Organometallic Routes to Cross-Conjugated Hydrocarbons

A THESIS SUBMITTED FOR THE DEGREE OF

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Declaration

Except where specific acknowledgements of others are made, the author carried out the work described in this thesis during the period of March 2009 to January 2013 in the Research School of Chemistry of the Australian National University, under the supervision of Professor Mick Sherburn. The material presented has not been submitted for any other degree and is less than 100,000 words in length.

Henry Toombs-Ruane

January 2013

Acknowledgements

My first thanks must go to my supervisor, Mick Sherburn. Thanks for the advice, the support, the guidance, and the banter. I haven't even finished and I'm already looking forward to our future collaborations.

And my thanks again to Mick for collecting together such a great group of guys and gals in the form of the Sherburn Group. It has been a pleasure to study (and not) with you all, and I hope that it can continue for a long time, either here, or from afar.

I am extremely grateful to Tony Herlt, Thomas Fallon, and Maxime Riou for their assistance in the laboratory. During my research I have also been fortunate enough to collaborate with Tony Willis and Michael Paddon-Row. If I had not had access to their vast knowledge, resources, and technical experience then I would never have been able to competently carry out research, let alone complete this thesis.

Studying at the Australian National University has given me the opportunity to intersect with many resident and visiting academics, in particular I am indebted to Ian Fairlamb, Bill Lording, Thomas Rauchfuss, Henning Hopf, Claude Spino, Martin Bennett, Scott Stewart, David Lupton, and Tony Hill for lending me their time and insights.

While my field has strayed significantly from my first forays into chemistry, it was Vladimir Golovko and Andy Pratt who—in my Honours year—showed me that chemistry is a field that can be both challenging and rewarding. And so I suppose I'll have to thank Vlad & Andy in every acknowledgement section I write.

I think there's an old adage about any given man not being an island. Perhaps it's something about independence and reliance coexisting; about the shared nature of the Human Experience. Or maybe it's about the buoyancy of flesh, and dying at sea. All this is a way of saying, thank you Julia. You've helped me more than I can possibly give thanks for; but more important than any help, you made any sacrifice worth it.

Finally, thanks mum, you really are the best! And Leah, hurry up with your novel.

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Publications

Some of the work in this thesis has been previously published:

Toombs-Ruane, H.; Osinski, N.; Fallon, T.; Wills, C.; Willis, A. C.; Paddon-Row, M. N.; Sherburn, M. S. Synthesis and Applications of Tricarbonyliron Complexes of Dendralenes. *Chem. Asian J.* **2011**, *6*, 3243–3250. This research is reported in Chapters 2 & 3.

Toombs-Ruane, H.; Pearson, E. L.; Paddon-Row, M. N.; Sherburn, M. S. On the Diels-Alder dimerisation of cross-conjugated trienes. *Chem. Commun.* **2012**, *48*, 6639–6641. This research is reported in Chapter 3.

Abbreviations

%	percentage yield
Δ	heat
°C	degree/s Celsius
Ac	acetyl
aq.	aqueous
Ar	aryl or argon
ASE	aromatic stabilisation energy
BDA	benzylideneacetone
BHT	2,6-di-*tert*-butyl-4-methylphenol
bp	boiling point
br	broad
brsm	based on recovered starting material
Bu	butyl
ca.	*circa* (approximately)
calc	calculated
CAN	ceric ammonium nitrate
cm^{-1}	wave number
COSY	correlated spectroscopy
CSI	chlorosulfonylisocyanate
δ	chemical shift
d	day/s or doublet/s
DA	Diels–Alder
dba	dibenzylideneacetone
DBU	1,8-diazabicyclo-[5.4.0]undec-7-ene
DFT	density functional theory
DMAP	4-dimethylaminopyridine
DME	dimethoxyethane
DMF	dimethylformamide
DIBAL	diisobutylaluminium hydride
DMSO	dimethylsulfoxide
dppf	1,1'-bis(diphenylphosphino)-ferrocene
EDG	electron donating group
EI	electron impact
equiv.	(molar) equivalent(s)
Et	ethyl
EWG	electron withdrawing group
eV	electron Volts
ESI	electrospray ionisation
FMO	frontier molecular orbital
Ft	tricarbonyliron
GC	gas chromatography
h	hour/s or Planck constant
HMBC	heteronuclear multiple bond coherence
LDA	lithium diisopropylamide
LRMS	low resolution mass spectrometry
hν	light/photochemistry
HMPA	hexamethylphosphoramide
HSQC	heteronuclear single quantum coherence
HOMO	highest occupied molecular orbital
HPLC	high pressure liquid chromatography
HRMS	high resolution mass spectrometry
HWE	Horner-Wadsworth-Emmons
Hz	Hertz
IMDA	intramolecular Diels–Alder
i-Pr	isopropyl
IR	infrared
J	coupling constant
KHMDS	potassium hexamethyldisilazide
lit.	literature
LUMO	lowest unoccupied molecular orbital
M	molar ($molL^{-1}$)
M^+	molecular ion

Me	methyl
min	minute
MHz	megahertz
mm Hg	millimetres of mercury
mol	mole
mol.	molar
mp	melting point
MS	mass spectroscopy
MVK	methyl vinyl ketone
m/z	mass to charge ratio
ν	absorption maxima (IR)
n-BuLi	*n*-butyl lithium
NLO	nonlinear optical
NMR	nuclear magnetic resonance
nOe	nuclear Overhauser effect
NOESY	nuclear Overhauser and exchange spectroscopy
Ph	phenyl
pin	pinacol
PMP	*para*-methoxyphenyl
PNP	*para*-nitrophenyl
ppm	parts per million
Pr	propyl
q	quartet
RCM	ring-closing metathesis
rt	room temperature
sat.	saturated
SM	starting material
SOI	secondary orbital interaction
t	time
t-Bu	*tert*-butyl
TBS	*tert*-butyldimethylsilyl
temp	temperature
Tf	trifluoromethanesulfonyl
THF	tetrahydrofuran
TLC	thin layer chromatography
TM	target material
TMM	trimethylenemethane
TS	transition state
Ts	*para*-toluenesulfonyl
p-TsOH	*para*-toluenesulfonic acid
v/v	volume concentration
v.i.	*vide infra* (see below)
v.s.	*vide supra* (see above)
vol.	volume
wt %	weight percent
ZCE	*Z*-cyclooctene

Abstract

Molecules with a high degree of unsaturation often have associated with them a concomitant level of instability. In fact, their instability is what hinders the preparation and synthetic utility of large swaths of polyunsaturated frameworks. One form of modulating and controlling that reactivity is the tricarbonyliron group; a functionality that coordinates to a portion of an unsaturated skeleton, often allowing the easy isolation and observation of the unstable compound.

This thesis explores the chemistry of cross-conjugated polyenes, and especially their relationship to the tricarbonyliron group, in one review, and three experimental chapters. Chapter 1 reviews the known chemistry of highly reactive polyenes, and their stabilisation through coordination to the tricarbonyliron group. Chapter 2 describes the preparation of tricarbonyliron complexes of the dendralenes. Chapter 3 investigates the curious reactivity of cross-conjugated trienes. Chapter 4 describes a new synthetic strategy towards preparing polyenes that are protected as organometallic complexes.

While the ability for the tricarbonyliron group to stabilise reactive polyenes has long been known, their applications in this respect have not been rigorously documented by review. In Chapter 1 we comprehensively review the literature on the tricarbonyliron complexes of unstable molecules, and uncover promising areas for future research. In particular, there remain several hydrocarbons of fundamental interest that have never been synthesised, whose preparation could be realised by using tricarbonyliron protection.

The dendralenes are a fundamental family of cross-conjugated oligoalkenes that only recently been accessed on a useful scale. The family of molecules has the power to rapidly form compounds with natural-product like complexity through a cascade of bond-forming reactions, but their synthetic utility is hampered by their instability and lack of selectivity. In Chapter 2 we describe the first targeted preparation of the tricarbonyliron complexes of the [3]-[6]dendralenes. We find that tricarbonyliron complexation not only protects the dendralenes from decomposition, but also selectively activates them to a broad range of reactions.

In Chapter 3 we report the first general synthesis of [3]dendralene molecules substituted at the 1-position. These compounds were prepared *via* cross-metathesis on the tricarbonyliron complex of [3]dendralene. With the elusive series of substituted dendralenes in hand, we report the surprising observation that the 1*E*-sub-class undergoes Diels-Alder dimerisation up to 200 times faster than the parent [3]dendralene. This stands in stark contrast to the behaviour of the 1*Z*-, 2- , & 3'-substituted [3]dendralenes, which are invariably more stable than the unsubstituted case. We explore the mechanistic rationale for this behaviour.

Finally, in Chapter 4 we use the knowledge gained in the synthetic efforts described in Chapters 2 & 3 to rationally develop a new, general method for the synthesis of polyene complexes via cross-coupling reactions. To verify our approach we use 2- & 2,3- substituted halobutadiene complexes to directly prepare the tricarbonyliron complexes of the dendralenes, as well as some new cross-conjugated frameworks.

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"Every passing hour brings the Solar System forty-three thousand miles closer to Globular Cluster M13 in Hercules—and still there are some misfits who insist that there is no such thing as progress."

Kurt Vonnegut, Jr.

1

Stabilisation of Hyper-Reactive Molecules By Tricarbonyliron

1.1 By Way Of An Introduction

1.1.1 Preamble

Due to the resurgence in interest in polyene systems there is a renewed urgency in understanding the ability of the tricarbonyliron group to stabilise and modulate the reactivity of an unstable η^4-polyene ligand, and thus it is worth investigating all of the systems that have been studied with a tricarbonyliron group stabilising a neutral polyene.

Unstable is a term often used imprecisely in organic chemistry.[1A] Even though 'unstable' is defined exactingly and unambiguously by IUPAC,[2] the term is still frequently used to mean a compound that has a high reactivity for undesired reaction pathways. Formally, "[stable] expresses a thermodynamic property, which is quantitatively measured by relative molar standard Gibbs energies," but this author is unsatisfied with the terminology which remains to him to describe a situation where a compound has a low (or high) proclivity for undergoing reactions which lead to its degradation. The obvious replacement for *stable* (used colloquially) is *unreactive*; unfortunately, describing a compound as *unreactive* often requires extensive further qualification. Even when used correctly, *stable* means different things to different chemists, as stability is a relative term. Here we define *highly reactive* as "cannot be readily handled or isolated under standard laboratory conditions," and *unstable* will be used as a corollary where the molecule in question has a significantly higher free energy than the compounds accessible by decomposition.[B]

1.1.2 Target: Fundamental Molecules

In synthetic organic chemistry there are broadly two fields of research, target oriented synthesis and reaction development. Target oriented synthesis is thought of as the *higher art*, while reaction development is more an *enabling technology*. Much has been written and said in the history of organic chemistry about the balance and the strife between these two complementary fields of research.[3] The validity of total synthesis as a field is often impugned by chemists and non-chemists alike.

> *"This is an important point: neither biology nor chemistry would be served best by a development in which all organic chemists would simply become biological such that, as a consequence, research at the core of organic chemistry and, therefore, progress in understanding the reactivity of organic molecules, would dry out. Progress at its core in understanding and reasoning is not only essential for organic chemistry itself, but for life science as a whole. Life science needs an*

[A] Inorganic chemists are often much more fastidious in this respect, as the observable differences, in their field, between thermodynamic stability and kinetic inertness are generally much more marked.

[B] The key point here is that there is no universal benchmark for stability or reactivity; at some point on an axis defining harshness of reaction conditions every molecule is highly reactive and at some point they are all inert. It is between these points that we arbitrarily define our default level of reactivity.

> *Organic Chemistry that remains strong."*
> ***Albert Eschenmoser*.[4]**

> *"I believe that chemical synthesis will make enormous contributions to human progress in the next century especially when coupled to biology and medicine. However, those developments will not be fully realized without great and continuing advances in the central disciplines of chemistry. There is so much that remains to be discovered, in my opinion, that today's chemistry will seem archaic to a 22nd century chemist."*
> ***Elias J. Corey*.[5]**

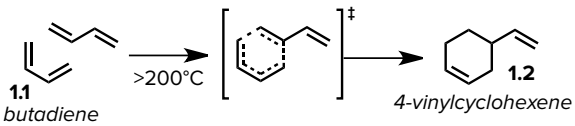
> *"These days, the discipline of natural product synthesis, both total and partial (semisynthesis), is an important field of investigation whose dividends stretch from new scientific knowledge to practical applications. Considered by many as the flagship of organic synthesis, natural product synthesis symbolizes the power of chemical synthesis at any given time and defines its scope and limitations."*
> ***K. C. Nicolaou*.[6]**

Fundamental molecules, unnatural though they may be, can be equally worthy objectives for targeted synthesis as natural products, and they can have as much scope for informing and defining the power and limitations of the field of chemical synthesis.

1.2 Polyene Protection

1.2.1 Alternative to Diene Protection

Dienes are employed in some of the most potent reactions in organic chemistry (e.g. the Diels-Alder reaction), but with great reactivity often comes great instability. Many dienes are stable under a range of conditions, for example butadiene takes very high temperatures or pressures to react in Diels-Alder reactions[7] (Scheme 1.1), but often the most interesting or synthetically useful dienes are also unstable.



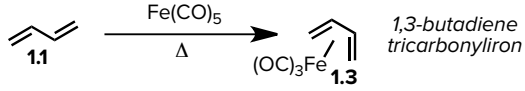
Scheme 1.1: Inherent stability of 1,3-butadiene.[7]

One of the less common ways to get around polyene instability is by avoiding the problem and using a modified approach, e.g. in the formal total synthesis of

triptolide, Miller and coworkers were faced with low yields when using an unstable triene, and thus only introduced the third alkene after the first two had reacted.[8]

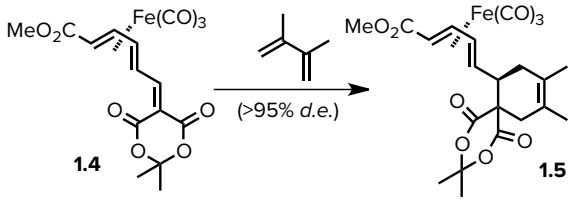
1.2.2 Tricarbonyliron Complexes of Dienes

The tricarbonyliron butadiene complex was first reported in 1930 (Scheme 1.2).[9] Since that time researchers faced with the prospect of an unstable diene have frequently turned to the tricarbonyliron moiety to generate a stable tricarbonyliron-diene complex.[10-14]



Scheme 1.2: First complexation of butadiene with tricarbonyliron (Reihlen *et al.* 1930).

Apart from stabilisation of a unstable diene, complexation with tricarbonyliron is commonly used in synthetic organic chemistry for two other purposes: as a stereochemical directing group (Scheme 1.3),[15,16] or to stabilise formation of an adjacent positive charge (and form a pentadienyl cation).[17] Most recent uses have focussed on their application for these purposes.[18]

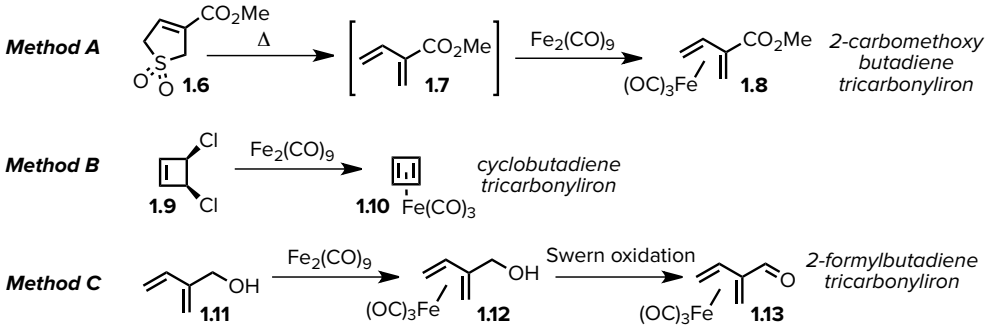


Scheme 1.3: Asymmetric induction with tricarbonyliron (Benvegnu *et al.* 1990).

The particular merits of tricarbonyliron stabilisation—as opposed to other kinds of diene stabilisation—are crucial to their usefulness to the synthetic organic chemist. The stability of the resultant complexes, the reliability of the methods developed to prepare and to remove tricarbonyliron groups (*vide infra*), and the ease of characterisation of the tricarbonyliron intermediates are all vital points in favour of tricarbonyliron stabilisation as opposed to other protecting groups. Tricarbonyliron is also surprisingly selective when compared with some other carbonylmetals (e.g. $Ru_n(CO)_m$ and $Os_n(CO)_m$) in its ability to form monomeric, rather than polymeric, organometallic complexes.

1.2.3 The Preparation of Tricarbonyliron Complexes of Unstable Polyenes

Conceptually, there are three different approaches to making the tricarbonyl complex of an unstable compound. Firstly (**A**), there is the possibility of adding [$Fe(CO)_3$] to an already prepared sample of the unstable compound, but this method requires very mild conditions for complexation, and is not tolerant of extremely unstable compounds (Scheme 1.4). Secondly (**B**), there is the possibility of treating some precursor to the desired unstable compound with complexation conditions, and generating the complex directly from the precursor; if the generation of the complex occurs as a stepwise process via the intermediacy of the unstable compound then this is arguably a subcategory of method **A**. Third (**C**) comes the option of carrying out complexation on a more stable precursor, which can then be converted into a complex of the unstable compound by separate successive synthetic steps. In the literature all three of these approaches have been taken to prepare the compounds described in this review (Scheme 1.4).



Scheme 1.4: Examples of each of the 3 classes of tricarbonyliron complexation discussed.

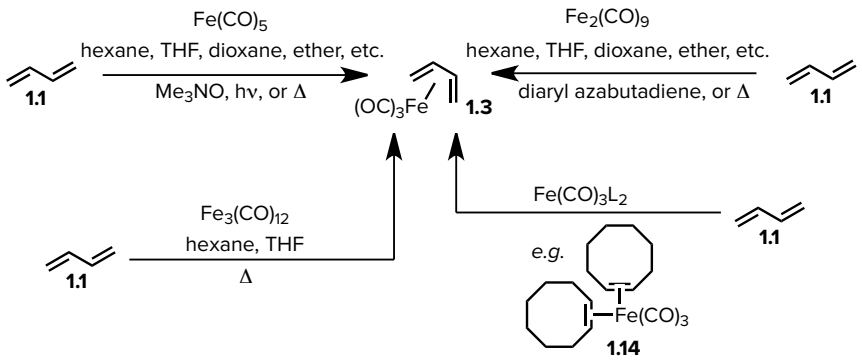
The approaches will be defined as methods **A**, **B**, or **C** for each compound that is discussed (Figure 1.2). Nicholson has reported[19] a method for determining the ability for a polyene to be complexed by the tricarbonyliron group. Relative bond-localisation energies were calculated for a range of polyunsaturated hydrocarbons which had been successfully complexed by the tricarbonyliron group, and on that basis Nicholson predicted a series of compounds that should form stable complexes under standard conditions; predictions which were borne out for *o*-xylylene and heptafulvene at least, (*v.i.*). But this method only takes into account one (**A**) of the three possible methods for preparing a tricarbonyliron complex of an unstable diene. Nicholson's bond localization energy calculations have been

corroborated by structure-resonance theory analysis by Herndon[20] and by theoretical studies by Dias.[21]

1.2.4 Reagents for Tricarbonyliron Complexation

There are many conditions in the literature for the complexation of 1,3-dienes with the tricarbonyliron moiety. Early methods used pentacarbonyliron, but researchers quickly figured out that diiron nonacarbonyl and triiron dodecacarbonyl generally form complexes more rapidly, and under milder conditions (Scheme 1.5).

The mechanism of complexation depends upon the source of the iron carbonyl, the solvent, and any additives, but generally involves the loss of one or more carbonyl ligands from an iron carbonyl centre, and subsequent coordination of one alkene of the 1,3-diene, followed by the other.[22] A curious consequence of the first step of complexation being loss of a CO ligand is that some of the most efficient means of tricarbonyliron-diene formation are also among the best at destroying that complex by further liberation of CO.[23,24]

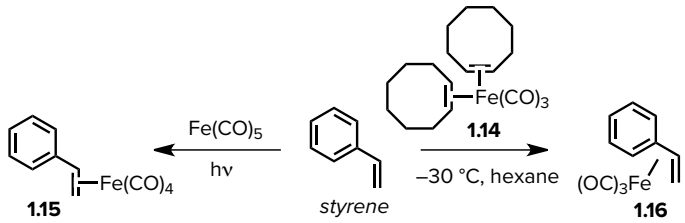


Scheme 1.5: Tricarbonyliron(butadiene) preparation.

Common complexation methods differ in the iron source (Scheme 1.5). $Fe(CO)_5$ is a neutral complex comprising a d^8-metal with five datively coordinated ligands, therefore it is an 18-electron complex and generally will only undergo dissociative substitution mechanisms, which require that at least one ligand is lost before a new one can ligate. $Fe_2(CO)_9$, $Fe_3(CO)_{12}$, and $Fe(CO)_3(L)_2$ are also 18-electron complexes, and during the mechanism of complexation $[Fe(CO)_4]$ is produced.

The second major class of tricarbonyliron complexation conditions that are commonly used are ones where a tricarbonyliron group is pre-complexed to some labile olefin-containing ligand. These kinds of complexation conditions are

discussed at length by Knölker.[25] His findings are that improvements can be made to the efficiency[C] of complexation by using tricarbonyliron transfer reagents like (benzylideneacetone)iron tricarbonyl (also called (BDA)$Fe(CO)_3$) and catalytic variants thereof.[26] In 1984, Grevels and coworkers[27] developed a reagent, **1.14**, for the coordination of dienes that had an unprecedented ability to isomerise and trap *s-cis* butadiene fragments from compounds which had previously been difficult to complex, and it was able to do this in dilute solution in hexane at −30 °C. A good point of comparison for the complexing power of Grevels' reagent (also formulated as $(ZCE)_2Fe(CO)_3$) is the result of a complexation with styrene, where Grevels' reagent is able to break the aromaticity of styrene to give the (η^4-styrene)$Fe(CO)_3$ complex **1.16**. Whereas, the aromaticity of styrene is not broken upon photochemical exposure of $Fe(CO)_5$, instead giving the (η^2-styrene)$Fe(CO)_4$ complex **1.15**.[28,29D] Grevels' reagent deserves more discussion as it has a special place in tricarbonyliron complexation chemistry (see Chapter 4).



Scheme 1.6: The carbonyliron complexation of styrene.[27,28]

In some rare cases, Collman's reagent (disodium tetracarbonyl ferrate)[30] ($Na_2[Fe(CO)_4]$), bis-tetrabutylammonium tetracarbonyl ferrate[31] ($[Bu_4N]_2[Fe(CO)_4]$), and bis-tetrabutylammonium octacarbonyl diferrate[32] ($[Bu_4N]_2[Fe_2(CO)_8]$) have been used as an iron tricarbonyl source where yields with neutral iron complexes are very low.[33]

[C] Efficiency in this case is not trivial to measure because iron carbonyl sources rapidly become prohibitively expensive if they must be used in excess early on in a synthesis. In general we take the view that the organic ligand will be the limiting reagent for which efficiency should be optimised; this view is in disagreement with much of the older inorganic literature, and perhaps reflects this author's organic bias.

[D] In follow up work it was possible to make the η^4-styrene complex photochemically (with significant effort), see Victor *et al.* 1972.

1.2.5 Methods for Tricarbonyliron Removal

The methods for removing the tricarbonyliron group vary in their sensitivity to the diene functionality, as well as their sensitivity to the molecule as a whole. In general, single-electron transfer oxidants are the reagents that allow for the lowest temperature and stoichiometry, while two-electron oxidants allow for more oxidatively mild conditions but require generally higher temperatures, reaction times, or stoichiometry (Figure 1.1). Apart from purely oxidative conditions it is also possible to demetalate photochemically, thermally, or with reducing conditions, but these are generally more specialised and require other functionality in the molecule, extremely resilient compounds, or result in the loss of diene functionality.

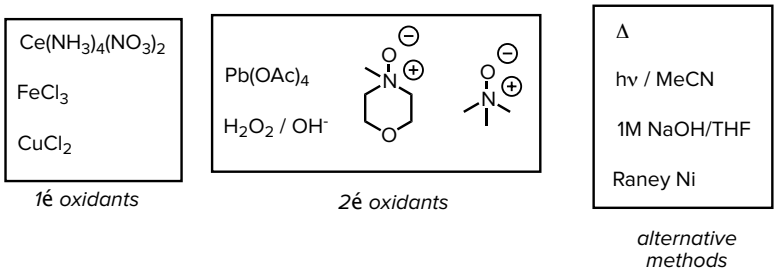


Figure 1.1: Demetalation agents.

Single-electron oxidants that have been used in the removal of tricarbonyliron groups from dienes include cerium ammonium nitrate (CAN),[11,34] ferric chloride,[35-37] and cupric chloride.[38] Reagents like CAN are among the most common for their ability to remove tricarbonyliron quickly and without heating, e.g. oxidations with CAN often take less than 15 minutes at 0 °C. Two-electron oxidants that have been used to demetalate a tricarbonyliron diene complex include trimethylamine N-oxide,[23,39] basic hydrogen peroxide,[40] lead tetraacetate,[41] and N-methyl morpholine N-oxide.[42] Tricarbonyliron groups have also been removed successfully *via* thermal conditions,[43] photochemical ligand removal,[44,45] photochemical ligand exchange,[24] nucleophilic ligand exchange,[46,47] and total hydrogenation with Raney nickel.[48]

1.3 Tricarbonyliron Complexes of Unstable Polyenes

Unstable polyenes have frequently been the objective of targeted synthesis efforts;[49] to the point where many of the compounds that have remained unsynthesised in this area have taken on mythic status. Interest in polyenes comes not just from aesthetic curiosity and ambition, but also genuine interest in the properties arising from the molecules' connectivity, as well as their electronic structure and interconnected π-systems.

Usually, aspects of organometallic chemistry are considered from either an organic or an inorganic perspective, depending on the professional inclination of the investigator. Tricarbonyliron-polyenes are hugely important to the inorganic community.[50,51] Herein we describe an organic chemist's perspective of tricarbonyliron-polyenes as: models of the naked ligand;[E] a controlled source of the reactive polyene, which can be generated using thermal,[43] photochemical,[44] or oxidative conditions[35] (see Chapter 3); or synthetically useful intermediates themselves, using the tricarbonyliron group to activate and direct reactivity (see Chapters 2, 3, and 4).

The simple organic compounds shown below (Figure 1.2) are archetypal examples of molecules which are too reactive to handle and observe under standard conditions. Each has been prepared as a complex with tricarbonyliron. They are mostly cyclic polyunsaturated hydrocarbons, with a few exceptions containing carbonyl groups, or lacking a ring.[F]

[E] Although the compound will be distorted by complexation to the metal centre there is still useful information to be gained from studying the complex's structure and properties.

[F] It is unclear to this author what external effects are driving the selectivity of the examples depicted. It may be that—of the polyenes—the cyclic variants are in general less stable, or it may be that there were methods amenable to the synthesis of complexes of cyclic polyenes over acyclic ones, or it may be due in part to the prejudice and vagaries of the organometallic community during the periods in which these complexes were made.

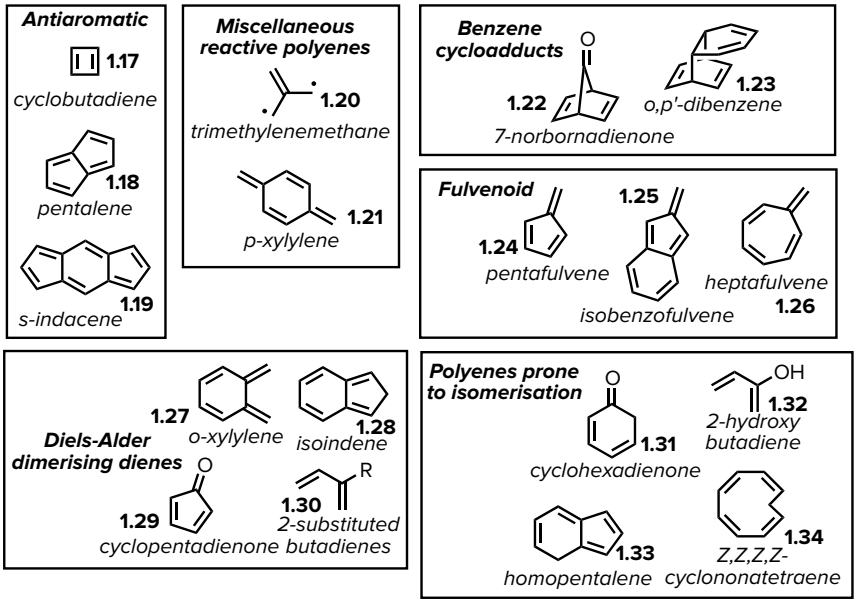


Figure 1.2: Reactive dienes which have been accessed as tricarbonyliron complexes.

Precise relationships between the polyenes (Figure 1.2) are difficult to pin down as each is closely related to the others. Because of this fundamental interconnectedness, any assignment of 'class' or 'group' is to some extent arbitrary. In Figure 1.2 polyenes are gathered by their common modes of decomposition, or, failing that, by an assignable structural feature. The *antiaromatic* compounds each contain a cyclic [4n]π-electron system in a fixed planar arrangement; their decomposition often involves [2+2] cycloadditions, but can be extremely complex. The *Diels-Alder dimerising dienes* have a very high tendency to react in concerted [4+2] cycloadditions with themselves. *Benzene cycloadducts* are polyenes that have a tendency to undergo a retro-Diels-Alder to form benzene. The *fulvenoid* hydrocarbons are vinylidene-expanded isomers of the aromatic annulenes; they have complicated decompositions often involving cycloadditions and polymerisation. *Isomerising polyenes* undergo very favourable tautomerisations or rapid unimolecular isomerisations to form more stable compounds. Remaining reactive polyenes are categorised as *miscellaneous*.

Key relationships between compounds and classes beyond those listed above are: cyclopentadienone is an oxa-fulvene, an acetylene-extruded norbornadienone, and a 4π-electron antiaromatic compound; cyclohexadienone is a methylene-expanded cyclopentadienone, and a highly reactive Diels-Alder diene; o-xylylene is an isomer of heptafulvene, which are both isomers of [8]annulene;

trimethylenemethane and cyclobutadiene are both triplet biradicals in the ground state; cyclononatetraene, homopentalene, and isoindene are all methylene-expanded 8π-electron antiaromatic ring-systems.

Part of our reason for compiling a compendium of tricarbonyliron-polyene compounds is to assess their known uses, their expected usefulness, and—if they are promising—attempt to repair the weaknesses of their preparation and uses in the future.

1.3.1 Antiaromatic Polyenes

The tricarbonyliron complexes of antiaromatic polyenes comprise the 4π-electron cyclobutadiene **1.17**, the 8π-electron pentalene **1.18**, and the 12π-electron *s*-indacene **1.19**. Each is highly reactive towards decomposition in its uncomplexed and unsubstituted form.

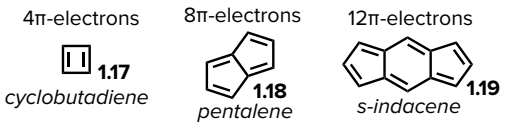


Figure 1.3: Antiaromatic polyenes that have been stabilised by the tricarbonyliron group.

CYCLOBUTADIENE

Cyclobutadiene, or [4]annulene, is the best known example of antiaromaticity, and is used as the archetypal example of the case where breaking Hückel's rule leads to a compound which is much less stable than similar non-aromatic compounds.[52] The preparation of cyclobutadiene tricarbonyliron was the subject of a review unto itself,[14] but its preparation and uses deserve another, albeit brief, retelling here.

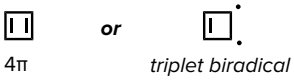
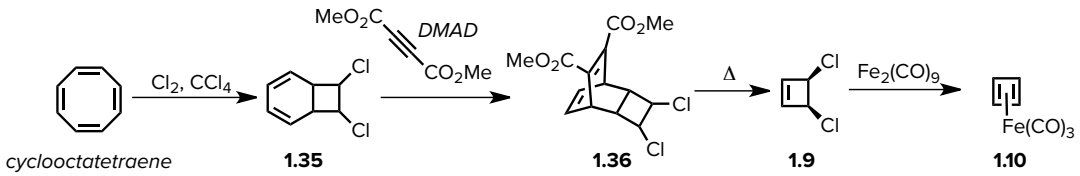


Figure 1.4: Cyclobutadiene, in its closed-shell singlet (left) or triplet (right) state.

Cyclobutadiene tricarbonyliron was hypothesized by Longuet-Higgens & Orgel[53] before it was synthesized by Pettit and coworkers in 1965.[54] The successful synthesis was achieved by the *in situ* elimination of chlorine from *cis*-3,4-dichlorocyclobutene, **1.9**, and concomitant complexation with tricarbonyliron(Scheme 1.7, Method **B**, see page 5). The reaction proceeds with

moderate yields (~40%)[G] and relatively mild conditions, and was later optimised and published as a robust procedure in *Organic Syntheses*.[55,56]



Scheme 1.7: Preparation of (Cyclobutadiene)Fe(CO)$_3$.[55,56]

Before Pettit and coworkers' successful synthesis of the parent cyclobutadiene tricarbonyliron complex, Dodge and coworkers prepared and crystallised the tetraphenyl derivative, **1.37** (Figure 1.5).[57] The molecular structures of these cyclobutadiene tricarbonyliron complexes, as determined by X-ray crystallography, are shown in Figure 1.5. The tricarbonyliron group converts the antiaromatic cyclobutadiene[58] into an aromatic[59,60] or *metalloaromatic*[61] system. The aromatisation of the ring explains the change in C–C bond lengths from the extremely alternant 1.34 Å and 1.57 Å in cyclobutadiene[62] to the delocalised 1.42 Å observed in the solid state for the complex.[63]

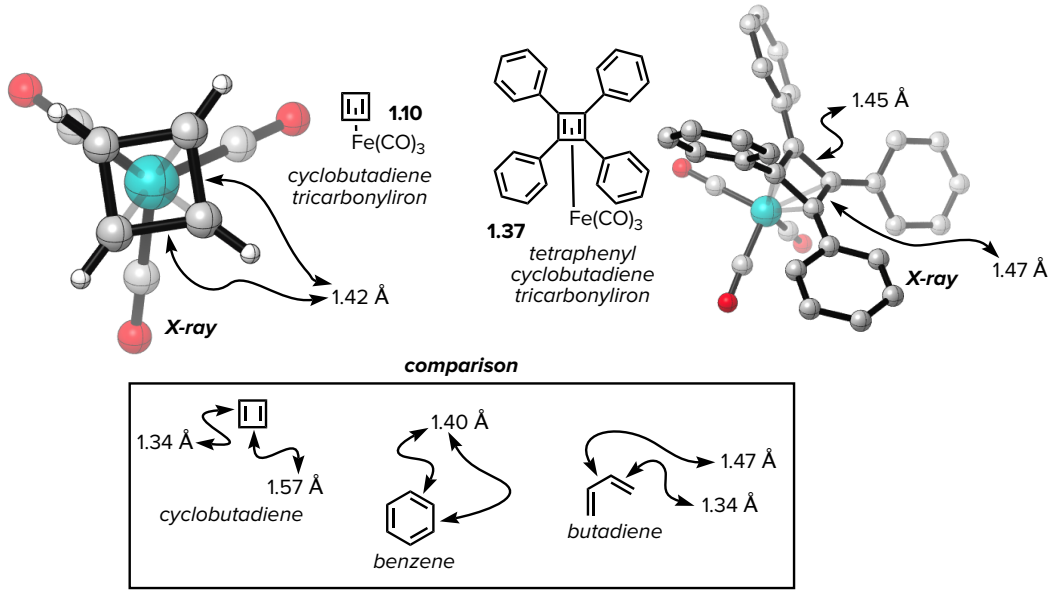
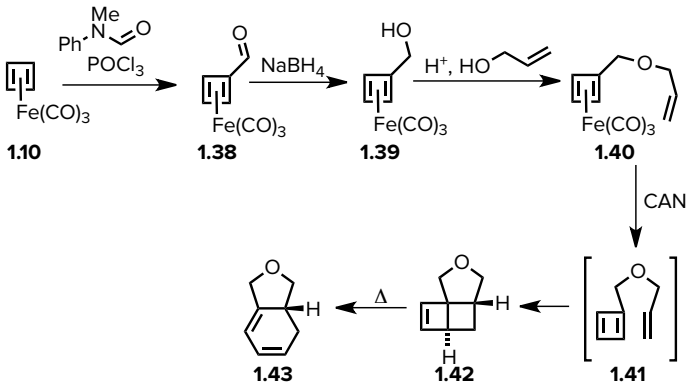


Figure 1.5: The molecular structure of cyclobutadiene tricarbonyliron (Left: Harvey *et al.* 1988,[63] Right: Dodge *et al.* 1965.[64]). Hydrogen atoms are excluded from some depictions of molecular structures in this chapter for clarity.

[G] Which is impressive considering the transformation and the extremely reactive nature of the likely intermediates.

(Cyclobutadiene)tricarbonyliron has been used to access [2+2] cycloadducts of cyclobutadiene by first introducing a tether for the appropriate dienophile[65H] by Vilsmeier-Haack formylation, followed by reduction, and Williamson ether synthesis (Scheme 1.8).[66] The adducts of the [2+2] cycloaddition are either cyclobutenes or substituted Dewar-benzenes[67] (with an alkynic dienophile), which could then be conveniently isomerised into 6-membered rings by a thermal 4π electrocyclic ring-opening.[65]



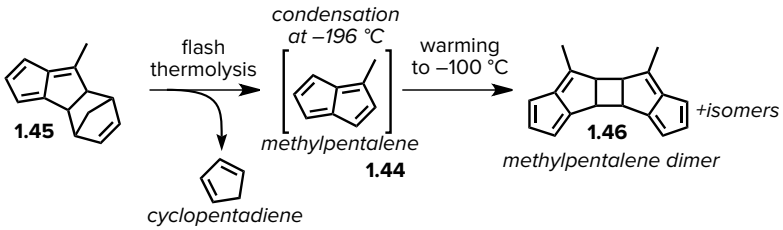
Scheme 1.8: Some reactions of (cyclobutadiene)tricarbonyliron.[65,66]

(Cyclobutadiene)tricarbonyliron was used to prepare and observe the reactivity of the unsubstituted and decomplexed cyclobutadiene for the first time.[11] The lengths one needs to go to stabilise cyclobutadiene in the absence of tricarbonyliron chemistry are best exemplified by Cram's 'taming' of cyclobutadiene.[68] In this paper cyclobutadiene is generated by the photochemical decarboxylation of γ-pyrone inside a hemicarcerand container molecule.[69]

PENTALENE

Pentalene is closely related to cyclobutadiene, as both are planar antiaromatic hydrocarbons. The parent pentalene, **1.18**, has not been directly observed or characterised. The observation of 1-methylpentalene, **1.44**, was reported by IR spectroscopic analysis at –196 °C. On warming from –140 °C to –100 °C these signals were replaced by signals belonging to a mixture of [2+2] dimers (Scheme 1.9).[70]

[H] Although this reaction is not a Diels-Alder, the terminology of dienophile is still convenient to use. Our use here mirrors use of the terminology in the literature.



Scheme 1.9: 1-Methylpentalene, as prepared by flash-thermolytic extrusion of cyclopentadiene, and observed by low temperature condensation onto NaCl plate for IR analysis. Dimers were isolated on warming past –140 °C.[70]

The preparation of pentalene and simple methyl substituted analogues was investigated extensively by Hafner and coworkers.[71,72] Results obtained by Hafner were similar to those obtained by De Mayo and coworkers (Scheme 1.9), in that pentalene itself was never fully characterised.[72-74] Stable pentalenes have been prepared, notably hexa(*p*-tolyl)-pentalene was prepared by Le Goff in 1962,[75] and has recently been examined by X-ray crystallography (Figure 1.6).[76]

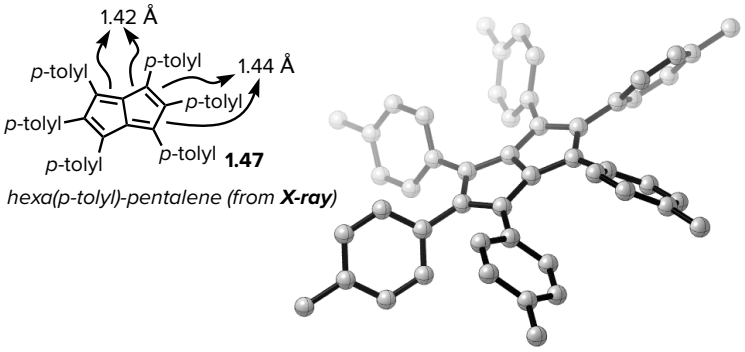


Figure 1.6: The molecular structure of hexa(*p*-tolyl)-pentalene from X-ray crystallography.[76]

Mono- (**1.48**) and bis(tricarbonyliron) (**1.49**, **1.50**) complexes of pentalene (Figure 1.7) have not yet been prepared, but they been investigated by DFT calculations, and it was proposed that they should be stable enough to be isolated.[77,78] Their lack of preparation is not necessarily an oversight, in the case of pentalene it seems there may be something special about the dinuclear complexes that have been reported (*v.i.*).

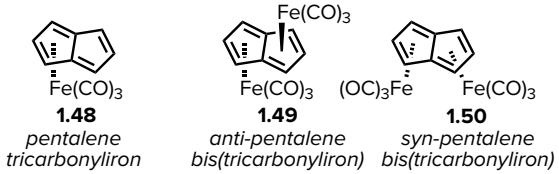
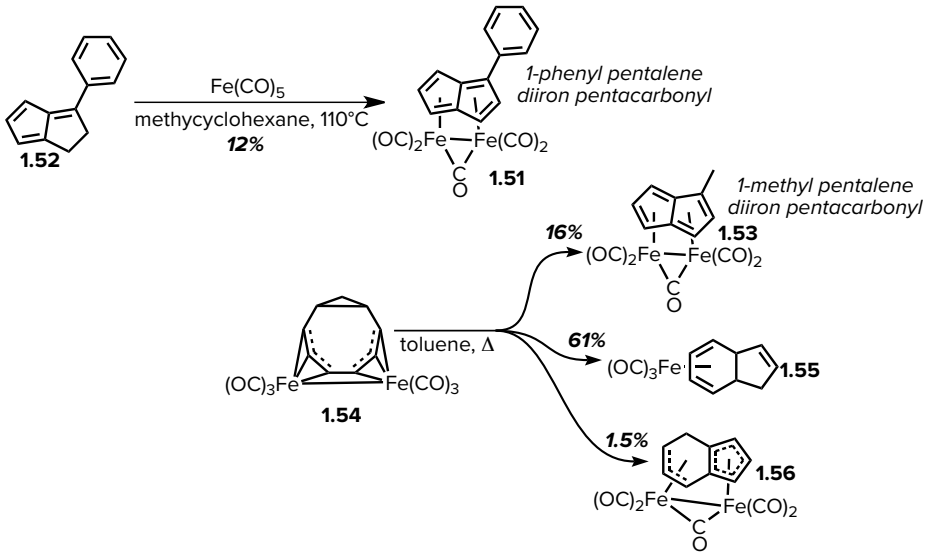


Figure 1.7: Mono- & bis(tricarbonyliron) complexes of pentalene (unreported).

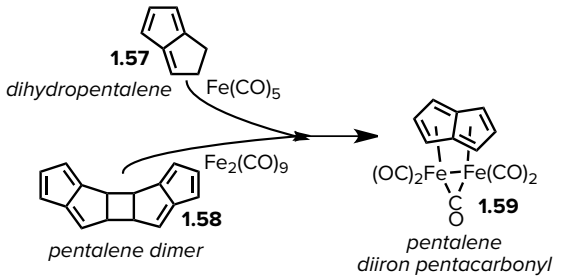
The first pentalene complex produced was not of the parent hydrocarbon, but was rather the 1-phenyl-substituted pentalene derivative, which was prepared as its diiron pentacarbonyl complex, **1.51**, by heating the substituted dihydropentalene **1.52** with iron pentacarbonyl at 110 °C for 12 h under nitrogen (Scheme 1.10, Method **B**, see page 5).[79] 1-Methyl pentalene diiron pentacarbonyl **1.53** was reported shortly after, prepared as a minor product from thermolysis of nonatetraene diiron hexacarbonyl[I] **1.54** in 16% yield (Scheme 1.10, Method **B**, see page 5).[80]



Scheme 1.10: Preparation of substituted pentalene diiron pentacarbonyls **1.51** & **1.53**. (Top: 1-phenyl pentalene,[79] bottom: 1-methyl pentalene.[80])

The diiron complex of the parent hydrocarbon was only recently reported by the $Fe(CO)_5/Fe_2(CO)_9$ mediated generation of pentalene and *in situ* complexation (Scheme 1.11, Method **B**, see page 5).[81]

[I] The nonatetraene diiron hexacarbonyl compound was not rigorously identified by Deganello and coworkers. We have tentatively assigned it here as a bis(allyl tricarbonyliron) complex by analogy with similar compounds.



Scheme 1.11: Pentalene carbonyliron complexation.[81]

Pentalene (and substituted analogues) appears to preferentially form diiron pentacarbonyl complexes upon direct complexation (Schemes 1.10–11). This mode of complexation is somewhat uncommon, as has been remarked upon by O'Hare and coworkers.[82] Curiously, the ligand appears to become somewhat *more* alternant in bond-length upon complexation when compared with the free polyene hexa(*p*-tolyl)-pentalene (Figure 1.8),[76] which is a characteristic usually associated with a lesser degree of aromaticity.[83] The diiron pentacarbonyl mode of complexation is reported in other cases where a cyclic 8π-electron system is complexed, including (cyclooctatetraene)$Fe_2(CO)_5$[84] and (cycloheptatrienide)$Fe_2(CO)_5[AsPh_4]$.[85]

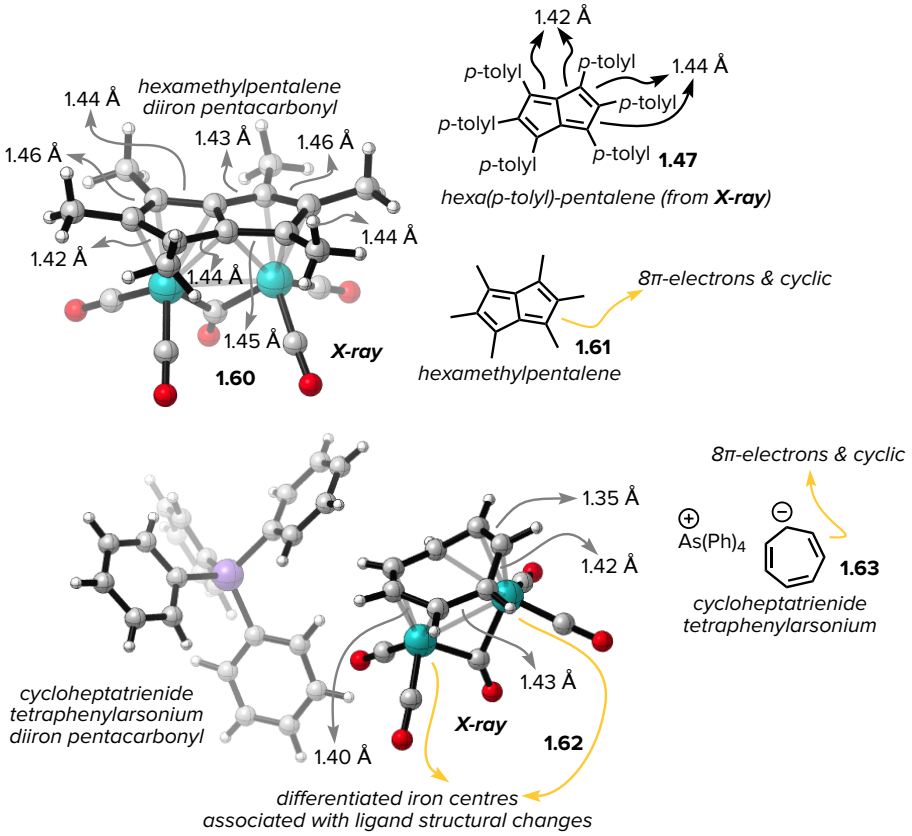


Figure 1.8: Molecular structures of hexamethylpentalene complex,[82] hexaphenylpentalene,[76] & cycloheptatrienide complex[85] by single crystal X-ray analysis.

Significant attempts have been made to access free pentalene from organometallic precursors containing pentalene as a ligand.[86] In spite of these efforts, no reports of successful isolation of the free pentalene from organometallic complexes have been made.

S-INDACENE

The indacenes are antiaromatic fused systems[J] (Figure 1.9) with 12π-electrons in a tricycle comprising a six-membered ring flanked by two five-membered rings. There are two possible configurations for such an arrangement, they are defined as *symmetrical* (called *s*-indacene, **1.19**) and *asymmetric* (called *as*-indacene, **1.64**). The asymmetric variant has been relatively little studied, and no successful synthesis of the parent *as*-indacene has been reported,[87] nor has it been generated as a tricarbonyliron complex. Symmetrical indacene has been prepared and

[J] They can be considered variously as annulene-like, expanded pentalenes, or bis-fulvenes.

partially characterised in its unsubstituted form.[73,88] The hydrocarbon has not been extensively investigated, with no reports of experimental studies since its initial preparation, and very little detail is known about its decomposition, except that it has been reported to have "*low thermal stability*."[89]

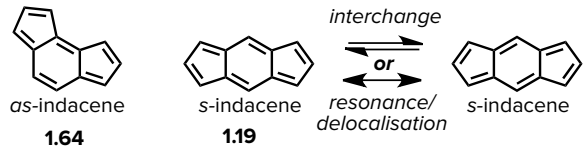


Figure 1.9: The indacene family of antiaromatic hydrocarbons.

The vague experimental information on the indacenes stands in stark contrast to the plethora of *ab initio* and density functional calculations on the family of compounds. In brief, the compounds have provoked a great deal of interest from theoreticians due to their display of *both* aromatic[90] and antiaromatic properties.[87,91-97K]

Analysis of the crystal structure of the stable derivative tetra(*t*ert-butyl) *s*-indacene[98,99] reveals that the bond lengths around the ring (Figure 1.10, C_{1-2} & C_{2-3}, etc.) are roughly equal, and thus that the π-system is delocalised. When first observed by Hafner and coworkers[99] and Dunitz and coworkers[98] this was hypothesised to be a "frozen transition state," in which the observed structure was not the 'true' ground-state. This view was clarified by follow-up calculations by Hertwig[87,100] that showed, unexpectedly, that the delocalised 12π-electron system corresponds to the likely ground-state structure.

K The trajectory of interest in the indacenes closely follows that for general interest in aromaticity. This is because the indacenes are used as one of the archetypal families of polyunsaturated hydrocarbons upon which to test new indices of aromaticity.

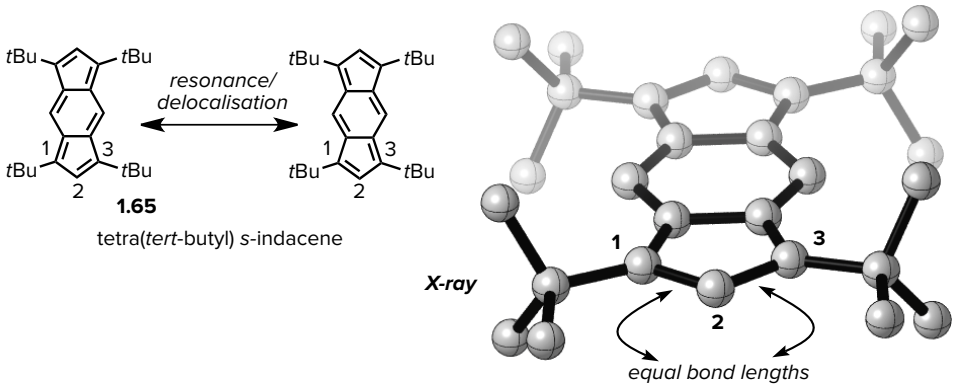


Figure 1.10: The molecular structure of tetra(*tert*-butyl) *s*-indacene. (X-ray structure determination: Hafner *et al.*[99] and Dunitz *et al.*[98])

The preparation of unsubstituted *s*-indacene tricarbonyliron complexes (Figure 1.11, **1.66**, **1.67** & **1.68**) has been modeled by density functional calculations,[101] but a successful synthesis has not been reported in the literature.

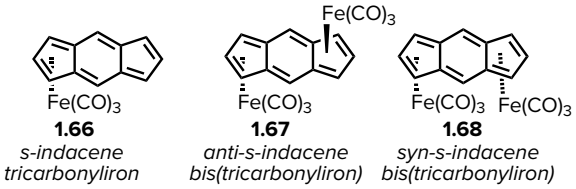
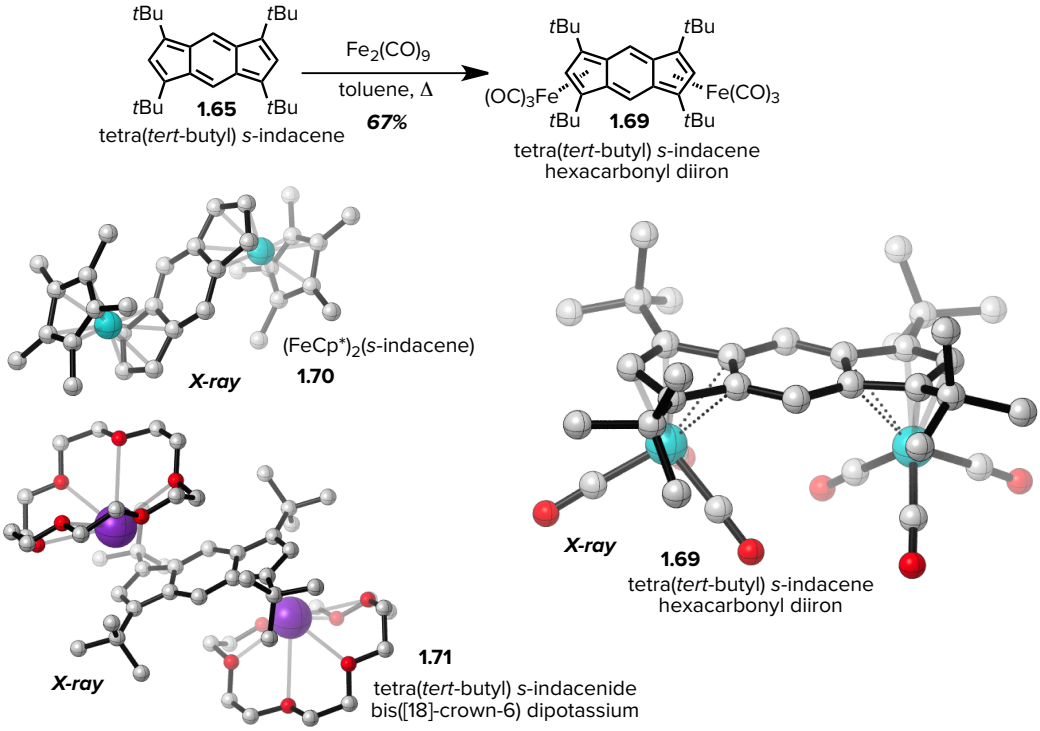


Figure 1.11: Mono- & bis(tricarbonyliron) complexes of *s*-indacene (unreported).

Only tetra-*tert*-butyl analogues of *s*-indacene tricarbonyliron complexes have been made, and were reported by O'Hare and coworkers in 1997 & 2000.[101,102] Complexation was achieved by heating the polyene to reflux in toluene with $Fe_2(CO)_9$ (Scheme 1.12, Method **A**, see page 5), affording the bis(tricarbonyliron) complex in good yield, in spite of the harsh conditions. The tricarbonyliron groups are *syn* to one another on the *s*-indacene ligand. This facial selectivity is in contrast to most indacene complex chemistry, where metal fragments are generally observed bonding *anti* to one another (e.g. **1.70** and **1.71**, Scheme 1.12). O'Hare and coworkers propose[102] that the iron groups are strongly coupled by the ligand, even though they lack direct connection, to explain the *syn*-facial selectivity.

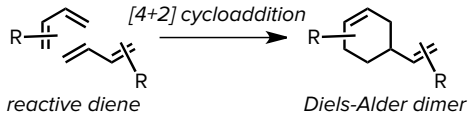


Scheme 1.12: Preparation and molecular structure of tetra-*tert*-butyl *s*-indacene hexacarbonyl diiron (X-ray: Cary *et al.*[102]), (X-ray of $(FeCp^*)_2$(*s*-indacene) by Manriquez *et al*, & X-ray of tetra(*tert*-butyl) *s*-indacenide bis([18]-crown-6) dipotassium by Cary *et al.*[103]).

If one could propose a good route to the parent *s*-indacene tricarbonyliron complex(es) (Figure 1.11), then one could hopefully prepare and study the uncomplexed parent hydrocarbon in a modern setting. This would provide experimental evidence that could be used to reinforce the many rigorous theoretical studies that have been reported.

1.3.2 Diels-Alder Dimerising Dienes

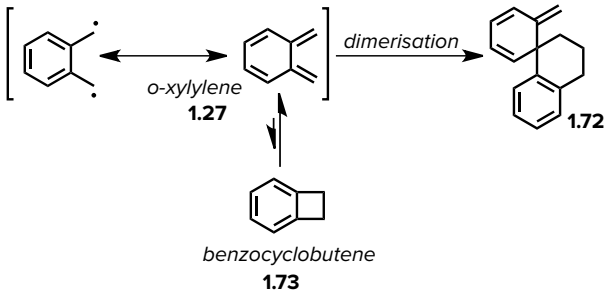
The Diels-Alder reaction is the cycloaddition of a dienophile to a diene, but in some cases the diene component is a sufficiently good dienophile that it can react with itself to form a substituted cyclohexene (Scheme 1.13). This kind of reactivity is often driven by either: (a) special stability of the Diels-Alder adduct, like the formation of aromatic rings as in the cases of *isoindene* and *o-xylylene* (see Scheme 1.14); or (b) by electronic destabilisation of the reactive diene, as it is with *cyclopentadienone* and the *2-substituted butadienes*.



Scheme 1.13: Diels-Alder dimerisation of dienes. In the case of highly reactive dienes, as discussed in this section, R is a substituent (or set of particular substituents) that makes this Diels-Alder dimerisation more favourable.

O-XYLYLENE

The formation of *o*-xylylene was inferred in 1961 from the isolation of its Diels-Alder dimers.[104,105] Even though this 1961 study did not isolate *o*-xylylene, its formation is implicit from the formation of the dimer. *o*-Xylylenes[L]—the parent hydrocarbon and the whole family of substituted derivatives—have been used extensively in organic synthesis[M] as reactive intermediates generated *in situ* as dienes in Diels-Alder reactions.[106] Their use as synthetic intermediates can be considered complementary to the use of benzyne, which is a reactive dienophile in Diels-Alder reactions.[107] The second-order rate constant for dimerisation of *o*-xylylene at 25 °C is approximately 10^4 $Lmol^{-1}s^{-1}$.[108,109] It is also possible for o-xylylene to undergo an electrocyclisation to form benzocyclobutene, **1.73**. This thermal process has been measured to have a barrier of approximately 40 kcal/mol,[110,111] and is endothermic by 13 kcal/mol.[112,113]



Scheme 1.14: The reactivity of *o*-xylylene.[108,111]

The first preparation of the parent *o*-xylylene tricarbonyliron complex **1.74** was reported by Roth and coworkers in 1967[114,115] The Roth synthesis of *o*-xylylene tricarbonyliron used the method based on the successful synthesis of cyclobutadiene tricarbonyliron **1.10** by Pettit and coworkers[54] from a 1,4-dihalo 2-butene system, which could be directly converted into the diene-iron complex

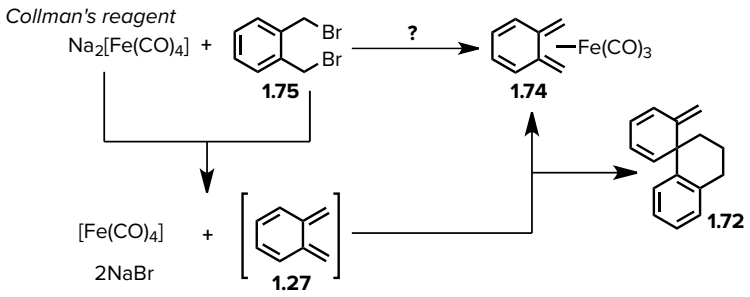
---

[L] Also called *o*-quinodimethanes.

[M] Their use is often limited to *intra*molecular Diels-Alder reactions due to their tendency to dimerise in *inter*molecular reactions.

(Scheme 1.7, Method **B**, see page 5). Unfortunately, under conditions similar to the Pettit procedure (which gives a greater than 40% yield of the cyclobutadiene complex **1.10**), the complexation with $Fe_2(CO)_9$ was optimised to give 4–6% of the *o*-xylylene complex **1.74**.

In 1991 Kerber & Ribakove[33] investigated and reviewed the methods for preparing *o*-xylylene in order to determine the mechanism of complexation. The successful methods were derivative of the one reported by Roth & Meier;[114] they all used 1,2-bis(bromomethyl)benzene **1.75** as a proto-diene, with differentiation in the iron source. Originally the reaction was presumed to operate in a similar manner to cyclobutadiene complexation as described by Pettit,[54] who said, "*It is not considered necessary that a free cyclobutadiene molecule appear as an intermediate in the reaction*," but—as discussed by Kerber & Ribakove—the bulk of the evidence is in favour of such a stepwise mechanism (Scheme 1.15), involving the release of the tetraene **1.27** into solution (Method **A**, see page 5)[N]. This insight allowed them to strategically use Collman's reagent (an anionic source of carbonyliron), in conjunction with diiron nonacarbonyl to increase complexation yields from a paltry 10% up to yields of 30–35%.[33]



Scheme 1.15: The complexation of *o*-xylylene.[33]

Curiously, these tricarbonyliron complexes appear not to have been used as a means to readily access *o*-xylylene in solution; this is in stark contrast to cyclobutadiene tricarbonyliron, one of the first uses of which was as a controlled source of cyclobutadiene.[11] The lack of practical synthetic use of *o*-xylylene tricarbonyliron as a source for *o*-xylylene is probably due to the consistently low

[N] Defining this approach is complicated, as it is difficult to determine mechanistically whether a given reaction is generating a polyene *in situ*, making it Method **A**, or whether it is directly forming the complex *via* some kind of organometallic intermediate, which would clearly be Method **B**.

yields, or the more exotic iron sources[116] required for even moderate yields of 25–35%.

The molecular structure of (*o*-xylylene)tricarbonyliron was determined by single crystal X-ray analysis (Figure 1.12).[117] Detailed information on the structure was useful to determine the degree of bond alternation in the ring, which showed bond lengths in between those of benzene and those of butadiene.

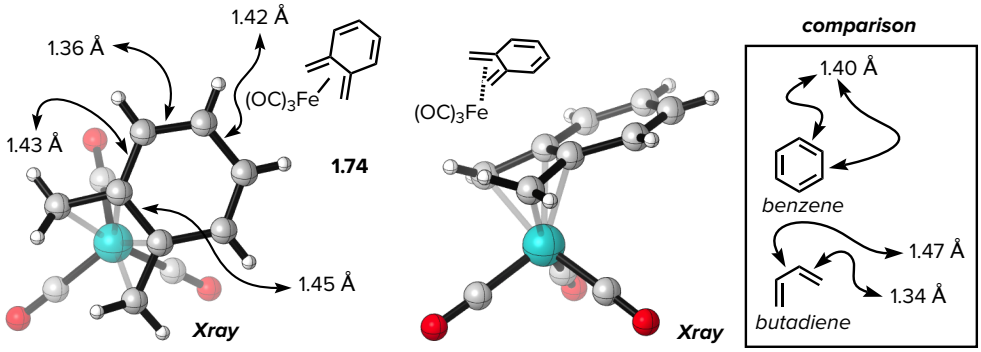
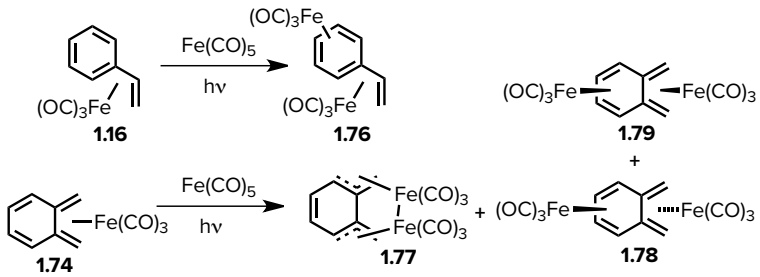


Figure 1.12: The molecular structure of tricarbonyliron(*o*-xylylene) from single crystal X-ray analysis.[117]

(*o*-Xylylene)tricarbonyliron has an *s-cis* 1,3-butadiene that remains uncomplexed, and so the logical extension of *o*-xylylene complex chemistry is to diiron complexes. The method developed for the double $Fe(CO)_3$-complexation of styrene[o] was extended to the coordination chemistry of *o*-xylylene.[29] The first fully characterised diiron complexes of *o*-xylylene were reported by Victor and coworkers in 1974 (Scheme 1.16).[118]

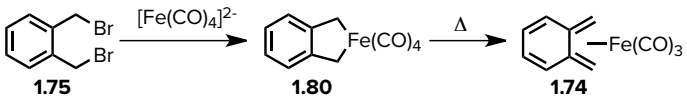


Scheme 1.16: The photochemical generation of bimetallic tricarbonyliron complexes.[29,118]

One can imagine an intermediate complex towards *o*-xylylene tricarbonyliron that retains the aromaticity of the 6π system. Such intermediates were reported by

[o] Which, with a formula of C_8H_8, is isomeric with *o*-xylylene.

Ullah and coworkers[119,120] (Scheme 1.17). These intermediates were subsequently converted into tricarbonyliron complexes of *o*-xylylenes (Method **B**/**C**, see page 5).[119] Girard and coworkers attempted to reproduce these results,[121] but did not isolate the reported novel intermediates or products. Complexes where *o*-xylylene behaves as a two- electron σ-donor ligand *via* the exocyclic methylene groups (as in complex **1.80**) occur mainly with metal atoms in medium to high oxidation states.[122] However, Tantillo and coworkers do calculate a reaction pathway that could potentially involve intermediates of this type, and they are predicted to be at least metastable (see *o,p'*-dibenzene for further discussion of this mechanism with a similar ferracycle, page 35).[123]

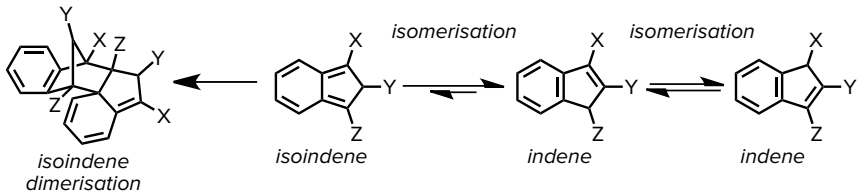


Scheme 1.17: *o*-Dimethylenebenzene η^2-Irontetracarbonyl intermediates (Ullah *et al.* 1984).

As *o*-xylylene is one of the most studied families of tricarbonyliron-diene complexes, many substituted complexes have been prepared.[116,121,124-129]

ISOINDENE

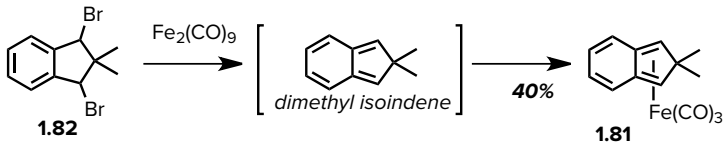
Isoindene is similar to several of the unstable compounds described here, most importantly for its reactivity is its close relationship to *o*-xylylene **1.27**, where the exocyclic diene is cyclised by incorporation of methylene. The main pathway for the decomposition of naked isoindene is its isomerisation to indene (Scheme 1.18). In fact, the isomerisation of indene to isoindene is a method that has been used to determine aromatic stabilisation energies (ASE).[130,131P] Substituted isoindenes can also decompose by Diels-Alder dimerisation (Scheme 1.18).



Scheme 1.18: Decomposition reactions of isoindene. Dimerisation versus isomerisation.

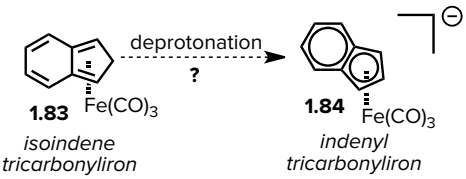
[P] It is not precisely indene-isoindene isomerisation that measures ASE, but the isomerisation of a cyclic pentadiene attached to an annulene. See Wannere *et al.* 2003 for further explanation and Herges *et al.* 2003 for an example.

Tricarbonyliron has been used to stabilise a substituted isoindene, as reported by Roth & Meier[114] alongside the first preparation *o*-xylylene (Scheme 1.19, Method **A**/**B**, see page 5). The prepared isoindene **1.81** was 2,2-dimethyl substituted so that it could not undergo the 1,5-hydrogen shifts associated with its rapid isomerisation to indene. 2,2-Dimethyl isoindene behaves more like a substituted *o*-xylylene than does the parent isoindene. Specifically, the compound undergoes Diels-Alder reactions.



Scheme 1.19: The preparation of 2,2-dimethyl isoindene tricarbonyliron.[114]

DFT computational studies have been done on the structure of the parent isoindene-tricarbonyliron complex **1.83**,[132] but its practical preparation is presumably precluded by the stability of the indenyl-tricarbonyliron complex **1.84** (Scheme 1.20). Indeed, attempts to prepare isoindene tricarbonyliron were reported to be unsuccessful.[33]



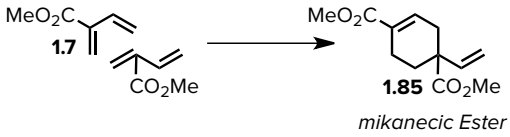
Scheme 1.20: The unreported isoindene tricarbonyliron complex.

2-SUBSTITUTED BUTADIENES

2-Substituted butadienes are one of the most important classes of highly reactive polyolefins that have been stabilised by the tricarbonyliron group due to the value in synthesis of the derived compounds, rather than merely as organometallic curiosities.[Q]

The instability of 2-acyl butadienes towards Diels-Alder dimerisation has been known for a long time, dating back to investigations in 1901 on the preparation and origin of mikanecic ester **1.85** (Scheme 1.21).[133]

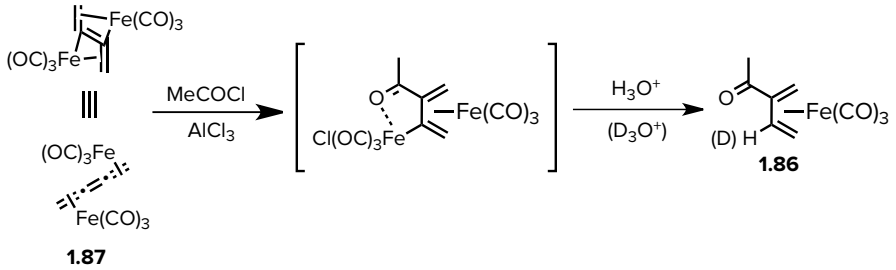
[Q] See Chapters 3 & 4 for more discussion on the reactions and uses of 2-substituted butadienes.



Scheme 1.21: The dimerisation of 2-carbomethoxybutadiene to form mikanecic ester.[133,134]

The exceptional reactivity of the unstable 2-substituted butadienes remained a source of ongoing research for the rest of the century.[135,136] Not all 2-substituted butadienes are inherently unstable (e.g. 2-methyl-1,3-butadiene, isoprene, is a stable, commercially available liquid); in general it appears that, for instability towards dimerisation, the diene 2-substituent must be a conjugating group[137,138] and/or electron withdrawing[139] as well as lacking in steric encumbrance at the reactive site (as necessitated by all Diels-Alder reactions).

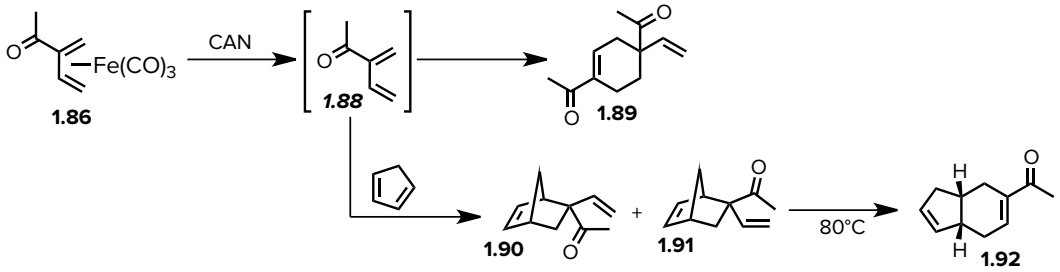
In 1981, Brion and coworkers reported[140] the preparation of 2-acetyl-1,3-butadienetricarbonyliron complex **1.86** resulting from the Lewis acid mediated decomposition of butatriene hexacarbonyldiiron[R] **1.87** (Scheme 1.22, Method **C**, see page 5).



Scheme 1.22: The preparation of 2-acetylbutadiene tricarbonyliron **1.86**.

The mechanism for the formation of the 2-acyl butadiene complex was unclear from their investigations, but was presumed to involve initial electrophilic addition in a Friedel-Crafts type manner, which would desymmetrise the molecule and lead to the migration of one of the two $Fe(CO)_3$ groups from the starting material into a stable η^4-butadiene complex while the other is oxidised to be a labile Fe^{2+} species, which could be proto-demetalated, or deutero-demetalated depending on the medium (i.e. H_2O or D_2O).

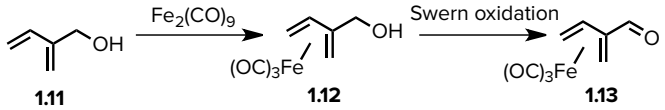
[R] Which is itself a tricarbonyliron complex of a fundamental class of polyenes.



Scheme 1.23: The release and reactivity of free 2-acetylbutadiene **1.88**.[140]

After preparation and isolation/purification of $Fe(CO)_3$ complex **1.86**, the highly reactive ligand **1.88** could be oxidatively released from the tricarbonyliron complex using CAN (Scheme 1.23). Attempts using standard conditions to isolate the naked ligand **1.88** led exclusively to isolation of the Diels-Alder dimer **1.89** (Scheme 1.23). The diene could also be reacted selectively in a Diels-Alder reaction with cyclopentadiene to give **1.90** & **1.91** (Scheme 1.23).

This work was expanded later by Martina, Brion, and co-authors in a series of papers that made various acyl derivatives of **1.86**,[10,141,142] including the 2-keto-, ester-, and aldehyde-derivatives (Method **C**, see page 5), and culminated in a 1986 paper entitled *Stabilisation de molecules hyperactives par complexation* on the practical preparation and reactivity of (2-formyl butadiene)tricarbonyliron, **1.13**.[143]



Scheme 1.24: The preparation of (2-formylbutadiene)$Fe(CO)_3$.[143]

Other classes of unstable acyclic 2-substituted butadienes that have been stabilised by the tricarbonyliron group are 2-chloro-,[144-146] 2-bromo-,[147] 2-sulfoxidyl-, 2-sulfonyl-, 2-cyano-,[146] and 2-stannylbutadiene[12] (Figure 1.13).

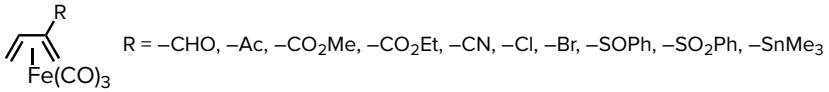
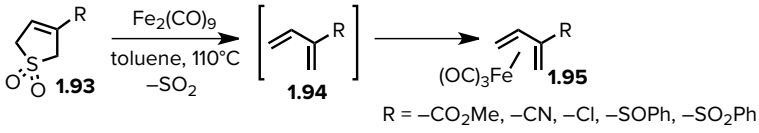


Figure 1.13: The unstable 2-substituted butadienes that have been made as their stabilised tricarbonyliron complexes.

These kinds of complexes (Figure 1.13) have been explored extensively, with the cited examples being only a select few. The synthesis of 2-substituted butadiene complexes by Yeh and coworkers[146] is particularly worthy of note, as it describes a general route to the complexes from relatively simple precursors (Method **A**,

Scheme 1.25, see page 5); although as sulfolene is itself a diene protecting group[148] there is some inelegance in exchanging one protecting group for another.



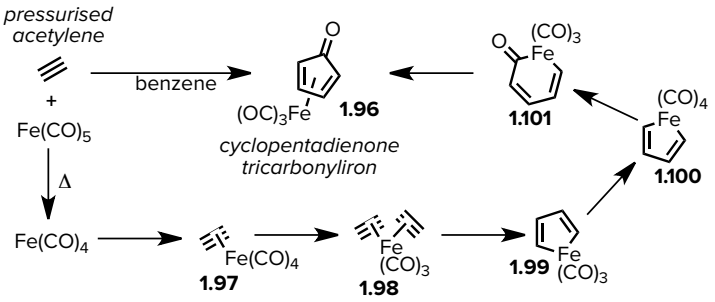
Scheme 1.25: The preparation of some 2-substituted butadiene complexes.[146]

The reactivity and instability of 2-substituted butadienes will be explored at some length in Chapter 3 (*v.i.*). 2-Halobutadiene tricarbonyliron complexes are particularly interesting, and they will be discussed in Chapter 4 (*v.i.*).

CYCLOPENTADIENONE

The family of cyclopentadienones are well known for their exceptionally high reactivity as dienes in Diels-Alder reactions.[149,150] Highly substituted cyclopentadienones can be stable enough to be commercially available (as in the case of the tetrachloro- and tetraphenyl- derivatives), but the unsubstituted case is substantially destabilised by an antiaromatic canonical structure.[151][s]

The tricarbonyliron complex of cyclopentadienone was reported Weiss and co-authors in 1960. The complex was prepared by a Pauson-Khand-like formal [2+2+1] cycloaddition between acetylene and a molecule of CO (Scheme 1.26, Method **B**, see page 5).[152-154]

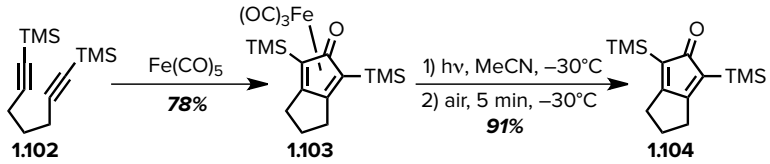


Scheme 1.26: The preparation of cyclopentadienone-tricarbonyliron (Weiss *et al.* 1960[152]), and proposed mechanistic pathway.[155]

[s] There is some dispute over the antiaromaticity of cyclopentadienone, *cf.* tropone. The latter has recently been measured to have *less* aromatic character than cycloheptatriene (Williams *et al.* 2012). By analogy, cyclopentadienone could have less antiaromatic character than cyclopentadiene. This author is unaware of any related investigations, but the high reactivity of cyclopentadiene could be in some part due to 4π 'antiaromatic character.'

The reaction proceeds by ligand substitution around $Fe(CO)_5$ with two molecules of acetylene (**1.98**), which then undergo an oxidative cyclisation to give ferracyclopentadiene **1.99**. Subsequent α-insertion of carbon monoxide, carbonyl association, and reductive elimination give the η^4-polyene complex **1.96** (Scheme 1.26).

Knölker and coworkers have substantially expanded the usefulness of the carbonyliron mediated [2+2+1] synthesis of cyclopentadienone complexes by developing methods for the efficient preparation of substituted cyclopentadienones, like **1.103** (Scheme 1.27).[156,157]



Scheme 1.27: The [2+2+1] preparation of substituted cyclopentadienone tricarbonyliron complexes.[24,155]

Knölker and coworkers have also designed new demetalation methods that allow access to the cyclopentadienone ligands without oxidative damage.[24,51] The introduction of good [2+2+1] cycloisomerisations has allowed carbonyliron(cyclopentadienone) complexes to be used as Shvo catalysts in catalytic hydrogen transfer reactions.[158,159]

1.3.3 Miscellaneous Polyenes

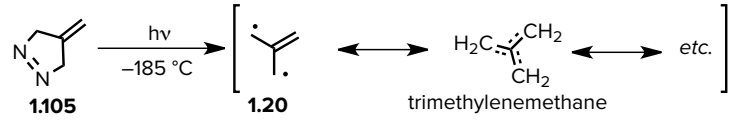
The miscellaneous polyenes comprise trimethylenemethane and *p*-xylylene. *p*-Xylylene can be considered as a dimer of trimethylenemethane, both in terms of connectivity and their bifurcated π-electron systems (Figure 1.14).

Figure 1.14: *Other* polyenes that have been stabilised by coordination of the tricarbonyliron group.

TRIMETHYLENEMETHANE

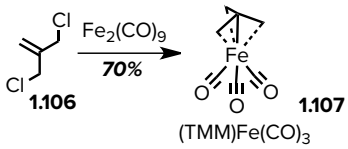
The chemistry of tricarbonyliron complexes is dominated by *s-cis* 1,3-butadiene, and its substituted and cyclic variants. But the tricarbonyliron group is not constrained to a Kekuléan worldview of only complexing to puritanical conjugated butadienes. Trimethylenemethane (TMM) is an example of a compound which

cannot be drawn as alternating single and double bonds—called a non-Kekulé molecule—but instead exists as a triplet biradical in the ground state (Scheme 1.28).[160] As a result of its inability to exist in an *all-paired up* ground state, the molecule is unstable and very reactive.[161T] Trimethylenemethane was the subject of theoretical interest for a long time[162] prior to its first observation as a hydrocarbon in 1966 by the elimination of dinitrogen from 4-methylene-Δ-pyrazoline at −185 °C (Scheme 1.28).[163,164]



Scheme 1.28: Trimethylenemethane, and it's low temperature preparation.[163]

The tricarbonyliron complex of trimethylenemethane was prepared the same year as the parent hydrocarbon was first observed.[165,166] The synthesis of trimethylenemethane was a targeted approach with an eye towards Nicholson's prediction[19] that: "the ability of unsaturated hydrocarbons to form diene-iron carbonyl complexes has been correlated with the expected loss of delocalization attendant on complexation." In terms of the electronics of the system (as it was understood at the time), trimethylenemethane would be similar to cyclobutadiene.[53] On this basis the preparation was approached in the same way as cyclobutadiene, and diiron nonacarbonyl was stirred with the dichloro-isobutene precursor **1.106** (Scheme 1.29, Method **B**, see page 5). The preparation was similarly successful to that of cyclobutadiene tricarbonyliron,[56] eventually reaching yields as high as 70%.[166] Further investigation into (TMM)Fe(CO)$_3$ led to several similar routes to its preparation.[166]



Scheme 1.29: Preparation of (TMM)Fe(CO)$_3$.[166]

The curious molecular structure of trimethylenemethane-tricarbonyliron (**1.107**, Figure 1.15) has been the subject of discussion and scrutiny since it was first proposed.[165] This interest continued through its proof by single-crystal X-ray diffraction,[167,168] and is still ongoing.[169,170] The structure of the

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[T] Curiously, trimethylenemethane is an isomer of butadiene (C_4H_6).

trimethylenemethane complex differs from other tricarbonyliron-polyene compounds not just in terms of its umbrella-shaped connectivity (Figure 1.15),[170] but also in the differentiated nature of the Fe–C bonding.[169]

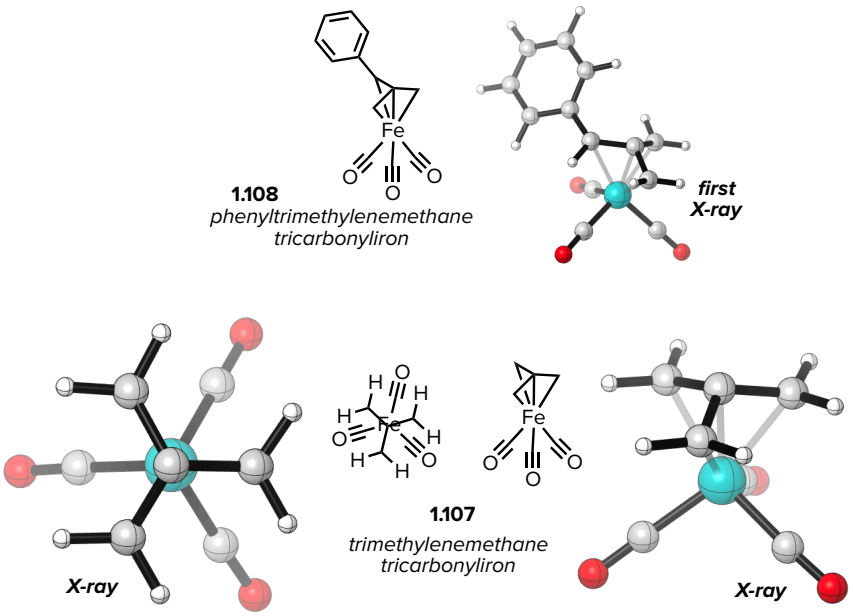


Figure 1.15: The structure of trimethylenemethane tricarbonyliron (top: Churchill *et al.* 1969,[167] bottom: Farrugia *et al.* 2006[169]).

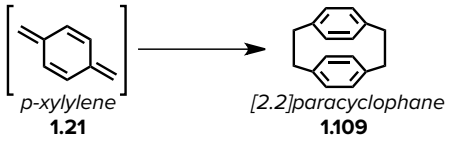
Trimethylenemethane complexes have been used in synthesis, an example being the formation of 2-substuted-1,3-butadiene complexes (*v.s.*).[141]

The *trimethylenemethane-type* (TMM-type) of coordination is not limited to molecules containing strictly trimethylenemethane moieties. Branched hydrocarbons with apparently stable bonds can also be complexed in this manner, even when there is a locked *s-cis* diene unit nearby (see the fulvenoids, page 36), the only requirement[u] is four sp^2 carbons in a branched arrangement.

P-XYLYLENE

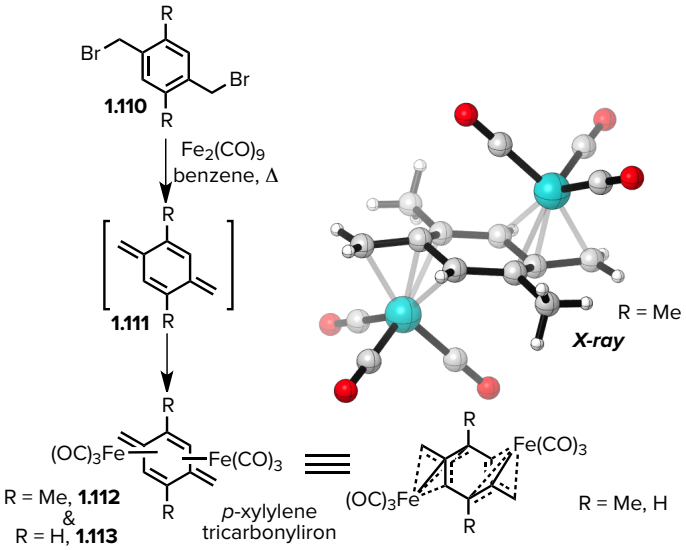
p-Xylylene is far less well-known and studied in organic synthesis than its *ortho* counterpart, but their similarity does extend to their high reactivity, where *p*-xylylene is perhaps best known for its ability to efficiently dimerise to give [2.2]paracyclophane (Scheme 1.30).[171]

[u] It is at least the only requirement that we are aware of.



Scheme 1.30: The synthetically useful dimerisation of *p*-xylylene.[171]

The bis(tricarbonyliron)-*p*-xylylene was prepared in 1.1% yield by heating 1,4-di(bromomethyl)benzene with diiron nonacarbonyl in benzene by Koray and coworkers in 1985 (Scheme 1.31, Method **B**, see page 5).[172] In contrast to the tricarbonyliron complexes of *o*-xylylene that have been prepared, *p*-xylylene can be made *only* as a dimetallic complex, and is coordinated as a bis-trimethylenemethane complex.



Scheme 1.31: The complexation of *p*-xylylene (X-ray: Koray *et al.*[172]).

The coordination mode differs because *p*-xylylene lacks any s-cis butadiene that can be complexed while leaving the rest of the molecule in a Kekulé state. The *p*-xylylene hexacarbonyldiiron complex was further investigated experimentally and theoretically.[173,174]

1.3.4 Benzene Cycloadducts

7-Norbornadienone and *o,p'*-dibenzene can be considered as the products of cycloaddition of benzene with carbon monoxide and benzene respectively (Figure 1.16). The high stability of benzene, and its accessibility by cycloreversion, puts these polyenes firmly on the side of the unstable.

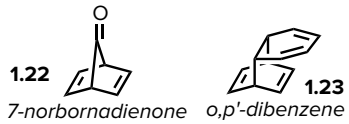
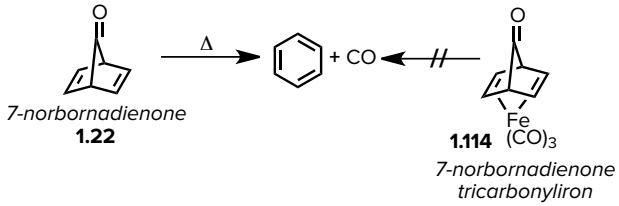


Figure 1.16: Formal cycloadducts of benzene that have been stabilised by coordination with the tricarbonyliron moiety.

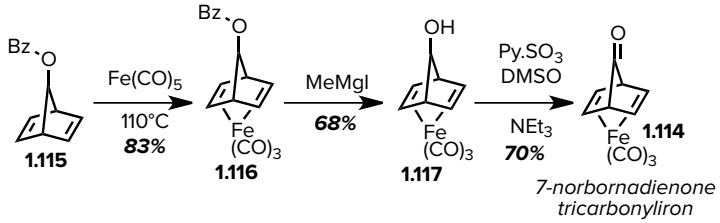
NORBORNADIENONE

The types of unwanted reactivity that can be ameliorated by the complexation of a tricarbonyliron group are not limited to cycloaddition or radical reactions, 7-norbornadienone is unstable towards a fast thermally-allowed[175] disrotatory cheletropic elimination, leading to benzene and carbon monoxide(Scheme 1.32). The compound was hypothesized,[176,177] but the only norbornadienones that could be isolated were benzo-substituted until Landesberg & Sieczkowski were able to successfully prepare the tricarbonyliron complex of 7-norbornadienone.[44,178]



Scheme 1.32: Norbornadienone tricarbonyliron stabilisation.[179]

The synthesis of tricarbonyl(7-norbornadienone)iron was achieved by first complexation of benzoyloxy precursor **1.115** with $Fe(CO)_5$ at 110°C (Scheme 1.33, Method **C**, see page 5), followed by cleavage of the ester, and subsequent Parikh-Doering oxidation ($Py.SO_3$, DMSO, NEt_3) of the secondary alcohol.[178,179] Samples of the purified tricarbonyliron complex **1.114** slowly decomposed at room temperature, which gives some indication of the instability which is being held at bay by the complexation (cold samples could be kept for years without degradation).



Scheme 1.33: Norbornadienone tricarbonyliron complexation.[179]

Norbornadienone is different than most of the tricarbonyliron-dienes mentioned here, because rather than a conjugated *s-cis*–1,3-butadiene, the complexed diene is

non-conjugated. The molecular structure of (7-norbornadienone)tricarbonyliron has not been determined by X-ray crystallography, but similar compounds have been observed. Shown in Figure 1.17 are the molecular structures of the bis-η^2 tricarbonyliron iron complexes of compounds closely related to (7-norbornadienone)tricarbonyliron.[180,181v]

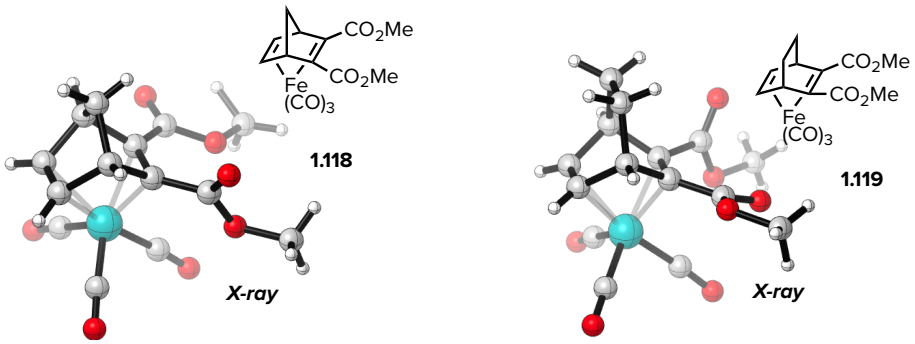
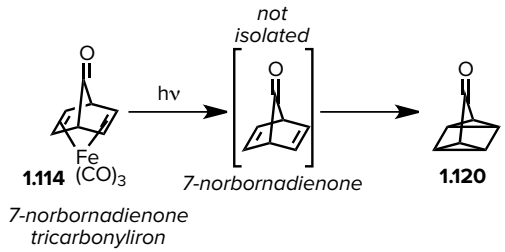


Figure 1.17: Bis-η^2 tricarbonyliron iron complexes of [2.2.1] and [2.2.2] dienes, by X-ray crystallographic analysis (Left: Watson *et al.*,[180] right: Irngartinger *et al.*[181]).

The first evidence for the uncomplexed 7-norbornadienone was obtained from photolysis of the tricarbonyliron complex **1.114**.[182 w] The evidence for the free 7-norbornadienone was the isolation of [2+2] cycloadduct **1.120** (Scheme 1.34). It was not until 1985 that direct spectroscopic evidence for free 7-norbornadienone was obtained by photolysis at 77 K.[183]



Scheme 1.34: Evidence for 7-norbornadienone.[44]

Pericyclic reactions of tricarbonyliron complexed η^4-polyenes are known (see discussion of cyclononatetraene, page 42), and so it was not immediately obvious that the tricarbonyliron group would be sufficiently stabilising to halt the

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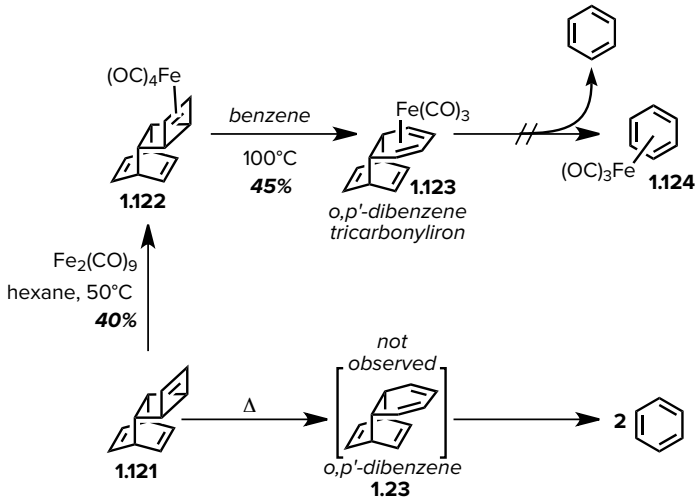
v Almost all tricarbonyliron complexes (that are stable and long-lived) can be classified as either *s-cis butadiene-*, *trimethylenemethane-*, or *bis(η^2-olefin)*-type complexes.

w Photochemical decomplexation of tricarbonyliron was known prior to this work (see Day and coworkers).

cheletropic elimination of CO. This is discussed to some extent by Grimme & Schneider[184] in their report on the synthesis of *o,p'*-dibenzene (*v.i.*).

O,P'-DIBENZENE

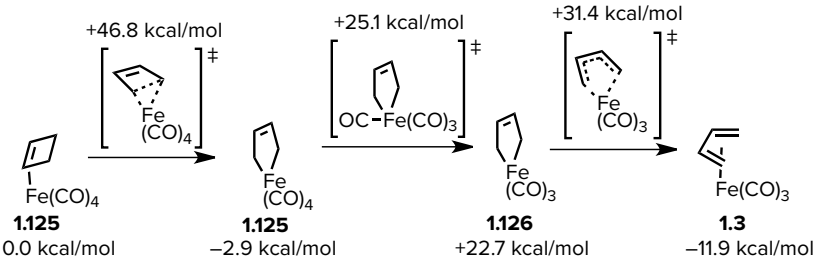
o,p'-Dibenzene is formally the [4+2] cycloadduct of two molecules of benzene, hence the instability is obvious, especially because the cycloreversion[185] of *o,p'*-dibenzene[186] to benzene is thermally allowed.[187] *o,p'*-Dibenzene was prepared by Grimme and coworkers from tetracyclic triene **1.121** (Scheme 1.35), by first generating tetracarbonyliron cyclobutene complex **1.122** (Method **C**, see page 5). This complex was converted to tricarbonyliron dibenzene **1.123** by heating in benzene; the process presumably proceeds by an iron-bound electrocyclic ring opening.[184]



Scheme 1.35: The tricarbonyliron complexation and stability of *o,p'*-dibenzene.[184]

Attempts to liberate *o,p'*-dibenzene from its tricarbonyliron complex, **1.123**, by the use of CAN led exclusively to the isolation of benzene.[184]

Tantillo and coworkers were curious about the mechanism of the metal-mediated 4π-electrocyclic ring-opening (**1.122**→**1.123**), and so investigated the possible pathways computationally with hybrid HF-DFT calculations (Scheme 1.36).[123] Although a concerted pericyclic pathway for the ring opening was possible, it was calculated to be significantly less favourable than one going *via* a σ-bound irontetracarbonyl **1.125**, and elimination of the ferracycle to give the tricarbonyliron-bound diene **1.3**.



Scheme 1.36: Calculated (hybrid HF-DFT) carbonyliron mediated 4π ring-opening (Tantillo *et al.* 2001[123]).

1.3.5 Fulvenoids

The fulvenoids have fundamental interest as one of the possible families of cross-conjugated isomers of cyclic aromatic (or antiaromatic) compounds (Figure 1.18). Pentafulvene is a highly reactive isomer of benzene, isobenzofulvene is a cross-conjugated isomer of naphthalene, and heptafulvene is isomeric with [8]annulene.[73] In general they are unstable towards dimerisation and polymerisation.

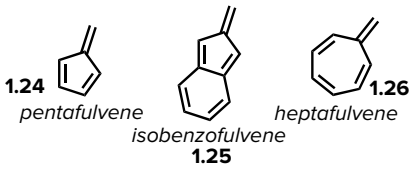
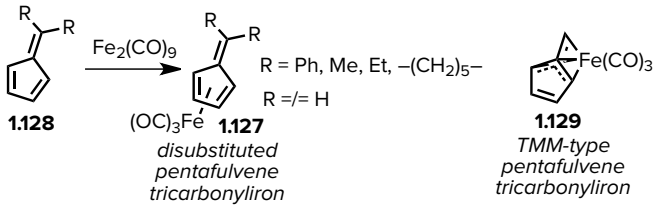


Figure 1.18: Unstable fulvenoids that have been stabilised by coordination of the tricarbonyliron moiety.

PENTAFULVENE

The fulvenes were prepared for the first time in 1900 by Thiele.[188] He also reported the preparation of unsubstituted pentafulvene **1.24**, noting only that it decomposed before it could be isolated or characterised.[189] It was not until over five decades later that pentafulvene could be fully characterised.[190,191] Tricarbonyliron complexes of pentafulvene have been made, but only of ω,ω-substituted[x] analogues (**1.127**, i.e. complexes of stable variants), especially the diphenyl derivative (Scheme 1.37).[192,193] Disubstituted pentafulvene-tricarbonyliron complexes were prepared by simply reacting the polyene with $Fe_2(CO)_9$ (Method **A**, see page 5).[194]

[x] Defined as disubstituted at the methylene position, or *6,6*.

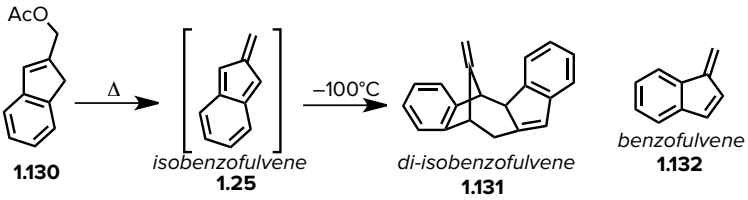


Scheme 1.37: Pentafulvene-tricarbonyliron complexes.[192]

Density functional calculations[195] and theoretical studies[21] have been done on the potential stability of the unreported parent pentafulvene-tricarbonyliron complex. No studies have been done on the potential TMM-type complexation (**1.129**, Scheme 1.37) of pentafulvene **1.24**, which is curious based on the observed stability of these kinds of tricarbonyliron complexes with other fulvenoid ligands (*v.i.*).

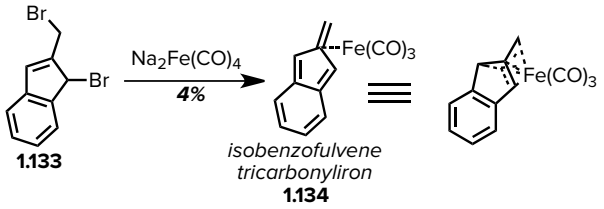
ISOBENZOFULVENE

Isobenzofulvene is one of the two possible C_4H_2 *benzannulated* pentafulvenes. While its isomer, benzofulvene (**1.132**),[196,197] is more stable than the parent pentafulvene, isobenzofulvene **1.25** is dramatically destabilised (Scheme 1.38),[198,199] with attempts to isolate the parent hydrocarbon leading to dimerisation, polymerisation, and frustration.[200,201]



Scheme 1.38: The stability of the benzofulvenes.[197,200]

Isobenzofulvene also contains the *o*-xylylene moiety, another frequently unstable skeleton which can be stabilised by tricarbonyliron complexation (as discussed in section 1.3.2, page 21). Isobenzofulvene-tricarbonyliron (**1.134**) was prepared by mixing Collman's reagent[30] with brominated hydrocarbon **1.133** (Method **B**, see page 5), and was isolated in a 4% yield (Scheme 1.39).[202] The use of Collman's reagent to eliminate bromine and concomitantly complex the polyene is unsurprising given the reagent's successful application to the *o*-xylylene family of polyenes (*v.s.*).[116]

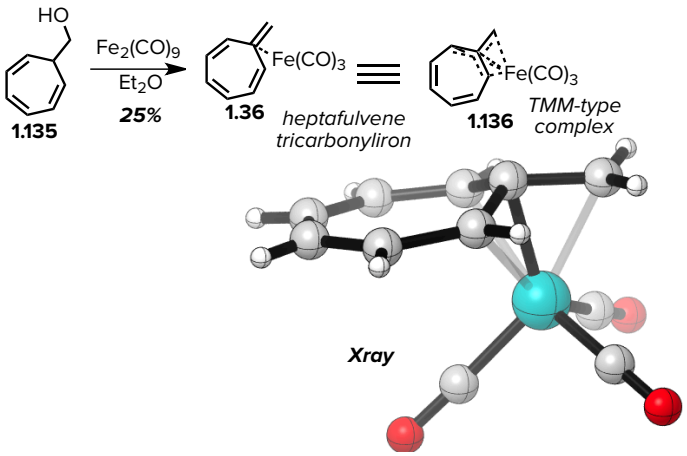


Scheme 1.39: Isobenzofulvene-tricarbonyliron preparation.[202]

No single crystal X-ray diffraction structure was obtained for the isolated isobenzofulvene-tricarbonyliron complex, but the near equivalency of vicinal coupling constants in the six-membered ring, obtained from ^{1}H NMR spectroscopic studies,[202] shows that there of the that there is significant bond-delocalisation,[203] which implies some degree of aromatisation. The selectivity for TMM-type complexation in the observed product is unsurprising given the resultant regeneration of aromaticity in the six-membered ring fused to the 'pentafulvene-unit' due to the coordination of the C_4 fragment.

HEPTAFULVENE

Heptafulvene was prepared and characterised as a dilute solution in propane several years before its complexation with tricarbonyliron.[204,205] The parent hydrocarbon was reported to polymerise upon concentration of a dilute solution, even at −60 °C, and so was a logical target for tricarbonyliron stabilisation.[206]

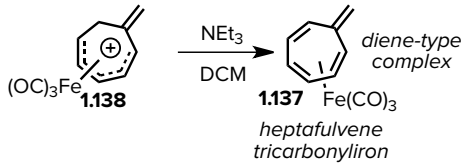


Scheme 1.40: Heptafulvene complexation and molecular structure from X-ray crystallographic analysis (X-ray: Churchill *et al.*[207]).

Heptafulvene-tricarbonyliron **1.136** was first prepared by elimination of water from 7-hydroxymethyl cycloheptatriene **1.135** with diiron nonacarbonyl (Scheme 1.40, Method **B**, see page 5).[208] Like isobenzofulvene, heptafulvene has a cross-conjugated polyene ring system, and thus can form a TMM-type complex with

tricarbonyliron. The formation of a TMM-type complex locks the tricarbonyliron in position, even when heated to temperatures that results in bond shift-isomerisation with similar 7-membered ring complexes.[209]

Shortly after its initial preparation, an isomeric form of heptafulvene tricarbonyliron, **1.137**, was reported (Scheme 1.41), which has tricarbonyliron coordinated to an *s-cis* butadiene unit inside the ring (Method **C**, see page 5).[210] Substituted variants of this complex were later investigated in more detail by Johnson and coworkers.[211]



Scheme 1.41: An alternative heptafulvene complexation.[211]

1.3.6 Polyenes Prone to Isomerisation

Tricarbonyliron complexes can be made of polyenes that tend to isomerise in their naked form, trapping their pre-isomerisation structure as a complex. Cyclohexadienone and hydroxybutadiene tend to undergo very favourable tautomerisations to form phenol or methyl vinyl ketone. Homopentalene and *Z,Z,Z,Z*-cyclononatetraene isomerise *via* rapid unimolecular reactions to form more stable compounds (Figure 1.19).

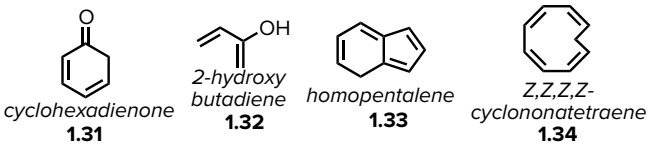


Figure 1.19: Polyenes prone to isomerisation that have been stabilised by coordination of the tricarbonyliron moiety.

CYCLOHEXADIENONE

Phenol is often used as the classic example in teaching keto-enol tautomerisation where the *enol* form is more stable than the *keto* form(Figure 1.20).[212] The stability of the enol form is due to the formation of the aromatic ring, and drives the equilibrium such that only 1 out of 10^{13} molecules is in the keto form.[213,214] In 1964, Birch and coworkers were the first to report the trapping of the tautomer of phenol as its tricarbonyliron complex.[215,216]

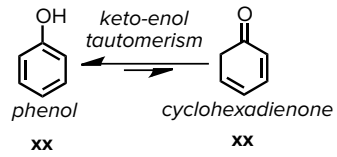
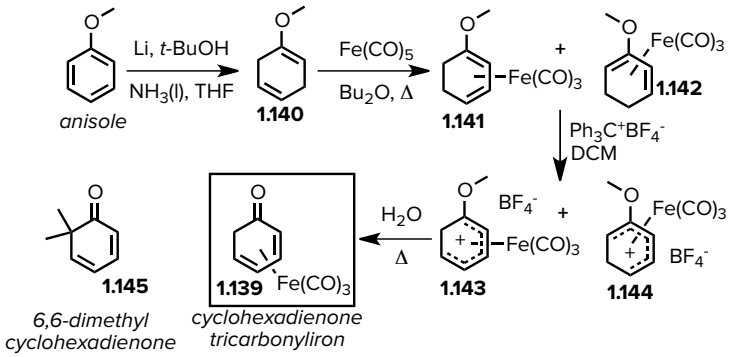


Figure 1.20: The keto-enol equilibrium for phenol lies firmly (by *thirteen* orders of magnitude) with the enol form.

Synthesis of complex **1.139** is a method **C** (see page 5)complexation (Scheme 1.42), where a more stable dienol is complexed, before being oxidised and hydrolysed to the unstable keto tautomer (Method **C**, see page 5). The preparation was formalised in a publication in *Organic Syntheses* in 1977 by Birch and coworkers.[217] The synthesis started from the Birch reduction of anisole to dienol ether **1.140**, followed by tricarbonyliron complexation to gave a mixture of isomers of the complexed dienol **1.141** & **1.142**, because the diene must be isomerised into conjugation during the complexation. Hydride is then abstracted from the cyclohexadiene tricarbonyliron, to give the stabilised pentadienyl cations **1.143** & **1.144**, which then gives the complex of cyclohexadienone on heating with water.



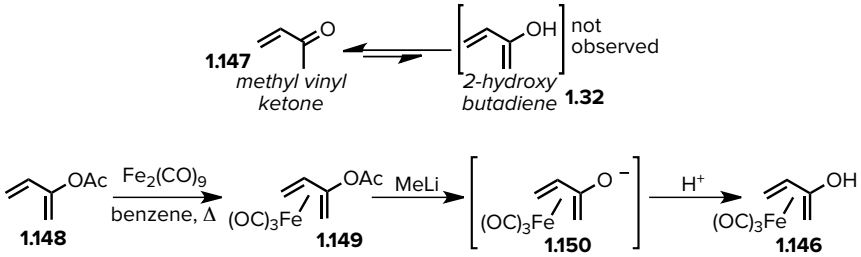
Scheme 1.42: Cyclohexadienone complexation.[217]

Cyclohexadienone is unstable not just to tautomerization but also Diels-Alder reaction (*cf.* cyclopentadienone, 2-acylbutadiene). This is shown by the 6,6-dimethyl case, **1.145** (Scheme 1.42), which can't tautomerise, but is reactive towards Diels-Alder reactions, even with the inhibitory steric bulk of the dimethyl substitution.[185,218]

Organic chemists have found use of the cyclohexadienone complex as an equivalent of an aryl cation,[219] where it can be used in the mild arylation of alkyl amines.[220]

1- & 2-HYDROXY 1,3-BUTADIENES

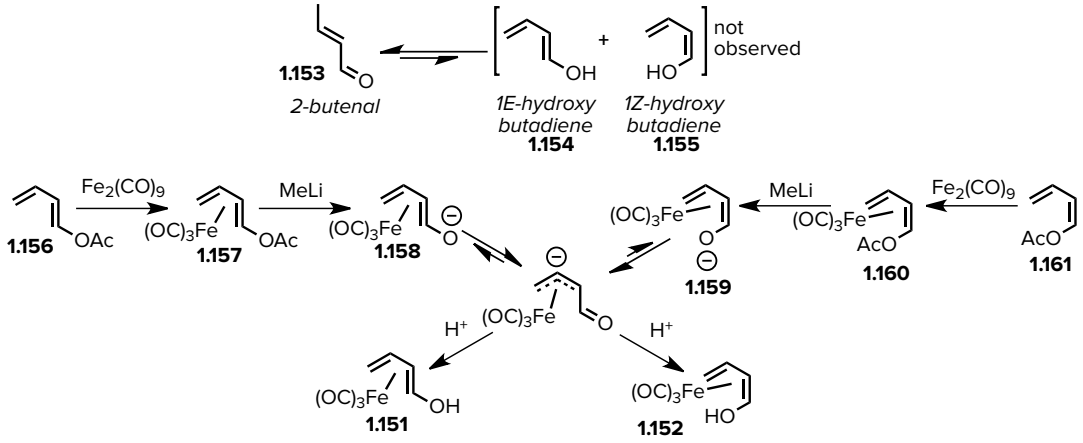
The complexation of cyclohexadienone is an example of the tricarbonyliron group stabilising an unfavourable *keto* tautomer, but the moiety can also stabilise unstable *enol* tautomers. For example, the enol tautomer of methylvinylketone can be trapped as the tricarbonyliron complex **1.146** (Scheme 1.43). [221,222]



Scheme 1.43: Trapping of MVK enol tautomer with tricarbonyliron.[221]

The enol tautomer complex **1.146** was first formed by DePuy and co-authors[221] by heating 2-acetoxybutadiene with di-iron nonacarbonyl in benzene (Scheme 1.43), followed by reaction with methyl-lithium, and subsequent acidification to give the oxygen sensitive enol tautomer (Method **C**, see page 5). The complex displays a useful umpolung reactivity with respect to MVK.

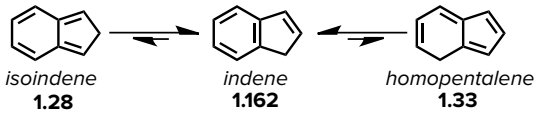
Complexes of the unstable enol tautomers, 1*E*/*Z*-hydroxybutadiene, i.e. **1.151** & **1.152**, (Scheme 1.44) can be prepared by the same method.[223,224]



Scheme 1.44: Trapping of unstable enol tautomer with tricarbonyliron.[223]

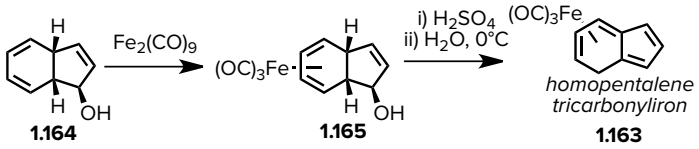
HOMOPENTALENE

Homopentalene is closely related to isoindene (*v.s.*) as both molecules undergo rapid aromatisation to indene (Scheme 1.45).[225]



Scheme 1.45: The isomerisation of homopentalene and isoindene to indene.

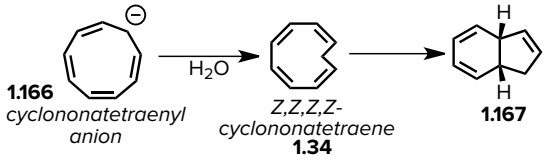
Homopentalene-tricarbonyliron *has*, unlike isoindene-tricarbonyliron (see *isoindene*, page 24), been made in its highly reactive, unsubstituted form, **1.163** (Scheme 1.46).[225] The successful synthesis was from bicyclic trienol **1.164**, which was coordinated with tricarbonyliron to give complex **1.165**, and finally isomerised and eliminated to give the homopentalene tricarbonyliron complex (Method **C**, see page 5).



Scheme 1.46: Homopentalene tricarbonyliron complexation.[225]

Z,Z,Z,Z-CYCLONONATETRAENE

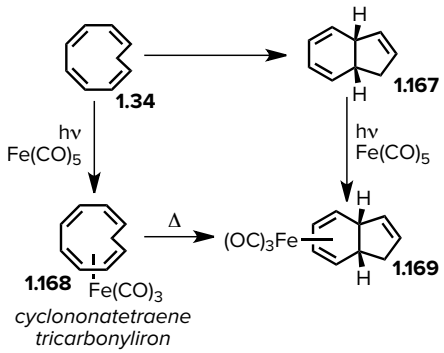
The methylene expanded annulenes are only slightly less well-known derivatives of the annulenes (see the [n]annulenes, page 46), with every chemist readily familiar with cyclopentadiene and cycloheptatriene.[Y] Between [8]annulene and [10]annulene resides cyclononatetraene, which can be observed as its "aromatic" anion (Scheme 1.47).[226]



Scheme 1.47: Cyclononatetraene preparation and decomposition.[226]

The hydrocarbon was prepared by Radlick & Alford in 1969 (Scheme 1.47),[226] where it was observed to rapidly undergo a 6π (thermal, disrotatory) electrocyclic ring closure to give the dihydro-indene structure **1.167**. Follow-up measurements[227] showed the hydrocarbon to have a half-life of ~50 minutes at 23°C.

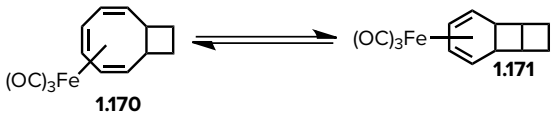
[Y] Or at least its oxidised congener, the tropylium ion.



Scheme 1.48: Cyclononatetraene complexation and isomerisation.[228]

The tricarbonyliron complex **1.168** was reported by Reardon & Brookhart in 1973 (Scheme 1.48, Method **A**, see page 5).[228] The preparation and stability of the complex are curious because the complex undergoes the same 6π-electrocyclisation as the uncomplexed hydrocarbon (to give compound **1.169**). The half-life of the complex was measured to be 48 minutes at 101 °C, and the isomerization obeys first-order kinetics. The precise mechanism by which this process occurs was studied by Reardon & Brookhart because the observation was so unusual. Brookhart determined that the observed first-order behaviour (along with the quantitative yield and lack of observable free ligand) of the isomerization was best explained by *"a unimolecular electrocyclic ring-closure of the bound cyclononatetraene ligand."* A mechanism involving dissociation and recombination of tricarbonyliron was ruled out by quantifying the barriers of such a process.[228]

The electrocyclic ring closures of tricarbonyliron-bound cyclic polyolefins is not exclusive to cyclononatetraene. Cotton and coworkers[229] reported the tricarbonyliron complexation and subsequent isomerisation of *cis*-bicyclo[6.2.0]deca–2,4,6-triene **1.170** (Scheme 1.49). Scholes and coworkers did follow-up mechanistic studies[230] on similar compounds to those worked on by Cotton *et al.*; they found more examples where electrocyclisation equilibria were perturbed by tricarbonyliron complexation.



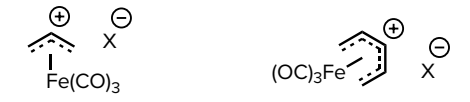
Scheme 1.49: Tricarbonyliron-bound electrocyclisation of *cis*-bicyclo[6.2.0]deca–2,4,6-triene.[229,230]

The reactions of tricarbonyliron(*Z*,*Z*,*Z*,*Z*-cyclononatetraene) have been summarised and discussed further by Deganello and coworkers[231] and Airoldi and

coworkers.[232] Electrocyclic ring-openings on cyclobutenes coordinated by iron have also been investigated experimentally[184] and computationally.[123]

1.3.7 η^3- and η^5-Tricarbonyliron Complexes

This review has focussed on the stabilisation of compounds which are very reactive when neutral and in their ground state. Obviously, many more compounds meet the requirements for high reactivity when charged derivatives are taken into account. π-Allyl[233] and π-pentadienyl[234] tricarbonyliron complexes have been known for a long time (Figure 1.21), and so won't be covered in any great detail here; also, the stabilising influence of tricarbonyliron has already been reviewed extensively in these cases (see Donaldson and others).[17,18,235] The only example considered in this review is the benzenonium ion (*v.i.*).

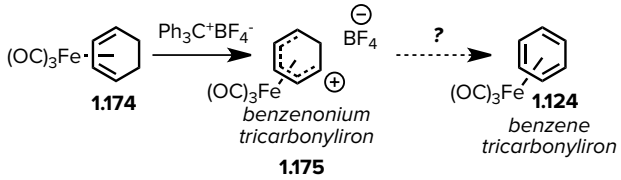


π-allyl complex **1.172** *π-pentadienyl complex* **1.173**

Figure 1.21: Allyl & pentadienyl tricarbonyliron complexes are well known.

BENZENONIUM ION (PROTONATED BENZENE)

Benzene obviously does not meet the requisite level of high reactivity, but, when protonated, benzene becomes a highly reactive pentadienyl cation. The lifetime of the benzenonium ion in aqueous solution is <100 picoseconds. The tricarbonyliron complex of benzenonium was first prepared by Fischer and coworkers in 1960,[236] by hydride abstraction from cyclohexadiene-tricarbonyliron **1.174** (Scheme 1.50). The stability imbued by the complexation of the tricarbonyliron group has been explained and quantified[237] by density functional calculations.



1.174 *benzenonium tricarbonyliron* **1.175** *benzene tricarbonyliron*

Scheme 1.50: Benzenonium-tricarbonyliron generation.[236]

The deprotonated tricarbonyliron-benzenonium, tricarbonyliron-benzene **1.124**, has not been synthesised (Scheme 1.50).[237] This is a notable gap in the literature since the structure, reactivity, and fluxionality of (cyclobutadiene)$Fe(CO)_3$ and

(cyclooctatetraene)$Fe(CO)_3$ have been so extensively investigated, and because deprotonation of pentadienyl cation tricarbonyliron complexes has been used successfully to generate cyclic polyene complexes.[210]

1.3.8 Complexes of Fundamental Polyenes

The fundamental polyenes can be subdivided into four different categories, or classes, which are the four possible combinations of the variable pairs: *acyclic* versus *cyclic*, and *through-conjugated* versus *cross-conjugated*. These alternate respectively to give the acyclic *linear polyenes* and *dendralenes*, and the cyclic *annulenes* and *radialenes* (Figure 1.22).[49]

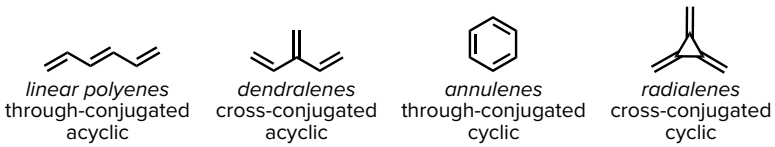
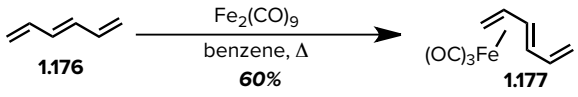


Figure 1.22: The fundamental classes of the polyenes.

Many of the highly reactive polyenes described in this chapter are related to, or derived from, the fundamental polyenes. It is worth discussing these compounds to some extent, even though they have mostly resisted complexation (or synthesis at all!).

LINEAR [N]POLYENES

The linear polyenes have an increasing degree of instability that correlates with increasing size, or chain length. Substitution can greatly increase the stability of even very long polyenes, as described recently by Zeeshan and co-authors.[238z] Of the complexes of the unsubstituted linear polyenes, the longest that has been made is of 1,3,5-hexatriene (Scheme 1.51, Method **A**, see page 5)[239], which is also the longest stable unsubstituted polyene. Substituted variants of longer polyenes have also been prepared.[240,241]

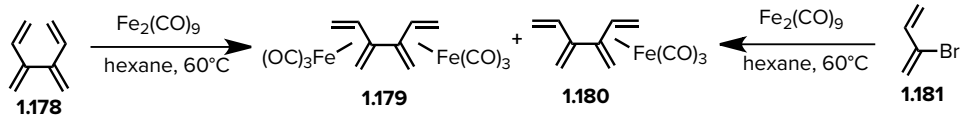


Scheme 1.51: Hexatriene complexation.[239]

[z] The supporting information to the cited document by Zeeshan *et al.* is very instructive on the effect of increasing chain length on stability, and the substitution patterns that have been incorporated to modify that stability. (http://pubs.acs.org/doi/suppl/10.1021/ol302577d)

[N]DENDRALENES

The [n]dendralenes are introduced and described in Chapter 2, along with all of the tricarbonyliron complexes of [3]dendralene that have been prepared. Greene and co-authors have reported the only prior tricarbonyliron complexes of an unsubstituted dendralene, **1.179** & **1.180** (Scheme 1.52, Methods **A** & **B**).[147]



Scheme 1.52: The preparation of tricarbonyliron[4]dendralene.[147]

[N]ANNULENES

The annulenes are possibly the best known of the fundamental polyenes, starting with cyclobutadiene, continuing through benzene and cyclo-octatetraene and higher.[49] The only unsubstituted [n]annulene higher than cyclobutadiene ([4]annulene, *v.s.*) that has been complexed by tricarbonyliron is [8]annulene, or cyclooctatetraene (COT), an anti-Hückel cyclic polyene (Figure 1.23). The (COT)$Fe(CO)_3$ complex has been very extensively studied, after its initial report by Manuel and co-authors.[242]

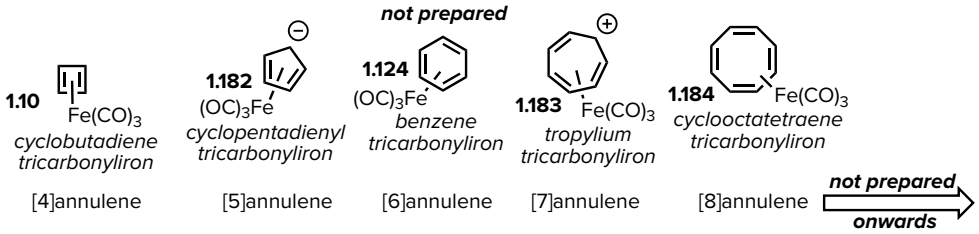


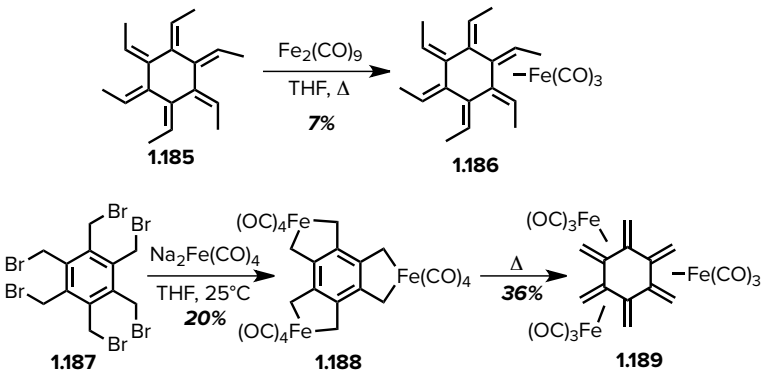
Figure 1.23: (Annulene)tricarbonyliron complexes.

Informally, higher non-neutral tricarbonyliron complexes of annulene-like polyenes have been prepared (Figure 1.23). Within this category are cyclopentadienyl tricarbonyliron[243] (*pseudo*-[5]annulene, a 6π-electron Hückel aromatic polyene) and tropylium tricarbonyliron[244-246] (*pseudo*-[7]annulene, a 6π-electron Hückel aromatic polyene).

[N]RADIALENES

The [n]radialenes are generally reactive towards a range of decomposition pathways that are not well understood. Complexation of a substituted [6]radialene was reported by Hopf and co-authors (Scheme 1.53, Method **A**, see page 5).[247] [6]Radialene is unstable, but the compound prepared by Hopf and coworkers, **1.185**, was not. A significant amount of work on tricarbonyliron complexes of *o*-

xylylene and derivatives has been done by Ullah and coworkers (see *o*-xylylene discussion).[119] This work evolved into the report of [6]radialene **1.189** [248-250] and Dewar benzene-type[120] derivatives of (*o*-quinone dimethane)tricarbonyliron complexes (Method **C**, see page 5).[33,121AA]



Scheme 1.53: Tricarbonyliron-[6]radialene complexes (top: Hopfner *et al.* 2003[247], bottom: Ullah *et al.* 1984[119]).

Neither unsubstituted [5]radialene—which has thus far resisted synthesis, isolation, and charaterisation[251]—nor its tricarbonyliron complex have not be prepared. [5]Radialene can be considered as a decahydro-monomeric unit of buckminsterfullerene (C_{60}),[252] and some recent DFT studies have been done on the possibility of making the tricarbonyliron complexes of the fullerenes, but these have not yet borne experimental fruit.[253]

[N]CUMULENES

Closely related to the alternant polyenes listed above are the cumulenes, which have a continuous series of C=C π-bonds. Cumulenes without substituents are purportedly very unstable compounds, with butatriene (Figure 1.24, [3]cumulene **1.191**) reported to polymerise completely within a few minutes of preparation.[254,255]

AA The reports by Ullah *et al.* describe the isolation and characterisation of intermediates which are not observed by authors performing similar (or identical) reactions (see Kerber & Ribakove *Organometallics* **1991**, *10*, 2848–2853, and Girard *et al. J. Am. Chem. Soc.* **1994**, *116*, 6427–6428.).

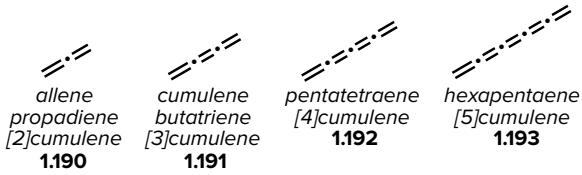
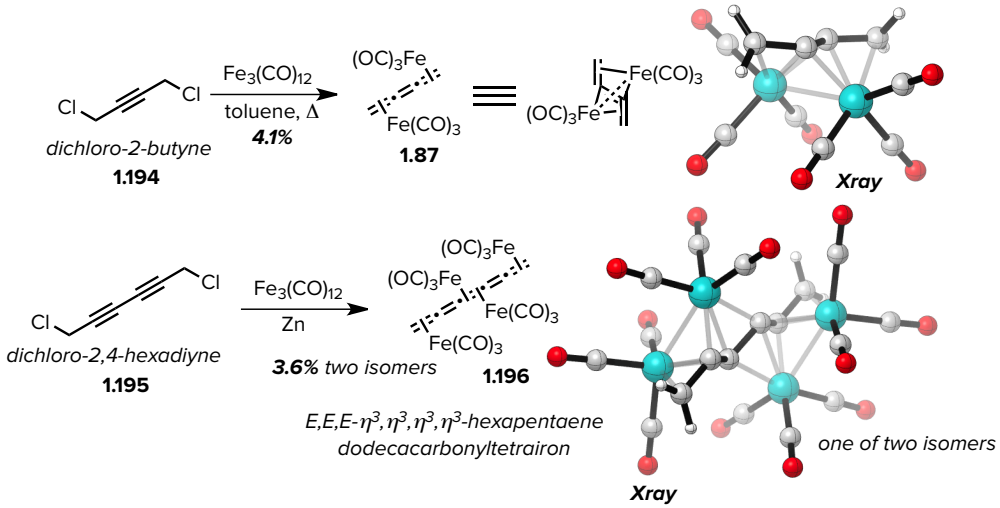


Figure 1.24: The first four cumulenes. The members of the cumulene family each have several interchangeable names.

Butatriene (or cumulene) has been very extensively studied as its bis(tricarbonyliron) complex,[255] and in fact was used synthetically to access 2-acetylbutadiene tricarbonyliron (*v.s.*).[140] The structure of bis(tricarbonyliron)butatriene is peculiar, with the normally linear ligand adopting a doubly bent configuration in order to coordinate to two *pseudo*-allylic bound tricarbonyliron groups (Scheme 1.54).[256-262]



Scheme 1.54: Cumulene tricarbonyliron complexation (top: Joshi *et al.* 1966,[256] X-ray: Gervasio *et al.* 2005,[262] bottom: Iyoda *et al.* 1991,[263] X-ray: *ibid.*).

This kind of coordination has been taken to the extreme with the preparation of (*E,E,E*-η³,η³,η³,η³-hexapentaene)dodecacarbonyl tetrairon **1.196** (Scheme 1.54, Method **A**/**B**, see page 5).[263]

1.4 Conclusions

Tricarbonyliron can be used to stabilise, and make unreactive, polyenes which would ordinarily be un-isolable. By itself this statement would need no

justification, no evidence, nor any review. The purpose of this review chapter was to show *how* the tricarbonyliron group has been used in this respect, and what the advantages and limitations of the functionality are. The approaches to the preparation of these complexes is critical, especially if they are to be proposed for general use. Trends and fashion in chemistry, as elsewhere in life, are cyclical. Organocatalysis rose,[264] and fell, before rising again;[265] so too did organometallic complexes of polyenes rise[54] and fall, alongside the chemistry of polyenes in general.[49]

Cyclic and acyclic polyenes have been extensively stabilised by the tricarbonyliron functionality (Figure 1.25). Most literature has focussed on cyclic, and through-conjugated polyenes, and in this respect the organometallic literature mirrors the organic.

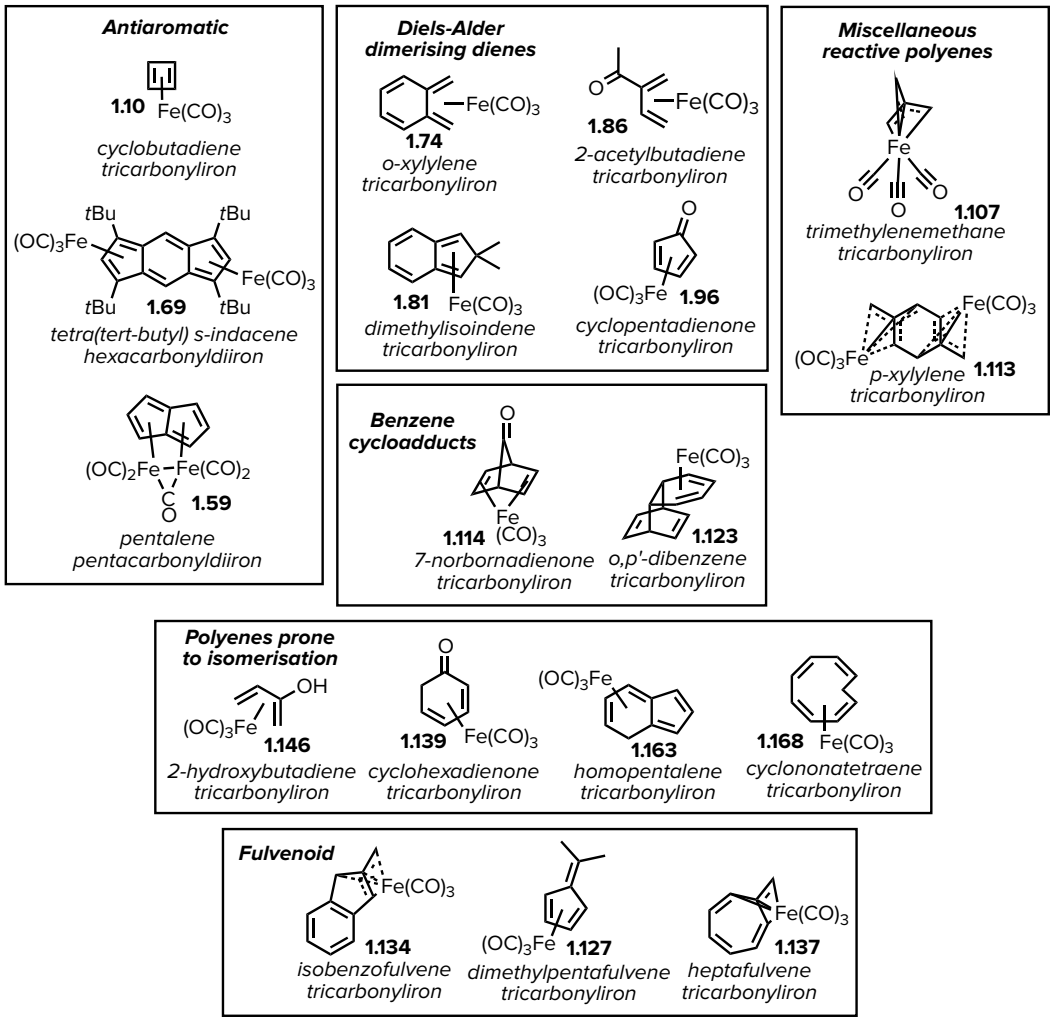


Figure 1.25: (Unstable polyene)-tricarbonyliron complexes.

Broadly, the classes of neutral compounds that have been stabilised by coordination to tricarbonyliron (Figure 1.25) can be classified as: Hückel antiaromatic, Diels-Alder reactive, isomerisable, benzene cycloadducts, fulvenoid, or some combination of the above. The ability of the tricarbonyliron group to deactivate (or passivate) a four-carbon fragment is demonstrated in its ability to halt Diels-Alder reactions, etc. but this passivation is not universal, and the ligand has been sometimes observed to undergo reactions that you might expect to be stopped, like electrocyclic ring closures or openings.

The stabilisation/deactivation of extremely reactive compounds by tricarbonyliron (Figure 1.25) has allowed their isolation, characterisation, and observation as models of the structure of the trapped ligand. Subsequent to trapping, the tricarbonyliron group has also been used to allow further derivatisation of the unstable polyene, and release of the ligand under controlled thermal, photochemical, or oxidative conditions. In their own right the polyene complexes have also found use in organometallic chemistry (e.g. cyclobutadiene, cyclopentadienones, etc.).

One of the key limitations in the preparation of tricarbonyliron complexes of unstable polyenes is the lack of good general preparative methods, the few exceptions to the low yields are either very specific to the compound (e.g. cyclobutadiene tricarbonyliron) or many steps from any potentially general intermediate (e.g. homopentalene tricarbonyliron). We believe that there is no *a priori* reason why tricarbonyliron-polyenes are no longer in favour, and that by re-opening the field of polyene chemistry we have necessarily turned to the tricarbonyliron group, as it is the only reliable way to control, direct, and protect the inherent reactivity of the polyenes.

2

Dendralene Complexes

2.1 Introduction

PREAMBLE

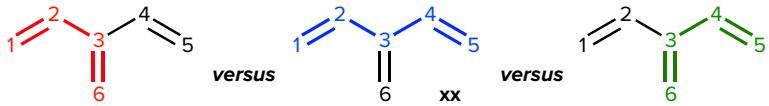
Making molecules that people haven't been able to make before has innate appeal to a synthetic organic chemist. If one can make a new molecule that enables new synthetic routes to complex targets, then all the better. And if there is a whole class of molecules that fit this description, then that must be best of all. The dendralenes are such molecules.

2.1.1 Cross-Conjugation

The dendralenes are a family of fundamental cross-conjugated polyenes, so before introducing the dendralenes, it would be good to know a little bit more about cross-conjugation. A "conjugated" system is traditionally defined[266] as one containing alternating single and multiple (double or triple) bonds, and that conjugation is responsible for a number of electronic and optical properties emergent from this kind of connectivity. The actual property of conjugation is the

interaction of one p-orbital with another across a σ-bond spacer.[2] The most significant effect of conjugation is electron delocalisation, which is the sharing of electron density between separate π-bonds in a conjugated system.[267] Synthetic organic chemists use conjugation and delocalisation—like many aspects of fundamental chemical interaction—superficially, in order to rationalise reaction outcomes.[268A]

Conceptually, conjugation can be further sub-divided into two different classes of connectivity, through-conjugation and cross-conjugation.[269] Through-conjugation comprises a system that is one conjugated π-bond after another in an unbranched chain,[267] whereas cross-conjugation is defined by branching or bifurcation points where the classical conjugation path is broken (Figure 2.1). Cross-conjugation has been more precisely defined by Phelan[266] as: *A [system] possessing three unsaturated groups, two of which, although conjugated to a third unsaturated centre, are not conjugated to each other*.



[3]dendralene

Figure 2.1: Highlighted dienes in [3]dendralene, shown in red, blue, and green. The diene in red shows conjugation between 6-3➔2-1 and the diene in green shows conjugation from 6-3➔4-5. Electrons cannot be delocalised from 1-2➔4-5. The conjugation path in [3]dendralene is said to be *bifurcated*, and is representative of other cross-conjugated systems.

To introduce the families of polyenes—and with it conjugation—it is instructive to successively connect ethylenes (as either –CH=CH–, or –C(=CH_2)– units), and examine the possibilities with each connection.[49] The simplest molecule containing a single alkene is ethylene (Figure 2.2). With ethylene there is no issue of conjugation, or isomeric forms. As a second alkene is introduced there is introduced the complication of cyclicality. Both 1,3-butadiene and cyclobutadiene are through-conjugated, with former acyclic and the latter cyclic. Upon arriving at three alkenes we take another step-up in complication, which is branchedness. Both 1,3,5-hexatriene and benzene are simply higher homologues of their 2-

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[A] This explanation is dismissive on its surface, but qualitative or hand-waving descriptions and understanding are types of heuristic thinking, and these kinds of heuristics are vital to one's ability to easily understand and apply chemical knowledge (see Graulich *et al. Chem. Soc. Rev.* **2010**, *39*, 1503–1512).

alkenic brethren, but [3]dendralene and [3]radialene cannot be categorised as such. [3]Dendralene is 'created'[B] from 1,3-butadiene by the insertion of a methylene group between the conjugated olefins, and hence bifurcating the conjugation path. The connectivity of [3]radialene can be rationalised by forming a bond between C(2) and C(4) of [3]dendralene to form a three-membered ring with three exocyclic double-bonds. These patterns of connectivity can be extended to compounds with four alkenes, and beyond (Figure 2.2).

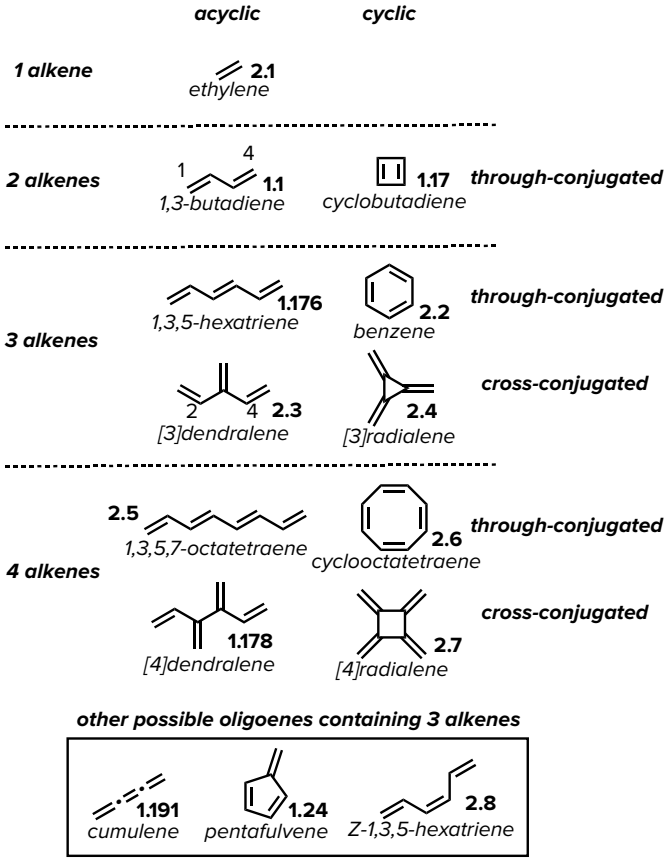


Figure 2.2: The possible connectivity of multiple alkenes. These connectivity patterns define the 'fundamental' classes of oligoalkenes (Figure 2.3).

Thus constructed are the families of oligoalkenes (Figure 2.3), the *linear polyenes*, the *dendralenes*, the *annulenes*, and the *radialenes*. The linear polyenes and the annulenes have been very extensively studied, both theoretically and experimentally. Experimentally, linear polyenes and annulenes have been prepared containing as many as 27[238] or 15[270] conjugated double bonds,

[B] Conceptual creation, not actual synthesis.

respectively. The cross-conjugated oligoalkenes have, by contrast, received relatively meagre attention. In fact, even five alkenes was thought to be too much for the dendralenes, with Hopf saying:[271] *even if [5]dendralene could be obtained by a preparatively simple route, it would presumably be difficult to study its chemical properties since it is presumably a very reactive substance*.[c] Similar difficulties have been reported in the preparation of the radialenes.[247,251,272]

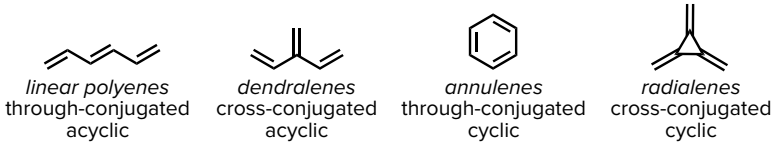


Figure 2.3: The 'fundamental' classes of oligoalkenes. The *linear polyenes*, the *dendralenes*, the *annulenes*, and the *radialenes*.

The four families described above are examples of 'pure' polyolefins, but there are many variants that were not touched upon, some examples of those containing three alkenes are given at the bottom of Figure 2.2. The *cumulenes* (of which butatriene, **1.191**, is an example) are a family of conjugated polyolefins, but they contain two orthogonal conjugated systems, rather than a single continuous system.[273-275] The *fulvenes* are sometimes considered to be fundamental polyolefins,[49] but are better described as *annulene–radialene* hybrids, *cf.* pentafulvene & cyclobutadiene. And finally, the *linear polyenes* can have either *E* or *Z* geometry about their disubstituted alkenes and still maintain through-conjugation, *cf. E*- & *Z*-1,3,5-hexatriene (Figure 2.2).

As a product of their altered connectivity, cross-conjugation differs from through-conjugation in two key ways. Firstly, cross-conjugated π-systems have a finite HOMO–LUMO gap; as the number of alkenes increases the gap stays roughly the same. Secondly, the branching nature of the cross-conjugated systems means that there is greater opportunity for steric interactions which force the branches out of plane, and thus out of conjugation.[276]

Cross-conjugation is the perennial next-big-thing in polyene chemistry.[266,272,276,277] In spite of this author's expressed cynicism, there seems to have been some recent theoretical advances that make cross-conjugated molecules of significant interest to material chemists looking for the ångström-scale circuit. Quantum interference

[c] This quote does not describe the current state of the art, but worry not, for this chemical cliffhanger is resolved in the very next section (2.1.2: The Dendralenes, p. 57), so read on.

controls charge-transfer,[278,279] and the bifurcated nature of cross-conjugated systems (Figure 2.1) means that all neutral closed-shell examples will show quantum interference.[279-285] As a consequence of this, cross-conjugated molecules have been proposed as molecular transistors for use in a hypothetical ångström-scale circuit.[279,281,286,287]

2.1.2 The Dendralenes

As introduced above, the dendralenes are a neglected class of fundamental oligoalkenes,[288] which had until recently eluded large-scale preparation and comprehensive study.[289,290] The carbon backbone of a dendralene is branched (Figure 2.4), having a series of outward facing methylene units, which gives the compounds an especially synthetically-undesirable appearance. Payne and coworkers discovered that the properties, both physical and chemical, of the dendralenes alternate with the number of alkenic subunits in the molecule.[291] The alternation of the dendralenes gives rise to sub-classification of the dendralenes as either *even* (e.g. [4]dendralene) or *odd* (e.g. [3]dendralene), based on the number of alkenes in the hydrocarbon. This behaviour was explained through computational studies by Paddon-Row,[292] which attributed the greater reactivity of **2.3** versus **1.178** to higher populations of reactive conformers and a more stable closed-shell singlet bispericyclic transition state for the Diels-Alder dimerisation.

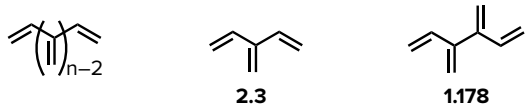


Figure 2.4: The [n]dendralenes.

The physical expression of this conformational preference is vividly exposed in the stability of the family: the even dendralenes can be stored neat at ambient temperature and remain unchanged for months,[293] in contrast, the odd dendralenes have half-lives on the order of hours under similar conditions (Figure 2.5).[291]

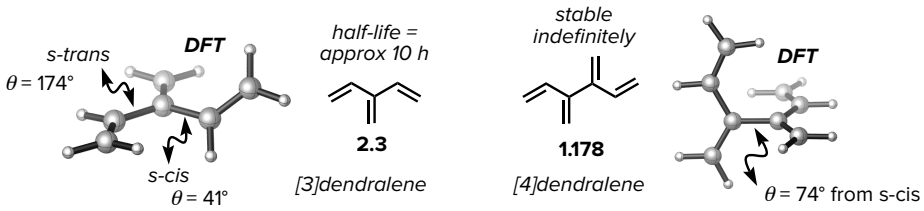
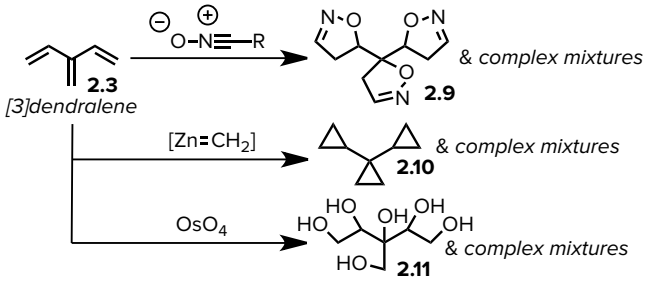


Figure 2.5: The lowest energy conformations of [3]dendralene and [4]dendralene.

We think of dendralenes as *fundamental* and *electronically fascinating* molecules, but thinking of them purely in this way dismisses their hidden synthetic utility. A utility that was highlighted by the use of the parent (i.e. the unsubstituted hydrocarbon) [3]-, [4]-, and [5]dendralenes to form frameworks with *natural-product-like complexity* in one step through cascades of pericyclic reactions.[293-295] Although the sequences at first appear to be too powerful *not* to have applications in synthesis, actual synthetic success with the dendralenes has been very limited.[288,296]

2.1.3 The Problem With the Dendralenes

We believe there to be three main problems with trying to apply dendralenes in synthesis: 1) odd members of the family are difficult to handle due to their inherent instability;[291,292,295,297] 2) there is a severe shortage of methods for preparing dendralenes;[288] and 3) most cascade processes involving dendralenes are insufficiently selective (Scheme 2.1).



Scheme 2.1: Lack of selectivity with reactions of [3]dendralene.

Dendralenes have promising potential as intermediates in synthetic organic chemistry, but their actual application is limited by the poor selectivity in the reactions that they have the most potential. In Diels-Alder reactions you have to work within the inherent selectivity of the dendralenes,[291] and even when you do that the selectivity is often mediocre[295] to poor.[293] Dendralenes have also been used successfully in Simmons-Smith reactions[298] to exhaustively cyclopropanate

the polyene, but there was no observable selectivity for reactions with less than saturating conditions (Scheme 2.1). Dihydroxylations and cycloadditions—other than the Diels-Alder reaction—have also met with limited success in reactions with the dendralenes (Scheme 2.1).

2.1.4 Aims: To Make and Use Tricarbonyliron[n]dendralenes

The dendralenes are unstable polyenes which have enormous unfulfilled synthetic potential, and so appeared to be perfect candidates for us to develop and test methodology to stabilise them and enhance their selectivity. To do this we proposed the use of the tricarbonyliron group to coordinate to the diene functionality in the dendralenes (Figure 2.6). We believed that coordination would help to block reactivity at one end of the molecule, enabling us to carry out reactions at unoccupied alkenic sites.

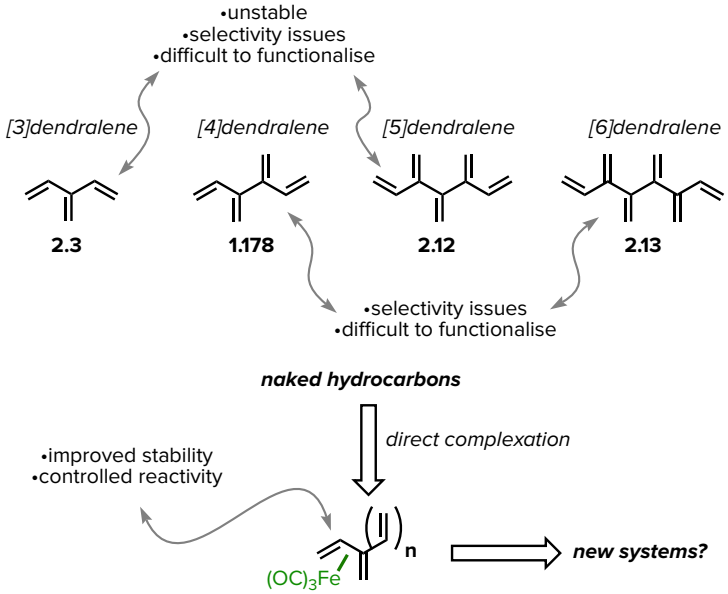


Figure 2.6: The problems of the [n]dendralenes can be solved with coordination chemistry.

We have access to multigram quantities of the parent [3]–[6]dendralenes, and so the ideal complexation would be a general reaction that could be carried out directly on any of the dendralenes with little optimisation (Figure 2.6). After preparing complexes of the available dendralenes, we would investigate the selectivity of the complexation.

With a selection of dendralene complexes in hand we would then target a range of transformations to assess the complexes' ability to control, direct and activate the

dendralenes towards reactions with which the parent hydrocarbon has poor reactivity or selectivity.

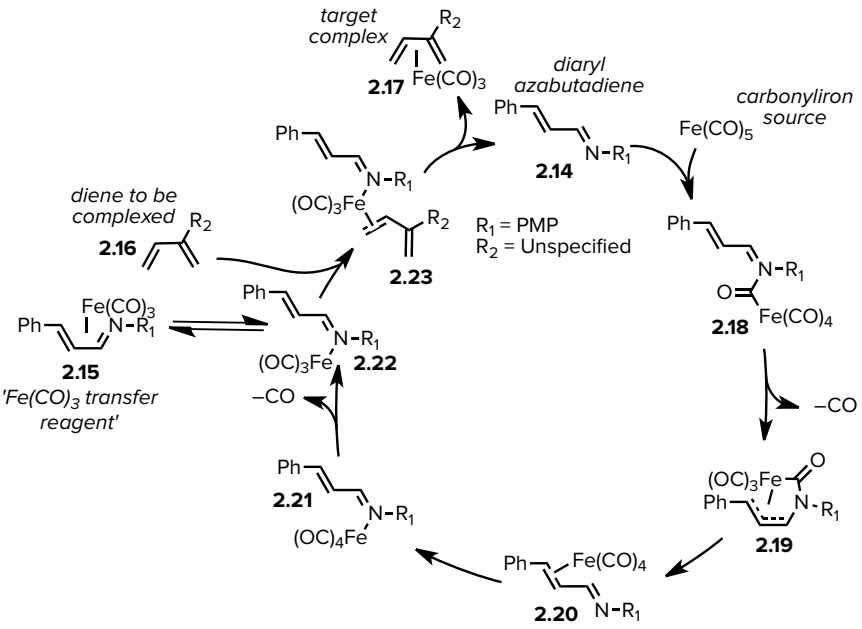
2.2 Complexing The Dendralene

In spite of the ostensibly obvious application to dendralenes, the preparation and reactions of metal complexes of dendralenes has been poorly investigated,[143,147,299][D] with only one early study describing direct complexation of a dendralene (the results reported by Greene and coworkers are described alongside our complexation of [4]dendralene, *v.i.*).[147]

There are many routes to tricarbonyliron complexes of polyenes, as discussed extensively in Chapter 1. The catalytic complexation of the [n]dendralenes was carried out by employing a slight modification on the experimental procedure described and developed by Knölker and coworkers.[25] The procedure is an evolution of classical chemistry that used (BDA)$Fe(CO)_3$ as a labile source of $Fe(CO)_3$.[230] The development is that diaryl azabutadienes are used rather than aryl enones. Their role is very similar, but catalytic—rather than stoichiometric—transfer reagent can be used because $Fe(CO)_3$ transfer is coupled the nucleophilic can activation of carbonyliron centres towards substitution.

The reaction involves the use of an inexpensive carbonyliron source, with a sub-stoichiometric amount of diaryl azabutadiene (Scheme 2.2). The imine nitrogen of diaryl azabutadiene **2.14** initiates the catalytic cycle by adding to one of the carbonyl ligands of a carbonyliron source.

[D] Much like most chemistry of the dendralenes.

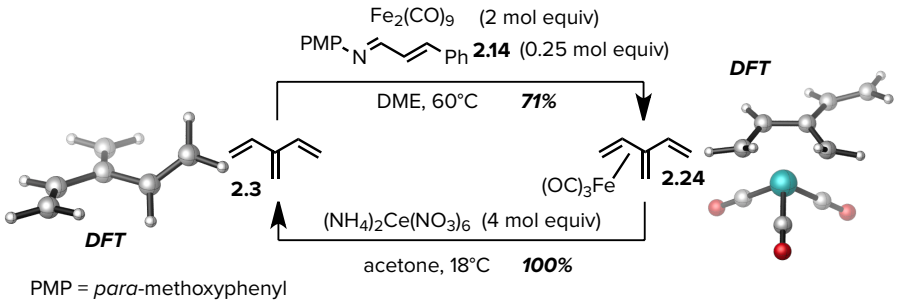


Scheme 2.2: Catalytic complexation of 2-substituted butadienes.[156]

After elimination of CO and rearrangement the complex is the equivalent of an $Fe(CO)_3$ transfer reagent, **2.15**. The desired diene, **2.16**, can then enter the catalytic cycle and receive the tricarbonyliron group by sequential η^2-coordination. The diaryl azabutadiene **2.14** is thus released. Aryl Schiff bases of cinnamaldehyde were found by Knölker[26] to be the best at transferring an equivalent of $Fe(CO)_3$ onto themselves, and then onto the desired diene catalytically.

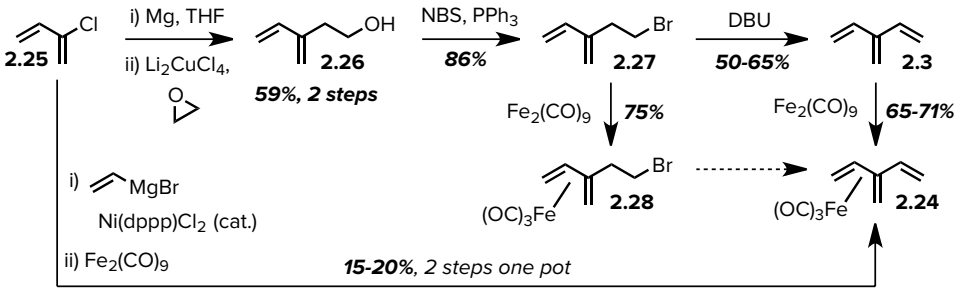
2.2.1 [3]Dendralene Complexation

We found that the tricarbonyliron complex of [3]dendralene **2.24** could be readily prepared in good yield on a multigram scale through an azabutadiene-catalyzed reaction of $Fe_2(CO)_9$ with the parent hydrocarbon **2.3** (Scheme 2.3).[25] Optimal conditions for the complexation reaction were found by varying solvent (THF and DME), temperature (60–85°C), and reagent stoichiometry. The best yields (65–71%) were obtained with DME at 60 °C, but this route required a multi-step preparation of neat [3]dendralene,[294] and the complexation of this unstable and volatile hydrocarbon.



Scheme 2.3: Optimised complexation of [3]dendralene.

Two different routes were taken to optimise the approach to the complex (Scheme 2.4). Complexation of an intermediate *en route* to 'neat' [3]dendralene should be higher yielding both during the complexation (as the reactant is less volatile) and in subsequent steps (as a tricarbonyliron-diene is a more stable moiety than a naked diene, and less dimerisation prone). Complexation of the immediate precursor, **2.27**, to [3]dendralene was slightly higher yielding than of [3]dendralene itself, but subsequent elimination was not as clean as the already successful route, so further optimisation in this direction was deemed a wasted effort. A much more efficient route was the preparation of [3]dendralene by the Kumada cross-coupling of chloroprene, **2.25**, directly with a commercially available solution of vinylmagnesium bromide in THF, followed by the addition of diiron nonacarbonyl and Knölker's azabutadiene catalyst[300] and heating to 60 °C. The isolated yield and purity obtained from the abridged approach compared favourably enough to be an improvement over the five step protocol previously reported.



Scheme 2.4: Different routes to tricarbonyliron[3]dendralene.

Once isolated, we observed that the complex of [3]dendralene was stable at ambient temperatures and pressures and could be handled in air and light under usual laboratory conditions as expected. Prolonged exposure to bright light and/or air did lead to decomposition of the tricarbonyliron complex of [3]dendralene (as it does to all tricarbonyliron complexes),[235,301] but the compounds could be

exposed to light/air for: weighing, transferring, and short reactions.[E] Unlike the hydrocarbon, it exhibited no tendency to dimerise. Furthermore, it could be converted into the hydrocarbon in quantitative yield[F] in seconds on exposure to cerium ammonium nitrate (CAN) in acetone.

DFT calculations[302][G] predict that the *cisoid* conformation for a tricarbonyliron-dendralene complex is about 4 kJmol^{-1} more stable than the corresponding *transoid* one (Figure 2.7). The described conformation is of the free alkene with respect to the tricarbonyliron-diene fragment. This is interesting because the *transoid* conformation is favored for the free [3]dendralene **2.3**. The next lowest energy conformation of [3]dendralene is *s-trans/s-trans*, about 3 kJmol^{-1} higher in enthalpy. We suspect that the apparent preference for the *s-cisoid* conformation in the complex results from the change in geometry about the terminal methylene carbon atoms of the complexed 1,3-butadiene unit: pyramidalisation on complexation with iron causes the methylene hydrogen atoms to move out of the plane, thereby reducing the destabilising inner H/H clash.

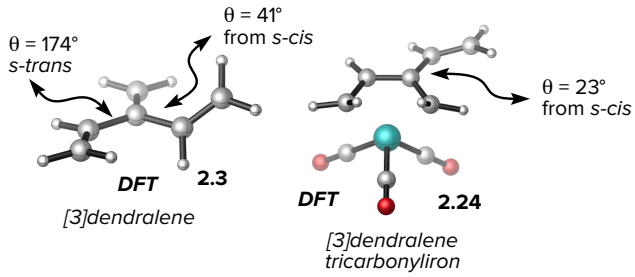


Figure 2.7: DFT calculated molecular structures of [3]dendralene and its tricarbonyliron complex.

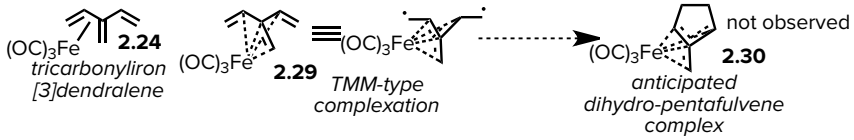
As introduced in Chapter 1, an alternative to *s-cis butadiene* tricarbonyliron complexes is the *trimethylenemethane mode* of complexation, wherein a cross-conjugated C_4 unit is coordinated to form an umbrella-like complex (Scheme 2.5).[170] This type of complexation is tolerated by—or possibly even preferred by—a large family of cyclic[172,208] and acyclic[166] polyenes when they are complexed with

[E] Long reactions were carried out with protection from light in the form of aluminium foil or amber glassware.

[F] Yield determined by ^{1}H NMR spectroscopic analysis; actual isolation of [3]dendralene from this reaction is very difficult due to its volatility.

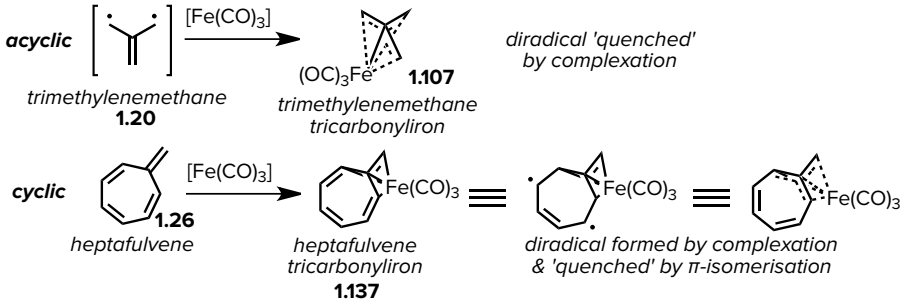
[G] DFT calculations reported in this chapter were performed at the B3LYP/6-31G(d) level of theory by Prof. Michael N. Paddon-Row unless otherwise stated.

tricarbonyliron. We do not observe any complexes of this type with reactions of carbonyliron sources with the dendralenes.



Scheme 2.5: Trimethylenemethane-type complexation and the dendralenes. TMM-type complexes of the dendralenes would presumably ring-close in a radical coupling reaction.

The absence of TMM-type complexation is presumably because neutral polyenes would form biradicals[H] (e.g. **2.29**, Scheme 2.5). This is not a problem with the parent TMM and derivatives where a biradical is 'quenched,' but with the dendralenes it would leave an unstabilised biradical that would presumably rapidly close to form a dihydro-pentafulvene complex, **2.30**. With the cyclic examples of TMM-type complexation, the biradical that would form from this π-electron localisation instead forms a new diene (Scheme 2.6).



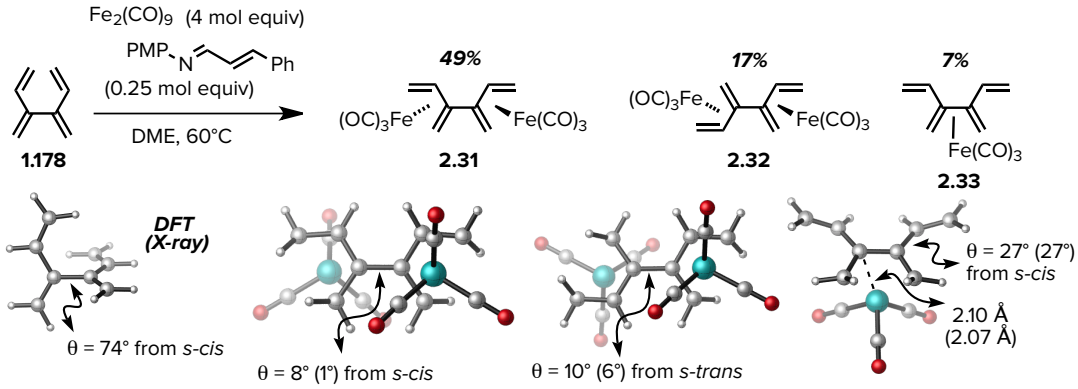
Scheme 2.6: The problem with acyclic trimethylenemethane-type complexation.

2.2.2 [4]Dendralene Complexation

Under exhaustive complexation conditions, [4]dendralene **1.178** gives a mixture of bis(tricarbonyliron) complexes **2.31** and **2.32** and the internal mono(tricarbonyliron) complex **2.33**. The chiral, C2-symmetric form of the bis(tricarbonyliron) complex **2.31** predominates over the meso-diastereomer **2.32** in a ratio of about 3 to 1 (see Scheme 2.7). This site selectivity is similar to that witnessed in uncatalyzed Diels–Alder reactions of [4]dendralene.[293] Initially we attempted to develop conditions which could selectively generate mono(tricarbonyliron) complexed [4]dendralene, but the mixtures were more

[H] Biradical is used synonymously with diradical throughout this thesis.

complex, and the internal mono-complex **2.33** could not be separated from the terminal mono-complex (**1.180**, see Scheme 2.8) by flash column chromatography. The complexation of [4]dendralene by diiron nonacarbonyl by Greene and coworkers in 1971 is the only report of a direct complexation of a dendralene in the literature.[147] Under similar conditions[I] we were unable to reproduce the reported results of 15 and 4% yields of the two diastereomeric diiron complexes and 26% of the terminal monoiron complex **1.180**. Specifically, under exhaustive conditions we were unable to isolate any of the terminal monoiron complex described as the major product of the reaction.[J]



Scheme 2.7: The tricarbonyliron complexation of [4]dendralene.

Molecular structures from single-crystal X-ray analyses of the three complexes were obtained, and lowest energy structures were calculated by DFT (Scheme 2.7). There is a good match between each X-ray crystal structure and the corresponding DFT-optimized minimum-energy structure; a result that adds weight to the premise that the conformations witnessed in the crystals are not dictated by packing forces. Whereas free [4]dendralene **1.178** prefers a conformation containing two *s-trans*-1,3-butadiene groups in a roughly orthogonal arrangement, all three complexes contain a [4]dendralene ligand adopting a roughly in-plane conformation.

[I] Greene *et al.* reports 1 equivalent of [4]dendralene to 2.6 equivalents of $Fe_2(CO)_9$ in 60-70 °C petroleum ether (ligroin) with heating.

[J] As the ratio of products obtained was found to be highly condition-dependent this in no way casts doubt on Greene's reported results.

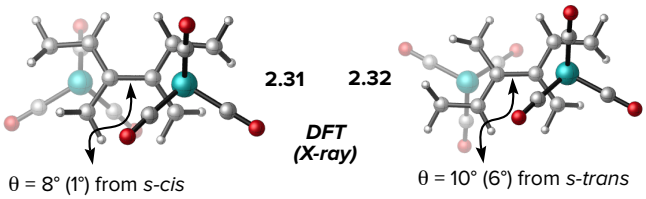


Figure 2.8: The molecular structures of bis(tricarbonyliron)-[4]dendralene complexes.

The structures of bis(tricarbonyliron)-[4]dendralene **2.31** & **2.32** are very similar, with the two tricarbonyliron group preferring an to reside on opposite faces (an *anti* conformation) in both (Figure 2.8). The dendralene ligand in both compounds is almost planar, perhaps indicating a high degree of conjugation between the complexed butadiene fragments and thus electronic communication between the metal centres. The relative stereochemistry in the bis(tricarbonyliron)-[4]dendralene is presumably set during the addition of the second tricarbonyliron fragment as it transitions from η^2- to η^4-coordination. If this is the case then the stereoselectivity of the complexation reaction is based on the conformational preference of the mono-terminal tricarbonyliron-[4]dendralene complex, and is unlikely to be optimisable.

The mono(tricarbonyliron)-[4]dendralene complex **2.33** has an analogous molecular structure to that calculated for tricarbonyliron[3]dendralene **2.24** (Figure 2.9). The vinyl groups pendant to the complexed butadiene are similarly positioned *s-cisoid* (23° and 27° from *s-cis*) to the butadiene fragment. On this basis, the selectivity and reactivity of **2.33** is predicted to be similar to that for **2.24**, for substrate-controlled reactions.

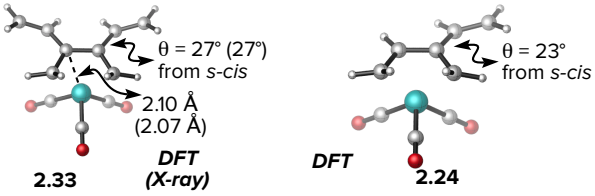
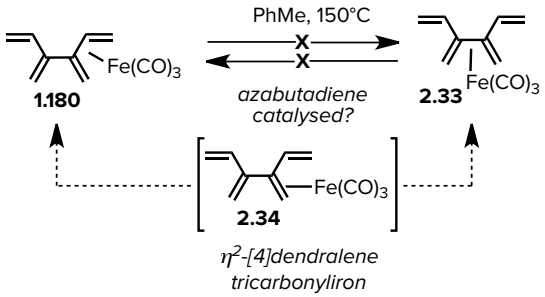


Figure 2.9: Comparison of molecular structures from DFT and X-ray analysis for tricarbonyliron [3] & [4]dendralene.

Evidently, for these complexes to be of use in synthesis, their integrity under standard reaction conditions must be maintained. Tricarbonyliron complexes of both acyclic and cyclic through-conjugated polyenes are known to exhibit fluxional behavior, with the tricarbonyliron group readily undergoing migration along a polyene chain.[303-313]

Intriguingly, migration does not occur in the unsubstituted dendralene series, as evidenced by the lack of interconversion witnessed between the two regioisomeric mono(tricarbonyliron) complexes of [4]dendralene, **1.180** and **2.33**, on heating solutions in toluene at 150 °C (Scheme 2.8). At this high temperature, degradation of the shift-isomers occurs at a rate significantly higher than any observable bond-shift isomerisation.



Scheme 2.8: Non-interconversion of shift-isomers of monoiron [4]dendralene.

Results obtained at high temperature do not necessarily rule out the possibility that there is a lower energy pathway for isomerisation under the reaction conditions, as the diaryl azabutadiene catalyst used in the complexation can labilise the formation of an η^2-olefin complex (i.e. **2.34**, Scheme 2.8),[300] which is believed to be the rate determining step in the shift-isomerisation of linear polyenes.[305] It is also possible that with Lewis acidic or Lewis basic substitution on the dendralene ligand that strongly basic[312,313] or strongly acidic[143,314] reaction conditions could lead to tricarbonyliron migration, but this should not play a role in the unsubstituted hydrocarbon case.

2.2.3 [5]Dendralene Complexation

The higher [n]dendralenes also deliver complexes under similar conditions as those reported for [3] & [4]dendralenes. The complication is that as the number of diene sites grows, so too does the number of potential isomers; issues of both site-selectivity and facial selectivity quickly become very complicated. Illustrative of this complication is the complexation of [5]dendralene (Figure 2.10), which comes equipped with two equivalent pairs of diene sites: **A** and **D** (*terminal*), and **B** and **C** (*internal*). Initial complexation of an $Fe(CO)_3$ unit can occur either *terminally* or *internally*, which subsequently can lead to complexation of a second $Fe(CO)_3$ unit, either *internally* (if initially *terminal*), or *terminally* (regardless of initial site), and either *syn* or *anti* to the first $Fe(CO)_3$ unit. These effects combine to allow the

formation of the following six products: **A** (or **D**), **B** (or **C**), *syn*-**AD**, *anti*-**AD**, *syn*-**AC** (or **BD**), and *anti*-**AC** (or **BD**).[K]

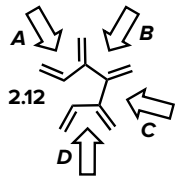
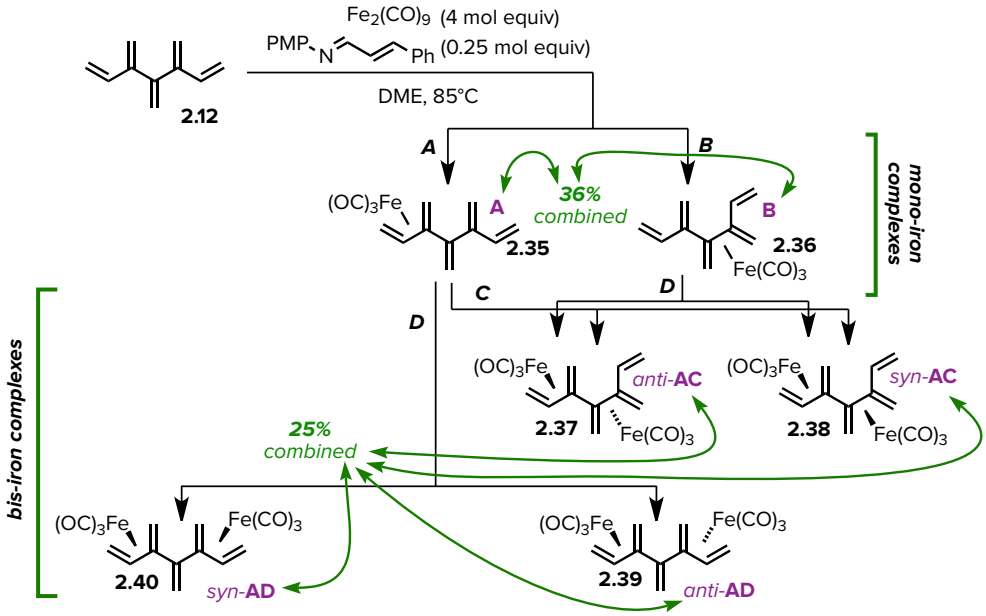


Figure 2.10: The potential complexation sites of [5]dendralene.

Our aim for the complexation reactions of the dendralenes was to get a general synthesis for the family, so that we could compare results and observed selectivity. Under "exhaustive" tricarbonyliron complexation conditions, [5]dendralene gave a mixture of all possible mono- and bis-$Fe(CO)_3$ complexes (Scheme 2.9). By flash column chromatography the fraction containing mono-adducts, **2.35** (A) & **2.36** (B) could be separated from bis-adducts, **2.37** (*anti*-AC), **2.38** (*syn*-AC), **2.39** (*anti*-AD), & **2.40** (*syn*-AD). The mono-iron complexes were collected in a combined yield of 36% (for two compounds), and the bis-adducts in a combined yield of 25% (for 4 compounds). Compounds **2.35** (A), **2.36** (B), **2.37** (*anti*-AC), & **2.38** (*syn*-AC) could not be isolated in pure form by column chromatography or HPLC, hence the structural assignment of these compounds is tentative and based on ^{1}H NMR spectroscopic examination and mass spectrometry. The ratio of **2.35** (A) to **2.36** (B) was observed to be approximately 5 to 1 by integration of crude ^{1}H NMR spectra.[L]

[K] Symmetry-equivalent combinations are given in brackets.

[L] A ratio of **2.37** (*anti*-AC) to **2.38** (*syn*-AC) to **2.39** (*anti*-AD) to **2.40** (*syn*-AD) could not be extracted from crude ^{1}H NMR spectra due to peak overlap.



Scheme 2.9: The tricarbonyliron complexation of [5]dendralene. The scheme can be followed from [5]dendralene with each product labelled in pink according to the scheme in Figure 2.10.

The reported results were our best attempts to push the reaction to complete conversion of mono-iron complexes. The complexation of [5]dendralene was monitored by ^{1}H NMR spectroscopy, but the mono-iron complexes were stubbornly resistant to further complexation. Addition of more diiron nonacarbonyl or longer reaction times led to decomposition rather than conversion.

The compounds **2.39** (*anti*-AD) & **2.40** (*syn*-AD) were isolated by crystallisation and their molecular structures determined by single-crystal X-ray diffraction (Figure 2.11). The structures are the first we have observed of tricarbonyliron[n]dendralene complexes adopting non-planar conformations in the hydrocarbon ligand.

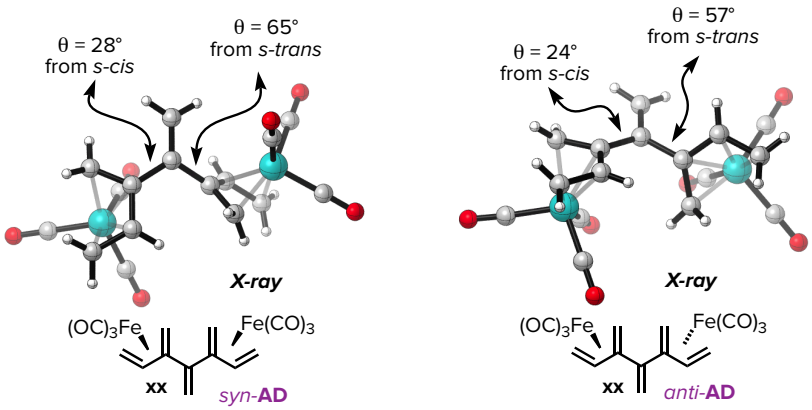


Figure 2.11: The molecular structures of the *terminal-terminal*-bis(tricarbonyliron) complexes of [5]dendralene, as determined by single-crystal X-ray diffraction.

In both cases (Figure 2.11), one of the (butadiene)tricarbonyliron fragments is almost in-plane and *s-cis* with the central alkene (as seen in other dendralene complexes), while the other is significantly out of plane and closer to *s-trans*. This differentiation in behaviour can be attributed to poor conjugation across the bifurcation point (i.e. cross-conjugation),[315] and implies poor electronic communication between the metal centres. On this basis we predict metal complexes of dendralenes higher than [4]dendralene to make poor functional materials in the ground state.[316]

2.2.4 [6]Dendralene Complexation

Just as the complexation of [5]dendralene was a significant step up in convolution from [4]dendralene, the same is true for [6]dendralene with respect to [5]dendralene. The fourteen potential combinations[M] of complexation for [6]dendralene are: **A** (or **E**), **B** (or **D**), **C**, *syn*-**AC** (or **CE**), *anti*-**AC** (or **CE**), *syn*-**AD** (or **EB**), *anti*-**AD** (or **EB**), *syn*-**AE**, *anti*-**AE**, *syn*-**BD**, *anti*-**BD**, *syn-syn*-**ACE**, *anti-anti*-**ACE**, or *syn-anti*-**ACE** (Figure 2.12). These possibilities can be subdivided according to their nuclearity, which is: three mononuclear, eight dinuclear, and three trinuclear.

[M] There would be many, many more possibilities if permutations were non-equivalent (e.g. if **AB** was not identical to **BA**), i.e. if the order of reaction of a diene had an impact on the overall product, as in the diene-transmissive Diels-Alder reaction.

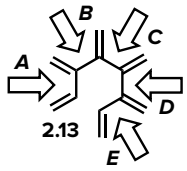
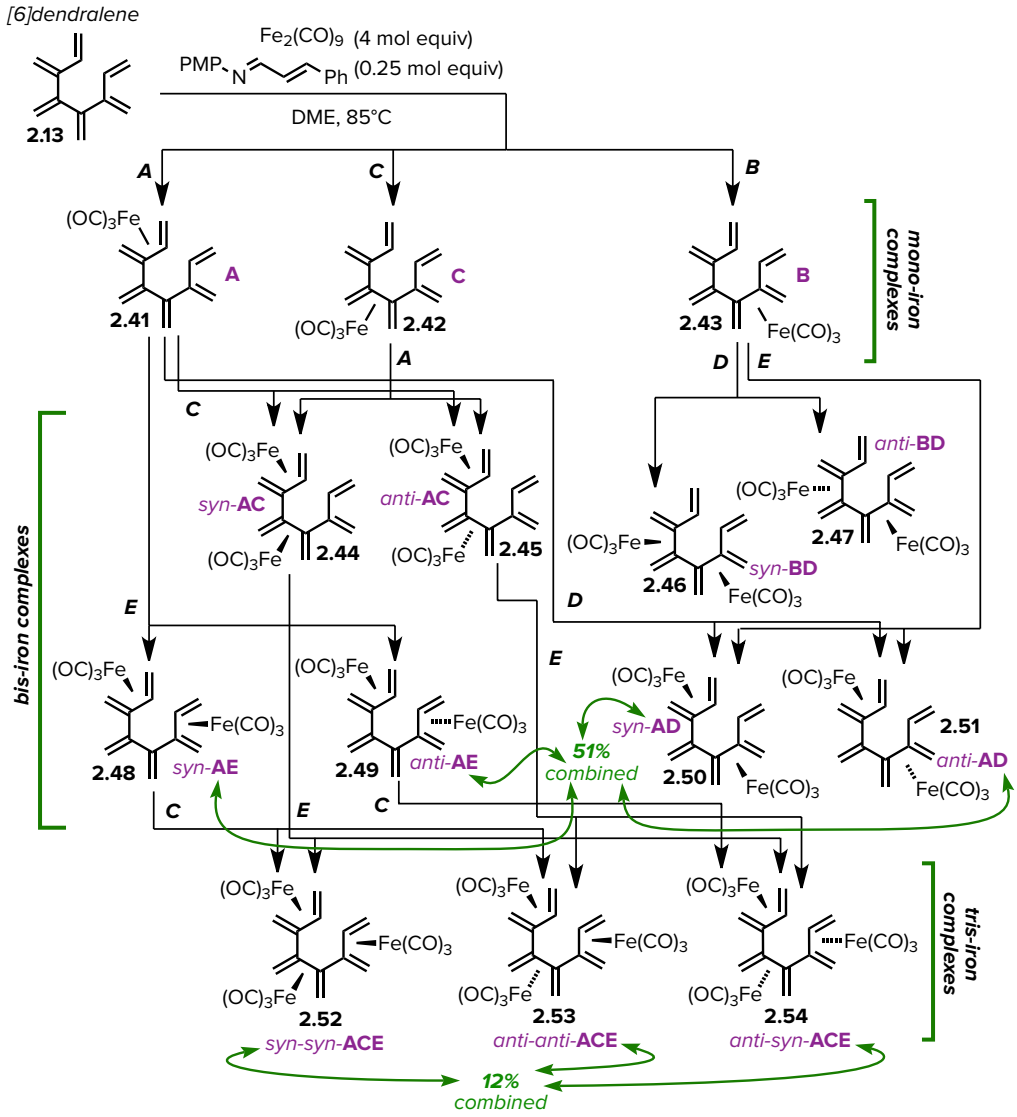


Figure 2.12: The potential complexation sites of [6]dendralene.

In contrast to the results of the complexation of [5]dendralene, [6]dendralene gave mostly bis(tricarbonyliron) [6]dendralene complexes **2.49** (*anti*-AE), **2.48** (*syn*-AE), **2.51** (*anti*-AD), & **2.50** (*syn*-AD) on reaction with diiron nonacarbonyl.

The isolated mixture of bis(tricarbonyliron)-[6]dendralene isomers **2.48**, **2.49**, **2.50**, & **2.51** accounted for more than half of the converted starting material (Scheme 2.10), The remainder of the recovered complexes were assigned by ^{1}H NMR spectroscopic analysis and mass spectrometry as a mixture of tris(tricarbonyliron) isomers **2.52**, **2.53**, & **3.54**. At this point the difficulty in separating diastereomeric mixtures of dendralene-iron complexes overcame our desire for analytically reportable ratios.

Regardless of the selectivity of the complexation, we knew that if the bis(tricarbonyliron)-[6]dendralene complexes underwent Diels-Alder reactions successfully at their exposed diene, then the mixture of diastereomers would be inconsequential. That is to say, that the tricarbonyliron groups are intended as practical protecting groups, and after their removal it doesn't particularly matter what face the tricarbonyliron group was on.

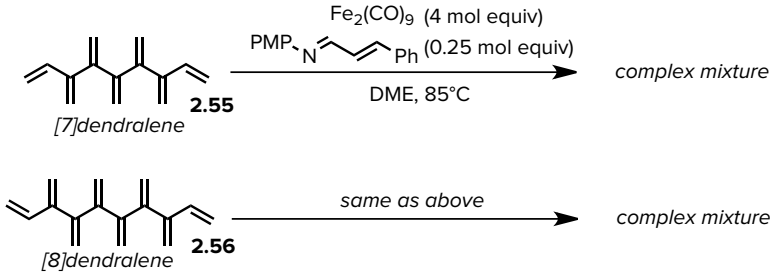


Scheme 2.10: The complexation of [6]dendralene, including degenerate pathways. The scheme can be followed from [6]dendralene with each compound (labelled in pink according to the scheme in Figure 2.12)) as an end- or branch-point.

Although the reaction arrows are not drawn as such, it is possible that equilibria exist between the complexes shown in Scheme 2.10. Such equilibria would significantly complicate any rational optimisation. We expect (and assume), like in the case for [4]dendralene, that shift-isomerisation does not occur to a significant extent during the complexation of [6]dendralene.

2.2.5 [7]&[8]Dendralene Complexation Attempts

The convexity in the coordination complexity of the lower dendralene series (3, 4, 5, & 6) should have been enough to halt further investigation of the higher dendralenes and their tricarbonyliron coordination. Regardless, we brashly set out to prepare the complexes of [7]- & [8]dendralene so that we could definitively establish or disprove alternating behaviour in the dendralenes and their complexation reactions. Unfortunately, the attempted complexation reactions were as unsatisfying as we had anticipated (Scheme 2.11).



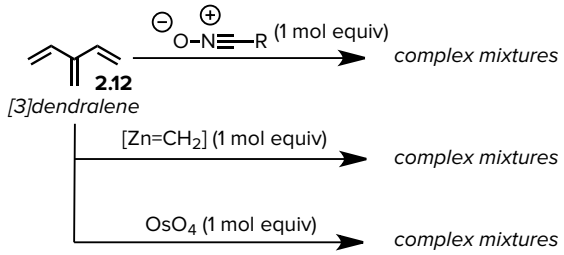
Scheme 2.11: The incomplete complexations of [7] and [8]dendralenes.

[7] & [8]Dendralenes gave mixtures of adducts under direct complexation conditions, and it was not possible to separate or isolate any of the compounds due to the limited scale of current [7] & [8]dendralene preparation methods. A more general understanding of [n]dendralene complexation will have to await the development of new methods.

2.3 Dendralene Complexes in Synthesis

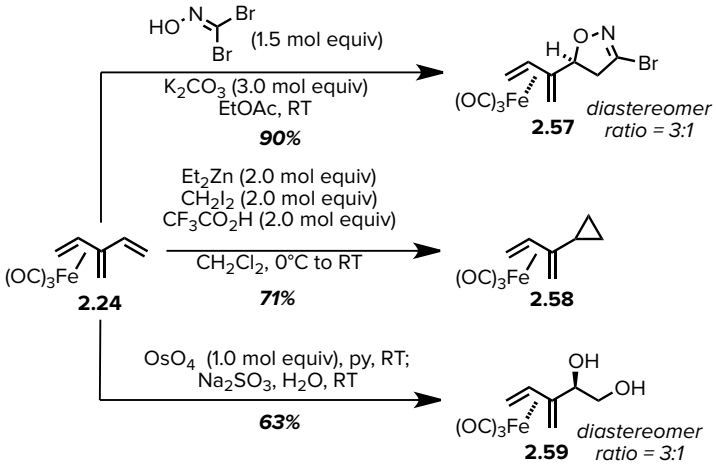
2.3.1 [3]Dendralene Tricarbonyliron In Synthesis

Attempts to react free [3]dendralene **2.3** with stoichiometric amounts of cyclopropanating agents or dipoles invariably led to the formation of complex mixtures (Scheme 2.12).



Scheme 2.12: Poor selectivity of [3]dendralene in [1+2] & [3+2] cycloisomerisations.

In contrast to the uncomplexed case, the tricarbonyliron complex of [3]dendralene **2.24** undergoes clean cycloaddition reactions[106,143] at the uncomplexed terminal alkene group, thereby leading to complexes of functionalized 1,3-butadienes **2.57**, **2.58**, and **2.59** (Scheme 2.13). These reactions are similar to those carried out by Lewis and coworkers on linear conjugated trienes[239] which were done to measure the reactivity of the alkene attached to a complexed diene. They were able to carry out a dihydroxylation on the free alkene, but were unable to cyclopropanate it.



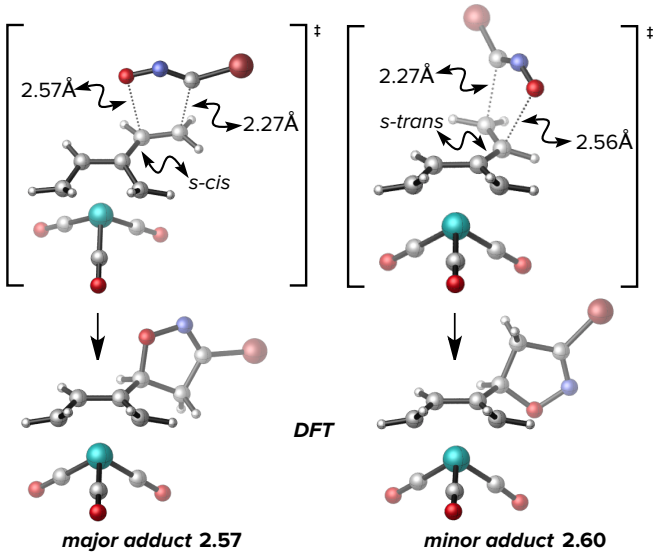
Scheme 2.13: Some reactions of tricarbonyliron[3]dendralene.

Mixtures of diastereomers (three to one) were produced in the 1,3-dipolar cycloaddition reactions of bromonitrile oxide (generated *in situ* from dibromoformaldoxime)[317-319][N] and OsO_4[320] with [3]dendralene–$Fe(CO)_3$ complex **2.24**. While it has not been possible to identify the major isomer experimentally,[O] insights have been gained through calculations. Scheme 2.14 depicts the DFT

[N] This is the same reaction/reagent that allowed Baran *et al.* and Barriault *et al.* to complete their 2009 and 2012 total syntheses of Vinigrol.

[O] NOESY and nOe-based NMR spectra were collected, but the lack of hydrogen on the $Fe(CO)_3$ group nullified attempts at NMR assignment of diastereomers.

transition-state structures leading to the two observed adducts. The TS leading to major adduct **2.57** involves the near in-plane, s-cis conformation of the dendralene with the dipole approaching from the uncomplexed face of the substrate. The TS for the minor adduct is 5.0 kJmol^{-1} less stable than that leading to the major adduct and results from addition to the uncomplexed face of [3]dendralene–Fe(CO)$_3$ **2.24** adopting the s-trans conformation. Regioisomeric TSs, involving approach of the dipole oxygen at the methylene terminus, were significantly (at least 9.6 kJmol^{-1}) higher in energy. Since the difference in transition state energies in these calculations appears to be dictated by the energy of the *s-cisoid* versus the *s-transoid* conformation of tricarbonyliron [3]dendralene, we believe they are sufficient to also explain the stereoselectivity of the OsO_4 osmate ester formation in the preparation of **2.59**. It would seem reasonable to extend this explanation to other additions to Fe(CO)$_3$-[3]dendralene complexes.

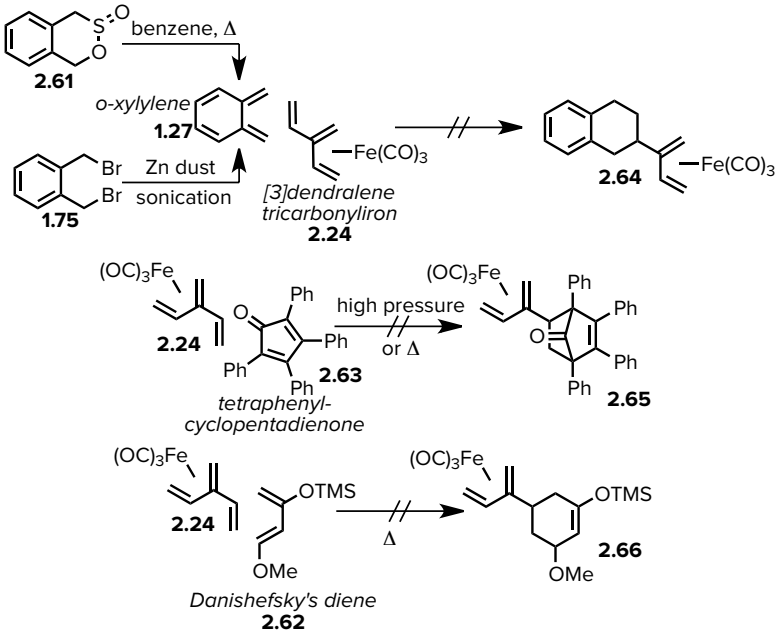


Scheme 2.14: Stereoselectivity of dipolar cycloadditions with tricarbonyliron[3]dendralene.

Samples of major isomer **2.57** contaminated with some minor isomer **2.60** that were left for an extended period could later be observed to contain only the major isomer. The two possibilities for this observation are that either the minor isomer is converted into the major isomer on standing, or that the minor isomer is less stable and selectively decomposes.

To capitalise on our success with dipolar cycloaddition reactions we sought to carry out [2+2] and [4+2] cycloadditions, and expand the variety of frameworks

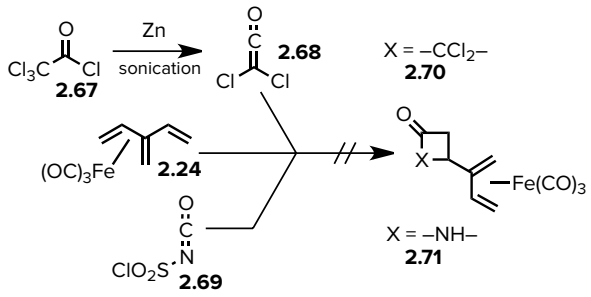
accessible from our tricarbonyliron[3]dendralene. The tricarbonyl group can typically be viewed as mildly electron donating,[35] and so we knew that carrying out Diels-Alder reactions on tricarbonyliron[3]dendralene would be difficult due to the lack of activation on the olefin that we wanted to react as dienophile.[321] Nevertheless we pursued several potent dienes that we knew to be highly reactive with even unactivated dienophiles (Scheme 2.15). Sultine **2.61** was prepared by the literature procedure,[322] but only unreacted starting material **2.24** and *o*-xylylene decomposition was observed. o-Xylylene **1.27** generated from zinc was similarly unreactive with complex **2.24**.[323] When *o*-xylylene failed we decided to be more systematic and turned to tetraphenylcyclopentadienone as a highly reactive electron-poor diene[149] and Danishefsky's diene **2.62** as a highly reactive electron-rich diene.[324,325] Unfortunately these too failed to give productive Diels-Alder cycloadduct at either high temperature (up to 100°C) or pressure (up to 16 kbar).



Scheme 2.15: Unsuccessful Diels-Alder reactions with tricarbonyliron[3]dendralene.

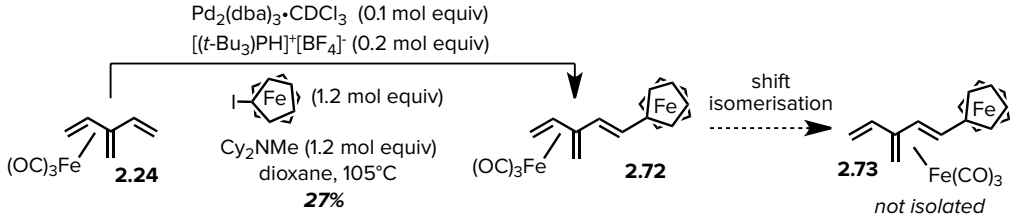
We hoped that in spite of the failure of tricarbonyliron[3]dendralene to react as a dienophile in Diels-Alder reactions that we would be able to achieve successful [2+2] cycloadditions. Here too all attempts were met with failure, and the tricarbonyliron group was presumably not able to survive the conditions; no starting material or reagents were observed in crude ^{1}H NMR spectra upon

attempted reaction of complex **2.24** with either dichloroketene, **2.68**, or chlorosulfonyl isocyanate, **2.69** (Scheme 2.16).



Scheme 2.16: Unsuccessful [2+2] cycloaddition attempts.

Tricarbonyliron[3]dendralene was successfully reacted with iodoferrocene in a palladium-catalysed Mizoroki-Heck cross-coupling reaction (Scheme 2.17). Low yields of the target ferrocenyl[3]dendralene tricarbonyliron complex, **2.72**, were isolated from the reaction. The catalyst and conditions were developed and optimised by Fu and coworkers[326-328] for the low temperature coupling of aryl chlorides with alkenes, and so it is particularly surprising that this substrate combination required high temperatures (105 °C) and long reactions (>12 hours) for high conversion. The reaction was carried out with several other aryl halides, but the product complex could not be separated from its shift-isomer **2.73**[P] that was formed as a byproduct of the reaction.[306]



Scheme 2.17: Successful Heck cross-coupling reaction with tricarbonyliron[3]dendralene.

The product, **2.72**, of the cross-coupling reaction demonstrates a use in the synthesis of a ferrocene-containing cross-conjugated system; applications of such structures in electronics devices have been suggested (Figure 2.13).[329,330]

[P] Although the shift-isomer was not isolated, its presence was confirmed by ^{1}H NMR spectroscopic analysis of crude and partially purified samples. The shift-isomers have mostly similar spectral properties to the terminally-complexed trienes, but have a distinctive pattern of a doublet-of-doublet, followed by a pair of coupled doublets (i.e. a terminal vinyl group) that was visible, along with other assignable resonances.

Biologically relevant carbonyliron complexes that have a ferrocene containing ligand have also been prepared by Rauchfuss and coworkers, where their mixed valence diiron nature was crucial to their desirable redox behaviour.[331]

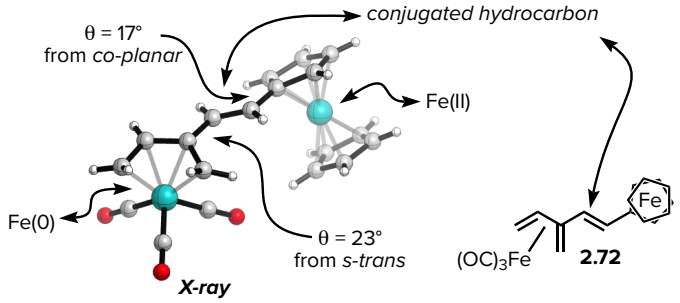
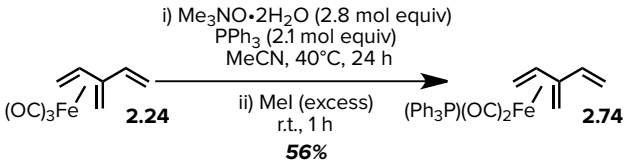


Figure 2.13: The molecular structure of ferrocenyl[3]dendralene tricarbonyliron (determined by single crystal X-ray diffraction).

Carbonyliron compounds can often be limited in their redox stability, because the complexes lose CO groups under oxidative conditions. Fortunately, it is possible to exchange ligands under oxidative conditions to make the complex more resistant to further oxidation.[332] Tricarbonyliron[3]dendralene was found to successfully undergo ligand exchange under these conditions by reaction with Me_3NO and PPh_3 (Scheme 2.18).[333Q]

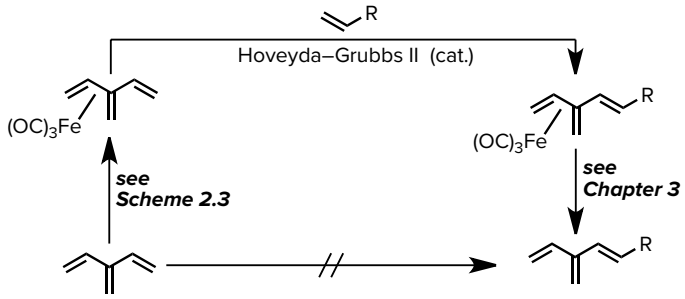


Scheme 2.18: Ligand exchange on tricarbonyliron[3]dendralene. This experiment was performed by Nik Osinski.[333]

Ligand exchange chemistry in combination with mixed valence compounds like complex **2.72** could allow the preparation of functional materials.

It is obvious in the modern era of organic synthesis to attempt to functionalise the free vinyl group on the tricarbonyliron[3]dendralene complex by metathesis chemistry. In fact, the cross metathesis reactivity of tricarbonyliron[3]dendralene, **2.24**, was so successful it has been expanded into its own section in Chapter 3 (Scheme 2.19).

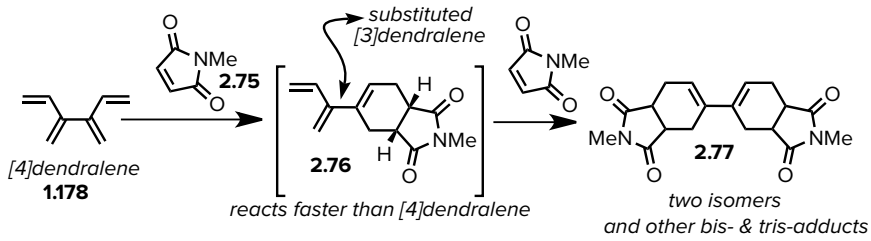
Q This experiment was performed by Nik Osinski under the supervision of Prof. Mick Sherburn.



Scheme 2.19: Successful tricarbonyliron[3]dendralene cross-metatheses (see Chapter 3).

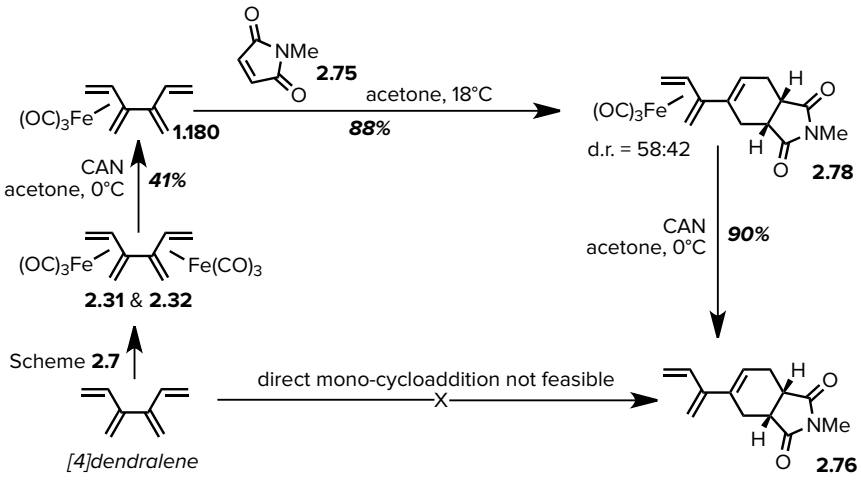
2.3.2 [4]Dendralene Tricarbonyliron In Synthesis

[4]Dendralene **1.178** undergoes a double cycloaddition reaction with dienophiles (like N-methylmaleimide, **2.75**): the second cycloaddition event is significantly faster than the first, so that the intermediate monoadduct **2.76** is not isolable, even if substoichiometric amounts of dienophiles are employed (Scheme 2.20).[291,293]



Scheme 2.20: The Diels-Alder reactivity of [4]dendralene towards N-methylmaleimide, **2.75**.

Monoadduct **2.76** is readily accessed (Scheme 2.21), however, through the tricarbonyliron complex **1.180** in a simple sequence that involves decomplexation of one tricarbonyliron group (**2.31**/**2.32**→**1.180**), cycloaddition (1.**180**→**2.78**), and decomplexation of the final tricarbonyliron group (**2.78**→**2.76**).

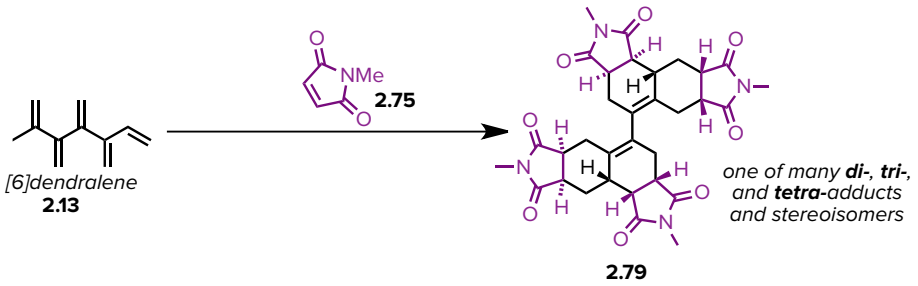


Scheme 2.21: Tricarbonyliron[4]dendralene to access previously inaccessible products.

Bis(tricarbonyliron)-[4]dendralene complexes **2.31** & **2.32** afford *terminal*-tricarbonyliron[4]dendralene **1.180** in a statistical yield alongside fully demetalated [4]dendralene and remaining starting material (Scheme 2.21). By removing one of the iron groups the terminal diene is now fully primed to undergo a Diels-Alder reaction with enforced selectivity. Diels-Alder reactions on 2-substituted dienes where the diene is not particularly activated (e.g. isoprene) often require high temperatures[334] or external activation.[335] In contrast, complex **1.180** undergoes the [4+2] cycloaddition at room temperature in just a few hours, implying that the butadienyl-tricarbonyliron group is more activating than we anticipated. During the reaction an inconsequential diastereomeric mixture is formed, which is subsequently simplified on oxidative removal of the tricarbonyliron group.

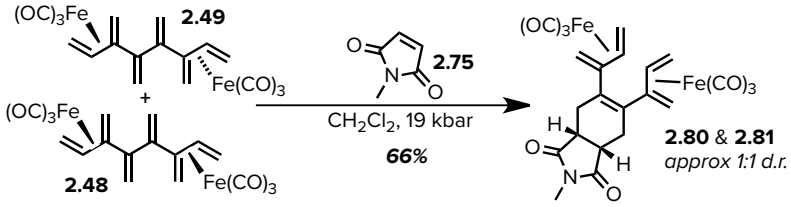
2.3.3 [6]Dendralene Hexacarbonyldiiron In Synthesis

[6]Dendralene **2.13** undergoes a multiple cycloaddition reactions with dienophiles (like N-methylmaleimide, **2.75**): after the first Diels-Alder reaction, subsequent reactions occur at a higher rate so that any intermediate monoadduct cannot be isolated, even if substoichiometric amounts of dienophiles are employed (Scheme 2.22). The reactivity profile of [6]dendralene is further complicated by the fact that many isomers of di-, tri-, & tetra-adducts are formed in the reaction due to poor stereo- & site-selectivity in the reactions.[336]



Scheme 2.22: [6]Dendralene in poorly selective Diels-Alder reactions.

Bis(tricarbonyliron)-[6]dendralene is prepared as a mixture of isomers (Scheme 2.10). The mixture can be directly treated with *N*-methylmaleimide in a Diels-Alder reaction 19 kbar (Scheme 2.23). After the reaction the unreactive isomers of bis(tricarbonyliron)-[6]dendralene can be removed by chromatography, and separating the two diastereomers of the Diels-Alder adduct, **2.80** & **2.81**.



Scheme 2.23: Tricarbonyliron[6]dendralene in a high-pressure Diels-Alder reaction.

Presumably each of the diastereomers, **2.48** & **2.49**, reacts highly stereoselectively with NMM, each giving only one product. There are three possible stereochemically distinct outcomes for this Diels-Alder reaction (Figure 2.14).

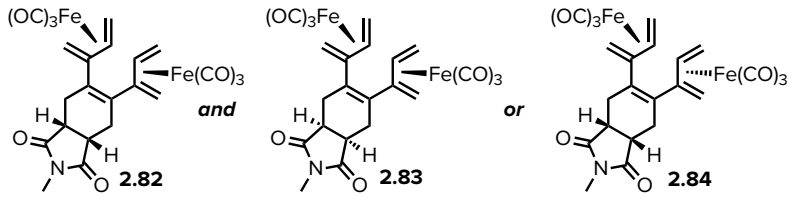
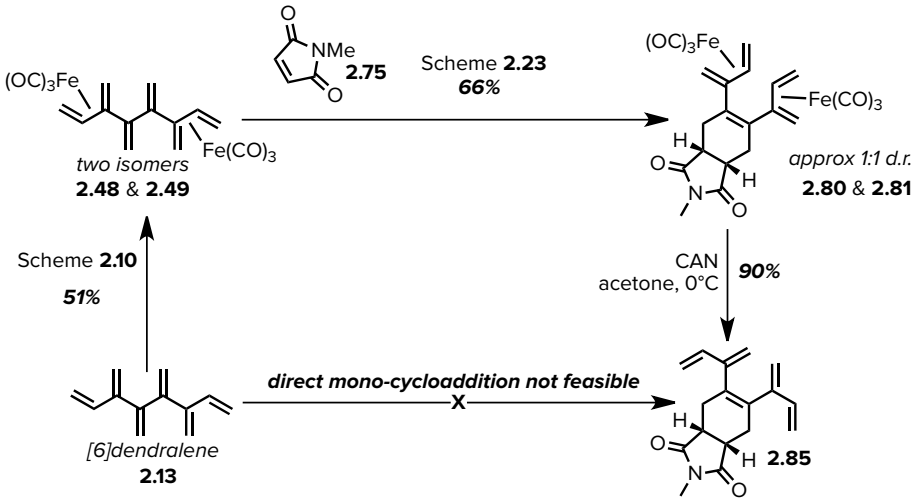


Figure 2.14: Possible stereochemistry of **2.80** & **2.81**.

High-pressure reactions (e.g. reactions at 19 kbar)[337] can be used to accelerate stubborn Diels-Alder reactions because of the highly negative activation entropy and activation volume of the pericyclic process. In this case, the steric bulk of the pair of tricarbonyliron groups, and their effect on the conformation of the internal diene, is what the high-pressure overcomes.

The Diels-Alder adducts, **2.80** & **2.81**, were isolated as a mixture of diastereomers; the mixture was inconsequential because removal of the tricarbonyliron group simplifies the question of stereoisomers by removing the iron-based stereocentres (Scheme 2.24). In this way we have selectively prepared the otherwise inaccessible internal Diels-Alder adduct, **2.85**, of [6]dendralene.



Scheme 2.24: [6]Dendralene Diels-Alder adduct, prepared selectively.

2.4 Conclusions

2.4.1 Progress

Tricarbonyliron complexes of [3]-, [4]-, [5]-, & [6]dendralenes were readily prepared as stable analogues of the corresponding [n]dendralenes (Figure 2.15). The complexes were prepared from the readily available hydrocarbons in one-step. After complexation, the compounds were stable towards a range of conditions, but the ligand could be readily released from the coordination compound by oxidation.

The tricarbonyliron complexes of [3], [4], and [6]dendralene were prepared with the moderate to good selectivity. Tricarbonyliron[3]dendralene was prepared as a single isomer in high yield. Bis(tricarbonyliron)[4]dendralene was prepared as a mixture of two diastereomers, and could be used to subsequently access *terminal*-tricarbonyliron[4]dendralene. Bis(tricarbonyliron)[6]dendralenes were formed with surprisingly high selectivity given the tremendously complicated possibilities for site and diastereoselectivity.

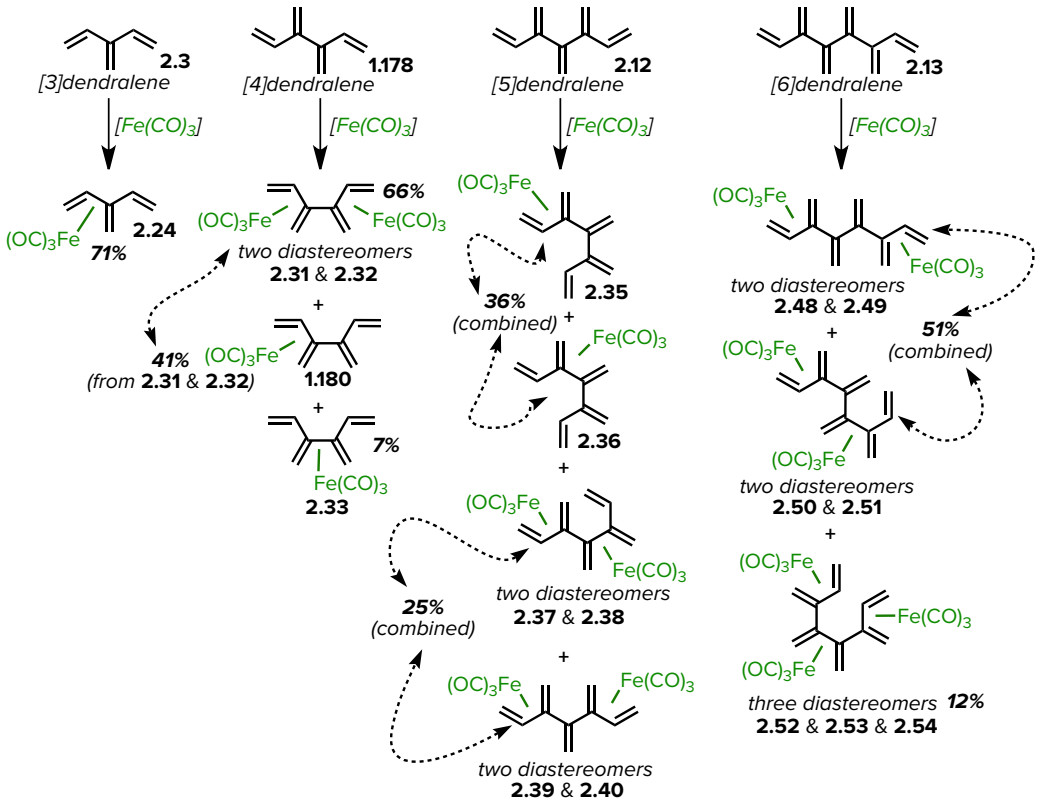
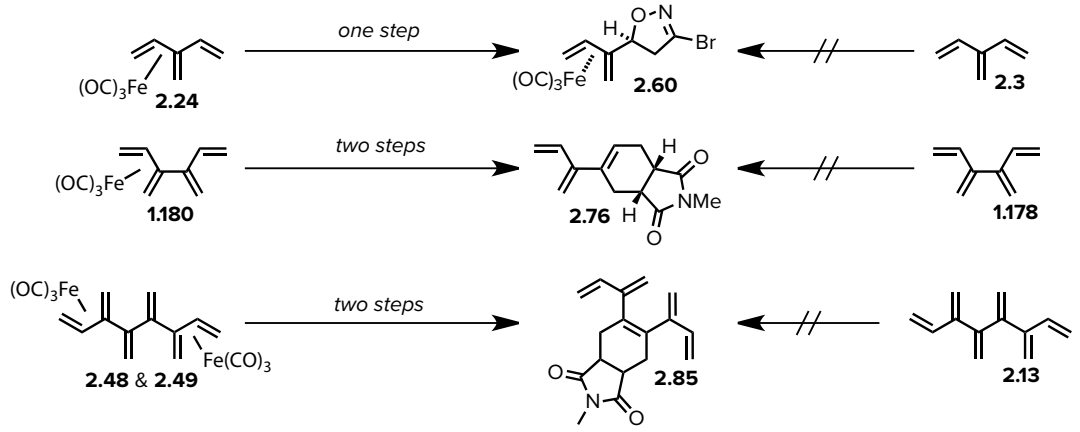


Figure 2.15: Tricarbonyliron[n]dendralene complexes prepared by direct metalation.

In measuring the selectivity of complexation for [3]-[6]dendralenes we also observed a curious alternation in behaviour, where [4] and [6]dendralenes gave selectively bis-terminal di-iron complexes, but [5]dendralene gave a mixture consisting mostly of mono-iron complexes.

These iron complexes greatly expand the synthetic potential of dendralenes by permitting transformations that cannot be achieved by direct reaction of the hydrocarbons (Scheme 2.25). Specifically, reactions can be carried out selectively at the terminal alkene of [3]dendralene, and Diels-Alder reactions can be executed selectively on [4]dendralene and [6]dendralene.



Scheme 2.25: Examples of the kinds of selectivity accessible with the tricarbonyliron[n]dendralenes.

2.4.2 Limitations

This work on the direct complexation of the [n]dendralenes is useful, but inherently limited by the dendralenes' innate selectivity (or lack thereof) for complexation. At the outset we aimed to test that innate selectivity as it would define the possible scope of our investigations. There is little room to optimise the complexation conditions, because although conditions did affect yields and ratios, we were not able to draw general rules that would allow us to develop better selectivity.

[3]Dendralene tricarbonyliron, **2.24**, allowed us to carry out many of the reactions we were interested in, but there were several classes of reactions in which it was unreactive or unstable.

Tricarbonyliron complexes of [4]dendralene were useful, but the ones we were most interested in accessing for synthetic applications, the monoiron-complexes **1.178** & **2.33**, were at best only formed as minor components of the direct complexation.

Under direct complexation conditions [5]dendralene gave a diverse mixture of adducts that were very difficult to separate from one another. This was a severe limitation of the methodology as a useful source of mono-*internal* tricarbonyliron[5]dendralene, **2.36**, was one of the goals of this research.

[6]Dendralene had significantly better selectivity than [5]dendralene under complexation conditions. The native selectivity for bis-*terminal* complexation limited the scope of the reactions we could test with these compounds.

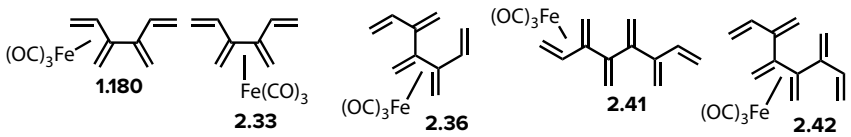


Figure 2.16: Some of the dendralene-complexes we were not able to directly prepare selectively.

All dendralenes had some degree of selectivity for the formation of terminal tricarbonyliron complexes. For the expansion of practical uses for the dendralene-tricarbonyliron complexes we would need a method for the generation of internally substituted dendralene complexes. The limitations of the research outlined in this chapter set the basis for the work reported in Chapter 4.

3

Cross-Conjugated Triene Stability

3.1 Introduction

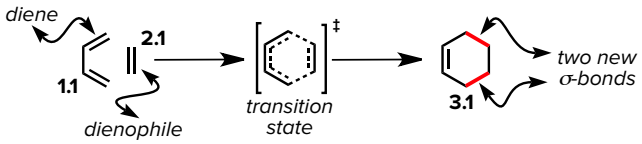
PREAMBLE

Cross-conjugated trienes are often highly reactive molecules. In some cases in attempting to prepare and isolate them they have been observed to undergo dimerisation *via* Diels-Alder, or Diels-Alder-like processes. We believed we could prepare them under mild conditions using the tricarbonyliron group.

The tricarbonyliron group is a very powerful protecting group for organic chemists interested in polyenes; it has the right balance of thermodynamic stability for enduring a synthetic sequence, and kinetic lability under the right conditions so it can be easily removed once its job is done. More than just for protection, the tricarbonyliron group can also activate a compound and allow reactions which are ordinarily unfruitful.

3.1.1 The Diels-Alder Reaction

The Diels-Alder reaction is one of the most powerful reactions (if not the most powerful outright) in organic synthesis.[338,339] The overall reaction involves a conjugated diene and a dienophile undergoing a concerted pericyclic cycloaddition to form a six-membered ring containing two new σ-bonds, and up to four new stereocentres (Scheme 3.1).

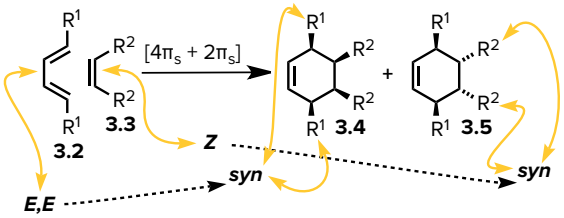


Scheme 3.1: The Diels-Alder reaction; one of the possible mechanisms.

A more comprehensive review of many of the aspects of the Diels-Alder reaction (particularly with respect to intramolecular variants) lies outside the scope of the present investigations, and so those aspects will not be extensively introduced.

DIELS-ALDER REACTION SELECTIVITY CONSIDERATIONS

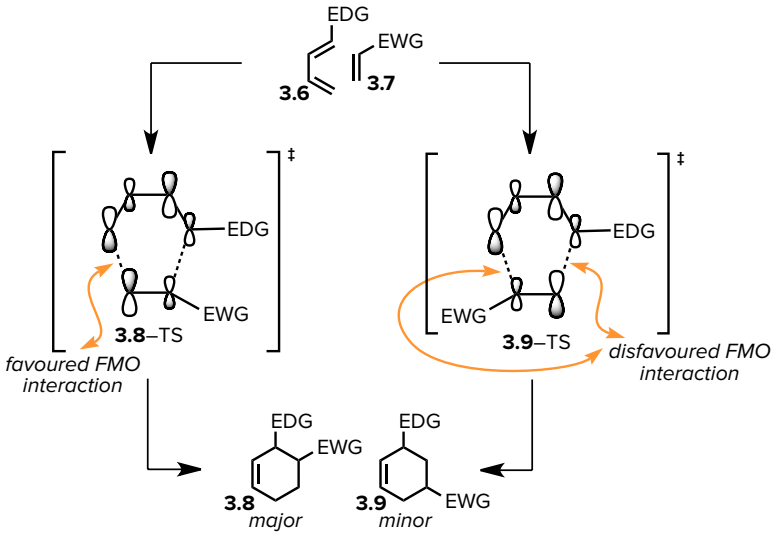
The Diels-Alder reaction has many stereochemical complications, these come hand-in-hand with the power of the reaction, these are: Alder's *cis*-principle, regioselectivity, endo/exo selectivity, and π-facial selectivity.[337] The Diels-Alder reaction mechanism is stereospecific. This means that the relative stereochemistry of the products is determined based on the geometry of the starting materials (Scheme 3.2). This is called *Alder's cis-principle*, and means that substituents that are *cis* in the starting materials are *cis* in the product(s). This is shown in Scheme 3.2, where *E,E* geometry in the diene leads to *cis* substitution in the product, and naturally *E,Z* would lead to *trans*. The stereospecificity of the reaction is due to the fact that there is an orbital symmetry requirement,[340] in that the reaction proceeds suprafacially with respect to both components.



Scheme 3.2: Diels-Alder *cis* stereospecificity, and the fixed relationship between starting material geometry and product stereochemistry.

Alder's cis principle is not to be confused with the diene conformational requirements for the reaction. The [4+2] cycloaddition demands the *s-cis* conformation in the diene component, and therefore dienes that are locked *s-cis* are often more reactive than equivalent dienes that are free to rotate; by the same token, locked *s-trans* dienes are unreactive.

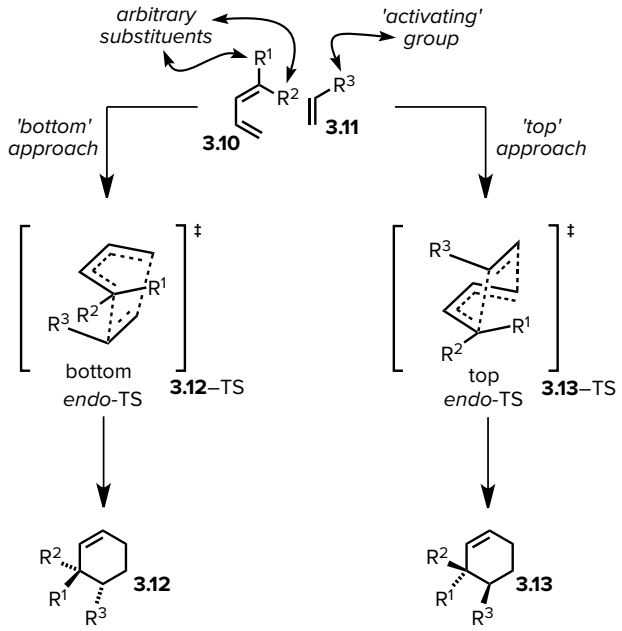
For unsymmetrical reactants there are two distinct ways in which they can associate (Scheme 3.3). The Diels-Alder reaction empirically favours the formation of 1,2- and 1,4-adducts (also called *ortho* and *para* adducts) with respect to the diene and dienophile activating substituents (*regioselectivity*). The explanation most prominently used to explain regioselectivity is frontier molecular orbital (FMO) theory,[341] based on the dominant orbital interaction between the highest occupied molecular orbital (HOMO) of one component and the lowest unoccupied molecular orbital (LUMO) of the other (Scheme 3.3).



Scheme 3.3: Diels-Alder regioselectivity, as dictated by FMO interactions between diene HOMO and dienophile LUMO.

The form of selectivity in the Diels-Alder reaction that has universally had the weakest explanation is *endo/exo selectivity*, which is the selectivity for the orientational relationship between the diene and dienophile (Scheme 3.4). This is commonly explained in the literature by *secondary orbital interactions* (SOIs), which tend to favour *endo* over *exo* products, and were first invoked by Woodward & Hoffman.[340] A transition state that is stabilised by SOIs has orbital interaction between the diene and dienophile, and these interactions are said to exist only in the transition state. There is significant dispute about the existence of SOIs, as it

seems that the observed selectivity can be explained by solvent effects, steric interactions, hydrogen bonding, and electrostatic forces.[342,343] SOIs, as proposed, are unobservable and unfalsifiable, and so are an inherently undesirable hypothesis, but stubbornly they persist.[344]



Scheme 3.4: *Endo* & *exo* selectivity of Diels-Alder reactions.

π-Facial selectivity is a well explained facet of Diels-Alder selectivity and is generally dictated by steric effects, where the dienophile approaches the diene from the π-face[A] with the least steric encumbrance. Occasionally other factors come into play, like polarisability or electrostatic interactions.[337]

FMO theory is useful to quickly explain the results of many Diels-Alder reactions,[341] but the theory has limitations,[345] especially when the reaction involves an orbital combination that is not HOMO(diene) and LUMO(dienophile).[135,137]

DIELS-ALDER REACTION MECHANISM

The precise mechanism of the Diels-Alder reaction has been the source of much discussion and controversy[346,347] since its initial report by Diels & Alder in 1928. The controversy and precise mechanism of the Diels-Alder cycloaddition is of

[A] This is a biased perspective, an equally valid view is that "the diene approaches the dienophile" or that "they approach each other." It is often easier to rationalise a reaction from the perspective of one of the reactants, but it is also necessary to acknowledge that this reasoning does not represent an impartial reality.

interest to us because we seek a fuller understanding of a series of Diels-Alder reactions later in this chapter.

Pericyclic reactions were defined by Woodward & Hoffman,[340] as "reactions in which all first-order changes in bonding relationships take place in *concert* on a closed curve."[B] The description was clarified by Dewar and coworkers in 1984[348] by defining *concerted* reaction as "one which takes place in a single kinetic step," and a "*synchronous* reaction is a concerted reaction in which all the bond-breaking and bond-forming processes take place in parallel, all having proceeded to comparable extents in the TS." "A *two step* reaction [now called *stepwise*] is one which takes place in two distinct steps, *via* a stable intermediate." In fact, much of the disagreement in the mechanism of the Diels-Alder reaction has arisen from disagreement about the definitions of *concerted*, *synchronous*, and *stepwise*, and their respective contributions towards the possible reaction pathways of a given Diels-Alder reaction. A spectrum of possible Diels-Alder reaction mechanisms from *concerted* to *stepwise* is shown in Figure 3.1.

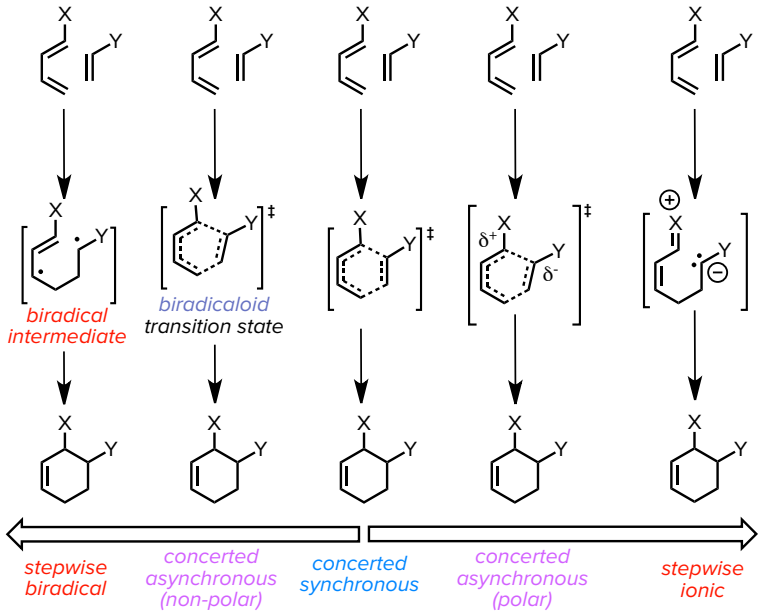


Figure 3.1: The spectrum of possible mechanisms for the Diels-Alder reaction. Substituents X & Y can dramatically effect which variant of the mechanism is taken.

[B] All emphasis in quoted statements is inserted by this author to clarify the contentious terms that are being discussed.

When Dewar proposed in 1984 that "multibond reactions cannot normally be synchronous"[348] he was widely derided in the chemical literature and community,[346,349] and his conclusions about synchronicity were soon disproven by his own calculations.[350,351] In a sense Dewar was right, although not in the manner intended, as the development of reaction dynamics led to the understanding that although *on average* there is no asynchronicity in most symmetrical pericyclic reactions (called *static* asynchronicity) they in general have some degree of *dynamic* asynchronicity in any individual example.[352] Synchronicity is a controversial aspect of the discussion of Diels-Alder reaction mechanisms because it describes the continuum of mechanisms between concerted reactions and those that are stepwise (Figure 3.1).

The debate on the mechanism of the Diels-Alder reaction has centered on whether or not there are discrete intermediates between starting materials and observed products.[347] The difference between such a stepwise–diradical and a pericyclic mechanism is more than mere terminology or semantics; if a discrete diradical intermediate is generally formed in Diels-Alder reactions then there are ways of extending their lifetime—such as by facilitating singlet to triplet relaxation[160c]—and thus potentially accessing new reactivity.

While the mechanism of the Diels-Alder reaction is still being clarified with new findings,[352] the consensus appears to be that most Diels-Alder reactions proceed through moderately- to highly-asynchronous concerted mechanisms,[353] with some low and variable proportion of products being derived from a discrete stepwise process.

We have thus far described the Diels-Alder reaction according to traditional Transition-State Theory, where *stepwise-biradical* and *pericyclic* are two separate pathways which the starting material 'chooses between' based on the respective free energies of activation. The modern understanding of reaction mechanisms is

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c There are chemists who believe that in spite of the evidence against discrete diradicals, that they are merely extremely short-lived (Raymond Firestone has said that no degree of stereospecificity could rule out a diradical mechanism, Houk, K. N. *et al. Acc. Chem. Res.* **1995**, *28*, 81–90), and are thus indistinguishable from a concerted mechanism. If a biradical is formed in the reaction in its excited singlet state it will be able to extremely rapidly close to form the cyclohexene adduct, but if it is allowed to relax to a triplet state then the intermediate would be much longer lived, allowing time for radical reactions and bond rotations.

that reactants travel dynamically on a three-dimensional potential energy surface, rather than committing to a specific mechanism (Figure 3.2).

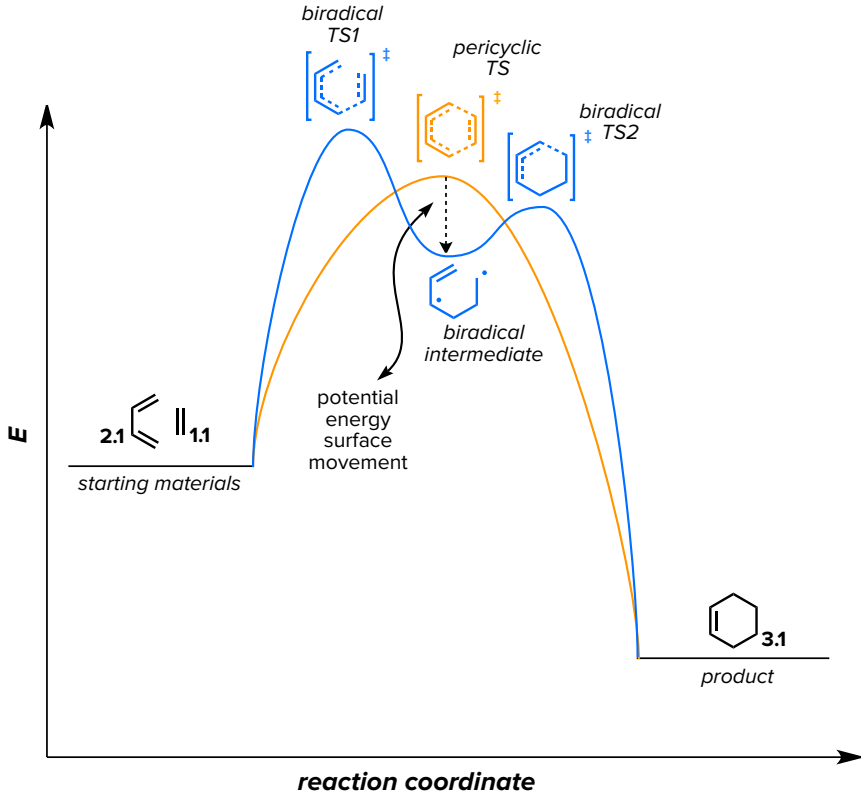


Figure 3.2: Reaction coordinate diagram depicting the Diels-Alder reaction between a hypothetical diene and dienophile (relative energy levels are arbitrary). Shown is the possibility for a *concerted* pericyclic mechanism to dynamically travel through a *stepwise* intermediate. This figure is a 2D cartoon representation of a 3D potential energy surface.[354]

From this perspective, it is possible that the transition states leading to diradical or zwitterionic intermediates may indeed be higher in energy than that of a concerted transition state, but that those intermediates are dynamically accessible *via* a common concerted transition state (Figure 3.2).[354]

A strictly biradical mechanism for the Diels-Alder reaction has been mostly abandoned in the modern academic literature.[D] In contrast to the stepwise-biradical mechanism, it is more generally accepted that highly polar Diels-Alder reactions can advance through ionic intermediates, and become *formal* Diels-

[D] Which is not to say that it has necessarily been thoroughly discredited, but just that the best arguments of its proponents—transition state asynchronicity, and examples of stepwise 'exceptions'—have been incorporated into generally accepted knowledge.

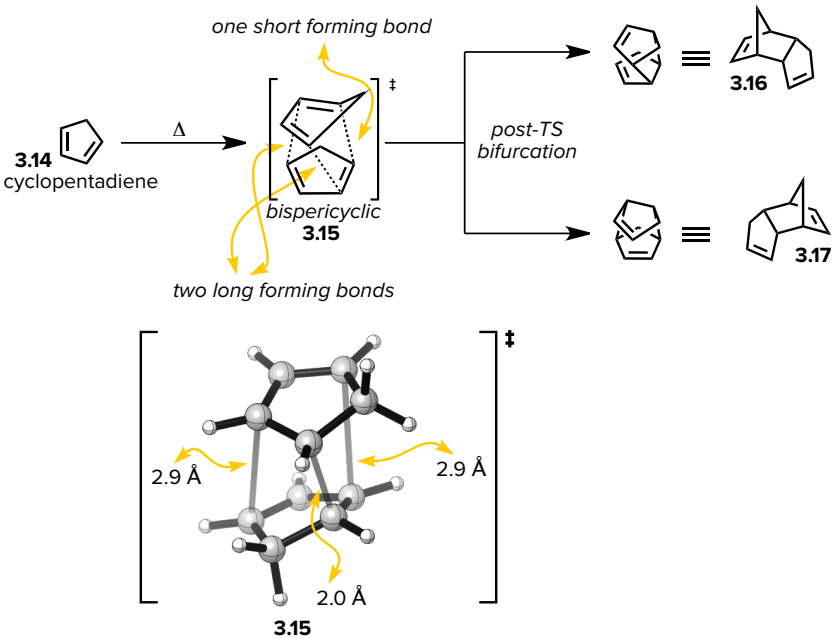
Alder reactions, or more precisely, a Michael/Aldol (or Michael/Mannich) domino sequence (Figure 3.1).[355-359]

From here onwards it will be assumed that the Diels-Alder reaction occurs exclusively *via* a concerted mechanism.

3.1.2 Bispericyclic Cycloaddition Reactions

The term *bispericyclic* was first used to describe a cycloaddition mechanism in 1977 by Snyder and coworkers[360] to describe a transition state in which a symmetry allowed $_{\pi}6_{s}$ movement of electrons is destabilised by the presence of a symmetry disallowed $_{\pi}8_{s}$ process. The term in this context was short-lived as further experiment[361] did not bear out preliminary results; and for two and a half decades the term was lost, until, when chance came, the term ensnared a new mechanism.

Bispericyclic was revived by Caramella and coworkers,[362] who discovered—while investigating the Diels-Alder dimerisation of cyclopentadiene—a transition state that could not be simply described as a pericyclic formation of two σ-bonds at the expense of two π-bonds (i.e. a Diels-Alder reaction). Density functional calculations indicated that the lowest energy pathway for the dimerisation of cyclopentadiene involved a bispericyclic transition state(Scheme 3.5).[362]

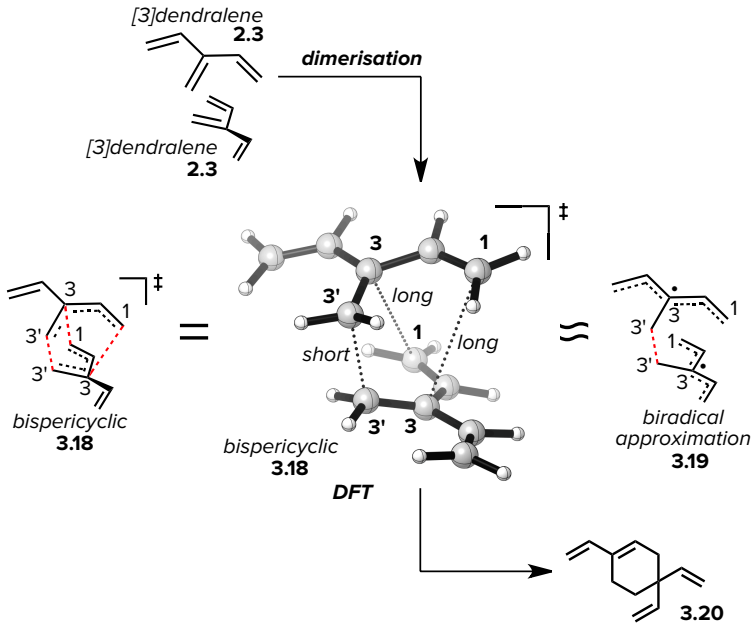


Scheme 3.5: Bispericyclic dimerisation of cyclopentadiene.[362]

The transition state of this *bispericyclic* pathway contains the partial formation of three bonds, one short and two long. After the transition state the pathway on the potential energy surface of the reaction bifurcates, with each of the resultant paths leading to enantiomeric products (**3.16** & **3.17** for cyclopentadiene dimerisation). This mechanism is so close in energy and structure of the transition state to a biradical mechanism that when it was first observed computationally by Caramella and coworkers it was called crypto-diradical.[363] Since its discovery, bispericyclic mechanisms for dimerisation have also been observed with methacrolein,[363] butadiene,[364,365] and cyclopentadienone.[150] Bispericyclic mechanisms have been reported only with dimerisations (i.e. where both dienes are identical), but there is no reason why non-identical dienes cannot undergo a bispericyclic cycloaddition.

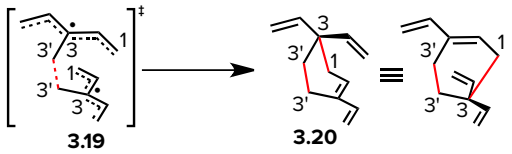
BISPERICYCLIC DIMERISATION OF [3]DENDRALENE

During studies on the dendralenes, Sherburn and coworkers observed rapid decomposition of some of the compounds during storage and handling.[294] Subsequent density functional calculations by Paddon-Row[292] showed that [3]dendralene can readily dimerise *via* a bispericyclic mechanism (Scheme 3.6).



Scheme 3.6: The bispericyclic dimerisation of [3]dendralene. The transition state structure (**3.18**) was determined by density functional calculations. Also shown is a biradical approximation of the transition state (**3.19**), where the long forming bonds are shown as unformed, leaving two pentadienyl radicals.[292]

The bispericyclic dimerisation of [3]dendralene is shown in Scheme 3.6. The transition state structure **3.18** has one short forming-bond at *ca.* 2.0 Å and two long forming bonds at *ca.* 3.3 Å, an asynchronicity of 1.3 Å. For comparison, Houk and coworkers describe a Diels-Alder transition state as *"extremely asynchronous"* where the difference between the short and long forming bonds is *ca.* 0.8 Å.[352] The degree of TS asynchronicity is high enough that a close approximation is that the short forming bond is fully formed, and the long bonds not formed at all in the TS, i.e. as biradical **3.19**. The geometry and electronic structure of such a transition state is best described by two pentadienyl radicals which are sufficiently strongly coupled through the developing C3'···C3' bond to produce a closed-shell singlet state **3.19** (Scheme 3.7).[292] This TS is termed a *biradicaloid* approximation. Closure to the [3]dendralene dimer occurs through two degenerate pathways involving C1–C3 bond formation.



Scheme 3.7: Biradicaloid dimerisation of [3]dendralene leading to two equivalent structures.[292]

A strict biradical mechanism is not entirely ruled out by these computational studies.[292E] A biradical mechanism would involve as a rate limiting step the formation of two pentadienyl radicals *via* a *syn* or *anti* approach of the [3]dendralenes in the transition state (Figure 3.3). Only the *anti*-TS (**3.22**) was calculated, as the *syn*-TS (**3.21**) is effectively the same as a bispericyclic-TS, and *anti*-TSs are generally lower in free energy due to higher entropy.[364] At a low level of theory, a biradical mechanism *via* an *anti*-TS was found to be very similar in transition state energy to a bispericyclic mechanism.

[E] See the supporting information of Paddon-Row & Sherburn 2012 for preliminary calculations and a discussion of the possibility of a biradical dimerisation.

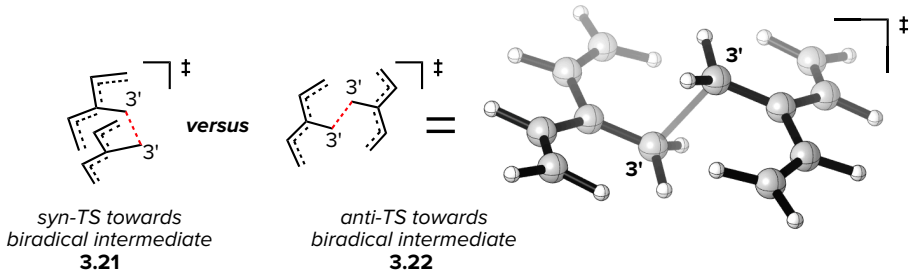


Figure 3.3: The possible biradical mechanism would involve as a rate limiting step the formation of two pentadienyl radicals and a C3'–C3' bond. This intermediate can be formed by an *anti*-, or a *syn*-approach of two molecules of [3]dendralene in the transition state.[292]

3.1.3 Substituted [3]Dendralenes

One can imagine four different ways to modify [3]dendralene with a single substituent: at C1 with E-configuration, at C1 with Z-configuration, at C2, and at C3'. The literature contains many examples of each of these, but there's a trend, only 1*Z*-, 2-, and 3'-substituents are reported to be stable, and substitution at C2 and C3' is far more common. (Figure 3.4).[288,366,367] In both cases, substituted derivatives **3.23** and **3.24** were found to be considerably more stable than the parent hydrocarbon **2.3**.

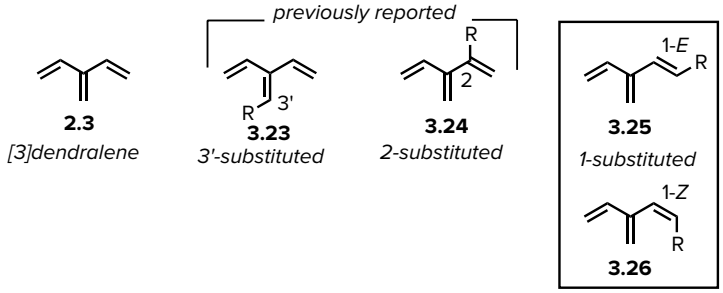


Figure 3.4: Possible substitution patterns on [3]dendralene.

The parent [3]dendralene has one potential diene and two potential dienophiles to react in a hypothetical Diels-Alder reaction. The different patterns for substitution on [3]dendralene (Figure 3.4) uniformly desymmetrise the dendralene, i.e. monosubstitution invariably creates two inequivalent diene sites, and hence the question of *site selectivity* (Figure 3.5) when participating in Diels-Alder reactions.

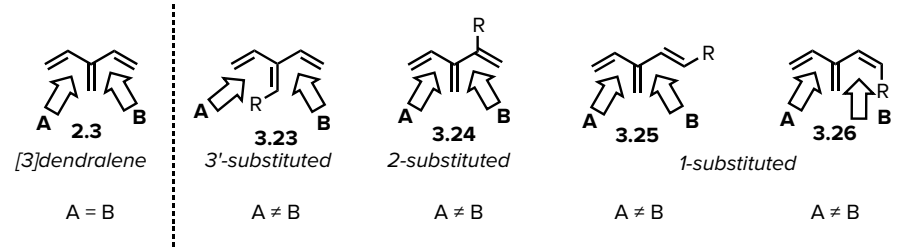


Figure 3.5: Site-selectivity with the substituted [3]dendralene series.

TERMINALLY-SUBSTITUTED [3]DENDRALENES

All published syntheses of 1-substituted [3]dendralenes involve reports of isolated examples (Figure 3.6).[368-373] All the reported 1*E*-substituted examples are of simple alkyl derivatives.[369-371] It is interesting to note that in 1971, **3.30** was reported as the least substituted dendralenic natural product by von Schantz and coworkers,[374,375] but in 1973 it was shown to be a misassignment of known terpene **3.33**.[375]

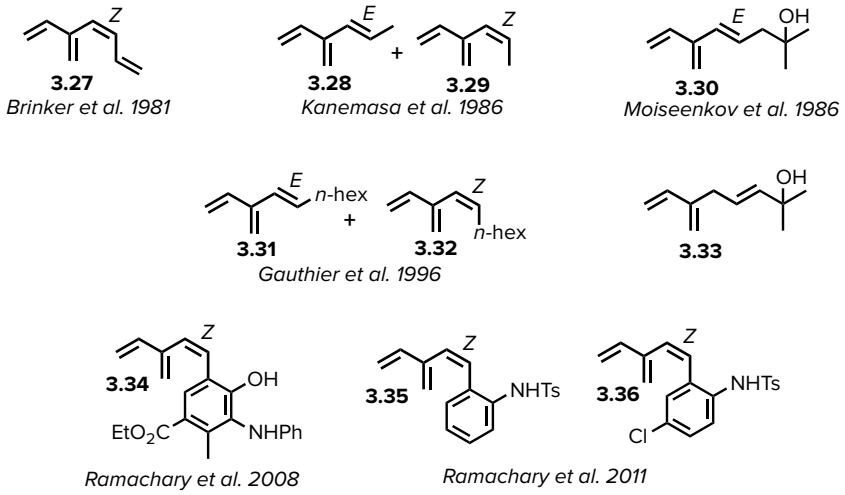
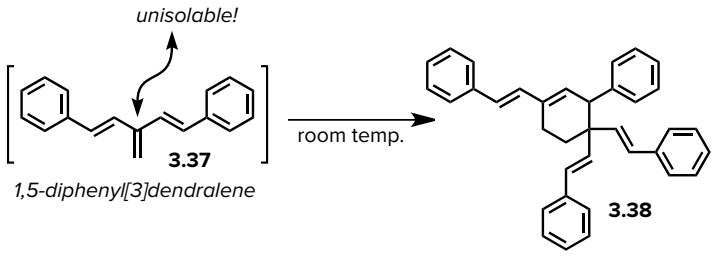


Figure 3.6: 1-Substituted [3]dendralenes.[368-373]

Mulzer and coworkers reported some time ago[376] that attempts to form 1*E*,5*E*-diphenyl-[3]dendralene (i.e. **3.37**) led to the isolation of the DA dimer[377,378][F] (Scheme 3.8) and, very recently, Singh & Ghosh showed that attempts to form 2-carboethoxy-1,5-diaryl [3]dendralenes also resulted in the isolation of DA dimers.[379]

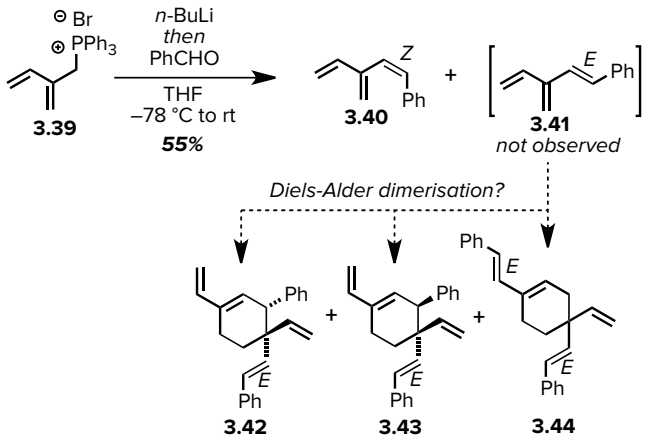
[F] This property is by no means limited to trienes. Mulzer *et al.* showed that 1,3-*E*-diphenyl-1,3-butadiene and related compounds exhibit the same, but less exaggerated, dimerisation behaviour.



Scheme 3.8: 1,5-Diphenyl [3]dendralene dimerisation.[376]

3.1.4 1*E*/*Z*-[3]Dendralenes *via* Wittig Olefinations

Earlier attempts towards a more general 1-substituted [3]dendralene synthesis in the Sherburn group[380][G] initially focussed on the direct formation of the 1,2-disubstituted C=C bond using Wittig reactions of the phosphonium salt **3.39** (Scheme 3.9). Surprisingly, reaction of the semi-stabilised ylide derived from **3.39** with benzaldehyde led to the generation of mixtures of four products: a *ca.* 1:1 ratio of 1*Z*-phenyl-[3]dendralene **3.40** and cyclohexenes **3.42**, **3.43** & **3.44**. Compounds **3.42**–**3.44** appeared to be the DA dimers of the 1*E*-phenyl-[3]dendralene isomer **3.41**, which would be an anticipated product since the Wittig reaction of semi-stabilised ylides is often non-stereoselective.[381]



Scheme 3.9: Wittig olefination on triphenylphosphonium salt **3.39** leads to a mixture of 1*Z*-phenyl[3]dendralene and dimers derived from 1*E*-phenyl[3]dendralene.

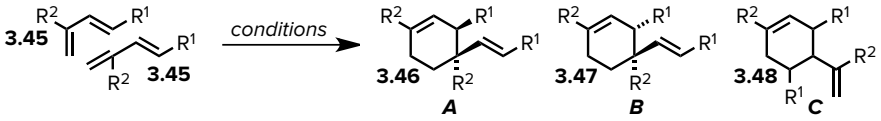
Similar results to those depicted in Scheme 3.9 were obtained in Wittig reactions of phosphonium salt **3.39** with substituted benzaldehydes. The isolation of DA

[G] The Wittig approaches to 1*Z*/*E*-[3]dendralenes reported in this introduction were carried out by Emma Pearson under the supervision of Michael Sherburn.

dimers **3.42**–**3.44** was surprising in light of the mild temperature (room temp.) and relatively low concentrations (0.1 M) employed in these reactions. Based on the result depicted in Scheme 3.9, it would appear that not two but *only one aromatic group* is required to promote facile DA dimerisation of a [3]dendralene, so long as that group is located at the 1-position. Furthermore, within the mono-substituted dendralene series, we note that the facile DA dimerisation behaviour *is specific to the 1E-aryl [3]dendralene isomer*: the 3'-phenyl,[382,383] 2-phenyl,[367] and 1*Z*-phenyl [3]dendralene[380] congeners are stable towards dimerisation and can be stored neat at ambient temperature.

3.1.5 Diels-Alder Dimerisation of 2-Substituted, and 1,3-Substituted 1,3-Butadienes

The identification of a bispericyclic mechanism for Diels-Alder dimerisation of [3]dendralene led us to believe that diene dimerisations might in general be bispericyclic, at least to some degree. This was reinforced by the finding that 1*E*-substitution led to very rapid dimerisation. We hypothesised that there was something special about aryl groups at this position based on the observed stability of 1*E*-methyl [3]dendralene compared to the inability to isolate the 1*E*-phenyl derivative. 1-Substituted dendralenes can be considered 1,3-disubstituted butadienes. Shown in Scheme 3.10 is the generalised dimerisation of 1,3-substituted butadienes, and accompanying it is Table 3.1, where we sought to collate all the related compounds we could find with dimerising butadienes.



Scheme 3.10: Diels-Alder dimerisation of 1,3-substituted 1,3-butadienes.

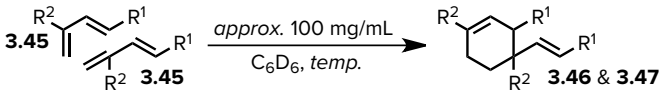
	reference	*(R^1 =)*	*(R^2 =)*	*reaction conditions*	***A*** : ***B*** : ***C***
1	384-386	H	Ph	neat, 160°C, 1 h, 90%	83:17 (A/B:C)
2	376,387	Ph	H	PhH, 130°C, 48 h, 91%	58:42 (A:B)
3	377,378,388,389	Ph	Ph	neat, 22°C, 6 h, 99%	>95:5 (A:B)
4	390	H	$CH=CH_2$	C_6D_6, 95°C, 22 h, 90%	>95:5 (A/B:C)
5	391	$CH=CH_2$	H	unreported, 40–50%	*A:B unreported*
6	376,377	Ph	CH=CHPh	triene not isolable, 75%	N/A *symmetrical*
7	134,136,392	H	CO_2Me	MeOH, r.t., 12 h, 58%	>95:5 (A/B:C)
8	139,393,394	H	CN	neat, 5°C, 3 months, >75%	>95:5 (A/B:C)
9	395	H	SO_2Ph	unreported	75:25 (A/B:C)

Table 3.1: Comparison of diastereo- and site-selectivity in 1,3-substituted 1,3-butadiene dimerisations.

It appears that it is a common phenomenon for butadienes substituted at the 1-position, the 2-position, or 1,3-disubstituted to be prone to Diels-Alder dimerisation (Table 3.1). The tendency towards dimerisation seems to be roughly in the order of 1,3- >> 2- > 1-substituted. In terms of the selectivity of the dimerisation, the diastereoselectivity appears to favour the formation of **A** over **B**, (Scheme 3.10) and for the site-selectivity of the reaction, the dienophilic alkene tends to be the 1,1-disubstituted alkene over the 1,2-disubstituted alkene (i.e. the formation of **A** & **B** is favoured over **C**). Unfortunately it is difficult to draw many conclusions from this information, as very few kinetic studies were done, so although the compounds were reported to be *'unstable'* and *'difficult to handle'* in most cases, an objective tendency towards dimerisation was not measured. Dimerisation experiments were typically done under what may be colloquially described as *overkill* conditions, e.g. entry 1, neat 2-phenylbutadiene was heated at 160 °C.[384]

RATE EFFECT OF 2-SUBSTITUTED VERSUS 1-SUBSTITUTED BUTADIENE DIMERISATION

Among the many investigations into the mechanism of the Diels-Alder reaction that were carried out in the 1980's and 1990's were a series of kinetic and stereoselectivity/stereospecificity *tests* by Mulzer and coworkers (Scheme 3.11, Table 3.2).[376-378] This research was based on the belief that the peculiar rate-enhancing abilities of a radicalophilic group (e.g. aryl groups) in Diels-Alder reactions could only be explained by a stepwise mechanism involving diradicals.



Scheme 3.11: Diels-Alder dimerisation of 1,3-butadienes.

	(R^1 =)	(R^2 =)	*temp.*	k_{rel}
1	Ph	Ph	50 °C	1×10^6
2	Ph	CH=CHPh	25 °C	$>10^8$
3	Ph	H	130 °C	1×10^3
4	Me	Ph	127 °C	300
5	Ph	Me	130 °C	90
6	t-Bu	Ph	130 °C	400
7	Ph	t-Bu	130 °C	9
8	H	H	—	1

Table 3.2: Rate comparison of 1-substituted 1,3-butadienes *versus* 2-substituted 1,3-butadienes. Rates (k_{rel}) are reported relative to butadiene in the gas phase (entry 8). Rates were measured by ^{1}H NMR in C_6D_6. (This table is a selection of the data collected by Mulzer and coworkers.)[376]

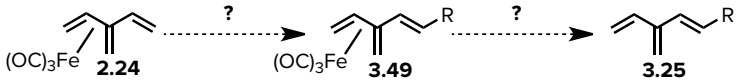
Pairwise comparisons can be made between entries in Table 3.2 in order to ferret out the effect of different substituents on dimerisation rates. 1,3-Diphenylbutadiene (Entry 1) has a dimerisation rate on the order of 10^6 times that of butadiene *cf.* 2-phenylbutadiene (Entry 3) which exhibits a rate smaller by a factor of 10^3. So rate enhancements can be additive in effect. Entry 4 *vs.* 5 and Entry 6 *vs.* 7 are comparisons which both show the same effect, where conjugating substituents at the 2-position have a greater positive impact on rate of dimerisation than the same substituent at the 1-position. This effect is on the order of a three-fold to a fifty-fold increase in rate.

The data provided by Mulzer and coworkers[376] is not comprehensive in its scope, and significantly more kinetic data would be needed to fully probe the nature of these effects.

3.1.6 Aims: Synthesis & Mechanism

The inability to prepare 1*E*-[3]dendralenes was vexing because we envisaged that the substitution pattern would be a useful route to preparing complex polycyclic compounds.

In Chapter 2 we described the preparation and isolation of the tricarbonyliron complex of [3]dendralene. We foresaw that the tricarbonyliron group would protect the [3]dendralene from dimerisation and allow us to access substituted [3]dendralenes in protected form. Thermally mild oxidative conditions could allow the observation of the free trienes for the first time (Scheme 3.12), and subsequent observation of their decomposition.



Scheme 3.12: The proposed general route to 1*E*-[3]dendralenes.

We were very interested in the mechanism of the dimerisation, this is because we wished to test our biradicaloid approximation of the transition state (Figure 3.7). Describing the mechanism accurately is more than just a semantic nicety, it allows us to predict what substituents are stabilising and destabilising, and shows us how to better control the Diels-Alder reactions of dendralenes in general. A dimerisation occurring by a *biradicaloid* mechanism should be accelerated by substitution with radicalophilic moieties proportional to their radical stabilising power; this is an aspect we sought to test.

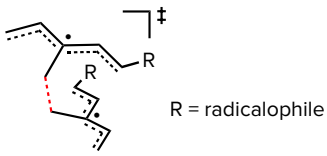
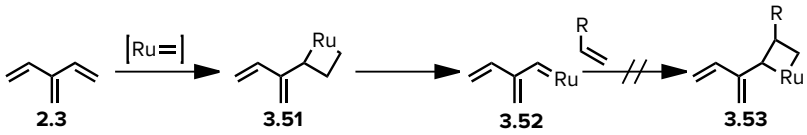


Figure 3.7: Testing the biradicaloid hypothesis by systematic modification of the substituent on a 1*E*-[3]dendralene.

3.2 Synthesis of 1*E*-[3]Dendralenes

3.2.1 1*E*-[3]Dendralene Complexes *via* Cross-Metathesis Reactions

Despite our best efforts, we have been unable to achieve successful metathesis reactions with naked [3]dendralene.[H] These results carry over to the higher dendralenes when the reaction attempted is a cross-metathesis reaction. The deleterious effect of conjugated dienes has been noted in the literature; it has been suggested[396] that the inactivity of the α,β-unsaturated carbene **3.52** generated after initial [2+2] and retro-[2+2] is to blame for the lack of productive reaction (Scheme 3.13).[397][I]



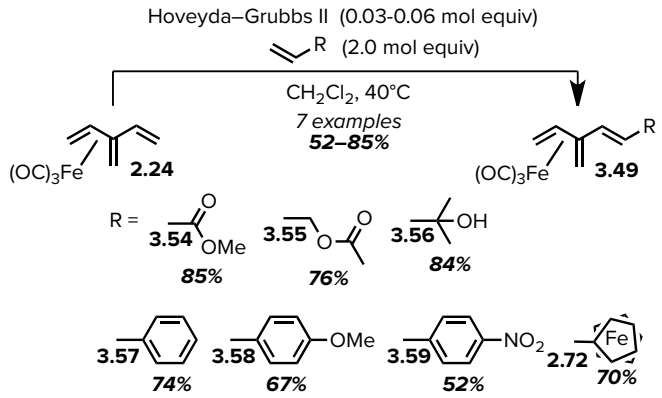
Scheme 3.13: The poor reactivity of [3]dendralene in cross-metathesis reactions.

In contrast to the results on the parent hydrocarbon, the tricarbonyliron complex of [3]dendralene **2.24** undergoes smooth cross-metathesis reactions with a range of alkene partners with either the Grubbs second-generation precatalyst[398] or, more conveniently,[J] the Hoveyda–Grubbs second-generation precatalyst[399,400] to form substituted products **3.49** with an *E*-alkene geometry (Scheme 3.14). The successful alkenic cross-metathesis partners can be labeled as either Type I or Type II in their metathesis behaviour according to the categorisation method reported by Chatterjee and coworkers.[401] This route allowed the general preparation of ester (**3.54** & **3.55**), 3° alcohol (**3.56**), aryl (**3.57**, **3.58**, & **3.59**), and metalloaromatic (**3.60**) substituted [3]dendralene complexes.

[H] This author carried out initial attempts at cross-metathesis on [3]- and [4]dendralene.

[I] A side-effect of this explanation is that for certain ring sizes it may be possible to carry out RCM on dendralenes as Schwab *et al.* report that α-β unsaturated carbenes can undergo slow and inefficient ring-closing metathesis.

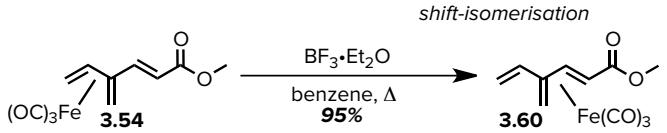
[J] The benzylidene precatalyst gave styrene self-, and cross-metathesis adducts that significantly complicated purification of some cross-metathesis products, especially during the scoping/optimisation stage of research.



Scheme 3.14: Cross-metathesis on tricarbonyliron[3]dendralene.

Type I and Type II alkenes were good cross-metathesis partners, but Type III alkenes such as α-methyl styrene or methyl methacrylate could not be induced to undergo metathesis with tricarbonyliron[3]dendralene under normal conditions.

For the cross-metathesis reactions that had lower yields, the explanation was usually a combination of shift-isomerisation of the product complex and incomplete conversion of starting material. Shift-isomerisation on the formation of similar compounds was reported in one of the only previous syntheses of 1*E*-substituted [3]dendralene complexes (Scheme 3.15).[10] This seems to occur more when the substituent is electron-withdrawing, such as with carbomethoxy or para-nitrophenyl substituents, due to the electron donating nature of the tricarbonyliron group.[35,305K]



reported by Martina & Brion *Tet. Lett.* **1982**, *23*, 865–868.

Scheme 3.15: Observed shift-isomerisation of 1*E*-carbomethoxy[3]dendralene tricarbonyliron complex.[10,143]

Some of the structures derived from cross-metathesis were amenable to analysis by single crystal X-ray diffraction (Figure 3.8). The X-ray derived molecular structures of the 1*E*-aryl[3]dendralene tricarbonyliron complexes show that the

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K This effect is discussed to some extent by Whitlock and coworkers (Whitlock *et al. J. Am. Chem. Soc.* **1971**, *93*, 2483–2492) in the shift-isomerisation of linear polyene tricarbonyliron complexes. It is clear that this is not the only determining factor in isomerisation, but seems to be a driving force in some cases.

cross-conjugated polyene ligand is almost fully conjugated and in-plane in the solid state.

Cross-conjugated polyenes connecting electron-rich moieties to electron-poor moieties have been explored for a long time.[402-404] This is due to the promising nonlinear optical (NLO) effects they exhibit, which have potential applications in functional materials and molecular machines & devices. The reported general route to substituted tricarbonyliron[3]dendralene complexes (Scheme 3.14) allows the preparation of new classes of compounds with potential NLO properties (Figure 3.8). If the electron-donating or withdrawing nature of the iron-containing terminus is not optimal it can be modified by ligand substitution,[332] which has been demonstrated in Chapter 2 (pages 71–77).

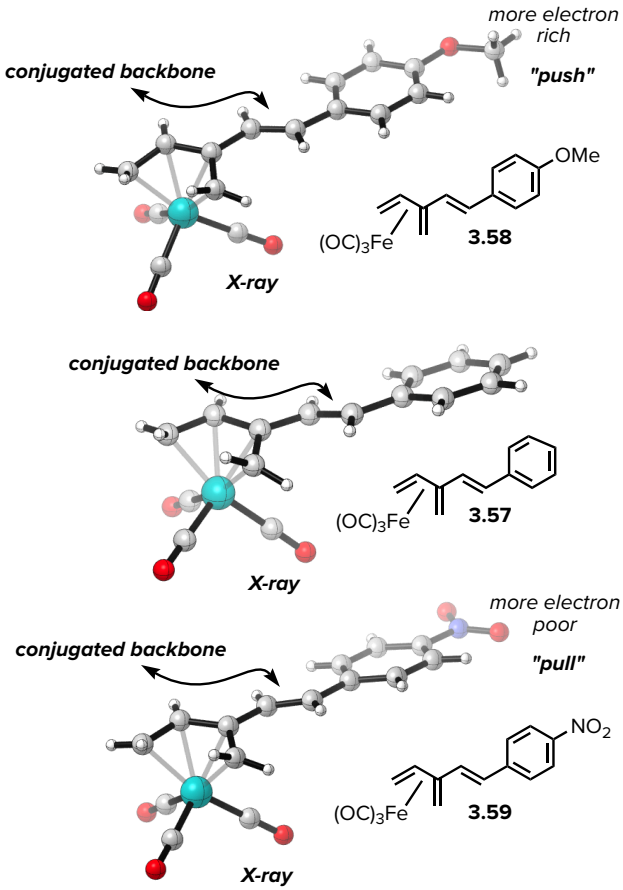
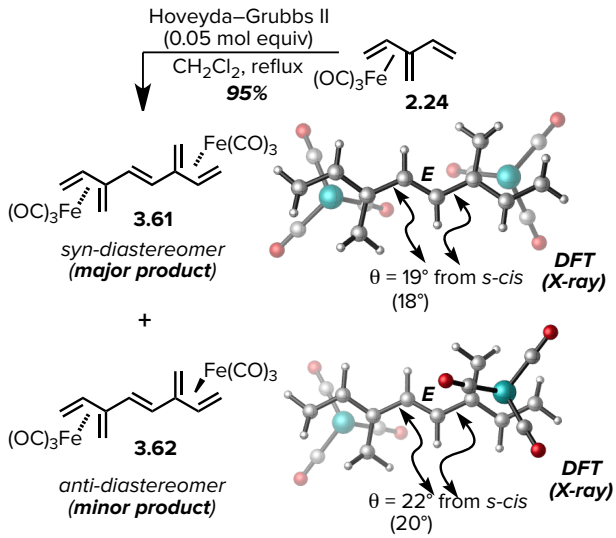


Figure 3.8: Molecular structures of 1*E*-aryl[3]dendralene tricarbonyliron complexes *via* single crystal X-ray diffraction.

3.2.2 Tricarbonyl[3]dendralene Dimer *via* Cross-Metathesis

The self-metathesis reaction of the tricarbonyliron complex of [3]dendralene **2.24** leads to an excellent yield of diastereomeric products **3.61** and **3.62** (*ca.* 2:1 ratio), from which the *E,s-cis,s-cis,syn* bis(tricarbonyliron) complex **3.61** is the major isomer, as demonstrated by single crystal X-ray analysis (Scheme 3.16). The DFT-optimised structure[L] (gas phase) correlates well with that seen in the crystal structure of the major isomer. The conformational preference of the ligand in structures **3.61** and **3.62**, with the uncomplexed alkene *s-cis* to the complexed diene, is consistent with that seen previously for the tricarbonyliron complex of [3]dendralene **2.24** (page 59).



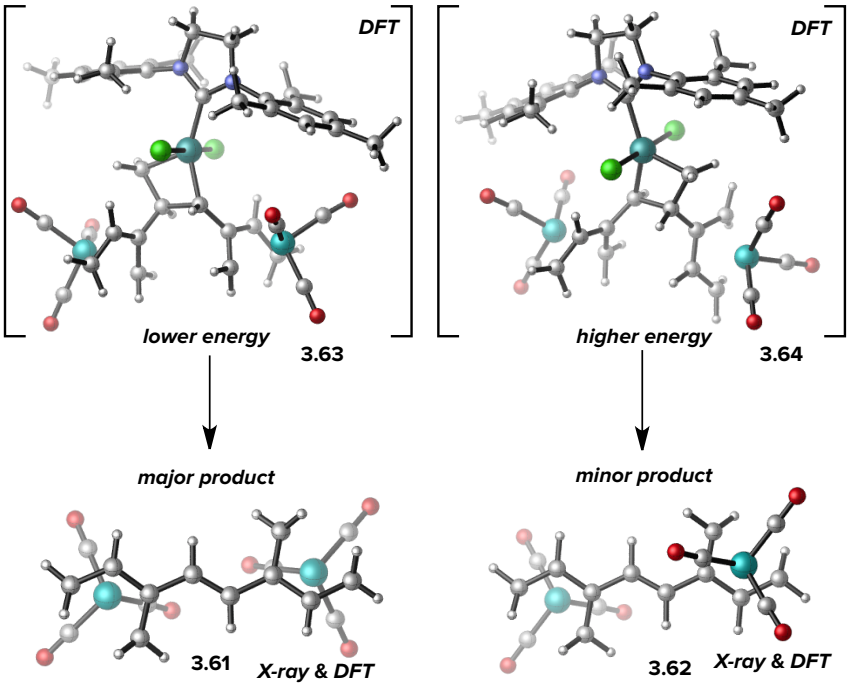
Scheme 3.16: Self–cross-metathesis of tricarbonyliron[3]dendralene.

Whereas the *syn* isomer **3.61** is favored experimentally, DFT calculations show that the *anti* diastereomer is the more stable structure to the extent that the equilibrium distribution is 68:32 in favor of *anti* diastereomer **3.62** and its conformers. Thus, the metathesis reaction does not appear to be under thermodynamic control. Experimentally, we see no change upon exposure of either complexes **3.61** or **3.62** to conditions significantly more forcing than those employed in the self-metathesis reaction (up to 0.50 molar equivalents of Hoveyda–Grubbs second-generation precatalyst, $CDCl_3$, 67 °C, 6 h). This result is

[L] DFT calculations reported in this chapter were performed at the B3LYP/6-31G(d) level of theory by Prof. Michael N. Paddon-Row unless otherwise stated.

consistent with self-metathesis products **3.61** and **3.62** being type IV olefins and spectators in cross-metathesis reactions.[401,405]

The *syn*-disposition of the $Fe(CO)_3$ groups is somewhat surprising, however, in light of the formation of the *anti*-isomers from direct complexation reactions. The DFT calculated structure of the ruthenacyclobutane intermediate[406,407M] towards the *syn* isomer **3.61** is 5 $kJmol^{-1}$ lower in energy than that leading to the minor product **3.62** (Scheme 3.17). Evidently, the two sterically bulky $Fe(CO)_3$ groups are accommodated well into the lower energy stereoisomeric intermediate.

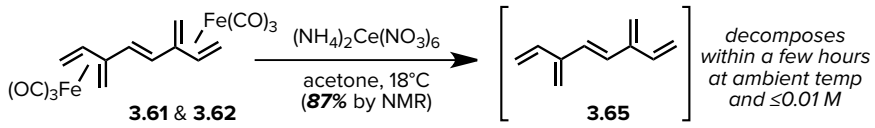


Scheme 3.17: Structure of the DFT calculated ruthenacyclobutane intermediates *en route* to the [3]dendralene–$Fe(CO)_3$ complex self-metathesis product.

Finally, upon oxidative decomplexation with CAN, 2,6-di(methylene)-1,4,7-octatriene **3.65**, one of the simplest acyclic structures with both linear conjugation and cross conjugation, is formed (Scheme 3.18). This highly reactive new hydrocarbon exhibits UV absorption maxima characteristic of both a through-conjugated diene and triene (λ_{max}=220 and 267 cm^{-1}). Further attempts were made to study this compound, but these attempts led to rapid decomposition of the

M Grubbs *et al.* (2001) make no claims as to whether the ruthenacyclobutane is an intermediate or a transition state; Piers *et al.* (2005) directly observe the 14-electron ruthenacyclobutane by NMR spectroscopy.

cross-conjugated pentaene into unidentified products. The inability to purify this compound after decomplexation was what initially led to the development of the oxidation/extraction protocol which allowed us to isolate cleanly the 1*E*-[3]dendralenes reported (*v.i.*).

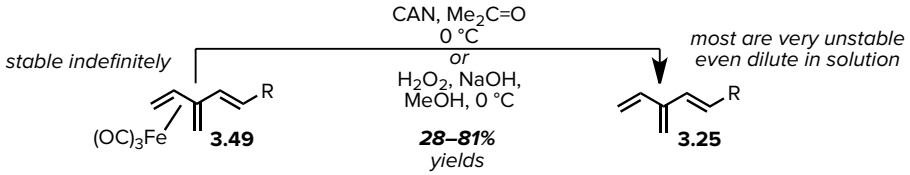


Scheme 3.18: Release of branched octapentaene **3.65**.

3.2.3 Decomplexation of Substituted [3]Dendralene Complexes

With **3.54**–**3.59**, & **2.72** in hand we had access to a broad range of stable dendralene precursors. Gratifyingly, oxidative decomplexation[408] was sufficiently rapid at 0 °C to generate, after workup, $CDCl_3$ solutions of 1*E*-aryl, alkyl and carbomethoxy-substituted [3]dendralenes **3.41**, & **3.66**–**3.71** that were free of DA dimerisation products and other contaminants, as shown by NMR spectroscopic analysis (Scheme 3.19).

CAN was used preferentially as the oxidative decomplexing agent (see Chapter 1 for a comparison of demetalation reagents, p. 8); the reaction was extremely rapid, giving complete conversion within 10 minutes at 0 °C. Initially CAN was used exclusively as the oxidative reagent, but this led to decomposition when used with the electron rich 4-methoxyphenyl group on **3.69**. Thus we were forced to develop conditions for two-electron oxidation that was tolerant of oxidation sensitive moieties, but that would still allow low temperatures and short reaction times to isolate and observe the unstable 1*E*-[3]dendralene. Although many two electron oxidants are known to remove tricarbonyliron, most require large excesses of reagent, high temperatures, and long reaction times.[39] We were able to find demetalation conditions, which had been developed by Franck-Neumann and coworkers in 1983,[40] that afforded clean 1*E*-[3]dendralene after minor modification.



R = –CO_2Me (**3.66**), –CH_2OAc (**3.67**), –$C(CH_3)_2$OH (**3.68**)

R = –Ph (**3.41**), 4-methoxyphenyl (**3.69**), 4-nitrophenyl (**3.70**), –ferrocenyl (**3.71**)

Scheme 3.19: Demetalation of substituted [3]dendralene tricarbonyliron complexes.

The reported preparation of free 1*E*-[3]dendralenes represents the first general syntheses of this elusive class of substituted dendralene.

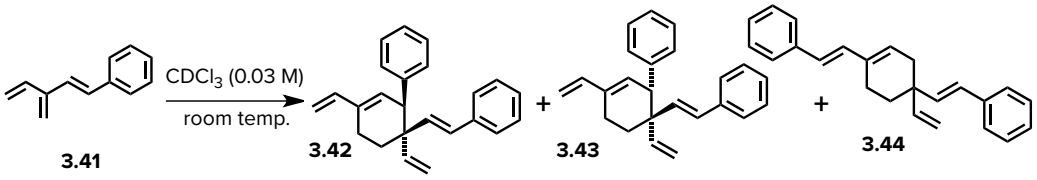
3.3 Diels–Alder Dimerisation of [3]Dendralenes

3.3.1 Half-Life of Dimerisation Measurements

To test the mechanism of the dimerisation of the 1*E*-[3]dendralenes, the phenyl variant, **3.41**, was arbitrarily chosen for method development.

1E-PHENYL[3]DENDRALENE

As expected, triene **3.41** underwent Diels-Alder dimerisation at 25 °C to form three isomeric cycloadducts, namely **3.42**–**3.44** (Scheme 3.20). In order to determine the mechanism, we needed a way to be able to accurately measure the half-lives of each of the prepared 1*E*-[3]dendralenes (**3.41**, & **3.66**–**3.71**) at a known concentration. A method was devised based on that reported by Mulzer and coworkers' kinetic studies.[376] Overall, the aim was to measure the instantaneous concentration at various points during the dimerisation *via* ^{1}H NMR spectroscopy and to use that data to deduce a half-life.

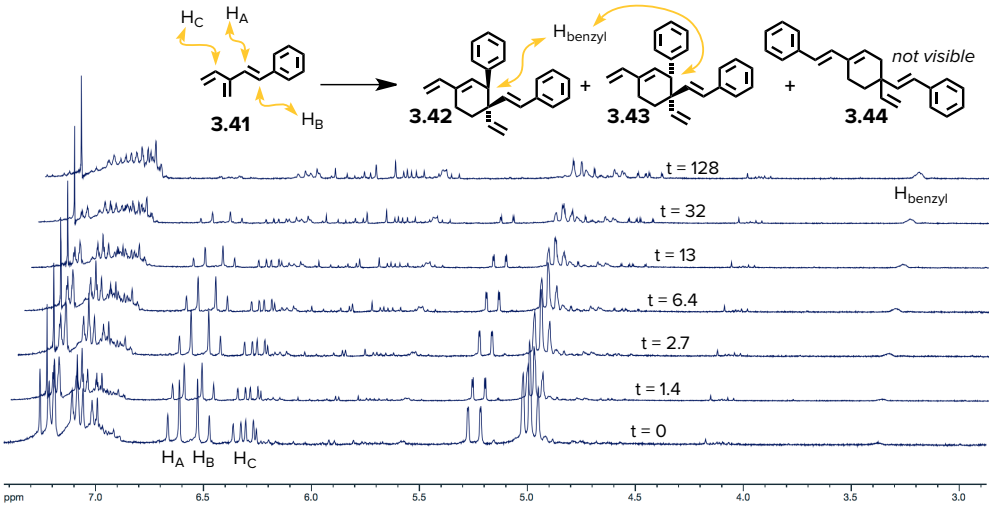


Scheme 3.20: The Diels-Alder dimerisation of 1*E*-phenyl[3]dendralene.

To this end, a *ca.* 0.5 mL volume solution of approximately 0.05 M concentration was made up of freshly prepared 1*E*-phenyl[3]dendralene, **3.41**, in an NMR tube dissolved in $CDCl_3$. To this solution was added 0.050 mL of a 0.166M (0.00833

mmol) standard solution of methylsulfonylmethane in $CDCl_3$ as an internal standard. The combined solution was mixed thoroughly and a ^1H NMR spectrum was recorded (Scheme 3.21).

This NMR spectrum was used to determine an accurate concentration of dendralene in solution by comparison of the internal standard with the peaks due to the dendralene, and the solution was diluted to 0.030 M with the appropriate volume of $CDCl_3$. A ^1H NMR spectrum of the diluted solution was taken to confirm the calculated concentration, and this spectrum was used as a measurement of initial concentration or *t_0 concentration*. The solution was held at 25.0 °C in a constant temperature bath and ^1H NMR spectra were collected regularly (Scheme 3.21).



Scheme 3.21: The Diels-Alder dimerisation of 1*E*-phenyl[3]dendralene and ^1H NMR overlay depicting 1*E*-phenyl[3]dendralene (bottom spectrum, **3.41**), being converted into its diastereomeric dimers (top spectrum, **3.42** & **3.43**).

The experiment was stopped at $4 \times t_{1/2}$ or if the concentration of analyte fell below the measurement error of the detection method.[409,410] The recorded ^1H NMR spectra were used to calculate the instantaneous concentration of the solution which was then correlated with the precise time that the spectrum was recorded. The decay of signal due to 1*E*-phenyl[3]dendralene over time was graphed on a scatter plot using KaleidaGraph (Figure 3.9).

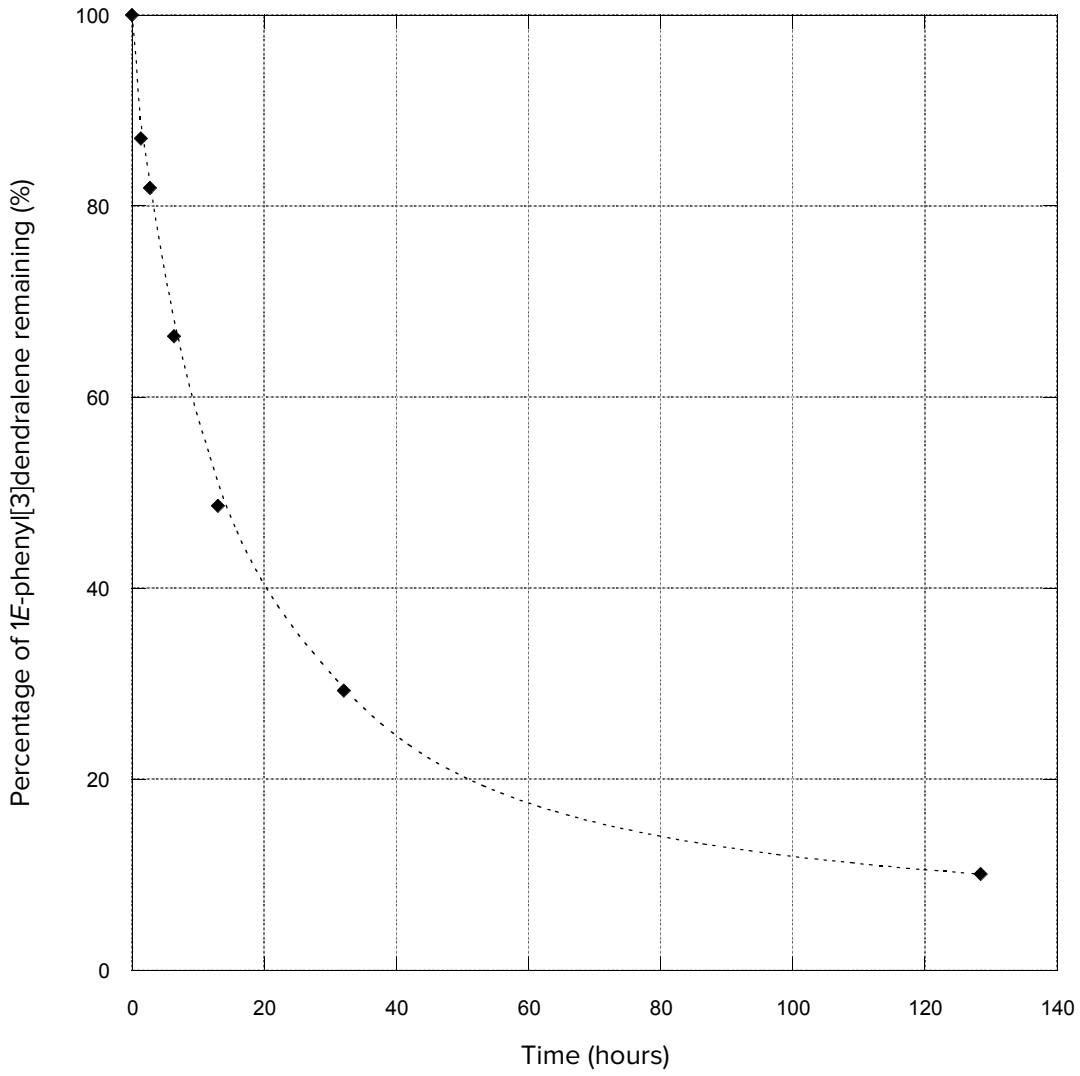


Figure 3.9: Observed decay of 1*E*-phenyl[3]dendralene in $CDCl_3$ (0.03 M).

It is possible to extract an approximate half-life from the graphed raw data by direct inspection of Figure 3.9, where the point of 50% consumption is about 10–15 hours from starting time.

For a more precise—and hopefully more accurate—half-life, a linear correlation is needed between concentration (in some form) and time.[411] The data was modified to have the *y-axis* as *1/[concentration]* ($Lmol^{-1}$) and again graphed on a scatter plot using KaleidaGraph, with the *x-axis* as *time in hours* (Figure 3.10). The gradient is thus *k* as in:

$$\frac{1}{[dendralene]} = \frac{1}{[dendralene]_0} + kt$$

and the half-life ($t_{1/2}$) is determined *via*:[412]

$$t_{1/2} = \frac{1}{k[dendralene]_0}$$

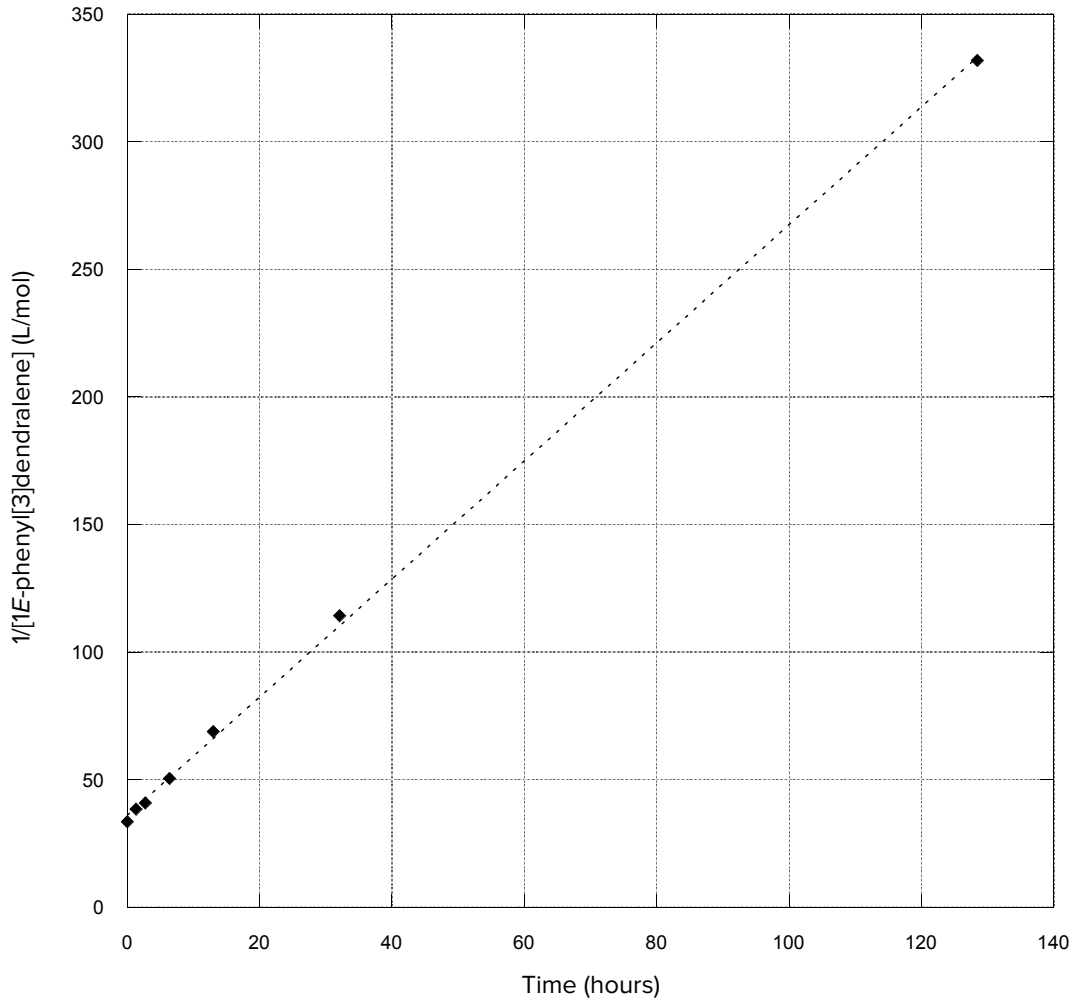
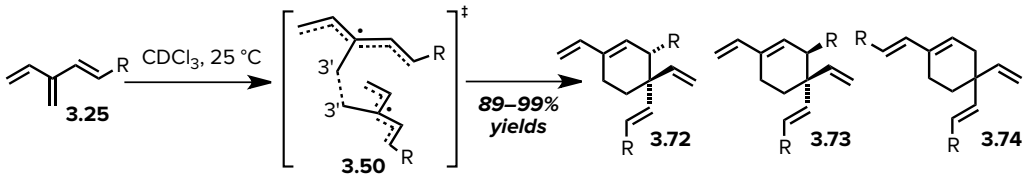


Figure 3.10: Plot to determine second-order half-life of 1*E*-phenyl[3]dendralene decay. The *inverse of concentration* is plotted against *time* to extract the half-life.

A value of 2.51 $Lmol^{-1}$ for *k* is extracted from the gradient of the curve in Figure 3.10. This gives a half-life of $1/(0.030 \times 2.51) = 13$ hours.[N]

The rest of the 1*E*-[3]dendralenes, **3.66**–**3.71**, underwent DA dimerisation at ambient temperature to each form up to three isomeric cycloadducts. In a similar manner to that reported for 1*E*-phenyl[3]dendralene, we could observe and measure the decay of the rest of the prepared 1*E*-[3]dendralenes (Scheme 3.22) by ^{1}H NMR spectroscopy (Table 3.3).



Scheme 3.22: Diels-Alder dimerisation of 1*E*-substituted-[3]dendralenes.

triene (R =)	*half-life (hours)*	*initial triene conc. (M)*	*cycloadduct ratio* **3.72** : **3.73** : **3.74**
4-nitrophenyl	1.7	0.030	56:44:00
$-CO_2Me$	8.6	0.030	39:32:29
phenyl	13	0.030	61:37:02
4-methoxyphenyl	15	0.028	59:33:08
$-CH_2OAc$	92	0.091	36:25:39
–H	150	0.087	—

Table 3.3: Half-life measurements and cycloadduct ratios for the dimerisation of 1*E*-[3]dendralenes.

As can be seen from the experimental half-life data provided in Table 3.3, the majority of 1*E*-substituted [3]dendralenes undergo DA dimerization significantly faster than the parent unsubstituted triene, [3]dendralene **2.3**. The acetoxymethyl-substituted system **3.67** is the odd one out, with a propensity to dimerise that is only slightly higher than the parent [3]dendralene. Aryl or carbomethoxy-substituted systems **3.66**, **3.69**, **3.70**, & **3.41** exhibit much faster dimerisations than **2.3**. The half-lives for the accelerated dimerisations have a spread of approximately a factor of ten from 1.7–15 hours, the slowest of which is still a factor of ten faster than the unsubstituted case, at 150 hours.

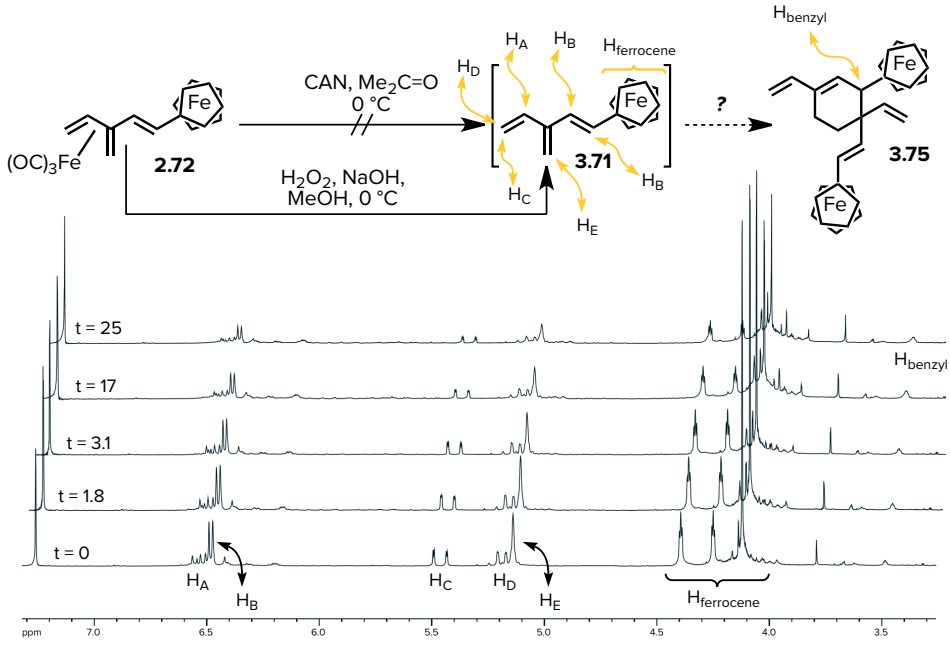
Interesting trends can be found on inspection of the ratios of the three DA dimers (**3.72**–**3.74**, Table 3.3). Perhaps π···π stacking between the two aryl groups

[N] The calculated half-life is 13.28 hours, but this value cannot be asserted to be accurate beyond two significant figures.

stabilises a TS leading to **3.72**, the dominant isomer formed during DA dimerisation of the 1*E*-aryl [3]dendralenes. These results are similar to those seen by Mulzer and coworkers[376] (and others) in the dimerisations of 1,3-diaryl butadienes.

3.3.2 Anomalous Results

The preparation and isolation of **3.71** (Scheme 3.23) was expected to provide another straightforward example of the scope of the predictive power of the pentadienyl radical as an approximation of the transition state of the bispericyclic mechanism. In other systems the ferrocenyl group has been shown to have a radical stabilising effect approximately in between the stabilising effect of a phenyl group and that of a 4-nitrophenyl group.[413,414]



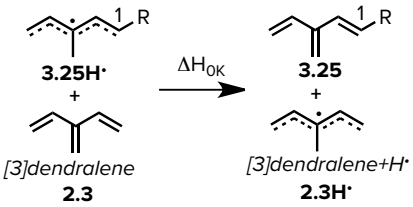
Scheme 3.23: The decomposition of 1*E*-ferrocenyl[3]dendralene and ^{1}H NMR overlay depicting 1*E*-ferrocenyl[3]dendralene (bottom spectrum, **3.71**) degrading over time. Unlike other dendralene dimerisations the loss of dendralenic peaks is not associated with a concommitant gain in obvious dimers.

The removal of the tricarbonyliron group from ferrocenyl[3]dendralene tricarbonyliron was complicated by the ferrocene hindering or inhibiting the single-electron oxidative-decomplexation *via* CAN conditions (Scheme 3.23). Tricarbonyliron complex **2.72** appeared to be resistant to limited amounts of CAN, and decomposed when exposed to an excess amount of CAN. The ligand **3.71** was successfully released by applying the optimised H_2O_2/OH^- conditions (*v.s.*).

Unfortunately, 1*E*-ferrocenyl[3]dendralene did not obey strict second order kinetics for dimerisation, nor were dimers observable in the crude product mixture.

3.3.3 Theoretical Explanation/Comparison With Experimental Results

The reactivity trends in the dimerisation of the 1*E*-substituted [3]dendralenes may be explained in terms of the recently proposed biradicaloid transition structure for the dimerisations of dendralenes (*v.s.* Scheme 3.6).[292] In order to determine the impact of the biradicaloid nature of the reaction, the enthalpies for the isodesmic reaction of [3]dendralene, **2.3**, with a substituted pentadienyl radical, **3.25H**$^{\bullet}$, were calculated (Scheme 3.24, Table 3.4). We proposed that if the reactivity of the 1*E*-[3]dendralenes closely tracked the stability of their respective pentadienyl radicals then the biradical model was a good approximation.



Scheme 3.24: Calculated pentadienyl radical stability relative to [3]dendralene based on the isodesmic reaction of substituted[3]dendralenes with [3]dendralene.

triene (R =)	*B3LYP*
4-nitrophenyl	11.8
phenyl	8.9
4-methoxyphenyl	8.7
$-CO_2Me$	7.0
$-CH_2OAc$	–0.3
–CH3	–0.9

Table 3.4: Enthalpies of stabilisation for the isodesmic reaction in Scheme 3.24 between [3]dendralene and 1*E*-substituted [3]dendralenes.
Calculated B3LYP/6-31G radical stabilisation enthalpies in KJ/mol at 0 K.

Comparing these radical stabilising energies (Table 3.4) with the experimental data (Table 3.3), the relative reactivities of the three aryl substituted dendralenes are correctly reflected in the relative radical stabilisation energies for these substituents. The methoxycarbonyl substituent is predicted to be slightly less effective than aryl groups at stabilising a pentadienyl radical but experimentally, it

lies between that of the 4-nitrophenyl and the phenyl systems. Nevertheless, theory correctly predicts that all four conjugating substituents will lead to faster DA dimerisations than alkyl substituents, which are predicted to have no stabilising influence on the pentadienyl radical.

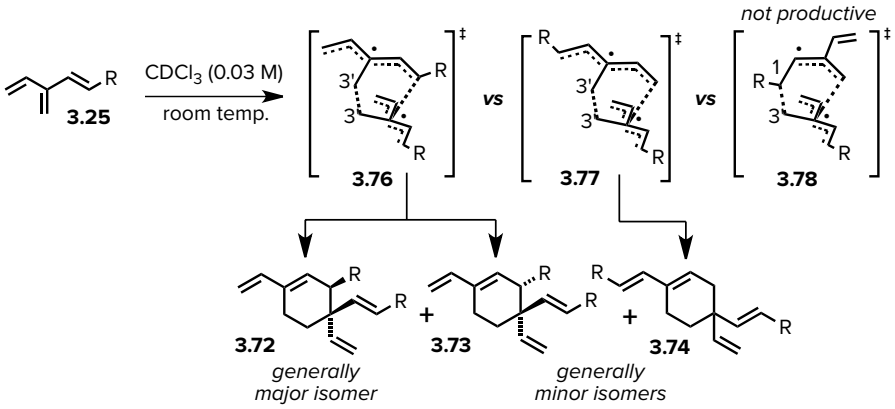


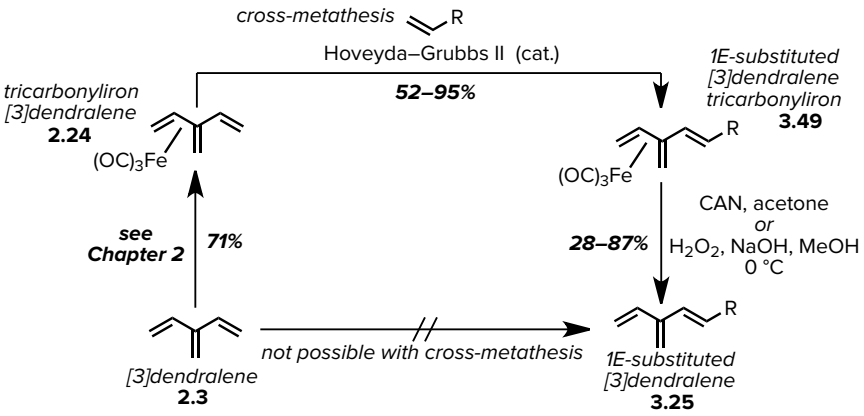
Figure 3.11: Possible biradicaloid transition states leading from 1-substituted [3]dendralenes to Diels-Alder dimers.

The biradicaloid TS model also explains the dienophile regio & site selectivity of the DA dimerisation. All three DA dimers **3.72**, **3.73**, & **3.74** (Scheme 3.11) result from the internal 1,1-disubstituted alkene functioning as dienophile, which can be formed from TS **3.76** or TS **3.77** (Scheme 3.11). If one of the two terminal alkenes were to react as dienophile then the TS would bear a much less stable allyl-radical component, as shown in TS **3.78**.

3.4 Conclusions

GENERAL PREPARATION OF 1E-[3]DENDRALENES

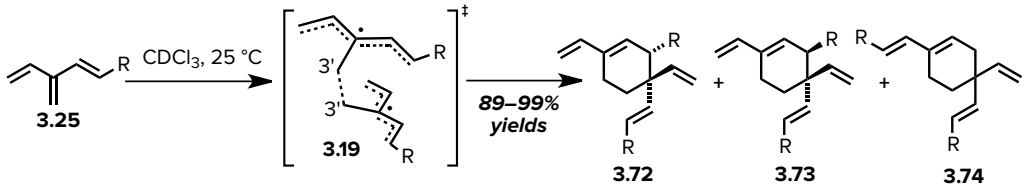
Reported in this chapter is the first example of cross-metathesis on a tricarbonyliron complex, which allows a fast and general preparation of the elusive 1*E*-[3]dendralene family in protected form (Scheme 3.25). These intermediates proved to be the lynchpin that allowed us to access a range of substituted 1*E*-[3]dendralenes under mild conditions for the first time.



Scheme 3.25: A general route to 1*E*-substituted[3]dendralenes *via* the previously unreported cross-metathesis of tricarbonyliron complexes. And liberation under mild conditions to allow studies on the 1*E*-[3]dendralenes for the first time.

BIRADICALOID/BISPERICYCLIC DIMERISATION OF 1E-[3]DENDRALENES

With access to a range of substituted 1*E*-[3]dendralenes, we were able to study their Diels-Alder dimerisation (Scheme 3.26). This was done by preparing a dilute solution (0.03 M or 0.09 M) at 25 °C and recording the change in concentration over time by ^{1}H NMR spectroscopy. The recorded half-lives varied from 1.7 to 150 hours, with conjugating substituents accelerating dimerisations relative to the unsubstituted case.



Scheme 3.26: The biradicaloid dimerisation of the 1*E*-[3]dendralenes to give substituted cyclohexenes decorated with many functional handles for further manipulation.

The biradicaloid behaviour of the dimerisation was probed by comparing a triene's rate of Diels-Alder dimerisation with its ability to stabilise a radical compared to [3]dendralene. Figure 3.12 clearly depicts the correlation between radical stability and Diels-Alder dimerisability. Conjugating substituents increase the rate of dimerisation roughly in line with the degree to which they stabilise a radical.

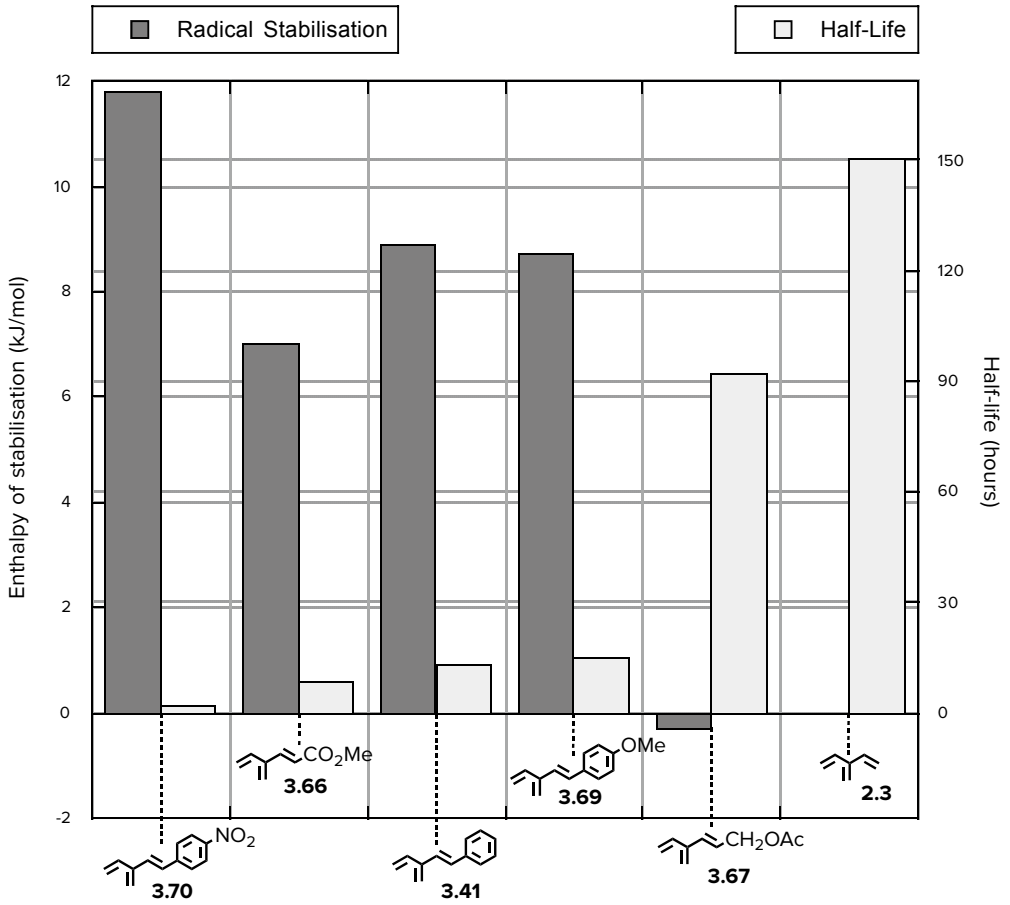


Figure 3.12: Comparison of a substituted dendralene's ability to stabilise a pentadienyl radical with its experimental half-life in solution (see Tables 3.3 and 3.4 for more detail). Calculated B3LYP/6-31G radical stabilisation enthalpies in KJ/mol at 0 K. Half-lives (hours) were measured at: 0.03 M (**3.41**, **3.66**, **3.69**, & **3.70**), or 0.09 M (**2.3** & **3.67**) in $CDCl_3$, at 25 °C.

PREDICTIVE VALUE OF THE BIRADICALOID MODEL

While a better understanding of some aspects of this Diels-Alder dimerisation must await further studies, it is abundantly clear that the positioning of a conjugating group at the 1*E*-site of [3]dendralene leads to a very reactive compound indeed. The biradicaloid approximation of the transition state seems to be a good model for how the substituted [3]dendralenes that we have tested dimerise, and should be relevant to the whole family of [n]dendralenes and their Diels-Alder reactions.

These results could be further strengthened by cross–Diels-Alder experiments wherein the electron-rich trienes (e.g. **3.69**) are reacted with electron-poor trienes (e.g. **3.70**). These kinds of experiments have been used by Spino[135] and others to

investigate the driving force and selectivity of non-traditional Diels-Alder reactions.

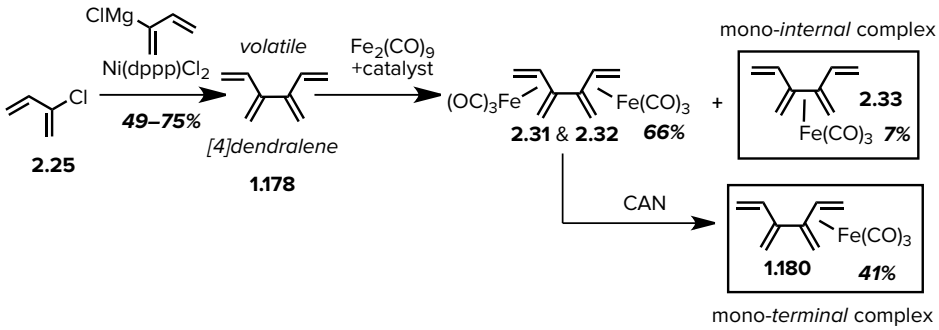
4

Cross–Coupling Reactions With Tricarbonyliron Halobutadienes

4.1 Introduction

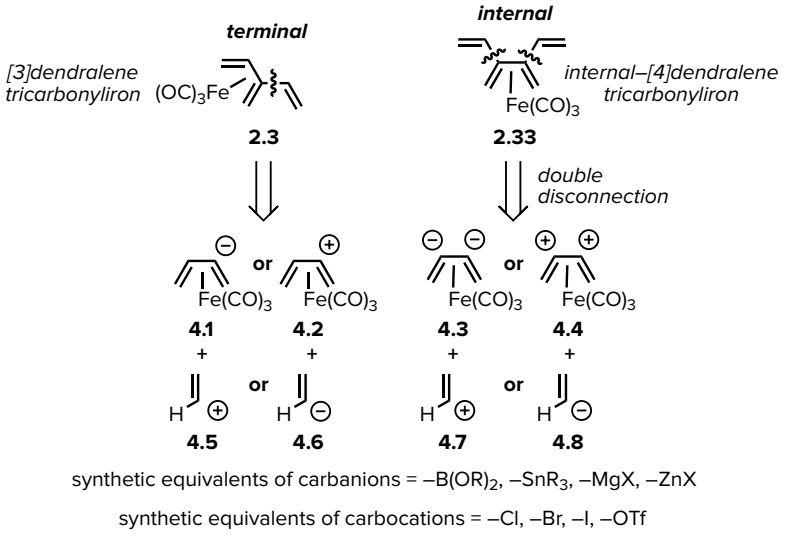
4.1.1 Pretext For A New Synthetic Approach

While carrying out the research described in Chapters 2 & 3 (pages 51 & 85, respectively) we ran into a problem: tricarbonyliron[n]dendralenes are synthetically useful, but most of the truly useful complexes cannot be made efficiently. For example, preparing the terminal tricarbonyliron complex of [4]dendralene, **1.180**, enables us to carry out selective Diels-Alder reactions, but preparing that complex requires at least three steps (Scheme 4.1). Similarly inelegant is the preparation of the internally complexed [4]dendralene, **2.33**, which is prepared directly in the complexation of volatile [4]dendralene in only a 7% yield (Scheme 4.1).



Scheme 4.1: Inefficient access to the mono-tricarbonyliron complexes of [4]dendralene.

It occurred to us that the kinds of compounds we wanted to make, e.g. **2.33** & **1.180**, (Scheme 4.1) could be classified as either terminal complexes, or as internal complexes. Analysing retrosynthetically, we saw that by disconnecting the C–C bonds of **2.3** & **2.33** shown in Scheme 4.2 we would have synthons **4.1**–**4.8** that could be used to access any of the protected dendralenes. In this way we could take the original concept of preparing polyenes protected as their tricarbonyliron complexes, but use a strategy that is both general and direct.[A]



Scheme 4.2: Retrosynthetic analysis of dendralene-tricarbonyliron complexes.

The tricarbonyliron dendralenes can be disconnected at the $C(sp^2)$–$C(sp^2)$ σ-bond shown in Scheme 4.2; bonds which are easily formed in the synthetic direction by palladium-catalysed cross-coupling reactions. The key starting materials for such an approach would be metallo- or halo-butadiene

[A] That is, *general* in scope, but *direct* in step-count.

tricarbonyliron complexes (**4.9**–**4.12**, Figure 4.1). Accessing these kinds of building blocks, and assessing their reactivity is thus the next rational step in utilising the dendralenes synthetically.

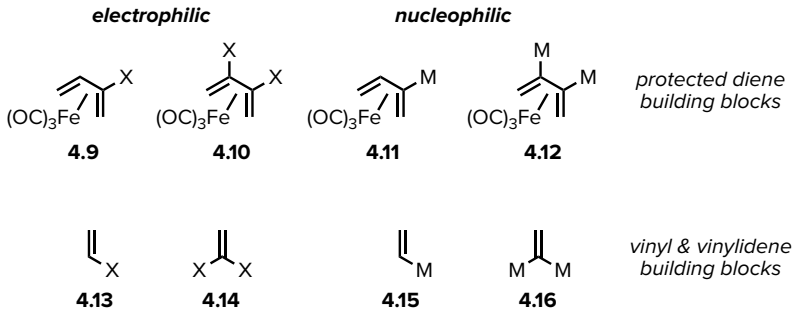
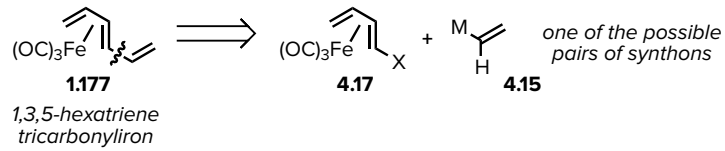


Figure 4.1: The key intermediates to building tricarbonyliron-protected dendralenes.

POSSIBILITY FOR APPLICATION TO OTHER POLYENES

Not only could the dendralenes be accessed in this way, but many different varieties of cross-conjugated polyene could be made protected as their tricarbonyliron complexes from the complexes in Figure 4.1. In principle it is also possible to access through-conjugated polyene complexes (such as **1.177**, Scheme 4.3) from very similar precursors as the cross-conjugated variants.



Scheme 4.3: 1,3,5-Hexatriene protected as a tricarbonyliron complex could be prepared *via* methods similar to those in Scheme 4.2 (*v.s.*).

AN OPPORTUNITY TO MAKE ELUSIVE FUNDAMENTAL POLYENES

Developing the complexation and cross-coupling chemistry of functionalised butadiene-tricarbonyliron complexes would thus allow us to access polyene compounds that have not yet been synthetically prepared. The chemistry of oligoalkenes has been explored haphazardly, and many interesting members have eluded synthesis. These include polyenes such as [5]radialene,[49,251] [13]annulene,[415] and cross-conjugated/through-conjugated hybrids like compounds **4.20** & **3.65** (Figure 4.2).[B]

[B] Compound **3.65** was reported for the first time in Chapter 3 (see page 108).

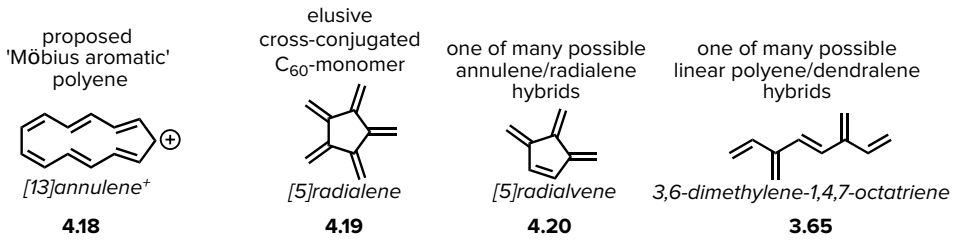
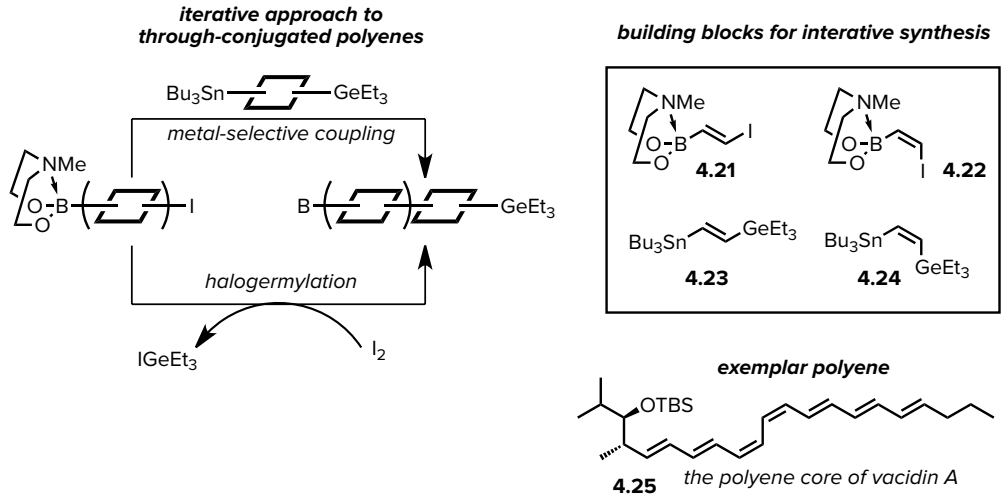


Figure 4.2: Elusive polyenes that might become accessible with the development of functionalised butadiene-tricarbonyliron complexes.

4.1.2 Butadiene–Iron Building Blocks

The described strategy is complementary to the modular preparation of polyenes envisaged by Burke.[416] Burke has described a system in which a great variety of linear polyenes containing a mixture of *E*-[417] and *Z*-[418] geometry can be prepared iteratively from a small collection of *building blocks* (e.g. polyene **4.25**, Scheme 4.4).[419] The complexed dienes we sought to prepare would also allow the integration of Burke's alkenic building blocks with our own, and thus a potentially broader strategy still.



Scheme 4.4: Burke's iterative coupling strategy allows the formation of many different polyenes from a small set of functionalised precursors.[419]

HALOBUTADIENE–TRICARBONYLIRON COMPLEXES

Before venturing into poorly explored territory we set about establishing which related compounds had been made previously.

Brune and coworkers report the first—and in most cases, only—studies on the various chlorine-substituted butadienes complexed by the tricarbonyliron group (Figure 4.3).[144,257,420-426] Brune seemingly prepared the complexes as a systematic

study on the bonding of tricarbonyliron-butadienes rather than for their potential uses as reactive intermediates. The complexes described herein were all prepared using direct complexation of an already prepared 1,3-butadiene (they are all examples of a Method **A** complexation, see page 5 for an explanation).

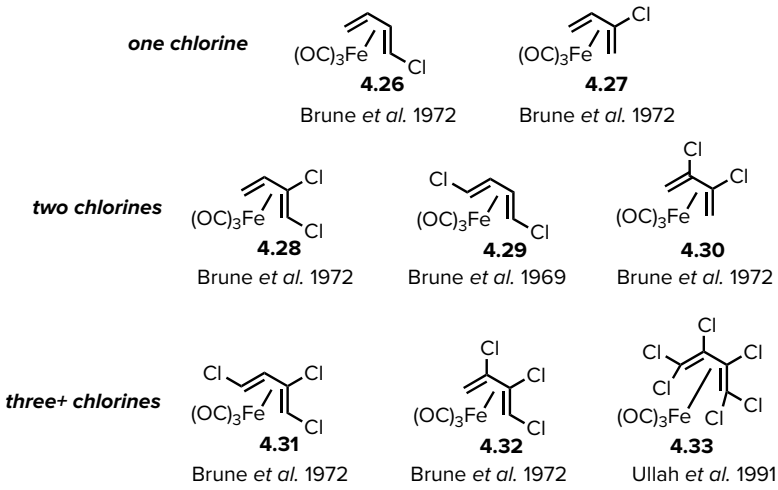
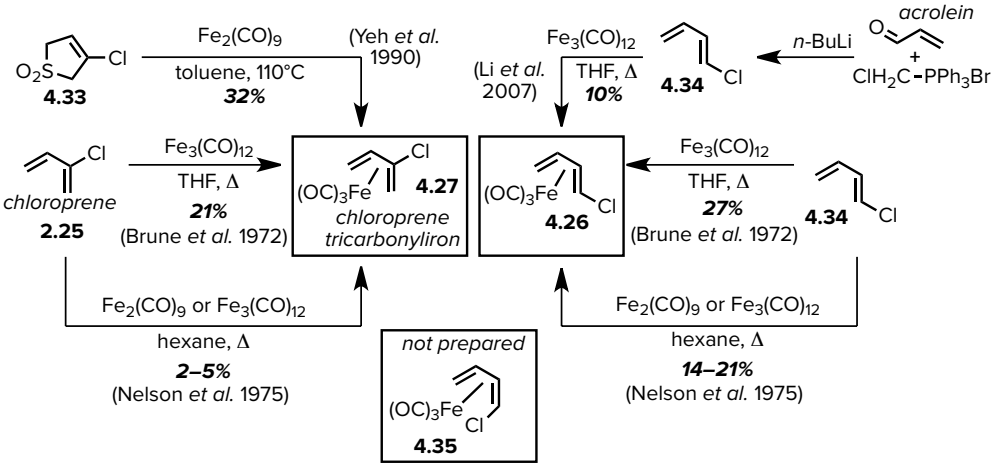


Figure 4.3: The literature known tricarbonyliron complexes of chlorobutadienes.

Chloroprene-tricarbonyliron, **4.27**, was reported for the first time in 1972 by Brune and coworkers as the result of direct complexation of chloroprene with triiron dodecacarbonyl (Scheme 4.5).[144] Nelson and coworkers rapidly followed up on this paper, but reported a significantly lower yield under very similar conditions.[145] Taking a slightly different tack, Yeh and coworkers were able to achieve a higher yield of the complex **4.27** by releasing chloroprene from sulfolene **4.33** using high temperature.[146]



Scheme 4.5: The literature reports of 1- & 2-chlorobutadiene tricarbonyliron complexes.[144-146,423,427]

The tricarbonyliron complex of 1*E*-chlorobutadiene, **4.26**, was prepared in effectively the same manner as the chloroprene complex (Scheme 4.5). Brune and coworkers reported its preparation in 27 % yield from the free diene,[423] and Nelson and coworkers reported 14–21 % yields of the same reaction.[145] Li and coworkers made 1*E*-chlorobutadiene, **4.34**, rather than purchasing (or otherwise acquiring) it,[428,429c] which unfortunately led to lower yields of the target complex. It is interesting to note that 1*Z*-chlorobutadiene tricarbonyliron, **4.35**, has not been reported in the literature.

Several tricarbonyliron complexes of dichlorobutadienes have been prepared, including 1,4-*E*,*E*-dichlorobutadiene (**4.29**), 1,2-*Z*-dichlorobutadiene (**4.28**), 2,3-dichlorobutadiene (**4.30**), and 1,4-dichloro-2,3-dimethyl-*E*,*E*-butadiene (**4.36**) (Scheme). Starting from cyclooctatetraene (**4.37**), 1,4-*E*,*E*-dichlorobutadiene (**4.38**) was prepared by Brune[420] according to the method of Criegee[430] and Avram,[431] before being complexed with triiron dodecacarbonyl to form compound **4.29**. The complex has subsequently been reported several more times in the literature.[423,432,433] This was soon followed by a 2,3-dimethyl substituted variant, **4.36**, that could be prepared relatively efficiently,[421] in spite of the multiple steps required to form the diene precursor.[434-436] 1,2-*Z*-Dichlorobutadiene, **4.39**, was prepared from chloroprene in two steps before the complex, **4.28**, was formed in 14 % yield.[423]

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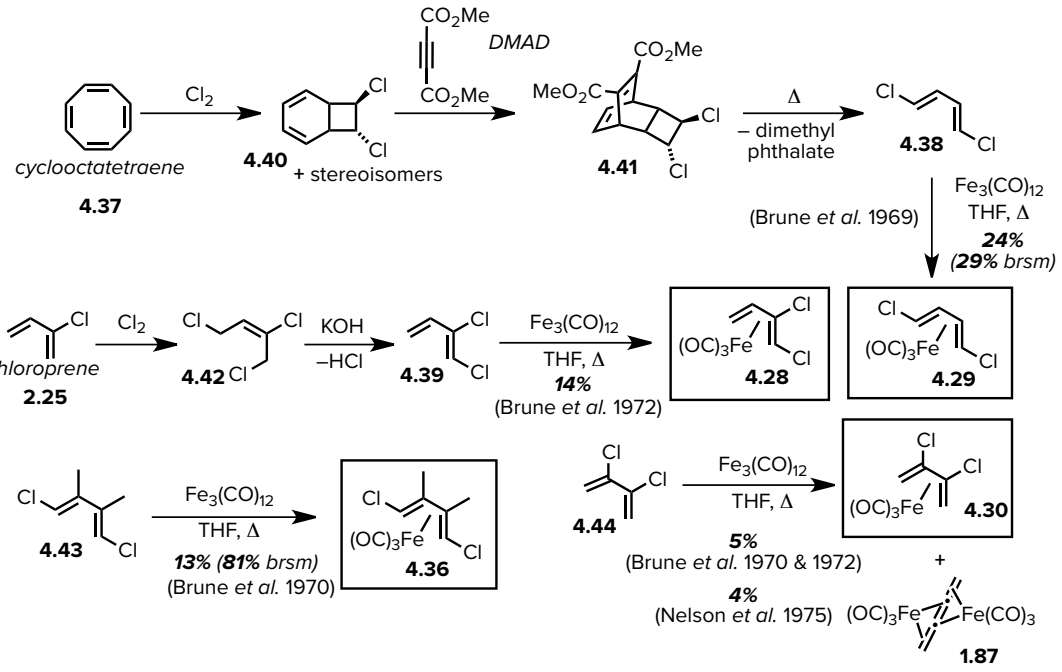
[c] 1*E*-Chlorobutadiene is a side-product from the industrial preparation of chloroprene, **2.25**.

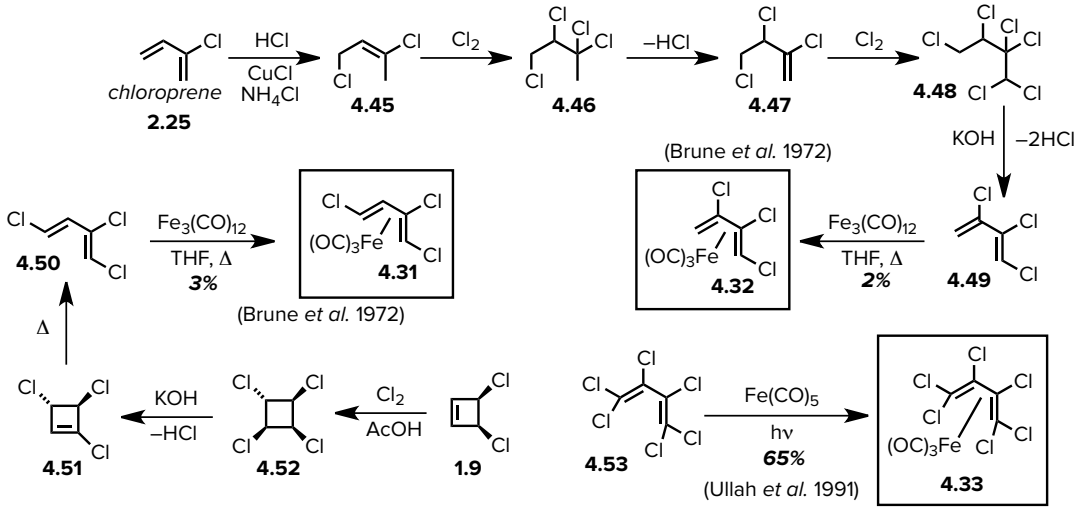


Scheme 4.6: The syntheses of the acyclic dichlorobutadiene tricarbonyliron complexes, including syntheses of the diene where appropriate.[144,257,420,421,423,427,432,433]

2,3-Dichlorobutadiene, **4.44**, was coordinated to a tricarbonyliron group by Brune and coworkers in 1972[144] by reaction of the readily available diene precursor[437] with $Fe_3(CO)_{12}$. The yields for the formation of 2,3-dichlorobutadiene-tricarbonyliron, **4.30** (4–5 %),[144,145] are the lowest for the simple chloro-butadienes described so far. This is due to the favourable elimination of $FeCl_2$ during the formation of the complex, and the generation of bis(tricarbonyliron)butatriene, **1.87**.[257]

The tricarbonyliron-dichlorobutadiene complexes that haven't been prepared are mostly examples where one of the chlorine atoms would be at the *inside* position of the *s-cis* diene unit (i.e. at the 1- or 4- positions with *Z*-configuration). The unfavourability of an internal substituent in the *s-cis* diene seems to be a recurring motif for 'gaps' in the complexation literature.

In 1972 Brune and coworkers described the preparation of two trichlorobutadiene-tricarbonyliron complexes[424] *via* painstaking iterative additions and eliminations from convenient feedstock chemicals (**2.25** & **1.9**, Scheme 4.7). Complexes **4.31** & **4.32** were formed in only 2 & 3 % yields, respectively, from their uncoordinated progenitors.



Scheme 4.7: Polychlorinated butadiene tricarbonyliron complexes and their preparation.[424,426]

Ullah and coworkers reported the synthesis of hexachlorobutadiene-tricarbonyliron, **4.33**, in 65 % yield (Scheme 4.7).[426] Despite repeated attempts by others,[423,424] this is the only report of the successful preparation of a halobutadiene that contains *inside* halo-substituents.

As part of their investigations, Brune and coworkers prepared some chloro-butadienes that did not form complexes when put under the same conditions ($Fe_3(CO)_{12}$, THF, Δ) as the dienes that successfully undergo complexation (Figure 4.4). 1,1,4-(*E*)-Trichlorobutadiene resisted forming complex **4.54**,[424] presumably due to the steric bulk of the *inside* chlorine atom hindering coordination of the iron centre. Both tetrachloro-butadienes also did not form complexes **4.55** & **4.56**;[423] it is unclear what force precludes tricarbonyliron complexation in these cases.[D]

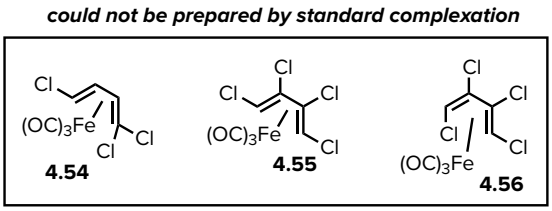
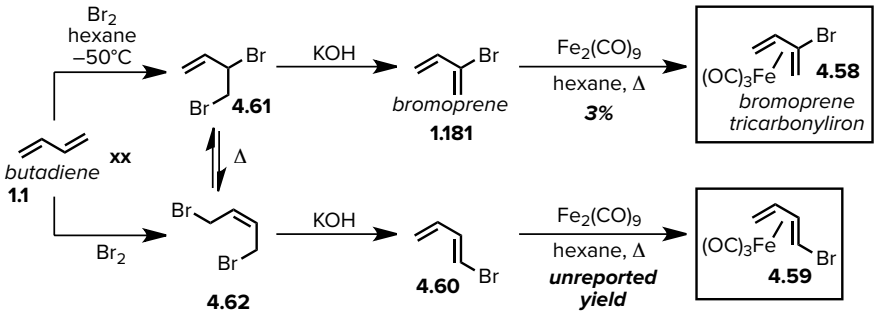


Figure 4.4: Polychlorinated butadienes that resisted tricarbonyliron complexation.[423,424]

[D] A straightforward argument based on steric effects of *internal* chlorines could be made if the 1,2,3,4-*Z,Z*-tetrachloro-1,3-butadiene precursor to **4.55** is a misassignment of the *E,E* isomer.

The only reported non-chlorine containing tricarbonyliron complexes of acyclic halobutadienes are of a pair of bromobutadienes that were described by Greene and coworkers in 1971 (Scheme 4.8).[147] Bromobutadienes **4.57** & **1.181** were prepared according to the method of Klebanskii and coworkers[438] and were then subjected to diiron nonacarbonyl in refluxing hexanes. The bromobutadiene complexes **4.58** & **4.59** were recovered as minor components of their respective reactions, with most of the material polymerising or otherwise decomposing.

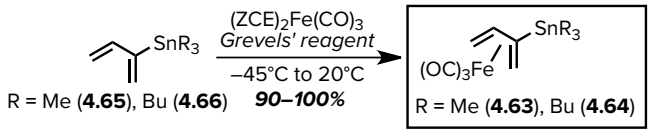


Scheme 4.8: Preparation of 1- & 2-bromobutadiene tricarbonyliron complexes.[147]

The poor yields for the complexes reported in this section may be low due to the ability of the tricarbonyliron group to insert into C–X bonds. In fact, reactions of metal carbonyls with halogenated hydrocarbons have long been known to result in the removal of the halogens;[256] in fact, it is one of the more common ways of forming tricarbonyliron complexes (as described in Chapter 1, p. 5).[439]

METALLOBUTADIENE–TRICARBONYLIRON COMPLEX

The only tricarbonyliron complexes of a 2-metallobutadiene that have been reported are 2-stannylbutadiene tricarbonyliron complexes **4.63** & **4.64**, which were prepared by Franck-Neumann and coworkers in 1989 (Scheme 4.9).[12] The successful approach by Franck-Neumann utilised Grevels' reagent (**1.14**) to directly complex the dienes under mild conditions (*v.i.*, page 138, for more discussion of Grevels' reagent). The authors report that low yields were obtained with other methods of tricarbonyliron complexation.

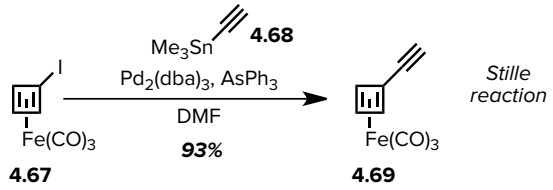


Scheme 4.9: The complexation of 2-stannylbutadiene with the tricarbonyliron group.[12]

4.1.3 Butadiene–Tricarbonyliron Complexes in Cross–Coupling

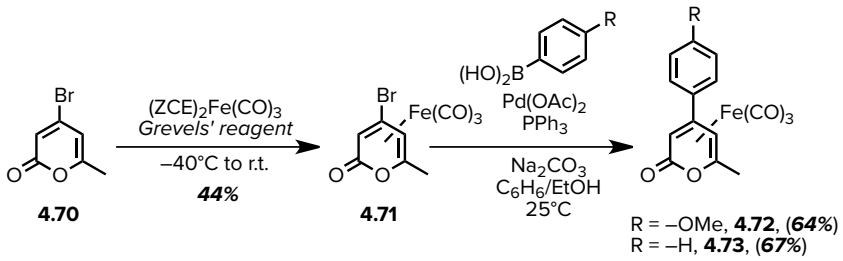
For halobutadiene-tricarbonyliron complexes to be useful in the modular construction of cross-conjugated polyenes they must be good partners in cross-coupling reactions. Some work has been done in this field, and the scope of what is known is described below.

Closely related to the acyclic butadiene-tricarbonyliron complexes are the cyclobutadiene complexes (see page 11 for more discussion on these complexes). Cross-coupling reactions have been carried out on derivatised cyclobutadiene-tricarbonyliron complexes by Bunz and coworkers.[440,441] Scheme 4.10 is representative of this work, where an iodobutadiene complex, **4.67**, can be induced to cross-couple with the stannylated acetylene **4.68** under Stille reaction conditions.



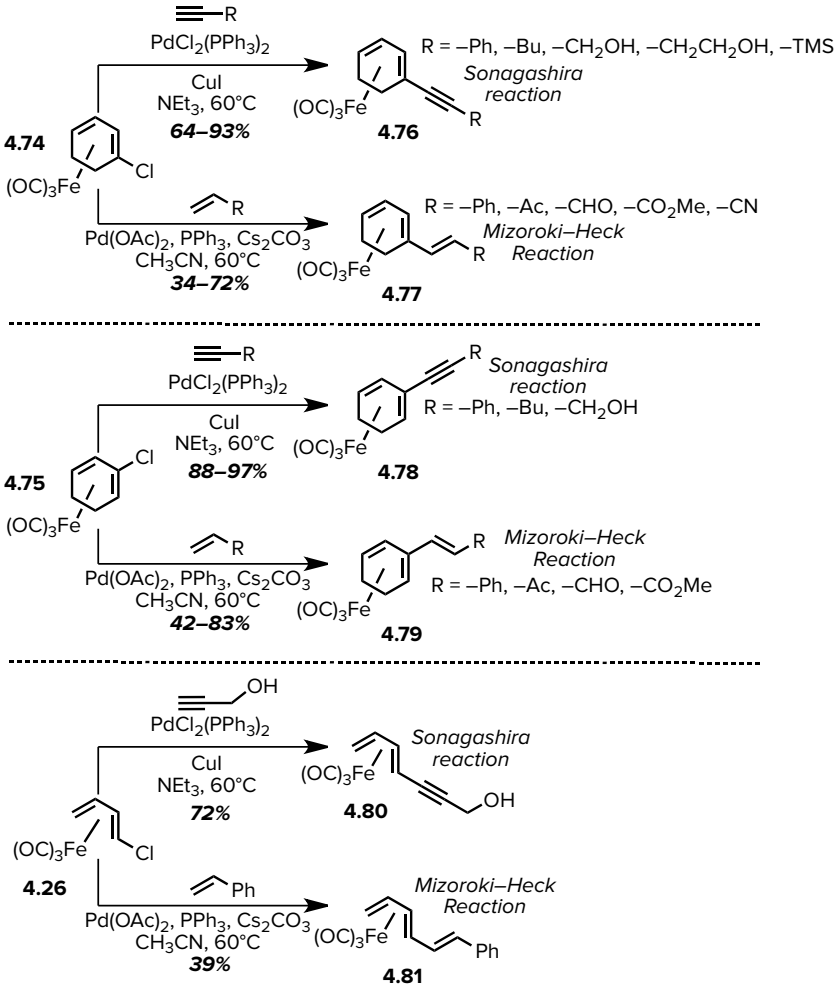
Scheme 4.10: Stille cross-coupling between iodocyclobutadiene-tricarbonyliron and trimethylstannyl acetylene.[440]

As part of a larger study on the chemistry of 2-pyrone tricarbonyliron complexes,[442] Fairlamb and coworkers reported a mild method for functionalising 2-pyrones using Suzuki–Miyaura reactions (Scheme 4.11).[301] The compound **4.70** resisted all common forms of tricarbonyliron complexation before succumbing to Grevels' reagent in a 44 % yield. Complex **4.71** was subsequently cross-coupled with phenyl boronic acid and *para*-methoxy phenyl boronic acid under palladium catalysis at 25 °C. These conditions are milder than those needed for the uncomplexed 2-pyrone **4.70**.[443]



Scheme 4.11: Suzuki–Miyaura cross-coupling reactions of (bromo-2-pyrone)tricarbonyliron complexes.[301]

The most relevant work to our planned cross-coupling approach to the tricarbonyliron-dendralenes is a series of cross-coupling reactions of chlorine-substituted cyclohexadiene-tricarbonyliron complexes reported by Chen & Li in 2007 (Scheme 4.12).[427]

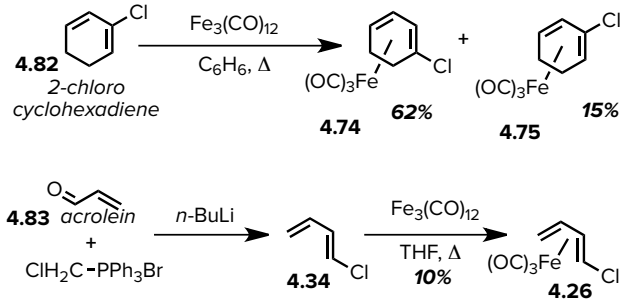


Scheme 4.12: Cross-coupling reactions carried out by Chen & Li on 1- & 2-chlorocyclohexadiene tricarbonyliron complexes.[427]

Chen & Li demonstrate successful Sonagashira and Mizoroki–Heck reactions on 1- & 2-chlorocyclohexadiene tricarbonyliron complexes **4.74** & **4.75** with a range of alkynic and alkenic coupling partners (Scheme 4.12). Both types of coupling reaction could also be carried out with 1-chloro-1,3-butadiene tricarbonyliron, **4.26**, but only one example of each reaction. The lack of further examples in the acyclic case was likely due to lack of material, because, of the three complexes reacted, it appears to be the most likely to generate interesting products. These examples show that there is at least some scope for cross-coupling reactions on

halogenated tricarbonyliron dienes. Of the possible C–C bond forming cross-coupling reactions known in the literature, it seems curious that only two were chosen for experimentation.

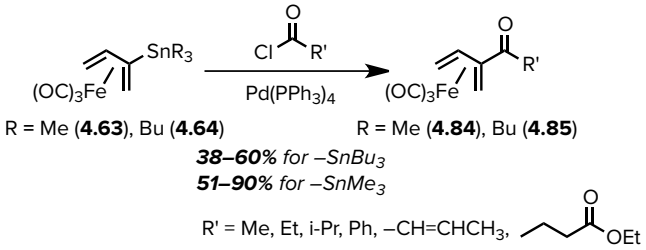
The complexes shown above (**4.74** & **4.75**, Scheme 4.12) were prepared by Chen & Li according to the procedure of Nametkin and coworkers, reported in 1975 (Scheme 4.13).[439,444,445] Both complexes are produced by the triiron dodecacarbonyl complexation of 2-chloro-1,3-cyclohexadiene **4.82**. This complexation then necessarily involves the isomerisation of the 1,3-diene to put the chlorine at the 1-position preferentially.[445] Such isomerisations have been observed in a number of other cases,[446] and occur *before* the formation of a rigid η^4-diene tricarbonyliron complex.[444,447] Some reactions of 1-chloro-1,3-butadiene tricarbonyliron **4.26** are also reported by Chen (Scheme 4.12); this compound was prepared in a manner similar to that of Brune and coworkers (Scheme 4.13).[423]



Scheme 4.13: Top: the preparation of 1- & 2-chlorocyclohexadiene tricarbonyliron complexes from 2-chlorocyclohexadiene.[444,445] Bottom: the preparation of 1-chlorobutadiene-tricarbonyliron.[427]

Apart from the work reported by Fairlamb[301] and Li,[427] the only other report of a tricarbonyliron-diene cross-coupling reaction is by Attwood and coworkers, who carried out palladium catalysis on triflates, as halide equivalents, pendant to a complexed cyclohexadiene.[448]

The tricarbonyliron butadiene complexes have also participated in coupling reactions where the nucleophilic and electrophilic functionality has been reversed, i.e. a metallo-substituted butadiene tricarbonyliron complex reacting with a C–X electrophile (Scheme 4.14).[12] Franck-Neumann and coworkers reported a series of acylations of the complexes **4.63** & **4.64** (see page 127 for their preparation) under palladium catalysed conditions. After a brief optimisation, they found that the $SnMe_3$ derivative gave the best yields with a range of acyl chlorides under mild conditions.



Scheme 4.14: The coupling of 2-stannylbutadiene tricarbonyliron complexes to a variety of acyl chlorides.[12]

While there are not an abundance of examples of $Fe(CO)_3$ reactions similar to those that we envisaged, there is significant precedent for a $Cr(CO)_3$ group (closely related to $Fe(CO)_3$) labilising C–X bonds of a coordinated arene towards radical reductions.[449,450] It has also been established in the literature that the $Cr(CO)_3$ & $Mn(CO)_3$ groups are compatible with—and can even activate—palladium catalysed cross-coupling reactions of coordinated ligands.[451,452]

Many of the possible tricarbonyliron complexes of chlorinated 1,3-butadienes have been prepared in the literature, but most of those compounds have not been used synthetically at all. Several cross-coupling reactions on these compounds and they have been used to make interesting complexes of polyunsaturated molecules. Nor has there been any rationale for using them in the targeted synthesis of specific useful or fundamental molecules.

4.1.4 Aims: A General Route to Cross-Conjugated Systems

The literature lacks any use of tricarbonyliron complexes in the modular preparation of polyunsaturated molecules. We envisaged a two-pronged approach to generalise the efficient preparation of tricarbonyliron complexes of cross-conjugated systems. In order to do this we set out to show that a wide range of reactions—especially cross-couplings—can be done on tricarbonyliron complexed halobutadienes. In particular we targeted chloroprene-tricarbonyliron and 2,3-dichlorobutadiene-tricarbonyliron (Figure 4.5) as the compounds that would give us the tricarbonyliron-dendralenes in the most efficacious manner.

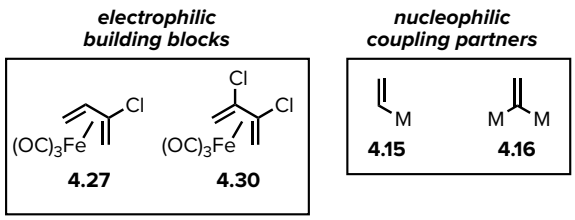
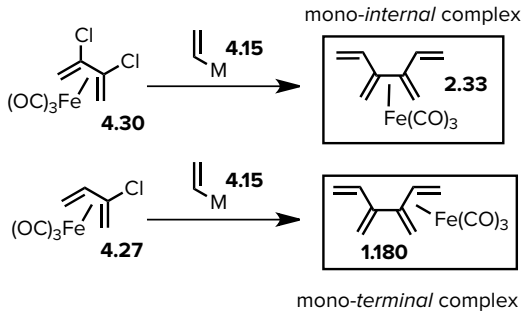


Figure 4.5: The key building blocks for making tricarbonyliron-dendralenes.

With these compounds we wished to establish that a broad spectrum of cross-coupling reactions, including Mizoroki–Heck, Suzuki–Miyaura, Stille, Negishi, & Sonagashira reactions, can be done on them in order to form the tricarbonyliron dendralenes. The dendralene complexes we targeted were those which previously eluded efficient synthesis, notably *terminal*- and *internal*-tricarbonyliron[4]dendralene (Scheme 4.15).



Scheme 4.15: A general route to tricarbonyliron-diene complexes in polyenes.

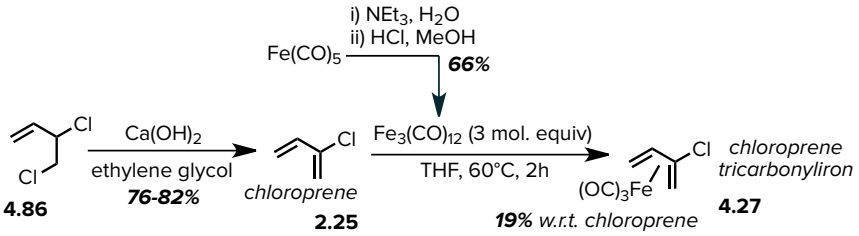
The potential scope of this synthetic approach was thus very broad. Our initial research was consequently focussed on specifically improving the synthesis of the tricarbonyliron-dendralenes. If we were successful that would validate our approach, and then we could expand it to other interesting conjugated systems.

4.2 Results: Remaking Dendralene Complexes

4.2.1 Building Blocks

The preparation of tricarbonyliron(chloroprene) has been reported 4 times in the literature, with yields ranging from 2–32% with respect to chloroprene. Of these syntheses the one that appeared to be the most practical for gram-scale preparation was reported in 1972 by Brune and coworkers.[144] The synthesis was effected by heating chloroprene with triiron dodecacarbonyl in a ratio of 3:1 in THF for 2 hours to give a 21% yield of (chloroprene)tricarbonyliron. As neither chloroprene nor triiron dodecacarbonyl are currently available for purchase from fine chemical suppliers, they were instead prepared according to literature procedures. To prepare triiron dodecacarbonyl, iron pentacarbonyl was heated with triethylamine in water overnight to afford $[Fe_3(CO)_{11}][HNEt_3]$, which was subsequently acidified in methanol, affording $Fe_3(CO)_{12}$ which crystallised out on heating.[453] The preparation was experimentally easy, and could be scaled up to

afford 180 grams of $Fe_3(CO)_{12}$ from a single sequence (Scheme 4.16). Chloroprene preparation has been optimised in-house, and can be distilled directly from a reaction vessel containing calcium hydroxide and ethylene glycol heated to 105 °C on up to a 150 gram scale, based on the published patent.[428]

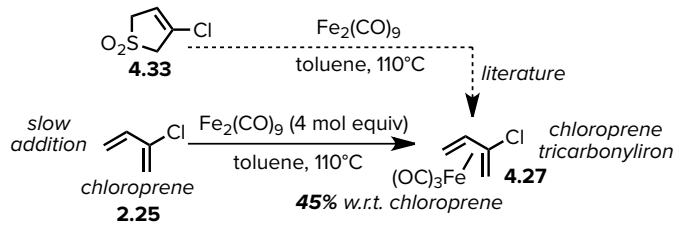


Scheme 4.16: The convergent preparation of tricarbonyliron(chloroprene).

(Chloroprene)tricarbonyliron **4.27** was prepared from chloroprene and $Fe_3(CO)_{12}$ in 19% yield by following the procedure of Brune and coworkers.[144] It is unclear what the appropriate stoichiometry is in this case, as although one can imagine up to three $[Fe(CO)_4]$ units can come from heating triiron dodecacarbonyl, it is likely to be lower, thus making triiron dodecacarbonyl the limiting reagent in the reaction, and dramatically increasing the overall effective yield. Such a discussion is purely academic, because we were not able to increase the efficiency of this reaction by varying the stoichiometry of the reaction from that initially reported by Brune *et al*.[144] Of more consequence is that by using this method we were able to obtain quantities in excess of 20 grams of (chloroprene)tricarbonyliron **4.27** from a single reaction, which was purified by a flash column chromatography and fractional vacuum distillation to separate the product from (butadiene)tricarbonyliron.[E]

Although we had a method to prepare tricarbonyliron(chloroprene) on the decagram scale, we were still interested in developing a higher yielding route, or one that did not require a complicated purification. Towards this end, we turned to a method for the preparation of tricarbonyliron(chloroprene) from 3-chlorosulfolene **4.33** (Scheme 4.17).[146]

[E] (1,3-Butadiene)tricarbonyliron was found to be an inert spectator under palladium-catalysed cross-coupling conditions, and so could be present in the (chloroprene)tricarbonyliron in proportions of up to 30% w/w (and probably higher, but we weren't interested in tested the proposition in such an extreme case). The fact that 'impure' fractions could be used made the preparation much more convenient, but these impure fractions do not contribute to the isolated yield we have reported.



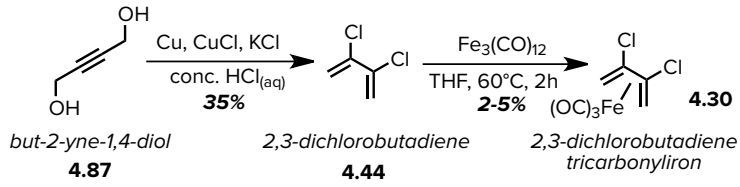
Scheme 4.17: Higher yielding, but less 'efficient' preparation of (chloroprene)tricarbonyliron.

The main benefit of using 3-chlorosulfolene (Scheme 4.17) is that under heating it brings about the slow release of chloroprene into solution.[392] We attempted to mimic this by simply slowly adding a solution of chloroprene to a pre-heated mixture of $Fe_2(CO)_9$ in toluene, which should allow us to access the higher yields and greater room for optimisation reported by Yeh.[146] We were indeed able to significantly increase our yields of isolated complex **4.27** relative to the prior approach (Scheme 4.16), unfortunately the high loadings of expensive diiron nonacarbonyl (4 mol. equiv *vs.* 0.3 mol. equiv $Fe_3(CO)_{12}$ required for complexation *cf.* Scheme 4.16), and the lack of significant increase in ease of isolation meant the approach wasn't an overall improvement. Possible further avenues for exploration here are the modification of the original Brune procedure to use slow addition of chloroprene to pre-heated triiron dodecacarbonyl.

With (chloroprene)tricarbonyliron, **4.27**, in hand we had one half of our two-pronged approach to a general route to cross-conjugated hydrocarbons complete (Scheme 4.15). In order for a truly general approach we also needed to selectively prepare hydrocarbons which are *internally* complexed by tricarbonyliron, for which we need the ability to 'grow the chain' in both directions.

Fortunately, both of the key reports on the preparation of (chloroprene)tricarbonyliron **4.27** also report the synthesis of (2,3-dichlorobutadiene)tricarbonyliron **4.30**.[144,145] Less fortunately, the reported yields of isolated (2,3-dichlorobutadiene)tricarbonyliron are universally lower than 5%, and multiple side-products must be removed by fractional vacuum distillation. Nevertheless, we were intent on establishing that the *strategy* was efficient; we remained confident that even though we would initially have low yields that we could follow-up with a more elegant second-generation synthesis. And so we prepared 2,3-dichlorobutadiene from but-2-yne-1,4-diol using the literature

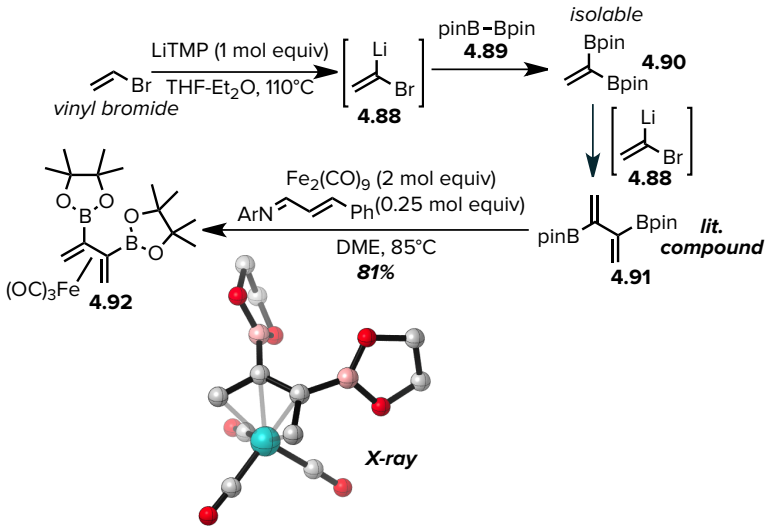
procedure[437F] We then followed the procedure reported by Brune and coworkers[144] to prepare the coordination compound **4.30**. Our reaction yields were low, as expected, and the yield was highly dependent on the source of dodecacarbonyl triiron.



Scheme 4.18: The preparation of 2,3-dichlorobutadiene tricarbonyliron.

Based on the success of 2-stannylated butadiene tricarbonyliron in acylation reactions (Scheme 4.14)[12] we were drawn to the idea of metalated-butadiene complexes for the potential of inverting or reversing the functionality of our halo-butadiene complexes, and so to massively expand the scope of the compounds accessible to us. We have had a longstanding interest in the practical preparation of cross-conjugated hydrocarbons, and so this author had ready access to the literature known[454] compounds 1,1-bis(pinacolatoboron)ethylene, and 2,3-bis(pinacolatoboron)butadiene, which are prepared by the low temperature deprotonation of vinyl bromide to generate a vinylcarbene equivalent **4.88** (Scheme 4.19). This vinyl carbenoid can then insert into the boron-boron bond of bis(pinacolatoboron) **4.89**, either once, or twice, depending on the stoichiometry. We were able to directly apply our optimised diene complexation conditions (described in Chapter 2) in order to complex 2,3-bis(pinacolatoboron)butadiene with tricarbonyliron.

[F] A witches brew of Cu, CuCl, KCl, dissolved in HCl, and heated!



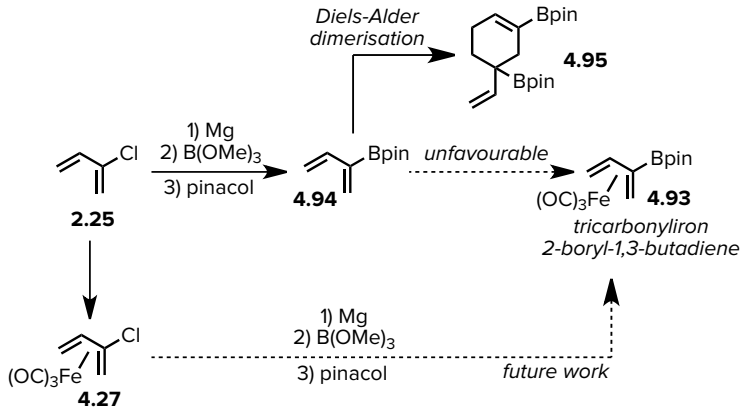
Scheme 4.19: Preparation and X-ray derived molecular structure of 2,3-bis(pinacolatoboron)butadiene tricarbonyliron. Hydrogen atoms and methyl groups have been omitted for clarity from the depicted molecular structure.

The preparation of 2,3-bis(pinacolatoboron)butadiene tricarbonyliron was achieved by heating diiron nonacarbonyl in dimethoxyethane with Knölker's diaryl azabutadiene catalyst,[26] which afforded the crystalline complex **4.92** in 81 % yield after flash column chromatography (Scheme 4.19). From the crystalline complex we were able to obtain a molecular structure from single crystal X-ray diffraction, which was satisfying as it allowed us to very rapidly confirm our structural assignment, as well as observe the degree of steric crowding about our hopefully reactive C–B bonds. It appeared that although one face of the C–B bond was very congested due to the $Fe(CO)_3$ group, the other face should be approachable by a transition metal complex. Structurally, the C–B bond lengths in the X-ray derived molecular structure were 1.56 and 1.58 Å, which is comparable to other C–B(pin) bonds that are reactive.[455,456]

Our main fear with the potential usefulness of the complex **4.92** was that the vicinal boron substituents would be cooperatively deactivating, thus making the bond too electron-poor to be reactive with palladium catalysts. This is visible in the poor cross-coupling reactivity of the uncomplexed 2,3-bis(pinacolatoboron)butadiene **4.91**.[457]

The only missing building block was thus the 2-pinacolatoboron-1,3-butadiene tricarbonyliron complex **4.93** (Scheme 4.20). Unfortunately, reports of the free diene, **4.94**, in the literature all note its reactivity towards Diels-Alder

dimerisation.[458-461] Rather than attempting to prepare the complex **4.93** directly, we envisaged modifying the substitution of the prepared chloroprene complex **4.27** when we needed to access the metallo-complex and its associated reactivity.

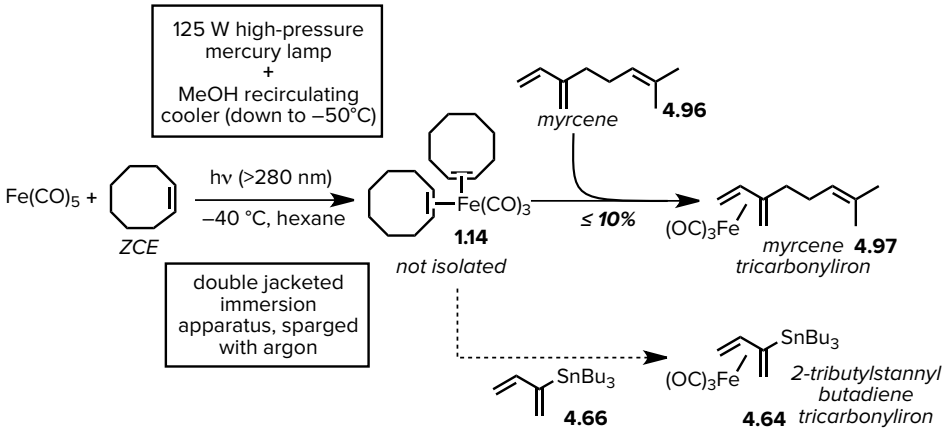


Scheme 4.20: Preparation and Diels-Alder dimerisation of 2-pinacolatoboron-1,3-butadiene.[459,461]

ATTEMPTED PREPARATION & USE OF GREVELS' REAGENT

To replace the 2-pinacolatoboron-tricarbonyliron complex **4.93** we looked to the only literature example of a mono-metallo-butadiene tricarbonyliron complex. In order to reproduce the only reported synthesis of 2-stannylbutadienes, and later extend this chemistry to include the pinacolato-boryl complex **4.93**, we required the use of Grevels' reagent[27] (**1.14**, see p. 138). Our initial attempts to prepare Grevels' reagent yielded no isolable material, and so we changed tack to attempt to use the reagent *in situ*[462-464] to avoid the complicated[27,465] isolation methods reported. Grevels' and coworkers reported the use of custom glassware;[466] we did our best to mimic that setup using the equipment available to us.

With jury-rigged equipment we were fighting fate by attempting to properly prepare such a delicate[465] reagent (Scheme 4.21), but by IR spectroscopy we did observe partial formation of the complexes (ZCE)$Fe(CO)_4$, **4.98**, & $(ZCE)_2Fe(CO)_3$, **1.14**, (ν_{max} (hexane) = 2076, 2000, 1994, 1973 cm^{-1} for **4.98**,[467] ν_{max} (hexane) = 2044, 1966 cm^{-1} for **1.14**,[27] reported). Myrcene, **4.96**, was added to the dilute –30 °C solution containing $(ZCE)_2Fe(CO)_3$, and the solvent rapidly removed under reduced pressure.



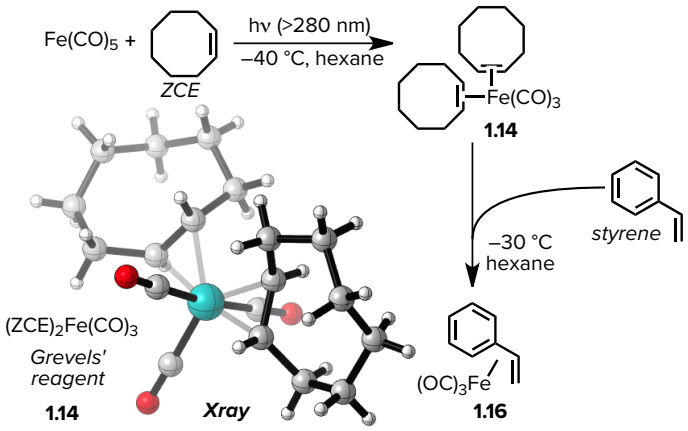
Scheme 4.21: Tricarbonyliron complexation of myrcene using Grevels' reagent generated *in situ*.

A small quantity of tricarbonyliron-myrcene (**4.97**)[468] was isolated from the reaction mixture (Scheme 4.21). This leads us to believe that with appropriate photochemical equipment we will be able to efficiently prepare 2-stannylbutadiene complexes in the future.[G]

GREVELS' REAGENT: THE ULTIMATE IN COMPLEXING POWER?

Grevels' reagent[27] (**1.14**, Scheme 4.22) has been used with great success in the literature to effect the tricarbonyliron complexation of even very deactivated molecules. Grevels' reagent—like many of the best reagents—is finely balanced on the edge of metastability, where it is just inert enough to exist and be handleable/isolable, but unstable enough to react with compounds normally resistant to complexation,[469] such as styrene (Scheme 4.22, mentioned previously on p. 6). Both the complex's inertness and instability are in large part due to the steric bulk of the *Z*-cyclooctene (ZCE) ring, as can be seen in its X-ray derived molecular structure in Scheme 4.22. Grevels and coworkers report the preparation of the reagent by irradiating a solution containing ZCE and $Fe(CO)_5$ at –40 °C, followed by recrystallisation at –78 °C, and filtration to isolate the crystalline complex.[27]

[G] Our photochemical apparatuses were destroyed in a laboratory fire (unrelated to the research reported in this thesis), which put planned follow-up experiments on hold.



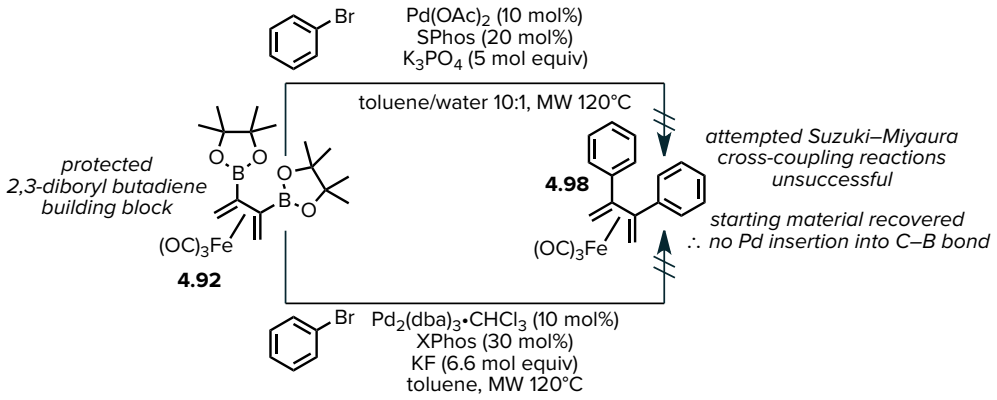
Scheme 4.22: Preparation, reactivity, and structure of Grevels' reagent.[27]

Grevels' reagent has been cited infrequently in the literature for an organometallic tool that is purportedly so powerful. A closer reading of some of the literature reports of its use shows why that is. Alexander and coworkers reported[465] the successful preparation of the reagent, but also noted that they were *"unable to dry the crystals in vacuo below 0 °C without their decomposing."* In a similar vein, Fairlamb and coworkers reported[301,470] that *"dramatic decomposition is observed if the solution is warmed too quickly."* The difficulties faced by even very experienced researchers meant that Grevels' reagent was probably best used only as a last resort, or for the preparation of complexes already confirmed to be useful.

4.2.2 A Unified, Selective Approach To Dendralene–Tricarbonyliron Complexes

PALLADIUM-CATALYSED CROSS-COUPLING REACTIONS OF TRICARBONYLIRON COORDINATED METALLOBUTADIENES

With 2,3-bis(pinacolatoboron)butadiene tricarbonyliron we sought to assuage our fears about its reactivity by using a range of optimised Suzuki–Miyaura cross-coupling reaction conditions to unite complex **4.92** with bromobenzene as a simple electrophilic component (Scheme 4.23). Sadly, the complex **4.92** remained inactive under conditions developed by Fu and coworkers,[328,471] as well as conditions pioneered by Buchwald and coworkers.[472,473]



Scheme 4.23: 2,3-Bis(pinacolatoboron)butadiene tricarbonyliron is *not* a good bis-nucleophile in cross-coupling reactions.

The lack of reactivity of 2,3-bis(pinacolatoboron)butadiene tricarbonyliron in palladium-catalysed cross-coupling reactions could be due to either steric or electronic deactivation. Electronic deactivation is possible, but free 2,3-bis(pinacolatoboron)butadiene **4.91** (Figure 4.7) is able to react in cross-coupling reactions[457] and the tricarbonyliron group is often considered slightly electron donating.[474] The steric bulk of the second Bpin group could hinder access of the palladium catalyst, especially when locked in the *s-cis* conformation by tricarbonyliron complexation, as shown in Figure 4.6.

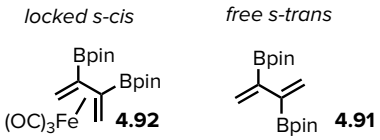


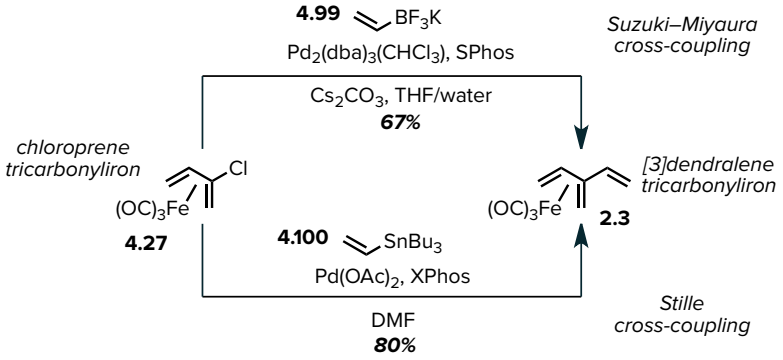
Figure 4.6: The conformational freedom of 2,3-bis(pinacolatoboron)butadiene.

Using complex **4.92** in cross-coupling reactions is worthy of further examination. Possible avenues for optimisation include altering the conditions, use of different catalysts, or modification of the boron-containing functionality. Reactivity could also be induced by merely employing more forcing conditions than those reported in Scheme 4.23.

In general, the nucleophilic component in a cross-coupling reaction is enhanced by being electron-rich, and the electrophilic component by being electron-poor. Thus, our lack of success with bis-nucleophile **4.92** only cemented our confidence in the imminent successful use of (halobutadiene)tricarbonyliron complexes **4.27** and **4.30** as electrophilic components in palladium-catalysed cross-coupling reactions.

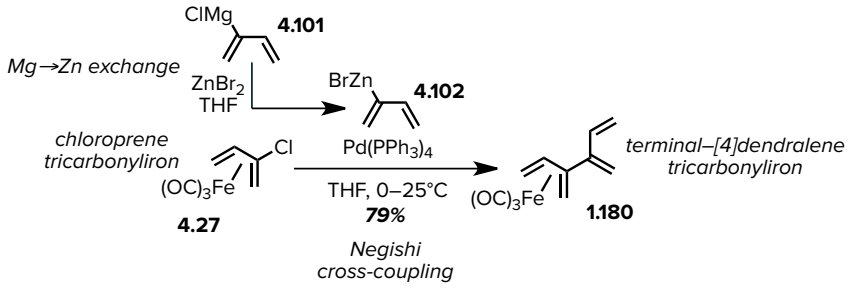
DENDRALENES VIA *TRICARBONYLIRON COORDINATED HALOBUTADIENES*

We were delighted to find that chloroprene-tricarbonyliron, **4.27**, successfully coupled with potassium trifluorovinylborate, **4.99**,[475,476] under Buchwald's Suzuki–Miyaura cross-coupling conditions (Scheme 4.24).[472,473] By this method we could produce tricarbonyliron[3]dendralene in 67 % yield from the chloroprene complex. Similarly, we could carry out Stille cross-coupling reactions[477] on chloroprene-tricarbonyliron, **4.27**, in the presence of vinyl tributyltin, **4.100**, to prepare [3]dendralene-tricarbonyliron in even higher yield (80 %).



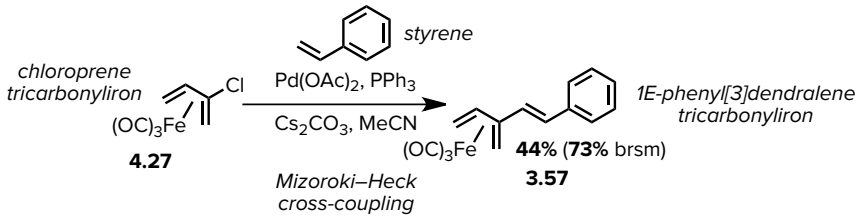
Scheme 4.24: Multiple routes to tricarbonyliron[3]dendralene with palladium.

To prepare the *terminal*-tricarbonyliron complex of [4]dendralene was one of the primary goals of this project. After a few unsuccessful Kumada reactions,[478,479] we were able to successfully prepare the complex **1.180** in good yield using Negishi cross-coupling chemistry (Scheme 4.25).[291] The organozinc reagent **4.102** could be generated *in situ* from the Grignard reagent **4.101**, itself prepared in one step from chloroprene. The reaction was preparatively very simple, and the target complex was recovered from the crude reaction mixture after filtration though a short silica plug. This simple process is in stark contrast to the inefficient multi-step route undertaken in Chapter 2 to prepare the same intermediate (pages 62 & 77).



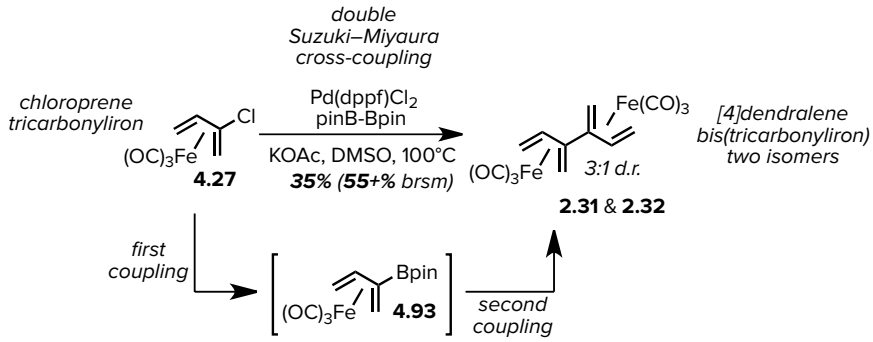
Scheme 4.25: Negishi cross-couplings solve access to mono-*terminal* tricarbonyliron[4]dendralene.

Mizoroki–Heck cross-coupling on chloroprene-tricarbonyliron gave us a new route to the series of 1*E*-substistuted-[3]dendralene complexes, such as compound **3.57** (Scheme 4.26). Even in unoptimised form, this result rendered obsolete our previous syntheses of this class of compounds *via* cross-metathesis and Mizoroki–Heck reactions on tricarbonyliron[3]dendralene (described on pages 71 & 102).



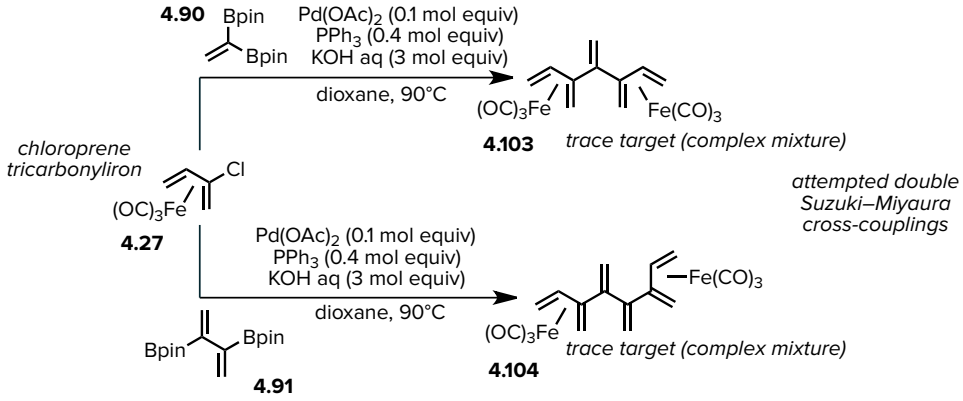
Scheme 4.26: 1*E*-Substituted tricarbonyliron[3]dendralenes from a common intermediate.

When electrophilic coupling partners are reacted with bis-nucleophiles (such as bis(pinacolatoboron), pinB–Bpin) they can react twice, i.e. at each of the nucleophilic moieties. This principle would allow us to make dendralenes that are terminated at each end with a tricarbonyliron group, the simplest of which would be bis(tricarbonyliron)-[4]dendralenes, **2.31** & **2.32** (Scheme 4.27). The desired dimerisation was effected by the use of '*one-pot Suzuki biaryl synthesis*' conditions.[480] These conditions generate a borylated version of the starting material *in situ*, which is then coupled to another equivalent of the starting material. The successful application of this reaction to chloroprene-tricarbonyliron, **4.27**, contains within it the first implicit use of 2-pinacolatoboron-1,3-butadiene tricarbonyliron, **4.93**.



Scheme 4.27: A selective synthesis of bis-*terminal* tricarbonyliron[4]dendralenes.

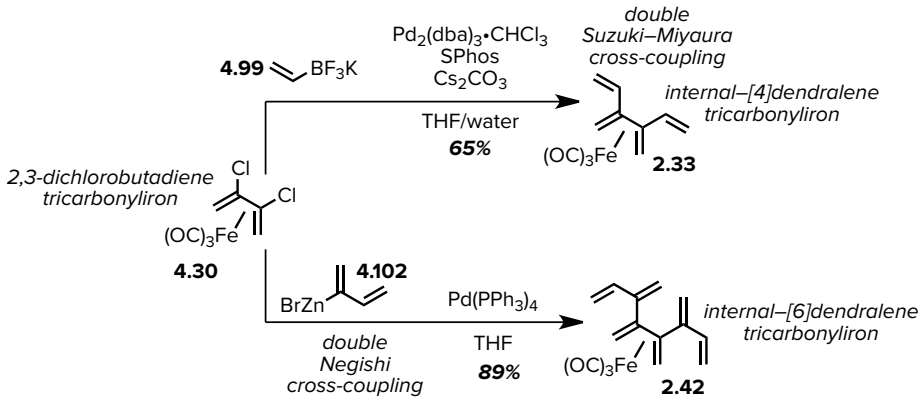
Vinylidenyl and butadienyl expanded versions of bis(pinacolatoboron), **4.90** and **4.91**, respectively, have been prepared in the literature (first described on page 127).[454,481] We planned to use these intermediates to directly prepare the bis-*terminal* tricarbonyliron complexes of [5]dendralene and [6]dendralene (Scheme 4.28). Unfortunately, we ran into a great deal of trouble when attempting to use these reagents with anything other than the most simple electrophilic coupling partner. ^{1}H NMR spectroscopic analysis of crude reaction mixtures showed some of the target materials **4.103** & **4.104**, but in our preliminary studies we did not have the opportunity to optimise the reaction beyond this point.



Scheme 4.28: Complications with Suzuki cross-couplings and bis-boron nucleophiles.

Possibly the most interesting and novel results of this research are the *double* cross-coupling reactions of the bis-electrophilic 2,3-dichlorobutadiene-tricarbonyliron complex, **4.30** (Scheme 4.29). Each of the C–Cl bonds could couple with one equivalent of the nucleophilic reagent. Under Suzuki–Miyaura conditions with potassium vinyltrifluoroborate, 2,3-dichlorobutadiene-tricarbonyliron afforded *internal*-tricarbonyliron [4]dendralene, **2.33**. For

comparison, the same compound is prepared as the minor product in 7 % yield on direct complexation of [4]dendralene with tricarbonyliron.



Scheme 4.29: *Internally*-complexed [4]- & [6]dendralenes *via* cross-coupling.

In the same way as *internal*-tricarbonyliron [4]dendralene, **2.33**, can be prepared (Scheme 4.29), so too can *internal*-tricarbonyliron [6]dendralene, **2.42**. This compound cannot be formed by direct tricarbonyliron complexation reaction with [6]dendralene, but is formed in good yield from the Negishi reaction of 2-butadienylzinc bromide with 2,3-dichlorobutadiene-tricarbonyliron.

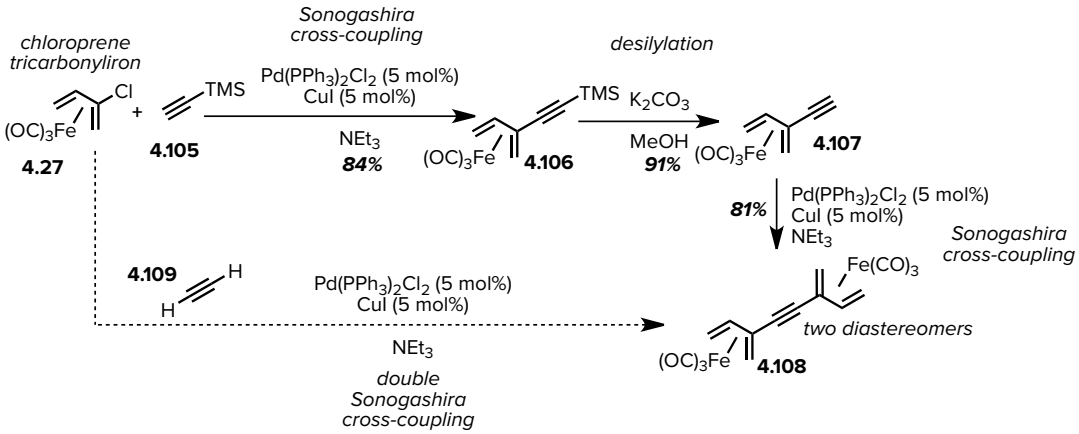
Evidently, if selective mono-coupling reactions on dichloride **4.30** can be carried out then an even greater range of structural types can be obtained. Experiments to test this possibility should be a high priority in future investigations in this area.

4.3 Results: Extension to Other Cross-Conjugated Systems

More than just a more elegant route to complexes of the dendralene family of hydrocarbons, we sought a general route to interesting conjugated systems. The next step was thus the Sonagashira reaction.

A Sonagashira reaction between acetylene and chloroprene-tricarbonyliron would give us exactly what we wanted, a very rapid route to a novel polyunsaturated hydrocarbon framework (Scheme 4.30). But, using acetylene directly in an untested reaction can also lead to a complicated optimisation, due to acetylene's volatility and flammability. Instead, TMS-acetylene, **4.105**, was used to allow us more control over each of the steps. After the successful Sonagashira reaction to

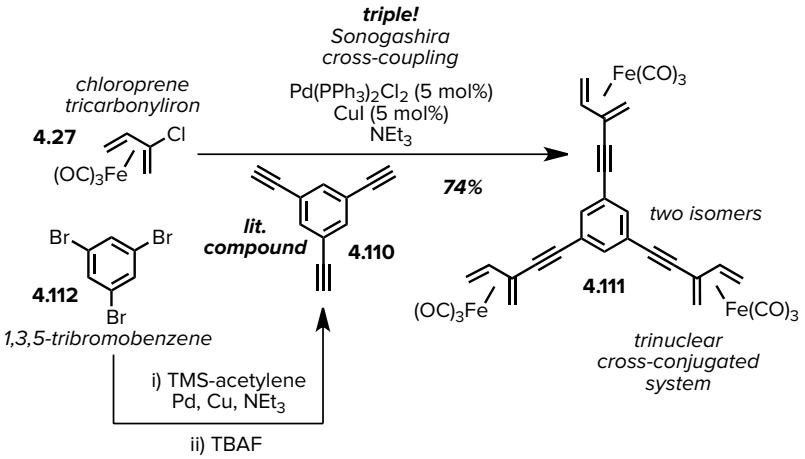
form complex **4.106**, desilylation was effected with potassium carbonate in methanol exposing the second alkynic terminus to allow a second Sonagashira cross-coupling reaction to form complex **4.108**. This sequence also gave us a route to access 2-ethynyl butadiene as its tricarbonyliron complex, **4.107**, the free hydrocarbon of which was reported by Hopf and coworkers.[482-484]



Scheme 4.30: Dehydro-dendralenes, and acetylene-expanded cross-conjugated systems.

To test the cross-coupling ability of tricarbonyliron-chloroprene *in extremis* we went looking for more challenging examples, where we came across trialkyne **4.110** (Scheme 4.31).[485H] Chloroprene-tricarbonyliron underwent a very successful ***triple*** Sonagashira cross-coupling with 1,3,5-triethynylbenzene[486] to form the cross-conjugated framework in **4.111**.

[H] Kindly provided to this author by Dr. Torsten Schwich.



Scheme 4.31: Sonogashira cross-coupling approach to a trinuclear cross-conjugated assembly.

The tris(tricarbonyliron) complex **4.111** was formed as mixture of two diastereomers, a *syn,syn*- and a *syn,anti*-isomer, of which the major isomer could be isolated and fully characterised. The major isomer is so-called, because crystals could not be grown that were suitable for single-crystal X-ray diffraction, and we cannot confidently assert which of the two possible isomers was prepared on the basis of NMR—or other—spectroscopic data. Due to the remoteness of the stereocenters (and their associated steric bulk) from each other, it is likely that the products were formed in statistical proportions. There are a total of eight possible stereoisomers in a molecule containing three stereocenters (2^3), and of these only two are *syn,syn*, the other six are *syn,anti*. If this is the case, the major product would be the *anti,syn* isomer over the *syn,syn* isomer in a 3:1 ratio.

Several other types of transformation were attempted on chloroprene-tricarbonyliron, including Grignard formation,[487] Kumada cross-coupling,[478] and radical hydro-dehalogenation[449] reactions. While initially unsuccessful, these reactions are representative of the possible future directions of this research.

4.3.1 Towards [5]Radialene

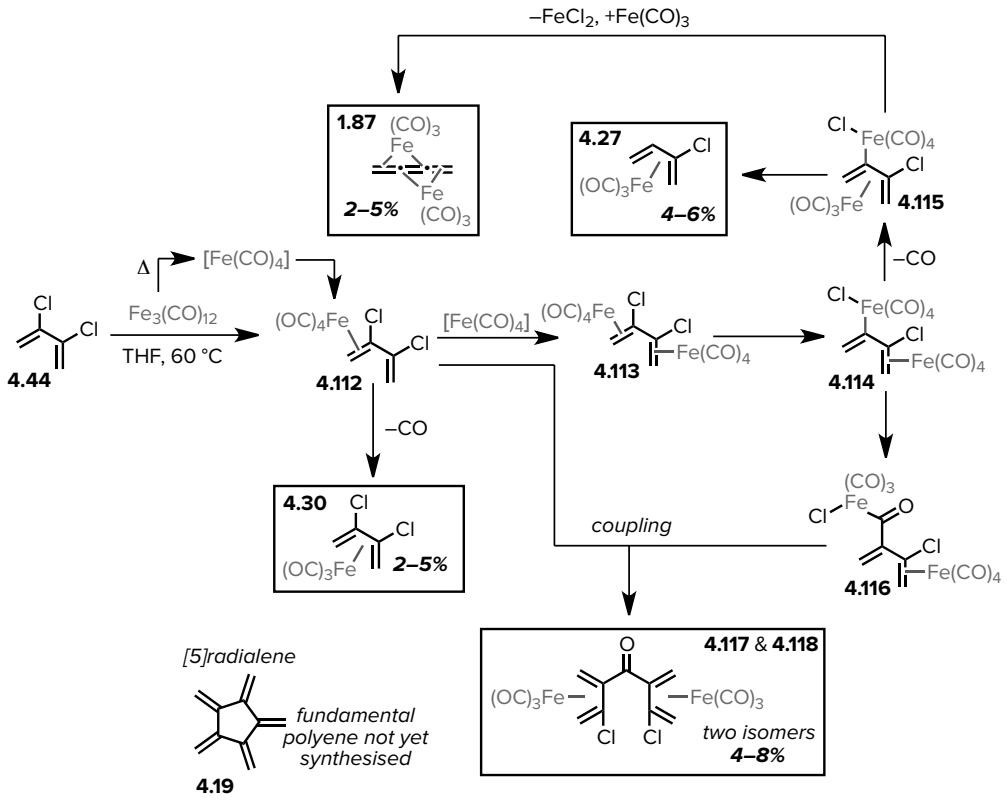
AN INTERESTING BYPRODUCT

One of the most significant results of this research came about serendipitously[I] while investigating the tricarbonyliron complexation of 2,3-dichlorobutadiene. We observed that alongside the formation of the desired complex **4.30** was the

[I] *Dans les champs de l'observation le hasard ne favorise que les esprits préparés.*—Louis Pasteur.

generation of multiple other tricarbonyliron complexes (Scheme 4.32). In fact, a total of *five* tricarbonyliron complexes are isolated from the complexation reaction in roughly equal amounts. Two of these side-products are the bis(tricarbonyliron) complex **1.117** & **1.118**, compounds that contains a cross-conjugated structure very familiar to us, an oxa-[5]dendralene, but curiously functionalised at each terminus with chlorine atoms. These compounds appear tantalisingly close to the cross-conjugated structure of [5]radialene, **4.19**, a compound that has thus far eluded successful synthesis.

In tricarbonyliron complexation reactions, the first step is the coordination of an $[Fe(CO)_4]$ group to one of the olefins in the diene (Scheme 4.32). In the case of 2,3-dichlorobutadiene it appears that the $[Fe(CO)_4]$ group can subsequently insert into a C–Cl bond (such as in **4.114**) and wreak havoc on the selectivity of the complexation.



Scheme 4.32: Proposed mechanism for the stepwise formation of each of the observed by-products (shown in boxes) from the complexation of 2,3-dichlorobutadiene. Isolated yields presumably do not reflect the true selectivity of the reaction.

Once a tricarbonyliron group has inserted it can then either eliminate (as in **1.87** & **4.27**) or undergo α-insertion of a CO ligand followed by coupling with another equivalent of 2,3-dichlorobutadiene to give complexes **4.117** & **4.118**. It was these final compounds that instigated this investigation into the reaction, because we believed we could use them to make [5]radialene (*v.i.*). Insertion byproducts such as complexes **4.117** & **4.118** have been observed in the literature on a few previous occasions.[145,147,256]

If Scheme 4.32 is an accurate representation of the mechanism then it is unsurprising that isolated yields from the reaction are very low, as many intermediates (some not shown) would be very reactive. This is especially true for intermediates lacking tricarbonyliron coordination at one or more site (the instability of 2-substituted butadienes is elaborated upon in Chapter 1, page 25). Selectivity for the formation of each of the side-products observed in this reaction is extremely difficult to measure with the analytical tools available in a synthetic organic laboratory. It may be possible to detect the presence of reactive intermediates *en route* to each of the isolated products using real-time reaction monitoring tools, such as *ReactIR* which carries out extremely rapid FTIR analysis on reaction mixtures. Without such information there was little scope for a rational optimisation of the formation of **4.117** & **4.118** (Scheme 4.32).

[5]RADIALENE – THE MISSING LINK

The [n]radialenes are a fundamental class of cross-conjugated oligoalkenes that contain an *n*-membered ring decorated with exocyclic methylene units (Figure 4.7, first mentioned on page 46). The [n]radialenes tend to be unstable, and so of the first four members of the family, only three have been synthesised. [3]Radialene was prepared by Dorko and coworkers[488,489] in 1963, [4]radialene was prepared by Griffin & Peterson[490,491]in 1962, and [6]radialene was prepared by Vollhardt and coworkers[492] in 1977. [5]Radialene—despite multiple attempts[251,493]—remains unknown.

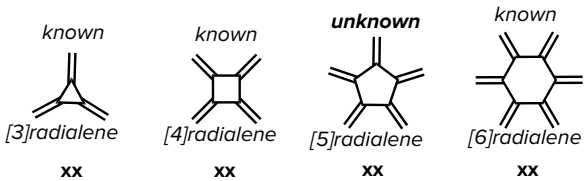
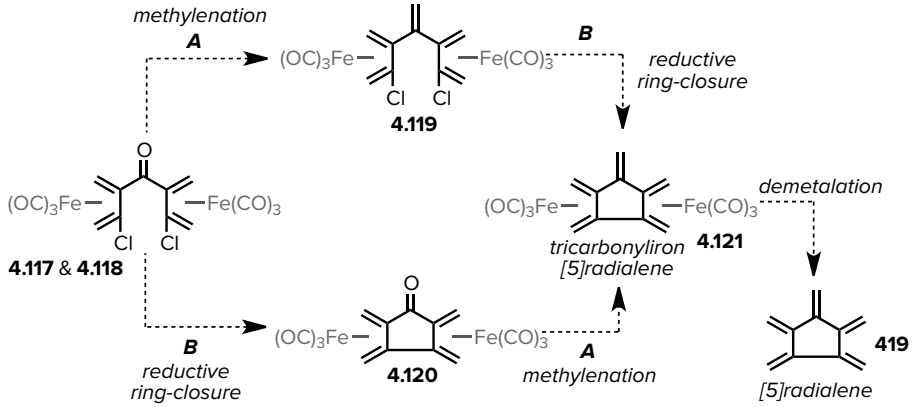


Figure 4.7: The first four [n]radialenes. Radialenes [3], [4], & [6] are known in the literature, but [5]radialene is not.

The complexes serendipitously prepared, **4.117** & **4.118**, are in effect only two steps away from an $Fe(CO)_3$ protected [5]radialene, **4.121** (Scheme 4.33). To get from **4.117** & **4.118** to **4.121** we planned two convergent paths of either methylenation (step **A**) followed by ring-closure (step **B**, i.e. **AB**), or vice versa (**BA**). Since both *syn*- and *anti*-diastereomers **4.117** & **4.118** are possible, a total of *four* routes to [5]radialene can be conceived.



Scheme 4.33: Attempted routes A→B & B→A towards a protected [5]radialene.

Initial attempts were made to translate the planned synthesis of complex **4.121** into reality (Scheme 4.33). Methylenation reactions (**A**) attempted on complexes **4.117** & **4.118** were Wittig, Petersen, and Petasis olefinations.[494] To take the other tack, tin[495] and boron[480] based conditions were also attempted to bring about reductive ring closures (**B**). These reactions have so far been unsuccessful.

To fully characterise these compounds, we set about growing crystal suitable for X-ray analysis of the bis(tricarbonyliron) coordinated complexes of **4.122** (Figure 4.8). One of the isomers out of **4.117** & **4.118** had been previously identified by Nelson and coworkers during the complexation of 2,3-dichlorobutadiene,[145] but the stereochemistry was undefined. By comparison with ^{1}H NMR spectroscopic data, we assign the compound isolated by Nelson and coworkers as the *syn*-isomer **4.118**.

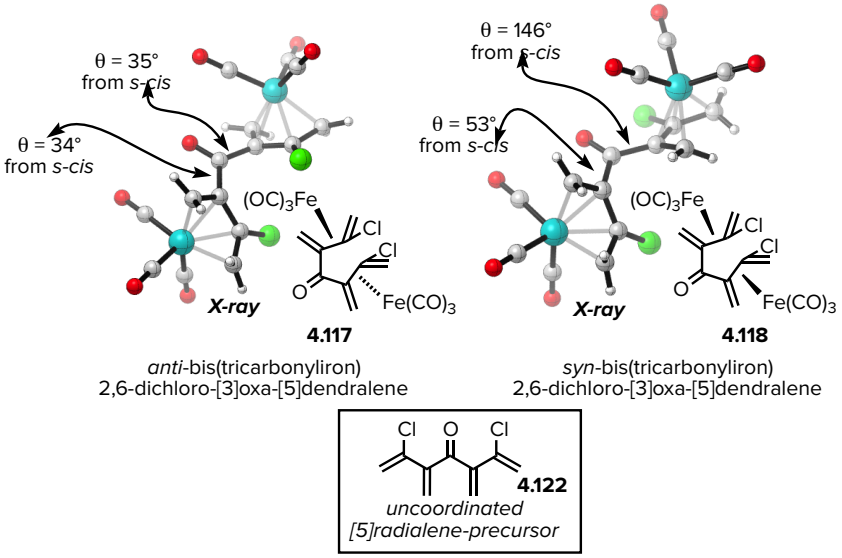
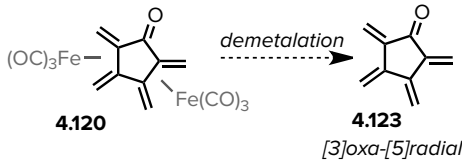


Figure 4.8: Molecular structures of bis(tricarbonyliron)-2,6-dichloro-[3]oxa-[5]dendralenes *via* single crystal X-ray crystallography. Tantalising intermediates on the way to [5]radialene.

There is presumably significant steric trauma associated with a *syn*-bis(tricarbonyliron) complexed [5]radialene. This assumption is backed up by analysis of the molecular structure derived from single-crystal X-ray diffraction of **4.118**, shown above (Figure 4.8), which has the carbons bearing the chlorine atoms almost completely rotated away from each other to minimise the steric clash of the tricarbonyliron groups.

In contrast to the steric impedance facing *syn*-complex **4.118**, observation of the molecular structure of *anti*-complex **4.117** indicates that the carbon atoms bearing the chlorines should be well-positioned to undergo the planned reductive C–C bond formation (*cf.* Scheme 4.33). This is observation is made with some confidence, as the structures shown in Figure 4.8 are very similar to those observed for bis(tricarbonyliron)-[5]dendralene (**2.39** & **2.40**, page 65), and the preferred conformations of the tricarbonyliron-dendralenes was confirmed by DFT analysis.

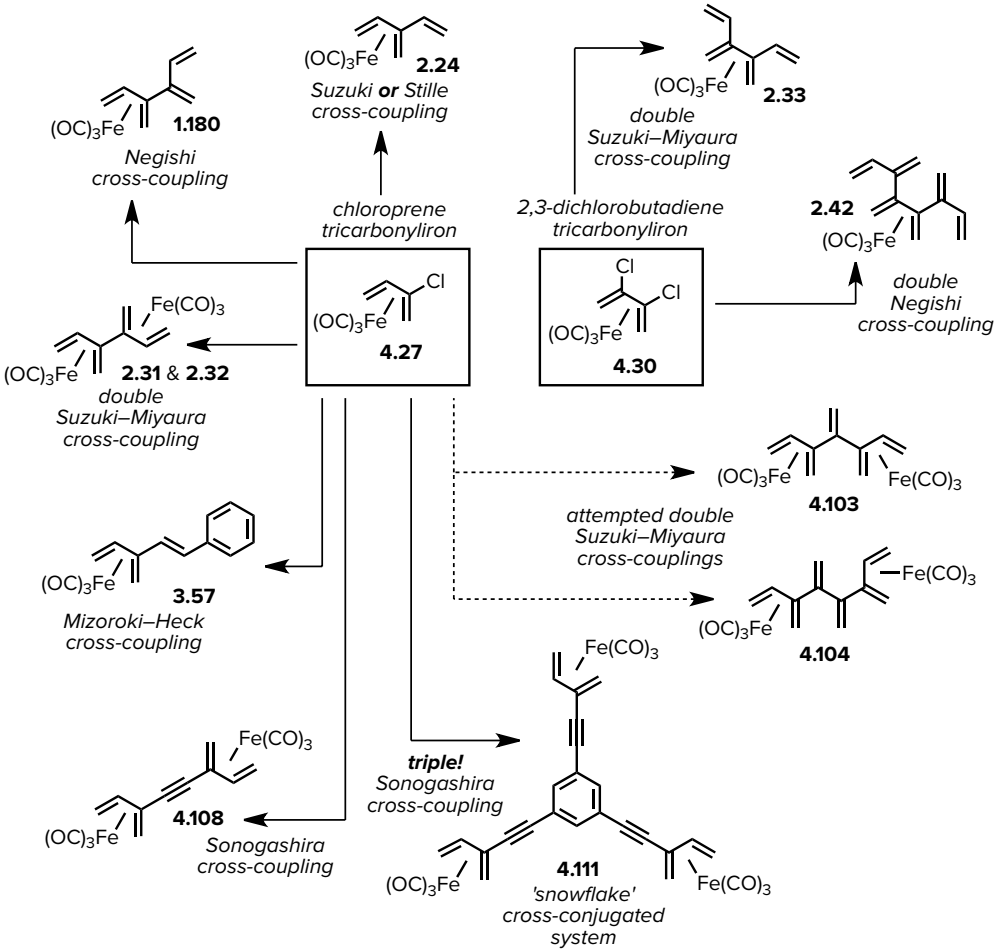
Obviously, synthesis of oxa-[5]radialene **4.123** (Scheme 4.34) could also be possible *via* the synthetic sequence *en route* to [5]radialene (Route **BA**, Scheme 4.33). [3]Oxa-[5]radialene is another unreported compound that would presumably be extremely reactive indeed.



Scheme 4.34: Targeted preparation of the unreported [3]oxa-[5]radialene.

4.4 Conclusions

Described in this chapter is a second generation synthesis of the tricarbonyliron-[n]dendralenes. This work arose from the need for a better synthesis of those [n]dendralene complexes that are selectively protected at particular diene sites, compounds like *internal- & terminal*-tricarbonyliron[4]dendralenes **1.180** & **2.33** (Scheme 4.35).



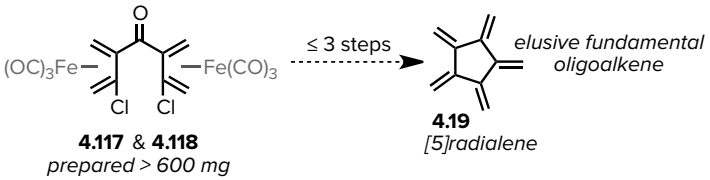
Scheme 4.35: Rapidly generated cross-conjugated frameworks from halobutadiene-tricarbonyliron building blocks.

Development of this methodology necessitated the large-scale preparation of literature-known complexes **4.27** & **4.30**, and the subsequent development of cross-coupling methodology compatible with these complexes. The tricarbonyliron[n]dendralenes **2.24**, **2.33**, **2.42**, **1.180**, **2.31**, & **2.32** were thus accessed *via* a range of different cross-coupling reactions (Scheme 4.35). As well as the parent dendralene complexes, 1*E*-substituted [3]dendralene complex **3.57** was also directly accessible from chloroprene-tricarbonyliron.

Not only was this methodology useful to prepare the tricarbonyliron[n]dendralenes more efficiently, but we were also able to prepare alkyne-containing cross-conjugated frameworks such as **4.108** & **4.111** (Scheme 4.35).

The weakest point of this work is the low yields in the preparation of the initial chlorodiene complexes. Ideally, these complexes would be made using Grevels' reagent, $(ZCE)_2Fe(CO)_3$, to prepare them under conditions mild enough to preclude side-reaction. This complexation method, once developed, could also be applied to prepare even more halodiene- and metallodiene-tricarbonyliron building blocks, so that this methodology can be truly general.

Although at present we cannot report the preparation of [5]radialene, we have made a pair of advanced intermediates (**4.117** & **4.118**) that should lead to its synthesis in short order (Scheme 4.36).



Scheme 4.36: Towards the first synthesis of [5]radialene.

5

Experimental

5.1 General Methods

NMR SPECTROSCOPY

^{1}H NMR spectra were recorded under standard conditions at 800 MHz, 600 MHz, 500 MHz, 400 MHz and 300 MHz using a *Bruker AVANCE 800*, *Bruker AVANCE 600*, a *Varian Unity INOVA 500*, *Varian MR400* or *Varian Mercury 300* spectrometer. Residual chloroform (δ 7.26 ppm) was used as an internal reference for ^{1}H NMR spectra measured in chloroform-*d*. Coupling constants (*J*) are quoted to the nearest 0.1 Hz. Assignment of proton signals was assisted by COSY, 1D-nOe, and NOESY experiments when necessary. ^{13}C NMR spectra were recorded at 200 MHz, 150 MHz, 125 MHz, 100 MHz or 75 MHz using a *Bruker AVANCE 800*, *Bruker AVANCE 600*, a *Varian Unity INOVA 500*, *Varian MR400* or *Varian Mercury 300* spectrometer. The central line of chloroform-*d* (δ 77.1 ppm) was used as an internal reference for ^{13}C NMR spectra recorded in this solvent. For other solvents, residues were assigned according to Fulmer and coworkers.[496]

Assignment of carbon signals was assisted by DEPT, HMBC, or HSQC experiments.

INFRARED SPECTROSCOPY, MASS SPECTROMETRY, & MELTING POINTS

IR spectra were recorded on a *Perkin–Elmer 1600* FTIR spectrometer as neat films on NaCl plates for oils, or as potassium bromide discs for solid products with only selected peaks being reported as characteristic. Low resolution mass spectra were recorded on a *Finnigan Polaris Q* ion trap mass spectrometer using electron impact (EI) ionisation mode at 40 or 70 eV, or a *VG Quattro II* triple quadrupole MS for electrospray ionisation (ESI). Low resolution mass spectra (*m/z*) were recorded with only major peaks being reported with intensities quoted as percentages of the base peak. High resolution mass spectra were recorded on a *VG Autospec* mass spectrometer operating at 70 eV for EI, or a *Bruker Apex3* 4.7T FTICR-MS for ESI. Positive ionisation was measured unless otherwise indicated. Melting points were measured on a *Reichert* melting point stage and are uncorrected.

CHROMATOGRAPHY

Analytical high performance liquid chromatography (HPLC) was performed using a *Shimadzu Prominence LC-20AD* chromatography pump and *SIL-20A* autosampler, on an *Alltima* silica 5 μm column (250 mm, 4.6 mm ID). Preparative HPLC was performed using a *Waters 600E* instrument on an *Alltima* silica 5 μm (250 mm, 22 mm ID), an *Alltima* silica 5 μm (250 mm, 10 mm ID), or a *Waters* silica 5 μm (150 mm, 19 mm ID) column unless otherwise specified. Analytical TLC was performed with *Merck* silica gel plates, precoated with silica gel *60 F254* (0.2 mm). Compounds on TLC were visualised by exposure to UV light and/or by dipping the plates in solutions of phosphomolybdic acid or vanillin followed by heating. Flash chromatography employed *Merck Kiesegel 60* (230–400 mesh) silica gel. Details of chromatographic conditions are indicated with each compound. UV-Vis spectra recorded using a *Shimadzu UV-Visible 2450* spectrometer.

REACTION CONDITIONS & REAGENT PURITY

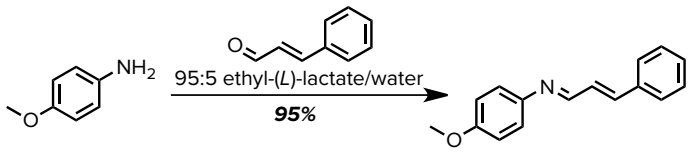
Reactions were conducted under a positive pressure of dry nitrogen in oven-dried glassware. A *LAUDA ecoline 006* constant temperature bath with a *LAUDA E300* temperature controller was used in kinetic and half-life experiments. Reaction conditions invoking microwave irradiation were carried out in a *CEM Discover and Explorer SP* microwave synthesis system. Solvents were dried using a solvent

purification system based on that described by Pangborn and co-workers,[497] dried over sodium wire and distilled from sodium benzophenone ketyl, or dried using standard laboratory methods.[498] Petrol refers to bp 40–60 °C petroleum spirits unless otherwise stated. All chemicals were purchased from *Aldrich*, *Alfa Aesar*, *Merck*, or *Strem* and used without further purification, or purified by standard procedures.[498] Solutions of *n*-BuLi or Grignard reagents were titrated against salicylaldehyde phenylhydrazone using the procedure of Love and coworkers.[499]

5.2 Experimental For Chapter 2

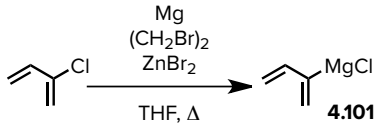
5.2.1 Tricarbonyliron Complexation of the Dendralenes

(E)-1-(4-METHOXYPHENYL)-4-PHENYL-1-AZA-1,3-BUTADIENE ***2.14***



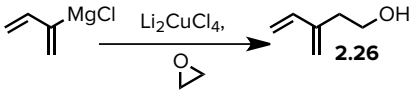
Compound **2.14** was prepared according to a slightly modified version of the procedure reported by Bennett and co-workers.[500] *p*-Anisidine (12.3 g, 100 mmol, 1.0 mol equiv) was dissolved in 95:5 ethyl-(*L*)-lactate : water (v/v) (50 mL). Cinnamaldehyde (12.6 mL, 100 mmol, 1.0 mol equiv) was added, the resulting solution was swirled until homogeneous and left to crystallise, which occurs spontaneously within seconds at room temperature. The *title compound* was isolated by vacuum filtration and washed with cold brine followed by water, then by pentane, and subsequently dried under a reduced pressure. The product was obtained as an ashen-yellow crystalline solid (22.48 g, 95%);
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.30 (t, J = 4.7 Hz, 1H), 7.55-7.52 (m , 2H), 7.43-7.34 (m, 3H), 7.24-7.20 (m, 2H), 7.13 (d, J = 3.5 Hz, 2H), 6.92 (dd, J = 6.5, 1.4 Hz, 2H), 3.83 (s, 3H) ppm.
^{1}H NMR spectroscopic data were in accordance with reported values.[25]

2-(1,3-BUTADIENYL)MAGNESIUM CHLORIDE **4.101**



To an oven-dried 2 L 3-neck round bottomed flask with magnetic stirrer, reflux condenser, and non-equalising addition funnel was added oven-dried magnesium turnings (42.5 g, 1.75 moles, 1.5 mol equiv.) under nitrogen. Enough THF (200 mL) was added to cover the magnesium, and the mixture was stirred at approx. 250 rpm. 1,2-dibromoethane (15 mL, 0.28 moles, 0.15 mol equiv.) was added slowly as an entrainer[501] (associated with vigorous gas evolution), followed by $ZnBr_2$ solution in THF (1.2 M, 10 mL, 12 mmol, 0.01 mol equiv.). A solution of THF (1 L), chloroprene[428] a (104 mL, 1.13 moles, 1.0 mol equiv.), and 1,2-dibromoethane (15 mL, 0.28 moles, 0.15 mol equiv.) was made up and added dropwise *via* addition funnel to maintain reflux. The reaction was then heated for 2 hours at reflux before it was titrated twice against of salicylaldehyde phenylhydrazone[499] (100 mg) in THF (10 mL) to give a concentration of 0.782 M (86% yield). The Grignard reagent could be stored for months in a light-protected Schlenk tube without significant degradation.

2-ETHANOLIC-1,3-BUTADIENE **2.26**



A solution of oven dried LiCl (2.00 g, 56.3 mmol, 0.12 mol equiv.) and anhydrous $CuCl_2$ (3.09 g, 28.2 mmol, 0.06 mol equiv.) in THF (300 mL) was prepared in a 2-neck round bottom flask with an equalising addition funnel and a dry-ice/acetone cooled cold-finger apparatus attached. A solution of ethylene oxide (20.6 g, 469 mmol, 1.0 mol equiv.) in THF (100 mL) (an approximately 4 M solution was targeted) was added *via* cannula to the reaction mixture and the mixture was heated to reflux (during later modifications it was found that this heating was unnecessary). Chloroprene Grignard reagent (0.782 M in THF, 600 mL, 469 mmol, 1.0 mol equiv.) was added *via* the addition funnel over 1 hour. Heating was continued for a further 2 h. The reaction was quenched by pouring the mixture

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[A] Although chloroprene is available industrially on the ton scale it is extremely difficult to obtain on the gram scale, and so chloroprene was prepared in the laboratory on 2 mole scale and in 77-85% yield according to the published patent (Tassara *et al.*).

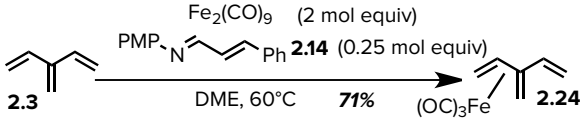
into a stirring 1 : 1 mixture of ether : water (1 L). The pH of the solution was adjusted to bring it to a pH of 4 (involved the addition of some 1N HCl), upon which a colour change and/or the generation of *gunk* in the aqueous phase was observed (the ether layer could be either extracted or decanted at this stage, decanting the first layer made further work-up less messy on a large scale). The ether layer was decanted and filtered through a plug of Celite. The aqueous layer was then extracted with more ether and the combined organic layers were dried with anhydrous magnesium sulfate. The magnesium sulfate was removed by vacuum assisted filtration and the solvent was removed under reduced pressure (0 °C, 40 Torr) and the resulting yellow/brown oil was purified by distillation[B] (care was required to stop the diene polymerising at this stage, and BHT was added to the distilling flask) (b.p. 61-66 °C / 20 Torr) affording the *title compound* **(2.26)** as a colourless oil (31.8416 g, 69 %). The *title compound* was converted into [3]dendralene according to the published procedure.[294]

b.p. 61-66 °C (20 Torr);

^{1}H NMR (300 MHz; $CDCl_3$): δ 6.44-6.34 (m, 1H), 5.26 (d, J = 17.6 Hz, 1H), 5.14-5.08 (m, 3H), 3.76 (q, J = 6.2 Hz, 2H), 2.52 (td, J = 6.4, 0.9 Hz, 2H) ppm.

^{1}H NMR spectroscopic data and physical data were in accordance with reported values.[148,390]

(3-METHYLENE-1,4-PENTADIENE)TRICARBONYLIRON ***2.24***



To a stirred solution of [3]dendralene[4] **(2.3)** (300 mg, 3.75 mmol, 1.0 mol equiv.) in distilled 1,2-dimethoxyethane (15 mL) was added $Fe_2(CO)_9$ (2.7249 g, 7.5 mmol, 2.0 mol equiv.) and (*E*)-1-(4-methoxyphenyl)-4-phenyl-1-aza-1,3-butadiene **2.14** (222 mg, 0.94 mmol, 0.25 mol equiv.). The reaction mixture was protected from light with aluminium foil, and stirred for 4 h at 60 °C. The solvent was removed under reduced pressure and the resulting orange/brown solid was purified by flash column chromatography (eluting with pentane on silica gel) affording **(2.24)** as a yellow oil (529 mg, 71%);

R_f 0.7 (pentane);

^{1}H NMR (300 MHz, $CDCl_3$): δ 6.52 (dd, J = 9.2, 10.2 Hz, 1H), 5.57 (d, J = 17.1 Hz,

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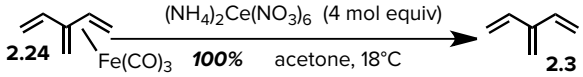
[B] Other experimentalists (J. Boyle *et al.*) have determined that the diene is *pure by NMR* at this stage and does not require distillation, even though it is discoloured.

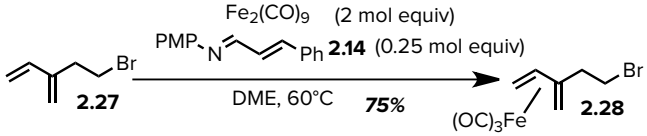
1H), 5.44 (t, *J* = 8.1 Hz, 1H), 5.15 (d, *J* = 10.5 Hz, 1H), 2.19 (dd, *J* = 2.4 Hz, 1.5 Hz, 1H), 1.80 (dd, *J* = 6.9, 2.4 Hz, 1H), 0.32 (dd, *J* = 9.3, 2.4 Hz, 1H), 0.15 (d, *J* = 2.7 Hz, 1H) ppm;
^{13}C NMR (75 MHz, $CDCl_3$): δ 211.1 (q), 137.2 (CH), 114.6 (CH_2), 101.0 (q), 85.7 (CH), 39.8 (CH_2), 37.5 (CH_2) ppm;
IR (thin film): ν_{max} = 3012, 2049, 1970 cm^{-1};
MS (EI): *m/z* (%): 220 ([*M*]$^{+\cdot}$, 18), 192 ([*M*]$^{+\cdot}$-CO, 35), 164 ([*M*]$^{+\cdot}$-2CO, 36), 136 ([*M*]$^{+\cdot}$-3CO, 100), 55.9 (51, $Fe^{+\cdot}$);
HRMS (EI): calculated for $C_9H_8FeO_3$ [*M*]$^{+\cdot}$: 219.9823; found 219.9828.

[3]DENDRALENE ***2.3***



To a stirred solution of compound **2.24** (4.0 mg, 0.018 mmol, 1.0 mol equiv) in acetone-d_6 (0.5 mL), a solution of cerium ammonium nitrate (20.0 mg, 0.037 mmol, 2.0 mol equiv) in acetone-d_6 (0.5 mL) was added dropwise at room temperature. Anisole (2.0 mg, 0.018 mmol, 1.0 mol equiv) was used as an internal standard for this transformation. Progress of the reaction was very rapid and followed by ^{1}H NMR spectroscopy. **2.3** was afforded as a solution in acetone-d_6 (1.5 mg/mL, 100% by NMR).
^{1}H NMR (300 MHz, $CDCl_3$): δ 6.45 (dd, *J* = 17.6, 10.5 Hz, 2H), 5.41 (d, *J* = 17.6 Hz , 2H), 5.15 (t, *J* = 5.3 Hz, 4H) ppm.
^{1}H NMR spectroscopic data were in accordance with reported values.[294]

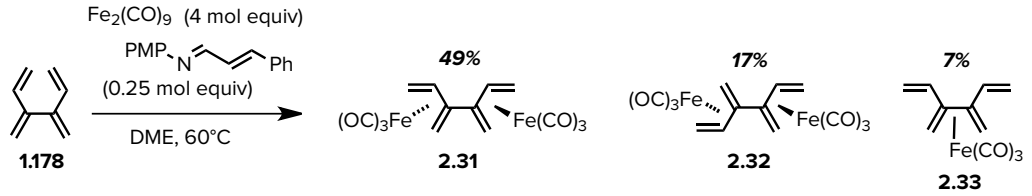
(5-BROMO-3-METHYLENEPENT-1-ENE)TRICARBONYLIRON ***2.28***



An amber glass round bottom flask fitted with reflux condenser was charged with diiron nonacarbonyl (1.13 g, 3.1 mmol, 2.0 mol equiv.) and (*E*)-1-(4-methoxyphenyl)-4-phenyl-1-aza-1,3-butadiene **2.14** (92 mg, 0.39 mmol, 0.25 mol equiv.). The reaction vessel was filled with nitrogen and a solution of 5-bromo-3-methylenepent-1-ene **2.27** (233.7 mg, 1.55 mmol, 1.0 mol equiv.) in DME (6.2 mL). The reaction mixture was protected from light with aluminium foil, and stirred for 2 h at 60 °C. The solvent was removed under reduced pressure and the resulting orange/brown solid was purified by flash column chromatography (eluting with pentane on silica gel) affording the *title compound* as a yellow oil (347

mg, 75% yield);
R_f 0.6 (hexane).
^{1}H NMR (300 MHz, $CDCl_3$): δ 5.37 (app t, J = 8.1 Hz, 1H), 3.71-3.54 (m, 2H), 2.98-2.89 (m, 1H), 2.82-2.72 (m, 1H), 1.80 (dd, J = 2.9, 1.5 Hz, 1H), 1.73 (dd, J =7.3, 2.9 Hz, 1H), 0.30 (d, J = 2.9 Hz, 1H), 0.13 (dd, J = 6.6, 3.0, Hz, 1H) ppm;
^{13}C NMR (75 MHz, $CDCl_3$): δ 211.1 (q), 103.0 (q), 85.8(CH), 42.7 (CH_2), 40.8 (CH_2), 38.7 (CH_2), 33.1 (CH_2) ppm.
IR (thin film): ν_{max} = 2927, 2049, 1970, 1263 cm^{-1};
MS (EI): *m/z* (%): 300.0 ([*M*]$^{+\cdot}$, 16), 274.0 (57), 243.9 (43), 215.9 (90), 187.9 (100), 56.0 (88);
HRMS (EI): calculated for $C_9H_9BrFeO_3$ [*M*]$^{+\cdot}$: 299.9084; found 299.9093.

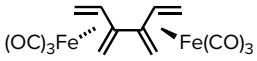
TRICARBONYLIRON COMPLEXATION OF [4]DENDRALENE



1.178 **2.31** **2.32** **2.33**

A 3.1 M solution of [4]dendralene[6] in THF (0.95 mL, 3.0 mmol, 1.0 mol equiv.) was added to a stirred suspension of $Fe_2(CO)_9$ (4.43 g, 12.0 mmol, 4.0 mol equiv.) and 1-(4-methoxyphenyl)-4-phenyl-1-aza-1,3-butadiene **2.14** (180 mg, 0.76 mmol, 0.25 mol equiv.) in distilled 1,2-dimethoxyethane (19 mL). The reaction mixture was protected from light with aluminium foil, and stirred for 140 h at reflux. The reaction mixture was filtered through a plug of Celite and washed thoroughly with pentane. The filtrate and washings were concentrated under reduced pressure. A separation using flash column chromatography (eluting with pentane on silica gel) yielded a mixture of the two bisadducts (**2.31** and **2.32)** (726 mg, 63%, 78 : 22 *d.r.*) separate from the internal mono adduct (**2.33)** (51 mg, 7%).

*HEXACARBONYL[(S-CIS-3,4-DIMETHYLENE-1,5-HEXADIENE)]DIIRON-ANTI **2.31***

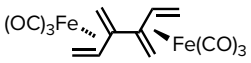


2.31

Compound **2.31** was obtained by normal phase HPLC (silica 5 μm, 250 mm x 22 mm, eluting with hexane). Compound **2.31** was recrystallized from a mixture of pentane and dichloromethane at -20 °C, to give yellow crystals;
R_f 0.55 (pentane);

m.p.: 98 °C (dichloromethane/pentane);
^{1}H NMR (300 MHz, $CDCl_3$): δ 5.68 (t, J = 8.1 Hz, 2H), 2.47 (dd, J = 3.3, 1.5 Hz, 2H), 1.89 (dd, J = 7.2, 2.4 Hz, 2H), 0.41 (dd, J = 9.0, 2.4 Hz, 2H), 0.25 (d, J = 3.0 Hz, 2H) ppm;
^{13}C NMR (75 MHz, $CDCl_3$): δ 210.6 (q), 102.1 (q), 82.0 (CH), 40.1 (CH_2), 37.6 (CH_2);
IR (KBr disc): ν_{max} = 2922, 2041, 1989, 1954 cm^{-1};
MS (EI): *m/z* (%): 385.9 (7, $[M]^{+\cdot}$), 357.9 (15, $C_{13}H_{10}Fe_2O_5^{+\cdot}$), 329.9 (73, $C_{12}H_{10}Fe_2O_4^{+\cdot}$), 301.9 (31, $C_{11}H_{10}Fe_2O_3^{+\cdot}$), 273.9 (41, $C_{10}H_{10}Fe_2O_2^{+\cdot}$), 245.9 (91, $C_9H_{10}Fe_2O^{+\cdot}$), 217.9 (100, $C_8H_{10}Fe_2^{+\cdot}$), 162.0 (46, $C_8H_{10}Fe^{+\cdot}$), 55.9 (41, $Fe^{+\cdot}$);
HRMS (EI): calculated for $C_{14}H_{10}Fe_2O_6$ $[M]^{+\cdot}$: 385.9184; found 385.9176.

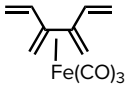
HEXACARBONYL[(S-TRANS-3,4-DIMETHYLENE-1,5-HEXADIENE)]DIIRON-ANTI ***(2.32)***



2.32

Compound **(2.32)** was obtained as a yellow solid from normal phase HPLC (silica 5 μm, 250 mm x 22 mm, eluting with hexane). Compound **(2.32)** was recrystallized from cold pentane to give yellow crystals;
R_f 0.55 (pentane);
m.p.: 163 °C (pentane);
^{1}H NMR (300 MHz, $CDCl_3$): δ 6.07 (t, J = 7.8 Hz, 2H), 2.16 (dd, J = 3.2, 1.5 Hz, 2H), 1.93 (dd, J = 7.1, 2.4 Hz, 2H), 0.40 (dd, J = 9.2, 2.4 Hz, 2H), 0.18 (d, J = 2.7 Hz, 2H) ppm;
^{13}C NMR (75 MHz, $CDCl_3$): δ 210.6 (q), 102.1 (q), 82.0 (CH), 40.1 (CH_2), 37.6 (CH_2);
IR (KBr disc): ν_{max} = 3016, 2042, 1985, 1958 cm^{-1};
MS (EI): *m/z* (%): 385.9 ($[M]^{+\cdot}$, 6), 357.9 ($[C_{13}H_{10}Fe_2O_5]^{+\cdot}$, 6), 329.9 ($[C_{12}H_{10}Fe_2O_4]^{+\cdot}$, 87), 301.9 ($[C_{11}H_{10}Fe_2O_3]^{+\cdot}$, 47), 273.9 ($[C_{10}H_{10}Fe_2O_2]^{+\cdot}$, 49), 246 ($[C_9H_{10}Fe_2O]^{+\cdot}$, 49), 218.0 ($[C_8H_{10}Fe_2]^{+\cdot}$, 95), 162.0 ($[C_8H_{10}Fe]^{+\cdot}$, 50), 55.9 ($[Fe]^{+\cdot}$, 15);
HRMS (EI): calculated for $C_{14}H_{10}Fe_2O_6$ $[M]^{+\cdot}$: 385.9180; found 385.9176.

*TRICARBONYL[INTERNAL-3,4-BIS(METHYLENE)-1,5-HEXADIENE]IRON **(2.33)***



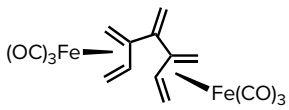
2.33

Compound **(2.33)** was recrystallized from pentane at -40 °C to give yellow crystals, which melted at room temperature to give a yellow oil (51 mg, 7%);
R_f 0.65 (pentane);
^{1}H NMR (300 MHz, $CDCl_3$): δ 6.99 (dd, J = 16.8, 10.5 Hz, 2H), 5.59 (dd, J = 16.8, 1.2 Hz, 2H), 5.26 (dd, J = 10.5, 1.2 Hz, 2H), 2.15 (d, J = 2.4 Hz, 2H), 0.13 (d, J = 2.7 Hz, 2H) ppm;
^{13}C NMR (75 MHz, $CDCl_3$): δ 210.7 (q), 133.7 (CH), 117.2 (CH_2) 99.5 (q), 37.6 (CH_2) ppm;
IR (thin film): ν_{max} = 2932, 2050, 1974 cm^{-1};
MS (EI): *m/z* (%): 246.0 (29, $[M]^{+\cdot}$), 218.0 (40, $C_{10}H_{10}FeO_2^{+\cdot}$), 190.0 (54, $C_9H_{10}FeO^{+\cdot}$), 162.0 (100, $C_8H_{10}Fe^{+\cdot}$), 55.9 (61, $Fe^{+\cdot}$);
HRMS (EI): calculated for $C_{11}H_{10}FeO_3$ $[M]^{+\cdot}$: 245.9979; found 245.9979.

TRICARBONYLIRON COMPLEXATION OF [5]DENDRALENE

To a stirred solution of [5]dendralene **2.12** (90 mg, 0.76 mmol, 1.0 mol equiv.) in distilled 1,2-dimethoxyethane (5 mL) was added $Fe_2(CO)_9$ (1.09 g, 3.03 mmol, 4.0 mol equiv.) and (*E*)-1-(4-methoxyphenyl)-4-phenyl-1-aza-1,3-butadiene **2.14** (45 mg, 0.19 mmol, 0.25 mol equiv.). The reaction mixture was protected from light with aluminium foil, and stirred for 24 h at 85 °C. The solvent was removed under reduced pressure and the resulting orange/brown solid was purified by flash column chromatography (eluting with pentane on silica gel) affording a mixture of mono-tricarbonyliron adducts of [5]dendralene, **2.35** & **2.36**, as yellow oil (74 mg, 36%), and a mixture of bis-tricarbonyliron adducts of [5]dendralene, **2.37**, **2.38**, **2.40**, & **2.39**, as a yellow solid (75 mg, 25%);

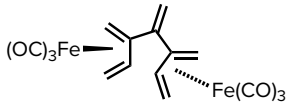
*TERMINAL-TERMINAL-SYN BISTRICARBONYLIRON[5]DENDRALENE **2.40***



An analytical sample of the *title compound* was obtained by HPLC (normal phase, eluent = heptane) as a yellow crystalline solid;
R_f 0.72 (pentane).
^{1}H NMR (500 MHz, $CDCl_3$): δ 5.67 (s, 2H), 5.57 (app t, J = 8.1 Hz, 2H), 2.17 (dd, J =

2.6, 1.8 Hz, 2H), 1.83 (dd, *J* = 7.1, 2.4 Hz, 2H), 0.33 (dd, *J* = 9.3, 2.4 Hz, 2H), 0.29 (d, *J* = 2.1 Hz, 2H) ppm;
^{13}C NMR (125 MHz, $CDCl_3$): δ 210.8 (q), 145.4 (q), 118.8 (CH_2), 104.1 (q), 88.9 (CH), 39.0 (CH_2), 38.8 (CH_2) ppm.
IR (KBr disc): ν_{max} = 3056, 3004, 2926, 2854, 2048, 1979, 1945, 1630 cm^{-1}
MS (EI): *m/z* (%): 411.9 ([*M*]$^{+\cdot}$, 5), 383.9 (2), 355.9 (73), 327.9 (36), 299.9 (23), 271.9 (100), 243.9 (83), 188.0 (31), 55.9 (33);
HRMS (EI): calculated for $C_{16}H_{12}Fe_2O_6$ [*M*]$^{+\cdot}$: 411.9333; found 411.9331.

TERMINAL-TERMINAL-ANTI BISTRICARBONYLIRON[5]DENDRALENE ***2.39***

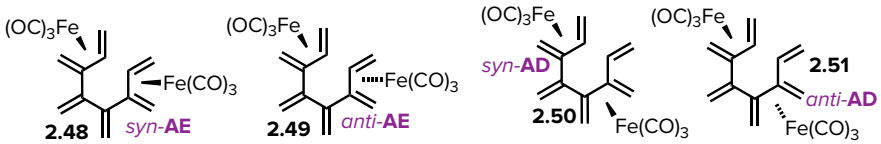


An analytical sample of the *title compound*, as a mixture with compounds **2.37** & **2.38**, was obtained by HPLC (normal phase, eluent = heptane). The *title compound* was further purified by low temperature recrystallisation from pentane;
R_f 0.72 (pentane).
^{1}H NMR (500 MHz, $CDCl_3$): δ 5.63-5.57 (m, 4H), 2.20 (dd, *J* = 2.6, 1.8 Hz, 2H), 1.80 (dd, *J* = 6.9, 2.4 Hz, 2H), 0.43 (dd, *J* = 2.9, 1.2 Hz, 2H), 0.31 (dd, *J* = 9.3, 2.4 Hz, 2H) ppm;
^{13}C NMR (125 MHz, $CDCl_3$): δ 210.9 (q), 145.4 (q), 118.7 (CH_2), 104.4 (q), 87.8 (CH), 40.4 (CH_2), 38.8 (CH_2) ppm.
IR (KBr disc): ν_{max} = 2927, 2852, 2049, 1977, 1628 cm^{-1}
MS (EI): *m/z* (%): 412.0 ([*M*]$^{+\cdot}$, 4), 384.0 (1), 355.9 (67), 328.0 (36), 300.0 (21), 272.0 (100), 244.0 (84), 188.0 (36), 55.9 (34);
HRMS (EI): calculated for $C_{16}H_{12}Fe_2O_6$ [*M*]$^{+\cdot}$: 411.9333; found 411.9342.

TRICARBONYLIRON COMPLEXATION OF [6]DENDRALENE

To a stirred solution of [6]dendralene **2.13** (100 mg, 0.63 mmol, 1.0 mol equiv.) in distilled 1,2-dimethoxyethane (5 mL) was added $Fe_2(CO)_9$ (924 g, 2.5 mmol, 4.0 mol equiv.) and (*E*)-1-(4-methoxyphenyl)-4-phenyl-1-aza-1,3-butadiene **2.14** (38 mg, 0.16 mmol, 0.25 mol equiv.). The reaction mixture was protected from light with aluminium foil, and stirred for 24 h at 85 °C. The solvent was removed under reduced pressure and the resulting orange/brown solid was purified by flash column chromatography (eluting with pentane on silica gel) affording a mixture of bis-tricarbonyliron adducts of [6]dendralene, **2.48**, **2.49**, **2.50**, & **2.51**, as a yellow

solid (140 mg, 51%), and a mixture of tris-tricarbonyliron adducts of [6]dendralene, **2.52**, **2.53**, & **2.54**, as a yellow solid (42 mg, 12%);

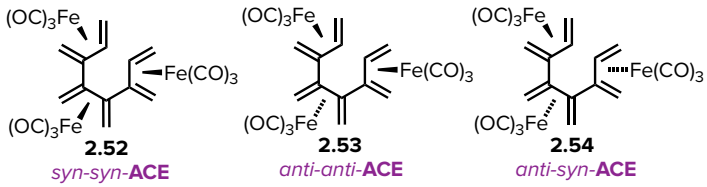


The compounds **2.48**, **2.49**, **2.50**, & **2.51** could not be separated from each other by flash column chromatography. Identification is tentatively proposed on the basis of crude ^{1}H spectroscopic data, and LR- & HR-MS (EI) data.

The *title compounds* were collected as a yellow solid (140 mg, 51% yield); R_f 0.46 (hexane).

MS (EI): *m/z* (%): 438.0 ([*M*]$^{+\cdot}$, 3), 410.0 ([*M–CO*]$^{+\cdot}$, 4), 382.0 ([*M–2CO*]$^{+\cdot}$, 39), 354.0 ([*M–3CO*]$^{+\cdot}$, 46), 326.0 ([*M–4CO*]$^{+\cdot}$, 37), 298.0 ([*M–5CO*]$^{+\cdot}$, 61), 270.0 ([*M–6CO*]$^{+\cdot}$, 100), 55.9 ([*Fe*]$^{+\cdot}$, 18);

HRMS (EI): calculated for $C_{18}H_{14}Fe_2O_6$ [*M*]$^{+\cdot}$: 437.9489; found 437.9485.



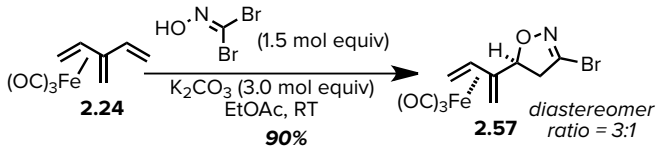
The compounds **2.52**, **2.53**, & **2.54** could not be separated from each other by flash column chromatography. Identification is tentatively proposed on the basis of crude ^{1}H spectroscopic data and LRMS (EI) data.

The *title compounds* were collected as a yellow solid (42 mg, 12% yield); R_f 0.31 (hexane).

MS (EI): *m/z* (%): 577.8 ([*M*]$^{+\cdot}$, 1), 549.9 ([*M–CO*]$^{+\cdot}$, 1), 521.9 ([*M–2CO*]$^{+\cdot}$, 7), 493.9 ([*M–3CO*]$^{+\cdot}$, 6), 465.9 ([*M–4CO*]$^{+\cdot}$, 3), 437.9 ([*M–5CO*]$^{+\cdot}$, 8), 409.9 ([*M–6CO*]$^{+\cdot}$, 6), 381.9 ([*M–7CO*]$^{+\cdot}$, 18), 353.9 ([*M–8CO*]$^{+\cdot}$, 9), 325.9 ([*M–9CO*]$^{+\cdot}$, 15), 149.0 (100).

5.2.2 Dendralene-Tricarbonyliron Complexes in Synthesis

*[3-BROMO-5-(BUTA-1,3-DIEN-2-YL)-4,5-DIHYDROISOXAZOLE]TRICARBONYLIRON **(2.57)***



Tricarbonyliron[3]dendralene **(2.24)** (22.0 mg, 0.1 mmol, 1.0 mol equiv) was dissolved in ethyl acetate (1 mL) and $KHCO_3$ (30.0 mg, 0.30 mmol, 3.0 mol equiv) was added in one portion to the rapidly stirred solution. To the stirring mixture was added dibromoformaldoxime (30.2 mg, 0.15 mmol, 1.5 mol equiv). The reaction was then stirred under nitrogen at room temperature, and the progress of the reaction was monitored by TLC. After 16 h the reaction mixture was partitioned with CH_2Cl_2 and a saturated solution of ammonium chloride. The aqueous layer was then extracted with CH_2Cl_2. The combined organic layers were washed with brine and dried with $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (eluting with 5% ethyl acetate/hexane on silica gel) to give the *title compound* as a yellow oil (30.6 mg, 90%, 3:1 ratio of diastereomers) (characterised as the major diastereomer);

R_f 0.25 (5% ethyl acetate/hexane);

^{1}H NMR (800 MHz, $CDCl_3$): δ 5.46 (dd, J = 8.3, 7.0 Hz, 1H), 5.16 (dd, J = 11.0, 8.3 Hz, 1H), 3.60 (dd, J = 17.5, 11.1 Hz, 1H), 3.28 (dd, J = 17.3, 9.3 Hz, 1H), 1.82 (dd, J = 7.0, 2.2 Hz, 1H), 1.75 (dd, J = 3.0, 1.4 Hz, 1H), 0.21 (dd, J = 9.2, 2.2 Hz, 1H), 5.46 (dd, J = 3.1, 0.9 Hz, 1H) ppm;

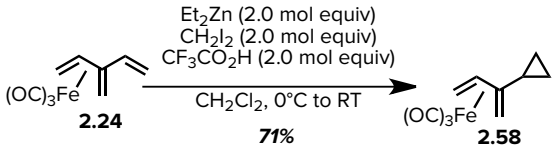
^{13}C NMR (200 MHz, $CDCl_3$): δ 210.3 (q), 136.7 (q), 102.4 (q), 83.0 (CH), 82.4 (CH), 48.5 (CH_2), 39.1 (CH_2), 37.8 (CH_2) ppm;

IR (KBr Disc): ν_{max} = 2927, 2052, 1990, 1978, 1962, 609 cm^{-1};

MS (EI): *m/z* (%): 342.9 ([M]$^{+\cdot}$, 1), 340.9 ([M]$^{+\cdot}$, 1), 312.9 ([M]$^{+\cdot}$-CO, 11), 284.9 ([M]$^{+\cdot}$-2CO, 10), 256.9 ([M]$^{+\cdot}$-3CO, 2), 178 (100), 138 (57), 55.9 (Fe$^{+\cdot}$, 20);

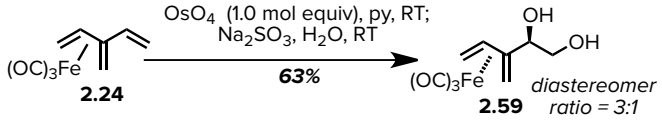
HRMS (EI): calculated for $C_{10}H_8FeNO_4$ [M]$^{+\cdot}$: 342.8966; found 342.8997.

TRICARBONYL[2-CYCLOPROPYL-1,3-BUTADIENE)IRON ***(2.58)***



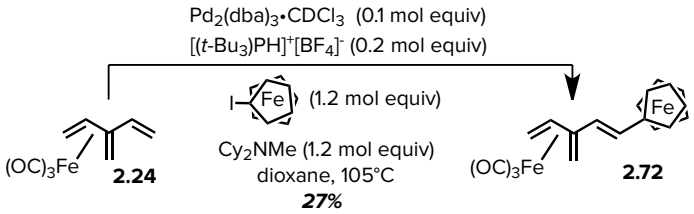
A solution of diethylzinc (1.0 M in hexane, 420 μL, 0.420 mmol, 2.0 equiv) was added *via* syringe to a dry round bottom flask containing CH_2Cl_2 (370 μL) at 0 °C. To this solution trifluoroacetic acid (32 μL, 0.42 mmol, 2.0 mol equiv) (distilled from 0.05 mol equiv trifluoroacetic anhydride) was added dropwise *via* syringe over 20 minutes, followed by the addition of diiodomethane (46 μL, 0.42 mmol, 2.0 mol equiv) (dried over $CaCl_2$ and distilled from copper powder) *via* syringe over 20 minutes. A solution of tricarbonyliron[3]dendralene **(2.24)** (46 mg, 0.209 mmol, 1.0 mol equiv) in CH_2Cl_2 (300 μL) was prepared in a dry, nitrogen filled round bottom flask and 'freeze-thaw' degassed under nitrogen and stirred at 0 °C. This solution of tricarbonyliron[3]dendralene is added to the diethylzinc / TFA / diiodomethane containing reaction mixture *via* cannula and the reaction allowed to warm to room temperature with stirring. A precipitate forms over the course of the reaction. The reaction mixture was quenched after two hours by the addition of a saturated solution of ammonium chloride (2 mL). The aqueous layer was extracted with CH_2Cl_2 and the combined organic solution was washed with water, followed by brine, then dried over $MgSO_4$ and filtered before being concentrated under reduced pressure to give the crude product as a pale yellow oil. The crude material was purified by flash column chromatography (eluting with pentane on silica gel) to give the *title compound* as a pale yellow oil (34.5 mg, 71%);
R_f 0.7 (pentane);
^{1}H NMR (400 MHz, $CDCl_3$): δ 5.26 (t, J = 7.3 Hz, 1H), 1.75-1.68 (m, 2H), 1.65 (dd, J = 4.4, 2.3 Hz, 1H), 0.98-0.91 (m, 1H), 0.87-0.80 (m, 1H), 0.76-0.69 (m, 1H), 0.65-0.59 (m, 1H), 0.06 (dd, J = 6.4, 2.4 Hz, 1H), 0.03 (d, J = 2 Hz, 1H) ppm;
^{13}C NMR (100 MHz, $CDCl_3$): δ 211.4 (q), 110.5 (q), 82.2 (CH), 38.2 (CH_2), 37.6 (CH_2), 16.2 (CH), 10.6 (CH_2), 6.9 (CH_2) ppm;
IR (thin film): ν_{max} = 3008, 2922, 2046, 1965 cm^{-1};
MS (EI): *m/z* (%): 234 ([*M*]$^{+\cdot}$, 22), 206 ([*M*]$^{+\cdot}$-CO, 60), 178 ([*M*]$^{+\cdot}$-2CO, 69), 150 ([*M*]$^{+\cdot}$-3CO, 59), 148 ([*M*]$^{+\cdot}$-$C_3H_2O_3$, 100), 55.9 ($Fe^{+\cdot}$, 52);
HRMS (EI): calculated for $C_{10}H_{10}FeO_3$ [*M*]$^{+\cdot}$: 233.9979; found 233.9980.

TRICARBONYL[H^4-3-METHYLENE-4-PENTENE-1,2-DIOL)IRON ***(2.59)***



Anhydrous pyridine (538 μL) was added to a round bottom flask containing Tricarbonyliron[3]dendralene (44.0 mg, 0.20 mmol, 1.0 mol equiv), and the reaction was subsequently stirred at room temperature. To the stirred reaction solution was added OsO_4 in anhydrous pyridine (0.39 M, 514 μL, 0.21 mmol, 1.0 mol equiv) dropwise *via* syringe. The reaction mixture was quenched after 1 h by addition of a saturated solution of sodium metabisulfite (8 mL). The aqueous mixture was extracted twice with CH_2Cl_2 and the combined organic solution was washed twice with water and dried over $MgSO_4$ and filtered before being concentrated under reduced pressure. The crude yellow solid was purified by flash column chromatography (eluting with 1:39:60 *i*-PrOH/EtOAc/hexane on silica gel) to give the *title compound* as a pale yellow crystalline solid (32 mg, 63%, 3:1 ratio of diastereomers) (characterised as the major diastereomer);
R_f 0.40 (40% ethyl acetate/hexanes);
m.p.: 85-86.5 °C (chloroform/hexane);
^{1}H NMR (800 MHz, $CDCl_3$): δ 5.61 (t, J = 8.1 Hz, 1H), 4.13 (d, J = 5.6 Hz, 1H), 3.96, (d, J = 11.1 Hz, 1H), 3.81 - 3.78 (m, 1H), 2.39 (s, 1H), 2.22 (s, 1H), 1.79 - 1.78 (m, 2H), 0.23 (d, J = 2.0 Hz, 1H), 0.20 (dd, J = 9.4 and 2.0 Hz, 1H) ppm;
^{13}C NMR (200 MHz, $CDCl_3$): δ 210.9 (q), 105.6 (q), 81.1 (CH), 74.6 (CH), 68.5 (CH_2) 40.2 (CH_2), 38.6 (CH_2) ppm;
IR (KBr disc): ν_{max} = 2917, 2046, 1984, 1960, 1099, 1063 cm^{-1};
MS (EI): *m/z* (%): 226.0 ([M]$^{+\cdot}$-CO, 14), 198.0 ([M]$^{+\cdot}$-2CO, 65), 170.0 ([M]$^{+\cdot}$-3CO, 58), 80.1 ([M]$^{+\cdot}$-$C_4H_2O_4$, 100), 55.9 ($Fe^{+\cdot}$, 22);
HRMS (EI): calculated for $C_9H_{10}FeO_5$ [M]$^{+\cdot}$: 253.9878; found 253.9866.

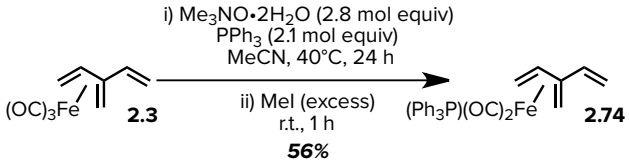
1E-FERROCENYL[3]DENDRALENE TRICARBONYLIRON ***2.72***



$Pd_2(dba)_3$•$CHCl_3$ (13 mg, 0.014 mmol, 0.1 mol equiv.), tris(*tert*-butyl)phosphonium tetrafluoroborate (8 mg, 0.028 mmol, 0.2 mol equiv.) and iodoferrocene (47 mg, 0.15 mmol, 1.1 mol equiv.) were rigorously degassed in a

one-piece apparatus—comprising a round-bottom flask and a condenser—under nitrogen. To the reaction mixture was added [3]Dendralene-tricarbonyliron (30 mg, 0.137 mmol, 1.0 mol equiv.), and dicyclohexyl methylamine (32 μL, 0.150 mmol, 1.1 mol equiv.), dissolved in dioxane (1 mL). The reaction was stirred at 105 °C for 22 hours. The reaction was quenched with water and the organic components extracted with ether. The ethereal fractions were combined and dried with magnesium sulfate and filtered through Celite. The solvent was subsequently removed under reduced pressure and the resulting brown solid was purified by flash column chromatography (eluting with hexane on silica gel) affording the *title compound* as a red powder (15 mg, 27% yield);
R_f 0.30 (hexane);
m.p.: 95-97 °C (hexane);
^{1}H NMR (800 MHz, $CDCl_3$): δ 6.69 (d, J = 15.9 Hz, 1H), 6.49 (d, J = 15.6 Hz, 1H), 5.41 (t, J = 7.8 Hz, 1H), 4.46 (s,1H), 4.36 (s, 1H), 4.28 (s, 2H), 4.11 (s, 5H), 2.30 (s, 1H), 1.80 (dd, J = 6.8, 2.4 Hz, 1H), 0.35 (dd, J = 6.2, 2.4 Hz, 1H), 0.18 (d, J = 2.5 Hz, 1H) ppm;
^{13}C NMR (200 MHz, $CDCl_3$): δ 211.1 (q), 128.2 (CH), 125.2 (CH), 102.6 (q), 84.5 (CH), 82.1 (q), 69.3 (CH), 69.2 (CH), 69.2 (CH), 68.1 (CH), 66.0 (CH), 39.5 (CH_2), 37.0 (CH_2) ppm;
IR (KBr disc): ν_{max} = 2037, 1967, 1951, 1632, 1473 cm^{-1};
MS (EI): *m/z* (%): 404.0 ([*M*]$^{+\cdot}$, 32), 320 ([*M*]$^{+\cdot}$-3CO, 100), 55.9 ([*Fe*]$^{+\cdot}$, 19);
HRMS (EI): calculated for $C_{19}H_{16}Fe_2O_3$ [*M*]$^{+\cdot}$: 403.9798; found 403.9793.

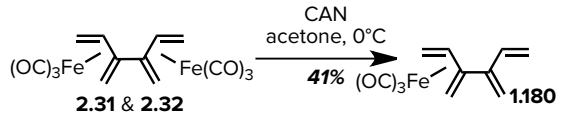
DICARBONYL TRIPHENYLPHOSPHINE[3]DENDRALENE IRON ***2.74***



This product was prepared by Nik Osinski[333] using a modified procedure of that reported by Adams and coworkers.[332] [3]Dendralene **2.3** (60.4 mg, 0.275 mmol, 1 mol equiv.), TMANO•2H_2O (48.9 mg, 0.440 mmol, 1.6 mol equiv.) and triphenyl phosphine (153.7 mg, 0.586 mmol, 2.1 mol equiv.) were dissolved in acetonitrile (1.1 mL). The reaction mixture was stirred for 15 h at room temperature. Then, a second portion of TMANO•2H_2O (38.0 mg, 0.342 mmol, 1.2 equiv.) was added, and the reaction mixture was stirred for another 24 h at 40 °C. The reaction mixture was filtered through a plug of silica and washed thoroughly with toluene. The washings were collected and solvent was removed under reduced pressure.

This was then re-dissolved in CH_3I (3 mL), to remove excess triphenyl phosphine, and stirred for 1 h. Further purification using flash column chromatography (40:1 hexane/Et_2O, silica gel) gave the title compound as a yellow oil (69.5 mg, 0.153 mmol, 55.6%);
R_f 0.24 (40:1 hexane/Et_2O);
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.56-7.34 (m, 15H), 6.50 (dd, J = 17.3, 10.5 Hz, 1H), 5.48 (d, J = 1.2 Hz, 1H), 5.42 (d, J = 0.9 Hz, 1H), 4.89 (t, J = 7.8 Hz, 1H), 1.85 (t, J = 2.1 Hz, 1H), 1.19-1.15 (m, 1H), -0.32 (t, J = 6.9 Hz, 1H), -0.48 (s, 1H);
^{13}C NMR (75 MHz, $CDCl_3$): δ 231.2 (q), 138.7 (CH), 136.7 (q), 136.2 (q), 133.4 (d, J_{CP} = 43.2 Hz, CH), 129.7 (CH), 128.2 (d, J_{CP} = 38.7 Hz, CH), 112.8 (CH_2), 97.7 (q), 86.6 (CH), 43.5 (CH_2);
IR (thin film): ν_{max} = 3003, 2045, 1975, 1916, 1480, 1434 cm^{-1};
MS (EI): *m/z* (%): 454.1 (6, $[M]^{+\cdot}$), 398.1 (66, $C_{24}H_{23}FeP^{+\cdot}$), 318.0 (89, $C_{18}H_{15}FeP^{+\cdot}$), 262.1 (100, $C_{18}H_{15}P^{+\cdot}$);
HRMS (EI): calculated for $C_{26}H_{23}FeO_2P$ $[M]^{+\cdot}$: 454.0785; found 454.0783.

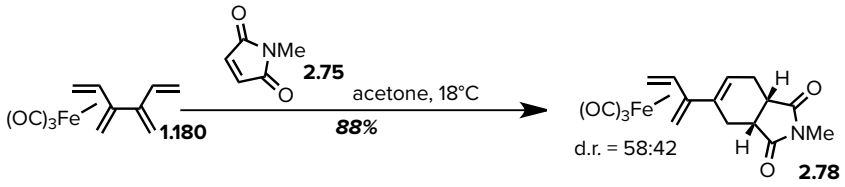
TRICARBONYL[TERMINAL-3,4-BIS(METHYLENE)-1,5-HEXADIENE]IRON ***(1.180)***



A mixture of **(2.31)** and **(2.32)** (266.5 mg, 0.69 mmol, 1 mol equiv.) was dissolved in 5 mL acetone and was ice-cooled. A solution of ceric ammonium nitrate (757.2 mg, 1.38 mmol, 2.0 mol equiv.) in dry acetone (10 mL) was added drop-wise to the mixture of the tricarbonyliron complexes of [4]dendralene. After addition was completed in 30 min., the reaction mixture was stirred for another 30 min. The mixture was quenched by the addition of a saturated solution of $NaHCO_3$ (20 mL). The resulting pale orange suspension was filtered, and extracted with dichloromethane (3 x 25 mL). The combined organic layers were washed with brine, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The mixture was purified by flash column chromatography (eluting with hexane on silica gel) to give **(1.180)** (69.5 mg, 41%) as a yellow oil;
R_f 0.65 (hexane);
^{1}H NMR (300 MHz, $CDCl_3$): δ 6.51 (dd, J = 17.1, 10.8 Hz, 1H), 5.65 (dd, J = 17.1 Hz, 1.5 Hz, 1H), 5.44-5.37 (m, 3H), 5.27 (dd, J = 10.8, 1.2 Hz, 1H), 2.10 (d, J = 1.5 Hz, 1H), 1.80 (dd, J = 7.1, 2.4 Hz, 1H), 0.29 (dd, J = 9.3, 2.4 Hz, 1H), 0.20 (d, J = 1.5 Hz, 1H) ppm;

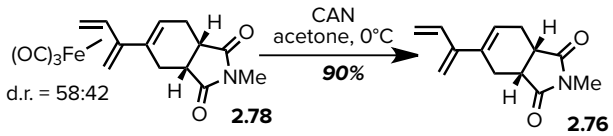
^{13}C NMR (75 MHz, $CDCl_3$): δ 211.0 (q), 145.2 (q), 135.7 (CH), 117.8 (CH_2), 115.2 (CH_2), 103.0 (q), 85.4 (CH), 39.6 (CH_2), 39.3 (CH_2);
IR (thin film): ν_{max} = 3092, 2051, 1995 cm^{-1};
MS (EI): *m/z* (%): 246.0 (6, $[M]^{+\cdot}$), 218.0 (27, $C_{10}H_{10}FeO_2^{+\cdot}$), 190.0 (43, $C_9H_{10}FeO^{+\cdot}$), 162.0 (100, $C_8H_{10}Fe^{+\cdot}$), 55.9 (21, $Fe^{+\cdot}$);
HRMS (EI): calculated for $C_{11}H_{10}FeO_3$ $[M]^{+\cdot}$: 245.9979; found 245.9982.

[5-(BUTA-1,3-DIEN-2-YL)-2-METHYL-3A,4,7,7A-TETRAHYDRO-1H-ISOINDOLE-1,3(2H)-DIONE]TRICARBONYLIRON ***(2.78)***



N-Methylmaleimide (**2.75**) (15.0 mg, 0.107 mmol, 1.0 mol equiv) and terminal-tricarbonyliron[4]dendralene (**1.180**) (26.3 mg, 0.107 mmol, 1 mol equiv) were dissolved in acetone-d_6 (0.5 mL) in a round bottom flask at ambient temperature and immediately transferred to an NMR tube to monitor reaction progress by ^{1}H NMR spectroscopy. The solvent was subsequently removed under reduced pressure and the resulting yellow/brown solid was purified by flash column chromatography (eluting with 10-20% ethyl acetate/hexane on silica gel) affording the *title compound* as a pale yellow solid mixture of diastereomers (25.9 mg, 88% yield, 58:42 diastereomeric ratio) (Characterised as the major diastereomer);
R_f: 0.42 (20% ethyl acetate/hexanes);
m.p.: 52-54 °C ($CDCl_3$);
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.19-6.16 (m, 1H), 5.40 (t, J = 9.3 Hz, 1H), 3.25-3.15 (m, 2H), 2.99 (s, 3H), 2.96 (dd, J = 5.7, 3.0 Hz, 1H), 2.76-2.69 (m, 1H), 2.39-2.33 (m, 2H), 2.02 (t, J = 2.0 Hz, 1H), 1.83 (dd, J = 7.3, 2.5 Hz, 1H), 0.30 (dd, J = 9.3, 1.9 Hz , 1H), 0.08 (t, J = 1.4 Hz, 1H) ppm;
^{13}C NMR (100 MHz, $CDCl_3$): δ 210.9 (q), 179.7 (q), 179.6 (q), 138.3 (CH), 125.3 (CH), 102.2 (q), 82.5 (q), 40.3 (CH), 40.0 (CH), 40.0 (CH_2), 39.1 (CH_2), 25.5 (CH_2), 25.1 (CH_2), 24.8 (CH_3) ppm;
IR (thin film): ν_{max} = 2920, 2850, 2048, 1972, 1777, 1699, 1435 cm^{-1};
MS (EI): *m/z* (%): 357.0 ($[M]^{+\cdot}$, 1), 329.0 ($[M]^{+\cdot}$-CO, 1), 301.0 ($[M]^{+\cdot}$-2CO, 38), 273.0 ($[M]^{+\cdot}$-3CO, 100), 55.9 ($Fe^{+\cdot}$, 13);
HRMS (EI): calculated for $C_{16}H_{15}FeNO_5$ $[M]^{+\cdot}$: 357.0300; found 357.0308.

5-(BUTA-1,3-DIEN-2-YL)-2-METHYL-3A,4,7,7A-TETRAHYDRO-1H-ISOINDOLE-1,3(2H)-DIONE ***(2.76)***



A solution of cerium ammonium nitrate (117.3 mg, 0.214 mmol, 2.0 mol equiv) in acetone-d_6 (1 mL) was added to a mixture of the diastereomers of **(2.78)** (40.3 mg, 0.113 mmol, 1.0 mol equiv) in acetone (0.5 mL) dropwise, and then stirred under nitrogen for 30 minutes. The reaction was quenched by adding a saturated solution of $NaHCO_3$ (2 mL). The resulting orange suspension was extracted with CH_2Cl_2 (5 mL) three times, washed with brine, dried over $MgSO_4$ and the solvent removed under a reduced pressure (40 mbar, 0 °C) to give a colourless oil, which was purified by flash column chromatography to give the *title compound* as a colourless oil (eluting with 20% ethyl acetate/hexanes on silica gel) (22.0 mg, 90%);

R_f 0.12 (20% ethyl acetate/hexanes);

^{1}H NMR (800 MHz, benzene-d_6): δ 6.22 (ddd, J = 17.4, 10.7 and 0.6 Hz, 1H), 5.68 - 5.66 (m, 1H), 5.15 (dd, J = 17.3 and 1.6 Hz, 1H), 5.00 (s, 1H), 4.98 (s, 1H), 4.95 (dd J = 10.7 and 1.3 Hz, 1H), 2.72, (dd, J = 15.2 and 2.9 Hz, 1H), 2.58 (s, 3H), 2.47 (ddd, J = 15.6, 6.7, 2.9 Hz, 1H) 2.32 (ddd, J = 9.7, 7.2 and 2.9 Hz, 1H), 2.36 (ddd, J = 10.0, 7.6, 2.8 Hz, 1H), 1.84 - 1.80 (m, 1H), 1.71 - 1.67 (m, 1H) ppm;

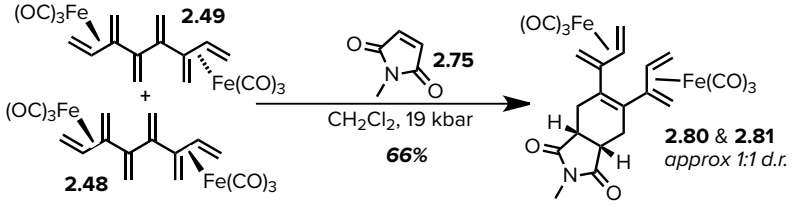
^{13}C NMR (200 MHz, benzene-d_6): δ 179.0 (q), 178.7 (q), 147.4 (q), 138.7 (q), 137.0 (CH), 124.7 (CH), 116.4 (CH_2), 113.5 (CH_2), 39.7 (CH), 39.0 (CH), 26.4 (CH_2), 24.5 (CH_3), 24.5 (CH_2) ppm;

IR (thin film): ν_{max} = 2918, 2849, 1776, 1697, 1435 cm^{-1};

MS (EI): *m/z* (%): 217.1 ([*M*]$^{+\cdot}$, 100), 132.1 ([*M*]$^{+\cdot}$-$C_3H_3O_2N$, 24), 117.1 (44), 112.1 (42), 91.1 (43);

HRMS (EI): calculated for $C_{13}H_{15}NO_2$ [*M*]$^{+\cdot}$: 217.1103; found 217.1104.

*HEXACARBONYL(5,6-DI(BUTA-1,3-DIEN-2-YL)-2-METHYL-3A,4,7,7A-TETRAHYDRO-1H-ISOINDOLE-1,3(2H)-DIONE)DIIRON **2.80** & **2.81***



A mixture of compounds **2.49** & **2.48** (165 mg, 0.38 mmol, 1.0 mol equiv.) and NMM (177 mg, 0.942 mmol, 2.5 mol equiv.) was dissolved in DCM () in a Teflon high-pressure reaction chamber. The vessel was subjected to high pressure (19 kbar) for 16 hours. The reaction mixture was concentrated under reduced pressure and the crude material purified by flash column chromatography (silica, 20% ethyl acetate/hexane), and the two isomers could be separated at this point or carried through to the next reaction as a mixture. The *title compound* was characterised as a single isomer (R_f of 0.31 *vs.* 0.22) of the mixture as a yellow solid (137 mg, 66% yield);

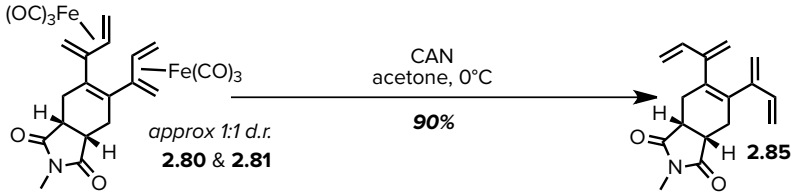
R_f = 0.31 (20% ethyl acetate/hexane).

^{1}H NMR (400 MHz; $CDCl_3$): δ 5.41 (t, J = 8.0 Hz, 2H), 3.23 (t, J = 1.9 Hz, 2H), 3.02 (s, 3H), 2.78 (d, J = 14.9 Hz, 2H), 2.59–2.54 (m, 2H), 1.86–1.83 (m, 4H), 0.35 (d, J = 2.2 Hz, 2H), 0.30 (dd, J = 9.4, 2.2 Hz, 2H) ppm;

MS (EI): *m/z* (%): 549.0 ([M]$^{+\cdot}$, 1), 493.0 (36), 465.0 (34), 437.0 (14), 409.0 (73), 381.0 (100), 353.0 (11), 325.1 (91), 55.9 (33);

HRMS (EI): calculated for $C_{23}H_{19}Fe_2NO_8$ [M]$^{+\cdot}$: 548.9809; found 548.9802.

*5,6-DI(BUTA-1,3-DIEN-2-YL)-2-METHYL-3A,4,7,7A-TETRAHYDRO-1H-ISOINDOLE-1,3(2H)-DIONE **2.85***



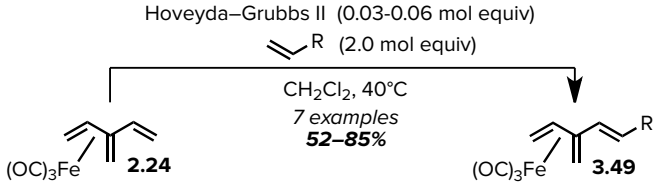
A mixture of complexes **2.80** & **2.81** (13.2 mg, 0.021 mmol, 1.0 mol equiv.) were dissolved in acetone (2 mL). To the solution was added cerium ammonium nitrate (69 mg, 0.13 mmol, 6.0 mol equiv.). The reaction mixture was quenched with $NaHCO_3$ (aqueous) after 20 minutes as TLC indicated the complete consumption of the starting material. The reaction mixture was extracted with ether, dried with magnesium sulfate, filtered, and the solvent removed under reduced pressure.

The crude product was obtained as a yellow oil, this oil was further purified by flash column chromatography (silica, 20% ethyl acetate/hexane) to afford the *title compound* as a white crystalline solid (5 mg, 90% yield);
R_f 0.25 (20% ethyl acetate/hexane).
^{1}H NMR (800 MHz; $CDCl_3$): δ 6.29 (dd, J = 17.4, 10.6 Hz, 2H), 5.09 (d, J = 10.5 Hz, 2H), 5.03 (d, J = 1.2 Hz, 2H), 4.93 (dd, J = 17.5, 0.8 Hz, 2H), 4.83 (s, 2H), 3.17 (app t, J = 3.1 Hz, 2H), 3.03 (s, 3H), 2.66 (m, 2H), 2.58-2.56 (m, 2H) ppm;
^{13}C NMR (201 MHz, $CDCl_3$): δ 179.5 (q), 147.7 (q), 137.5 (CH), 134.9 (q), 117.0 (CH_2), 115.7 (CH_2), 40.1 (CH), 30.0 (CH_2), 25.0 (CH_3) ppm.
MS (EI): *m/z* (%): 269.1 ([M]$^{+\cdot}$, 18), 155.1 (19), 83.9 (100);
HRMS (EI): calculated for $C_{17}H_{19}NO_2$ [M]$^{+\cdot}$: 269.1416; found 269.1417.

5.3 Experimental For Chapter 3

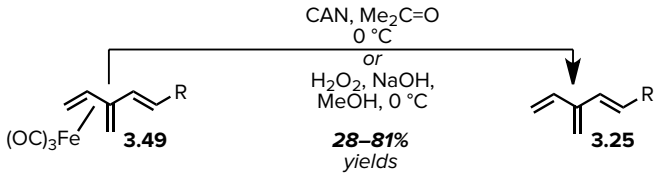
5.3.1 General Procedures

*GENERAL PROCEDURE 1 (**GP-1**): FOR THE CROSS METATHESIS OF TRICARBONYLIRON[3]DENDRALENE*



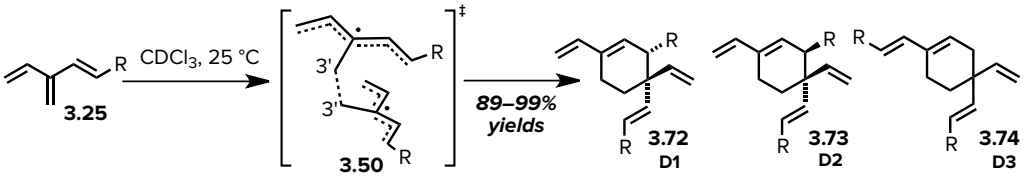
A solution of tricarbonyliron[3]dendralene[3] **2.24** (1.0 mol equiv.) and the vinylic cross-metathesis partner (2.0 mol equiv) in CH_2Cl_2 (0.1 M) was added *via* cannula to a flask containing Hoveyda–Grubbs second generation catalyst (0.05 mol equiv.) under nitrogen. The resulting mixture was then heated to reflux with stirring for 16 h, and protected from light by aluminium foil. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography affording the *substituted [3]dendralene complex* **3.49**.

*GENERAL PROCEDURE 2 (**GP-2**): FOR THE DECOMPLEXATION OF TRICARBONYLIRON[3]DENDRALENES WITH CERIUM AMMONIUM NITRATE.*



To a rapidly stirred solution of the tricarbonyliron complex **3.49** in acetone or acetone-d_6 (0.02–0.05 M) at 0 °C was added cerium ammonium nitrate (3.0 mol equiv.) as a solid. The solution was left stirring, open to air, for 15 minutes or until completion, as determined by TLC. The orange solution was quenched by addition of saturated NH_4Cl (0.5 vol. equiv. relative to the solvent) and diluted with isopentane (*ca.* 3 vol. equiv. relative to acetone). The two layers were separated and the organic layer was washed with water and dried ($MgSO_4$). If the decomplexed compound was stable to isolation (i.e. for **3.67** & **3.68**) then the solvent was removed under reduced pressure and the residue was purified by flash chromatography. If the compound was unstable towards isolation (i.e. for **3.41**, **3.66**, **3.69–3.71**) then the isopentane solution of the compound was added to a small volume of $C_2D_2Cl_4$ and the isopentane was rapidly removed under reduced pressure (20 mbar) at 0 °C, then at higher vacuum (1–2 mbar) for one minute, and the deuterated solution could be stored over extended periods at –78 °C without change. For compounds **3.41** & **3.66** $CDCl_3$ could be used in the place of isopentane to carry out the extraction, in these cases the $CDCl_3$ volume was carefully reduced on a rotary evaporator until approximately 0.5 mL remained. These solutions could then be treated in the same way as the $C_2D_2Cl_4$ solution above.

*GENERAL PROCEDURE 3 (**GP-3**): FOR THE MONITORING OF THE DIMERISATION OF UNSTABLE TERMINALLY SUBSTITUTED DENDRALENES & THE FORMATION OF DIMERS **D1**, **D2**, & **D3***



A *ca.* 0.4–0.6 mL volume solution of approximately 0.05 M concentration was made up of the dendralene **3.25** in $CDCl_3$ or $C_2D_2Cl_4$ in an NMR tube. To this

solution was added 0.050 mL of a 0.166M (0.00833 mmol) standard solution of methylsulfonylmethane in $CDCl_3$ as an internal standard. The combined solution was mixed thoroughly and a ^1H NMR spectrum was recorded. The NMR spectrum was used to determine an accurate concentration of dendralene in solution by comparison of the internal standard with the peaks due to the dendralene, and the solution was diluted to 0.030 M with the appropriate volume of $CDCl_3$ or $C_2D_2Cl_4$. A ^1H NMR spectrum of the diluted spectrum was taken to confirm the calculated concentration, and this spectrum was used as an 'initial concentration measurement' or 't_0 concentration.' The solution was held at 25.0 °C in a constant temperature bath and ^1H NMR spectra were collected regularly to measure the rate of dimerisation of the unstable dendralene and derive a half-life. The experiment was stopped at $4 \times t_{1/2}$ or if the concentration of analyte fell below the measurement error of the detection method.[409,410] The recorded ^1H NMR spectra were used to calculate the instantaneous concentration of the solution which was then correlated with the precise time that the spectrum was recorded. The resulting data was plotted on a scatter plot using Microsoft Excel or KaleidaGraph with the x-axis as time (hours) and the y-axis as 1/[concentration] (L mol^{-1}). The gradient is thus k as in:

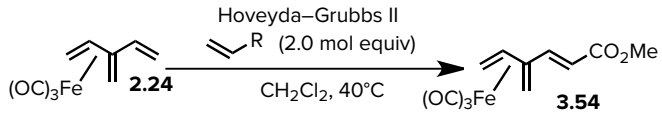
$$\frac{1}{[dendralene]} = \frac{1}{[dendralene]_0} + kt$$

and $t_{1/2}$ is determined *via*:[412]

$$t_{1/2} = \frac{1}{k[dendralene]_0}$$

5.3.2 Synthesis of 1*E*-[3]Dendralenes

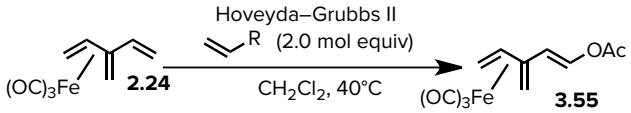
TRICARBONYL[(E)-METHYL 4-METHYLENE-2,5-HEXADIENOATE)IRON ***(3.54)***



A solution of tricarbonyliron[3]dendralene **(2.24)** (24.2 mg, 0.110 mmol, 1.0 mol equiv.) and methyl acrylate (17.4 mg, 0.182 mmol, 2.0 mol equiv) in CH_2Cl_2 (1 mL) was added *via* cannula to a one-piece refluxing round bottom flask containing Grubbs second generation catalyst (3.9 mg, 0.005 mmol, 0.05 mol equiv.). The resulting mixture was then heated to reflux with stirring under nitrogen for 16 h

(**GP-1**). The solvent was subsequently removed under reduced pressure and the resulting brown solid was purified by flash column chromatography (eluting with 20% CH_2Cl_2/pentane, on silica gel) affording the *title compound* as a yellow solid (25.9 mg, 85% yield);
R_f 0.15 (20% CH_2Cl_2/hexane);
m.p.: 61-62 °C (chloroform/hexane);
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.53 (d, J = 15.4 Hz, 1H), 6.17 (d, J = 15.3 Hz, 1H), 5.58 (dd, J = 9.5, 7.3 Hz, 1H), 3.78 (s, 3H), 2.12 (dd, J = 2.9, 1.5 Hz, 1H), 1.94 (dd, J = 7.4, 2.2 Hz, 1H), 0.51 (dd, J = 9.4, 3.0 Hz, 1H), 0.21 (d, J =2.9 Hz, 1H) ppm;
^{13}C NMR (100 MHz, $CDCl_3$): δ 210.0 (q), 166.7 (q), 117.7 (CH), 95.3 (q), 89.5 (CH), 51.8 (CH_3), 41.7 (CH_2), 37.1 (CH_2) ppm;
IR (KBr disc): ν_{max} = 2924, 2060, 1991, 1965, 1713, 1633, 1435 cm^{-1};
MS (EI): *m/z* (%): 278.0 ([*M*]$^{+\cdot}$, 23), 250.0 ([*M*]$^{+\cdot}$-CO, 55), 222.0 ([*M*]$^{+\cdot}$-2CO, 69), 194.0 ([*M*]$^{+\cdot}$-3CO, 100), 55.9 ([*Fe*]$^{+\cdot}$, 72);
HRMS (EI): calculated for $C_{10}H_{11}FeO_5$ [*M*]$^{+\cdot}$: 277.9878; found 277.9881.

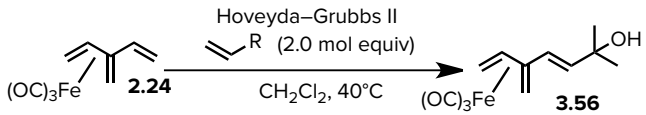
TRICARBONYL[(E)-1-ACETOXY-4-METHYLENE-2,5-HEXADIENE)IRON ***(3.55)***



A solution of tricarbonyliron[3]dendralene (**2.24)** (50.0 mg, 0.223 mmol, 1.0 mol equiv.) and *(Z)*-1,4-diacetoxy-but-2-ene (78.5 mg, 0.455 mmol, 2.0 mol equiv) in CH_2Cl_2 (1 mL) was added *via* cannula to a one-piece refluxing round bottom flask containing Grubbs second generation catalyst (19.0 mg, 0.01 mmol, 0.1 mol equiv.) (**GP-1**). The resulting mixture was then heated to reflux and stirred for 16 h. The solvent was subsequently removed under reduced pressure and the resulting brown solid was purified by flash column chromatography (eluting with 5% ethyl acetate/hexane on silica gel) affording the *title compound* as a yellow oil (50.6 mg, 76% yield);
R_f 0.36 (20% ethyl acetate/hexanes);
^{1}H NMR (300 MHz, $CDCl_3$): δ 6.48 (d, J = 15.4 Hz, 1H), 6.05-6.14 (m, 1H), 5.42 (t, J = 8.1 Hz, 1H), 4.57-4.70 (m, 2H), 2.14 (d, J = 3 Hz, 1H), 2.08 (s, 3H), 1.80 (dd, J = 7.2, 2.2, 1H), 0.32 (dd, J = 8.8, 2.2, 1H), 0.13 (d, J = 3 Hz, 1H) ppm;
^{13}C NMR (75 MHz, $CDCl_3$): δ 210.7 (q), 170.7 (q), 133.9 (CH), 124.0 (CH), 99.4 (q), 85.9 (CH), 64.1 (CH_2), 39.9 (CH_2), 37.5 (CH_2), 20.9 (CH_3) ppm;
IR (thin film): ν_{max} = 3009, 2053, 1966, 1742, 1231 cm^{-1};

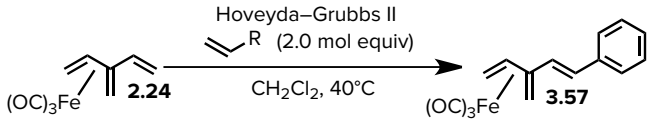
MS (EI): *m/z* (%): 292.0 ([*M*]$^{+\cdot}$, 12%), 264.0 ([*M*]$^{+\cdot}$-CO, 27) , 236.0 ([*M*]$^{+\cdot}$-2CO, 81) , 208.0 ([*M*]$^{+\cdot}$-3CO, 94) , 55.9 ([*Fe*]$^{+\cdot}$, 80);
HRMS (EI): calculated for $C_{12}H_{12}FeO_5$ [*M*]$^{+\cdot}$: 292.0034; found 292.0012.

TRICARBONYL[(E)-2-METHYL-5-METHYLENEHEPTA-3,6-DIEN-2-OL] IRON ***3.56***



Prepared *via* **GP-1** using **2.24** (440 mg, 2.0 mmol, 1.0 mol equiv.), 2-methylbut-3-en-2-ol (344 mg, 4.0 mmol, 2.0 mol equiv.), Hoveyda–Grubbs second generation catalyst (63 mg, 0.1 mmol, 0.05 mol equiv.), and CH_2Cl_2 (20 mL). The yellow oil was purified by flash column chromatography (silica gel, 5:95→20:80 ethyl acetate/hexane) affording the *title compound* as a yellow oil (469 mg, 84% yield); R_f 0.41 (20% ethyl acetate/hexane).
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.42 (d, J = 15.7 Hz, 1H), 6.15 (d, J = 15.7 Hz, 1H), 5.49-5.26 (m, 1H), 2.18 (s, 1H), 1.78 (dd, J = 6.9, 2.4 Hz, 1H), 1.37 (s, 3H), 1.35 (s, 3H), 0.31 (dd, J = 9.2, 2.4 Hz, 1H), 0.13 ppm (d, J = 2.4 Hz, 1H);
^{13}C NMR (100 MHz, $CDCl_3$): δ 211.1 (q), 138.1 (CH), 126.4 (CH), 100.7 (q), 85.7 (CH), 71.0 (q), 39.7 (CH_2), 37.7 (CH_2), 30.0 (CH_3), 29.9 (CH_3) ppm.
IR (thin film): ν_{max} =2976, 2046, 1962, 1474, 1364 cm^{-1}
MS (EI): *m/z* (%): 278.0 ([*M*]$^{+\cdot}$, 36), 250.0 (47), 222.0 (72), 194.1 (80), 176.0 (100), 55.9 (73);
HRMS (EI): calculated for $C_{12}H_{14}FeO_4$ [*M*]$^{+\cdot}$: 278.0241; found 278.0243.

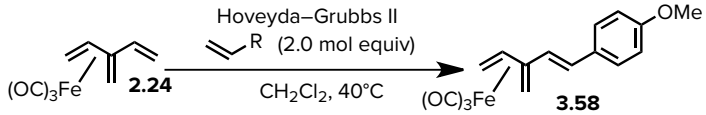
TRICARBONYL(E)-3-METHYLENE-1-PHENYL-1,4-PENTADIENE)IRON ***(3.57)***



A solution of tricarbonyliron[3]dendralene **(2.24)** (20.0 mg, 0.091 mmol, 1.0 mol equiv.) and styrene (18.9 mg, 0.182 mmol, 2.0 mol equiv) in CH_2Cl_2 (1 mL) was added *via* cannula to a one-piece refluxing round bottom flask containing Hoveyda-Grubbs second generation catalyst (3.9 mg, 0.005 mmol, 0.05 mol equiv.) (**GP-1**). The resulting mixture was then heated to reflux with stirring under nitrogen for 16 h. The solvent was subsequently removed under reduced pressure and the resulting brown solid was purified by flash column chromatography

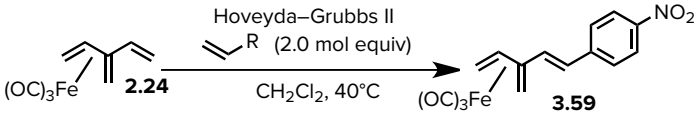
(eluting with hexane on silica gel) affording the *title compound* as a yellow oil (20.3 mg, 74% yield);
R_f 0.21 (5% CH_2Cl_2/pentane);
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.48-7.28 (m, 5H), 7.92 (s, 2H), 5.54 (t, J = 7.8 Hz, 1H), 2.33 (s, 1H), 1.86 (dd, *J* = 6.9, 2 Hz, 1H), 0.40 (dd, *J* = 9.3, 2 Hz, 1H), 0.23 (d, *J* = 2 Hz, 1H) ppm;
^{13}C NMR (75 MHz, $CDCl_3$): δ 210.9 (q), 136.3 (q), 129.2 (CH), 128.7 (CH), 128.5 (CH), 128.1 (CH), 126.7 (CH), 101.2 (q), 85.7 (CH), 39.9 (CH_2), 37.4 (CH_2) ppm;
IR (thin film): ν_{max} = 3029, 2045, 1965, 1496, 959 cm^{-1};
MS (EI): *m/z* (%): 296.0 ([*M*]$^{+\cdot}$, 12%), 268.0 ([*M*]$^{+\cdot}$-CO, 46), 240.0 ([*M*]$^{+\cdot}$-2CO, 62), 212.1 ([*M*]$^{+\cdot}$-3CO, 100), 55.9 ([*Fe*]$^{+\cdot}$, 44);
HRMS (EI): calculated for $C_{15}H_{12}FeO_3$ [*M*]$^{+\cdot}$: 296.0136; found 296.0135.

TRICARBONYL((E)-1-(3-METHYLENEPENTA-1,4-DIEN-1-YL)-4-METHOXYBENZENE)IRON ***3.58***



Prepared *via* **GP-1** using **2.24** (453 mg, 2.06 mmol, 1.0 mol equiv.), *p*-methoxystyrene (557 mg, 4.0 mmol, 2.0 mol equiv.), Hoveyda–Grubbs second generation catalyst (85 mg, 0.12 mmol, 0.06 mol equiv.), and CH_2Cl_2 (20 mL). The yellow solid was purified by flash column chromatography (silica gel, 5:95 ethyl acetate/hexane) affording the *title compound* as a yellow crystalline solid (451 mg, 67% yield);
R_f 0.43 (5:95 ethyl acetate/hexane);
mp: 75–78 °C (ether/hexane).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (d, *J* = 8.5 Hz, 2H), 6.90–6.86 (m, 3H), 6.76 (d, *J* = 5.8 Hz, 1H), 5.51 (m, 1H), 3.83 (s, 3H), 2.32 (dd, *J* = 2.6, 1.5 Hz, 1H), 1.83 (dd, *J* = 6.8, 2.4 Hz, 1H), 0.38 (dd, *J* = 9.1, 2.3 Hz, 1H), 0.21 (d, *J* = 2.1 Hz, 1H) ppm;
^{13}C NMR (100 MHz, $CDCl_3$): δ 211.1 (q), 159.7 (q), 129.2 (q), 129.0 (CH), 128.1 (CH), 126.3 (CH), 114.2 (CH), 102.1 (q), 85.2 (CH), 55.4 (CH_3), 39.8 (CH_2), 37.5 (CH_2) ppm.
IR (KBr disc): ν_{max} = 2042, 1994, 1979, 1958, 1603 cm^{-1};
MS (EI): *m/z* (%): 356.0 (5), 326.1 ([*M*]$^{+\cdot}$, 14), 298.1 (56), 270.1 (70), 242.0 (100), 56.0 ([*Fe*]$^{+\cdot}$, 30);
HRMS (EI): calculated for $C_{16}H_{14}FeO_4$ [*M*]$^{+\cdot}$: 326.0241; found 326.0242.

*TRICARBONYL[-(E)-1-(3-METHYLENEPENTA-1,4-DIEN-1-YL)-4-NITROBENZENE)IRON **3.59***



Prepared *via* **GP-1** using **2.24** (454 mg, 2.06 mmol, 1.0 mol equiv.), *p*-nitrostyrene (550 mg, 4.0 mmol, 2.0 mol equiv.), Hoveyda–Grubbs second generation catalyst (63 mg, 0.10 mmol, 0.05 mol equiv.), and CH_2Cl_2 (20 mL). The yellow solid was purified by flash column chromatography (silica gel, 20:80 CH_2Cl_2/hexane) affording the *title compound* as a bright yellow crystalline solid (366 mg, 52% yield);

R_f 0.12 (20:80 CH_2Cl_2/hexane);

mp: 108–110 °C ($CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (d, J = 8.8 Hz, 2H), 7.58 (d, J = 8.8 Hz, 2H), 7.10 (d, J = 16.1 Hz, 1H) , 6.93 (d, J = 15.8 Hz, 1H), 5.51 (t, J = 8.1 Hz, 1H), 2.29 (dd, J = 2.9, 1.5 Hz, 1H), 1.92 (dd, J = 7.0, 2.6 Hz, 1H), 0.48 (dd, J = 9.5, 2.6 Hz, 1H), 0.25 (d, J = 2.6 Hz, 1H) ppm;

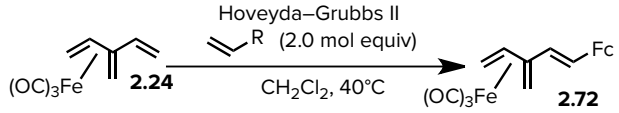
^{13}C NMR (100 MHz, $CDCl_3$): δ 210.5 (q), 147.1 (q), 142.9 (q), 133.7 (CH), 127.2 (CH), 126.5 (CH), 124.2 (CH), 99.2 (q), 87.3 (CH), 40.9 (CH_2), 37.3 (CH_2) ppm.

IR (KBr disc): ν_{max} = 2928, 2045, 1976, 1593, 1519, 1340 cm^{-1};

MS (EI): *m/z* (%): 341.0 ([*M*]$^{+\cdot}$, 14), 313.0 (34), 285.0 (100), 257.0 (22), 227.0 (73), 55.9 ([*Fe*]$^{+\cdot}$, 40);

HRMS (EI): calculated for $C_{15}H_{11}FeNO_5$ [*M*]$^{+\cdot}$: 340.9987; found 340.9992.

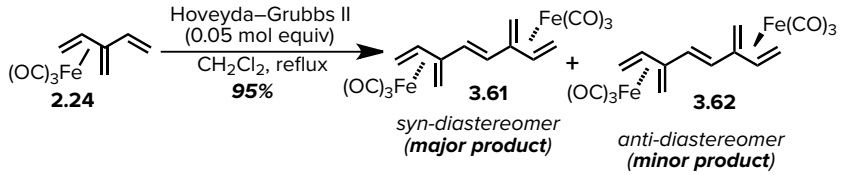
*TRICARBONYL[(E)-1-FERROCENYL-3-METHYLENE -1,4-PENTADIENE)IRON VIA CROSS-METATHESIS **(2.72)***



A solution of tricarbonyliron[3]dendralene **(2.24)** (37.5 mg, 0.170 mmol, 1.0 mol equiv.) and vinylferrocene (72.4 mg, 0.342 mmol, 2.0 mol equiv) in CH_2Cl_2 (1 mL) was added *via* cannula to a one-piece refluxing round bottom flask containing Hoveyda-Grubbs second generation catalyst (5.0 mg, 0.008 mmol, 0.05 mol equiv.) (**GP-1**). The resulting mixture was then heated to reflux and stirred for 16 h. The solvent was subsequently removed under reduced pressure and the resulting brown solid was purified by flash column chromatography (eluting with hexane on silica gel) affording the *title compound* as a red powder (48.1 mg, 70%

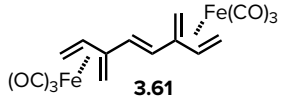
yield); R_f 0.30 (hexane);
Spectroscopic data were in accordance with reported values, see page 166.

HOMO-CROSS METATHESIS OF TRICARBONYLIRON[3]DENDRALENE



A solution of tricarbonyliron[3]dendralene **(2.24)** (177.8 mg, 0.808 mmol, 2.0 mol equiv.) in CH_2Cl_2 (2 mL) was added *via* cannula to a one-piece refluxing round bottom flask containing Hoveyda-Grubbs second generation catalyst (30.0 mg, 0.05 mmol, 0.06 mol equiv.) (**GP-1**). The resulting mixture was then heated to reflux and stirred for 16 h. The solvent was then removed under reduced pressure and the resulting brown solid was passed through a plug of silica (eluting with pentane) affording a mixture of compounds **3.61** and **3.62** as a yellow solid (159 mg, 95%, 64:36 *d.r.*).

HEXACARBONYL[(E)-3,6-DIMETHYLENEOCTA-1,4,7-TRIENE]DIIRON-SYN ***(3.61)***

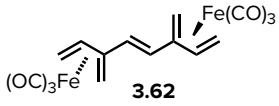


syn-diastereomer
(major product)

Further purification to give an analytically pure sample of the *title compound* was carried out on normal phase HPLC (10 μm silica, 250 x 22 mm, eluting with hexane, ret. time: 16.6 min) to give the major product **3.61** as a yellow crystalline solid;
R_f 0.26 (hexane);
m.p.: 96-99 °C (hexane);
^{1}H NMR (300 MHz, $CDCl_3$): δ 6.74 (s, 2H), 5.48 (t, J = 9.0 Hz, 2H), 2.19 (d, J = 2.7 Hz, 2H), 1.83 (dd, J = 7.0, 2.3 Hz, 2H), 0.36 (dd, J = 9.4, 2.3 Hz, 2H), 0.18 (d, J = 2.7 Hz, 2H) ppm;
^{13}C NMR (75 MHz, $CDCl_3$): δ 210.5 (q), 130.0 (CH), 99.9 (q), 86.1 (CH), 40.0 (CH_2), 37.2 (CH_2) ppm;
IR (KBr disc): ν_{max} = 2926, 2046, 1973, 1962 cm^{-1};
MS (EI): *m/z* (%): 411.9 ([*M*]$^{+\cdot}$, 6), 383.9 ([*M*]$^{+\cdot}$-CO, 4), 355.9 ([*M*]$^{+\cdot}$-2CO, 44), 327.9 ([*M*]$^{+\cdot}$-3CO, 20), 299.9 ([*M*]$^{+\cdot}$-4CO, 9), 271.9 ([*M*]$^{+\cdot}$-5CO, 55), 244.0 ([*M*]$^{+\cdot}$-6CO,

100), 55.9 ($Fe^{+\cdot}$, 40);
HRMS (EI): calculated for $C_{16}H_{12}Fe_2O_6$ $[M]^{+\cdot}$: 411.9333; found 411.9331.

HEXACARBONYL[(E)-3,6-DIMETHYLENEOCTA-1,4,7-TRIENE]DIIRON-ANTI ***3.62***

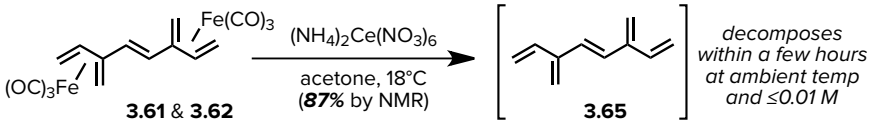


3.62

anti-diastereomer
(minor product)

Further purification to give an analytically pure sample of the *title compound* was carried out on normal phase HPLC (10 μm silica, 250 x 22 mm, eluting with hexane, ret. time: 15.2 min) to give the minor product **3.62** as a yellow crystalline solid;
R_f 0.29 (hexane);
m.p.: 181-183 °C (decomposition) (chloroform/toluene);
^{1}H NMR (300 MHz, $CDCl_3$): δ 6.71 (s, 2H), 5.50 (t, J = 8.2 Hz, 2H), 2.22 (dd, J = 2.3, 1.1 Hz, 2H), 1.83 (dd, J = 7.0, 2.3 Hz, 2H), 0.38 (dd, J = 9.3, 2.9 Hz, 2H), 0.21 (d, J = 2.9 Hz, 2H) ppm;
^{13}C NMR (75 MHz, $CDCl_3$): δ 210.6 (q), 129.0 (CH), 99.6 (q), 85.8 (CH), 40.2 (CH_2), 37.9 (CH_2) ppm;
IR (KBr disc): ν_{max} = 2041, 1961, 1482, 980, 960 cm^{-1};
MS (EI): *m/z* (%): 411.9 ($[M]^{+\cdot}$, 18), 383.9 ($[M]^{+\cdot}$-CO, 9), 355.9 ($[M]^{+\cdot}$-2CO, 83), 327.9 ($[M]^{+\cdot}$-3CO, 50), 299.9 ($[M]^{+\cdot}$-4CO, 41), 271.9 ($[M]^{+\cdot}$-5CO, 83), 244.0 ($[M]^{+\cdot}$-6CO, 100), 55.9 ($Fe^{+\cdot}$, 59);
HRMS (EI): calculated for $C_{16}H_{12}Fe_2O_6$ $[M]^{+\cdot}$: 411.9333; found 411.9336.

(E)-3,6-DIMETHYLENEOCTA-1,4,7-TRIENE ***3.65***



3.61 & **3.62** **3.65**

A solution of ceric ammonium nitrate (115 mg, 0.210 mmol, 5.8 mol equiv.) in dry acetone-d_6 (0.5 mL) was added drop-wise to a mixture of **3.61** and **3.62** (14.9 mg, 0.036 mmol, 1.0 mol equiv) dissolved in acetone-d_6 (0.5 mL) and cooled in an ice-bath. After addition was completed in 2 min., the reaction mixture was stirred for another 5 min, end-point can be judged by loss of starting material spot on TLC (**GP-2**). The mixture was quenched by the addition of saturated $NaHCO_3$ solution (1 mL). The resulting pale orange suspension was extracted with benzene-d_6 (2

mL). The combined organic layers were washed with brine (1 mL), and filtered through a basic alumina plug, to give the *title compound* as a yellow solution in acetone/benzene. The product could not be isolated in solvent-free form, and aqueous work up results in significant losses of material. The yield of the transformation was determined as 87% (±5%) by ^{1}H NMR spectroscopy, through an experiment conducted under the same conditions with durene added as an internal standard.

UV/Vis: λ_{max} = 220, 267 nm;

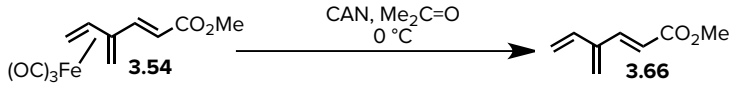
^{1}H NMR (800 MHz, 1:1 acetone-d_6 : benzene-d_6 calibrated against residual benzene): δ 6.51 (s, 2H), 6.38 (dd, J = 17.4, 10.8 Hz, 2H), 5.32 (d, J = 17.4 Hz, 2H), 5.07 (s, 2H), 5.05 (s, 2H), 5.00 (d, J = 10.9 Hz, 2H) ppm;

^{13}C NMR (200 MHz, 1:1 acetone-d_6 : benzene-d_6 calibrated against residual benzene): δ 145.3 (q), 137.0 (CH), 130.4 (CH), 116.6 (CH_2), 116.5 (CH_2) ppm;

MS (EI): *m/z* (%): 272.0 (10), 264.2 (2[M]$^{+\cdot}$, 1), 244.0 (20), 132.1 ([M]$^{+\cdot}$, 26), 117.1 ([M]$^{+\cdot}$-CH_3, 57), 91.1 (70);

HRMS (EI): calculated for $C_{10}H_{12}$ [M]$^{+\cdot}$: 132.0939; found 132.0939.

*(E)-METHYL 4-METHYLENE-2,5-HEXADIENOATE (**3.66**)*



Tricarbonyl[(4-6η^4)-(*E*)-methyl 4-methylene-2,5-hexadienoate)iron **3.54** (15 mg, 0.055 mmol, 1.0 mol equiv.), cerium ammonium nitrate (91 mg, 0.17 mmol, 3.0 mol equiv.), and acetone-d_6 (2 mL) were combined according to **GP-2**, using $CDCl_3$ to extract the unstable dendralene. The *title compound* was characterised as a yellow $CDCl_3$ solution (0.0235 mmol, 42% yield);

R_f 0.15 (25:75 diethyl ether/pentane).

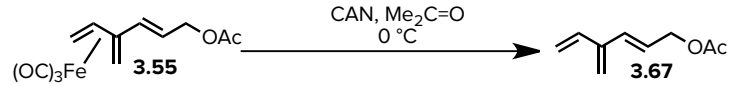
^{1}H NMR (300 MHz; CDCl3): δ 7.20 (d, J = 15.9 Hz, 1H), 6.23 (dd, J = 17.4, 10.9 Hz, 1H), 5.88 (d, J = 15.9 Hz, 1H), 5.32–5.20 (m, 3H), 5.04 (d, J = 10.9 Hz, 1H), 3.56 (s, 3H) ppm;

^{13}C NMR (75 MHz; $CDCl_3$): δ 206.8 (q), 143.6 (CH), 142.1 (q), 134.0 (CH), 121.0 (CH_2), 119.6 (CH), 116.9 (CH_2), 51.3 (CH_3) ppm.

MS (EI): *m/z* (%): 138.1 ([M]$^{+\cdot}$, 23) , 118.0 (68) , 79.1 (100);

HRMS (EI): calculated for $C_8H_{10}O_2$ [M]$^{+\cdot}$: 138.0681; found 138.0681.

*(E)-1-ACETOXY-4-METHYLENE-2,5-HEXADIENE (**3.67**)*



Tricarbonyl[(4-6η⁴)-(*E*)-1-acetoxy-4-methylene-2,5-hexadiene]iron **3.55** (58 mg, 0.20 mmol, 1.0 mol equiv.), cerium ammonium nitrate (329 mg, 0.60 mmol, 3.0 mol equiv.), and acetone (8 mL) were combined according to **GP-2**. The yellow oil was purified by flash column chromatography (silica gel, 5:95 diethyl ether/pentane) affording the *title compound* as a colourless oil (25 mg, 81 % yield); R_f 0.17 (5:95 diethyl ether/pentane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.43 (dd, J = 17.2, 10.6 Hz, 1H), 6.39 (d, J = 15.6 Hz, 1H), 5.94 (dt, J = 15.8, 6.3 Hz, 1H), 5.39 (d, J = 17.5 Hz, 1H), 5.18–5.14 (m, 3H), 4.64 (d, J = 6.1 Hz, 2H), 2.09 (s, 3H) ppm;

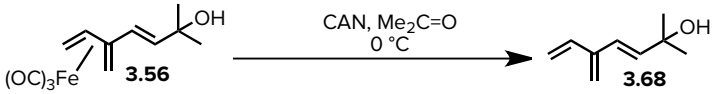
^{13}C NMR (100 MHz, $CDCl_3$): δ 170.9 (q), 143.4 (q), 135.8 (CH), 132.9 (CH), 125.1 (CH), 116.5 (CH_2), 116.1 (CH_2), 65.0 (CH_2), 21.1 (CH_3) ppm;

IR (thin film): ν_{max} = 3090, 2940, 1742, 1239, 968, 899 cm^{-1}.

MS (EI): *m/z* (%): 152.0 ([*M*]$^{+\cdot}$, 13), 110.0 (12), 95.0 (20), 91.0 (100), 83.9 (45);

HRMS (EI): calculated for $C_9H_{12}O_2$ [*M*]$^{+\cdot}$: 152.0837; found 152.0838.

*(E)-2-METHYL-5-METHYLENEHEPTA-3,6-DIEN-2-OL (**3.68**)*



Tricarbonyliron-(E)-2-methyl-5-methylenehepta-3,6-dien-2-ol **3.56** (98 mg, 0.35 mmol, 1.0 mol equiv.), cerium ammonium nitrate (580 mg, 1.1 mmol, 3.0 mol equiv.), and acetone (5 mL) were combined according to **GP-2**. The *title compound* was characterised as a yellow oil (0.0235 mmol, 70% yield);

The *title compound* was characterised as a colourless oil (34 mg, 70% yield); R_f 0.21 (20% ethyl acetate/hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.41 (dd, J = 17.2, 10.5 Hz, 1H), 6.29 (d, J = 16.1 Hz, 1H), 5.97 (d, J = 15.6 Hz, 1H), 5.36 (dd, J = 17.6, 1.5 Hz, 1H), 5.13-5.09 (m, 3H), 1.90 (br s, 1H), 1.34 (s, 6H) ppm;

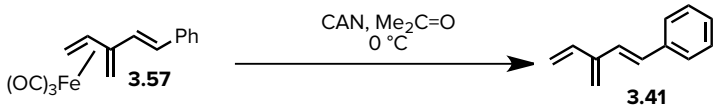
^{13}C NMR (100 MHz, $CDCl_3$): δ 143.8, 139.3, 136.3, 125.1, 115.6, 115.1, 70.8 (q), 29.8 (CH_3) ppm.

IR (thin film): ν_{max} =3391, 3088, 2974, 971, 911 cm^{-1}

MS (EI): *m/z* (%): 145.1 ([*M*]$^{+\cdot}$, 35), 137.1 (45), 123.1 (36), 95.1 (100);

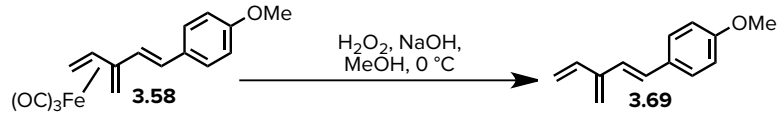
HRMS (EI): calculated for $C_9H_{14}O_1$ [*M*]$^{+\cdot}$: 138.1043; found 138.1044.

*(E)-(3-METHYLENEPENTA-1,4-DIEN-1-YL)BENZENE (**3.41**)*



Tricarbonyl[(4-6η⁴)-(*E*)-(3-methylenepenta-1,4-dien-1-yl)benzene)iron **3.57** (18 mg, 0.0615 mmol, 1.0 mol equiv.), cerium ammonium nitrate (101 mg, 0.185 mmol, 3.0 mol equiv.), and acetone-d_6 (2 mL) were combined according to **GP-2**, using $CDCl_3$ to extract the unstable dendralene. The *title compound* was characterised as a yellow $CDCl_3$ solution (0.0245 mmol, 40% yield);
R_f 0.35 (2:98 CH_2Cl_2/pentane).
^{1}H NMR (800 MHz; CDCl3): δ 7.35 (d, J = 8.0 Hz, 2H), 7.24 (dd, J = 8.0, 7.3 Hz, 2H), 7.17–7.15 (m, 1H), 6.77 (d, J = 16.2 Hz, 1H), 6.65 (d, J = 16.2 Hz, 1H), 6.46 (dd, J = 17.4, 10.8 Hz, 1H), 5.40 (dd, J = 17.3, 1.4 Hz, 1H), 5.18–5.11 (m, 3H) ppm;
^{13}C NMR (200 MHz; $CDCl_3$): δ 144.1 (q), 137.0 (q), 135.8 (CH), 130.1 (CH), 128.4 (CH), 127.49 (CH), 127.41 (CH), 126.3 (CH), 115.7 (CH2), 115.3 (CH2) ppm.
MS (EI): *m/z* (%): 312.2 (2[M]$^{+\cdot}$, 22), 156.1 ([M]$^{+\cdot}$, 100), 141.1 (51), 128.1 (42), 115.0 (28);
HRMS (EI): calculated for $C_{12}H_{12}$ [M]$^{+\cdot}$: 156.0939; found 156.0935.

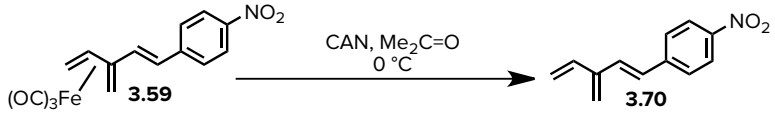
*(E)-1-(3-METHYLENEPENTA-1,4-DIEN-1-YL)-4-METHOXYBENZENE (**3.69**)*



To a rapidly stirred solution of tricarbonyl[(4-6η⁴)-(*E*)-1-(3-methylenepenta-1,4-dien-1-yl)-4-methoxybenzene)iron **3.58** (14 mg, 0.042 mmol, 1.0 mol equiv.) in methanol (0.01–0.05 M) (dissolution was aided by heating) was added 30% aqueous hydrogen peroxide (0.26 mL, 6.0 mL/mmol). The solution was cooled to 0 °C. NaOH (10 mg, 0.25 mmol, 6.0 mol equiv.) was added dropwise as a solution in MeOH, and the mixture was left stirring, open to air, for 30 minutes. The brown suspension was quenched by addition of saturated aqueous $Na_2S_2O_3$ (1 vol equiv. relative to the hydrogen peroxide) and diluted with isopentane (*ca.* 2 vol equiv. relative to the methanol). The two layers were separated and the organic layer was washed with water and dried ($MgSO_4$), then filtered. The isopentane solution of **3.69** was added to a small volume of $C_2D_2Cl_4$ (0.5 mL) and the isopentane was removed under reduced pressure (20 mbar) at 0 °C on a rotary evaporator, then the remaining traces of isopentane were removed by increasing the vacuum to 1–2 mbar for one minute. The $C_2D_2Cl_4$ solution could be stored over extended

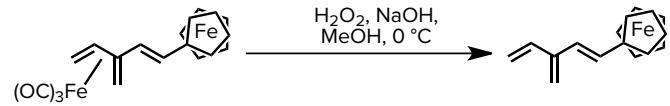
periods at –78 °C without change. The *title compound* was characterised as a yellow $C_2D_2Cl_4$ solution (0.0153 mmol, 28% yield);
R_f 0.44 (5:95 Et_2O/pentane).
^{1}H NMR (400 MHz; $C_2D_2Cl_4$): δ 7.40 (d, J = 8.7 Hz, 2H), 6.89 (d, J = 8.8 Hz, 2H), 6.74 (app d, J = 4.4 Hz, 2H), 6.57 (dd, J = 17.2, 10.8 Hz, 1H), 5.52 (d, J = 17.8 Hz, 1H), 5.24 (app dd, J = 11.1, 0.7 Hz, 3H), 3.83 (s, 3H) ppm;
^{13}C NMR (100 MHz; $C_2D_2Cl_4$): δ 160.6 (q), 145.5 (q), 137.4 CH), 131.20 (q), 131.09 (CH), 129.2 (CH), 127.0 (CH), 117.5 (CH_2), 116.5 (CH_2), 115.5 (CH), 56.8 (CH_3) ppm.
MS (EI): *m/z* (%): 186.1 ([*M*]$^{+\cdot}$, 100), 155.1 (56), 86.0 (75);
HRMS (EI): calculated for $C_{13}H_{14}O$ [*M*]$^{+\cdot}$: 186.1045; found 186.1048.

*(E)-1-(3-METHYLENEPENTA-1,4-DIEN-1-YL)-4-NITROBENZENE (**3.70**)*



Tricarbonyl[(4-6η^4)-(*E*)-1-(3-methylenepenta-1,4-dien-1-yl)-4-nitrobenzene]iron **3.59** (22 mg, 0.064 mmol, 1.0 mol equiv.), cerium ammonium nitrate (106 mg, 0.19 mmol, 3.0 mol equiv.), and acetone-d_6 (2 mL) were combined according to **GP-2**, using $C_2D_2Cl_4$ to extract the unstable dendralene. The *title compound* was characterised as a yellow $C_2D_2Cl_4$ solution (0.0314 mmol, 49% yield);
R_f 0.10 (25:75 CH_2Cl_2/pentane).
^{1}H NMR (800 MHz, $C_2D_2Cl_4$): δ 8.18 (d, J = 8.8 Hz, 2H), 7.57 (d, J = 8.8 Hz, 2H), 7.01 (d, J = 16.2 Hz, 1H), 6.78 (d, J = 16.2 Hz, 1H), 6.55 (dd, J = 17.4, 10.8 Hz, 1H), 5.52 (dd, J = 17.4, 1.1 Hz, 1H), 5.38 (d, J = 14.0 Hz, 2H), 5.28 (d, J = 10.9 Hz, 1H) ppm;
^{13}C NMR (200 MHz, $C_2D_2Cl_4$): δ 146.5 (q), 143.7 (q), 143.5 (q), 134.9 (CH), 132.5 (CH), 127.9 (CH), 126.9 (CH), 124.0 (CH), 118.3 (CH_2), 116.9 (CH_2) ppm.
MS (EI): *m/z* (%): 201.1 ([*M*]$^{+\cdot}$, 99), 154.1 (100), 128.1 (73), 77.0 (48);
HRMS (EI): calculated for $C_{12}H_{11}NO_2$ [*M*]$^{+\cdot}$: 201.0790; found 201.0788.

*1E-FERROCENYL[3]DENDRALENE (**3.71**)*

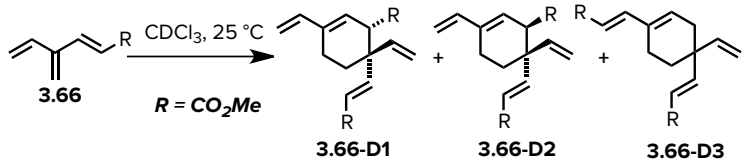


To a rapidly stirred solution of tricarbonyl[(4-6η^4)-(*E*)-1-(3-methylenepenta-1,4-dien-1-yl)-ferrocene)iron **2.72** (27 mg, 0.065 mmol, 1.0 mol equiv.) in methanol (0.05 M) (dissolution was aided by heating) was added 30% aqueous hydrogen peroxide (0.4 mL, 6.0 mL/mmol). The solution was cooled to 0 °C. NaOH (16 mg,

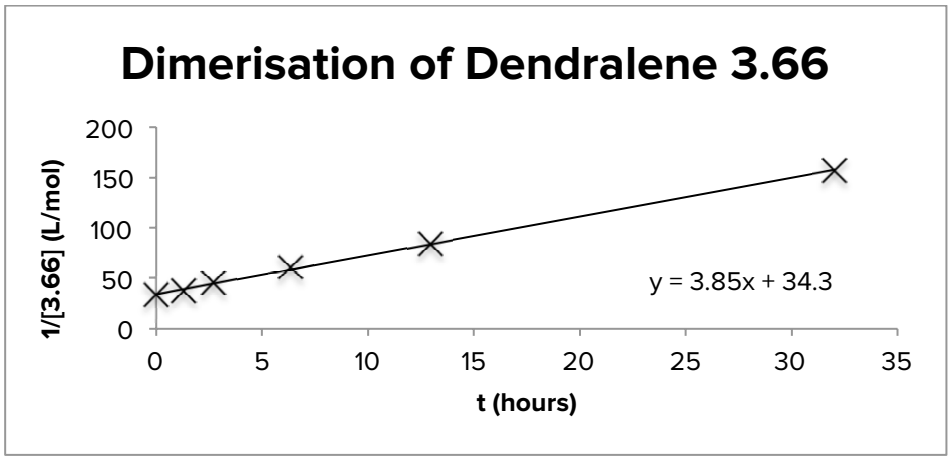
0.40 mmol, 6.0 mol equiv.) was added dropwise as a solution in MeOH, and the mixture was left stirring, open to air, for 30 minutes. The brown suspension was quenched by addition of saturated aqueous $Na_2S_2O_3$ (1 vol equiv. relative to the hydrogen peroxide) and diluted with $CDCl_3$ (*ca.* 5 vol equiv. relative to the methanol). The two layers were separated and the organic layer was washed 3 times with water, and dried ($MgSO_4$), then filtered. The $CDCl_3$ solution of **3.71** was reduced under reduced pressure (20 mbar) at 0 °C on a rotary evaporator, until the volume was approximately 1.0 mL. The *title compound* was characterised as a yellow *d*-chloroform solution (0.0144 mmol, 22% yield);
^{1}H NMR (300 MHz; $CDCl_3$): δ 6.54 (dd, J = 11.2, 6.1 Hz, 1H), 6.48 (d, J = 4.8 Hz, 2H), 5.46 (dd, J = 17.4, 1.6 Hz, 1H), 5.19 (dd, J = 10.8, 1.4 Hz, 1H), 5.14 (s, 2H), 4.39 (t, J = 1.8 Hz, 2H), 4.25 (t, J = 1.8 Hz, 2H), 4.12 (s, 5H) ppm;
Further analytical data was not collected for complex **3.71**, so assignment is based only on ^{1}H NMR spectroscopic data.

5.3.3 Diels-Alder Dimerisation of 1*E*-[3]Dendralenes

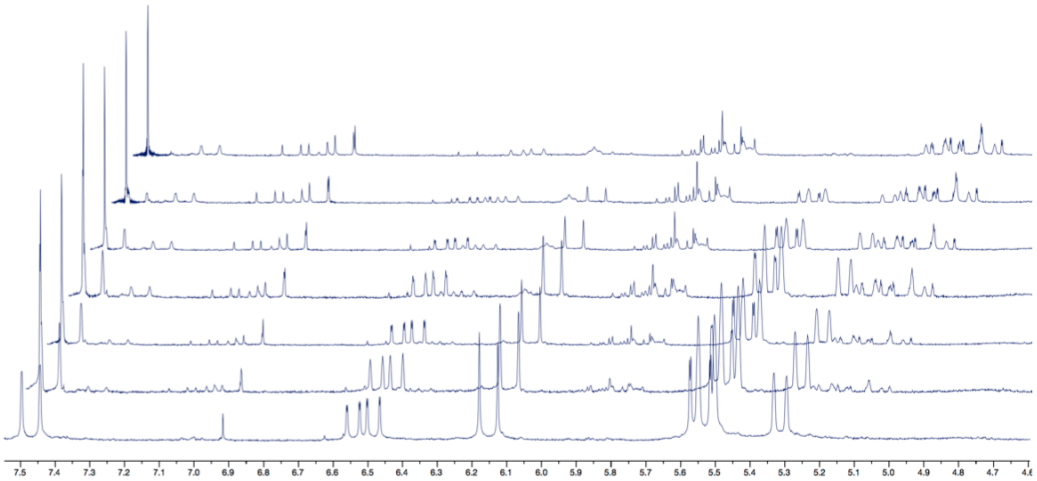
*DIMERISATION OF (**3.66**)*



A solution of **3.66** in $CDCl_3$ (0.55 mL, 0.043 mol L^{-1}) containing methylsulfonylmethane as an internal standard (0.00833 mmol) was diluted to 0.78 mL by addition of $CDCl_3$ to give a 0.030 mol L^{-1} solution. The solution was then treated according to **GP-3**. The observed half-life was 8.6 hours at a concentration of 0.030 mol L^{-1}.



The loss of **3.66** indicated by the points recorded in the graph above can be observed directly in the NMR spectral overlay presented below. Also observed is the concomitant formation of compounds **3.66-D1**, **3.66-D2**, and **3.66-D3**. By ^{1}H NMR spectroscopy, the ratio of products **3.66-D1**:**3.66-D2**:**3.66-D3** was 28:22:50 respectively.

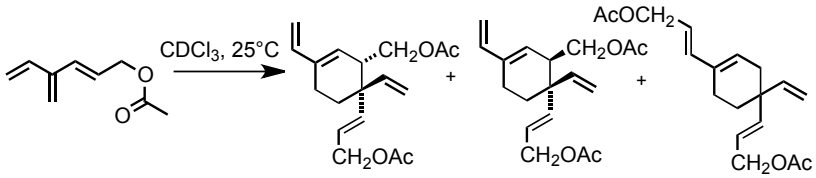


The crude mixture of dimers was purified by flash column chromatography (silica gel, 10:90 ethyl acetate/hexane) affording a mixture of **3.66-D1** and **3.66-D2** as a colourless oil (0.0057 mmol, 49% by ^{1}H NMR spectroscopy);
R_f 0.30 (10:90 ethyl acetate/hexane).
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.04 (d, J = 16.0 Hz, 1H), 6.96 (d, J =16.0 Hz, 1H), 6.36 (dd, J = 17.5, 10.8 Hz, 2H), 5.90–5.77 (m, 4H), 5.71 (app. d, J = 3.5 Hz, 2H), 5.21–5.02 (m, 8H), 3.72 (app. d, J = 2.8 Hz, 6H), 3.64 (s, 6H), 3.39 (br. s, 2H), 2.39–2.04 (m, 6H), 1.83–1.73 (m, 2H) ppm;
^{13}C NMR (150 MHz, $CDCl_3$): δ 172.2 (two coincident signals), 167.0, 166.9, 152.5, 151.6, 140.8, 139.8, 138.6, 138.5, 138.2, 138.1, 123.4, 123.3, 120.5, 120.2, 115.8, 115.1,

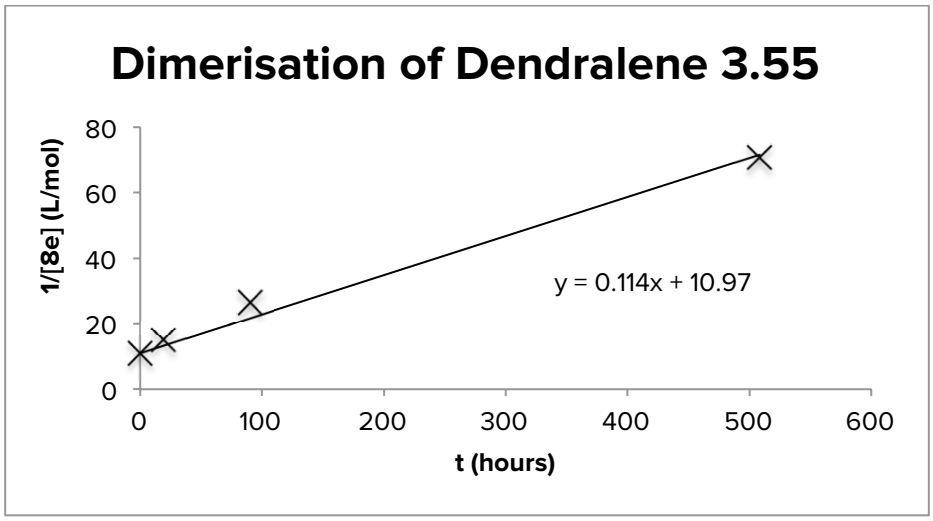
112.7, 112.7, 51.9, 51.8, 51.6, 51.5, 49.9, 49.8, 43.7, 43.6, 28.5, 28.1, 21.0, 21.0 ppm.
IR (thin film): ν_{max} = 3154, 2953, 1718, 908 cm^{-1}; MS (EI): *m/z*: 276.1 ($[M]^{+\cdot}$);
HRMS (EI): calculated for $C_{16}H_{20}O_4$ $[M]^{+\cdot}$: 276.1362; found 276.1365.

3.66-D3 was isolated as a colourless oil (0.0057 mmol, 49% by ^1H NMR spectroscopy);
R_f 0.22 (10:90 ethyl acetate/hexane);
^1H NMR (300 MHz; $CDCl_3$): δ 7.27 (d, J = 15.6 Hz, 1H), 6.88 (d, J = 16.0 Hz, 1H), 6.14 (s, 1H), 5.79–5.68 (m, 3H), 5.06 (app dd, J = 33.3, 14.1 Hz, 2H), 3.74 (s, 3H), 3.73 (s, 3H), 2.35 (br s, 2H), 2.16 (br s, 2H), 1.79 (t, J = 6.5 Hz, 2H) ppm;
^{13}C NMR (75 MHz; $CDCl_3$): δ 167.1 (q, two coincident signals), 153.2 (CH), 147.0 (CH), 141.5 (CH), 135.0 (CH), 134.3 (CH), 119.5 (CH), 115.3 (CH), 114.5 (CH_2), 51.59 (CH_3), 51.53 (CH_3), 41.6 (q), 34.4 (CH_2), 30.9 (CH_2), 21.5 (CH_2) ppm.
IR (thin film): ν_{max} = 3153, 2953, 1717 cm^{-1};
MS (EI): *m/z* (%): 276.1 ($[M]^{+\cdot}$, 6), 244.1 (36), 216.1 (20), 137.1 (11), 79.1 (100);
HRMS (EI): calculated for $C_{16}H_{20}O_4$ $[M]^{+\cdot}$: 276.1362; found 276.1365.

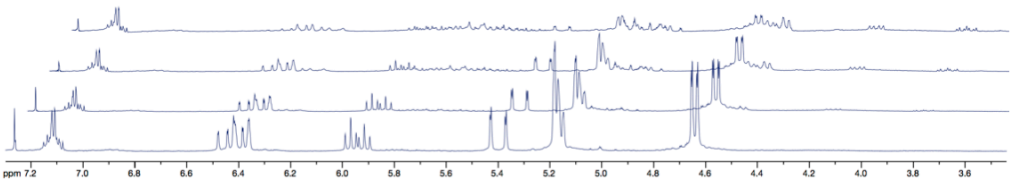
*DIMERISATION OF (**3.55**)*



A solution of **3.55** in $CDCl_3$ (0.45 mL, 0.091 mol L^{-1}) containing methylsulfonylmethane as an internal standard (0.00833 mmol) was treated according to **GP-3**. The observed half-life was 92 hours at a concentration of 0.091 mol L^{-1}.



The loss of **3.55** indicated by the points recorded in the graph above can be observed directly in the NMR spectral overlay presented below. Also observed is the concomitant formation of compounds **3.55-D1**, **3.55-D2**, and **3.55-D3**. By ^{1}H NMR spectroscopy, the ratio of products was 36:25:39 for **3.55-D1**:**3.55-D2**:**3.55-D3** respectively.



The crude mixture of dimers was purified by flash column chromatography (silica gel, 2:98 to 5:95 ethyl acetate/hexane) affording a mixture of all three dimers **3.55-D1–3** as a colourless oil; R_f 0.46 (10:90 EtOAc/hexane). Separation was achieved by reverse phase HPLC (60:40 acetonitrile/water, Waters XBridge Prep C18 5 μm OBD 19 × 150 mm).

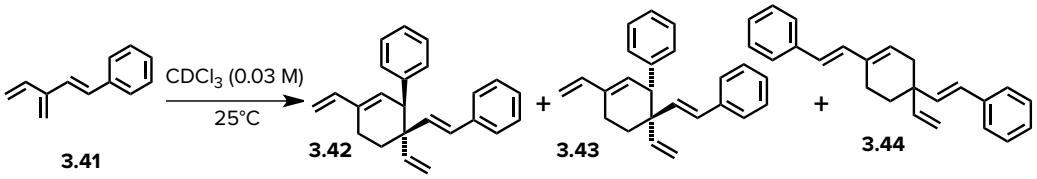
3.55-D1 was isolated as a colourless oil (0.0066 mmol, 32% by ^{1}H NMR spectroscopy); retention time 8.9 minutes (17 mL/minute, 60:40 acetonitrile/water),
^{1}H NMR (400 MHz; $CDCl_3$): δ 6.36 (dd, J = 17.5, 10.8 Hz, 1H), 5.90 (dd, J = 17.6, 10.9 Hz, 1H), 5.77 (d, J = 15.9 Hz, 1H), 5.70–5.69 (m, 1H), 5.59 (dt, J = 15.9, 6.3 Hz, 1H), 5.15–5.06 (m, 3H), 4.99 (d, J = 10.7 Hz, 1H), 4.53 (dd, J = 6.3, 1.0 Hz, 2H), 4.18 (dd, J = 10.9, 5.0 Hz, 1H), 3.83 (dd, J = 11.0, 8.2 Hz, 1H), 2.56 (t, J = 2.6 Hz, 1H), 2.18 (t, J = 2.1 Hz, 2H), 2.05 (s, 3H), 2.04 (s, 3H), 1.83–1.69 (m, 2H) ppm;

^{13}C NMR (100 MHz, $CDCl_3$): δ 171.1, 170.9, 142.8, 139.1, 137.7, 136.7, 127.9, 124.3, 114.2, 111.8, 65.36, 65.23, 43.1, 42.5, 30.6, 29.8, 21.26, 21.10 ppm.
IR (thin film): ν_{max} = 2929, 1733, 908 cm^{-1};
MS (EI): *m/z* (%): 304.2 ($[M]^{+\cdot}$, 2), 244.1 (30), 184.1 (51), 92.1 (100);
HRMS (EI): calculated for $C_{18}H_{24}O_4$ $[M]^{+\cdot}$: 304.1675; found 304.1676.

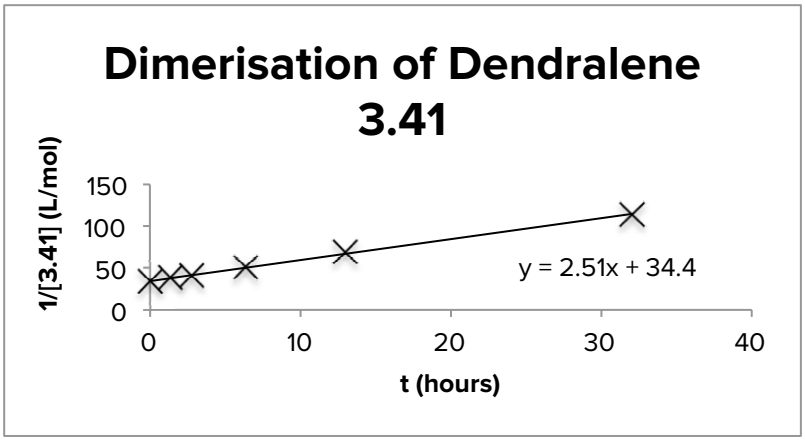
3.55-D2 was collected as a *ca.* 1:1 mixture with **3.55-D1**, as a colourless oil (0.0045 mmol **3.55-D2**, yield of **10e3.55-D2** 22% by ^{1}H NMR spectroscopy); retention time 8.4 minutes (17 mL/minute, 60:40 acetonitrile/water),
^{1}H (300 MHz; $CDCl_3$): δ 6.37 (dd, *J* = 17.5, 10.7 Hz, 2H), 5.95–5.75 (m, 4H), 5.70–5.54 (m, 4H), 5.16–4.98 (m, 8H), 4.54 (t, *J* = 6.9 Hz, 4H), 4.18 (ddd, *J* = 10.9, 4.9, 0.6 Hz, 2H), 3.83 (ddd, *J* = 11.1, 8.2, 3.1 Hz, 2H), 2.55 (br s, 2H), 2.19 (br s, 4H), 2.06–2.05 (m, 12H), 1.86–1.67 (m, 4H) ppm;
^{13}C NMR (75 MHz, $CDCl_3$): δ 171.2 (two coincident peaks), 171.1, 170.9, 142.8 (two coincident peaks), 140.3, 140.1, 139.1, 137.8 (two coincident peaks), 136.7, 136.7, 127.9 (two coincident peaks), 124.4, 123.5, 115.2, 114.2, 111.8 (two coincident peaks), 65.5, 65.4, 65.3, 65.2, 43.2, 43.1, 42.6, 42.5, 30.60, 30.5, 29.8 (two coincident peaks), 21.3 (two coincident peaks), 21.1 (two coincident peaks) ppm.
IR (thin film): ν_{max} = 2929, 1733, 908 cm^{-1};
MS (EI): *m/z* (%): 304.2 ($[M]^{+\cdot}$, 38), 288.1 (100);
HRMS (EI): calculated for $C_{18}H_{24}O_4$ $[M]^{+\cdot}$: 304.1675; found 304.1676.

3.55-D3 was isolated as a colourless oil (0.0071 mmol, 35% by ^{1}H NMR spectroscopy); retention time 7.8 minutes (17 mL/minute, 60:40 acetonitrile/water);
^{1}H NMR (400 MHz; $CDCl_3$): δ 6.26 (d, *J* = 15.7 Hz, 1H), 5.78–5.68 (m, 3H), 5.60 (dt, *J* = 15.5, 6.8 Hz, 1H), 5.51 (dt, *J* = 15.7, 6.3 Hz, 1H), 5.05–4.94 (m, 2H), 4.59 (d, *J* = 6.7 Hz, 2H), 4.52 (dt, *J* = 6.3, 1.3 Hz, 2H), 2.21 (s, 2H), 2.13-2.10 (m, 2H), 2.06 (s, 3H), 2.05 (s, 3H), 1.69 (t, *J* = 6.6 Hz, 2H) ppm;
^{13}C NMR (100 MHz; $CDCl_3$): δ 171.0, 171.0, 143.4, 141.3, 137.4, 134.3, 128.4, 122.4, 119.6, 113.2, 65.53, 65.36, 41.2, 34.7, 31.5, 29.8, 21.9, 21.1 ppm.
IR (thin film): ν_{max} =2924, 2951, 1732, 909 cm^{-1};
MS (EI): *m/z* (%): 304.2 ($[M]^{+\cdot}$, 4), 262.1 (100);
HRMS (EI): calculated for $C_{18}H_{24}O_4$ $[M]^{+\cdot}$: 304.1675; found 304.1678.

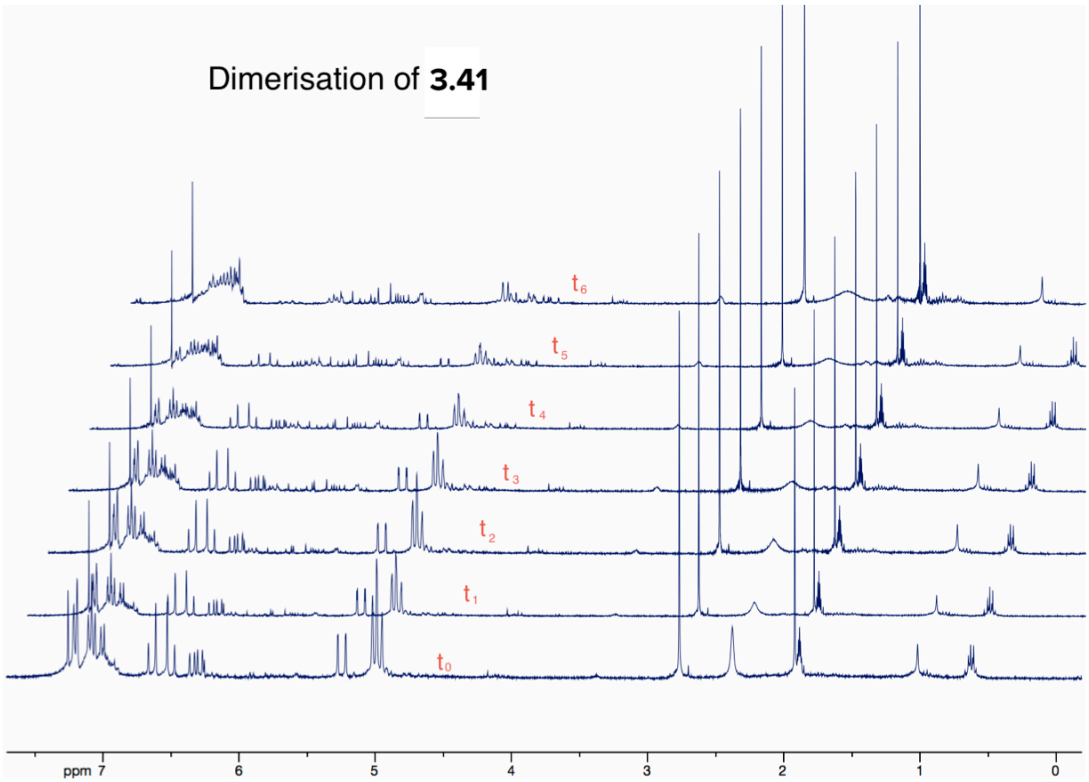
*DIMERISATION OF (**3.41**)*



A solution of **3.41** in $CDCl_3$ (0.80 mL, 0.0307 mol L^{-1}) containing methylsulfonylmethane as an internal standard (0.00833 mmol) was diluted to 0.82 mL by addition of $CDCl_3$ to give a 0.030 mol L^{-1} solution. The solution was then treated according to **GP-3**. The observed half-life was 13 hours at a concentration of 0.030 mol L^{-1}.



The loss of **3.41** indicated by the points recorded in the graph above can be observed directly in the NMR spectral overlay presented below. Also observed is the concomitant formation of compounds **3.42**, **3.43**, and **3.44**. The ratio of **3.42**:**3.43**:**3.44** is consistent with that obtained in the Wittig reaction of **3.39** with benzaldehyde.



The solvent was removed under reduced pressure and the residue was purified first by flash chromatography (silica gel, 5:95 Et_2O/hexane) then by HPLC (Porasil preparative column, 0.5:99.5 EtOAc/hexane).

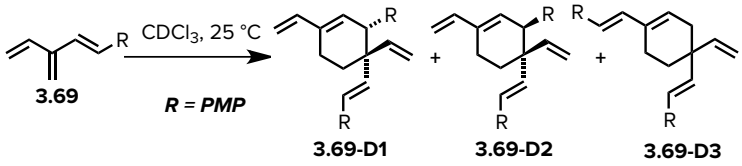
Analysis of the crude mixture by ^{1}H NMR spectroscopy indicated the ratio of products was 61:37:2 for **3.42**:**3.43**:**3.44** respectively.

A mixture of dimers **3.42** and **3.43** were isolated as a colourless oil (26.8 mg, 0.09 mmol, 35%, **3.42**:**3.43**, 62:38).
^{1}H NMR (500 MHz; $CDCl_3$): δ 7.42-7.19 (m, 10H **3.42**, 10H **3.43**), 6.53-6.46 (m, 2H **3.42** 2H **3.43**), 6.35 (d, *J* = 16.4 Hz, 1H **3.43**), 6.22 (d, *J* = 16.3 Hz, 1H **3.42**), 6.06 (d, *J* = 16.4 Hz, 1H **3.42**), 6.01 (dd, *J* = 17.6, 10.9 Hz, 1H **3.43**), 5.88-5.83 (m, 1H **3.42**, 1H **3.43**), 5.27-5.19 (m, 2H **3.42**, 2H **3.43**), 5.07 (br d, *J* = 10.5 Hz, 1H **3.42**, 1H **3.43**), 4.97 (d, *J* = 10.8 Hz, 1H **3.43**), 4.90 (d, *J* = 17.5 Hz, 1H **3.42**), br 3.66 (s, 1H **3.42**, 1H **3.43**), 2.49-2.44 (m, 1H **3.42**, 1H **3.43**), 2.38-2.30 (m, 1H **3.42**, 1H **3.43**), 2.08-1.87 (m, 2H **3.42**, 2H **3.43**) ppm;
^{13}C NMR (125 MHz, $CDCl_3$, d1 = 60 s): *δ* 143.9, 142.6, 141.4, 141.3, 139.5 (two coincident signals), 138.0, 137.9, 136.5, 136.4, 136.3, 135.3, 131.1 (two coincident signals), 130.4 (two coincident signals), 128.8, 128.7 (two coincident signals), 128.5, 127.8 (two coincident signals), 127.2, 127.0, 126.7 (two coincident signals),

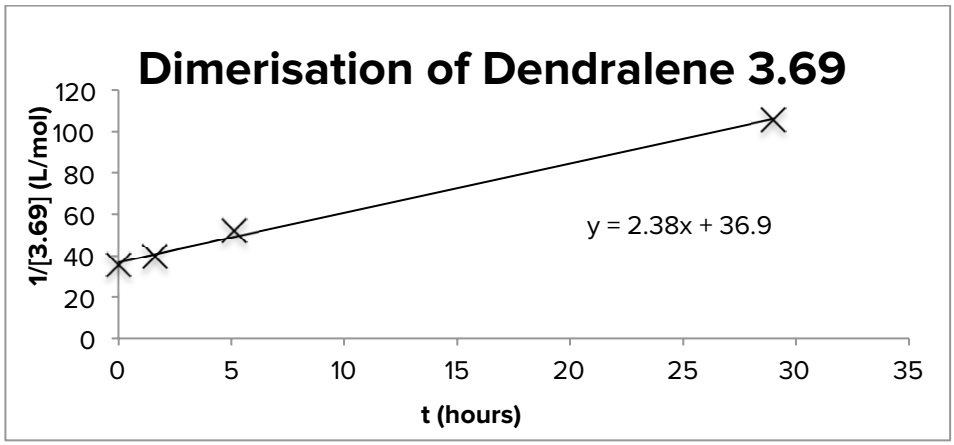
126.3 (two coincident signals), 126.2, 114.1, 113.9, 111.5 (two coincident signals), 51.7, 51.3, 45.3, 29.4, 29.3 and 21.5 (two coincident signals) ppm.
IR (thin film) ν = 3026, 1642, 1603, 1494, 1450 cm^{-1};
MS (70 eV, EI): *m/z* (%): 312 (58) $[M]^{+\cdot}$, 156 (100);
HRMS (70 eV, EI): calc for $C_{24}H_{24}$ $[M]^{+\cdot}$: 312.1878; found 312.1873.

3.44 was isolated as a colourless oil (2.5% yield calculated *via* ^1H NMR).
^1H NMR (500 MHz, $CDCl_3$): δ 7.44–7.17 (10H, m), 6.80 (1H, d, J = 16.1 Hz), 6.44 (1H, d, J = 16.1 Hz), 6.38, (1H, d, J = 16.3 Hz), 6.22 (1H, d, J = 16.3 Hz), 5.95–5.92 (1H, m), 5.90 (1H, dd, J = 17.6, 10.7 Hz), 5.13–5.06 (2H, m), 2.44–2.21 (4H, m) and 1.92–1.84 (2H, m) ppm;
^{13}C NMR (125 MHz, $CDCl_3$): δ 144.2, 137.9, 137.8, 136.4, 135.5, 131.9, 128.7, 128.6, 128.2, 128.1, 127.2, 127.1, 126.3 (two coincident signals), 125.5, 113.1, 41.7, 35.4, 32.1 and 22.2 ppm.
IR (thin film) ν = 2920, 1634, 1447 cm^{-1};
MS (70 eV, EI): *m/z* (%): 312 (24) $[M]^{+\cdot}$, 156 (100);
HRMS (70 eV, EI): calc for $C_{24}H_{24}$ $[M]^{+\cdot}$: 312.1878; found 312.1879.

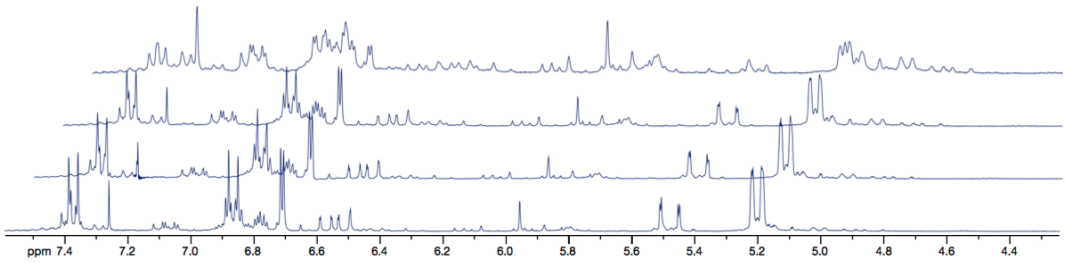
*DIMERISATION OF (**3.69**)*



A solution of **3.69** in $C_2D_2Cl_4$ (0.55 mL, 0.0773 mol L^{-1}) containing methylsulfonylmethane as an internal standard (0.00833 mmol) was diluted to 1.42 mL by addition of $CDCl_3$ to give a 0.028 mol L^{-1} solution. The solution was then treated according to **GP-3**. The observed half-life was 15 hours at a concentration of 0.028 mol L^{-1}.



The loss of **3.69** indicated by the points recorded in the graph above can be observed directly in the NMR spectral overlay presented below. Also observed is the concomitant formation of compounds **3.69-D1**, **3.69-D2**, and **3.69-D3.** By ^{1}H NMR spectroscopy, the ratio of products **3.69-D1**:**3.69-D2**:**3.69-D3** was 59:33:8 respectively.



The crude mixture of dimers was purified by flash column chromatography (silica gel, 1:99 to 5:95 EtOAc/hexane) followed by HPLC (Porasil preparative column, 5:95 EtOAc/hexane). Dimer **3.69-D1** was isolated as a colourless oil (0.011 mmol, 57% by ^{1}H NMR spectroscopy);

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.15 (2H, d, J = 8.8 Hz), 7.13 (2H, d, J = 8.8 Hz), 6.68 (2H, d, J = 8.8 Hz), 6.62 (2H, d, J = 8.8 Hz), 6.50 (1H, dd, J = 17.5, 10.9 Hz), 6.17 (1H, d, J = 16.3 Hz), 5.99, (1H, dd, J = 17.5, 10.8 Hz), 5.91 (1H, d, J = 16.3 Hz), 5.85 (1H, d, J = 4.1 Hz), 5.27–5.15 (3H, m), 5.06 (1H, d, J = 10.9 Hz), 3.80 (6H, s), 3.59 (1H, br s), 2.51–2.24 (2H, m) and 2.04–1.80 (2H, m) ppm;

^{13}C NMR (125 MHz, $CDCl_3$): δ 158.8, 158.3, 144.3, 139.6, 136.0, 133.4, 133.3, 131.5, 131.4, 130.8, 121.1, 127.2, 113.9, 113.7, 113.1, 111.2, 55.3 (two coincident signals), 50.5, 45.2, 29.2 and 21.5 ppm.

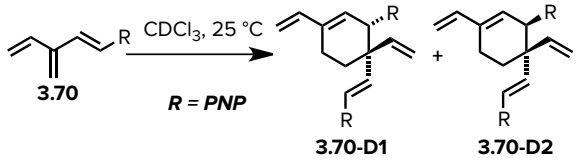
IR (thin film) ν = 1607, 1510, 1247 cm^{-1}; MS (70 eV, EI): m/z (%): 372 (91) $[M]^+$, 186 (95), 155 (100);

HRMS (70 eV, EI): calc for $C_{26}H_{28}O_2$ $[M]^+$: 372.2089; found 372.2088;

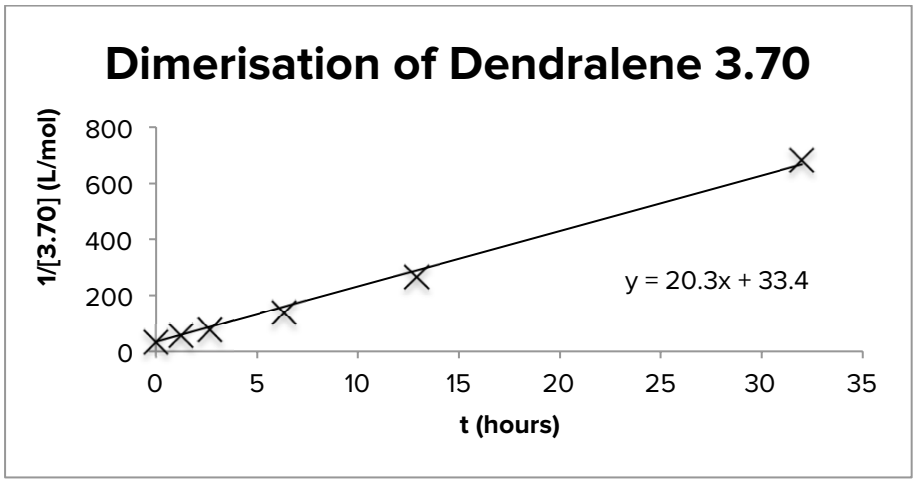
And dimer **3.69-D2** was isolated as a colourless oil (0.0064 mmol, 32% by ^{1}H NMR spectroscopy);
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32 (2H, d, J = 9.1 Hz), 7.09 (2H, d, J = 9.1 Hz), 6.90–6.81 (4H, m), 6.47 (1H, dd, J = 17.4, 10.8 Hz), 6.39 (1H, d, J = 16.5 Hz), 6.15, (1H, d, J = 16.5 Hz), 5.83 (2H, dd, J = 17.5, 10.8 Hz), 5.20 (1H, d, J = 17.8 Hz), 5.03 (1H, d, J = 10.8 Hz), 4.94 (1H, dd, J = 10.9, 1.5 Hz), 4.87 (1H, dd, J = 17.5, 1.5 Hz), 3.82 (3H, s), 3.81 (3H, s), 3.58 (1H, br s), 2.49–2.24 (2H, m) and 2.04–1.85 (2H, m) ppm;
^{13}C NMR (125 MHz, $CDCl_3$): δ 158.9 (two coincident signals), 144.5, 135.5, 134.4, 130.8, 130.6, 130.0, 127.4 (two coincident signals), 127.2, 124.9, 114.1, 114.0, 113.9, 112.8, 55.4 (two coincident signals), 41.6, 35.5, 32.2 and 22.3 ppm.
IR (thin film) v = 1510, 1247 cm^{-1};
MS (70 eV, EI): m/z (%): 372 (57) $[M]^{+\cdot}$, 186 (100), 155 (53);
HRMS (70 eV, EI): calc for $C_{26}H_{28}O_2$ $[M]^{+\cdot}$: 372.2089; found 372.2090.

And **3.69-D3** as a colourless oil (0.0016 mmol, 8% by ^{1}H NMR spectroscopy);
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31 (4H, pseudo t, J = 8.9 Hz), 6.86 (2H, d, J = 8.9 Hz), 6.82 (2H, d, J = 8.9 Hz), 6.66 (1H, d, J = 16.0 Hz), 6.38 (1H, d, J = 16.0 Hz), 6.31 (1H, d, J = 16.4 Hz), 6.06 (1H, d, J = 16.4 Hz), 5.92–5.82 (2H, m), 5.09 (1H, dd, J = 4.5, 1.2 Hz), 5.04 (1H, dd, J = 10.9, 1.3 Hz), 3.80 (3H, s), 3.79 (3H, s), 2.38–2.27 (4H, m) and 1.84 (2H, t, J = 6.3 Hz) ppm;
^{13}C NMR (125 MHz, $CDCl_3$): δ 158.9 (two coincident signals), 144.5, 135.5, 134.4, 130.8, 130.6, 130.0, 127.4 (two coincident signals), 127.2, 124.9, 114.1, 114.0, 113.9, 112.8, 55.4 (two coincident signals), 41.6, 35.5, 32.2 and 22.3 ppm.
IR (thin film) v = 1510, 1247 cm^{-1};
MS (70 eV, EI): m/z (%): 372 (57) $[M]^{+\cdot}$, 186 (100), 155 (53);
HRMS (70 eV, EI): calculated for $C_{26}H_{28}O_2$ $[M]^{+\cdot}$: 372.2089; found 372.2090.

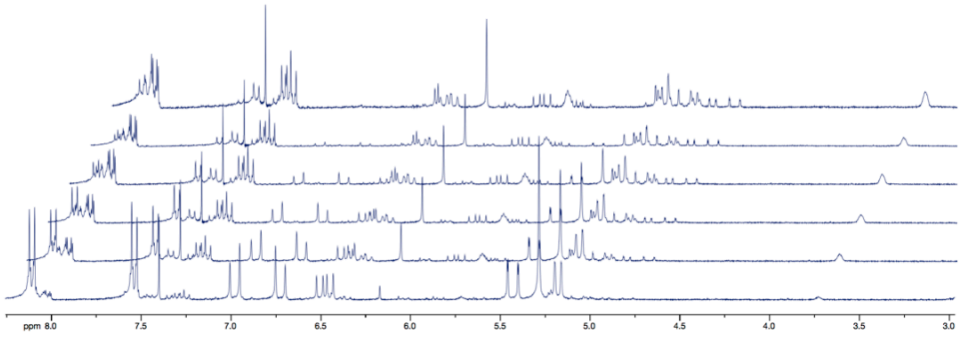
*DIMERISATION OF **3.70***



A solution of **3.70** in $C_2D_2Cl_4$ (1.05 mL, 0.030 mol L^{-1}) containing methylsulfonylmethane as an internal standard (0.00833 mmol) was treated according to **GP-3**. The observed half-life was 1.7 hours at a concentration of 0.030 mol L^{-1}.



The loss of **3.70** indicated by the points recorded in the graph above can be observed directly in the NMR spectral overlay presented below. Also observed is the concomitant formation of compounds **3.70-D1** and **3.70-D2**. By ^{1}H NMR spectroscopy, the ratio of products **3.70-D1**:**3.70-D2** was 56:44 respectively.



The crude mixture of dimers was purified by flash column chromatography (silica gel, 5:95 EtOAc/hexane). Dimer **3.70-D1** was isolated as a colourless oil (0.0087 mmol, 55% by ^{1}H NMR spectroscopy);

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.11 (2H, d, J = 8.9 Hz), 8.10 (2H, d, J = 8.9 Hz), 7.32 (2H, d, J = 8.9 Hz), 7.27 (2H, d, J = 8.9 Hz), 6.46 (1H, dd, J = 17.6, 11.0 Hz), 6.23 (1H, d, J = 16.4 Hz), 6.18 (1H, d, J = 16.4 Hz), 5.92 (1H, dd, J = 17.6, 10.9 Hz), 5.78 (1H, brd, J = 3.9 Hz), 5.30 (1H, d, J = 11.0 Hz), 5.27 (1H, d, J = 17.6 Hz), 5.20 (1H, d, J = 17.6 Hz), 5.12 (1H, d, J = 10.9 Hz), 3.76 (1H, br s), 2.50–2.55 (1H, m), 2.39–2.31 (1H, m) and 2.01–1.90 (2H, m) ppm;

^{13}C NMR (125 MHz, $CDCl_3$): δ 149.1, 147.1, 147.0, 143.8, 142.4, 139.2, 138.9, 137.6, 131.2, 128.7, 128.2, 126.7, 124.3, 123.2, 115.5, 113.0, 51.1, 45.7, 29.1 and 21.5 ppm.

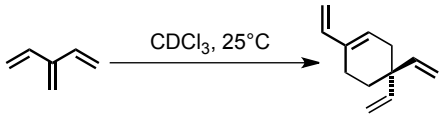
IR (thin film) v = 1595, 1514, 1344 cm^{-1};

MS (70 eV, EI): m/z (%): 402 (28) $[M]^{+\cdot}$, 201 (100), 155 (52);

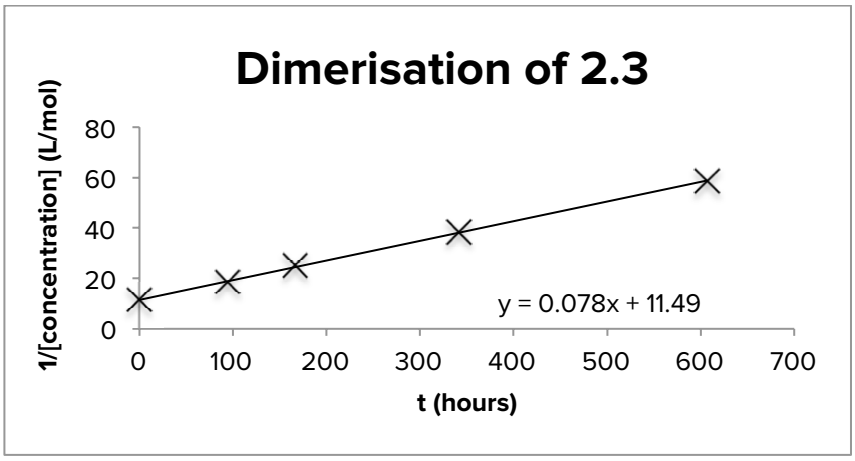
HRMS (70 eV, EI): calc for $C_{24}H_{22}N_2O_4$ $[M]^{+\cdot}$: 402.1580; found 402.1586;

Dimer **3.70-D2** was isolated as a colourless oil (0.0068 mmol, 43% by ^{1}H NMR spectroscopy);
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.18 (2H, d, J = 8.7 Hz), 8.14 (2H, d, J = 8.7 Hz), 7.48 (2H, d, J = 8.7 Hz), 7.31 (2H, d, J = 8.7 Hz), 6.52 (1H, d, J = 16.5 Hz), 6.45, (1H, d, J = 16.5 Hz), 6.46 (1H, dd. J = 17.6, 10.8 Hz), 5.81–5.77 (1H, m), 5.74 (1H, dd, J = 17.6, 10.8 Hz), 5.26 (1H, d, J = 17.6 Hz), 5.11 (1H, d, J = 10.8 Hz), 5.00 (1H, dd, J = 10.8, 1.0 Hz), 4.86 (1H, dd, J = 17.6, 1.0 Hz), 3.75 (1H, br s), 2.54–2.46 (1H, m), 2.36–2.27 (1H, m) and 2.03–1.91 (2H, m) ppm;
^{13}C NMR (125 MHz, $CDCl_3$): δ 149.0, 147.2, 147.1, 144.0, 141.2, 140.6, 138.9, 137.8, 131.3, 128.6, 128.1, 127.0, 124.3, 123.2, 115.6, 113.1, 51.3, 45.9, 29.0 and 21.6 ppm.
IR (thin film) v = 1595, 1515, 1343 cm^{-1}; MS (70 eV, EI): m/z (%): 402 (31) $[M]^{+\cdot}$, 201 (100), 155 (59);
HRMS (70 eV, EI): calc for $C_{24}H_{22}N_2O_4$ $[M]^{+\cdot}$: 402.1580; found 402.1584.

*DIMERISATION OF **2.3** TO GIVE **3.20***



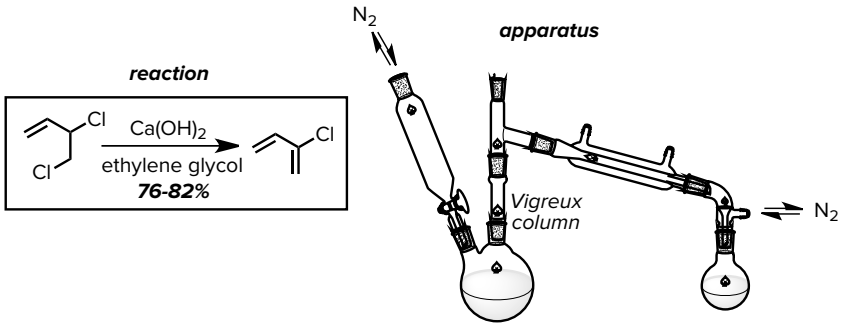
A solution of **2.3** in $CDCl_3$ (0.55 mL, 0.38 mol L^{-1}) containing methylsulfonylmethane as an internal standard (1 mmol) was diluted to 2.45 mL by addition of $CDCl_3$ to give a 0.087 mol L^{-1} solution. The solution was then treated according to **GP-3**. The observed half-life was 150 hours at a concentration of 0.087 mol L^{-1}. All spectroscopic data for **3.20** corresponded to that reported in the literature.[294]



5.4 Experimental For Chapter 4

5.4.1 Remaking the Tricarbonyliron-Dendralenes

2-CHLOROBUTADIENE ***2.25***



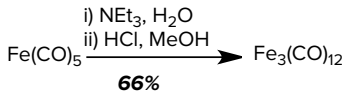
2-Chloro-1,3-butadiene (chloroprene) was prepared based on the patent submitted by Tassara & Baudoin.[428] A two-necked round bottom flask is prepared fitted with a non-equalising addition funnel and a Vigreux column that is further fitted with a distillation kit (*v.s.*), the receiving flash of which is charged with several crystals of BHT and grams of $CaCO_3$. The reaction flask is charged with $Ca(OH)_2$ (88.9 g, 1.2 mol, 1.0 mol equiv) and ethylene glycol (800 mL) and heated to 105°C. Several millilitres of 1,2-dichlorobut-3-ene is added *via* addition funnel and the heat of the reaction is modified until chloroprene can be seen condensing in the Vigreux column. 1,2-Dichlorobut-3-ene (a total of 250 g, 2.0 mol, 1.7 mol equiv) is then added dropwise *via* addition funnel, maintaining a constant rate of distillation. Chloroprene is distilled up and collected up to 60°C, in the receiving flask containing BHT and $CaCO_3$ cooled in an ice-bath. It is finally decanted into a vial

and stored at –15–30°C in a freezer to prevent dimerisation and polymerisation. The *title compound* was collected as a pungent, colourless oil (142 g, 80% yield); b.p. = 58–60°C

^{1}H NMR (400 MHz; $CDCl_3$): δ 6.42 (ddd, J = 16.5, 10.4, 0.6 Hz, 1H), 5.67 (dq, J = 16.5, 0.7 Hz, 1H), 5.42-5.38 (m, 2H), 5.31 (ddt, J = 10.4, 1.5, 0.8 Hz, 1H).

^{1}H NMR spectroscopic data and physical data were in accordance with reported values.[428,429]

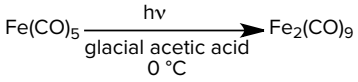
TRIIRON DODECACARBONYL



Triiron dodecacarbonyl was prepared according to the method reported by McFarlane & Wilkinson.[453,502] Oxygen-free water (480 mL) and triethylamine (166 mL, 1.64 mol, 1.5 mol. equiv) was added to a degassed round bottom flask fitted with a reflux condenser and under nitrogen. $Fe(CO)_5$ (220 mL, 1.12 mol, 1.0 mol equiv) was added to the reaction vessel and the reaction heated to 80 °C for 12 h with vigorous stirring. The dark red reaction mixture was then cooled, filtered through a Buchner funnel and the residue ($[NEt_3H][Fe_3(CO)_{11}]$) washed with water. The residue was dissolved in methanol (1.2 L) and transferred into a round bottom flask fitted with a reflux condenser. HCl (1:1 mixture of conc. HCl to water, 2 L) was slowly added to the mixture, which was subsequently heated to 100 °C for 3 hours. At this point the reaction has clarified to a pale green solution containing floating chunks of crystalline triiron dodecacarbonyl. The product is removed by filtration and washed with copious water, methanol, and finally, hexane. The solid is dried under a reduced pressure and exposure to air is minimised.

The *title compound* was isolated as a dark green crystalline solid[c] (180 g, 66% yield).

DIIRON NONACARBONYL

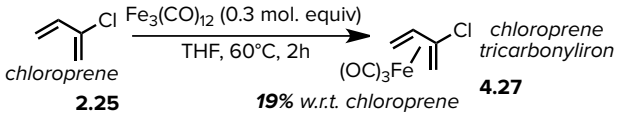


Diiron nonacarbonyl was prepared according to the method reported by Braye & Hübel.[503] Three cold-finger reaction apparatuses were prepared, with the tubing

[c] Larger crystals could be obtained by Soxhlet extraction with hexane. In the experience of this author that was unnecessary, unless one particularly wants to use a Soxhlet extraction apparatus.

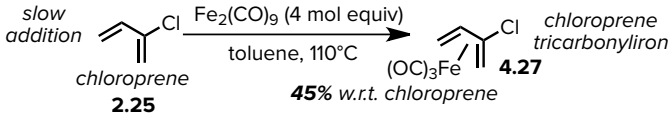
for the coolant connected in series and terminated at each end at a Julabo recirculating refrigeration unit set to –5°C. A solution of $Fe(CO)_5$ (134 mL, 1.0 mol, 1.0 mol equiv) in glacial acetic acid (266 mL) is prepared, and distributed equally between the cold-finger reaction apparatuses, each containing a magnetic stirring rod and under an atmosphere of nitrogen. The reaction vessels were then placed into an aluminium-foil lined bucket containing a magnetic stirrer and a 125W high-pressure mercury lamp. The reactions are irradiated for 12 h with constant stirring, cooling and steady flow of nitrogen (all are critical for safety). The orange crystalline product is then collected by filtration and washed with water, ethanol, and ether, and dried under reduced pressure with minimal exposure to air. In some rare cases material generated in this way was pyrophoric. Instructions for dealing with pyrophoric material were reported by Braye & Hübel.[503]
The *title compound* was isolated as a bright orange crystalline solid (48 g, 27% yield).

TRICARBONYL(2-CHLOROBUTADIENE)IRON ***4.27***



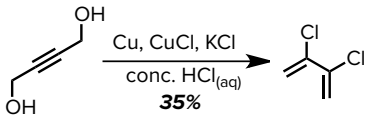
Tricarbonyliron-chloroprene was prepared according to the method reported by Brune and coworkers.[144,146] An oven dried round bottom flask fitted with reflux condenser was charged with triiron dodecacarbonyl (100g, 0.2 mol, 1.0 mol equiv), which was then covered with THF (200 mL) under an atmosphere of nitrogen. To the suspension was added chloroprene (53g, 0.6 mol, 3.0 mol equiv.) as a solution in THF (50 mL) over a period of 15 minutes. The reaction was then heated to 60°C for a period of 3 hours. The solvent was removed from the reaction mixture under reduced pressure and the crude oil purified by flash column chromatography (silica, hexane). The *title compound* was collected as a mixture with butadiene-tricarbonyliron, which was subsequently removed by fractional distillation under reduced pressure (b.p = 70 °C, 10 mbar).
The *title compound* was characterised as a yellow oil (21.1 g, 19% yield);
R_f 0.57 (hexane).
b.p = 70 °C (10 mbar);
^{1}H NMR (300 MHz; $CDCl_3$): δ 5.74 (dd, *J* = 8.4, 7.1 Hz, 1H), 2.27 (dd, *J* = 4.2, 1.5 Hz, 1H), 1.64 (dd, *J* = 7.0, 2.7 Hz, 1H), 0.59 (dd, *J* = 4.2, 0.9 Hz, 1H), -0.17 (dd, *J* = 8.6, 2.7 Hz, 1H).

^{1}H NMR spectroscopic data and physical data were in accordance with reported values.[144,145]



Tricarbonyliron-chloroprene was prepared according to a modification of the method reported by Yeh and coworkers.[146] An oven dried round bottom flask fitted with reflux condenser was charged with diiron nonacarbonyl (4.1 g, 11.3 mmol, 2.0 mol equiv.) and toluene (10 mL). The reaction mixture was heated to 110°C. Once at high temperature, a solution of chloroprene (0.50 g, 5.8 mmol, 1.0 mol equiv.) in toluene (2 mL) was added dropwise *via* syringe over a period of an hour. Once addition was complete another portion of diiron nonacarbonyl (4.1 g, 11.3 mmol, 2.0 mol equiv.) was added and the reaction heated for a further hour. The reaction mixture was allowed to cool, and the solvent was carefully removed under reduced pressure. The complex **4.27** was subsequently purified as above.
The *title compound* was isolated as a yellow oil (595 mg, 45% yield); Spectroscopic data were in accordance with reported values (*v.s.*).

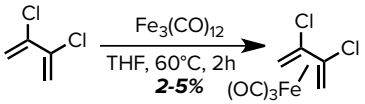
2,3-DICHLOROBUTADIENE **4.44**



2,3-Dichlorobutadiene was prepared according to the method of Stewart.[437] A multi-neck round bottom flask containing a large magnetic stirrer was charged with Cu (6g, 0.094 mol, 0.05 mol equiv.), CuCl (80g, 0.81 mol, 0.4 mol equiv.), KCl (40g, 0.42 mol, 0.2 mol equiv.), and BHT (0.8g, 3.6 mmol, 0.002 mol equiv.). To the solids was added concentrated HCl (36%, 350mL) and monobutyl diethylene glycol (butyl digol, 120 mL). The flask was fitted with a distillation head and non-equalising addition funnel and heated to 110°C under nitrogen. To the reaction mixture was added dropwise but-2-yn-1,4-diol **4.82** (172g, 2.0 mol, 1.0 mol equiv.) as a solution in concentrated HCl (36%, 170mL). While the diol **4.82** is being added the temperature of the reaction is raised to 130°C to induce 'steam' distillation of the product. The *title compound* is collected in the receiving flask as the organic phase of a biphasic mixture with concentrated HCl. The organic phase was found to be the more dense and was separated by decanting with a Pasteur pipette and neutralised and dried with anhydrous K_2CO_3. The crude organic

material was found to be mostly pure by ^{1}H NMR spectroscopy, but was further purified by fractional distillation at 50–54 °C (100 mbar). The *title compound* was isolated as a viscous, pungent, pale yellow oil (74.7 g, 35% yield);
b.p. = 50–54 °C (100 mbar).
^{1}H NMR (300 MHz; $CDCl_3$): δ 6.01 (d, J = 1.0 Hz, 2H), 5.61 (d, J = 1.0 Hz, 2H) ppm.
^{1}H NMR spectroscopic data and physical data were in accordance with reported values.[257,437]

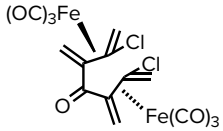
TRICARBONYL(2,3-DICHLOROBUTADIENE)IRON ***4.30***



Tricarbonyl(2,3-dichlorobutadiene)iron was prepared according to a slightly modified procedure of those reported by Brune *et al.*, & Nelson *et al.*[144,145] A nitrogen filled, oven dried round bottom flask fitted with reflux condenser was charged with triiron dodecacarbonyl (25 g, 0.05 mol, 1 mol equiv.) and covered with THF (80 mL). To the reaction vessel was added 2,3-dichlorobutadiene (24 g, 0.20 mol, 4 mol equiv.) as a solution in THF (20 mL) over 15 minutes. The reaction mixture was subsequently heated for 2 hours at 60 °C. The solvent was removed under reduced pressure and the residue dissolved in dichloromethane. The suspension was filtered through a plug of silica, eluting with dichloromethane, and solvent was removed under reduced pressure again. The residue was dissolved in 25:75 DCM/hexane and separated by flash column chromatography (silica, hexane). The first fraction (mixture containing spots R_f 0.7–0.8) was collected and ^{1}H NMR analysis indicated the presence of the *title compound* alongside complexes **1.87** & **4.27**. The *title compound* was separated from complex **1.87** *via* fraction distillation under reduced pressure (50 °C, 4.8 mbar). At the high temperatures employed in this distillation, complex **4.27** is selectively decomposed. The *title compound* was isolated as an orange-red oil (450 mg, 3% yield);
R_f 0.7 (hexane);
bp = 50 °C (4.8 mbar);
^{1}H NMR (300 MHz; $CDCl_3$): δ 2.20 (d, J = 4.1 Hz, 2H), 0.25 (d, J = 4.1 Hz, 2H) ppm.
The spectroscopic and physical data recorded above were in accordance with that reported in the literature.[144]

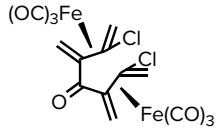
Further elution of the flash column containing complex 4.30 with 15→25% DCM/hexane afforded the compounds **4.117** & **4.118** shown below.

HEXACARBONYL(ANTI-(4′-6′)2,6-DICHLORO-3,5-DIMETHYLENEHEPTA-1,6-DIEN-4-ONE)DIIRON ***4.117***



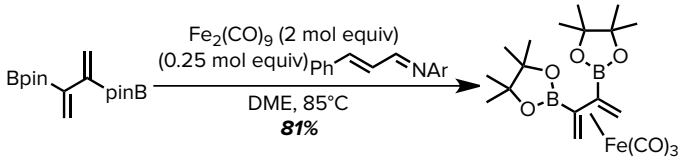
The *title compound* was isolated and further purified by recrystallisation (1:1 $CDCl_3$/hexane) as a yellow–orange crystalline solid (454 mg, 2% yield);
R_f 0.43 (25% CH_2Cl_2/hexane).
^{1}H NMR (300 MHz; CDCl3): δ 2.30 (app t, J = 3.9 Hz, 4H), 0.72 (d, J = 3.9 Hz, 2H), 0.15 (d, J = 3.0 Hz, 2H) ppm;
^{13}C NMR (75 MHz, $CDCl_3$): δ 208.9 (br C_q), 198.9 (C_q), 109.9 (C_q), 101.9 (C_q), 42.4 (CH_2), 39.1 (CH_2) ppm.
MS (EI): *m/z* (%): 481.8 ([*M*]$^{+\cdot}$, 1), 453.8 ([*M–CO*]$^{+\cdot}$, 2), 425.8 ([*M–2CO*]$^{+\cdot}$, 2), 396.8 ([*M–3CO*]$^{+\cdot}$, 42), 369.8 ([*M–4CO*]$^{+\cdot}$, 19), 341.8 ([*M–5CO*]$^{+\cdot}$, 22), 313.8 ([*M–6CO*]$^{+\cdot}$, 23), 187.9 (100), 55.9 ([*Fe*]$^{+\cdot}$, 29);
HRMS (EI): calculated for $C_{14}H_8Cl_2{}^{56}Fe_2O_6$ [*M–CO*]$^{+\cdot}$: 453.8397; found 453.8382.

HEXACARBONYL(SYN-(4′-6′)2,6-DICHLORO-3,5-DIMETHYLENEHEPTA-1,6-DIEN-4-ONE)DIIRON ***4.118***



The *title compound* was isolated and further purified by recrystallisation as a yellow crystalline solid (360 mg, 2% yield);
R_f 0.29 (25% CH_2Cl_2/hexane).
^{1}H NMR (300 MHz; $CDCl_3$): δ 2.32 (d, J = 4.2 Hz, 1H), 2.08 (d, J = 3.0 Hz, 1H), 0.71 (d, J = 4.2 Hz, 1H), 0.04 (d, J = 3.0 Hz, 1H) ppm.
^{1}H NMR spectroscopic data and physical data were in accordance with that reported in the literature.[145]

TRICARBONYL(2,3-BIS(PINACOLATOBORON)BUTADIENE)IRON ***4.92***



An oven dried, nitrogen filled round bottom flask was prepared containing 2,3-bis(pinacolatoboron)-1,3-butadiene[454] (217 mg, 0.71 mmol, 1 mol equiv.), diiron nonacarbonyl (516 mg, 1.4 mmol, 2 mol equiv.), and (*E*)-4-methoxy-*N*-((*E*)-3-phenylallylidene)aniline (42 mg, 0.18 mmol, 0.25 mol equiv.). The reaction mixture was protected from light with aluminium foil, and stirred for 4 h at 85 °C. The solvent was removed under reduced pressure and the resulting orange/brown solid was purified by flash column chromatography (eluting with pentane on silica gel) affording the *title compound* as a pale yellow crystalline solid (257 mg, 81% yield);

^{1}H NMR (300 MHz; $CDCl_3$): δ 1.97 (d, J = 1.5 Hz, 2H), 1.31 (s, 24H), 0.38 (d, J = 1.4 Hz, 2H) ppm;

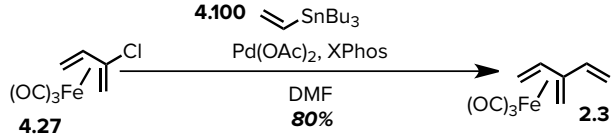
^{13}C NMR (75 MHz, $CDCl_3$): δ 211.4 (C_q), 84.4 (C_q), 46.1 (CH_2), 24.9 (C_q), 24.8 (CH_3) ppm.

IR (thin film): ν_{max} = 2986, 2043, 1967, 1142 cm^{-1};

MS (EI): *m/z* (%): 446.1 ([*M*]$^{+\cdot}$, 1), 390.1 (30), 362.1 (100), 279.1 (13);

HRMS (EI): calculated for $C_{19}H_{28}{}^{11}B_2FeO_7$ [*M*]$^{+\cdot}$: 446.1371; found 446.1367.

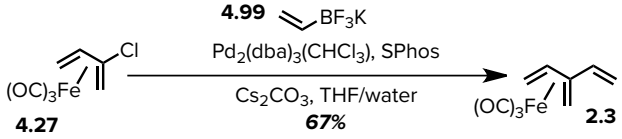
STILLE REACTION TOWARDS TRICARBONYLIRON[3]DENDRALENE ***2.3***



$Pd(OAc)_2$ (8 mg, 0.01 mmol, 0.05 mol equiv.), XPhos (8 mg, 0.02 mmol, 0.10 mol equiv.), chloroprene-tricarbonyliron (44 mg, 0.2 mmol, 1.0 mol equiv.), DMF (0.8 mL) and tributylstannyl ethylene (76 mg (70µL), 0.24 mmol, 1.2 mol equiv.) were combined in a one-piece refluxing apparatus. The reaction vessel was heated to 60°C under an atmosphere of nitrogen for 15 hours. The mixture was diluted with ether, and washed with copious water. The solution was dried with magnesium sulfate, filtered, and concentrated under reduced pressure. The *title compound* was purified by column chromatography (silica, hexane) and isolated as a yellow oil (35 mg, 80% yield);

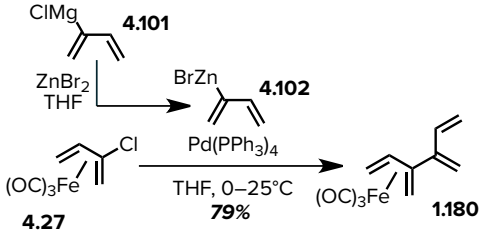
Spectroscopic data were in accordance with reported values, see page 157.

*SUZUKI–MIYAURA REACTION TOWARDS TRICARBONYLIRON[3]DENDRALENE **2.3***



$Pd_2(dba)_3$·$CHCl_3$ (6.5 mg, 0.02 mmol, 0.03 mol equiv.), SPhos (5 mg, 0.04 mmol, 0.06 mol equiv.), Cs_2CO_3 (214 mg, 0.6 mmol, 3 mol equiv.), chloroprene-tricarbonyliron (46 mg, 0.2 mmol, 1.0 mol equiv.), potassium ethylene-trifluoroborate (58 mg, 0.4 mmol, 2 mol equiv.), THF (0.9 mL), and deoxygenated water (0.1 mL) were combined in a microwave reactor vial. The reaction was then subjected to microwave irradiation in a microwave reactor apparatus (100 °C, 200 W) for 1 hour. The mixture was diluted with ether, and washed with brine and copious water. The solution was dried with magnesium sulfate, filtered, and concentrated under reduced pressure. The *title compound* was purified by column chromatography (silica, hexane) and was isolated as a yellow oil (40 mg, 67% yield);
Spectroscopic data were in accordance with reported values, see page 157.

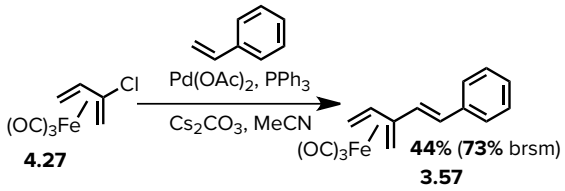
*NEGISHI REACTION TO FORM TERMINAL TRICARBONYLIRON[4]DENDRALENE **1.180***



To a stirred mixture of $ZnBr_2$ (1.13 M, 0.80 mL, 0.9 mmol, 1.5 mol equiv.) in THF (6 mL), Grignard reagent **4.101** (0.50 M, 1.44 mL, 0.72 mmol, 1.2 mol equiv.) was added dropwise at 0 °C to generate 2-zincobutadiene **4.102** *in situ*. The mixture was stirred for 20 min over which time it was allowed to warm to room temperature. To the solution, chloroprene complex **4.27** (140 mg, 0.6 mmol, 1.0 mol equiv.) was added, followed by $Pd(PPh_3)_4$ (35 mg, 0.03 mmol, 0.05 mol equiv.) and the solution allowed to stir at room temperature under nitrogen for 3 hours. At which point TLC indicated complete consumption of starting material, and reaction mixture was quenched by addition of water and the organic components were extracted with ether. The ethereal fractions were combined and dried with magnesium sulfate and filtered. The solvent was removed under

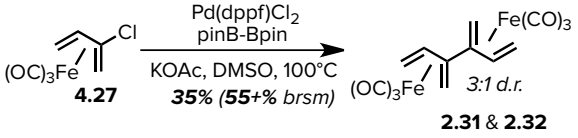
reduced pressure to afford the crude product. The product was purified by flash column chromatography (silica, hexane) to afford the *title compound* as a yellow oil (116 mg, 79% yield);
Spectroscopic data were in accordance with reported values, see page 168.

*MIZOROKI–HECK REACTION TO FORM 1E-PHENYL-[3]DENDRALENE **3.57***



$Pd(OAc)_2$ (9.5 mg, 0.02 mmol, 0.1 mol equiv.), PPh_3 (2.6 mg, 0.01 mmol, 0.05 mol equiv.), chloroprene-tricarbonyliron (48 mg, 0.2 mmol, 1.0 mol equiv.), acetonitrile (3 mL) were combined in a one-piece refluxing apparatus and stirred for 3 hours. To the reaction vessel was added styrene (83 mg (92µL), 0.8 mmol, 4 mol equiv.). The reaction was then heated to 60°C under an atmosphere of nitrogen for 1 hour. The mixture was diluted with CH_2Cl_2, and washed with copious water. The solution was dried with magnesium sulfate, filtered, and concentrated under reduced pressure. The *title compound* was purified by column chromatography (silica, hexane) and was isolated as a yellow oil (26 mg, 44% (73% brsm) yield);
Spectroscopic data were in accordance with reported values, see page 176.

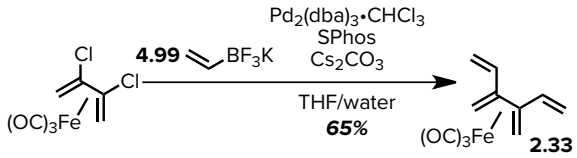
*SUZUKI–MIYAURA REACTION TO FORM BISTRICARBONYLIRON [4]DENDRALENE COMPLEXES **2.31** & **2.32***



$PdCl_2$(dppf) (9.5 mg, 0.02 mmol, 0.1 mol equiv.), chloroprene-tricarbonyliron (92 mg, 0.4 mmol, 1.0 mol equiv.), KOAc (118 mg, 1.2 mmol, 3.0 mmol), bis(pinacolatoboron) (51 mg, 0.2 mmol, 0.5 mol equiv.), dioxane (2 mL) were combined in a one-piece refluxing apparatus under nitrogen. The reaction was then heated to 105 °C overnight. The mixture was diluted with CH_2Cl_2, and washed with copious water. The solution was dried with magnesium sulfate, filtered, and concentrated under reduced pressure. The *title compounds* were purified by column chromatography (silica, hexane) and were isolated as a yellow

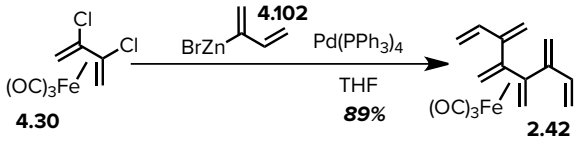
solid (27 mg, 35% (55% brsm) yield, 3:1 d.r.);
Spectroscopic data were in accordance with reported values, see pages 159 & 160.

*NEGISHI REACTION TO FORM INTERNAL TRICARBONYLIRON[4]DENDRALENE **2.33***



$Pd_2(dba)_3$•$CHCl_3$ (3 mg, 0.03 mmol, 0.03 mol equiv.), SPhos (5 mg, 0.06 mmol, 0.06 mol equiv.), Cs_2CO_3 (214 mg, 0.66 mmol, 3 mol equiv.), 2,3-dichloro-1,3-butadiene-tricarbonyliron (29 mg, 0.11 mmol, 1.0 mol equiv.), potassium ethylene-trifluoroborate (59 mg, 0.44 mmol, 4 mol equiv.), THF (0.9 mL), and deoxygenated water (0.1 mL) were combined in a microwave reactor vial. The reaction was then subjected to microwave irradiation in a microwave reactor apparatus (100 °C, 200 W) for 1 hour. The mixture was diluted with ether, and washed with brine and copious water. The solution was dried with magnesium sulfate, filtered, and concentrated under reduced pressure. The *title compound* was purified by column chromatography (silica, hexane) and was isolated as a yellow oil (18 mg, 65% yield);
Spectroscopic data were in accordance with reported values, see page 161.

*TRICARBONYLIRON(4:6)-[6]DENDRALENE **2.42***

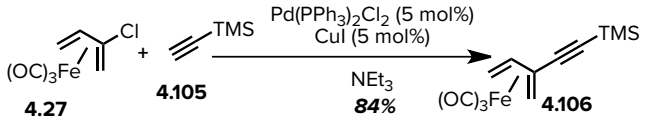


To a stirred mixture of $ZnBr_2$ (1.13 M, 0.29 mL, 0.33 mmol, 3.0 mol equiv.) in THF (2.5 mL), Grignard reagent **4.101** (0.50 M, 0.52 mL, 0.26 mmol, 2.4 mol equiv.) was added dropwise at 0°C to generate 2-zincobutadiene **4.102** *in situ*. The mixture was stirred for 20 min over which time it was allowed to warm to room temperature. To the solution, dichloride **4.30** (28.5 mg, 0.11 mmol, 1.0 mol equiv.) was added, followed by $Pd(PPh_3)_4$ (12.7 mg, 0.011 mmol, 0.1 mol equiv.) and the solution allowed to stir at room temperature under nitrogen for 3.5 hours. At which point TLC indicated complete consumption of starting material, and reaction mixture was quenched by addition of water and the organic components were extracted with ether. The ethereal fractions were combined and dried with magnesium sulfate and filtered. The solvent was removed under reduced pressure

to afford the crude product. The product was purified by flash column chromatography (silica, hexane) to afford the *title compound* as a yellow oil (29 mg, 89% yield);
R_f 0.33 (hexane).
^{1}H NMR (800 MHz; $CDCl_3$): δ 6.47 (ddd, *J* = 17.4, 10.7, 0.7 Hz, 1H), 5.44 (t, *J* = 0.6 Hz, 1H), 5.33 (dt, *J* = 17.4, 0.5 Hz, 1H), 5.27 (t, *J* = 1.1 Hz, 1H), 5.13 (dd, *J* = 10.7, 0.6 Hz, 1H), 1.75 (d, *J* = 2.4 Hz, 1H), 0.39 (d, *J* = 2.4 Hz, 1H) ppm;
^{13}C NMR (201 MHz; CDCl3): δ 210.9, 143.4, 139.0, 122.0, 116.5, 106.9, 39.8 ppm.
MS (EI): *m/z* (%): 298.0 ($[M]^{+\cdot}$, 1), 270.0 ($[M–CO]^{+\cdot}$, 2), 242.0 ($[M–2CO]^{+\cdot}$, 63), 214.0 ($[M–3CO]^{+\cdot}$, 100), 55.9 (41).

5.4.2 Extension to Other Cross-Conjugated Systems

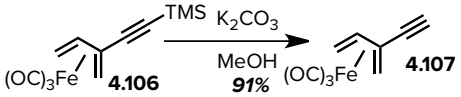
*TRICARBONYL(TRIMETHYL(3-METHYLENEPENT-4-EN-1-YN-1-YL)SILANE) IRON **4.106***



Chloroprene-tricarbonyliron (47 mg, 0.2 mmol, 1.0 mol equiv.) was dissolved in triethylamine (2 mL) in a one-piece apparatus comprising a round-bottom flask and a condenser under nitrogen. To the reaction mixture were added $PdCl_2(PPh_3)_2$ (10 mg, 0.01 mmol, 0.05 mol equiv.) and cuprous iodide (3 mg, 0.01 mmol, 0.05 mol equiv.), successively. The reaction was stirred for five minutes, then trimethylsilyl acetylene was added *via* syringe (29 μL, 0.24 mol, 1.2 mol equiv.). The reaction was stirred at 45°C for 3 hours. The reaction was quenched with water and the organic components extracted with ether. The ethereal fractions were combined and dried with magnesium sulfate and filtered. The solvent was removed under reduced pressure to afford the crude product as a brown oil. The crude product was dissolved in hexane and purified by flash column chromatography (silica, hexane). The *title compound* was characterised as a yellow oil (49 mg, 84% yield);
R_f 0.50 (hexane).
^{1}H NMR (400 MHz, $CDCl_3$): *δ* 5.68-5.64 (m, 1H), 2.03 (s, 1H), 1.76 (dd, *J* = 6.7, 2.4 Hz, 1H), 0.30 (d, *J* = 2.4 Hz, 1H), 0.21 (s, 9H), 0.17 (d, *J* = 2.4 Hz, 1H) ppm;
^{13}C NMR (100 MHz, $CDCl_3$): *δ* 210.3 (q), 104.0 (q), 91.4 (q), 89.7 (CH), 84.3 (q), 43.7 (CH_2), 39.5 (CH_2), –0.1 (CH_3) ppm.
IR (thin film): ν_{max} = 2962, 2164, 2055, 1977, 1251 cm^{-1}

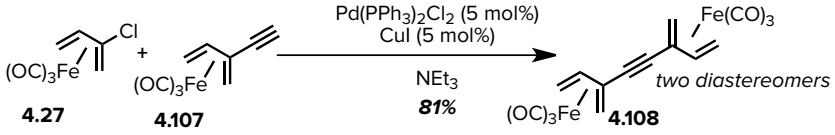
MS (EI): *m/z* (%): 290.0 ([*M*]$^{+\cdot}$, 3), 262.0 (15), 234.0 (31), 206.0 (100), 135.1 (26);
HRMS (EI): calculated for $C_{12}H_{14}FeO_3Si$ [*M*]$^{+\cdot}$: 290.0062; found 290.0076.

TRICARBONYL(3-METHYLENEPENT-1-EN-4-YNE)IRON ***4.107***



K_2CO_3 (25.4 mg, 0.183 mmol, 2.0 mol equiv.) was added to a solution of compound **4.106** (26.6 mg, 0.092 mmol, 1.0 mol equiv.) dissolved in methanol (0.5 mL). The suspension was allowed to stir for 30 minutes. The mixture was quenched by addition of sat. aq. ammonium chloride and the organic components were thrice extracted from the aqueous layer with ether. The combined organic layers were dried with magnesium sulfate, filtered, and concentrated under reduced pressure. The *title compound* was purified by filtration through a silica plug (hexane) characterised as a pale yellow oil (16 mg, 91% yield);
R_f 0.50 (hexane).
^{1}H NMR (800 MHz; $CDCl_3$): δ 5.73-5.71 (m, 1H), 2.76 (s, 1H), 2.05 (dd, *J* = 2.7, 1.4 Hz, 1H), 1.80 (dd, *J* = 7.0, 2.7 Hz, 1H), 0.34 (dd, *J* = 2.7, 1.0 Hz, 1H), 0.22 (dd, *J* = 9.3, 2.7 Hz, 1H) ppm;
^{13}C NMR (201 MHz; CDCl3): δ 209.9 (C_q), 90.2 (CH), 83.1 (C_q), 82.7 (C_q), 74.0 (CH), 43.3 (CH_2), 39.5 (CH_2) ppm.
MS (EI): *m/z* (%): 218.0 ([*M*]$^{+\cdot}$, 38), 216.1 (100);
HRMS (EI): calculated for $C_9H_6FeO_3$ [*M*]$^{+\cdot}$: 217.9666; found 217.9668.

HEXACARBONYL(3,6-DIMETHYLENEOCTA-1,7-DIEN-4-YNE)DIIRON ***4.108***



Chloroprene-tricarbonyliron (38 mg, 0.17 mmol, 1.0 mol equiv.) was dissolved in triethylamine (2 mL) in a one-piece apparatus comprising a round-bottom flask and a condenser under nitrogen. To the reaction mixture were added $PdCl_2(PPh_3)_2$ (9 mg, 0.01 mmol, 0.05 mol equiv.) and cuprous iodide (3 mg, 0.01 mmol, 0.05 mol equiv.), successively. The reaction was stirred for five minutes, then complex **4.107** (37 mg, 0.17 mol, 1 mol equiv.). The reaction was stirred at 45°C for 5 hours. The reaction was quenched with water and the organic components extracted with ether. The ethereal fractions were combined and dried with magnesium sulfate

and filtered. The solvent was removed under reduced pressure to afford the crude product as a brown oil. The crude product was dissolved in hexane and purified by flash column chromatography (silica, hexane). The *title compound* was characterised as the major diastereomer, a yellow crystalline solid (56 mg, 81% yield);

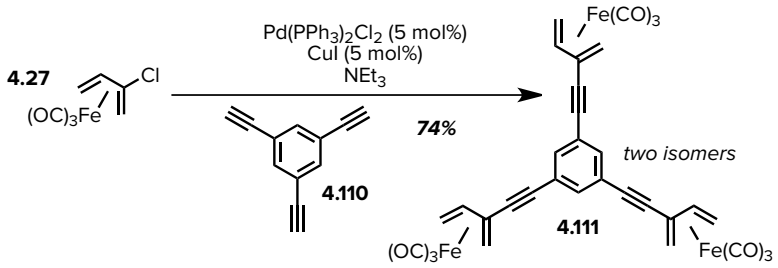
^{1}H NMR (800 MHz; $CDCl_3$): δ 5.74 (ddd, *J* = 9.3, 7.0, 1.2 Hz, 1H), 2.09 (ddd, *J* = 4.2, 2.7, 1.4 Hz, 1H), 1.84 (dt, *J* = 7.0, 2.5 Hz, 1H), 0.40-0.39 (m, 1H), 0.28 (dt, *J* = 9.3, 3.0 Hz, 1H);

^{13}C NMR (201 MHz; CDCl3): δ 209.9 (C_q), 89.9 (CH), 85.0 (C_q), 83.6 (C_q), 43.3 (CH_2), 39.7 (CH_2) ppm.

MS (EI): *m/z* (%): 409.9 ($[M]^{+\cdot}$, 7), 353.9 (80), 325.9 (85), 269.9 (100), 55.0 (33);

HRMS (EI): calculated for $C_{16}H_{10}Fe_2O_6$ $[M]^{+\cdot}$: 409.9176; found 409.9178.

NONACARBONYL(1,3,5-TRIS(3-METHYLENEPENT-4-EN-1-YN-1-YL)BENZENE)TRIIRON ***4.111***



Chloroprene-tricarbonyliron (151 mg, 0.66 mmol, 3.3 mol equiv.) was dissolved in triethylamine (4 mL) in a round-bottom flask with a condenser under nitrogen. To the reaction mixture were added $PdCl_2(PPh_3)_2$ (21 mg, 0.03 mmol, 0.15 mol equiv.) and cuprous iodide (6 mg, 0.03 mmol, 0.15 mol equiv.), successively. The reaction was stirred for five minutes, then 1,3,5-trisacetylenylbenzene was added (30 mg, 0.2 mol, 1. mol equiv.). The reaction was stirred at 45°C for 1 hour. The reaction was quenched with water and the organic components were extracted with ether. The ethereal fractions were combined and dried with magnesium sulfate and filtered. The solvent was removed under reduced pressure to afford the crude product as a dark red oil. The crude product was dissolved in hexane and purified by flash column chromatography (silica, 20% DCM/hexane). The *title compound* was characterised as the major (presumably *syn,anti*) isomer, which was a yellow solid (107 mg, 74% yield);

R_f = 0.35 (20% DCM/hexane).

^{1}H NMR (800 MHz; $CDCl_3$): δ 7.58-7.58 (m, 1H), 5.79-5.76 (m, 1H), 2.13 (dt, *J* = 2.6, 1.3 Hz, 1H), 1.88-1.87 (m, 1H), 0.43 (dt, *J* = 2.5, 1.2 Hz, 1H), 0.32 (ddt, *J* = 9.3, 2.5,

1.2 Hz, 1H) ppm;
^{13}C NMR (201 MHz; CDCl3): δ 210.0 (C_q), 134.6 (CH), 123.4 (C_q), 89.9 (CH), 89.8 (C_q), 83.9 (C_q), 83.7 (C_q), 43.1 (CH_2), 39.8 (CH_2) ppm.
MS (EI): *m/z* (%): 697.9 ([*M–CO*]$^{+\cdot}$, 2), 669.9 ([*M–2CO*]$^{+\cdot}$, 6), 641.9 ([*M–3CO*]$^{+\cdot}$, 7), 613.9 ([*M–4CO*]$^{+\cdot}$, 6), 585.9 ([*M–5CO*]$^{+\cdot}$, 8), 557.9 ([*M–6CO*]$^{+\cdot}$, 3), 529.9 ([*M–7CO*]$^{+\cdot}$, 12), 501.9 ([*M–8CO*]$^{+\cdot}$, 6), 473.9 ([*M–9CO*]$^{+\cdot}$, 13), 269.1 (100);
HRMS (EI): calculated for $C_{33}H_{18}{}^{56}Fe_3O_9$ [*M*]$^{+\cdot}$: 725.8999; found 725.9006.

Appendix

X-Ray Crystallographic Data

X-ray crystallography reports for compounds **1.180**, **2.31**, **2.32**, **2.33**, **2.39**, **2.40**, **2.72**, **3.57**, **3.58**, **3.59**, **4.92**, **4.117**, & **4.118** are provided on the DVD on the inside back cover of this thesis. Single crystal X-ray analyses were performed by Dr. Anthony Willis.

Computational Data

Density functional computation reports for the results reported in Chapter 2 are provided on the DVD on the inside back cover of this thesis. DFT calculations were performed by Prof. Michael Paddon-Row using the Gaussian 03 program.[§]

§ Gaussian 03, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

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Publications

Toombs-Ruane, H. *et al.* Synthesis and Applications of Tricarbonyliron Complexes of Dendralenes. *Chem. Asian J.* **6**, 3243–3250 (**2011**) - Reproduced by permission of *John Wiley & Sons*.[504] Pages 213–220.

Toombs-Ruane, H., Pearson, E. L., Paddon-Row, M. N. & Sherburn, M. S. On the Diels-Alder dimerisation of cross-conjugated trienes. *Chem. Commun.* **48**, 6639–6641 (**2012**) - Reproduced by permission of *The Royal Society of Chemistry*.[297] Pages 221–223.

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Synthesis and Applications of Tricarbonyliron Complexes of Dendralenes

Henry Toombs-Ruane,[a] Nik Osinski,[a] Thomas Fallon,[a] Cindy Wills,[a] Anthony C. Willis,[a] Michael N. Paddon-Row,*[b] and Michael S. Sherburn*[a]

Abstract: [3]Dendralene and [4]dendralene are converted smoothly into tricarbonyliron complexes. The structures of four complexes analyzed by DFT and single-crystal X-ray analysis show that, in contrast to free hydrocarbons, complexed dendralenes prefer a roughly in-plane conformation. The complexes are stable towards $Fe(CO)_3$ group migration up to 150 °C. The synthetic value of $Fe(CO)_3$ complexation in the dendralene series is demonstrated through a variety of selective synthetic manipulations (Diels–Alder reaction, dipolar cycloaddition, Simmons–Smith cyclopropanation, dihydroxylation, olefin cross metathesis) that are not achievable by direct transformation of the free hydrocarbons. Application to the synthesis of a previously unreported, highly reactive linear/cross-conjugated hydrocarbon is also described.

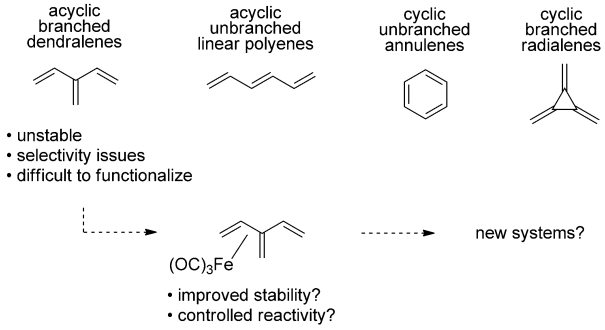
Keywords: dendralenes · density functional calculations · hydrocarbons · metathesis · synthesis design

Introduction

Dendralenes are a neglected, yet fundamental, class of acyclic branched oligoalkenes.[1] A short time ago, we discovered that the physical and chemical properties of the dendralenes alternate with the number of alkene subunits in the molecule; behavior that was traced by DFT calculations to an alternation in the conformational preferences in even and odd dendralenes.[2] The result of this alternating pattern is dramatic: when stored neat at ambient temperatures, the even dendralenes are unchanged over months, whereas the odd dendralenes have half-lives in the order of hours.

The parent [3]-, [4]-, and [5]dendralenes can be used directly to create complex structures with natural-product-like complexity in one step through cascades of pericyclic reactions.[3–5] Despite the enormous potential of such sequences, applications in synthesis are very limited.[1–5] We have identified three problems inhibiting the application of dendralenes in synthesis: 1) odd members of the family are difficult to handle due to their inherent instability;[2,5] 2) there is a severe shortage of methods for dendralenes synthesis;[1] and 3) most cascade processes involving dendralenes are insufficiently selective.[3–5]

Herein, we introduce a method that addresses these shortfalls by way of the η^4-(1,3-butadiene)tricarbonyliron complexes[6] of the hydrocarbons (Scheme 1). Specifically, we



Scheme 1. Proposed strategy to overcome the stability/reactivity issues of dendralenes with [3]dendralene as an example.

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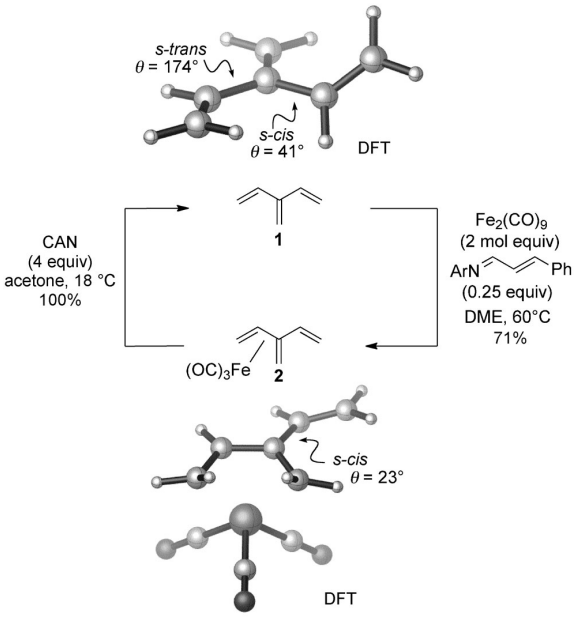
show that these readily prepared compounds 1) attenuate the reactivity of the more reactive members of the family; 2) enhance the synthetic potential of the dendralenes by allowing reaction outcomes that cannot be achieved directly from the parent hydrocarbons; and 3) allow the rapid synthesis of new dendralenes and related, unprecedented structures.

Results and Discussion

The complexation of unstable dienes by the $Fe(CO)_3$ group to generate stable complexes is well established.[6–8] Nevertheless, the preparation and reactions of metal complexes of dendralenes has been poorly investigated,[9–11] with only one early study describing direct complexation of a dendralene.[9] We found that the tricarbonyliron complex of [3]dendralene **2** could be readily prepared in good yield on a multigram scale through an azabutadiene-catalyzed[12] reaction of $Fe_2(CO)_9$ with the parent hydrocarbon **1** (Scheme 2).

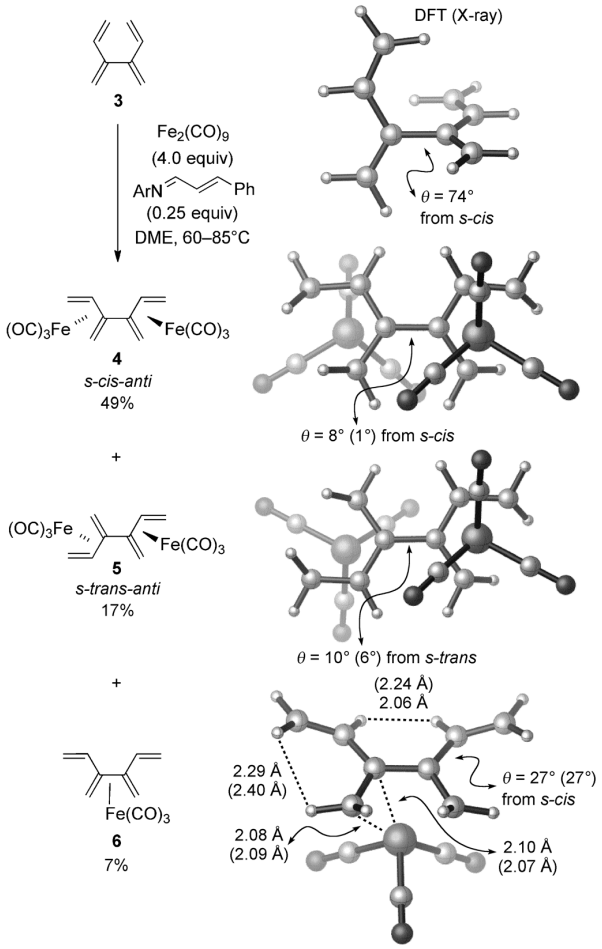


Scheme 2. Complexation and decomplexation of [3]dendralene **1** and the calculated lowest energy conformations of the hydrocarbon and the $Fe(CO)_3$ complex. Ar = 4-methoxyphenyl, DME = 1,2-dimethoxyethane.

As expected, the complex was stable at ambient temperatures and pressures and could be handled in air and light under usual laboratory conditions. Unlike the hydrocarbon, it exhibited no tendency to dimerize. Furthermore, it could be converted into the hydrocarbon in quantitative yield in seconds on exposure to ceric ammonium nitrate (CAN) in acetone.

DFT calculations[13,7] predict that the *cisoid* conformation for the tricarbonyliron complex is about 4 kJ mol^{-1} more stable than the corresponding *transoid* one. This is interesting because the *transoid* conformation is favored for the free [3]dendralene (Scheme 2). We suspect that the preference for the *s-cisoid* conformation in the complex results from the geometry about the terminal methylene carbon atoms of the complexed 1,3-butadiene unit: pyramidalization on complexation with iron causes the methylene hydrogen atoms to move out of the plane, thereby reducing the destabilizing inner H/H clash.

Under exhaustive complexation conditions, [4]dendralene **3** gives a mixture of bis(tricarbonyliron) complexes **4** and **5** and the internal mono(tricarbonyliron) complex **6**, with the chiral, C_2-symmetric form of the bis(tricarbonyliron) complex **4** predominating over the *meso*-diastereomer **5** (Scheme 3).[14] This site selectivity is similar to that wit-



Scheme 3. Complexation of [4]dendralene and calculated structures of the products. Ar = 4-methoxyphenyl. Molecular structures from single-crystal X-ray analysis and DFT-calculated minimum-energy structures of complexes are very similar throughout. Selected parameters from theory and experiment (in brackets) are included.

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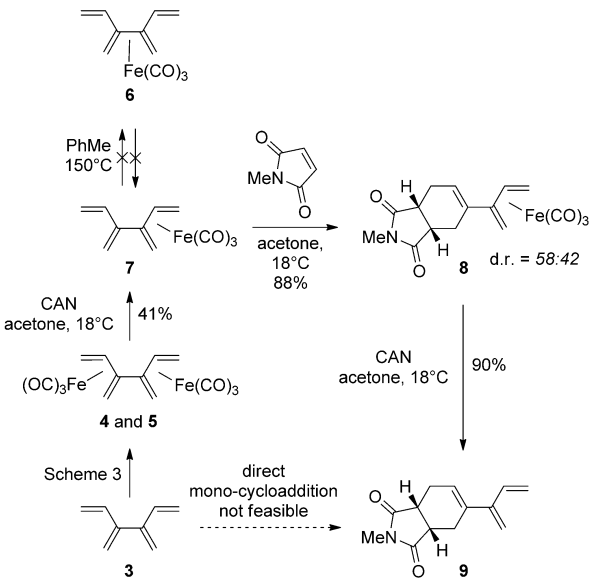
nessed in uncatalyzed Diels–Alder reactions of [4]dendralene.[4] The higher [*n*]dendralenes also deliver complexes under similar conditions.[15]

Molecular structures from single-crystal X-ray analyses of the three complexes were obtained,[16] and lowest energy structures were calculated by DFT.[13] There is a good match between each X-ray crystal structure and the corresponding DFT-optimized minimum-energy structure;[13] a result that adds weight to the premise that the conformations witnessed in the crystals are not dictated by packing forces. Whereas free [4]dendralene **3** prefers a conformation containing two *s-trans*-1,3-butadiene groups in a roughly orthogonal arrangement, all three complexes contain a [4]dendralene ligand adopting a roughly in-plane conformation.

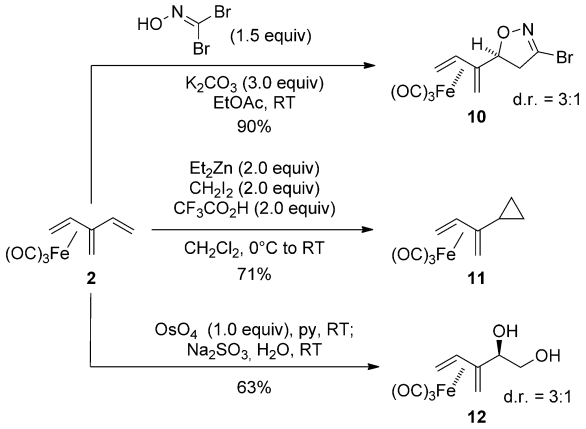
Evidently, for these complexes to be of use in synthesis, their integrity under standard reaction conditions must be maintained. Tricarbonyliron complexes of both acyclic and cyclic linear conjugated polyenes are known to exhibit fluxional behavior, with the tricarbonyliron group readily undergoing migration along a polyene chain.[17] Intriguingly, migration does not occur in the unsubstituted dendralene series, as evidenced by the lack of interconversion witnessed between the two regioisomeric mono(tricarbonyliron) complexes of [4]dendralene, **6** and **7**, on heating solutions in toluene at 150 °C (Scheme 4). The preparation of a structure



Scheme 4. Lack of fluxional behavior in complexes of dendralenes and access to structures that are inaccessible directly from dendralenes.

that is not accessible by direct transformation of [4]dendralene **3** is also depicted in Scheme 4. Thus, free [4]dendralene **3** undergoes a double cycloaddition reaction with dienophiles: the second cycloaddition event is significantly faster than the first, so that the intermediate monoadduct **9** is not isolable, even if substoichiometric amounts of dienophiles are employed.[2,4] Monoadduct **9** is readily accessed, however, through the tricarbonyliron complex **7** in a simple, high yielding sequence that involves decomplexation of one tricarbonyliron group (**4/5**→**7**), cycloaddition (**7**→**8**), and decomplexation (**8**→**9**).

The tricarbonyliron complex of [3]dendralene **2** undergoes smooth cycloaddition reactions[18] at the uncomplexed terminal alkene group, thereby leading to complexes of functionalized 1,3-butadienes **10**, **11**, and **12** (Scheme 5). Attempts to react free [3]dendralene **1** with stoichiometric amounts of cyclopropanating agents[19] or dipoles invariably led to the formation of complex mixtures.



Scheme 5. Cycloaddition reactions with the tricarbonyliron complex of [3]dendralene. py = pyridine.

Mixtures of diastereomers (3:1) were produced in the 1,3-dipolar cycloaddition reactions of bromonitrile oxide[20] and OsO_4 with [3]dendralene–$Fe(CO)_3$ complex **2**. While it has not been possible to identify the major isomer experimentally, insights have been gained through calculations. Figure 1 depicts the DFT transition-state structures (TSs) leading to the two observed adducts. The TS leading to major adduct **10** involves the near in-plane, *s-cis* conformation of the dendralene with the dipole approaching from the uncomplexed face of the substrate. The TS for the minor adduct is 5.0 kJ mol^{-1} less stable than that leading to the major adduct and results from addition to the uncomplexed face of the [3]dendralene–$Fe(CO)_3$ molecule adopting the *s-trans* conformation. Regioisomeric TSs, involving approach of the dipole oxygen at the methylene terminus, were significantly (at least 9.6 kJ mol^{-1}) higher in energy.

Despite our best efforts, we have been unable to achieve successful metathesis reactions with naked [3]dendralene.[21] In contrast, the tricarbonyliron complex of [3]dendralene **2** undergoes smooth cross-metathesis reactions with a range of alkene partners with either the Grubbs second-generation precatalyst[22] or, more conveniently,[23] the Hoveyda–Grubbs second-generation precatalyst[24] to form substituted products **13** with an *E*-alkene geometry (Scheme 6). The last ex-

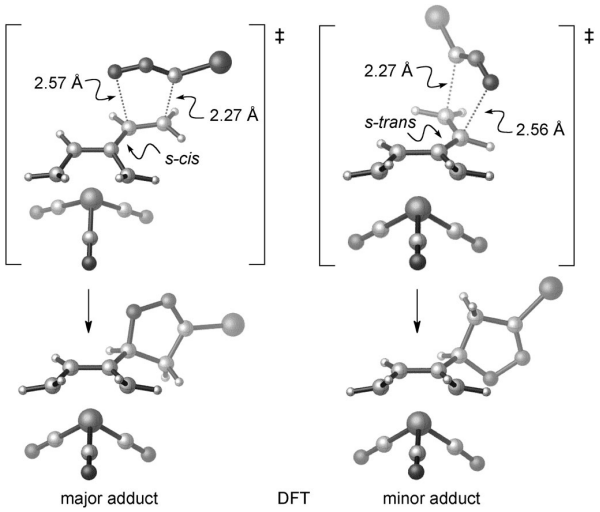
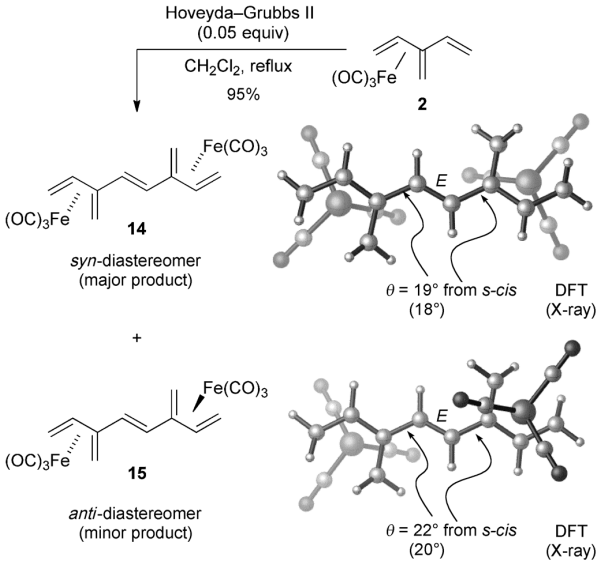
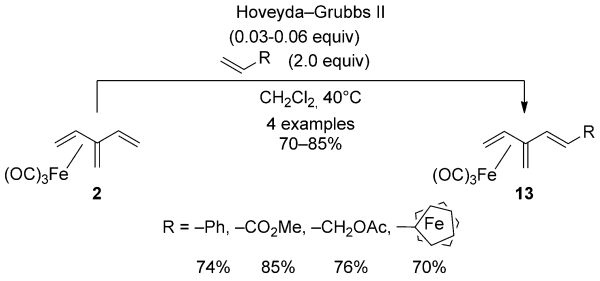


Figure 1. Calculated diastereomeric TSs and products from the 1,3-dipolar cycloaddition reaction of bromonitrile oxide with [3]dendralene–$Fe(CO)_3$ complex **2**.



Scheme 7. Self-metathesis of [3]dendralene–$Fe(CO)_3$ complex **2**. DFT-calculated structures are also shown.



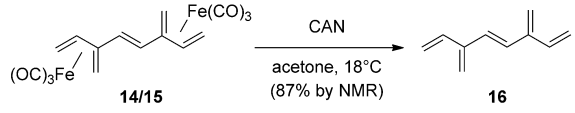
Scheme 6. Synthesis of substituted [3]dendralene–$Fe(CO)_3$ complexes through cross metathesis.

ample demonstrates an application of this method in the synthesis of a ferrocene-containing cross-conjugated system; applications of such structures in electronics devices have been suggested.[25]

The self-metathesis reaction of the tricarbonyliron complex of [3]dendralene **2** leads to an excellent yield of diastereomeric products **14** and **15** (ca. 2:1 ratio), from which the *E,s-cis,s-cis,syn* bis(tricarbonyliron) complex **14** is the major isomer, as demonstrated by single-crystal X-ray analysis (Scheme 7).[16] Once again, the DFT-optimized structure[13] (gas phase) correlates well with that seen in the crystal structure of the major isomer. The conformational preference of the ligand in structures **14** and **15**, with the uncomplexed alkene *s-cis* to the complexed diene, is consistent with that seen previously for the tricarbonyliron complex of [3]dendralene **2** (Scheme 2).

Whereas *syn* isomer **14** is favored experimentally, DFT calculations show that the *anti* diastereomer is the more stable structure to the extent that the equilibrium distribution is 68:32 in favor of *anti* diastereomer **15** and its conformers. Thus, the metathesis reaction does not appear to be under thermodynamic control. Experimentally, we see no change upon exposure of either **14** or **15** to conditions significantly more forcing than those employed in the self-metathesis reaction (up to 0.50 equivalents of Hoveyda–Grubbs second-generation precatalyst, $CDCl_3$, 67 °C, 6 h). This result is consistent with self-metathesis products **14** and **15** being type IV olefins and spectators in cross-metathesis reactions.[26]

Finally, upon oxidative decomplexation with CAN, 2,6-di(methylene)-1,4,7-octatriene **16**, one of the simplest acyclic structures with both linear conjugation and cross conjugation, is formed (Scheme 8). This reactive new hydrocarbon exhibits UV absorption maxima characteristic of both a linear conjugated diene and triene (λ_{max} = 220 and 267 cm^{-1}).



Scheme 8. Decomplexation yields a new fundamental hydrocarbon.

Conclusion

Tricarbonyliron complexes of dendralenes were readily prepared as stable analogues of dendralenes. These iron complexes greatly expand the synthetic potential of dendralenes by permitting transformations that cannot be achieved by direct reaction of the hydrocarbons.

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Experimental Section

General Methods

^{1}H NMR spectra were recorded under standard conditions at 800, 600, 500, 400, and 300 MHz by using Bruker AVANCE 800, Bruker AVANCE 600, a Varian Unity INOVA 500, Varian MR400, or Varian Mercury 300 spectrometers, respectively. Residual chloroform (δ = 7.26 ppm) was used as an internal reference for ^{1}H NMR spectra measured in $CDCl_3$. Coupling constants (J) are quoted to the nearest 0.1 Hz. ^{13}C NMR spectra were recorded at 200, 150, 125, 100, or 75 MHz by using Bruker AVANCE 800, Bruker AVANCE 600, a Varian Unity INOVA 500, Varian MR400, or Varian Mercury 300 spectrometers, respectively. $CDCl_3$ (δ = 77.1 ppm) was used as an internal reference for ^{13}C NMR spectra recorded in this solvent. Assignment of carbon signals was assisted by DEPT or HSQC experiments. IR spectra were recorded on a Perkin–Elmer 1600 FTIR spectrometer as neat films on NaCl plates for oils or as KBr discs for solid products. Low-resolution mass spectra were recorded on a Finnigan Polaris Q ion-trap mass spectrometer using electron impact (EI+) ionization mode at 40 or 70 eV. High-resolution mass spectra were recorded on a VG Autospec mass spectrometer operating at 70 eV. Melting points were measured on a Reichert melting point stage and are uncorrected. Analytical high-performance liquid chromatography (HPLC) was performed by using a Shimadzu Prominence LC-20AD chromatograph pump and SIL-20A autosampler on an Alltima Silica 5 μm column (250 mm, 4.6 mm ID). Preparative HPLC was performed by using a Waters 600E instrument on Altima silica 5 μm (250 mm, 22 mm ID), Altima silica 5 μm (250 mm, 10 mm ID), or Waters silica 5 μm (150 mm, 19 mm ID) columns. Analytical TLC was performed with Merck silica gel plates, precoated with silica gel 60 F254 (0.2 mm). Flash chromatography employed Merck Kieselgel 60 (230–400 mesh) silica gel. UV/Vis spectra were recorded by using a Shimadzu UV-Visible 2450 spectrometer.

Reactions were conducted under a positive pressure of dry argon or nitrogen in oven-dried glassware. Solvents were dried by using a solvent purification system based on that described by Pangborn and co-workers,[27] dried over sodium wire, and distilled from sodium benzophenone ketyl, or dried by using standard methods. Petrol refers to b.p. 40–60 °C petroleum spirits unless otherwise stated. Commercially available chemicals were purified by standard procedures[28] or used as purchased.

*(η^4-3-Methylene-1,4-pentadiene)tricarbonyliron (**2**)*

$Fe_2(CO)_9$ (2.7249 g, 7.5 mmol, 2.0 equiv) and (*E*)-1-(4-methoxyphenyl)-4-phenyl-1-aza-1,3-butadiene[29] (222 mg, 0.94 mmol, 0.25 equiv) were added to a stirred solution of **1**[3] (300 mg, 3.75 mmol, 1.0 equiv) in distilled DME (15 mL). The reaction mixture was protected from light with aluminum foil and stirred for 4 h at 60 °C. The solvent was removed under reduced pressure and the resulting orange/brown solid was purified by flash column chromatography (eluting with pentane on silica gel) to afford **2** as a yellow oil (529 mg, 71 %). R_f = 0.7 (pentane); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.52 (dd, J = 9.2, 10.2 Hz, 1 H), 5.57 (d, J = 17.1 Hz, 1 H), 5.44 (t, J = 8.1 Hz, 1 H), 5.15 (d, J = 10.5 Hz, 1 H), 2.19 (dd, J = 2.4 Hz, 1.5 Hz, 1 H), 1.80 (dd, J = 6.9, 2.4 Hz, 1 H), 0.32 (dd, J = 9.3, 2.4 Hz, 1 H), 0.15 ppm (d, J = 2.7 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 211.1 (q), 137.2 (CH), 114.6 (CH_2), 101.0 (q), 85.7 (CH), 39.8 (CH_2), 37.5 ppm (CH_2); IR (thin film): $\tilde{\nu}_{max}$ = 3012, 2049, 1970 cm^{-1}; MS (EI): *m*/*z* (%): 220 (18) $[M]^+$, 192 (35) $[M-CO]^+$, 164 (36) $[M-2CO]^+$, 136 (100) $[M-3CO]^+$, 55.9 (51) $[Fe]^+$; HRMS (EI): *m*/*z* calcd for $C_9H_8FeO_3$ $[M]^+$: 219.9823; found: 219.9828.

*[3]Dendralene (**1**)*

A solution of CAN (20.0 mg, 0.037 mmol, 2.0 equiv) in [D$_6$]acetone (0.5 mL) was added dropwise at room temperature to a stirred solution of **2** (4.0 mg, 0.018 mmol, 1.0 equiv) in [D$_6$]acetone (0.5 mL). Anisole (2.0 mg, 0.018 mmol, 1.0 equiv) was used as an internal standard for this transformation. The progress of the reaction was rapid and followed by ^{1}H NMR spectroscopy. Compound **1** was afforded as a solution in [D$_6$]acetone (1.5 mg mL^{-1}, 100 %, as determined by NMR spectroscopy). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.45 (dd, J = 17.6, 10.5 Hz, 2 H), 5.41 (d, J = 17.6 Hz, 2 H), 5.15 ppm (t, J = 5.3 Hz, 4 H). Spectroscopic data were in accordance with reported values.[2]

Tricarbonyliron Complexation of [4]Dendralene

A 3.1 M solution of [4]dendralene[4] in THF (0.95 mL, 3.0 mmol, 1.0 mol equiv) was added to a stirred suspension of $Fe_2(CO)_9$ (4.43 g, 12.0 mmol, 4.0 mol equiv) and 1-(4-methoxyphenyl)-4-phenyl-1-aza-1,3-butadiene[29] (180 mg, 0.76 mmol, 0.25 mol equiv) in distilled DME (19 mL). The reaction mixture was protected from light with aluminum foil and stirred for 140 h at reflux. The reaction mixture was filtered through a plug of Celite and washed thoroughly with pentane. The filtrate and washings were concentrated under reduced pressure. Separation by flash column chromatography (eluting with pentane on silica gel) yielded a mixture of the two bisadducts **4** and **5** (726 mg, 63 %, 78:22 diastereomeric ratio (d.r.)) separate from the internal monoadduct **6** (51 mg, 7 %).

*Compound **4***

Compound **4** was obtained by normal-phase HPLC (silica 5 μm, 250 mm × 22 mm, eluting with hexane) and recrystallized from a mixture of pentane and dichloromethane at −20 °C to give yellow crystals. R_f = 0.55 (pentane); m.p. 98 °C (dichloromethane/pentane); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.68 (t, J = 8.1 Hz, 2 H), 2.47 (dd, J = 3.3, 1.5 Hz, 2 H), 1.89 (dd, J = 7.2, 2.4 Hz, 2 H), 0.41 (dd, J = 9.0, 2.4 Hz, 2 H), 0.25 ppm (d, J = 3.0 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 210.6 (q), 102.1 (q), 82.0 (CH), 40.1 (CH_2), 37.6 ppm (CH_2); IR (KBr disc): $\tilde{\nu}_{max}$ = 2922, 2041, 1989, 1954 cm^{-1}; MS (EI): *m*/*z* (%): 385.9 (7) $[M]^+$, 357.9 (15) $[C_{13}H_{10}Fe_2O_5]^+$, 329.9 (73) $[C_{12}H_{10}Fe_2O_4]^+$, 301.9 (31) $[C_{11}H_{10}Fe_2O_3]^+$, 273.9 (41) $[C_{10}H_{10}Fe_2O_2]^+$, 245.9 (91) $[C_9H_{10}Fe_2O]^+$, 217.9 (100) $[C_8H_{10}Fe_2]^+$, 162.0 (46) $[C_8H_{10}Fe]^+$, 55.9 (41) $[Fe]^+$; HRMS (EI): *m*/*z* calcd for $C_{14}H_{10}Fe_2O_6$ $[M]^+$: 385.9184; found: 385.9176.

*Compound **5***

Compound **5** was obtained as a yellow solid from normal-phase HPLC (silica 5 μm, 250 mm × 22 mm, eluting with hexane) and was recrystallized from cold pentane to give yellow crystals. R_f = 0.55 (pentane); m.p. 163 °C (pentane); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.07 (t, J = 7.8 Hz, 2 H), 2.16 (dd, J = 3.2, 1.5 Hz, 2 H), 1.93 (dd, J = 7.1, 2.4 Hz, 2 H), 0.40 (dd, J = 9.2, 2.4 Hz, 2 H), 0.18 ppm (d, J = 2.7 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 210.6 (q), 102.1 (q), 82.0 (CH), 40.1 (CH_2), 37.6 (CH_2); IR (KBr disc): $\tilde{\nu}_{max}$ = 3016, 2042, 1985, 1958 cm^{-1}; MS (EI): *m*/*z* (%): 385.9 (6) $[M]^+$, 357.9 (6) $[C_{13}H_{10}Fe_2O_5]^+$, 329.9 (87) $[C_{12}H_{10}Fe_2O_4]^+$, 301.9 (47) $[C_{11}H_{10}Fe_2O_3]^+$, 273.9 (49) $[C_{10}H_{10}Fe_2O_2]^+$, 246 (49) $[C_9H_{10}Fe_2O]^+$, 218.0 (95) $[C_8H_{10}Fe_2]^+$, 162.0 (50) $[C_8H_{10}Fe]^+$, 55.9 (15) $[Fe]^+$; HRMS (EI): *m*/*z* calcd for $C_{14}H_{10}Fe_2O_6$ $[M]^+$: 385.9180; found: 385.9176.

*Compound **6***

Compound **6** was recrystallized from pentane at −40 °C to give yellow crystals, which melted at room temperature to give a yellow oil (51 mg, 7 %). R_f = 0.65 (pentane); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.99 (dd, J = 16.8, 10.5 Hz, 2 H), 5.59 (dd, J = 16.8, 1.2 Hz, 2 H), 5.26 (dd, J = 10.5, 1.2 Hz, 2 H), 2.15 (d, J = 2.4 Hz, 2 H), 0.13 ppm (d, J = 2.7 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 210.7 (q), 133.7 (CH), 117.2 (CH_2) 99.5 (q), 37.6 (CH_2) ppm; IR (thin film): $\tilde{\nu}_{max}$ = 2932, 2050, 1974 cm^{-1}; MS (EI): *m*/*z* (%): 246.0 (29) $[M]^+$, 218.0 (40) $[C_{10}H_{10}FeO_2]^+$, 190.0 (54) $[C_9H_{10}FeO]^+$, 162.0 (100) $[C_8H_{10}Fe]^+$, 55.9 (61) $[Fe]^+$; HRMS (EI): *m*/*z* calcd for $C_{11}H_{10}FeO_3$ $[M]^+$: 245.9979; found: 245.9979.

*Compound **7***

A mixture of **4** and **5** (266.5 mg, 0.69 mmol, 1 equiv) was dissolved in acetone (5 mL) and was cooled on an ice bath. A solution of CAN (757.2 mg, 1.38 mmol, 2.0 equiv) in dry acetone (10 mL) was added dropwise to the mixture of the tricarbonyliron complexes of [4]dendralene. After addition was completed in 30 min, the reaction mixture was stirred for another 30 min. The mixture was quenched by the addition of a saturated solution of $NaHCO_3$ (20 mL). The resulting pale orange suspension was filtered and extracted with dichloromethane (3 × 25 mL). The combined organic layers were washed with brine, dried over anhydrous

$MgSO_4$, and concentrated under reduced pressure. The mixture was purified by flash column chromatography (eluting with hexane on silica gel) to give **7** as a yellow oil (69.5 mg, 41%). R_f=0.65 (hexane); ^{1}H NMR (300 MHz, $CDCl_3$): δ=6.51 (dd, J=17.1, 10.8 Hz, 1H), 5.65 (dd, J=17.1 Hz, 1.5 Hz, 1H), 5.44–5.37 (m, 3H), 5.27 (dd, J=10.8, 1.2 Hz, 1H), 2.10 (d, J=1.5 Hz, 1H), 1.80 (dd, J=7.1, 2.4 Hz, 1H), 0.29 (dd, J=9.3, 2.4 Hz, 1H), 0.20 ppm (d, J=1.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=211.0 (q), 145.2 (q), 135.7 (CH), 117.8 (CH_2), 115.2 (CH_2), 103.0 (q), 85.4 (CH), 39.6 (CH_2), 39.3 ppm (CH_2); IR (thin film): $\tilde{\nu}_{max}$=3092, 2051, 1995 cm^{-1}; MS (EI): m/z (%): 246.0 (6) $[M]^+$, 218.0 (27) $[C_{10}H_{10}FeO_2]^+$, 190.0 (43) $[C_9H_{10}FeO]^+$, 162.0 (100) $[C_8H_{10}Fe]^+$, 55.9 (21) $[Fe]^+$; HRMS (EI): m/z calcd for $C_{11}H_{10}FeO_3$ $[M]^+$: 245.9979; found: 245.9982.

Compound ***8***

N-Methylmaleimide (NMM) (15.0 mg, 0.107 mmol, 1.0 equiv) and **7** (26.3 mg, 0.107 mmol, 1 equiv) were dissolved in [D$_6$]acetone (0.5 mL) in a round-bottomed flask at ambient temperature and immediately transferred to an NMR tube to monitor the progress of the reaction by ^{1}H NMR spectroscopy. The solvent was subsequently removed under reduced pressure and the resulting yellow/brown solid was purified by flash column chromatography (eluting with 10–20% ethyl acetate/hexane on silica gel) to afford **8** as a pale yellow solid mixture of diastereomers (25.9 mg, 88%, 58:42 d.r.; characterized as the major diastereomer). R_f= 0.42 (20% ethyl acetate/hexanes); m.p. 52–54 °C ($CDCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ=6.19–6.16 (m, 1H), 5.40 (t, J=9.3 Hz, 1H), 3.25–3.15 (m, 2H), 2.99 (s, 3H), 2.96 (dd, J=5.7, 3.0 Hz, 1H), 2.76–2.69 (m, 1H), 2.39–2.33 (m, 2H), 2.02 (t, J=2.0 Hz, 1H), 1.83 (dd, J=7.3, 2.5 Hz, 1H), 0.30 (dd, J=9.3, 1.9 Hz, 1H), 0.08 ppm (t, J=1.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=210.9 (q), 179.7 (q), 179.6 (q), 138.3 (CH), 125.3 (CH), 102.2 (q), 82.5 (q), 40.3 (CH), 40.0 (CH), 40.0 (CH_2), 39.1 (CH_2), 25.5 (CH_2), 25.1 (CH_2), 24.8 ppm (CH_3); IR (thin film): $\tilde{\nu}_{max}$=2920, 2850, 2048, 1972, 1777, 1699, 1435 cm^{-1}; MS (EI): m/z (%): 357.0 (1) $[M]^+$, 329.0 (1) $[M-CO]^+$, 301.0 (38) $[M-2CO]^+$, 273.0 (100) $[M-3CO]^+$, 55.9 (13) $[Fe]^+$; HRMS (EI): m/z calcd for $C_{16}H_{15}FeNO_5$ $[M]^+$: 357.0300; found: 357.0308.

Compound ***9***

A solution of CAN (117.3 mg, 0.214 mmol, 2.0 equiv) in [D$_6$]acetone (1 mL) was added dropwise to a mixture of the diastereomers of **8** (40.3 mg, 0.113 mmol, 1.0 equiv) in acetone (0.5 mL) and then stirred under nitrogen for 30 min. The reaction was quenched by adding a saturated solution of $NaHCO_3$ (2 mL). The resulting orange suspension was extracted with CH_2Cl_2 (3×5 mL), washed with brine, dried over $MgSO_4$, and the solvent removed under a reduced pressure (40 mbar, 0 °C) to give a colorless oil, which was purified by flash column chromatography to give **9** as a colorless oil (eluting with 20% ethyl acetate/hexanes on silica gel) (22.0 mg, 90%). R_f=0.12 (20% ethyl acetate/hexanes); ^{1}H NMR (800 MHz, [D$_6$]benzene): δ=6.22 (ddd, J=17.4, 10.7, 0.6 Hz, 1H), 5.68–5.66 (m, 1H), 5.15 (dd, J=17.3, 1.6 Hz, 1H), 5.00 (s, 1H), 4.98 (s, 1H), 4.95 (dd, J=10.7, 1.3 Hz, 1H), 2.72, (dd, J=15.2, 2.9 Hz, 1H), 2.58 (s, 3H), 2.47 (ddd, J=15.6, 6.7, 2.9 Hz, 1H) 2.32 (ddd, J=9.7, 7.2, 2.9 Hz, 1H), 2.36 (ddd, J=10.0, 7.6, 2.8 Hz, 1H), 1.84–1.80 (m, 1H), 1.71–1.67 ppm (m, 1H); ^{13}C NMR (200 MHz, [D$_6$]benzene): δ=179.0 (q), 178.7 (q), 147.4 (q), 138.7 (q), 137.0 (CH), 124.7 (CH), 116.4 (CH_2), 113.5 (CH_2), 39.7 (CH), 39.0 (CH), 26.4 (CH_2), 24.5 (CH_3), 24.5 ppm (CH_2); IR (thin film): $\tilde{\nu}_{max}$=2918, 2849, 1776, 1697, 1435 cm^{-1}; MS (EI): m/z (%): 217.1 (100) $[M]^+$, 132.1 (24) $[M-C_3H_3O_2N]^+$, 117.1 (44), 112.1 (42), 91.1 (43); HRMS (EI): m/z calcd for $C_{13}H_{15}NO_2$ $[M]^+$: 217.1103; found: 217.1104.

Compound ***10***

Compound **2** (22.0 mg, 0.1 mmol, 1.0 equiv) was dissolved in ethyl acetate (1 mL) and $KHCO_3$ (30.0 mg, 0.30 mmol, 3.0 equiv) was added in one portion to the rapidly stirred solution. Dibromoformaldoxime (30.2 mg, 0.15 mmol, 1.5 equiv) was added to the stirring mixture. The reaction was then stirred under nitrogen at room temperature and the progress of the reaction was monitored by TLC. After 16 h, the reaction mixture was partitioned with CH_2Cl_2 and a saturated solution of ammonium chloride. The aqueous layer was then extracted with CH_2Cl_2. The combined organic layers were washed with brine and dried with $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (eluting with 5% ethyl acetate/hexane on silica gel) to give **10** as a yellow oil (30.6 mg, 90%, 3:1 d.r.; characterized as the major diastereomer). R_f=0.25 (5% ethyl acetate/hexane); ^{1}H NMR (800 MHz, $CDCl_3$): δ=5.46 (dd, J=8.3, 7.0 Hz, 1H), 5.16 (dd, J=11.0, 8.3 Hz, 1H), 3.60 (dd, J=17.5, 11.1 Hz, 1H), 3.28 (dd, J=17.3, 9.3 Hz, 1H), 1.82 (dd, J=7.0, 2.2 Hz, 1H), 1.75 (dd, J=3.0, 1.4 Hz, 1H), 0.21 (dd, J=9.2, 2.2 Hz, 1H), 5.46 ppm (dd, J=3.1, 0.9 Hz, 1H); ^{13}C NMR (200 MHz, $CDCl_3$): δ=210.3 (q), 136.7 (q), 102.4 (q), 83.0 (CH), 82.4 (CH), 48.5 (CH_2), 39.1 (CH_2), 37.8 ppm (CH_2); IR (KBr Disc): $\tilde{\nu}_{max}$= 2927, 2052, 1990, 1978, 1962, 609 cm^{-1}; MS (EI): m/z (%): 342.9 (1) $[M]^+$, 340.9 (1) $[M]^+$, 312.9 (11) $[M-CO]^+$, 284.9 (10) $[M-2CO]^+$, 256.9 (2) $[M-3CO]^+$, 178 (100), 138 (57), 55.9 (20) $[Fe]^+$; HRMS (EI): m/z calcd for $C_{10}H_8FeNO_4$ $[M]^+$: 342.8966; found: 342.8997.

Compound ***11***

A solution of diethylzinc (1.0 M in hexane, 420 μL, 0.420 mmol, 2.0 equiv) was added by syringe to a dry round-bottomed flask containing CH_2Cl_2 (370 μL) at 0 °C. Trifluoroacetic acid (TFA; 32 μL, 0.42 mmol, 2.0 equiv; distilled from 0.05 equiv trifluoroacetic anhydride) was added dropwise by syringe to this solution over 20 min, followed by the addition of diiodomethane (46 μL, 0.42 mmol, 2.0 equiv; dried over $CaCl_2$ and distilled from copper powder) by syringe over 20 min. A solution of **2** (46 mg, 0.209 mmol, 1.0 equiv) in CH_2Cl_2 (300 μL) was prepared in a dry, nitrogen-filled, round-bottomed flask and freeze–thaw degassed under nitrogen and stirred at 0 °C. This solution of tricarbonyliron[3]dendralene was added to the diethylzinc/TFA/diiodomethane-containing reaction mixture by cannula and the reaction was allowed to warm to room temperature with stirring; a precipitate formed over the course of the reaction. The reaction mixture was quenched after 2 h by the addition of a saturated solution of ammonium chloride (2 mL). The aqueous layer was extracted with CH_2Cl_2 and the combined organic solution was washed with water, followed by brine, then dried over $MgSO_4$, and filtered before being concentrated under reduced pressure to give the crude product as a pale yellow oil. The crude material was purified by flash column chromatography (eluting with pentane on silica gel) to give **11** as a pale yellow oil (34.5 mg, 71%). R_f=0.7 (pentane); ^{1}H NMR (400 MHz, $CDCl_3$): δ=5.26 (t, J=7.3 Hz, 1H), 1.75–1.68 (m, 2H), 1.65 (dd, J=4.4, 2.3 Hz, 1H), 0.98–0.91 (m, 1H), 0.87–0.80 (m, 1H), 0.76–0.69 (m, 1H), 0.65–0.59 (m, 1H), 0.06 (dd, J=6.4, 2.4 Hz, 1H), 0.03) ppm (d, J=2 Hz, 1H; ^{13}C NMR (100 MHz, $CDCl_3$): δ=211.4 (q), 110.5 (q), 82.2 (CH), 38.2 (CH_2), 37.6 (CH_2), 16.2 (CH), 10.6 (CH_2), 6.9 ppm (CH_2); IR (thin film): $\tilde{\nu}_{max}$=3008, 2922, 2046, 1965 cm^{-1}; MS (EI): m/z (%): 234 (22) $[M]^+$, 206 (60) $[M-CO]^+$, 178 (69) $[M-2CO]^+$, 150 (59) $[M-3CO]^+$, 148 (100) $[M-C_3H_2O_3]^+$, 55.9 (52) $[Fe]^+$; HRMS (EI): m/z calcd for $C_{10}H_{10}FeO_3$ $[M]^+$: 233.9979; found: 233.9980.

Compound ***12***

Anhydrous pyridine (538 μL) was added to a round-bottomed flask containing tricarbonyliron[3]dendralene (44.0 mg, 0.20 mmol, 1.0 equiv) and the reaction was subsequently stirred at room temperature. OsO_4 in anhydrous pyridine (0.39 M, 514 μL, 0.21 mmol, 1.0 equiv) was added dropwise by syringe to the stirred reaction solution. The reaction mixture was quenched after 1 h by the addition of a saturated solution of sodium metabisulfite (8 mL). The aqueous mixture was extracted twice with CH_2Cl_2 and the combined organic solution was washed twice with water and dried over $MgSO_4$ and filtered before being concentrated under reduced pressure. The crude yellow solid was purified by flash column chromatography (eluting with 1:39:60 isopropanol/ethyl acetate/hexane on silica gel) to give **12** as a pale yellow crystalline solid (32 mg, 63%, 3:1 d.r.; characterized as the major diastereomer). R_f=0.40 (40% ethyl acetate/hexanes); m.p. 85–86.5 °C (chloroform/hexane); ^{1}H NMR (800 MHz, $CDCl_3$): δ=5.61 (t, J=8.1 Hz, 1H), 4.13 (d, J=5.6 Hz, 1H), 3.96, (d, J=11.1 Hz, 1H), 3.81–3.78 (m, 1H), 2.39 (s, 1H), 2.22 (s, 1H), 1.79–1.78 (m, 2H), 0.23 (d, J=2.0 Hz, 1H), 0.20 ppm (dd, J=9.4, 2.0 Hz, 1H); ^{13}C NMR (200 MHz, $CDCl_3$): δ=210.9 (q), 105.6 (q), 81.1 (CH), 74.6 (CH), 68.5 (CH_2) 40.2 (CH_2), 38.6 ppm (CH_2); IR (KBr disc): $\tilde{\nu}_{max}$=

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2917, 2046, 1984, 1960, 1099, 1063 cm^{-1}; MS (EI): *m/z* (%): 226.0 (14) $[M-CO]^+$, 198.0 (65) $[M-2CO]^+$, 170.0 (58) $[M-3CO]^+$, 80.1 (100) $[M-C_4H_2O_4]^+$, 55.9 (22) $[Fe]^+$; HRMS (EI): *m/z* calcd for $C_9H_{10}FeO_5$ $[M]^+$: 253.9878; found: 253.9866.

Compound ***13a***

A solution of **2** (20.0 mg, 0.091 mmol, 1.0 equiv) and styrene (18.9 mg, 0.182 mmol, 2.0 equiv) in CH_2Cl_2 (1 mL) was added by cannula to a one-piece refluxing round-bottomed flask containing Hoveyda–Grubbs second-generation catalyst (3.9 mg, 0.005 mmol, 0.05 equiv). The resulting mixture was then heated to reflux with stirring under nitrogen for 16 h. The solvent was subsequently removed under reduced pressure and the resulting brown solid was purified by flash column chromatography (eluting with hexane on silica gel) to afford **13a** as a yellow oil (20.3 mg, 74%). R_f=0.21 (5% CH_2Cl_2/pentane); ^{1}H NMR (300 MHz, $CDCl_3$): δ= 7.48–7.28 (m, 5H), 7.92 (s, 2H), 5.54 (t, J=7.8 Hz, 1H), 2.33 (s, 1H), 1.86 (dd, J=6.9, 2 Hz, 1H), 0.40 (dd, J=9.3, 2 Hz, 1H), 0.23 ppm (d, J=2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=210.9 (q), 136.3 (q), 129.2 (CH), 128.7 (CH), 128.5 (CH), 128.1 (CH), 126.7 (CH), 101.2 (q), 85.7 (CH), 39.9 (CH_2), 37.4 ppm (CH_2); IR (thin film): $\tilde{\nu}_{max}$=3029, 2045, 1965, 1496, 959 cm^{-1}; MS (EI): *m/z* (%): 296.0 (12) $[M]^+$, 268.0 (46) $[M-CO]^+$, 240.0 (62) $[M-2CO]^+$, 212.1 (100) $[M-3CO]^+$, 55.9 (44) $[Fe]^+$; HRMS (EI): *m/z* calcd for $C_{15}H_{12}FeO_3$ $[M]^+$: 296.0136; found: 296.0135.

Compound ***13b***

A solution of **2** (24.2 mg, 0.110 mmol, 1.0 mol equiv) and methyl acrylate (17.4 mg, 0.182 mmol, 2.0 mol equiv) in CH_2Cl_2 (1 mL) was added by cannula to a one-piece refluxing round-bottomed flask containing Grubbs second-generation catalyst (3.9 mg, 0.005 mmol, 0.05 equiv). The resulting mixture was then heated to reflux with stirring under nitrogen for 16 h. The solvent was subsequently removed under reduced pressure and the resulting brown solid was purified by flash column chromatography (eluting with 20% CH_2Cl_2/pentane on silica gel) to afford **13b** as a yellow solid (25.9 mg, 85%). R_f=0.15 (20% CH_2Cl_2/hexane); m.p. 61–62 °C (chloroform/hexane); ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.53 (d, J= 15.4 Hz, 1H), 6.17 (d, J=15.3 Hz, 1H), 5.58 (dd, J=9.5, 7.3 Hz, 1H), 3.78 (s, 3H), 2.12 (dd, J=2.9, 1.5 Hz, 1H), 1.94 (dd, J=7.4, 2.2 Hz, 1H), 0.51 (dd, J=9.4, 3.0 Hz, 1H), 0.21 ppm (d, J=2.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=210.0 (q), 166.7 (q), 117.7 (CH), 95.3 (q), 89.5 (CH), 51.8 (CH_3), 41.7 (CH_2), 37.1 ppm (CH_2); IR (KBr disc): $\tilde{\nu}_{max}$= 2924, 2060, 1991, 1965, 1713, 1633, 1435 cm^{-1}; MS (EI): *m/z* (%): 278.0 (23) $[M]^+$, 250.0 (55) $[M-CO]^+$, 222.0 (69) $[M-2CO]^+$, 194.0 ($[M-3CO]^+$ 100), 55.9 (72) $[Fe]^+$; HRMS (EI): *m/z* calcd for $C_{10}H_{11}FeO_5$ $[M]^+$: 277.9878; found: 277.9881.

Compound ***13c***

A solution of **2** (50.0 mg, 0.223 mmol, 1.0 equiv) and *(Z)*-1,4-diacetoxy-but-2-ene (78.5 mg, 0.455 mmol, 2.0 mol equiv) in CH_2Cl_2 (1 mL) was added by cannula to a one-piece refluxing round-bottomed flask containing Grubbs second-generation catalyst (19.0 mg, 0.01 mmol, 0.1 equiv). The resulting mixture was then heated to reflux and stirred for 16 h. The solvent was subsequently removed under reduced pressure and the resulting brown solid was purified by flash column chromatography (eluting with 5% ethyl acetate/hexane on silica gel) to afford **13c** as a yellow oil (50.6 mg, 76%). R_f=0.36 (20% ethyl acetate/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$): δ=6.48 (d, J=15.4 Hz, 1H), 6.05–6.14 (m, 1H), 5.42 (t, J=8.1 Hz, 1H), 4.57–4.70 (m, 2H), 2.14 (d, J=3 Hz, 1H), 2.08 (s, 3H), 1.80 (dd, J=7.2, 2.2, 1H), 0.32 (dd, J=8.8, 2.2, 1H), 0.13 ppm (d, J=3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=210.7 (q), 170.7 (q), 133.9 (CH), 124.0 (CH), 99.4 (q), 85.9 (CH), 64.1 (CH_2), 39.9 (CH_2), 37.5 (CH_2), 20.9 ppm (CH_3); IR (thin film): $\tilde{\nu}_{max}$=3009, 2053, 1966, 1742, 1231 cm^{-1}; MS (EI): *m/z* (%): 292.0 (12)$[M]^+$, 264.0 (27) $[M-CO]^+$, 236.0 (81) $[M-2CO]^+$, 208.0 (94) $[M-3CO]^+$, 55.9 (80) $[Fe]^+$; HRMS (EI): *m/z* calcd for $C_{12}H_{12}FeO_5$ $[M]^+$: 292.0034; found: 292.0012.

Compound ***13d***

A solution of **2** (37.5 mg, 0.170 mmol, 1.0 equiv) and vinylferrocene (72.4 mg, 0.342 mmol, 2.0 equiv) in CH_2Cl_2 (1 mL) was added by cannula to a one-piece refluxing round-bottomed flask containing Hoveyda–Grubbs second-generation catalyst (5.0 mg, 0.008 mmol, 0.05 equiv). The resulting mixture was then heated to reflux and stirred for 16 h. The solvent was subsequently removed under reduced pressure and the resulting brown solid was purified by flash column chromatography (eluting with hexane on silica gel) to afford **13d** as a red powder (48.1 mg, 70%). R_f= 0.30 (hexane); m.p. 95–97 °C (hexane); ^{1}H NMR (800 MHz, $CDCl_3$): δ= 6.69 (d, J=15.9 Hz, 1H), 6.49 (d, J=15.6 Hz, 1H), 5.41 (t, J=7.8 Hz, 1H), 4.46 (s,1H), 4.36 (s, 1H), 4.28 (s, 2H), 4.11 (s, 5H), 2.30 (s, 1H), 1.80 (dd, J=6.8, 2.4 Hz, 1H), 0.35 (dd, J=6.2, 2.4 Hz, 1H), 0.18 ppm (d, J=2.5 Hz, 1H); ^{13}C NMR (200 MHz, $CDCl_3$): δ=211.1 (q), 128.2 (CH), 125.2 (CH), 102.6 (q), 84.5 (CH), 82.1 (q), 69.3 (CH), 69.2 (CH), 69.2 (CH), 68.1 (CH), 66.0 (CH), 39.5 (CH_2), 37.0 ppm (CH_2); IR (KBr disc): $\tilde{\nu}_{max}$=2037, 1967, 1951, 1632, 1473 cm^{-1}; MS (EI): *m/z* (%): 404.0 (32) $[M]^+$, 320 (100) $[M-3CO]^+$, 55.9 (19) $[Fe]^+$; HRMS (EI): *m/z* calcd for $C_{19}H_{16}Fe_2O_3$ $[M]^+$: 403.9798; found: 403.9793.

Homo-cross-metathesis of ***2***

A solution of **2** (177.8 mg, 0.808 mmol, 2.0 equiv) in CH_2Cl_2 (2 mL) was added by cannula to a one-piece refluxing round-bottomed flask containing Hoveyda–Grubbs second-generation catalyst (30.0 mg, 0.05 mmol, 0.06 equiv). The resulting mixture was then heated to reflux and stirred for 16 h. The solvent was then removed under reduced pressure and the resulting brown solid was passed through a plug of silica (eluting with pentane) to afford a mixture of compounds **14** and **15** as a yellow solid (159 mg, 95%, 64:36 d.r.).

Compound ***14***

Further purification to give an analytically pure sample of **14** was carried out on normal-phase HPLC (10 μm silica, 250×22 mm, eluting with hexane, retention time: 16.6 min) to give the major product **14** as a yellow crystalline solid. R_f=0.26 (hexane); m.p. 96–99 °C (hexane); ^{1}H NMR (300 MHz, $CDCl_3$): δ=6.74 (s, 2H), 5.48 (t, J=9.0 Hz, 2H), 2.19 (d, J=2.7 Hz, 2H), 1.83 (dd, J=7.0, 2.3 Hz, 2H), 0.36 (dd, J=9.4, 2.3 Hz, 2H), 0.18 ppm (d, J=2.7 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=210.5 (q), 130.0 (CH), 99.9 (q), 86.1 (CH), 40.0 (CH_2), 37.2 ppm (CH_2); IR (KBr disc): $\tilde{\nu}_{max}$=2926, 2046, 1973, 1962 cm^{-1}; MS (EI): *m/z* (%): 411.9 (6) $[M]^+$, 383.9 (4) $[M-CO]^+$, 355.9 (44) $[M-2CO]^+$, 327.9 (20) $[M-3CO]^+$, 299.9 (9) $[M-4CO]^+$, 271.9 (55) $[M-5CO]^+$, 244.0 (100) $[M-6CO]^+$, 55.9 (40) $[Fe]^+$; HRMS (EI): *m/z* calcd for $C_{16}H_{12}Fe_2O_6$ $[M]^+$: 411.9333; found: 411.9331.

Compound ***15***

Further purification to give an analytically pure sample of **15** was carried out on normal-phase HPLC (10 μm silica, 250×22 mm, eluting with hexane, retention time: 15.2 min) to give the minor product **15** as a yellow crystalline solid. R_f=0.29 (hexane); m.p. 181–183 °C (decomposition) (chloroform/toluene); ^{1}H NMR (300 MHz, $CDCl_3$): δ=6.71 (s, 2H), 5.50 (t, J=8.2 Hz, 2H), 2.22 (dd, J=2.3, 1.1 Hz, 2H), 1.83 (dd, J= 7.0, 2.3 Hz, 2H), 0.38 (dd, J=9.3, 2.9 Hz, 2H), 0.21 ppm (d, J=2.9 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=210.6 (q), 129.0 (CH), 99.6 (q), 85.8 (CH), 40.2 (CH_2), 37.9 ppm (CH_2); IR (KBr disc): $\tilde{\nu}_{max}$=2041, 1961, 1482, 980, 960 cm^{-1}; MS (EI): *m/z* (%): 411.9 (18) $[M]^+$, 383.9 ($[M-CO]^+$ 9), 355.9 (83) $[M-2CO]^+$, 327.9 (50) $[M-3CO]^+$, 299.9 (41) $[M-4CO]^+$, 271.9 (83) $[M-5CO]^+$, 244.0 (100) $[M-6CO]^+$, 55.9 (59) $[Fe]^+$; HRMS (EI): *m/z* calcd for $C_{16}H_{12}Fe_2O_6$ $[M]^+$: 411.9333; found: 411.9336.

Compound ***16***

A solution of CAN (115 mg, 0.210 mmol, 5.8 equiv) in dry [D_6]acetone (0.5 mL) was added dropwise to a mixture of **14** and **15** (14.9 mg, 0.036 mmol, 1.0 equiv) dissolved in [D_6]acetone (0.5 mL) and cooled on an ice bath. After addition was completed in 2 min, the reaction mixture was stirred for another 5 min; the end point was judged by loss of the starting material spot on TLC. The mixture was quenched by the addition of a saturated solution of $NaHCO_3$ (1 mL). The resulting pale orange suspension was extracted with [D_6]benzene (2 mL). The combined organic layers were washed with brine (1 mL) and filtered through a basic alumi-

na plug to give **16** as a yellow solution (acetone/benzene, ca. 1:3). The product could not be isolated in solvent-free form and aqueous workup resulted in significant loss of material. The yield of the transformation was determined to be 87% (±5%) by ^{1}H NMR spectroscopy, through an experiment conducted under the same conditions with durene added as an internal standard. ^{1}H NMR (800 MHz, 1:1 [D_6]acetone/[D_6]benzene calibrated against residual benzene): $\delta = 6.51$ (s, 2H), 6.38 (dd, $J = 17.4$, 10.8 Hz, 2H), 5.32 (d, $J = 17.4$ Hz, 2H), 5.07 (s, 2H), 5.05 (s, 2H), 5.00 ppm (d, $J = 10.9$ Hz, 2H); ^{13}C NMR (200 MHz, 1:1 [D_6]acetone/[D_6]benzene calibrated against residual benzene): $\delta = 145.3$ (q), 137.0 (CH), 130.4 (CH), 116.6 (CH_2), 116.5 ppm (CH_2); UV/Vis: $\lambda_{max} = 220$, 267 nm; MS (EI): *m*/*z* (%): 272.0 (10), 264.2 (1) $[2M]^+$, 244.0 (20), 132.1 (26) $[M]^+$, 117.1 (57) $[M-CH_3]^+$, 91.1 (70); HRMS (EI): *m*/*z* calcd for $C_{10}H_{12}$ $[M]^+$: 132.0939; found: 132.0939.

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On the Diels–Alder dimerisation of cross-conjugated trienes†

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The first general synthesis of 1-substituted [3]dendralenes has led to the discovery that conjugating groups significantly enhance the rate of Diels–Alder dimerisation relative to both the parent [3]dendralene and to other substituted systems.

Interest in the dendralene family of fundamental hydrocarbons (Fig. 1) is increasing,[1] a fact that is ascribable to the ease by which they can be elaborated into polycyclic systems through diene-transmissive Diels–Alder (DA) sequences.[2,3] Members of the [*n*]dendralene family higher than the triene **1** ($n = 3$) and tetra-ene **2** ($n = 4$) were reported for the first time only twelve years ago[4] and higher members of the series ($n = 5$–8) were made available in useful amounts only in 2009.[5] [3]Dendralene **1** is the most reactive of the parent hydrocarbons in Diels–Alder (DA) cycloadditions, both in reactions with the dienophile *N*-methylmaleimide and in DA dimerisations. In contrast, [4]dendralene **2** is the least reactive of the series of [*n*]dendralenes ($n = 3$–8).[5] The difference in stability between **1** and **2** is dramatic: whereas **2** can be stored neat at ambient temparature over extended periods without noticeable change, **1** has a half life of around 10 h under these conditions. This behaviour was explained through computational studies, which attributed the greater reactivity of **1** *versus* **2** to higher populations of reactive conformers and a more stable closed-shell singlet bis-pericyclic transition state for the DA dimerisation.[6]

Three sites for substitution are available about a [3]dendralene framework and previous reports have detailed the synthesis and properties of the 3′- and 2-substituted derivatives, **3** and **4** respectively (Fig. 1).[1,7,8] In both cases, substituted derivatives **3** and **4** were found to be considerably more stable than the parent hydrocarbon **1**. Herein we report a general synthetic approach to the remaining series, namely 1-substituted [3]dendralenes **5**. We report the unexpected observation that, in stark contrast to the behaviour of **3** and **4**, members of sub-class **5** are prone to rapid DA dimerisation *up to 200 times faster than parent triene* **1**. We define the structural requirements for this reactivity and we explain it, with the assistance of DFT calculations.

All published syntheses of 1-substituted [3]dendralenes involve reports of isolated examples.[9] Our plan for a more general 1-substituted [3]dendralene synthesis initially focussed on the direct formation of the 1,2-disubstituted C=C bond using Wittig reactions of the previously unreported phosphonium salt **6**[10] (Scheme 1). Surprisingly, reaction of the semi-stabilised ylide derived from **6** with benzaldehyde led to the generation of mixtures of four products: a *ca.* 1 : 2 ratio of 1*Z*-phenyl-[3]dendralene **7a** and cyclohexenes **9a**, **10a** and **11a**. Compounds **9a–11a** appear to be the DA dimers of the 1*E*-phenyl-[3]dendralene isomer **8a**, which would be an anticipated product since the Wittig reaction of semi-stabilised ylides is often poorly stereoselective.[11] Similar results to those depicted in Scheme 1 were obtained in Wittig reactions of phosphonium salt **6** with substituted benzaldehydes.

The isolation of DA dimers **9a–11a** was surprising in light of the mild temperature (*i.e.* room temperature) and relatively low concentrations (0.1 M) employed in these reactions.[10] Nevertheless, Mulzer and coworkers reported some time ago[12] that attempts to form 1*E*,5*E*-diphenyl-[3]dendralene (*i.e.* the 5*E*-phenyl analogue of **8a**) led to the isolation of the DA dimer[13] and, very recently, Singh and Ghosh[14] showed that attempts to form 2-carboethoxy-1,5-diaryl-[3]dendralenes also resulted in the isolation of DA dimers. Based on the result depicted in Scheme 1, it would appear that not two but

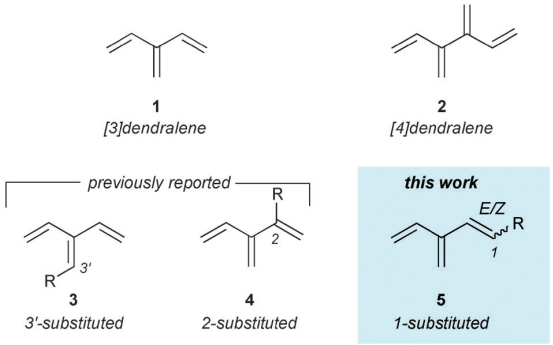

Fig. 1 The parent [3]- and [4]dendralenes and the possible monosubstituted trienes.

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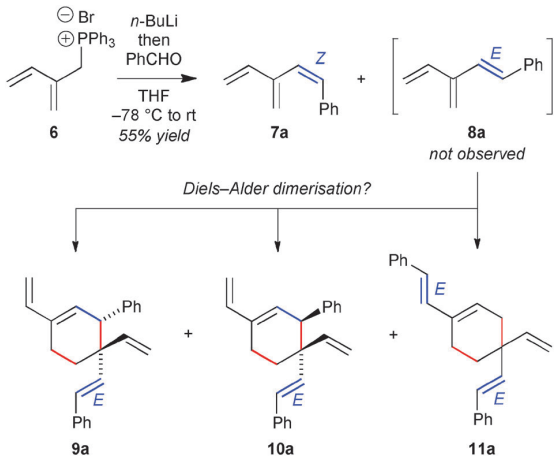
† Electronic supplementary information (ESI) available: experimental procedures and characterisation data, ^{1}H and ^{13}C NMR spectra of all new compounds and computational details. See DOI: 10.1039/c2cc32520a

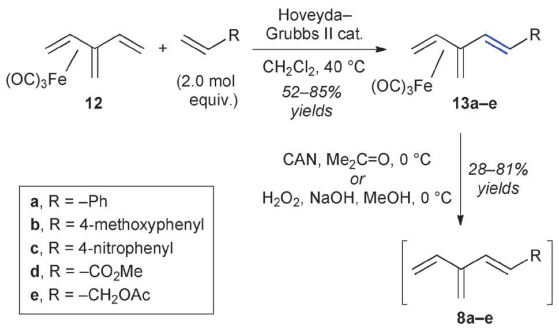


Scheme 1 Wittig approach to 1-substituted [3]dendralenes.

only one aromatic group is required to promote facile DA dimerisation of a [3]dendralene, so long as the group is located at the 1-position. Furthermore, within the mono-substituted dendralene series, we note that the facile DA dimerisation behaviour is *specific to the* 1*E*-*aryl*-[*3*]*dendralene isomer*: the 3′-phenyl-,[15] 2-phenyl-[8] and 1*Z*-phenyl-[3]dendralene congeners are stable towards dimerisation and can be stored neat at ambient temperature.

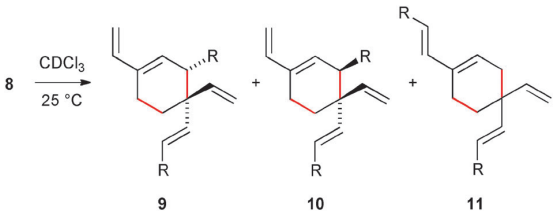
Both the intermediacy of 1*E*-phenyl-[3]dendralene **8a** and its rapid DA dimerisation are implied from the result depicted in Scheme 1. A synthetic approach that could provide an authentic sample of the triene would provide stronger evidence by allowing the direct observation of the dimerisation event. We recently demonstrated that **12**, the iron tricarbonyl complex of the parent [3]dendralene, undergoes cross metathesis with various olefins to gave stable, isolable complexes of 1*E*-substituted [3]dendralenes **13** (Scheme 2).[16] This work was extended to complexes **13a–e**, carrying aryl, alkyl and ester substituents. Gratifyingly, oxidative decomplexation[17] was sufficiently rapid at 0 °C to generate, after workup, $CDCl_3$ solutions of 1*E*-aryl, alkyl and carboethoxy-substituted [3]dendralenes **8a–e** that were free of DA dimerisation products and other contaminants, as shown by NMR spectroscopic analysis.[10]

As expected, trienes **8a–e** underwent DA dimerisation at ambient temperature to form three isomeric cycloadducts, namely **9–11**. As can be seen from the experimental half-life



Scheme 2 Optimised synthesis of 1*E*-substituted [3]dendralenes.

Table 1 Experimental half life measurements for DA dimerisation of 1*E*-substituted [3]dendralenes[a]

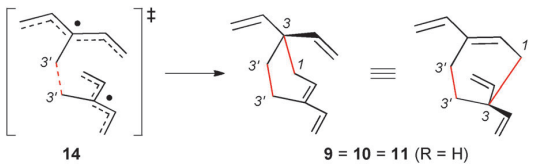


Starting triene **8** (R =)	Half life ($t_{1/2}$/h)	Starting triene conc. (M)	Cycloadduct ratio **9**:**10**:**11**
c (4-nitrophenyl)	1.7	0.030	56:44:0
d (–CO_2Me)	8.6	0.030	39:32:29
a (Ph)	13	0.030	61:37:2
b (4-methoxyphenyl)	15	0.028	59:33:8
e (–CH_2OAc)	92	0.091	36:25:39
1 (–H)	150	0.087	—

[a] Overall yields for the dimerisation are in the range 89–99%, as measured by ^{1}H NMR spectroscopy.

data provided in Table 1, the majority of 1*E*-substituted [3]dendralenes undergo DA dimerisation significantly faster than the parent unsubstituted triene **1**.[18] The acetoxymethyl-substituted system **8e** is the odd one out, with a propensity to dimerise that is only slightly higher than the parent [3]dendralene. Aryl or carbomethoxy-substituted systems **8a–d** exhibit much faster dimerisations than **1**.

These findings may be explained in terms of the recently proposed biradicaloid transition structure (TS) for the dimerisations of dendralenes.[6] DFT calculations revealed that [3]dendralene dimerised *via* a bispericyclic TS, whose geometry and electronic structure is best described by two pentadienyl radicals which are sufficiently strongly coupled through the developing C3′···C3′ bond to produce a closed-shell singlet state **14** (Scheme 3).[6] Closure to the [3]dendralene dimer occurs through two degenerate pathways involving C1–C3 bond formation.

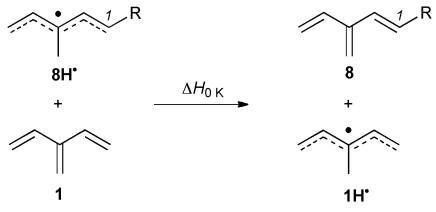


Scheme 3 Biradicaloid TS leading to [3]dendralene dimer.

This biradicaloid model predicts that the introduction of a radical stabilising substituent at C1 of [3]dendralene should accelerate the dimerisation reaction, relative to the parent cognate system. This prediction was verified by calculating the stabilisation enthalpies at 0 K ($\Delta H_{0\,K}$) of 1-substituted pentadienyl radicals, defined by the reaction **8H**$^\bullet$ + **1** → **8** + **1H**$^\bullet$. This equation and the B3LYP/6-31G(d) $\Delta H_{0\,K}$ values are given in Table 2.

Comparing these radical stabilising energies with the experimental data, the relative reactivities of the three aryl substituted dendralenes are correctly reflected in the relative radical stabilisation energies for these substituents. The methoxycarbonyl

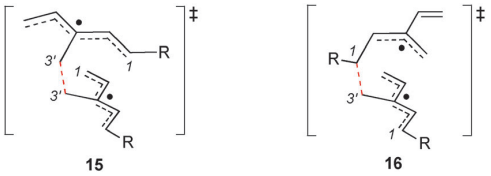
Table 2 Calculated B3LYP/6-31G(d) radical stabilisation enthalpies in kJ mol^{-1} at 0 K



R	B3LYP
$-CH_3$	−0.9
$-CH_2OAc$	−0.3
$-CO_2Me$	7.0
4-Methoxyphenyl	8.7
Phenyl	8.9
4-Nitrophenyl	11.8

substituent is predicted to be slightly less effective than aryl groups at stabilising a pentadienyl radical but experimentally, it lies between that of the 4-nitrophenyl and the phenyl systems. Nevertheless, theory correctly predicts that all four conjugating substituents will lead to faster DA dimerisations than alkyl substituents, which are predicted to have no stabilising influence on the pentadienyl radical.

The biradicaloid TS model also explains the dienophile site selectivity of the DA dimerisation. All three DA dimers **9**, **10** and **11** (Table 1) result from the internal 1,1-disubstituted alkene functioning as dienophile, which can be formed from TS **15** (Scheme 4). If one of the two terminal alkenes were to react as dienophile then the TS would bear a much less stable allyl radical component, as shown in TS **16**.



Scheme 4 Possible biradicaloid TSs leading to 1-substituted [3]dendralene dimers.

Interesting trends can be found on inspection of the ratios of the three DA dimers (Table 1). Perhaps $\pi\cdots\pi$ stacking between the two aryl groups stabilises a TS leading to **9**, the dominant isomer formed during DA dimerisation of the 1*E*-aryl-[3]dendralenes, whereas the TS *en route* to this isomer could be destabilised by steric strain when R = alkyl. While a better understanding of some aspects of this DA dimerisation must await further studies, it is abundantly clear that the positioning of a conjugating group at the 1*E*-site of [3]dendralene leads to a very reactive compound indeed.

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4aRS, 9aSR)- Tricarbonyl[C, 2,3,C-η-(1,4-epoxy-1,5-bis(dimethoxymethyl)-2,3-dimethylidene-1,2,3,4,4a,9,9a,10-octahydroanthracene)]iron. *Helv. Chim. Acta* **1989**, *72*, 906–916.

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