 ¹ NMR spectrum of 3-11 recorded in CDCl₃ at 500 MHz.
Figure 5.68 $^{13}$C$\{^1\text{H}\}$ NMR spectrum of 3-11 recorded in CDCl$_3$ at 126 MHz.

Figure 5.69 $^{31}$P$\{^1\text{H}\}$ NMR spectrum of 3-11 recorded in CDCl$_3$ at 121 MHz.
5.2. NMR Spectra – Branched Complexes and Their Organic Precursors

(Chapter 3)

Figure 5.70 $^1$H NMR spectrum of 3-12 recorded in CDCl$_3$ at 500 MHz.

Figure 5.71 $^{13}$C{$^1$H} NMR spectrum of 3-12 recorded in CDCl$_3$ at 126 MHz.
Figure 5.72 $^{13}$P-$^1$H NMR spectrum of 3-12 recorded in CDCl$_3$ at 126 MHz.
5.2. NMR Spectra – Branched Complexes and Their Organic Precursors

(Chapter 3)

Figure 5.73 $^1$H NMR spectrum of 3-13\textsuperscript{a} recorded in CDCl\textsubscript{3} at 500 MHz.

Figure 5.74 $^{13}$C{$^1$H} NMR spectrum of 3-13\textsuperscript{a} recorded in CDCl\textsubscript{3} at 126 MHz. The signals marked with "#" were not observed in the 1D NMR spectrum. The gHMBC NMR spectrum confirmed the presence of the two signals, though (see Figure 3.4 on page 253)
Figure 5.75 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of 3-13* recorded in CDCl$_3$ at 121 MHz.

Figure 5.76 $^1\text{H}$ NMR spectrum of 3-14 recorded in CDCl$_3$ at 500 MHz.
Figure 5.77 $^{13}\text{C}^{\text{1H}}$ NMR spectrum of 3-14 recorded in CDCl$_3$ at 126 MHz.

Figure 5.78 $^{31}\text{P}^{\text{1H}}$ NMR spectrum of 3-14 recorded in CDCl$_3$ at 121 MHz.
Figure 5.79 ¹H NMR spectrum of 3-15* recorded in CDCl₃ at 500 MHz.

Figure 5.80 ¹³C{¹H} NMR spectrum of 3-15* recorded in CDCl₃ at 126 MHz.
5.2. NMR Spectra – Branched Complexes and Their Organic Precursors

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Figure 5.81 $^{31}\text{P}^{1}\text{H}$ NMR spectrum of 3-15* recorded in CDCl$_3$ at 121 MHz.

Figure 5.82 $^1\text{H}$ NMR spectrum of 3-16 recorded in CDCl$_3$ at 500 MHz.
Figure 5.83 $^{13}\text{C}^{[1\text{H}]}$ NMR spectrum of 3-16 recorded in CDCl$_3$ at 126 MHz.

Figure 5.84 $^{31}\text{P}^{[1\text{H}]}$ NMR spectrum of 3-16 recorded in CDCl$_3$ at 121 MHz.
5.2. NMR Spectra – Branched Complexes and Their Organic Precursors

(Chapter 3)

Figure 5.85 $^1$H NMR spectrum of 3-17* recorded in CDCl$_3$ at 500 MHz.

Figure 5.86 $^{13}$C($^1$H) NMR spectrum of 3-17* recorded in CDCl$_3$ at 126 MHz.
Figure 5.87 $^{31}\text{P}^{[1\text{H}]}$ NMR spectrum of 3-17* recorded in CDCl$_3$ at 121 MHz.

Figure 5.88 $^1\text{H}$ NMR spectrum of 3-18 recorded in CDCl$_3$ at 500 MHz.
Figure 5.89 $^{13}$C{$^1$H} NMR spectrum of 3-18 recorded in CDCl₃ at 126 MHz.

Figure 5.90 $^{31}$P{$^1$H} NMR spectrum of 3-18 recorded in CDCl₃ at 121 MHz.
Figure 5.91 $^1$H NMR spectrum of 3-19\textsuperscript{b} recorded in CDCl$_3$ at 500 MHz.

Figure 5.92 $^{13}$C($^1$H) NMR spectrum of 3-19\textsuperscript{b} recorded in CDCl$_3$ at 126 MHz.
Figure 5.93 $^{31}\text{P}^1\text{H}$ NMR spectrum of 3-19 recorded in CDCl$_3$ at 121 MHz.
Figure 5.94 $^1$H NMR spectrum of 3-20 recorded in CDCl$_3$ at 500 MHz.

Figure 5.95 $^{13}$C($^1$H) NMR spectrum of 3-20 recorded in CDCl$_3$ at 126 MHz.
5.2. NMR Spectra – Branched Complexes and Their Organic Precursors

(Chapter 3)

Figure 5.96 $^{31}\text{P}^{(1\text{H})}$ NMR spectrum of 3-20 recorded in CDCl$_3$ at 121 MHz.

Figure 5.97 $^1\text{H}$ NMR spectrum of 3-21 recorded in CDCl$_3$ at 500 MHz.
Figure 5.98 $^{13}$C{$^1$H} NMR spectrum of 3-21 recorded in CDCl$_3$ at 126 MHz.

Figure 5.99 $^{31}$P{$^1$H} NMR spectrum of 3-21 recorded in CDCl$_3$ at 121 MHz.
5.2. NMR Spectra – Branched Complexes and Their Organic Precursors

(Chapter 3)

**Figure 5.100** $^1$H NMR spectrum of 3-22* recorded in CDCl$_3$ at 500 MHz.

**Figure 5.101** $^{13}$C($^1$H) NMR spectrum of 3-22* recorded in CDCl$_3$ at 126 MHz.
Figure 5.102 $^{31}\text{P}^{1\text{H}}$ NMR spectrum of 3-22 recorded in CDCl$_3$ at 121 MHz.
Figure 5.103 $^1$H NMR spectrum of 3-27 recorded in CDCl$_3$ at 500 MHz.

Figure 5.104 $^{13}$C($^1$H) NMR spectrum of 3-27 recorded in CDCl$_3$ at 126 MHz.
Figure 5.105 $^1$H NMR spectrum of 3-28 recorded in CDCl$_3$ at 500 MHz.

Figure 5.106 $^{13}$C{$^1$H} NMR spectrum of 3-28 recorded in CDCl$_3$ at 126 MHz.
Figure 5.107 $^1$H NMR spectrum of 3-29 recorded in CDCl$_3$ at 500 MHz.

Figure 5.108 $^{13}$C-$^1$H NMR spectrum of 3-29 recorded in CDCl$_3$ at 126 MHz.
Figure 5.109 $^{31}\text{P}^{[\text{H}]}$ NMR spectrum of 3-29 recorded in CDCl$_3$ at 121 MHz.

Figure 5.110 $^1\text{H}$ NMR spectrum of 3-30 recorded in C$_6$D$_6$ at 300 MHz.
Figure 5.111 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of 3-30 recorded in C$_6$D$_6$ at 121 MHz.
Figure 5.112 $^1$H NMR spectrum of 3-33 recorded in CDCl$_3$ at 500 MHz.

Figure 5.113 $^{13}$C($^1$H) NMR spectrum of 3-33 recorded in CDCl$_3$ at 126 MHz.
Figure 5.114 $^1$H NMR spectrum of 3-34* recorded in CDCl$_3$ at 500 MHz.

Figure 5.115 $^{13}$C($^1$H) NMR spectrum of 3-34* recorded in CDCl$_3$ at 126 MHz.
Figure 5.116 $^1$H NMR spectrum of 3-35 recorded in CDCl$_3$ at 500 MHz.

Figure 5.117 $^{13}$C($^1$H) NMR spectrum of 3-35 recorded in CDCl$_3$ at 126 MHz.
5.2. NMR Spectra – Branched Complexes and Their Organic Precursors
(Chapter 3)

Figure 5.118 $^1$H NMR spectrum of 3-36 recorded in CDCl$_3$ at 500 MHz.

Figure 5.119 $^{13}$C($^1$H) NMR spectrum of 3-36 recorded in CDCl$_3$ at 126 MHz.
Figure 5.120 $^1$H NMR spectrum of 3-37 recorded in CDCl$_3$ at 500 MHz.

Figure 5.121 $^{13}$C/$^1$H NMR spectrum of 3-37 recorded in CDCl$_3$ at 126 MHz.
5.2. NMR Spectra – Branched Complexes and Their Organic Precursors

(Chapter 3)

Figure 5.122 $^1$H NMR spectrum of 3-38 recorded in CDCl$_3$ at 500 MHz.

Figure 5.123 $^{13}$C($^1$H) NMR spectrum of 3-38 recorded in CDCl$_3$ at 126 MHz.
Figure 5.124 $^1$H NMR spectrum of 3-38A recorded in CDCl$_3$ at 500 MHz.

Figure 5.125 $^1$H NMR spectrum of 3-39 recorded in CDCl$_3$ at 500 MHz.
Figure 5.126 $^{13}\text{C}^{(1\text{H})}$ NMR spectrum of 3-39 recorded in CDCl$_3$ at 126 MHz.

Figure 5.127 $^{31}\text{P}^{(1\text{H})}$ NMR spectrum of 3-39 recorded in CDCl$_3$ at 121 MHz.
**Figure 5.128** $^1\text{H}$ NMR spectrum of 3-40 recorded in CDCl$_3$ at 500 MHz.

**Figure 5.129** $^{13}\text{C}$NMR spectrum of 3-40 recorded in CDCl$_3$ at 126 MHz.
Figure 5.130 $^{31}\text{P}\{^{1}\text{H}\}$ NMR spectrum of 3-40 recorded in CDCl$_3$ at 121 MHz.

Figure 5.131 $^{1}\text{H}$ NMR spectrum of 3-41 recorded in CDCl$_3$ at 500 MHz.
Figure 5.132 $^{13}\text{C}^{1}\text{H}$ NMR spectrum of 3-41 recorded in CDCl$_3$ at 126 MHz.

Figure 5.133 $^{31}\text{P}^{1}\text{H}$ NMR spectrum of 3-41 recorded in CDCl$_3$ at 121 MHz.
Figure 5.134 $^1$H NMR spectrum of 3-42 recorded in CDCl$_3$ at 500 MHz.

Figure 5.135 $^{13}$C{$^1$H} NMR spectrum of 3-42 recorded in CDCl$_3$ at 126 MHz.
Figure 5.136 $^{31}P\{^1H\}$ NMR spectrum of 3-42 recorded in CDCl$_3$ at 121 MHz.

Figure 5.137 $^1H$ NMR spectrum of 3-43 recorded in CDCl$_3$ at 300 MHz.
5.2. NMR Spectra – Branched Complexes and Their Organic Precursors  

(Chapter 3)

Figure 5.138 $^{31}$P-$^1$H NMR spectrum of 3-43 recorded in CDCl$_3$ at 121 MHz.

Figure 5.139 $^1$H NMR spectrum of 3-44 recorded in CDCl$_3$ at 500 MHz.
Figure 5.140 $^{13}$C{$^{1}$H} NMR spectrum of 3-44 recorded in CDCl$_3$ at 126 MHz.

Figure 5.141 $^{31}$P{$^{1}$H} NMR spectrum of 3-44 recorded in CDCl$_3$ at 121 MHz.
5.2. NMR Spectra – Branched Complexes and Their Organic Precursors

(Chapter 3)

Figure 5.142 $^1$H NMR spectrum of 3-45 recorded in CDCl$_3$ at 500 MHz.

Figure 5.143 $^{13}$C($^1$H) NMR spectrum of 3-45 recorded in CDCl$_3$ at 126 MHz.
Figure 5.144 $^{31}\text{P}^{[1\text{H}]}$ NMR spectrum of 3-45 recorded in $\text{C}_6\text{D}_6$ at 121 MHz.
5.2. NMR Spectra – Branched Complexes and Their Organic Precursors

Figure 5.145 $^1$H NMR spectrum of 3-46 recorded in CDCl$_3$ at 500 MHz.

Figure 5.146 $^{13}$C($^1$H) NMR spectrum of 3-46 recorded in CDCl$_3$ at 126 MHz.
Figure 5.147 $^{31}\text{P}^{(1)}\text{H}$ NMR spectrum of 3-46 recorded in CDCl$_3$ at 121 MHz.

Figure 5.148 $^1\text{H}$ NMR spectrum of 3-47 recorded in C$_6$D$_6$ at 300 MHz.
5.2. NMR Spectra – Branched Complexes and Their Organic Precursors

(Chapter 3)

Figure 5.149 $^{31}\text{P}^{1\text{H}}$ NMR spectrum of 3-47 recorded in C$_6$D$_6$ at 121 MHz.

Figure 5.150 $^1\text{H}$ NMR spectrum of 3-48 recorded in CDCl$_3$ at 500 MHz.
Figure 5.151 $^{13}$C{\textsuperscript{1}H} NMR spectrum of 3-48 recorded in CDCl\textsubscript{3} at 126 MHz.

Figure 5.152 $^{31}$P{\textsuperscript{1}H} NMR spectrum of 3-48 recorded in CDCl\textsubscript{3} at 162 MHz.
5.2. NMR Spectra – Branched Complexes and Their Organic Precursors

(Chapter 3)

Figure 5.153 $^1$H NMR spectrum of 3-52$^b$ recorded in C$_6$D$_6$ at 500 MHz.

Figure 5.154 $^{13}$C($^1$H) NMR spectrum of 3-52$^b$ recorded in C$_6$D$_6$ at 126 MHz.
Figure 5.155 $^{31}\text{P}^{[\text{H}]}$ NMR spectrum of 3-52$^b$ recorded in C$_6$D$_6$ at 121 MHz.

Figure 5.156 $^1\text{H}$ NMR spectrum of 3-55$^b$ recorded in C$_6$D$_6$ at 500 MHz.
Figure 5.157 $^{31}$P{${}^1$H} NMR spectrum of 3-55$^b$ recorded in C$_6$D$_6$ at 121 MHz.

Figure 5.160 $^1$H NMR spectrum of 3-58$^b$ recorded in C$_6$D$_6$ at 300 MHz.
Figure 5.158 $^1$H NMR spectrum of 3-56$^b$ recorded in CDCl$_3$ at 300 MHz.

Figure 5.159 $^{31}$P{$^1$H} NMR spectrum of 3-56$^b$ recorded in C$_6$D$_6$ at 121 MHz.
5.2. NMR Spectra – Branched Complexes and Their Organic Precursors
(Chapter 3)

Figure 5.161 $^{31}\text{P}$$^1\text{H}$ NMR spectrum of 3-58$^b$ recorded in C$_6$D$_6$ at 121 MHz.
5.3 X-Ray Crystallographic Data Table
Table 2.1: X-ray Crystallographic Data Table

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### Notes
- Table 2.1 includes X-ray crystallographic data for several compounds or complexes, with columns for property or condition, formula, crystal size, color, and space group.
5.4 Costing Tables

5.4.1 Star-Shaped Ruthenium Acetylide Complexes
(Chapter 1)
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<td>n-BuLi (2.5M n-Hex)</td>
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<td>-</td>
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<tr>
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<td>-</td>
<td>2</td>
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<td>85</td>
<td>1.00</td>
<td>0.0082</td>
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<td>0.0070</td>
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<td>85</td>
<td>1000.00</td>
<td>8.2079</td>
<td>756.2791</td>
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<tr>
<td>2-45*</td>
<td>484.51</td>
<td>0.0082</td>
<td>3.977</td>
<td>(RuCl3 x 3H2O)</td>
<td>207.43</td>
<td>75</td>
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<td>0.0109</td>
<td>2.2701</td>
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<td>0.0082</td>
<td>3.977</td>
<td>Dimethylsulfoxide</td>
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<td>8.00</td>
<td>0.0876</td>
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<td>90</td>
<td>1.00</td>
<td>0.0029</td>
<td>1.7859</td>
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<td>0.0026</td>
<td>1.743</td>
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<td>1.743</td>
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<td>Cul</td>
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Table 5.5 Costing table of octupolar ruthenium acetylide complex 2-9* (part 1/2).

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<th>Reaction</th>
<th>Cost (AUD)</th>
<th>Concentration</th>
<th>Yield (%)</th>
<th>Charge (mol)</th>
<th>Price (AUD/kg)</th>
<th>Total Cost (AUD)</th>
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<td>0.0029</td>
<td>1.786</td>
<td>2-2*</td>
<td>150.17</td>
<td>98</td>
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<td>9.00</td>
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<tr>
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<td>0.0029</td>
<td>1.786</td>
<td>Cul</td>
<td>190.45</td>
<td>98</td>
</tr>
<tr>
<td>1-maleic acid</td>
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<td>98</td>
<td>0.10</td>
<td>0.0001</td>
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<td>61.392</td>
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<td>0.0029</td>
<td>1.786</td>
<td>Pd(PPh3)4</td>
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<td>0.0030</td>
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<td>1.109</td>
<td>Triethylamine</td>
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<td>74</td>
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Total cost [AUD]: 311
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<th>Required amount (g)</th>
<th>SM / Reagent</th>
<th>M (SM) [g/mol]</th>
<th>Reported yield [%]</th>
<th>Equiv. Used</th>
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<th>m (SM) required [g]</th>
<th>Price (Aldrich) [$/mol]</th>
<th>Cost for ran. [$]</th>
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<td>2-9*</td>
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<td>1.00</td>
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5.4. Costing Tables
## Table 5.7
Costing table of octopolar ruthenium acetylide complex 2.10* (part 2/2)

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<th>1.00</th>
<th>0.0048</th>
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<td>0.0044</td>
<td>2.905</td>
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<td>90</td>
<td>7.20</td>
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Table 5.23: Costing table of octupolar ruthenium acetate complex 2-54* (part 4/6)
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