Syntheses, Electrochemical, Linear Optical, and Cubic Nonlinear Optical Properties of Ruthenium Alkynyl-Functionalized Oligo(phenylenevinylene) Stars

Zhiwei Chen,^[a] Christopher J. Jeffery,^[b] Mahbod Morshedi,^[b] Graeme J. Moxey,^[b] Adam Barlow,^[b] Xinwei Yang,^[b] Bandar A. Babgi,^[b,c] Gulliver T. Dalton,^[b] Michael D. Randles,^[b] Matthew K. Smith,^[b] Chi Zhang,^[a] Marek Samoc,^[d] Marie P. Cifuentes,^[a,b] Mark G. Humphrey^{*,[a,b]}

Contribution to the Special Issue of *ChemPlusChem* celebrating the Singapore Golden Jubilee.

Organometallic Complexes for Nonlinear Optics. Part 54. Part 53: H. J. Zhao, P. V. Simpson, A. Barlow, G. J. Moxey, M. Morshedi, N. Roy, R. Philip, C. Zhang, M. P. Cifuentes and M. G. Humphrey, submitted.

Abstract: The syntheses of *trans*-[Ru(C≡CC₆H₄-4-CHO)(C≡CC₆H₄-4-R)(dppe)₂] [R = H **9a**, NO₂ **9b**, CHO **9c**, C≡CC₆H₃-3,5-Et₂ **9d**, (*E*)-CH=CHC₆H₄-4-Bu^t **9e**], *trans*-[Ru(C≡CC₆H₄-4-R)Cl(dppe)₂] [R = C≡CC₆H₃-3,5-Et₂ **11a**, (*E*)-CH=CHC₆H₄-4-Bu^t **11b**, (*E*)-CH=CHC₆H₄-4-NO₂ **11c**], 1,2,4,5-{*trans*[(dppe)₂(RC₆H₄C≡C)Ru{C≡CC₆H₄-4-(*E*)-CH=CH}]}₂C₆H₂ [R = H **14a**, C≡CC₆H₃-3,5-Et₂ **14b**, (*E*)-CH=CHC₆H₄-4-Bu^t **14c**], 1-*I*-3,5-{*trans*[(L₂)₂(R)Ru{C≡CC₆H₄-4-(*E*)-CH=CH}]}₂C₆H₃ (L₂ = dppe, R = Cl **15a**; L₂ = dppe, R = C≡CPh **15b**, R = C≡CC₆H₄-4-NO₂ **15c**), 1-Me₃SiC≡C-3,5-{*trans*[(L₂)₂(R)Ru{C≡CC₆H₄-4-(*E*)-CH=CH}]}₂C₆H₃ (L₂ = dppe, R = Cl **16a**; L₂ = dppe, R = C≡CPh **16b**), 1-HC≡C-3,5-{*trans*[(dppe)₂(R)Ru{C≡CC₆H₄-4-(*E*)-CH=CH}]}₂C₆H₃ (R = Cl **17a**, R = C≡CPh **17b**) and 1,3,5-{*trans*[(dppe)₂(3,5-R₂-C₆H₃C≡C)Ru{C≡CC₆H₄-4-(*E*)-CH=CH}]}₃C₆H₃ [R = (*E*)-CH=CHC₆H₄-4-C≡C-*trans*-[Ru(C≡CPh)(dppe)₂] **18**] are reported, together with those of the precursor alkynes 1-RC≡C-3,5-Et₂C₆H₃ (R = SiMe₃ **2**, H **3**, C₆H₄-4-C≡CSiMe₃ **5**, C₆H₄-4-C≡CH **6**). The identities of **9c**, **9d**, **9e**, **11a** and *trans*-[Ru{C≡CC₆H₄-4-(*E*)-CH=CHC₆H₄-4-Bu^t}₂(dppe)₂] (**12** and **12'**)

were confirmed by single-crystal X-ray diffraction studies. The electrochemical properties of **9a-9e**, **11a-11b**, **14a-14c**, **15a-15c**, **16b**, **17a**, **17b**, and **18** were assessed by cyclic voltammetry; the studies reveal that potentials for the fully/quasi-reversible metal-centered oxidation processes decrease on introduction of solubilizing alkyl substituents and increase on increasing acceptor substituent strength; other structural variations have little impact. UV-vis-NIR spectroscopic studies on these complexes reveal lowest-energy MLCT bands that red-shift on increasing acceptor substituent strength, blue-shift on alkyl incorporation, and gain in intensity on progression from linear to star complexes. Low temperature UV-vis-NIR spectroelectrochemical studies of **14a-c** show the appearance of an intense low-energy band at 7400-7900 cm⁻¹ that is red-shifted on π -system lengthening and alkyl substituent incorporation. The cubic nonlinear optical properties of **9d**, **9e**, **14a-c**, **15a-c**, **16b**, **17a-b** and **18** were assayed by femtosecond Z-scan studies at benchmark wavelengths (750 and 800 nm) in the near IR, with nonlinearity increasing on nitro incorporation; the values for the *E*-ene-linked dendrimers in these studies are much larger than yne-linked analogues. **9d**, **9e**, **14a-c** and **18** were further examined by broad spectral range femtosecond Z-scan studies; the cruciform complexes have appreciable multiphoton absorption cross-sections, with maximal values close to two- and three-times the wavelength of the linear optical absorption maxima.

- [a] Z. Chen, Prof. C. Zhang, Prof. M. P. Cifuentes, Prof. M. G. Humphrey
School of Chemical and Material Engineering, Jiangnan University,
Wuxi 214122, Jiangsu Province, China.
E-mail: Mark.Humphrey@anu.edu.au
- [b] C. J. Jeffery, Dr M. Morshedi, Dr G. J. Moxey, Dr A. Barlow, X. Yang, Dr B. A. Babgi, Dr G. T. Dalton, Dr M. D. Randles, Dr M. K. Smith, Assoc. Prof. M. P. Cifuentes, Prof. M. G. Humphrey
Research School of Chemistry, Australian National University
Canberra, ACT 2601, Australia.

[c] Permanent address:
Asst. Prof. B. A. Babgi
Department of Chemistry, Faculty of Science, King Abdulaziz
University, P.O. Box 80203, Jeddah 21589, Saudi Arabia

[d] Prof. M. Samoc
Research School of Physics and Engineering,
Australian National University
Canberra, ACT 2601, Australia.
Current address:
Advanced Materials Engineering and Modeling Group,
Faculty of Chemistry, Wrocław University of Technology,
Wrocław 50-370, Poland.

Introduction

The nonlinear optical (NLO) properties of molecular materials have attracted significant interest.^[1] While the majority of studies have focused on purely organic molecules, recent comparisons of NLO parameters have shown that organometallics can outperform organics, even when the data are scaled for molecular weights, molecular volumes, numbers of electrons strongly participating in polarization, or even costs of production.^[2] The results from these performance comparisons, coupled to the additional functionality inherent in metal complexes (a diversity of

FULL PAPER

geometries, performance tuning by co-ligand modification, and the possibility of switching by reversible metal-centered oxidation) have helped drive the continuing interest in organometallics as potential NLO materials,^[3] and to maintain them as a genuine alternative to organics.

One structure-NLO property relationship that was developed in early studies of purely organic molecules was the observation of an increase in NLO merit on replacing an yne-linkage in a π -bridging unit with an *E*-ene linkage, an outcome ascribed to orbital energy mismatch of p orbitals of *sp*-hybridized acetylenic carbons with the p orbitals of *sp*²-hybridized phenyl carbons;^[4] this effect is presumably in combination with the increased propensity for oligo(phenyleneethynylene) (OPE) units to rotate out of π -system coplanarity when compared to oligo(phenylenevinylene) (OPV) analogues, reducing efficient π -delocalization. Metal alkynyl complexes were contemporaneously shown to function as efficient NLO materials,^[5] and they continue to provoke interest, but despite the favourable characteristics of *E*-ene-linked species, the vast majority of studies of the NLO properties of metal alkynyl complexes have considered those with an OPE-based rather than OPV-based π -bridge. We report herein studies directed at addressing this deficiency, including the syntheses of metal alkynyl complexes with OPV-based bridges by a methodology that employs an unusual “chemistry-on-complex” approach at a pendant formyl group, comprehensive evaluation of the electrochemical and spectroscopic properties of the new complexes, structural and spectroelectrochemical studies of selected examples, and an evaluation of their cubic NLO parameters; some of these results have been published in a preliminary form.^[6]

Results and Discussion

Previous studies with metal alkynyl complexes have established several outcomes that influenced the research described herein. NLO activity has been shown to increase on proceeding from 14-electron complexes to 18-electron complexes,^[7] and from 3d metals to 4d and 5d metals,^[8] focusing subsequent research efforts on 18 valence electron ruthenium and osmium alkynyl complexes. While less efficient in an absolute sense than their osmium congeners, ruthenium alkynyl complexes bearing two bidentate diphosphines were found to provide a favourable balance of reactivity and NLO efficiency,^[9] so the studies summarized below concentrated on this combination.

Several ruthenium complexes bearing phenylenevinylene-containing alkynyl ligands have been reported previously,^[9b, 10] but all were prepared by reaction of a (chloro)ruthenium precursor with a pre-formed *E*-ene-bearing alkyne. To enhance flexibility in the synthesis of such complexes, in the chemistry described below we explored the possibility of using pre-formed (4-formylphenylethynyl)ruthenium complexes in Horner-Wadsworth-Emmons coupling with phosphonate esters. One further point guided the synthetic studies. Alkynyl ligands with multiple phenyleneethynylene units have been shown to afford complexes with significant NLO properties,^[9c, 10d, 11] but these extended π -systems are often accompanied by reduced solubility of the complexes in common organic solvents. With this in mind, the syntheses targeted bis(alkynyl)ruthenium complexes containing solubilizing alkyl groups on the terminal aryl ring.

Synthesis of acetylenes

Two new alkynes bearing solubilizing alkyl groups were targeted for eventual attachment at the periphery of the ruthenium-containing OPE stars. Thus, 1,3-diethyl-5-((4-ethynylphenyl)ethynyl)benzene (**5**) was prepared via successive Sonogashira coupling^[12]/deprotection reactions in four steps (Scheme 1). 2,6-Diethyl-4-iodobenzene (**1**) was readily obtained via a standard diazotization reaction of 2,6-diethyl-4-iodoaniline^[13] with sodium nitrite and fluoroboric acid that afforded 1-iodo-3,5-diethylphenyldiazonium fluoroborate, and a subsequent *in situ* treatment with sodium methoxide in methanol. Sonogashira coupling of **1** with trimethylsilylacetylene using PdCl₂(PPh₃)₂/CuI as catalysts afforded 3,5-diethyl-1-(trimethylsilyl)ethynylbenzene (**2**) in good yield, desilylation of which under basic conditions gave 1,3-diethyl-5-ethynylbenzene (**3**). A second Sonogashira coupling using 1-iodo-4-(trimethylsilyl)ethynylbenzene^[14] afforded the π -extended derivative 4-(3,5-Et₂C₆H₃C≡C)C₆H₄C≡CSiMe₃ (**4**), which was then treated with KOH to give 1-(4-HC≡CC₆H₄C≡C)-3,5-Et₂C₆H₃ (**5**) in excellent yield. The new compounds were obtained as oils and characterized using IR, proton and carbon NMR spectroscopy, and EI and high-resolution mass spectrometry. A downfield shift in the NMR signal for the proton *para* to the iodo/ethynyl is seen on proceeding from **1** and **2** (6.99 ppm) to **3** and **4** (7.06 ppm), a similar downfield shift in the acetylenic proton being seen in proceeding from **3** (3.01 ppm) to **5** (3.16 ppm). The stilbenylacetylene **8** was obtained from a *trans*-halogenation of (*E*)-1-(4-*tert*-butylphenyl)-2-(4-bromophenyl)ethene^[15] with butyl lithium/iodine that gave the iodo derivative (**6**) (Scheme 1). Compound **6** was then coupled to trimethylsilylacetylene under Sonogashira conditions to give (*E*)-1-(4-trimethylsilyl)ethynylphenyl)-2-(4-*tert*-butylphenyl)ethene (**7**), deprotection using potassium hydroxide giving (*E*)-1-(4-*tert*-butylphenyl)-2-(4-ethynylphenyl)ethene (**8**). Compounds **6–8** were characterized by IR, ¹H and ¹³C NMR, and EI and high resolution ESI mass spectrometry.

Scheme 1. Syntheses of acetylenes **5** and **8**.

FULL PAPER

Synthesis of (4-(formylphenyl)alkynyl)ruthenium complexes

The obvious complexes from which to attempt on-complex Horner-Wadsworth-Emmons coupling, *trans*-[Ru(C≡CC₆H₄-4-CHO)Cl(L)₂] (L₂ = dppe, dppe), have been reported previously^[9c] and were therefore employed in the present studies, but we also targeted several new ruthenium alkynyl complexes in which the *trans*-chloro ligand was replaced with alkynyl ligands to enhance stability. The preparation of the 4-(formylphenyl)alkynyl complexes **9a** and **9b** employed established procedures for the syntheses of ruthenium alkynyl complexes, with the reactions of *trans*-[Ru(4-C≡CC₆H₄R)Cl(dppe)₂] (R = CHO,^[9c] NO₂^[16]) with the required terminal acetylene and ammonium or sodium hexafluorophosphate under basic conditions affording ruthenium bis(alkynyl) complexes in acceptable yields (Scheme 2). The reactions can be monitored by NMR spectroscopy, with the phosphorus resonance shifting from around 49 ppm for the mono(alkynyl) complexes to 54.1 (**9a**) and 53.7 (**9b**) ppm on formation of the bis(alkynyl) derivatives, and the proton spectrum showing an upfield shift of the aldehyde proton from 9.99 to 9.81 ppm on formation of **9a**, and a corresponding resonance appearing at 9.86 ppm for complex **9b**. The order of introduction of the alkynyl ligands is crucial, formation of **9b** by reaction of 4-nitrophenylacetylene^[12] with *trans*-[Ru(4-C≡CC₆H₄CHO)Cl(dppe)₂] under similar conditions being attempted without success. The bis-(4-formylarylalkynyl) complex **9c** was prepared from *cis*-[RuCl₂(dppe)₂]^[17] using an excess of acetylene in refluxing dichloromethane, the product being readily identified by the NMR signals at 53.6 ppm for the equivalent phosphorus centers and at 9.87 ppm for the aldehyde protons.

Scheme 2. Syntheses of (4-formylphenyl)ethynylruthenium complexes **9a-9c**. [Ru] = *trans*-[Ru(κ²-dppe)₂] = *trans*-[Ru(κ²-PPh₂CH₂CH₂PPh₂)₂].

Ruthenium alkynyl complex formation can frequently be facilitated by the use of the pre-formed five-coordinate [RuCl(dppe)₂]⁺ cation.^[18] In the present studies, the five-coordinate complex cation as its hexafluorophosphate salt [RuCl(dppe)₂]⁺PF₆⁻ (**10**) was conveniently prepared in over 95% yield directly from *cis*-[RuCl₂(dppe)₂]^[17] using NaPF₆ in dichloromethane. Reaction of **10** with **5** followed by treatment with NEt₃ afforded *trans*-[Ru(C≡CC₆H₄-4-C≡CC₆H₃-3,5-Et₂)Cl(dppe)₂] (**11a**) in 56% yield (Scheme 3). Formation of the unsymmetrical bis(alkynyl) complex *trans*-[Ru(C≡CC₆H₄-4-CHO)(C≡CC₆H₄-4-C≡CC₆H₃-3,5-Et₂)(dppe)₂] (**9d**) was achieved in 46% yield after prolonged stirring of 4-ethynylbenzaldehyde^[19] with **11a**. The transformation from the 5-coordinate cationic complex to the mono- and bis-alkynyl complexes was readily confirmed through the ³¹P NMR resonances for the dppe ligands, with the two triplets observed for **10** (55.9, 83.7 ppm) being replaced by characteristic singlets at 49.2 (**11a**) and 53.3 ppm (**9d**). A similar sequence of

reactions using [RuCl(dppe)₂]⁺PF₆⁻ (**10**) with **8** afforded *trans*-[Ru(C≡CC₆H₄-4-(*E*)-CH=CHC₆H₄Bu^t-4)Cl(dppe)₂] (**11b**), together with trace amounts of the symmetric bis(alkynyl) *trans*-[Ru(C≡CC₆H₄-4-(*E*)-CH=CHC₆H₄Bu^t-4)₂(dppe)₂] (**12**), and then *trans*-[Ru(C≡CC₆H₄-4-CHO)(C≡CC₆H₄-4-(*E*)-CH=CHC₆H₄Bu^t-4)(dppe)₂] (**9e**) following reaction of **11b** with 4-HC≡CC₆H₄CHO. All complexes were characterized by IR, ¹H and ¹³C NMR spectroscopy, and EI and high resolution ESI mass spectrometry. As expected, the remote alkyl ligand variations have little effect on the ¹H NMR aldehyde proton resonance (9.81-9.89 ppm for **9a-e**).

Scheme 3. Syntheses of (4-formylphenylethynyl)ruthenium complexes **9d** and **9e**. [Ru] = *trans*-[Ru(κ²-dppe)₂] = *trans*-[Ru(κ²-PPh₂CH₂CH₂PPh₂)₂].

Extension of the classical stereospecific Horner-Wadsworth-Emmons C=C bond formation reaction to metal-containing (4-formylphenyl)ethynyl complexes was then explored as a new route to metal-ethynyl-functionalized stilbenes. Our initial attempt examined synthesis of the previously-reported complex *trans*-[Ru(C≡CC₆H₄-4-(*E*)-CH=CHC₆H₄-4-NO₂)Cl(dppe)₂]^[9b] (Scheme 4). *trans*-[Ru(C≡CC₆H₄-4-CHO)Cl(dppe)₂]^[9c] was reacted with sodium hydride and 4-O₂NC₆H₄CH₂P(O)(OEt)₂ in THF for 5 h, the latter prepared via an Arbuzov reaction of 1-(bromomethyl)-4-nitrobenzene with triethyl phosphite, to give the stereospecifically-coupled (4-{4-nitrophenyl-(*E*)-ethynyl}phenyl)ethynyl product (**11c**) in a greater overall yield than the published procedure [which involves coupling of the preformed (*E*)-1-(4-nitrophenyl)-2-(4-ethynylphenyl)ethene to the ruthenium center]. A similar coupling of the tri-substituted benzylic phosphonate 1,3,5-C₆H₃(CH₂PO(OEt)₂)₃^[20] and excess *trans*-[Ru(C≡CC₆H₄-4-CHO)Cl(dppe)₂] over 40 h afforded **13a** in acceptable yield, confirming the applicability of this chemistry-on-complex method for the multi-site incorporation of *E*-ene linkages into ruthenium alkynyl complexes.

FULL PAPER

Scheme 4. Syntheses of **11c** and **13a** by Horner-Wadsworth-Emmons reactions. [Ru] = *trans*-[Ru(κ^2 -dppe)₂].

Having demonstrated this methodology on known complexes, we then extended it to the formation of new *E*-ene-linkage-containing ruthenium alkynyl cruciform complexes (Scheme 5). Treatment of 1,2,4,5-C₆H₂{CH₂P(O)(OEt)₂}₄^[20] with the (4-formylphenylethynyl)ruthenium complexes **9a**, **9d** and **9e** and sodium hydride in 1,2-dimethoxyethane for 24–48 h afforded the tetra-ruthenium star complexes **14a–c** in good yields. Formation of the bis(alkynyl) complex environments was confirmed by monitoring the ³¹P NMR spectra (appearance of resonances at ca. 53 ppm).

Scheme 5. Syntheses of ene-linkage-containing ruthenium alkynyl cruciform complexes **14a–c**. [Ru] = *trans*-[Ru(κ^2 -dppe)₂].

The methodology was then employed in the construction of a ruthenium-alkynyl-containing stilbenyl dendrimer. The target necessitated the construction of a 1-A-3,5-B₂-functionalized arene to serve as the branching point in the dendrimer arms. In the present studies, introduction of a branching point required the use of a 3,5-substituted iodobenzene, for which treatment with trimethylsilylacetylene under Sonogashira conditions followed by removal of the silyl protecting group afforded the required 3,5-substituted "wedge" complexes (Scheme 6). Attempts to form the dpdm-ligated ruthenium wedge complex **15a** by reaction of the bis(phosphonate ester) 1-I-C₆H₃-3,5-{CH₂PO(OEt)₂}₂ with *trans*-[Ru(C≡CC₆H₄-4-CHO)Cl(dpdm)₂] resulted in low yields of the desired product, and attempts to optimize the reaction by changing the base (sodium ethoxide or potassium *tert*-butoxide), reaction temperature and reaction times lead to decomposition of the (4-formylphenyl)alkynyl ruthenium complex. In contrast, synthesis of the dppe-ligated ruthenium wedge complex **15b** from **9a** was achieved in 59% yield using a threefold excess of potassium *tert*-butoxide in refluxing THF, although the same conditions afforded only a small amount of the nitro-substituted analogue **15c** from **9b**. In each case, the ¹H NMR spectrum shows the disappearance of the aldehyde peak due to the (4-formylphenyl)ethynyl ligand of the starting complexes at 9.8–10.0 ppm. In **15c**, the protons *ortho* to the nitro substituent resonate downfield of the usual phenyl region at 7.95 ppm. The disappearance of the resonances due to the phosphonate ester at 25.9 ppm in the ³¹P NMR spectra is consistent with the formation of the wedge complexes. The IR spectra of these wedge compounds show characteristic alkynyl ν (C≡C) bands at

2059, 2072 and 2046 cm⁻¹ for **15a–c**, respectively. The alkynyl ν (C≡C) stretching frequency remains unchanged in **15a** compared to that of the starting complex; in contrast, the loss of the electron withdrawing aldehyde group in the formation of **15b** sees the alkynyl ν (C≡C) band shift to 2072 cm⁻¹ from 2046 cm⁻¹ in **9a**. In **15c**, the (4-nitrophenyl)ethynyl ligand affords a band at 2046 cm⁻¹, as is found with **9b**. The ESI mass spectrum of **15a** reveals exchange of chloro ligand with solvent (MeCN), a peak being seen at 2270 mass units ([M - Cl + MeCN]⁺), as well as a peak corresponding to loss of chloride at 2230 mass units ([M - Cl]⁺). The FAB mass spectra of **15b** and **15c** display molecular ions at 2453 and 2543 mass units, respectively, with **15b** fragmenting by loss of the phenylethynyl ligand and iodo group, and **15c** via loss of the nitro substituent.

Scheme 6. Syntheses of ene-linkage-containing "wedge" complexes **17a** and **17b**. [Ru] = *trans*-[Ru(κ^2 -PPh₂(CH₂)_nPh₂)₂] [n = 1 (dpdm), 2 (dppe)].

Sonogashira coupling of the iodo complexes **15a** and **15b** with excess trimethylsilylacetylene afforded the ethynyl derivatives **16a** and **16b**, respectively, subsequent deprotection with potassium carbonate affording moderate yields of the desired alkyne-terminated wedge complexes **17a** and **17b** (Scheme 6). All wedge complexes were characterized by IR and NMR spectroscopy and mass spectrometry. The ν (C≡C) bands in the IR spectra show a shift to lower energy on alkylation at the iodo substituent (**15a**, **15b** at 2060 and 2072 cm⁻¹, respectively), the latter remaining invariant between the trimethylsilyl- and terminal-alkyne complexes (**16b** at 2056 cm⁻¹ and **17b** at 2057 cm⁻¹). All show a single phosphorus NMR signal, confirming persistence of the *trans*-disposition of the diphosphine ligands (53.9–54.4 ppm for the dppe complexes, and -5.9 ppm for the dpdm examples). A molecular ion is observed for **16b** at 2422 mass units in both the HR ESI and FAB mass spectra, displaying the expected isotope pattern. Fragmentation occurs by the loss of the trimethylsilyl group or the phenylethynyl ligand. No molecular ion is observed in the ESI mass spectrum of **17a**, a fragment due to the loss of both chloro ligands and the ethynyl group being seen at 2077 mass units. The molecular ion is observed in the FAB mass

FULL PAPER

spectrum of **17b** (2350 mass units) with the characteristic loss of a phenylethynyl ligand.

The ethynyl-substituted "wedge" complex **17b** was then coupled to the previously-reported triruthenium complex **13a**^[10a, 10b] to form the nonaruthenium dendrimer **18** (Scheme 7). The reaction was monitored by ³¹P NMR spectroscopy, with the disappearance of the resonance at 50.1 ppm due to the mono(alkynyl) ruthenium environments at **13a** and replacement by a signal at 54.2 ppm due to the resulting bis(alkynyl) ruthenium centers of **18**.

Scheme 7. Synthesis of the dendritic complex **18**. [Ru] = *trans*-[Ru(κ^2 -dppe)₂] = *trans*-[Ru(κ^2 -PPh₂CH₂CH₂PPh₂)₂].

Structural studies

The compositions of compounds **9c**, **9d**, **9e**, **11a**, **12'** and **12''** were confirmed by single-crystal X-ray diffraction studies. The molecular structures are displayed in Figures S1 (**9c**), 1 (**9d**), 2 (**9e**), S2 (**11a**), S3 (**12'**), S4 and S5 (**12''**), and selected bond length and angle data are collected in the relevant figure captions. The bond lengths and angles about the key C/Cl-Ru-C(1)-C(2)-C(3) units in structures **9c**, **9d**, **9e**, and **11a** are not unusual (see, for example refs [11, 21]), falling within the ranges of the literature precedents for arylalkynylbis(diphosphine)ruthenium complexes; for example, the Ru-C(1) vectors for the mono(alkynyl)(chloro)bis(diphosphine)ruthenium complexes [2.037(8) (**11a**)] and the bis(alkynyl)bis(diphosphine)ruthenium complexes [2.074(4) (**9c**), 2.070(10), 2.063(9) (**9d**), 2.065(7), 2.076(6) (**9e**)] are not unexpected. In contrast, Ru-C(1) parameters for **12'** [2.108(5)] and **12''** [2.149(4)] are both very long, possibly an artefact of the substitutional disorder in these specific structural studies.

Cyclic voltammetry studies

Cyclic voltammetry (CV) data for the complexes prepared in these studies are collected in Table 1. All complexes show an oxidation process between 0.48 and 0.76 V assigned to the Ru^{II/III} oxidation. Ratios for the forward and reverse current peaks range from 0.8 to 1.0, and peak separations are equivalent to, or in some cases up to 0.03 V more than, ΔE for the ferrocene/ferrocenium internal standard, indicating that these processes are fully or quasi-reversible. The potentials for the oxidation processes vary in a fairly systematic fashion. **11a**, which contains solubilizing ethyl groups on the terminal phenyl ring, shows a fully reversible

oxidation process at 0.51 V, somewhat lower than that required to oxidize its non-alkylated analogue **11d** (0.55 V),^[22] and presumably due to the slight electron-releasing effect of the alkyl groups. Replacement of the yne linkage furthest from the metal center with an *E*-ene-linked *tert*-butyl-substituted phenyl group, in proceeding from **11d** to **11b** (0.56 V), has little effect on

Figure 1. Molecular structure of *trans*-[Ru(C≡CC₆H₄-4-CHO)(C≡CC₆H₄-4-C≡CC₆H₃-3,5-Et₂)(dppe)₂] (**9d**), with thermal ellipsoids set at the 30% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ru1-C1 2.070(10), Ru1-C21 2.063(9), Ru1-P1 2.373(2), Ru1-P2 2.353(2), Ru1-P3 2.372(2), Ru1-P4 2.357(2), C1-Ru1-C21 178.9(4), C1-Ru1-P1 80.5(3), C1-Ru1-P2 89.5(2), C1-Ru1-P3 98.7(3), C1-Ru1-P4 90.7(2), C21-Ru1-P1 98.5(3), C21-Ru1-P2 90.8(2), C21-Ru1-P3 82.3(3), C21-Ru1-P4 89.0(2), P1-Ru1-P2 81.63(8), P1-Ru1-P3 179.21(9), P1-Ru1-P4 98.50(8), P2-Ru1-P3 98.45(8), P2-Ru1-P4 179.80(10), P3-Ru1-P4 81.43(8).

Figure 2. Molecular structure of *trans*-[Ru(C≡CC₆H₄-4-CHO)(C≡CC₆H₄-4-(*E*)-CH=CHC₆H₄-4-Bu)(dppe)₂] (**9e**), with thermal ellipsoids set at the 30% probability level. Hydrogen atoms and lattice dichloromethane molecules have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ru1-C1 2.065(7), Ru1-C21 2.076(6), Ru1-P1 2.3667(15), Ru1-P2 2.3596(15), Ru1-P3 2.3532(15), Ru1-P4 2.3659(15), C1-Ru1-C21 179.7(3), C1-Ru1-P1 98.28(17), C1-Ru1-P2 91.81(17), C1-Ru1-P3 87.83(17), C1-Ru1-P4 81.30(17), C21-Ru1-P1 81.44(17), C21-Ru1-P2 88.33(17), C21-Ru1-P3 92.03(16), C21-Ru1-P4 98.98(17), P1-Ru1-P2 82.56(5), P1-Ru1-P3 97.66(5), P1-Ru1-P4 179.58(6), P2-Ru1-P3 179.60(7), P2-Ru1-P4 97.42(5), P3-Ru1-P4 82.36(5).

the potential for the oxidation process. The similar electronic environment of the metal atom in these related complexes has been noted previously, structural changes occurring remote to the metal center having only minor effects on the potentials for the oxidation processes.^[10d] Replacement of the chloro ligand by a 4-formylphenylethynyl group, to form the unsymmetrical bis(alkynyl) complexes *trans*-[Ru(C≡CC₆H₄-4-CHO)(C≡CC₆H₄-4-R)(dppe)₂] (**9**), results in an increase in potentials for the metal-centered oxidation processes. For the (4-formylphenylethynyl)(phenylethynyl) examples **9a-9c**, $E_{1/2}$ increases with increasing electron-withdrawing character of the phenylethynyl substituent, with R = H (**9a**, 0.61 V) < R = CHO (**9c**,

FULL PAPER

0.72 V) < R = NO₂ (**9b**, 0.75 V), as expected. Extension of the π -bridge of **9a** [via a second phenylethynyl unit R = C $\equiv$ CC₆H₃-3,5-Et₂ or a stilbenyl group R = (E)-CH=CHC₆H₄-4-Bu^t] results in little change in $E_{1/2}$.

Potentials of the oxidation processes for the cruciform complexes 1,2,4,5-(*trans*-[(dppe)₂(RC₆H₄C $\equiv$ C)Ru{C $\equiv$ CC₆H₄-4-(E)-CH=CH}])₄C₆H₂ (**14**) are all found in the narrow range 0.51–0.55 V, with the diethyl-substituted yne-linked complex (R = C $\equiv$ CC₆H₃-3,5-Et₂, **14b**, 0.55 V) again requiring a higher potential than the *tert*-butyl-substituted ene-linked example [R = (E)-CH=CHC₆H₄-4-Bu^t, **14c**, 0.51 V]. The "wedge" complexes **15–17** are oxidized at comparable potentials, with only a slight variation observed on moving from the 1-iodo-substituted core **15b** (0.53 V) through the 1-trimethylsilylethynyl- (**16b**, 0.52 V) and ethynyl- (**17b**, 0.56 V) analogues, and a slight decrease in the reversibility of the process at each step. Substitution with the electron-withdrawing nitro group (**15c**, 0.63 V) affords a shift to higher potentials, as expected. The chloro-terminated dppe-containing wedge complexes **15a** (0.62 V) and **17a** (0.59 V) require a slightly higher potential for metal-centered oxidation than their phenylethynyl-containing analogues **15b** and **17b**.

The general invariance in the potentials for the metal-localized oxidation process in these complexes reflects the similar chemical environment of the metal atom in each case. The single oxidation process observed in the sweep range (0 to 1.6 V) is due to the symmetry of the molecules and the lack of interaction between the metal centers. The dendritic complex **18** also shows a single oxidation process (0.52 V), in agreement with the pseudo-equivalent metal environments seen in the ³¹P NMR data. Complexes containing the nitro group also show an irreversible nitro-centered reduction process at -1.14 V (**9b**), -0.98 V (**11c**), and -1.33 V (**15c**).

Linear optical studies

The UV-vis-NIR spectra for all complexes (Table 1) show characteristic bands at lowest energy [absorption maxima in the range 380–490 nm (26300–20400 cm⁻¹)], assigned from DFT calculations on related ruthenium alkynyl complexes as due to metal-to-ligand charge transfer, specifically Ru d_{yz} → C₂R in nature.^[23] Nitro-substituted complexes are transparent at frequencies below 22000 cm⁻¹, while all other complexes are transparent below 26000 cm⁻¹. Alkyl introduction at the distal aryl ring of *trans*-[Ru(C $\equiv$ CC₆H₄-4-C $\equiv$ CPh)Cl(dppe)₂] (λ_{max} 25800 cm⁻¹)^[22] to give **11a** (26300 cm⁻¹, +500 cm⁻¹) results in a slight hypsochromic shift in the MLCT band, whereas replacement of the -yne linkage with an *E*-ene group and introduction of a *tert*-butyl group, to give **11b** (25000 cm⁻¹, -800 cm⁻¹), produces a bathochromic shift. Linear optical spectrum of the nitro-substituted *E*-ene-linked complex **11c** (20500 cm⁻¹) contains the lowest-energy transition, as expected.^[9c]

Substitution of the chloro ligand with a phenylethynyl unit, on proceeding from *trans*-[Ru(C $\equiv$ CC₆H₄-4-CHO)Cl(dppe)₂] (λ_{max} 24200 cm⁻¹)^[9c] to *trans*-[Ru(C $\equiv$ CC₆H₄-4-CHO)(C $\equiv$ CC₆H₄-4-R)(dppe)₂] (**9a–c**), results in a decrease in the energy of the MLCT, the electron-withdrawing nature of the phenylethynyl substituent determining the size of the shift (R = H, **9a**, 23900 cm⁻¹, -300 cm⁻¹) < CHO (**9c**, 23500 cm⁻¹, -700 cm⁻¹) < R = NO₂ (**9b**, 21600 cm⁻¹, -2600 cm⁻¹). Similarly, a red shift is observed on moving from (chloro)ruthenium alkynyl complexes **11a** and **11b** to the

corresponding (4-formylphenylethynyl) complexes **9d** (24200 cm⁻¹, □□□□□□□□) and **9e** (23800 cm⁻¹, -1200 cm⁻¹).

Compared to the monometallic complexes (**9** and **11**), the cruciform complexes 1,2,4,5-(*trans*-[(dppe)₂(RC₆H₄C $\equiv$ C)Ru{C $\equiv$ CC₆H₄-4-(E)-CH=CH}])₄C₆H₂ (**14**) show a significant increase in the extinction coefficient of the MLCT band, an effect noted previously with trisubstituted benzene-cored analogues such as the star complex 1,3,5-(*trans*-[(dppe)₂(PhC $\equiv$ C)Ru(C $\equiv$ CC₆H₄-4-C $\equiv$ C)])₃C₆H₃ (**19b**, ϵ 11.6 × 10⁴ M⁻¹ cm⁻¹).^[24] In the present studies, the increase in absorbance at λ_{max} for **14b** (R = C $\equiv$ CC₆H₃-3,5-Et₂, ϵ 20.0 × 10⁴ M⁻¹ cm⁻¹) and **14c** [R = (E)-CH=CHC₆H₄-4-Bu^t, 21.6 × 10⁴ M⁻¹ cm⁻¹] is approximately two-fold over that of **14a** (R = H, 11.5 × 10⁴ M⁻¹ cm⁻¹), containing the shorter terminal phenylethynyl ligand, and two-fold over the trimetallic complex **19b**. Transition energies are lower for the cruciform star complexes **14b** (25300 cm⁻¹) and **14c** (22700 cm⁻¹) than for the related mononuclear chloro complexes **11a** (26300 cm⁻¹) and **11b** (25000 cm⁻¹) and, again, the ene-linked complex **14b** shows the lowest-energy MLCT band. Compared to the trimetallic star complexes, i.e. the yne-linked **19b** (24300 cm⁻¹) and the *E*-ene-linked **13b** (23800 cm⁻¹),^[10b] the cruciform star complexes show a higher-energy MLCT band.

Table 1. Cyclic voltammetric and linear optical data.^[a]

Complex ^[b] R	$E_{1/2}$ ^[c] [Δ <i>E</i> , (<i>i</i> _{pa} / <i>i</i> _{pc}) (V)]	λ_{max} (nm) (ϵ □ □ (10 ⁴ M ⁻¹ cm ⁻¹))
<i>trans</i> -[Ru](C $\equiv$ CC ₆ H ₄ -4-CHO)(C $\equiv$ CC ₆ H ₄ -4-R)		
H (9a)	0.61 [0.07, 0.9]	418 (2.3), 313 (1.9)
NO ₂ (9b)	0.75 [0.07, 0.8]	463 (2.3), 411 (sh, 2.0)
CHO (9c)	0.72 [0.07, 0.8]	426 (4.0)
C $\equiv$ CC ₆ H ₃ -3,5-Et ₂ (9d)	0.63 [0.07, 1]	414 (5.2)
(E)-CH=CHC ₆ H ₄ -4-Bu ^t (9e)	0.58 [0.07, 1]	420 (6.1)
<i>trans</i> -[Ru](C $\equiv$ CC ₆ H ₄ -4-R)Cl		
C $\equiv$ CC ₆ H ₃ -3,5-Et ₂ (11a)	0.51 [0.09, 1]	380 (2.9)
(E)-CH=CHC ₆ H ₄ -4-Bu ^t (11b)	0.56 [0.07, 1]	400 (4.1)
(E)-CH=CHC ₆ H ₄ -4-NO ₂ (11c)	0.56 [1] ^[9c]	489 (2.6) ^{[d] [9c]}
1,3,5-(<i>trans</i> -(R)[Ru](C $\equiv$ CC ₆ H ₄ -(E)-4-CH=CH)) ₃ C ₆ H ₃ ^[10b]		
Cl (13a)	0.51 [0.9]	426 (8.7) ^[d]
C $\equiv$ CPh (13b)	0.49 [1]	421 (13.0) ^[d]
1,2,4,5-(<i>trans</i> -(RC ₆ H ₄ C $\equiv$ C)[Ru](C $\equiv$ CC ₆ H ₄ -4-(E)-CH=CH)) ₄ C ₆ H ₂		
H (14a)	0.54 [0.11, 1]	421 (11.5), 325 (11.5)
C $\equiv$ CC ₆ H ₃ -3,5-Et ₂ (14b)	0.55 [0.07, 1]	395 (20.0), 297 (14.6)
(E)-CH=CHC ₆ H ₄ -4-Bu ^t (14c)	0.51 [0.09, 1]	441 (21.6), 315 (13.9)
1-I-3,5-(<i>trans</i> -(R)[Ru](C $\equiv$ CC ₆ H ₄ -4-(E)-CH=CH)) ₂ C ₆ H ₃		
Cl ^[e] (15a)	0.62 [0.10, 1]	406
C $\equiv$ CPh (15b)	0.53 [0.09, 1]	425 (6.6), 320 (6.7).
C $\equiv$ CC ₆ H ₄ -4-NO ₂ (15c)	0.63 [0.06, 1]	481 (3.2), 417 (3.7), 312 (3.9)
1-Me ₃ SiC $\equiv$ C-3,5-(<i>trans</i> -(R)[Ru](C $\equiv$ CC ₆ H ₄ -4-(E)-CH=CH)) ₂ C ₆ H ₃		
Cl ^[e] (16a)		411 (6.8)
C $\equiv$ CPh (16b)	0.52 [0.16, 0.9]	421 (7.2), 319 (7.5)
1-HC $\equiv$ C-3,5-(<i>trans</i> -(R)[Ru](C $\equiv$ CC ₆ H ₄ -4-(E)-CH=CH)) ₂ C ₆ H ₃		
Cl ^[e] (17a)	0.59 [0.11, 0.8]	402, 317

FULL PAPER

C≡CPh	(17b)	0.56 [0.15, 0.8]	417, 320
1,3,5-{ <i>trans</i> -(3,5-R ₂ C ₆ H ₃ C≡C)[Ru](C≡CC ₆ H ₄ -4-(<i>E</i>)-CH=CH)] ₃ C ₆ H ₃			
{(<i>E</i>)-CH=CHC ₆ H ₄ -4-	(18)	0.52 [0.14, 0.8]	417, 322
C≡C}[Ru](C≡CPh)			

[a] Measured as CH₂Cl₂ solutions. [b] [Ru] = *trans*-[Ru(dppe)₂]. [c] Pt disc working-, Pt wire auxiliary-, and Ag/AgCl reference electrodes; ferrocene /ferrocenium redox couple at 0.56 V (*i*_{pc}/*i*_{pa} 0.9 -1, Δ*E*_p 0.07-0.09 V). [d] Measured as THF solutions. [e] [Ru] = *trans*-[Ru(dppm)₂].

Spectroelectrochemical studies

In situ oxidation of metal-containing complexes using an optically transparent thin-layer electrochemical (OTTLE) cell offers a convenient method for accessing spectroscopic data of the oxidized metal complexes, and has been employed widely with ruthenium alkynyl complexes.^[10d, 22-23, 25] Application of potentials slightly higher than indicated by the cyclic voltammetric data to dichloromethane solutions of the star complexes **14a-c** resulted in reversible conversion to the tetracationic (formally Ru^{III})₄ complexes [**14a-c**]⁴⁺; isosbestic points are observed in the transformations in each case (Figures 3, S6), and comparative UV-vis-NIR data have been collected in Table 2. All complexes show the emergence of low-energy NIR absorption bands, assigned to alkynyl-to-Ru^{III} charge transfer,^[23b] with the band for **14b** (7600 cm⁻¹), containing the extended π -delocalizable ligand, occurring at a slightly lower energy than that of **14a** (7900 cm⁻¹); the *E*-ene-linked complex **14c** shows the lowest energy band (7300 cm⁻¹). These bands are significantly red-shifted compared to those of the bis(alkynyl) complex trications *trans*-[Ru(C≡CPh)(C≡CC₆H₄-4-C≡CPh)(dppe)₂]⁺ (8400 cm⁻¹)^[23a] and [1,3,5-{*trans*-[(dppe)₂(PhC≡C)Ru(C≡CC₆H₄-4-C≡C)]₃C₆H₃}]³⁺ (8400 cm⁻¹).^[23b] This large bathochromic effect is likely due to the *E*-ene-linked cruciform nature of complexes **14**, rather than the increase in the number of metal centers, because the tri-substituted nonaruthenium nonacation [1,3,5-{*trans*-[(dppe)₂(PhC≡C)Ru(C≡CC₆H₄-4-C≡C)]₃C₆H₃(C≡C)]₂C₆H₃(C≡C)(dppe)₂Ru(C≡CC₆H₄-4-C≡C)]₃C₆H₃]⁹⁺ shows the corresponding low energy band at 8400 cm⁻¹ (measured in THF, ϵ ca. 8 x 10⁴ M⁻¹ cm⁻¹).^[23b] Vibronic progressions evident in the spectra of [**14a-c**]⁴⁺ at ca. 9000 cm⁻¹ can be attributed to ν (C≡C), as noted previously in similar complexes.^[23a] The absorption intensities for the lowest-energy bands for the cruciform star complexes [**14a-c**]⁴⁺ are uniformly higher than those observed for the related trimetallic star complexes [ϵ ca. 12 vs 8 (x 10⁴ M⁻¹ cm⁻¹)], with the *E*-ene-linked complex **14c** showing the highest ϵ .

Cubic hyperpolarizability studies

The third-order optical nonlinearities of the cruciform, wedge and dendritic molecules **14a-c**, **15a-c**, **16a**, **16b**, **17a**, **17b** and **18** were assessed by the Z-scan technique^[26] at a benchmark wavelength of 750 nm, chosen because it corresponds to a region of optical transparency for all of these complexes (reducing the effects of resonance enhancement), and also because of its technological importance (it corresponds to a wavelength region of enhanced transparency of biological materials such as tissue); an NLO performance comparison in this wavelength region is therefore of interest. Measurements were carried out in dichloromethane except for those of **15b** and **16b**, which were measured in THF for

solubility reasons; the resultant data are collected in Table 3. At this wavelength, all new complexes exhibit negative nonlinear refraction and positive nonlinear absorption, consistent with the presence of two-photon resonance effects. The real components of the cubic nonlinearities, in particular, are characterized in most cases by large error margins, rendering development of structure-property relationships problematic. Nevertheless, some comparisons may usefully be made. Focusing on the wedge complexes, replacing the bidentate diphosphine co-ligand dppm by dppe at the ruthenium centers (proceeding from **15a** to **15b** or **17a** to **17b**)

Table 2. UV-vis-NIR data for cruciform complexes 1,2,4,5-{*trans*-(dppe)₂(RC₆H₄C≡C)Ru(C≡CC₆H₄-4-(*E*)-CH=CH)]₄C₆H₂ in the resting (**14a-c**) and tetra-oxidized ([**14a-c**]⁴⁺) forms. [a]

R		λ (cm ⁻¹) (ϵ □ [a])	λ (cm ⁻¹) (ϵ □ [b])
H	14a	22200 (11.5), 30700 (11.2)	[14a] ⁴⁺ 7900 (11.6), 16600 (2.6, sh), 20900 (4.2), 26000 (7.9), 38300 (19.7)
C≡CC ₆ H ₃ -3,5-Et ₂	14b	24900 (20.0), 32100 (13.4, sh), 37000 (15.8, sh)	[14b] ⁴⁺ 7600 (11.9), 16300 (2.3, sh), 20800 (7.3), 21900 (8.1), 25500 (11.1), 32100 (14.9, sh), 38000 (20.3)
(<i>E</i>)-CH=CHC ₆ H ₄ -4-Bu ^t	14c	31600 (14.4), 23700 (21.7)	[14c] ⁴⁺ 7400 (18.1), 9800 (3.3, sh), 16300 (2.9, sh), 20000 (9.2), 28300 (16.3), 30000 (14.6, sh), 38000 (19.9)

[a] CH₂Cl₂. [b] □ 10⁴ M⁻¹ cm⁻¹.

Figure 3. UV-vis-NIR spectral progressions during oxidation of cruciform complex 1,2,4,5-{*trans*-

FULL PAPER

(dppe)₂(RC₆H₄C≡C)Ru{C≡CC₆H₄-4-(*E*)-CH=CH}₂ (R = H, **14a**) (top), and overlay of the spectra for [**14a-c**]⁴⁺ (R = C≡CC₆H₃-3,5-Et₂ (**14b**), R = (*E*)-CH=CHC₆H₄-4-Bu^t (**14c**)) (bottom), in CH₂Cl₂.

results in no change in the nonlinearity. The addition of the electron-withdrawing nitro substituent to the arylalkynyl ligand (proceeding from **15b** to **15c**) results in a two-fold increase in the nonlinearity. While being mindful of variations resultant upon a difference in measurement wavelength (750 nm vs 800 nm, illustrated by data for **9d-e** and **14a-c** at both wavelengths: Table S2), the nonlinearity $|\gamma|$ varies little between the two classes of wedge complex (with yne- or *E*-ene-containing π -bridges). As

FULL PAPER

Table 3. Linear optical and cubic nonlinear optical data for selected complexes.^{a, b}

Complex R		λ_{max} (nm)	γ_{real} (10^{-36} esu)	γ_{imag} (10^{-36} esu)	$ \gamma $ (10^{-36} esu)	σ_2 (10^{-50} cm ⁴ s)
1,3,5-(<i>trans</i> -(R)[Ru]{C $\equiv$ CC ₆ H ₄ -(<i>E</i>)-4-CH=CH}) ₃ C ₆ H ₃ measured at 800 nm						
Cl ^[10b]	(13a) ^[c]	426	-4600 $\pm$ 2000	4200 $\pm$ 800	6200 $\pm$ 2000	1000 $\pm$ 200
C $\equiv$ CPh ^[10b]	(13b) ^[c]	421	-11200 $\pm$ 3000	8600 $\pm$ 2000	14000 $\pm$ 4000	2100 $\pm$ 500
1,3,5-(<i>trans</i> -(R)[Ru]{C $\equiv$ CC ₆ H ₄ -4-C $\equiv$ C}) ₃ C ₆ H ₃ measured at 800 nm						
Cl ^[27]	(19a) ^[c]	414	-330 $\pm$ 100	2200 $\pm$ 500	2200 $\pm$ 600	530 $\pm$ 120
C $\equiv$ CPh ^[27]	(19b) ^[c]	411	-600 $\pm$ 200	2900 $\pm$ 500	3000 $\pm$ 600	700 $\pm$ 120
1,2,4,5-(<i>trans</i> -(RC ₆ H ₄ C $\equiv$ C)[Ru]{C $\equiv$ CC ₆ H ₄ -(<i>E</i>)-CH=CH}) ₄ C ₆ H ₂						
H	(14a)	440	-38200 $\pm$ 7790	7370 $\pm$ 3100	38900 $\pm$ 8380	2090 $\pm$ 880
C $\equiv$ CC ₆ H ₃ Et ₂ -3,5	(14b)	393	-36000 $\pm$ 10600	14200 $\pm$ 5800	38700 $\pm$ 12000	4020 $\pm$ 1640
(<i>E</i>)-CH=CHC ₆ H ₄ Bu ^t -4	(14c)	415	-36000 $\pm$ 10600	14200 $\pm$ 5800	38700 $\pm$ 12000	4020 $\pm$ 1640
1-I-3,5-(<i>trans</i> -(R)[Ru]{C $\equiv$ CC ₆ H ₄ -(<i>E</i>)-CH=CH}) ₂ C ₆ H ₃						
Cl ^[d]	(15a)	406	-1800 $\pm$ 490	300 $\pm$ 70	1800 $\pm$ 500	
C $\equiv$ CPh	(15b) ^[c]	425	-2200 $\pm$ 260 ^[e]	220 $\pm$ 60 ^[e]	2200 $\pm$ 260 ^[d]	
C $\equiv$ CC ₆ H ₄ NO ₂ -4	(15c)	481	-4200 $\pm$ 1,500	1500 $\pm$ 420	4500 $\pm$ 1600	
1-Me ₃ SiC $\equiv$ C-3,5-(<i>trans</i> -(R)[Ru]{C $\equiv$ CC ₆ H ₄ -(<i>E</i>)-CH=CH}) ₂ C ₆ H ₃						
Cl ^[d]	(16a)	411	-510 $\pm$ 500	4700 $\pm$ 1500	4700 $\pm$ 2000	1100 $\pm$ 360
C $\equiv$ CPh	(16b) ^[c]	421	-2100 $\pm$ 140	410 $\pm$ 60	2100 $\pm$ 150	
1-HC $\equiv$ C-3,5-(<i>trans</i> -(R)[Ru]{C $\equiv$ CC ₆ H ₄ -(<i>E</i>)-CH=CH}) ₂ C ₆ H ₃						
Cl ^[d]	(17a)	402	-1900 $\pm$ 230	140 $\pm$ 20	1900 $\pm$ 230	
C $\equiv$ CPh	(17b)	417	-1900 $\pm$ 260	300 $\pm$ 40	1900 $\pm$ 260	
1,3,5-(<i>trans</i> -(3,5-R ₂ C ₆ H ₃ C $\equiv$ C)[Ru]{C $\equiv$ CC ₆ H ₄ -(<i>E</i>)-CH=CH}) ₃ C ₆ H ₃						
(<i>E</i>)-CH=CHC ₆ H ₄ -4-	(18)	417	-6700 $\pm$ 770	1300 $\pm$ 130	6800 $\pm$ 780	
C $\equiv$ C)[Ru](C $\equiv$ CPh)						
1,3,5-{ <i>trans</i> -(3,5-R ₂ C ₆ H ₃ C $\equiv$ C)[Ru](C $\equiv$ CC ₆ H ₄ -4-C $\equiv$ C)} ₃ C ₆ H ₃ ^[27] measured at 800 nm						
(C $\equiv$ C)[Ru](C $\equiv$ CPh)	(20) ^[c]	402	-5050 $\pm$ 500	20100 $\pm$ 2000	20700 $\pm$ 2000	4800 $\pm$ 500

^[a] Measurements are referenced to the nonlinear refractive index of silica $n_2 = 3 \times 10^{-16}$ cm² W⁻¹. ^[b] Complexes measured as CH₂Cl₂ solutions and at 750 nm with [Ru] = *trans*-Ru(dppe)₂ unless otherwise specified. ^[c] Measured as THF solutions. ^[d] [Ru] = *trans*-Ru(dppm)₂.

FULL PAPER

expected for a relatively subtle change at these large molecules, replacing the iodo substituent with either $\text{C}\equiv\text{CSiMe}_3$ or $\text{C}\equiv\text{CH}$ does not significantly affect the nonlinearity (**15b**, **16b**, **17b**).

Focusing on the dendrimer complexes, proceeding from the zero-generation yne-linked dendrimers (**19a**, **19b**) to the comparable *E*-ene-linked dendrimers (**13a**, **13b**) results in a marked increase in the nonlinear response. Although increasing the dendrimer generation, in moving from the zero- (**19b**) to first-generation yne-linked dendrimer (**20**) results in an approximately ten-fold increase in the nonlinearity, this effect is not seen with *E*-ene-linked dendrimers (proceeding from **13b** to **18**); in fact the nonlinearity decreases by a factor of two. This may be caused by an increasing loss of coplanarity in moving to **18**, or by the wavelength dependence of the response (although the near coincidence of the linear optical absorption maxima suggests that this may not be a critical factor). Finally, the observed nonlinearities of the cruciform complexes at this benchmark wavelength are the largest from the present study. The overall $|\gamma|$ values are dominated by very large γ_{real} contributions – while the energies of transitions for complexes across the present study are similar, it is noteworthy that the extinction coefficients for the lowest energy one-photon absorption bands for **14a-c** are much larger than those for the other complexes, and this may suggest significantly enhanced resonance effects.

The impressive NLO coefficients at the aforementioned benchmark wavelengths prompted a more detailed study of selected examples over the relatively broad spectral range 500–1600 nm, with a particular focus on the cruciform star complexes. Representative σ_2 and γ spectral dependences (those for **14a**) are displayed in Figure 4, the remainder being shown in Figures S7 (**9d**), S8 (**9e**), S9 (**14b**), S10 (**14c**), and S11 (**18**), while maximal data are collected in Table S3. All complexes studied are multiphoton absorbers, showing positive imaginary components of the third-order nonlinearity in the range 500–1500 nm. These complexes exhibit large apparent two-photon absorption (2PA) cross-sections at short wavelengths (500/520 nm), which is probably a combination of 2PA and excited-state absorption/reverse saturable absorption (ESA/RSA) due to the measurements being undertaken at the low-energy end of the linear absorption; the reported 2PA values at such wavelengths should therefore be considered with caution. The monometallic compounds (**9d** and **9e**) have a common 2PA peak at 640 nm, the ethenyl-linked **9e** having a larger cross-section. The 2PA maxima are at lower energies for **9e** than **9d** in the range 740–900 nm, consistent with the lower-energy MLCT in the linear absorption spectrum (to which these 2PA maxima are correlated).

The monometallic compounds, **9d** and **9e**, are “building blocks” for the formation of **14b** and **14c**, respectively. Addition of the monomer **9d/9e** to the core to afford **14b/14c** appreciably changes the 2PA spectrum; 2PA maxima are shifted to lower energy by around 20–40 nm, and the maximal values of the cross-section at these wavelengths increase seven- to ten-fold. A strong response at around 1150 nm also appears, which correlates closely with three times the wavelength of the lowest energy linear absorption band, and probably arises from three-photon absorption. This low-energy nonlinear absorption band is at a shorter wavelength than that observed for the 1,3,5-substituted analogue **18** (1300 nm), possibly a consequence of changing the core geometry of these star complexes. Attempts at “tuning” the NLO properties with alteration of the capping groups appear to

give negligible changes in the values of the NLO parameters (while being mindful of the associated errors), although the longer-peripheral π -system-containing **14b** and **14c** have stronger nonlinear absorptive properties at the longer wavelength maxima than does the phenyl-capped complex **14a**. This behavior may indicate that the NLO properties are overwhelmingly influenced by the core geometry rather than the peripheral substitution.

Figure 4. (top) Plot of σ_2 (blue) for **14a** overlaid on the UV-visible spectrum (black), and including plots of the UV-visible spectrum at twice (red) and three-times (green) the wavelength. (bottom) The real (red) and imaginary (black) parts of the third-order hyperpolarizability of **14a**.

Conclusions

The studies described herein have demonstrated useful outcomes from both the synthetic and materials perspectives. The “chemistry-on-complex” stereospecific formation of *E*-configured stilbene groups by Horner-Wadsworth-Emmons coupling of metal-ethynyl-functionalized benzaldehydes employed in this work has been shown to afford facile access to a range of “star” complexes, with both 1,3,5-trisubstituted arene and 1,2,4,5-tetrasubstituted arene (cruciform) geometries. Formyl substituents on arenes are ubiquitous in organic chemistry and undergo a broad range of reactions and consequent functionalization; the scope for analogous “chemistry-on-complex” transformation of metal-ethynyl-derivatized benzaldehydes remains to be explored, but the present studies have provided a glimpse of the potential.

Access to the range of ruthenium alkynyl-functionalized oligo(phenylenevinylene) stars, which the present studies has afforded, has permitted both an internal comparison of their

FULL PAPER

properties across the complexes described here, and an external comparison to those of the extant ruthenium alkynyl-functionalized oligo(phenyleneethynylene) analogues, allowing several structure-property outcomes to be highlighted. Alkyl substituents were employed in the present work to ensure sufficient solubility, but their electron-releasing nature is reflected in increased ease of oxidation and a blue-shift in optical absorption maximum. Incorporation of nitro substituents increases the potentials of the metal-centered oxidation processes, red-shifts the optical absorption maximum, and increases the maximal value of the cubic NLO properties. Progression from 1,3,5-trisubstituted arene core to 1,2,4,5-tetrasubstituted arene (cruciform) core results in a substantial increase in linear optical absorption maximum extinction coefficient, a decrease in energy of the LMCT band in the spectrum of the oxidized form, and a significant increase in maximal values of the nonlinear absorption. Finally, replacing the yne-linkages from the extant complexes with the *E*-ene linkages in the present work results in a blue-shift in optical absorption maximum, a red-shift in the LMCT band in the spectrum of the oxidized form, and an increase in nonlinear absorption cross-section; thus, the OPV-based star complexes from the present study exhibit enhanced nonlinearities with a slight gain in optical transparency.

Acknowledgements

We thank the Australian Research Council (ARC) for financial support. M.D.R. was the recipient of an Australian Postgraduate Award, X.Y. is the recipient of a China Scholarship Council ANU Postgraduate Scholarship, M.P.C. thanks the ARC for Australian Research Fellowships, and M.G.H. thanks the ARC for Australian Professorial Fellowships. M.S. acknowledges the NCN grant DEC-2013/10/A/ST4/00114.

Keywords

Organometallic chemistry • Molecular electrochemistry • Nonlinear optics • Transition metals

Supporting Information

Complete details of the syntheses and characterization of compounds **1-5**, **7**, and **8**, and complexes **9a-9e**, **10**, **11a-11c**, **13a**, **14a-14c**, **15a-15c**, **16a**, **16b**, **17a**, **17b**, and **18**, crystallographic studies of **9c-9e**, **11a**, **12'**, and **12''**, electrochemical studies of all new complexes, spectroelectrochemical studies of **14a-14c**, single-wavelength nonlinear optical studies of **15a-15c**, **16b**, **17a**, **17b**, and **18**, and broad spectral range nonlinear optical studies of **9d**, **9e**, **14a-14c**, and **18** are reported in the Supporting Information, available on the WWW under <http://dx.doi.org/10.1002/cplu.2015xxxxx>.

References

- [1] a) W. W. Boyd, *Nonlinear Optics*, 3rd ed., Academic Press, Amsterdam, **2008**; b) R. L. Sutherland, D. G. McLean, K. Sean, *Handbook of Nonlinear Optics*, 2nd ed, Marcel Dekker, New York, **2003**.
- [2] T. Schwich, M. P. Cifuentes, P. A. Gugger, M. Samoc, M. G. Humphrey, *Adv. Mater.* **2011**, 23, 1433-1435.
- [3] a) J. P. L. Morrall, G. T. Dalton, M. G. Humphrey, M. Samoc, *Adv. Organomet. Chem.* **2007**, 55, 61-136; b) M. E. Thompson, P. E. Djurovich, S. Barlow, S. Marder, in *Comprehensive Organometallic Chemistry III*, Vol. 12 (Eds.: R. H. Crabtree, D. M. P. Mingos), Elsevier, Oxford, **2007**, pp. 101-194; c) M. G. Humphrey, T. Schwich, P. J. West, M. P. Cifuentes, M. Samoc, in *Comprehensive Inorganic Chemistry II*, Vol. 8 (Eds.: J. Reedijk, K. Poeppelemeier), Elsevier, Oxford, UK, **2012**, pp. 781-835.
- [4] L.-T. Cheng, W. Tam, S. R. Marder, A. E. Stiegman, G. Rikken, C. W. Spangler, *J. Phys. Chem.* **1991**, 95, 10643-10652.
- [5] a) P. L. Porter, S. Guha, K. Kang, C. C. Frazier, *Polymer* **1991**, 32, 1756-1760; b) W. J. Blau, H. J. Byrne, D. J. Cardin, A. P. Davey, *J. Mater. Chem.* **1991**, 1, 245-249; c) T. B. Marder, G. Lesley, Z. Yuan, H. B. Fyfe, P. Chow, G. Stringer, I. R. Jobe, N. J. Taylor, I. D. Williams, S. K. Kurtz, in *Materials for Nonlinear Optics: Chemical Perspectives* (Eds.: S. R. Marder, J. E. Sohn, G. D. Stucky), ACS, Washington DC, **1991**, pp. 605-615; d) L. K. Myers, C. Langhoff, M. E. Thompson, *J. Am. Chem. Soc.* **1992**, 114, 7560-7561; e) I. R. Whittall, M. G. Humphrey, M. Samoc, J. Swiatkiewicz, B. Luther-Davies, *Organometallics* **1995**, 14, 5493-5495; f) Z. Yuan, N. J. Taylor, R. Ramachandran, T. B. Marder, *Appl. Organomet. Chem.* **1996**, 10, 305-316; g) S. Houbrechts, K. Clays, A. Persoons, V. Cadierno, P. M. Gamasa, J. Gimeno, *Organometallics* **1996**, 15, 5266-5268.
- [6] C. J. Jeffery, M. P. Cifuentes, G. T. Dalton, T. C. Corkery, M. D. Randles, A. C. Willis, M. Samoc, M. G. Humphrey, *Macromol. Rapid Commun.* **2010**, 31, 846-849.
- [7] a) I. R. Whittall, M. G. Humphrey, S. Houbrechts, A. Persoons, D. C. R. Hockless, *Organometallics* **1996**, 15, 5738; b) I. R. Whittall, M. P. Cifuentes, M. G. Humphrey, B. Luther-Davies, M. Samoc, S. Houbrechts, A. Persoons, G. A. Heath, D. Bogsanyi, *Organometallics* **1997**, 16, 2631-2637.
- [8] a) A. M. McDonagh, M. P. Cifuentes, M. G. Humphrey, S. Houbrechts, J. Maes, A. Persoons, M. Samoc, B. Luther-Davies, *J. Organomet. Chem.* **2000**, 610, 71-79; b) C. E. Powell, M. P. Cifuentes, A. M. McDonagh, S. Hurst, N. T. Lucas, C. D. Delfs, R. Stranger, M. G. Humphrey, S. Houbrechts, I. Asselberghs, A. Persoons, D. C. R. Hockless, *Inorg. Chim. Acta* **2003**, 352, 9-18.
- [9] a) A. M. McDonagh, I. R. Whittall, M. G. Humphrey, D. C. R. Hockless, B. W. Skelton, A. H. White, *J. Organomet. Chem.* **1996**, 523, 33-40; b) A. M. McDonagh, I. R. Whittall, M. G. Humphrey, B. W. Skelton, A. H. White, *J. Organomet. Chem.* **1996**, 519, 229-235; c) S. Hurst, M. P. Cifuentes, J. P. L. Morrall, N. T. Lucas, I. R. Whittall, M. G. Humphrey, I. Asselberghs, A. Persoons, M. Samoc, B. Luther-Davies, A. C. Willis, *Organometallics* **2001**, 20, 4664 - 4675.
- [10] a) S. K. Hurst, N. T. Lucas, M. G. Humphrey, T. Isoshima, K. Wostyn, I. Asselberghs, K. Clays, A. Persoons, M. Samoc, B. Luther-Davies, *Inorg. Chim. Acta* **2003**, 350, 62-76; b) S. K. Hurst, M. G. Humphrey, T. Isoshima, K. Wostyn, I. Asselberghs, K. Clays, A. Persoons, M. Samoc, B. Luther-Davies, *Organometallics* **2002**, 21, 2024-2026; c) I. R. Whittall, M. G. Humphrey, M. Samoc, B. Luther-Davies, *Angew. Chem., Int. Ed. Engl.* **1997**, 36, 370-371; d) L. Rigamonti, B. Babgi, M. P. Cifuentes, R. L. Roberts, S. Petrie, R. Stranger, S. Righetto, A. Teshome, I. Asselbergh, K. Clays, M. G. Humphrey, *Inorg. Chem.* **2009**, 48, 3562-3572; e) I. R. Whittall, M. G. Humphrey, A. Persoons, S. Houbrechts, *Organometallics* **1996**, 15, 1935-1941.
- [11] B. Babgi, L. Rigamonti, M. P. Cifuentes, T. C. Corkery, M. D. Randles, T. Schwich, S. Petrie, R. Stranger, A. Teshome, I. Asselbergh, K. Clays, M. Samoc, M. G. Humphrey, *J. Am. Chem. Soc.* **2009**, 131, 10293-10307.
- [12] S. Takahashi, Y. Kuroyama, K. Sonogashira, N. Hagihara, *Synthesis* **1980**, 627-630.

FULL PAPER

- [13] I. Ehlers, P. Maity, J. Aubé, B. König, *Eur. J. Org. Chem.* **2011**, 2474-2490.
- [14] O. Lavastre, S. Cabioch, P. H. Dixneuf, J. Vohlidal, *Tetrahedron* **1997**, *53*, 7595-7604.
- [15] S. Barlow, C. Risko, S.-J. Chung, N. M. Tucker, V. Coropceanu, S. C. Jones, Z. Levi, J.-L. Brédas, S. R. Marder, *J. Am. Chem. Soc.* **2005**, *127*, 16900-16911.
- [16] D. Touchard, P. Haquette, S. Guesmi, L. L. Pichon, A. Daridor, L. Toupet, P. H. Dixneuf, *Organometallics* **1997**, *16*, 3640-3648.
- [17] K. A. Green, M. P. Cifuentes, T. C. Corkery, M. Samoc, M. G. Humphrey, *Angew. Chem. Int. Ed.* **2009**, *48*, 7867-7870.
- [18] N. Gauthier, C. Olivier, S. Rigaut, D. Touchard, T. Roisnel, M. G. Humphrey, F. Paul, *Organometallics* **2008**, *27*, 1063-1072.
- [19] W. B. Austin, N. Bilow, W. J. Kellegan, K. S. Y. Lau, *J. Org. Chem.* **1981**, *46*, 2280-2286.
- [20] A. Winter, C. Friebe, M. D. Hager, U. S. Schubert, *Eur. J. Org. Chem.* **2009**, 801 - 809.
- [21] a) A. M. McDonagh, M. P. Cifuentes, I. R. Whittall, M. G. Humphrey, M. Samoc, B. Luther-Davies, D. C. R. Hockless, *J. Organomet. Chem.* **1996**, *526*, 99-103; b) S. K. Hurst, M. G. Humphrey, J. P. Morrall, M. P. Cifuentes, A. Samoc, B. Luther-Davies, A. C. Willis, *J. Organomet. Chem.* **2003**, *670*, 56 - 65; c) Z. Li, A. M. Beatty, T. P. Fehlner, *Inorg Chem* **2003**, 5707-5714; d) Q. Ge, T. S. A. Hor, *Dalton Trans.* **2008**, 2929-2936; e) G. A. Koutsantonis, G. I. Jenkins, P. A. Schauer, B. Szczepaniak, B. W. Skelton, C. Tan, A. H. White, *Organometallics* **2009**, *28*, 2195-2205; f) C. Olivier, S. De Sousa, L. Ducasse, B. Kauffmann, T. Toupance, *Chem. Eur. J.* **2014**, *20*, 7017-7024.
- [22] M. P. Cifuentes, C. E. Powell, M. G. Humphrey, G. A. Heath, M. Samoc, B. Luther-Davies, *J. Phys. Chem. A* **2001**, *105*, 9625-9627.
- [23] a) C. E. Powell, M. P. Cifuentes, J. P. L. Morrall, R. Stranger, M. G. Humphrey, M. Samoc, B. Luther-Davies, G. A. Heath, *J. Am. Chem. Soc.* **2003**, *125*, 602-610; b) M. P. Cifuentes, C. E. Powell, J. P. Morrall, A. M. McDonagh, N. T. Lucas, M. G. Humphrey, M. Samoc, S. Houbrechts, I. Asselberghs, K. Clays, A. Persoons, T. Isoshima, *J. Am. Chem. Soc.* **2006**, *126*, 10819-10832.
- [24] A. M. McDonagh, C. E. Powell, J. P. Morrall, M. P. Cifuentes, M. G. Humphrey, *Organometallics* **2003**, *22*, 1402-1413.
- [25] a) C. E. Powell, M. G. Humphrey, M. P. Cifuentes, J. P. Morrall, M. Samoc, B. Luther-Davies, *J. Phys. Chem. A* **2003**, *107*, 11264-1266; b) G. T. Dalton, M. P. Cifuentes, S. Petrie, R. Stranger, M. G. Humphrey, M. Samoc, *J. Am. Chem. Soc.* **2007**, *129*, 11882-11883.
- [26] M. Sheik-Bahae, A. A. Said, T. Wei, D. J. Hagan, E. W. van Stryland, *IEEE J. Quantum Electr.* **1990**, *26*, 760-769.
- [27] A. M. McDonagh, M. G. Humphrey, M. Samoc, B. Luther-Davies, *Organometallics* **1999**, *18*, 5195-5197.

Entry for the Table of Contents

FULL PAPER

(4-Formylphenylethynyl)ruthenium complexes such as that at right are shown to undergo “chemistry-on-complex” Horner-Wadsworth-Emmons coupling, affording a range of tri- and tetra-ruthenium-functionalized star molecules and a nonaruthenium dendrimer. The products are NLO-active, with linear optical properties that are redox-switchable.

Zhiwei Chen, Christopher J. Jeffery, Mahbod Morshedi, Graeme J. Moxey, Adam Barlow, Xinwei Yang, Bandar A. Babgi, Gulliver T. Dalton, Michael D. Randles, Matthew K. Smith, Chi Zhang, Marek Samoc, Marie P. Cifuentes, Mark G. Humphrey*

Page No. -Page No.

Syntheses, Electrochemical, Linear Optical, and Cubic NLO Properties of Ruthenium Alkynyl-Functionalized Oligo(phenylenevinylene) Stars