



**MOLECULAR WIRES:
SYNTHESES, ELECTROCHEMISTRY AND
PROPERTIES OF METAL COMPLEXES CONTAINING
CARBON CHAINS**

by

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ABSTRACT

This thesis describes the synthesis, properties and reactions of transition metal complexes containing poly-ynyl ligands.

A review of the literature relating to metal complexes containing the poly-ynyl ligand is given in Chapter 1.

The rich chemistry associated with poly-ynyl complexes containing the $W(CO)_3Cp$ fragment is extended by capping of the carbon chain by the redox-active group, Fc to give a series of complexes, $\{W(CO)_3Cp\}(C\equiv C)_nFc$ ($n = 1 - 4$). Chapter 2 details the syntheses and reactions of these complexes differing only by the number of carbon atoms in the bridge. The redox properties of the ferrocenyl nucleus show a moderate increase in oxidation potential, which can be correlated with increasing chain length. The reactions of these complexes with $Co_2(CO)_8$ and tetracyanoethene (tcne) are investigated. In all cases, the reactions apparently occur under steric control. The novel vinylidene cluster $Co_2W(\mu_3-CCPhFc)(\mu_3-PPhCH_2PPh_2)(CO)_5Cp$ (**2.5**) was obtained from **2.1** and $Co_2(\mu-dppm)(CO)_6$. Reactions of **2.1** with tcne gave the cyclobutenyl (**2.11**) and buta-1,3-dien-2-yl (**2.12**) complexes by cycloaddition to the $C\equiv C$ triple bond and subsequent ring-opening. In the presence of silica gel, **2.12** reacts with MeOH to give the chelating imino complex $W\{C[=C(CN)_2C(OMe)=NH]CFc=C(CN)_2\}(CO)_2Cp$ (**2.13**).

The preparation of an iron/ruthenium butadiyndiyl complex **3.14** is described in Chapter 3. The complex undergoes three reversible 1-electron oxidation processes as shown by cyclic voltammetry. Chemical oxidation with one or two equivalents of $[FcH][PF_6]$ gave the mono- and di-oxidised complexes respectively. A detailed investigation into the spectroscopic and electronic properties is given. The oxidation potentials fall midway between the diiron and diruthenium parent complexes. The structure of the carbon bridge in the di-oxidised complex cannot be unequivocally assigned as no ^{13}C resonances of the chain are available. It is likely that the structure is somewhere between butadiynyl ($-C\equiv C-C\equiv C-$) and cumulenyl ($=C=C=C=C=$) in nature. The electronic properties suggest the mono-oxidised complex is a Class II

system. The electronic coupling parameter V_{AB} , calculated from the NIR transition, gives a value of 188 cm^{-1} (0.023 eV) which is high for Class II complexes but much lower than those of Class III complexes of this type (V_{AB} ca 0.4 – 0.7 eV).

The chemistry of gold(I) complexes containing butadiynyl ligands is relatively unexplored. The linear coordination and possibility of aurophilic interactions prompted the synthesis of several complexes containing $\text{Au}(\text{PR}_3)$ units. Linear rods of up to 13 atoms in length were formed. Chapter 4 details the synthesis of several gold butadiynyl and poly-ynyl complexes bearing phosphine ligands.

Chapter 5 describes the synthesis and properties of some complexes used as starting materials in previous chapters. As well as these, several novel complexes are described which were envisaged as intermediates on route to new poly-ynyl complexes and whose structures were determined by X-ray studies. A series of butadiynyl complexes containing ruthenium fragments is described and the cyclic voltammograms recorded. A comparison between several known ruthenium butadiyndiyl complexes is made. All the complexes showed a large degree of electronic communication between the ruthenium centres. Changing of the ligands on the ruthenium to give non-symmetrical butadiyndiyl complexes did not diminish this communication. The reactions of butadiynyl complexes with triflic acid are also discussed.

STATEMENT

This thesis contains no material which has been accepted for the award of any other degree or diploma in any university and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference is given in the text of this thesis.

I consent to this thesis being made available for photocopy or loan.

10/9/02

Mark E. Smith

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Au cul, à la tete, surtout au cul, et pourvu que ca glisse!

ABBREVIATIONS

In general

Å	angstroms
acac	acetylacetonate
Ar	aryl
Av.	average
bipy	bipyridine
b.p.	boiling point
Bu	butyl
ⁿ Bu	normal butyl
^t Bu	tertiary butyl
ca.	circa
calc.	calculated
Cp	cyclopentadienyl
Cp*	pentamethycyclopentadienyl
Cy	cyclohexyl
d	days
dbu	1,8-diazabicyclo[5.4.0]undec-7-ene
dippe	1,2-bis(diisopropylphosphino)ethane
dmpe	1,2-bis(dimethylphosphino)ethane
dmsO	dimethylsulphoxide
dppe	1,2-bis(diphenylphosphino)ethane
dppm	bis(diphenylphosphino)methane
e.g.	for example
en	ethylenediamine
Et	ethyl
eV	electron volt
Fc	ferrocenyl
g	grams
h	hours
HOMO	highest occupied molecular orbital
Hz	hertz
K	Kelvins

L	ligand or litres
LUMO	lowest unoccupied molecular orbital
[ML _n]	general metal-ligand fragment
M	metal or molarity
Me	methyl
mg	milligram
MHz	megahertz
min.	minutes
mL	millilitres
mmol	millimole
MO	molecular orbital
OAc	acetate
O ^t Bu	tertiary butoxide
OTf	triflate
Ph	phenyl
ⁱ Pr	isopropyl
ppn	bis(triphenylphosphine)iminium
r.t.	room temperature
R _f	retardation factor (TLC)
Rc	ruthenocenyl
SOMO	semi-occupied molecular orbital
tcne	tetracyanoethylene
thf	tetrahydrofuran
tmeda	tetramethylenediamine
tol	tolyl
TLC	thin layer chromatography
V	Volts
X	anion

For Cyclic Voltammetry

E°	formal electrode potential
SCE	standard calomel electrode

For Electronic Absorption Spectroscopy (UV / Vis, NIR)

λ	wavelength
ϵ	extinction coefficient
IVCT	intervalence charge transition

For Infrared Spectroscopy (IR)

br	broad
cm^{-1}	wavenumbers (reciprocal centrimetres)
m	medium
s	strong
sh	shoulder
vs	very strong
vw	very broad
w	weak

For Mass Spectrometry

ES	Electrospray
M	molecular ion
m/z	mass per unit charge

For Nuclear Magnetic Resonance Spectroscopy (NMR)

δ	chemical shift
d	doublet
dd	doublet of doublets
dt	doublet of triplets
J	coupling constant
m	multiplet
ppm	parts per million
s	singlet

t triplet

For Spectroelectrochemistry

OTTLE optical transparent thin layer electrode

Chapter 1

Introduction

During the past decade there has been rapid growth in the field of molecular electronics.¹ The continual push to make electronic devices smaller and faster has spawned the field of nanotechnology. There have been increasing numbers of reports of organic or organometallic molecules with tailor-made properties such as recognition or switching ability.²⁻¹⁶ A prerequisite to the development of super-molecules incorporating these devices is the construction of efficient and modular electron conveyors.

By definition, a molecular wire is a “one dimensional molecule allowing a through-bridge exchange of an electron/hole between its remote ends/terminal groups, themselves able to exchange electrons with the outside world”.¹⁷

Before being considered as a molecular wire a given compound should have a proven ability to convey electrons. However, experimental evaluation of the electron conduction capability is not always a simple task and only three means have been devised so far.

(1) The direct measurement of the bulk conductivity of the material, either from amorphous solid, or a crystal. This approach gives only statistical information about the molecular conductivity, since it is strongly dependant on the solid-state structure of the material.^{18,19}

(2) The direct measurement of the conductivity of a single molecule.

(3) In order to get information on the discrete species, a convenient way is to look at the electronic interaction between the redox-active termini using electrochemistry (cyclic voltammetry) (see below).

The idea of forging electronic components from single molecules was first proposed in 1974 by researchers at IBM. But it took until 1996 to make a key breakthrough. By adding thiol molecules to polyphenylene, they were able to anchor molecules to a gold sheet and for the first time, run a current through them. In polyphenylene, the molecular orbitals overlap, forming a conducting channel along the length of the molecule.^{20,21}

Organic molecules featuring conjugated π -electron networks were initially targeted as potential molecular wires. These molecules are usually sufficiently stable enough to allow purification by chromatographic techniques resulting in the isolation of molecules of impressive length. High yield stepwise linear syntheses enabled molecules up to 128 Å in length to be isolated starting from simple building blocks (Figure 1).^{22,23} These organic wires were diverse in composition due to the large number of unsaturated organic units and could be obtained with either flexible or rigid cores.

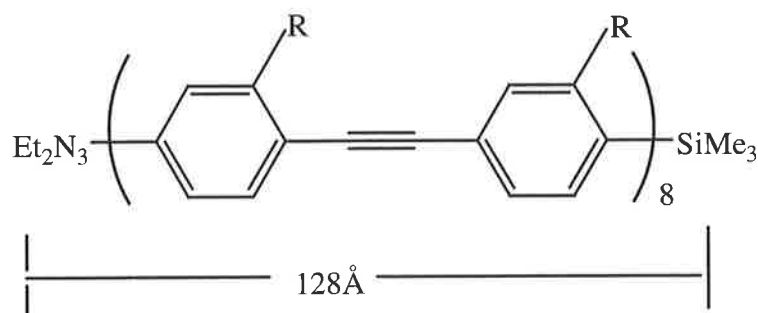


Figure 1: An organic molecular wire, R = 3-ethylheptyl.

Transition metals have long been used to stabilise reactive organic molecules with extended π conjugation. This is a result of not only the steric protection afforded by the bulky metal fragment, but the ability of the metal d-orbitals to overlap with the π -orbitals of the organic moiety. However, there are to date, no examples of a “working” molecular wire in which an organic unit bridges two transition metal centres. The simplest form would be a complex in which two redox active transition metal centres are linked by a chain of carbon atoms.

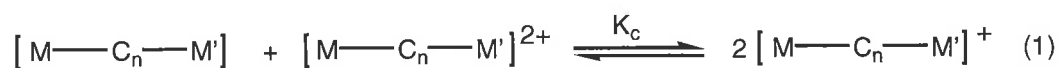
Consider a complex in which two identical redox active centres, each with a 1-electron oxidised product, are linked by a bridging organic ligand. The redox centres are distinguished by the labels M and M'. Under the Robin and Day classifications, there are two extreme scenarios possible:

(a) The bridging ligand does not allow any electronic interaction between M and M' (the ligand is an insulator). This compound may be described as a Class I material.²⁴ The E° values for the oxidation of M and M' will be essentially identical, differing only by a small statistical factor [$\Delta E^\circ = 2(RT/F)\ln 2$].²⁵ The voltametric wave will have the shape of a 1-electron process, but its magnitude will correspond to that of a 2-electron process.

(b) There are very strong interactions between M and M' (the ligand is a conductor). These complexes are described as Class III materials.²⁴ The two E° values will be significantly different, and in the cyclic voltammogram (CV) two well separated waves, each corresponding to a 1-electron process, will be observed. In general, the extent of the interaction between the metal centres will be reflected by the magnitude of ΔE° ($\Delta E^\circ = |E^\circ_2 - E^\circ_1|$).²⁶ It has been suggested that for complexes in this Class, $\Delta E^\circ > 200$ mV usually.⁷

However, it should be noted that the relationship between ΔE° and electron delocalisation is not always simple, especially for weakly interacting redox centres (Class II materials), due to the effects of structural reorganisation, solvent and ion pairing. In this case, spectroscopic techniques can be used to distinguish the metal centres.

For complexes of the type $M-C_n-M$, the degree of electronic delocalisation between two equivalent termini, M, is gauged by the comproportionation constant, K_c , for the equilibrium shown in Equation 1.



K_c can be calculated from the electrode potentials $E_{1/2}(2+/1+)$ and $E_{1/2}(1+/0)$ ^{27,28} from Equation 2.

$$K_c = (\exp\{F[E_{1/2}(2+/1+)-E_{1/2}(1+/0)]/RT\}) \quad (2)$$

The separation of the oxidation waves, ΔE° , also gives an indication of the degree of electronic communication between the metal centres along the organic bridge. A molecular wire should be a Class III material with well separated waves in the CV. These waves should also be reversible as this indicates the complex is chemically stable in each of its accessible redox states.

The simplest organic bridge is one in which a chain of carbon atoms links two metal centres. No discussion will be made here on complexes in which two metal centres are linked by one, two or three carbon atoms.

At the beginning of the work described in this thesis there were only a small number of $\{ML_n\}C\equiv CC\equiv C\{ML_n\}$ complexes known. Presently, however, there are several groups researching this area, each group using different metal centres. Table 1 lists many of the known butadiyndiyl complexes and the number of observed and isolated redox states.

Table 1. Bridged butadiyndiyl binuclear complexes, $\{ML_n\}C\equiv CC\equiv C\{ML_n\}$.

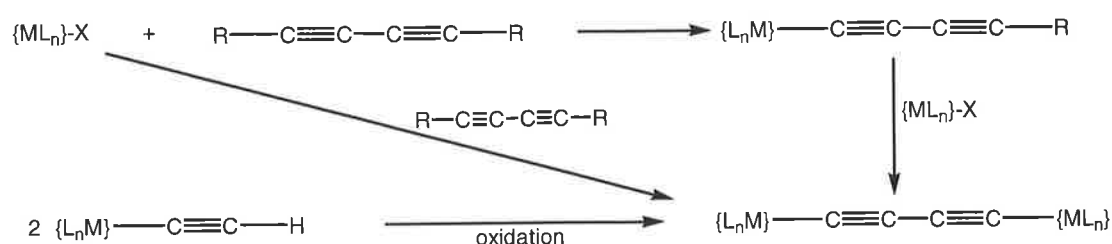
Complex	ML_n	Obs./isol. redox. st. ^a	refs
1.1	Mo(CO) ₂ Tp'	2/1	29
1.2	W(CO) ₂ Tp'	2/1	29
1.3	W(CO) ₃ Cp	1/1	30
1.4	Mn(dmpe) ₂ I	3/3	31
1.5	Re(NO)(PPh ₃)Cp*	3/3	32
1.6	Re(NO)(P(tol) ₃)Cp*	3/1	33
1.7	Re(CO) ₃ (bipy)	1/1	34
1.8	Fe(CO) ₂ Cp	1/1	35
1.9	Fe(dppe)Cp*	4/3	36
1.10	Fe(dippe)Cp*	4/3	37
1.11	Ru(PPh ₃) ₂ Cp	5/3	38
1.12	Ru(PPh ₃)(PMe ₃)Cp	5/1	39
1.13	Ru(dppe)Cp*	5/3	40
1.14	Ru(dppm)Cp*	5/1	40
1.15	Os(PPh ₃) ₂ Cp	5/1	41
1.16	Os(dppe)Cp*	5/1	41
1.17	Rh(CO)(P ^t Pr ₃) ₂	1/1	42
1.18	Ni(PPh ₃)Cp	1/1	35
1.19	Ni(CN)(NH ₃) ₃	1/1	43
1.20	PdCl(P ⁿ Bu ₃) ₂	1/1	44
1.21	PtCl(P ⁿ Bu ₃) ₂	1/1	45
1.22	Au(PCy ₃)	1/1	46

^aObserved/isolated redox states of the compound.

SECTION A

(i) Synthesis

As illustrated in Scheme 1, the synthesis of $\{\text{ML}_n\}\text{C}\equiv\text{CC}\equiv\text{C}\{\text{ML}_n\}$ complexes can be accomplished in three general ways.



Scheme 1. General synthetic methodologies for the formation of $\{\text{ML}_n\}\text{C}\equiv\text{CC}\equiv\text{C}\{\text{ML}_n\}$.

(a) Syntheses from diacetylide anions and metal-halide complexes

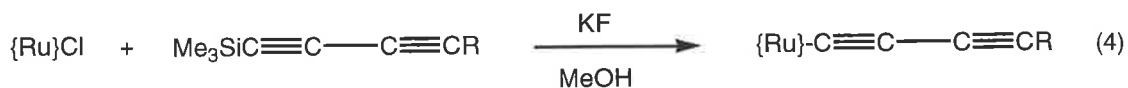
The acetylenic hydrogens of 1,3-diynes are about as acidic as those of 1-alkynes and diynes and are therefore readily metallated.⁴⁷ The dianionic diacetylide reagent $\text{LiC}\equiv\text{CC}\equiv\text{CLi}$ has been used to prepare the dinuclear complexes **1.8**⁴⁸ and **1.11**³⁸ from reactions with $\text{FeCl}(\text{CO})_2\text{Cp}$ or $[\text{Ru}(\text{thf})(\text{PPh}_3)_2\text{Cp}][\text{PF}_6]$ respectively (Equation 3).



$\{\text{ML}_n\} = \text{Fe}(\text{CO})_2\text{Cp}$, $\text{Ru}(\text{PPh}_3)_2\text{Cp}$; $\text{X} = \text{Cl}$ or thf .

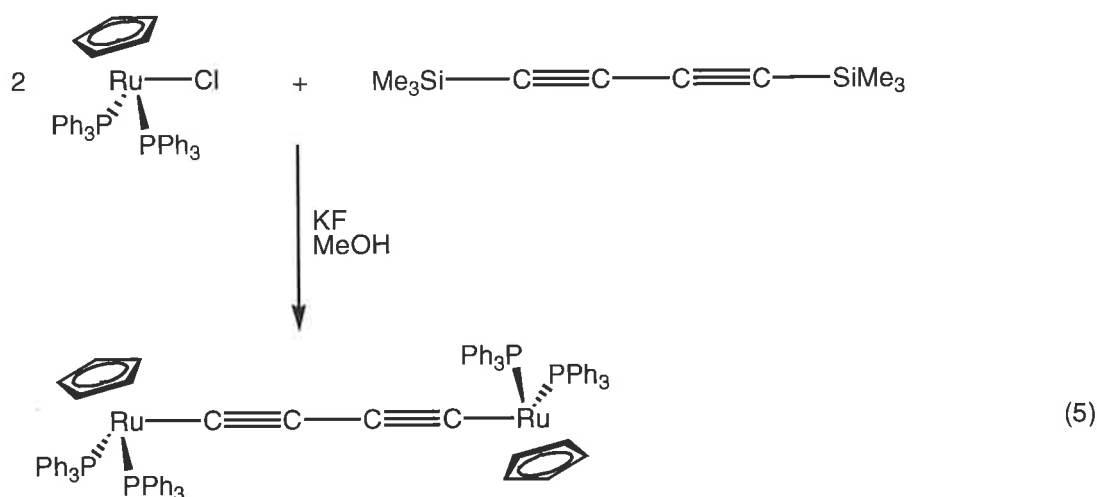
(b) Metal Exchange and Coupling Reactions Involving Group 14 Diynyl Reagents.

Preparative organic poly-ynyl chemistry has long used Group 14 reagents such as trialkylsilyl moieties⁴⁹ or tetravalent tin reagents^{50,51} as protecting and stabilising groups in the construction of carbon-carbon bonds. Fluoride-catalysed desilylation of trimethylsilyl-substituted diynes in the presence of metal halides affords σ -diynyl complexes in high yield in reactions that are thought to proceed via the vinylidene or silyl-vinylidene (Equation 4).^{52,53} More recently, Bruce et al.⁵⁴ have shown that this reaction can be applied to a large number of trimethylsilyl capped butadiynes.



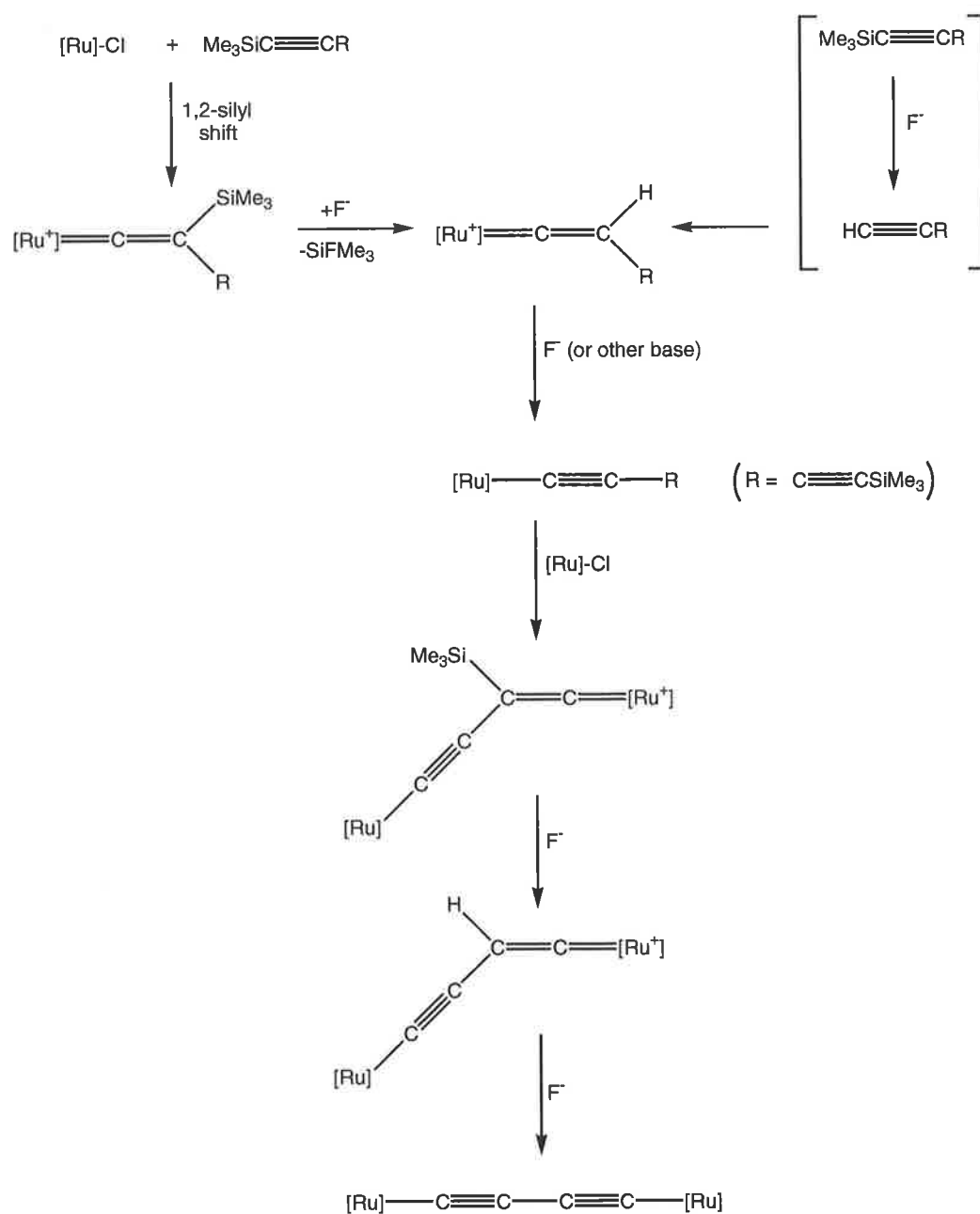
$[\text{Ru}] = \text{Ru}(\text{PPh}_3)_2\text{Cp}$, $\text{R} = \text{Ph}$, $\text{C}\equiv\text{CPh}$.

Bruce et al. have focused their research on the $\text{Ru}(\text{PR}_3)_2\text{Cp}$ endgroup. Several papers have been published on acetylide^{38,55,56} and 1,3-butadiyne^{38,39,57} complexes containing this metal fragment. The butadiynyl complex, **1.11**, has been synthesised and is shown in Equation 5).^{39,57}



Synthesis of **1.11**.

The mechanism for the formation of this complex has been the subject of debate. Recently, Bruce et al. reported analogous reactions with longer chain homologues and aryl substituents to probe the mechanism.⁵⁴ The key step in these reactions is the 1,2-silyl shift to give a vinylidene (Scheme 2) which is deprotonated by fluoride. The reaction is driven by the precipitation of the ethynyl complexes.

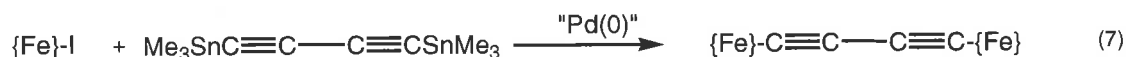
Scheme 2. $[\text{Ru}] = \text{Ru}(\text{PPh}_3)_2\text{Cp}$.

It has been shown that the PPh_3 ligands of **1.11** could be replaced with other phosphines. When **1.11** was treated with excess PMe_3 , two of the PPh_3 ligands were exchanged for PMe_3 giving $\{\text{Cp}(\text{PPh}_3)(\text{PMe}_3)\text{Ru}\}\text{C}\equiv\text{CC}\equiv\text{C}\{\text{Ru}(\text{PMe}_3)(\text{PPh}_3)\text{Cp}\}$ (**1.12**). The synthesis of $\{\text{Cp}^*(\text{dppe})\text{Ru}\}\text{C}\equiv\text{CC}\equiv\text{C}\{\text{Ru}(\text{dppe})\text{Cp}^*\}$ (**1.13**)⁴⁰ was analogous to that of Lapinte and co-workers (Scheme 7). More recently, osmium was introduced into this chemistry and has shown a very promising start. The synthesis was analogous to that used for the iron and ruthenium analogues using the $\text{Os}(\text{dppe})\text{Cp}^*$ fragment instead to form $\{\text{Cp}^*(\text{dppe})\text{Os}\}\text{C}\equiv\text{CC}\equiv\text{C}\{\text{Os}(\text{dppe})\text{Cp}^*\}$ (**1.16**).⁴¹

The Stille reaction (Equation 6), in which an aryl-, alkenyl-, or alkynyl-stannane is cross-coupled with an aryl or vinyl halide, pseudo-halide, or arenediazonium salt in the presence of a $\text{Pd}(0)$ catalyst, is a common method for the preparation of new carbon-carbon bonds.⁵⁸ It has been demonstrated recently that a similar approach may be used to form new metal-carbon bonds.



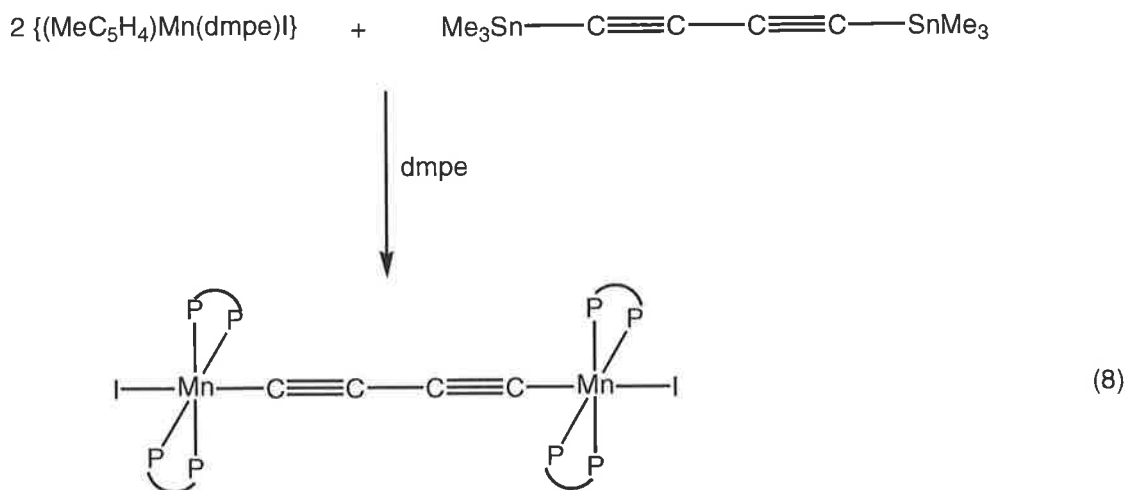
Treatment of $\text{FeI}(\text{CO})_2\text{Cp}$ with $\text{HC}\equiv\text{CC}\equiv\text{CSnMe}_3$ in the presence of $\text{PdCl}_2(\text{NCMe})_2$ (5 mol%) gives $\text{Fe}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{CO})_2\text{Cp}$.⁵⁹ The diyndiyl complex **1.8** was obtained in a similar fashion from $\text{FeI}(\text{CO})_2\text{Cp}$ and one-half equivalent of $\text{Me}_3\text{SnC}\equiv\text{CC}\equiv\text{CSnMe}_3$ (Equation 7).⁵⁹ More recently, this reaction has been extended to alkynyl complexes of Ru, Mo and W.⁶⁰



$\{\text{Fe}\} = \text{Fe}(\text{CO})_2\text{Cp}$.

Berke et al. have recently reported the synthesis of a manganese $\{\text{ML}_n\}\text{C}\equiv\text{CC}\equiv\text{C}\{\text{ML}_n\}$ complex (Equation 9).³¹

According to Equation 8, the green low-spin d^5 Mn(II) complex, $\{\text{I}(\text{dmpe})_2\text{Mn}\}\text{C}\equiv\text{CC}\equiv\text{C}\{\text{Mn}(\text{dmpe})_2\text{I}\}$ (**1.4**) is obtained from $\{(\text{MeC}_5\text{H}_4)\text{Mn}(\text{dmpe})\text{I}\}$ and half an equivalent of bis(trimethylstannyl)-1,3-butadiyne in the presence of dmpe.³¹

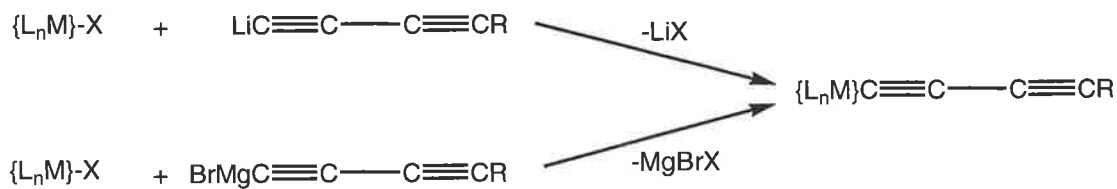


Synthesis of **1.4**.

Secondly, the metal fragments can be added in a stepwise fashion, which involves the isolation of a butadiynyl complex. This can also be achieved in a number of ways.

Both the methods discussed for the simultaneous addition of two metal fragments to the C_4 chain can be utilised in the formation of the monometallic butadiynyl complexes.

Treatment of $\text{HC}\equiv\text{CC}\equiv\text{CR}$ ($\text{R} = \text{H}$, alkyl, trialkylsilyl, aryl) with one equivalent of BuLi or EtMgBr affords $\text{LiC}\equiv\text{CC}\equiv\text{CR}$ ⁶¹ or $\text{BrMgC}\equiv\text{CC}\equiv\text{CR}$ ⁴⁷ respectively (Scheme 3).



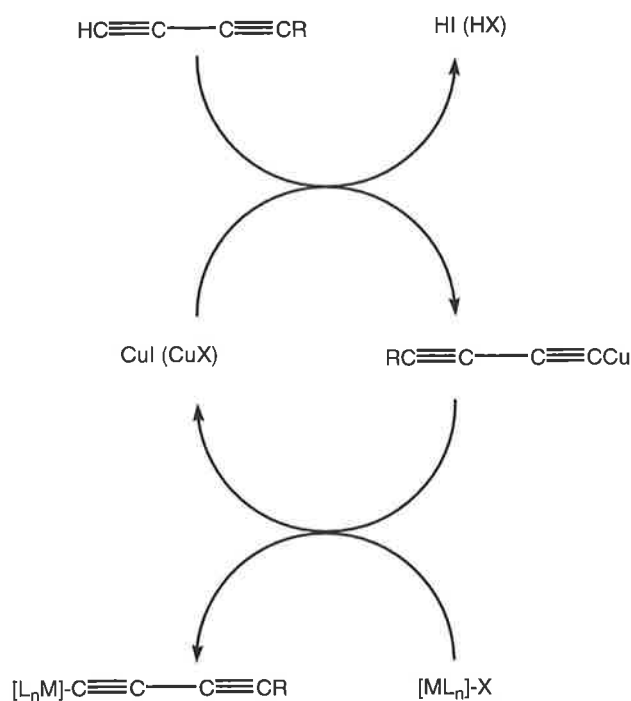
Scheme 3.

Similarly, the air-stable crystalline diyne, $\text{Me}_3\text{SiC}\equiv\text{CC}\equiv\text{CSiMe}_3$, can be readily desilylated with $\text{MeLi}\cdot\text{LiBr}$ to give the SiMe_3 -protected synthon $\text{LiC}\equiv\text{CC}\equiv\text{CSiMe}_3$.⁴⁷

(c) Cu(I)-Catalysed Reactions of 1,3-Diynes with Metal-Halide Complexes

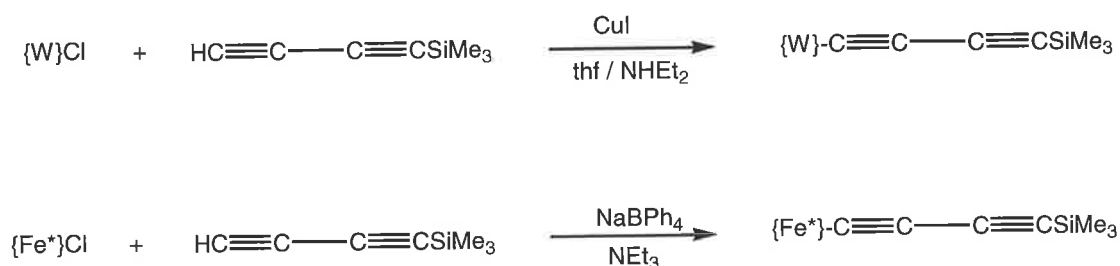
There is considerable precedence for the use of CuI to catalyse reactions between metal halides and 1-alkynes.^{44,62} The copper(I)-catalysed reactions between buta-1,3-diyne and a variety of Group 10 complexes in amine solvents under mild conditions were initially reported in 1977, when the *cis*- and *trans*-isomers of $\text{Pt}(\text{C}\equiv\text{CC}\equiv\text{CH})_2(\text{PBU}_3)_2$ were obtained from the corresponding dihalide complexes and $\text{HC}\equiv\text{CC}\equiv\text{CH}$ with retention of geometry at the metal centre.^{44,62} This reaction has been successfully applied to the preparation of diynyl complexes featuring metals across the periodic table.⁶³

While the mechanisms of these reactions have not been investigated in detail, it is likely that an intermediate copper(I) alkynyl is formed, which undergoes an alkynyl-halide exchange with the $[\text{ML}_n]\text{-X}$ species, resulting in the formation of the transition metal σ -alkynyl complex and a Cu(I) halide, which completes the catalytic cycle (Scheme 4).^{44,55,62}



Scheme 4.

The useful reagent $\text{LiC}\equiv\text{CC}\equiv\text{CSiMe}_3$ is sufficiently nucleophilic to displace halides from a wide variety of transition metal halides. Alternatively, $\text{HC}\equiv\text{CC}\equiv\text{CSiMe}_3$ can be coupled directly to metal fragments using CuI ⁶⁴ or NaBPh_4 ⁶⁵ (Scheme 5).

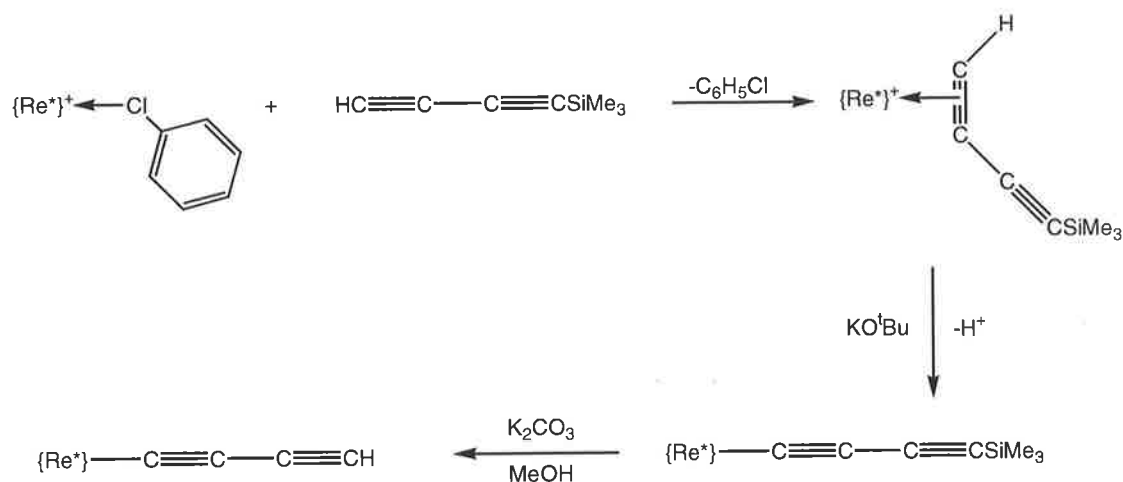


Scheme 5. $\{\text{W}\} = \text{W}(\text{CO})_3\text{Cp}$, $\{\text{Fe}^*\} = \text{Fe}(\text{dppe})\text{Cp}^*$.

The silylated diynyl complexes can be readily proto-desilylated by standard methods, such as treatment with $[\text{NBu}_4]\text{F}$ or KOH/MeOH to give the corresponding terminal diynyl complexes. These procedures have the advantage of avoiding the preparation of terminal diyne reagents.

(d) Miscellaneous Preparations

Gladysz and co-workers⁶⁶ have prepared the trimethylsilylbutadiynyl complex $\text{Re}(\text{C}\equiv\text{CC}\equiv\text{CSiMe}_3)(\text{NO})(\text{PPh}_3)\text{Cp}^*$ by the multi-step synthesis illustrated in Scheme 6. The key step in this approach is the preparation and subsequent deprotonation of the η^2 -alkyne complex $[\text{Re}(\eta^2\text{-HC}_2\text{C}\equiv\text{CSiMe}_3)(\text{NO})(\text{PPh}_3)\text{Cp}^*]^+$. The SiMe_3 protecting group was readily removed in methanolic K_2CO_3 to give the terminal diyne complex $\text{Re}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{NO})(\text{PPh}_3)\text{Cp}^*$ (Scheme 6).



Scheme 6. $\{\text{Re}^*\} = \text{Re}(\text{NO})(\text{PPh}_3)\text{Cp}^*$.

The synthesis of $\{\text{ML}_n\}\text{C}\equiv\text{CC}\equiv\text{C}\{\text{ML}_n\}$ complexes from the butadiynyl complexes can be achieved by a second copper-catalysed coupling reaction. Alternatively, the silyl-protected butadiynyl complexes can be deprotected in situ and coupled to another metal fragment.

(e) Coupling Reactions of $\{\text{ML}_n\}\text{C}\equiv\text{CH}$ Complexes.

The preparation of symmetrical diynes is often accomplished by oxidative coupling of 1-alkynes. Whilst many different reaction conditions have been established for the homo-coupling of terminal organic alkynes there are few examples of coupling reactions of $\text{C}\equiv\text{CH}$ units in the metal coordination sphere.

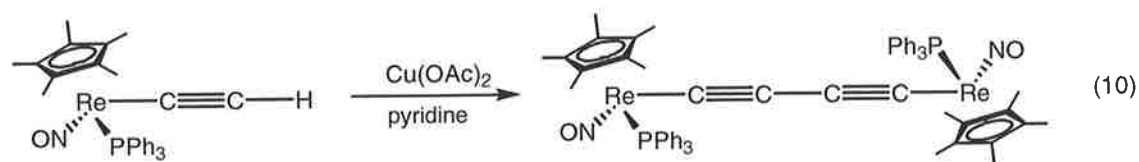


$\{\text{ML}_n\} = \text{Ni}(\text{PPh}_3)\text{Cp}, \text{Fe}(\text{CO})_2\text{Cp}$.

Hay conditions ($\text{CuCl} / \text{tmeda}, \text{O}_2, \text{r.t.}$)⁶⁷ have been used to prepare a number of diyndiyl complexes $\{\text{ML}_n\}\text{C}\equiv\text{CC}\equiv\text{C}\{\text{ML}_n\}$ [$\text{ML}_n = \text{Ni}(\text{PPh}_3)\text{Cp}$; **1.18**, $\text{Fe}(\text{CO})_2\text{Cp}$; **1.8**] by oxidative coupling of $\{\text{ML}_n\}\text{C}\equiv\text{CH}$ (Equation 9).³⁵

The chiral rhenium endgroup used by Gladysz and coworkers, $\text{Re}(\text{NO})(\text{PPh}_3)\text{Cp}^*$, has been used to cap carbon chains from two to twenty atoms in length.⁶⁸ The

butadiyndiyl complex, $\{\text{Cp}^*(\text{PPh}_3)(\text{NO})\text{Re}\}\text{C}\equiv\text{CC}\equiv\text{C}\{\text{Re}(\text{NO})(\text{PPh}_3)\text{Cp}^*\}$ (**1.5**), was synthesised by Eglington coupling of the rhenium ethynyl (Equation 10).⁶⁹



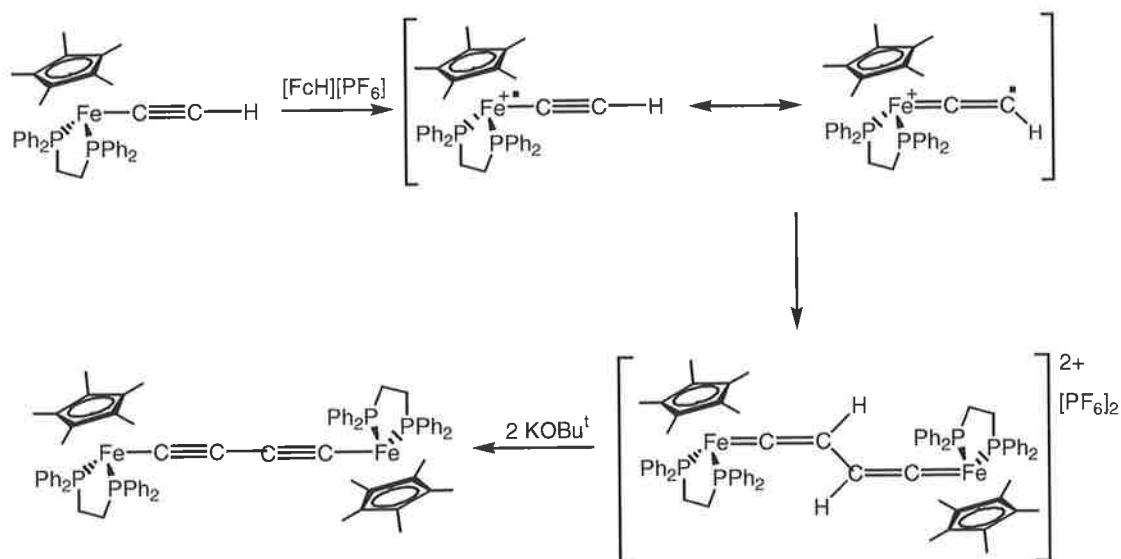
Synthesis of **1.5**.

While the reaction in Equation 10 is performed with racemic rhenium acetylide and thus gives a mixture of diastereomers, for the ease of discussion, this point will be omitted. It is worth noting that crystallisation affords samples enriched in one or other of the diastereomers and further reactions were done using diastereomerically pure samples.

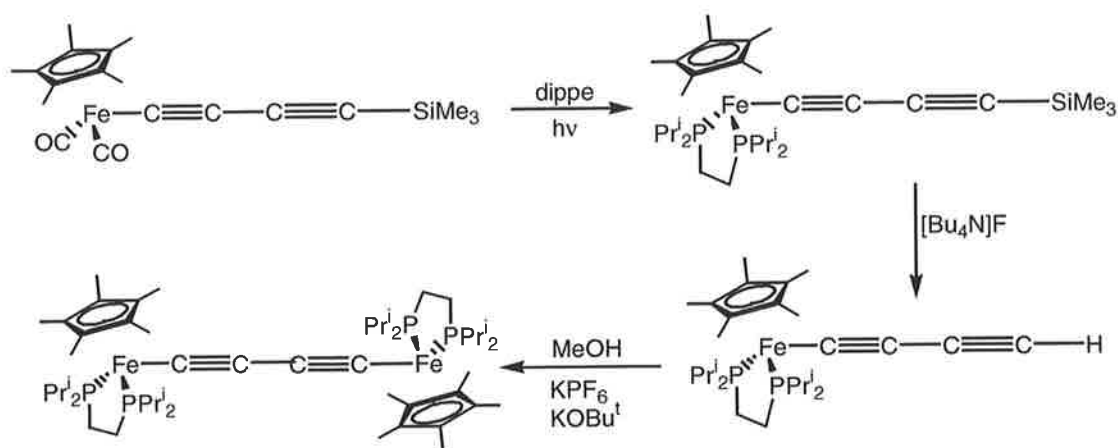
An identical reaction was used to transform the $\text{P}(\text{tol})_3$ -containing rhenium-ethynyl $\text{Re}(\text{C}\equiv\text{CH})(\text{NO})(\text{P}(\text{tol})_3)\text{Cp}^*$ to the butadiyndiyl complex, $\{\text{Cp}^*(\text{P}(\text{tol})_3)(\text{NO})\text{Re}\}\text{C}\equiv\text{CC}\equiv\text{C}\{\text{Re}(\text{NO})(\text{P}(\text{tol})_3)\text{Cp}^*\}$ (**1.6**).³³

Lapinte et al. have long used the $\text{Fe}(\text{dppe})\text{Cp}^*$ unit to stabilise carbon chains.⁷ The diyndiyl complex $\{\text{Cp}^*(\text{dppe})\text{Fe}\}\text{C}\equiv\text{CC}\equiv\text{C}\{\text{Fe}(\text{dppe})\text{Cp}^*\}$ (**1.9**) was synthesised^{36,70} in a two-step procedure from the iron ethynyl $\text{Fe}(\text{C}\equiv\text{CH})(\text{dppe})\text{Cp}^*$ shown in Scheme 7.

Oxidation of $\text{Fe}(\text{C}\equiv\text{CH})(\text{dppe})\text{Cp}^*$ with $[\text{FcH}][\text{PF}_6]$ gave the 17-electron species $[\text{Fe}(\text{C}\equiv\text{CH})(\text{dppe})\text{Cp}^*][\text{PF}_6]$ (Scheme 7). Usually, 17-electron species dimerise through a metal-metal interaction,^{71,72} but in the case of the $[\text{Fe}(\text{C}\equiv\text{CH})(\text{dppe})\text{Cp}^*]^+$ cation, the extreme steric crowding about the metal centres prevents the metal centres from approaching close enough for any significant interaction to occur. Instead, coupling occurs between the ethynyl ligands to yield the bis-vinylidene $[\{\text{Cp}^*(\text{dppe})\text{Fe}\}=\text{C}=\text{CHCH}=\text{C}=\{\text{Fe}(\text{dppe})\text{Cp}^*\}][\text{PF}_6]_2$ which upon treatment with KO^tBu gave the desired butadiyndiyl complex **1.9**.³⁶

Scheme 7. Synthesis of **1.9**.

As an extension to this elegant chemistry, Lapinte and coworkers have replaced the dppe ligand for the more electron releasing ligand, dippe. The synthesis of the C_4 complex was very different for the dippe analogue and is shown in Scheme 8.³⁷ The known⁷³ trimethylsilylbutadiynyl complex, $\text{Fe}(\text{C}\equiv\text{CC}\equiv\text{CSiMe}_3)(\text{CO})_2\text{Cp}^*$ was converted to the butadiyndiyl complex, $\{\text{Cp}^*(\text{dippe})\text{Fe}\}\text{C}\equiv\text{CC}\equiv\text{C}\{\text{Fe}(\text{dippe})\text{Cp}^*\}$ (**1.10**) in three steps by replacing the carbonyl ligands with a dippe ligand, followed by proto-desilylation to give the terminal butadiynyl complex which is then capped by another $\text{Fe}(\text{dippe})\text{Cp}^*$ fragment (Scheme 8).³⁷

Scheme 8. Synthesis of **1.10**.

SECTION B

(i) Theoretical Calculations

To gain further insight into the electronic structure of **1.11** and the structural and physical properties of the complexes formed upon oxidation, extended Hückel (EH) (Figure 2) and density functional (DF) molecular orbital calculations were carried out on the model complexes $[\{\text{Cp}(\text{PH}_3)_2\text{Ru}\}\text{C}\equiv\text{CC}\equiv\text{C}\{\text{Ru}(\text{PH}_3)_2\text{Cp}\}]^{n+}$ ($n = 0 - 4$). To aid discussion, the carbons of the chain are labelled as follows: $\text{Ru}-\text{C}_\alpha-\text{C}_\beta-\text{C}_\beta'-\text{C}_\alpha'-\text{Ru}$

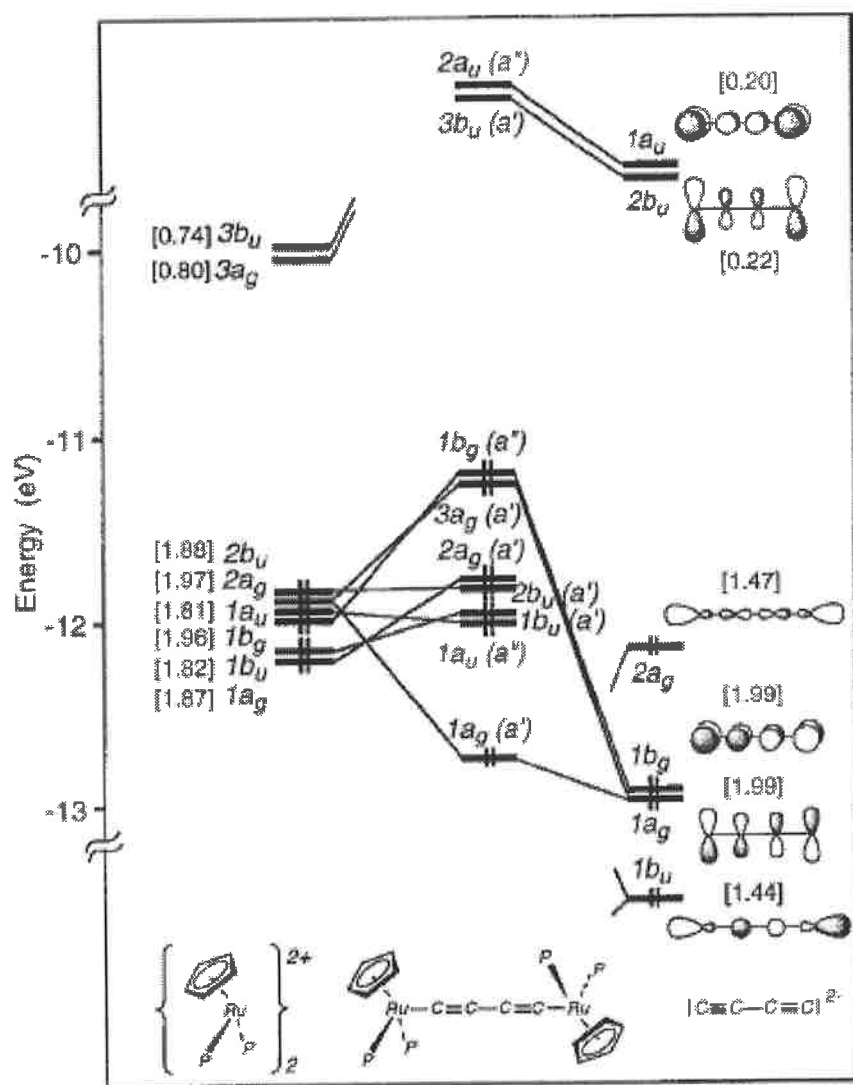


Figure 2. EH orbital interaction diagram for the neutral model complex $\{\text{Cp}(\text{PH}_3)_2\text{Ru}\}\text{C}\equiv\text{CC}\equiv\text{C}\{\text{Ru}(\text{PH}_3)_2\text{Cp}\}$ of C_{2h} symmetry (labels in the C_s symmetry group in parentheses). FMO occupations after interaction given in brackets.

The HOMOs are delocalised over the entire six-atom Ru-C₄-Ru chain, and it may be concluded that any oxidation process, which involves loss of electrons from these orbitals, will not be exclusively metal-centred. The HOMOs are antibonding between Ru and C_α and between C_β and C_{β'}, but bonding between C_α and C_β. Thus, the computational studies suggest that shortening of the M-C and C-C single bonds and lengthening of the C≡C triple bonds are to be expected upon oxidation of {Cp(PH₃)₂Ru}C≡CC≡C{Ru(PH₃)₂Cp}.

In addition, it should be noted that the HOMOs are well separated from the high-lying LUMOs (3.37 eV) and are also removed from the other occupied metallic MOs, as illustrated in Figure 2. Therefore, {Cp(PH₃)₂Ru}C≡CC≡C{Ru(PH₃)₂Cp} should be capable of losing up to four electrons and give rise to a series of five oxidation states, as was experimentally observed for **1.11**.

Comparison of models with different ligands surroundings suggests that molecules containing strong-electron-donating ligands should be more readily oxidised.

(ii) Cyclic Voltammetry

As mentioned previously, a convenient way to look at the electronic interaction between the redox-active termini is using electrochemistry (cyclic voltammetry). Table 2 lists the oxidation potentials and the separation between the oxidation waves for several complexes. The comproportionation constant, K_c has been reported in most cases. However, this value depends on the temperature at which the cyclic voltammogram is run. To enable a comparison, K_c was re-calculated using T = 293 K. Assuming that the oxidation potentials are not significantly affected by temperature, this allows a direct comparison to be made between all the complexes in Table 2.

Table 2. Electrochemical data for $\{ML_n\}C\equiv CC\equiv C\{ML_n\}^a$.

Complex	$\{ML_n\}$	E_1	E_2	E_3	E_4	1+/2+	2+/3+	3+/4+	$^bK_c \times 10^8$	$^cK_c \times 10^8$	Ref
1.4	Mn(dmpe) ₂ I	d	d			0.63			540	450	31
1.5	Re(NO)(PPh ₃)Cp*	0.01	0.54			0.53			11	9.2	69
1.6	Re(NO)(P(tol) ₃)Cp*	-0.22	0.31			0.53			11	9.2	33
1.9	Fe(dppe)Cp*	-0.69	0.03	0.95		0.72	0.92		16000	15000	36
1.10	Fe(dippe)Cp*	-0.97	-0.18	0.81		0.79	0.99		n/r	230000	37
1.11	Ru(PPh ₃) ₂ Cp	-0.23	0.41	1.03	1.68	0.64	0.62	0.65	1500	660	57
1.12	Ru(PPh ₃)(PMe ₃)Cp	-0.26	0.33	0.97	1.46	0.59	0.64	0.49	2100	950	57
1.13	Ru(dppe)Cp*	-0.43	0.23	1.02	1.51	0.66	0.79	0.49		1400	40
1.16	Os(dppe)Cp*	-0.61	0.15	0.80	1.20	0.76	0.55	0.40		71000	41

^aSee individual references for details of the electrochemical experiments, potentials given in volts (V). ^b K_c reported. ^c K_c re-calculated for T = 298 K using Equation 2. ^dThe separation of the two oxidation waves is given (0.63 V) but the actual potentials are yet to be reported. n/r = not reported

While the oxidation potentials of the $\text{Mn}(\text{dmpe})_2\text{I}$ containing complex, **1.4** have yet to be published, the potential difference between the two observed redox processes has been reported as 0.63 V.³¹

Both the rhenium-containing butadiyndiyl complexes listed in Table 2 show two reversible 1-electron oxidations. When the PPh_3 ligand was replaced by the more electron-releasing ligand $\text{P}(\text{tol})_3$, each oxidation is more facile by 0.23 V. In both cases the separation of the two oxidation waves was 0.53 V which is the lowest of all the complexes reported in Table 3.

The iron butadiyndiyl complex, **1.9** undergoes three reversible 1-electron oxidation processes as assayed by cyclic voltammetry (-0.69, 0.03, 0.95 V).³⁶ Attempts to prepare and isolate the tri-cation complex failed. In an effort to decrease the oxidation potential of the third oxidation, the *dppe* ligand was replaced by the more electron-releasing ligand, *dippe*.³⁷ The CV of **1.10** shows three well-separated and reversible waves (-0.97, -0.18, +0.81 V). Comparison of these potential values with those obtained in the related *dppe* series showed that the substitution of *dppe* by *dippe* induces a positive shift of the three redox potentials of 0.29, 0.26 and 0.14 V. There is also an increase in the separation of the waves (*dippe*, $\Delta E^\circ = 0.79$ V; *dppe*, $\Delta E^\circ = 0.72$ V) which shows that increasing the electron density at the metal centre increases the amount of communication between the metal centres.

As already mentioned, **1.11** undergoes a series of three reversible 1-electron oxidations (-0.23, +0.41 and +1.03 V) and a fourth irreversible oxidation (+1.68 V) (Figure 3).⁵⁷ The separations of the waves are similar ($\Delta E^\circ \sim 0.6$ V) and are an indication of the strength of the electronic communication between the two ruthenium centres across the C_4 bridge. While the first three oxidation processes were confirmed as 1-electron steps, the irreversible fourth wave in the CV appears to be a multi-electron wave by comparison of the peak currents. This may be taken as an indication of the existence of an ECE mechanism in which the tetra-cationic species, once generated at the electrode surface, undergoes a rapid chemical transformation to a new species which is then subject to a further oxidative process at the applied potential.

The more electron rich ruthenium complex, **1.13** shows three reversible 1-electron oxidations and a fourth irreversible oxidation, the first two lower (ca. 0.2 V) than the Ru(PPh₃)₂Cp containing complex, **1.11**.

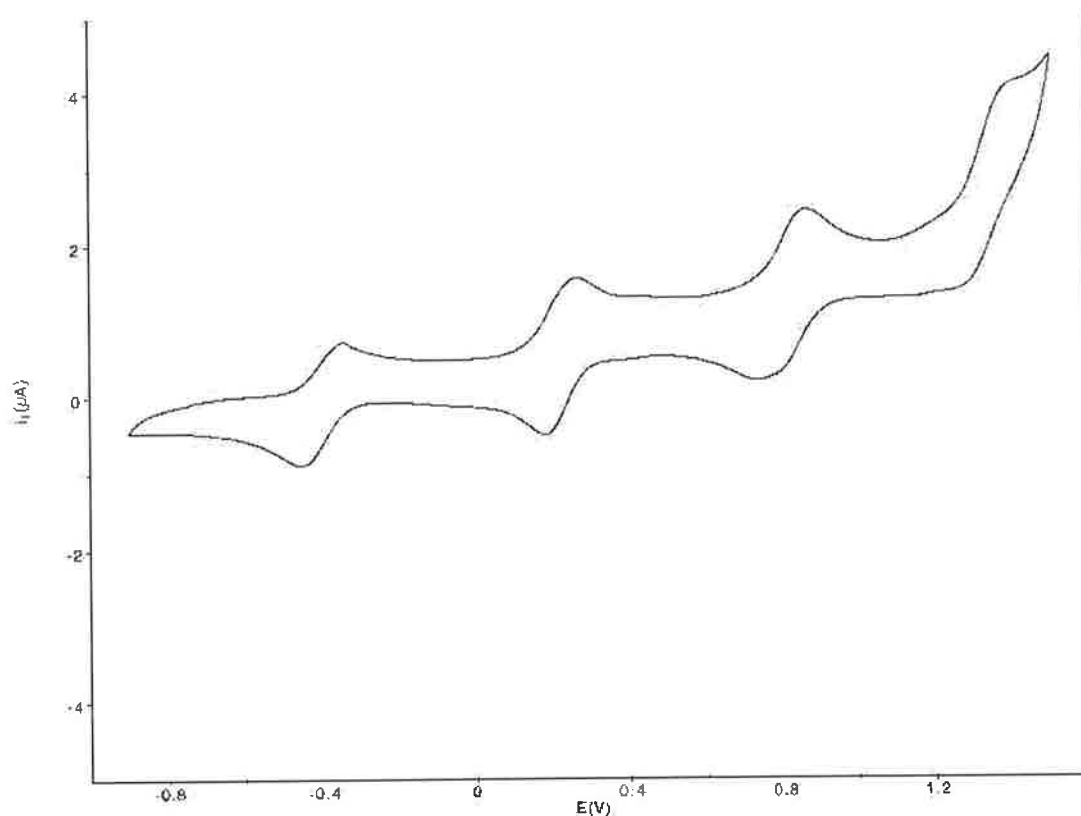


Figure 3. Cyclic voltammogram of **1.11**.

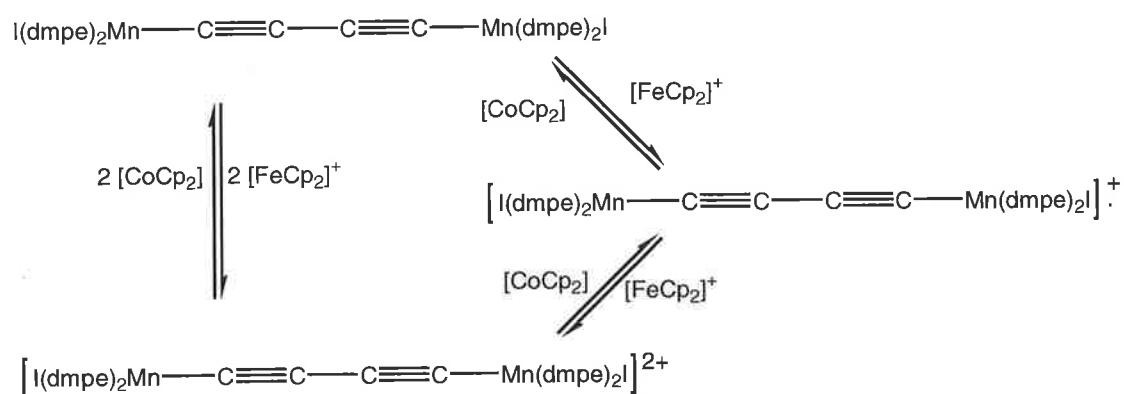
Of current interest in this research group is **1.16** which like its ruthenium analogues, shows three reversible 1-electron oxidations and a fourth irreversible oxidation. It is worth noting that ΔE° (0.76 V) is larger than both **1.9** (0.71 V) and **1.13** (0.66 V). This indicates a larger degree of electronic communication between the two osmium termini. The third oxidation is the one of most interest as it is even lower than that of **1.9** and is the lowest reported to date.

As previously mentioned, K_c is the equilibrium constant for the dissociation reaction in Equation 1. It is a direct measure of the thermodynamic stability of the mono-oxidised complex. A higher K_c implies the mono-oxidised complex is more stable. The K_c values calculated for the mono-oxidised species of the complexes in Table 2

range between $9.2 \times 10^8 - 2.3 \times 10^{13}$ and are larger than has been found for the well-known Creutz-Taube ion $\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-pyrazine})$ [$K_c = 10^{6.6}$ (aqueous solution),⁷⁴ $10^{7.3}$ (acetonitrile solution)⁷⁵]. The ΔE° ($|E_2 - E_1| = 0.53 - 0.79$ V) values found for the complexes listed in Table 2 reflect a large degree of electronic interaction between the metal centres through the C_4 bridge in all cases.

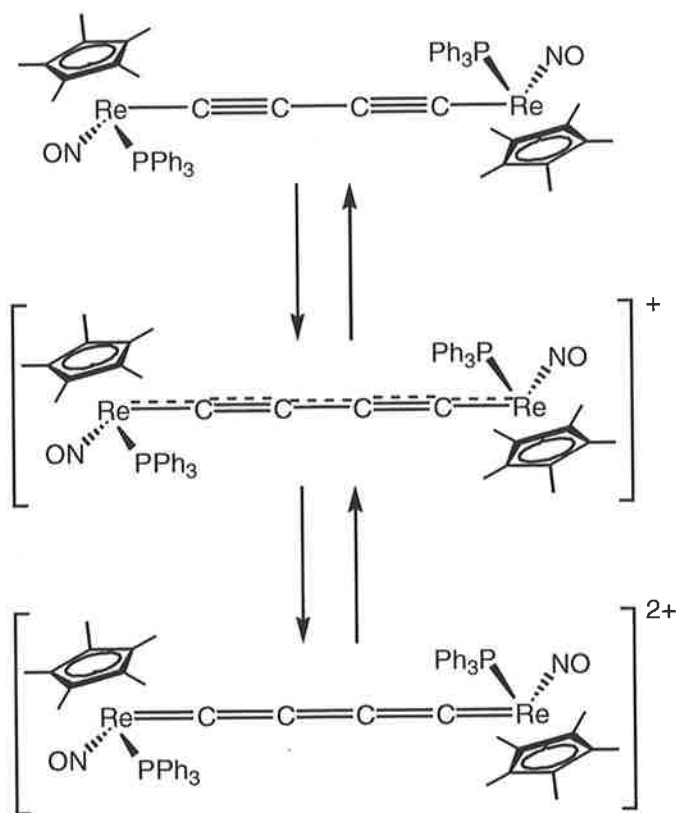
(iii) Chemical Oxidation

Chemically, **1.4** can be oxidised stepwise to the mono- and di-oxidised complexes using $[\text{FcH}][\text{PF}_6]$. Both oxidation steps are reversible and thus, addition of either one or two equivalents of cobaltocene to the mono- and di-oxidised complexes respectively gave back the neutral complex (Scheme 9).



Scheme 9. Oxidation of **1.4**.

Oxidation of the neutral complex **1.5** with one or 2.5 equivalents of AgPF_6 gave the mono- and di-oxidised complexes, $[\mathbf{1.5}][\text{PF}_6]_n$ ($n = 1, 2$) as is shown in Scheme 10. The reversibility of these reactions was examined by the reduction of the mono-oxidised complex with sodium naphthalenide to give back **1.5**.

Scheme 10. Oxidation of **1.5**.

As previously mentioned, attempts to prepare the trication of **1.9** failed. Chemical oxidation with one or two equivalents of $[\text{FcH}][\text{PF}_6]$ gave the mono- and di-cations respectively. The nature of the C_4 bridge in the three different oxidation states was probed by spectroscopic and electronic techniques. In the case of the dippe derivative, **1.10** the trication was chemically accessible. Oxidation of the dication with an equivalent of AgPF_6 gave the only known butadiyndiyl trication, $[\mathbf{1.10}][\text{PF}_6]_3$.

Chemical oxidation of **1.11** with 1 or 2.5 equivalents of AgPF_6 gave the series $[\mathbf{1.11}][\text{PF}_6]_n$ ($n = 0 - 2$). The $\text{Ru}(\text{dppe})\text{Cp}^*$ complex, **1.13** could also be oxidised to the mono- and di-oxidised complexes using the appropriate equivalents of $[\text{FcH}][\text{PF}_6]$. All attempts to prepare the tri and tetra-cations were unsuccessful in both the ruthenium series.

(iv) Structural Characterisation

Several of the complexes discussed have been characterised by X-ray studies, including many of the oxidised species. This enables a discussion of the structural changes associated with oxidation. Selected crystallographic data is listed in Table 3.

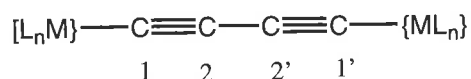


Figure 4. Atom labelling scheme for $\{ML_n\}C\equiv CC\equiv C\{ML_n\}$ complexes.

Figure 4 shows the atom labelling scheme for the carbon chain of $\{ML_n\}C\equiv CC\equiv C\{ML_n\}$ complexes that are used in the following discussion of X-ray structural data.

The neutral complex, **1.5** exhibits $C\equiv C$ and $C-C$ bond lengths (1.202(7), 1.389(5) Å) very close to those in butadiyne (1.218(2), 1.384(2) Å)⁷⁶ and three other structurally characterised $MC\equiv CC\equiv CM$ species ($M = Ru/Re/Rh$: 1.217(4)/1.19(2)/1.205(5), 1.370(6)/1.43(4)/1.388(7) Å).^{34,38,42} The ReC_4Re linkage is somewhat bent with bond angles at carbon of 174.4(5) and 176.8(9) Å.

The di-oxidised complex, **[1.5][PF₆]₂** exhibits $Re=C$ bond lengths (1.909(7)/1.916(7) Å) close to that in a related compound with a $^+Re=C=C=C=Mn$ linkage (1.91(1) Å).⁷⁷ The $C=C$ bond lengths (1.263(10)/1.260(10), 1.305(10) Å) are near those of butatriene (1.283(5) – 1.318(5) Å).⁷⁸

The Fe-C distance contracts slightly upon oxidation (1.889(9)/1.885(8) – 1.830(8) Å) in the dppe series (**1.9** – **[1.9][PF₆]**). The $C\equiv C$ bond is lengthened while the $C-C$ distance contracts slightly. The value of 1.236(9) Å for C_1-C_2 in **[1.9][PF₆]** is a little long for a $C\equiv C$ bond, indicating a change in the bonding along the carbon chain upon oxidation. While the neutral complex is essentially linear there is a much greater distortion in the mono-oxidised complex with angles at carbon of 167 and 177°.

Table 3. Crystallographic data for $[\{ML_n\}C\equiv CC\equiv C\{ML_n\}]^{n+}$.

Complex	$[ML_n]$	M-C ₁ , M-C _{1'}	C ₁ -C ₂ , C _{1'} -C _{2'}	C ₂ -C _{2'}	M-C ₁ -C ₂ , M-C _{1'} -C _{2'}	C ₁ -C ₂ -C ₃ , C ₂ -C ₃ -C ₄	Ref
1.4	Mn(dmpe) ₂ I	1.798(15)	1.263(17)	1.33(3)	n/r	n/r	31
[1.4][PF₆]	Mn(dmpe) ₂ I	1.763(2)	1.275(3)	1.313(5)	n/r	n/r	31
[1.4][BPh₄]₂	Mn(dmpe) ₂ I	1.768(4)	1.289(5)	1.295(5)	n/r	n/r	31
1.5	Re(NO)(PPh ₃)Cp*	2.037(5)	1.202(7)	1.389(5)	174.4(5)	176.8(6)	69
[1.5][PF₆]₂	Re(NO)(PPh ₃)Cp*	1.909(7)	1.263(10)	1.305(10)	168.5(7)	177.8(9)	69
		1.916(7)	1.260(10)		171.4(7)	175.4(9)	79
1.9	Fe(dppe)Cp*	1.889(9)	1.22(1)	1.37(1)	175(1)	177(1)	
		1.885(8)	1.22(1)		179(1)	176(1)	36
[1.9][PF₆]	Fe(dppe)Cp*	1.830(8)	1.236(9)	1.36(1)	167.0(6)	177(1)	37
[1.10][PF₆]₃	Fe(dippe)Cp*	1.79(1)	1.27(1)	1.30(1)	175.1(9)	178.7(9)	54
cis-1.11	Ru(PPh ₃) ₂ Cp	2.00(1)	1.20(2)	1.38(2)	177(1)	178(2)	38
trans-1.11	Ru(PPh ₃) ₂ Cp	2.001(3)	1.217(4)	1.370(6)	178.9(2)	177.2(3)	40
1.13	Ru(dppe)Cp*	2.001(3)	1.223(4)	1.382(4)	176.6(3)	176.9(3)	
		2.003(3)	1.218(4)		177.1(3)	178.0(3)	40
[1.13][PF₆]	Ru(dppe)Cp*	1.931(2)	1.248(3)	1.338(3)	165.6(2)	178.0(2)	40
[1.13][PF₆]₂	Ru(dppe)Cp*	1.858(5)	1.280(7)	1.294(7)	175.6(4)	176.7(6)	
		1.856(5)	1.269(7)		170.1(4)	174.2(6)	
	HC≡CC≡CH		1.218(2)	1.384(2)			76
	H ₂ C=C=C=CH ₂		1.283(5)	- 1.318(5)			78

n/r = not reported.

For the trication, **[1.10][PF₆]₃** the bond lengths show the C₄ bridge is intermediate between a butadiyne (1.218(2) / 1.384(2) Å) and butatriene (1.283(5) / 1.318(5) Å) formulation (C₁₋₂ 1.27(1), C_{2-2'} 1.33(1) Å).³⁷ The FeC₄Fe axis is essentially linear with bond angles at carbon of 175 - 177°. Comparison of the C-C bond distances with the mono-oxidised complex, **[1.9][PF₆]** (1.236(9) / 1.36(1) Å) indicates an elongation of the C₁₋₂ bond and a shortening of the C_{2-2'} bonds.

Two forms of **1.11** were structurally characterised differing in the relative arrangement of the two Ru(PPh₃)₂Cp fragments, these being *cis* and *trans*. Coordination about the ruthenium atoms is nearly octahedral and is entirely consistent with previously observed structures of complexes containing the Ru(PPh₃)₂Cp moiety. The Ru(dppe)Cp* analogue has also been characterised crystallographically as well as both the mono- and di-oxidised complexes. The most interesting parts of the structures relate to the coordination of the C₄ fragments.

The Ru-C distance is experimentally equivalent for the three neutral ruthenium complexes (2.00(1) – 2.003(3) Å). The C₁-C₂ bond distances of 1.20(2) – 1.223(4) Å are close to that of butadiyne (1.218(2) Å) as is the C₂-C_{2'} bond distance of 1.370(6) – 1.382(4) Å vs 1.384(2) Å).

Upon oxidation the Ru-C distance decreases (2.001(3)/2.003(3) – 1.931(2) – 1.858/1.856(5) Å) indicating a change in bonding from diyne to cumulenic. The C₁-C₂ and C₂-C_{2'} distances also confirm this with an increase in C₁-C₂ (1.218/1.223(4) – 1.248(3) – 1.269/1.280(7) Å) and a decrease in C₂-C_{2'} (1.382(4) – 1.338(3) – 1.294(7) Å). In the case of the di-oxidised complex **[1.13][PF₆]₂**, all the C-C distances are very similar (1.269(7) – 1.294(7) Å) and are close to that of butatriene (1.283(5) – 1.318(5) Å).

All the neutral complexes (excluding **1.4**) listed in Table 3 show C₁-C₂ distances between 1.217 – 1.233 Å and C₂-C_{2'} distances between 1.370 – 1.389 Å. The bond distances for butadiyne (1.218, 1.384 Å) are also listed in Table 3 and fall in the ranges for the butadiyndiyl complexes. This confirms that for all the complexes, the carbon chain is diyne in nature. The angles at carbon for all the complexes range

between $174.4 - 179^\circ$. This shows that there is a slight degree of bending in the carbon chains when compared to butadiyne (180°). It should be noted that the values reported for butadiyne are from a gas phase electron diffraction study. Therefore, the bending in the carbon chain of the butadiyndiyl complexes can be explained by crystal packing forces.

Upon oxidation the M-C distance decreases, C_1-C_2 increases and C_2-C_2' decreases for all the series listed in Table 3 (excluding **1.4**). This shows as the complexes are oxidised, there is a change in bonding along the MC_4M chain from diynyl towards cumulenenic. The iron complexes however, do not show such a large change and it is suggested that the di-oxidised complexes has a structure closer to diynyl than cumulenenic.

It is reported that the CC bond lengths show the C_4 bridge goes from a butadiyne (1.263(17), 1.33(3) Å) in the neutral complex, **1.4** to a butatriene formulation (1.289(5), 1.295(5) Å) in the di-oxidised complex, **[1.4][BPh₄]₂**. However, when the neutral complex, **1.4** is compared to butadiyne (1.218(2), 1.384(2) Å)⁷⁶ it appears the assignment of a butadiyne structure does not fit the data. In fact, the CC bond lengths more closely resemble those of butatriene (1.283(5) – 1.318(5) Å).⁷⁸ The mono-oxidised complex, **[1.4][PF₆]** has CC bond lengths in between those of the neutral and di-oxidised species.

(v) Spectroscopy (IR, NIR, UV/VIS)

The IR data for several complexes and the oxidised versions are listed in Table 4. The change in the $\nu(CC)$ frequencies as the complexes are oxidised gives an idea of the structure of the carbon bridge. In addition, the NIR transition for the mono-oxidised complexes is discussed. This inter-valence charge transfer band (IVCT) is characteristic of the formally mixed-valence nature $[M(II)/M(III)]$ of these complexes.⁸⁰

Table 4. IR data for $[\{ML_n\}C\equiv CC\equiv C\{ML_n\}]^{n+}$ (cm^{-1}).

Complex	ML_n	$n = 0$	$n = 1$	$n = 2$	Ref
1.4	Mn(dmpe) ₂ I	2127, 1805	2123, 1805	2107, 1607	³¹
1.5	Re(NO)(PPh ₃)Cp*	1964	1872	^a	⁶⁹
1.9	Fe(dppe)Cp*	1955, 1880	1973, 1880	2160, 1050	³⁶
1.11	Ru(PPh ₃) ₂ Cp	1971, 1956	1855	1767	⁵⁷

^aNot observed.

Further insight into the nature of the C₄ bridge in **[1.4][X]_n** ($n = 0, 1$; $X = PF_6$, $n = 2$; $X = BPh_4$) can be obtained from the IR spectra. The $\nu(CC)$ absorptions are only marginally shifted relative to those of the neutral complex for the mono-oxidised complex (2127, 1805 vs 2123, 1805 cm^{-1}). No $\nu(CC)$ absorptions are observed for the di-oxidised complex.

The IR spectra of the series **[1.5][PF₆]_n** ($n = 0 - 2$) show a decrease in energy for $\nu(CC)$ ($n = 0$, 1964; $n = 1$, 1872; $n = 2$, not observed cm^{-1}) and an increase in energy for $\nu(NO)$ ($n = 0$, 1623; $n = 1$, 1665; $n = 2$, 1719 cm^{-1}).⁶⁹ These trends show that the C₄ ligand goes from diynediyl in the neutral complex to cumulenic in the di-oxidised form. The mono-oxidised complex shows a IVCT band in the NIR spectra at ca 1200 nm. No solvent dependence was observed and thus this complex can be classified as a Class III complex.

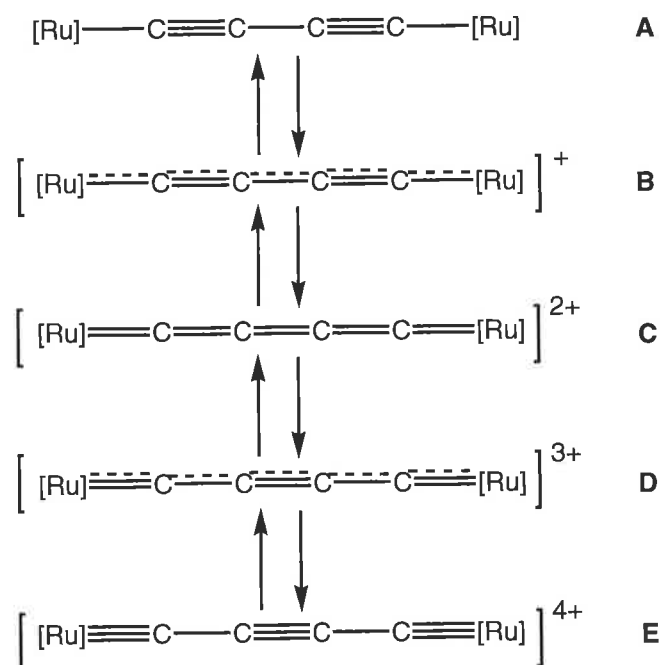
The IR spectra of **[1.9][PF₆]_n** ($n = 0$, 1955, 1880; $n = 1$, 1973, 1880; $n = 2$, 2160, 1950 cm^{-1}) show a shift toward the higher energy ($n = 0 < 1 < 2$).³⁶ This indicates that on oxidation there is little change in the bond order, which would be expected if the π -orbitals of the C₄ bridging group were to participate in the delocalisation of the spin density. The NIR spectra of the mono-oxidised complex shows a large IVCT band at ~1300 nm with virtually no solvent dependency (CH₃CN, 1298; MeOH, 1274; CH₂Cl₂, 1302 nm) which shows that the mono-oxidised complex behaves as a Class III system.

The IR $\nu(\text{CC})$ absorptions for $[\mathbf{1.11}][\text{PF}_6]_n$ ($n = 0 - 2$) are listed in Table 4 and show a steady decrease in frequency indicating the bond order is decreasing upon oxidation. The single $\nu(\text{CC})$ band for the mono-oxidised complex is midway between those of the related neutral and di-oxidised species. This observation provides strong evidence that the unpaired electron is delocalised over the molecule on the IR time scale (ca 10^{-13} s) and, consequently, that the metal centres are equivalent. A NIR transition at ~ 1950 nm is also observed for $[\mathbf{1.11}][\text{PF}_6]$ and is assigned to an IVCT. The position of ν_{max} was found to be solvent independent and was observed for $[\mathbf{1.5}][\text{PF}_6]$ and $[\mathbf{1.9}][\text{PF}_6]$. The $\nu(\text{CC})$ band at 1767 cm^{-1} for $[\mathbf{1.11}][\text{PF}_6]_2$ shows the complex has a cumulenic type structure.

Unfortunately, despite their apparent thermodynamic stability, efforts to prepare the tri- and tetra-oxidised species, by chemical oxidation of the di-oxidised complex were unsuccessful, primarily due to the lack of a suitable oxidising reagent. In order to gain insight in to the nature of the carbon bridge in these species a spectro-electrochemical study (IR, NIR, visible and UV), in which the species to be studied were generated by electrolysis in a modified spectrometer cell, was undertaken.

The electrogenerated tri-oxidised species is characterised by a single $\nu(\text{CC})$ band at 1627 cm^{-1} , the observation of which suggests a further decrease in the $\text{C}\equiv\text{C}$ bond order in the C_4 bridge.

The quadruply-oxidised species is highly reactive and was only observed as a transient species. The $\nu(\text{CC})$ band at 1936 cm^{-1} is likely to be due to a complex formed by a chemical reaction of the tetra-oxidised species. Scheme 11 shows the structural changes in the C_4 bridge associated with oxidation. While it is tempting to attribute the $\nu(\text{CC})$ band to the species indicated by structure **E** in Scheme 11, this is unlikely since this complex is centrosymmetric and the $\text{C}\equiv\text{C}$ is formally IR-inactive.



Scheme 11. Valence bond structures of $[1.11]^{n+}$ ($n = 0 - 4$).

(vi) *NMR Spectroscopy*

The carbons of the chain were observed in the ^{13}C labelled complex of **1.5** and showed two complex signals at δ 95.8/96.4 assigned to C_α and δ 117.5/116.4 assigned to C_β . The former was assigned from the phosphorous coupling. Oxidation of **1.5** to the dication causes the signals in the ^1H and ^{31}P NMR spectra to be shifted downfield. The dication is diamagnetic and the ^{13}C enriched version enabled the resonances of the C_4 bridge to be observed. A doublet of doublet of doublets at δ 305.1 (J_{CC} 77.0, 40.7 Hz, J_{CP} 12.3 Hz) was assigned to $\text{Re}=\text{C}$ while a doublet of doublets at δ 213.5 (J_{CC} 77.0, 40.7 Hz) was assigned to $\text{Re}=\text{C}=\text{C}$.

A low temperature ^{31}P NMR study of **1.9** shows two sharp singlets (C_7D_8 , δ 99.5, 110.9) with the same intensity. Upon warming the two signals broaden and coalesce at 200 K. In the ^{13}C NMR spectra, a triplet ($^2J_{\text{PC}} = 41$ Hz) at δ 99.7 was assigned to C_α while a singlet at δ 110.2 was assigned to C_β . The mono-oxidised species give only broad resonances in the ^1H NMR spectra and no ^{31}P NMR spectra could be obtained. This is due to the paramagnetic nature of this complex. The di-oxidised complex, $[1.9][\text{PF}_6]_2$ shows two singlets in the ^{31}P NMR spectra at δ 89.1 and 88.2. This upfield

shift is observed in the ^1H NMR spectra as well, where the Cp^* protons are observed as a singlet at δ -6.03.

Few comparisons can be made in the ruthenium series due to the limited solubility of the neutral complex, **1.11**. The carbons of the chain were not observed. Sharp, well-defined resonances were found in the ^1H NMR spectra of the isolated di-oxidised species, suggesting that this complex is diamagnetic. The Cp signal was shifted downfield in the ^1H and ^{13}C NMR spectra of the di-oxidised relative to the neutral complex.

In contrast to the $\{\text{ML}_n\}\text{C}\equiv\text{CC}\equiv\text{C}\{\text{ML}_n\}$ systems already discussed, the neutral complex **1.4** is a low-spin d^5 Mn(II) complex. The low-spin character of this complex is shown by NMR spectroscopy where the methylene protons of the dmpe ligand appear in a typical region for low-spin Mn(II)(dmpe) $_2$ complexes.^{81,82} The ^1H NMR resonances of the mono-oxidised complex, which has only one unpaired electron, are less paramagnetically shifted than the neutral complex. The di-oxidised complex is diamagnetic, again shown by ^1H NMR spectroscopy. No ^{13}C NMR data are reported.

(vii) ESR Spectroscopy

The delocalisation of the odd-electron in **[1.5][PF $_6$]** was probed by ESR.⁶⁹ An undecet (g 2.02, CH_2Cl_2) with an $A_{\text{iso,Re}}$ value of 98 G and broad individual lines (ΔH_{pp} 49 G) was observed. Rhenium has two isotopes with spin 5/2, but since the magnetic moments are very close they can be treated as a single spin system. The undecet indicates that the two rhenium atoms are equivalent on the rapid ESR time scale (ca. 10^{-9} s) and thus the odd electron is delocalised over both rhenium end groups.

The ESR spectrum of **[1.9][PF $_6$]** displays three features corresponding to the three components of the g -tensor as expected for low-spin d^5 Fe(III) with pseudo-octahedral geometry. A value of g_{iso} (2.102) was calculated and compares well with other Fe(III)-containing complexes.⁷ In contrast to **[1.9][PF $_6$]** the tri-cation **[1.10][PF $_6$] $_3$** is ESR silent in the 300 – 80 K range. At 4 K, however, a partially resolved signal is observed displaying two distinct g -tensor components ($g_1 = 2.5527$, $g_2 = 2.0308$). It is assumed

that the signal at 2.0308 corresponds to unresolved g_2 and g_3 components. The g values are quite different from those observed in **[1.10][PF₆]**.³⁷

No ESR experiments have been performed on the ruthenium C_4 systems to date.

(viii) ⁵⁷Fe Mössbauer Spectroscopy

⁵⁷Fe Mössbauer spectroscopy is a very sensitive probe for identifying the electronic environment of iron. Quadrupole splittings (QS) and isomer shifts (IS) can provide insight into the nature of the bonds to iron.^{7,83} A comparison of the ⁵⁷Fe Mössbauer spectra for **[1.9]ⁿ⁺** ($n = 0 - 2$) is shown in Table 5.

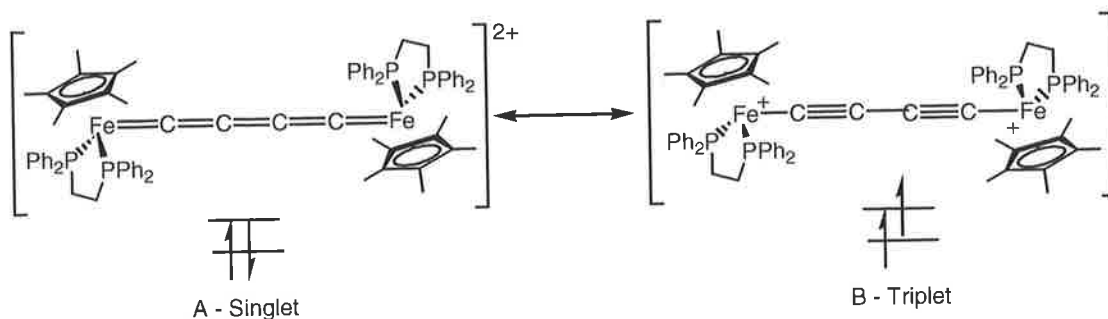
Table 5. Mössbauer data for **[1.9]ⁿ⁺** ($n = 0 - 2$).^a

n	QS (mm/s)	IS (mm/s)
0	2.07	0.27
1	1.32	0.21
2	1.05	0.18

^aAt T = 77 K. QS = quadrupole splitting, IS = isomer shift.

The QS of the mono-oxidised complex is close to the average value of the neutral and di-oxidised complexes. A consequence of the average value of QS should be a weak contribution from the bridging C_4 ligand to the delocalisation of the unpaired electron. The observation of a single doublet for the QS shows that the two iron nuclei are equivalent on the ⁵⁷Fe Mössbauer time scale (10^9 s⁻¹). The value of QS for the di-oxidised complex is half that of the neutral complex and is typical of pure Fe(III) centres. Thus the di-oxidised complex can be thought of as containing an Fe(III)- C_4 -Fe(III) fragment.

A spin equilibrium is observed for the di-oxidised complex, which has a singlet ground state. The separation between the singlet and triplet states, however, is so low ($J = -18$ cm⁻¹) that both are thermally populated even at liquid nitrogen temperature. As a dyndiyl structure is expected for the triplet state, the C_4 ligand mediates both energetic and magnetic communication between the metal termini. A schematic representation is shown in Scheme 12.



Scheme 12. Resonance structures of **[1.9][PF₆]₂**.

The decrease in the IS value as the complex is sequentially oxidised is consistent with a decrease in electron density at the metal centre.

Three 1-electron oxidations using one equivalent of [FcH][PF₆] (twice) and one equivalent of AgPF₆ were carried out successively to give the complexes **[1.10][PF₆]_n** (*n* = 0 – 3).

Table 6. ⁵⁷Fe Mössbauer data for **[1.10]ⁿ⁺** (*n* = 0 – 3).

<i>n</i>	QS (mm/s)	IS (mm/s)
0	2.06	0.26
1	1.33	0.24
2	1.047	0.191
3	0.985	0.163

^aAt *T* = 77 K. QS = quadrupole splitting, IS = isomer shift.

The trend in the ⁵⁷Fe Mössbauer data for **[1.10]ⁿ⁺** is similar to that of the related dppe series. The neutral complex gives a doublet QS (2.06 mm/s) typical of a pure iron(II) system. The spectrum of the tri-oxidised complex recorded at zero field showed a single doublet (77 K, mm/s vs Fe, IS = 0.163, QS = 0.985), unambiguously establishing that the two iron termini are equivalent on the ⁵⁷Fe Mössbauer time scale. The experimental QS might be compatible with two 17-electron Fe(III) termini,⁸⁴ but this does not allow the exclusion of an Fe(II)-cumulenyl formulation. Indeed, it was found recently that complexes with an Fe=C double bond give ⁵⁷Fe Mössbauer spectra very similar to those of the Fe(III) 17-electron species [Cp*Fe(dppe)(R)][PF₆].⁸⁵ Moreover, it is noteworthy that the ⁵⁷Fe Mössbauer spectrum of the tri-oxidised

species displays a single doublet with parameters close to the di-oxidised complex. These results indicate that the oxidation of the di-oxidised complex could not take place at the metal centres, but rather on the all-carbon chain.

SECTION C

(i) Heterobimetallic complexes, $\{ML_n\}C\equiv CC\equiv C\{ML'_m\}$

While the study of homobimetallic C_4 complexes has steadily increased, the heterobimetallic C_4 complexes are a newly discovered area. Table 7 lists the known complexes $\{ML_n\}C\equiv CC\equiv C\{M'L'_m\}$.

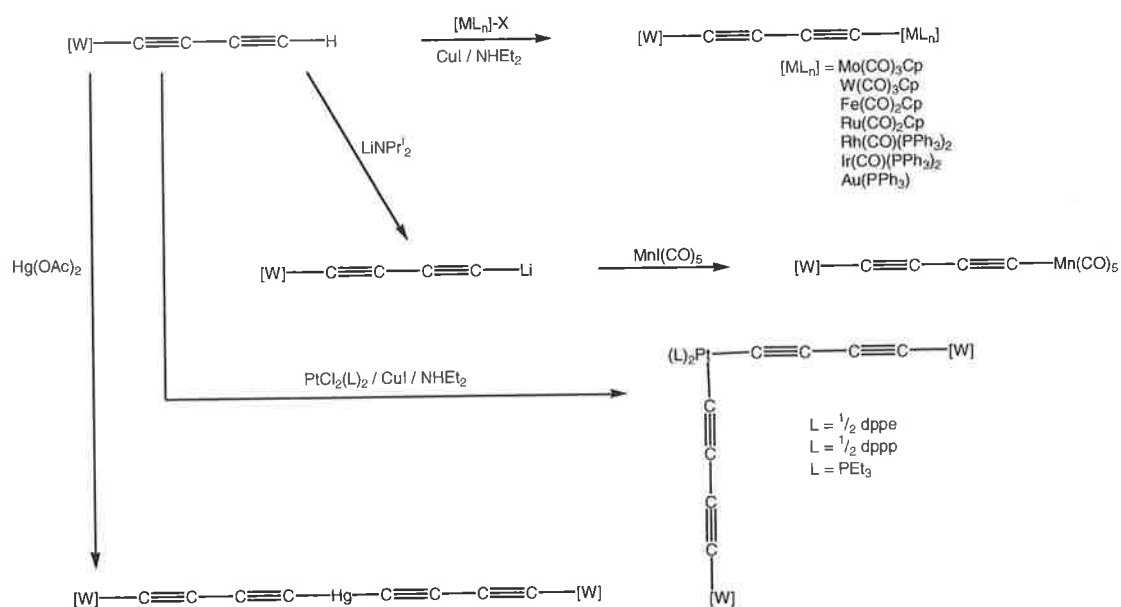
Table 7. Heterobimetallic butadienyldiyl complex, $\{ML_n\}C\equiv CC\equiv C\{M'L'_m\}$.

$\{ML_n\}$	$\{M'L'_m\}$	Ref
Re(NO)(PPh ₃)Cp*	<i>trans</i> -Rh(CO)(PPh ₃) ₂	86
Re(NO)(PPh ₃)Cp*	<i>trans</i> -Pd(PEt ₃) ₂ Cl	86
Fe(dppe)Cp*	Fe(CO) ₂ Cp*	73
Fe(dppe)Cp*	Fe(CO) ₂ Cp [#]	73
Fe(CO)(L)Cp; L = CO, PPh ₃	M(CO) ₃ Cp; M = W, Mo	48
W(CO) ₃ Cp	Mo(CO) ₃ Cp	63
W(CO) ₃ Cp	Mn(CO) ₅	63
W(CO) ₃ Cp	M(CO) ₂ Cp; M = Fe, Ru	63
W(CO) ₃ Cp	Ru(PPh ₃) ₂ Cp	63
W(CO) ₃ Cp	M(CO)(PPh ₃) ₂ ; M = Rh, Ir	63
W(CO) ₃ Cp	Au(PPh ₃)	63
Fe(dppe)Cp*	Re(NO)(PPh ₃)Cp*	87

Cp[#] = pentaphenyl-cyclopentadiene.

In addition to the complexes listed in Table 7 the following heterobimetallic complexes are known containing two $\{ML_n\}C\equiv CC\equiv C$ groups attached to a third metal centre:⁶³ *cis*-Pt(L)₂(C≡CC≡C{W(CO)₃Cp}) (L = ½ dppe, ½ dppp, PEt₃) and Hg(C≡CC≡C{W(CO)₃Cp})₂.

Scheme 13 shows the versatility of the $\{ML_n\}C\equiv CC\equiv CH$ complex as the diynyl hydrogen can be substituted with metal fragments from Groups 6–12.⁶³



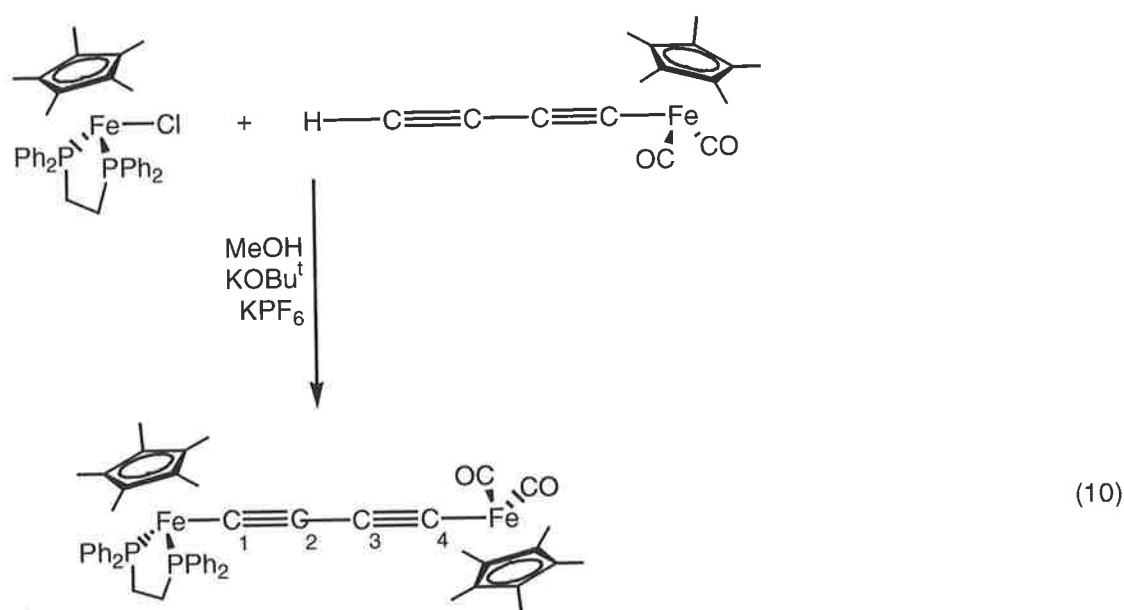
Scheme 13. Syntheses of heterobinuclear complexes containing the $W(CO)_3Cp$ group.⁶³

Of the $\{ML_n\}C\equiv CC\equiv C\{M'L'_m\}$ complexes mentioned, electrochemical studies of very few have been reported. In the case of *trans*- $\{Cp^*(NO)(PPh_3)Re\}C\equiv CC\equiv C\{PdCl(PEt_3)_2\}$, the cyclic voltammogram showed one reversible and one irreversible oxidation, assigned to the rhenium centres and the palladium centre respectively. When compared to similar rhenium-containing complexes it was concluded that there was very little electronic communication between the rhenium and palladium centres.⁸⁶ The ESR spectrum generated *in situ* by adding an equivalent of $[Fch][PF_6]$ to *trans*- $\{Cp^*(NO)(PPh_3)Re\}C\equiv CC\equiv C\{PdCl(PEt_3)_2\}$ in an ESR tube showed the odd electron is not delocalised as is the case for **1.5**. Instead, the odd electron is localised mainly on the rhenium centre.

(ii) $\{Cp^*(dppe)Fe\}C\equiv CC\equiv C\{Fe(CO)_2Cp^*\}$ (**1.23**).

(a) *Synthesis*

Treatment of $Fe(C\equiv CC\equiv CH)(CO)_2Cp^*$, KPF_6 and $KOBu^t$ in MeOH with one equivalent of $FeCl(dppe)Cp^*$ gave the binuclear butadiyndiyl complex, $\{Cp^*(dppe)Fe\}C\equiv CC\equiv C\{Fe(CO)_2Cp^*\}$ (**1.23**) as shown in Equation 10.⁷³



Synthesis of **1.23**.

(b) *Structural characterisation*

The structure of **1.23** was determined by X-ray diffraction. The data shows that the Fe-C and $C\equiv C$ bond lengths are shorter on the electron-rich side of the molecule than on the electron-poor side. This is in agreement with the polarisation of the electron density from the donor $Fe(P)_2$ centre to the acceptor $Fe(CO)_2$ group. Comparison of the bond angles shows a deviation from linearity at the $Fe(CO)_2$ moiety when compared to the $Fe_5(P)_2$ end [$Fe-C_1-C_2$ $177.8(8)^\circ$, $Fe-C_4-C_3$ $172.0(1)^\circ$]. The C_1-C_2 bond length ($1.21(1)$ Å) is very close to that of butadiyne ($1.218(2)$ Å) whereas the C_3-C_4 bond is significantly longer ($1.24(1)$ Å). The length of the C_2-C_3 single bond ($1.36(1)$ Å) is shorter than the C-C bond distance of butadiyne ($1.384(2)$ Å). As a result of this, a strong electronic communication between the two iron fragments is believed to occur via the carbon bridge.⁷³

(c) Cyclic Voltammetry

The cyclic voltammogram of **1.23** shows two 1-electron oxidations at -0.36 and 0.74 V. The first oxidation is reversible and indicates the thermal stability of the mono-oxidised complex. The second oxidation becomes reversible at higher scan rates. A comparison between the potentials of the mononuclear complexes and **1.23** is given in Table 8.

Table 8. Electrochemical for **1.23** and related complexes.⁷³

Complex	E_1 (V)	E_2 (V)	ΔE (V)
1.23	-0.36	0.74^a	1.10
$\text{Fe}(\text{C}\equiv\text{CC}\equiv\text{CSiMe}_3)(\text{dppe})\text{Cp}^*$	0.00		
$\text{Fe}(\text{C}\equiv\text{CC}\equiv\text{CSiMe}_3)(\text{CO})_2\text{Cp}^*$	1.15^b		

^aQuasi-reversible. ^bNon-reversible.

The comparison of the oxidation potentials of **1.23** with those of the related monomers confirms the strong electronic communication between the metal centres across the carbon bridge. Moreover, the role of the C_4 bridge is illustrated by comparison of the oxidation potential of $\text{Fe}(\text{C}\equiv\text{CC}\equiv\text{CSiMe}_3)(\text{dppe})\text{Cp}^*$. The first oxidation potential of **1.23** is 0.3 V more thermodynamically favourable than for $\text{Fe}(\text{C}\equiv\text{CC}\equiv\text{CSiMe}_3)(\text{dppe})\text{Cp}^*$.

The increase of the reversibility of the second oxidation process when compared to $\text{Fe}(\text{C}\equiv\text{CC}\equiv\text{CSiMe}_3)(\text{CO})_2\text{Cp}^*$ and the decrease in the potential indicates a strong communication across the C_4 bridge and a stabilisation of the di-oxidised complex.

On the basis of the CV results, oxidation of **1.23** was carried out with $[\text{FcH}][\text{PF}_6]$ to give the mono-oxidised complex $[\text{1.23}][\text{PF}_6]$.

(d) ^{57}Fe Mössbauer Data

The ^{57}Fe Mössbauer parameters of mono-nuclear and binuclear half-sandwich iron species are very different for Fe(II) and Fe(III). Table 9 lists the ^{57}Fe Mössbauer parameters for **1.23** and $[\text{1.23}][\text{PF}_6]$.

Table 9. ^{57}Fe Mössbauer fitting parameters for $[\mathbf{1.23}][\text{PF}_6]_n$ ($n = 0 - 2$).^a

n	QS (mm/s)	QS (mm/s)	IS (mm/s)	IS (mm/s)
	Fe(II)	Fe(III)	Fe(II)	Fe(III)
0	1.973		0.237	
	1.974		0.029	
1	-0.028	0.206	1.990	0.992

^aT = 80 K. QS = quadrupole splitting, IS = isomer shift.

The ^{57}Fe Mössbauer spectrum of **1.23** shows two doublets with almost the same QS. Depending on the electron density at the iron centres, the IS are quite different and are assigned to $\text{Fe}(\text{dppe})\text{Cp}^*$ (IS 0.237 mm/s) and $\text{Fe}(\text{CO})_2\text{Cp}^*$ (IS = 0.029 mm/s) on the basis of the IS values for the mononuclear complexes. The spectrum of $[\mathbf{1.23}][\text{PF}_6]$ also shows two doublets. The QS values clearly show that oxidation is mainly localised on the $\text{Fe}(\text{dppe})\text{Cp}^*$ fragment. Characteristic parameters of a 17-electron low-spin Fe(III) centre are observed, whereas the IS and QS of the $\text{Fe}(\text{CO})_2\text{Cp}^*$ moiety corresponds to a pure Fe(II) centre.

(e) Spectroscopy

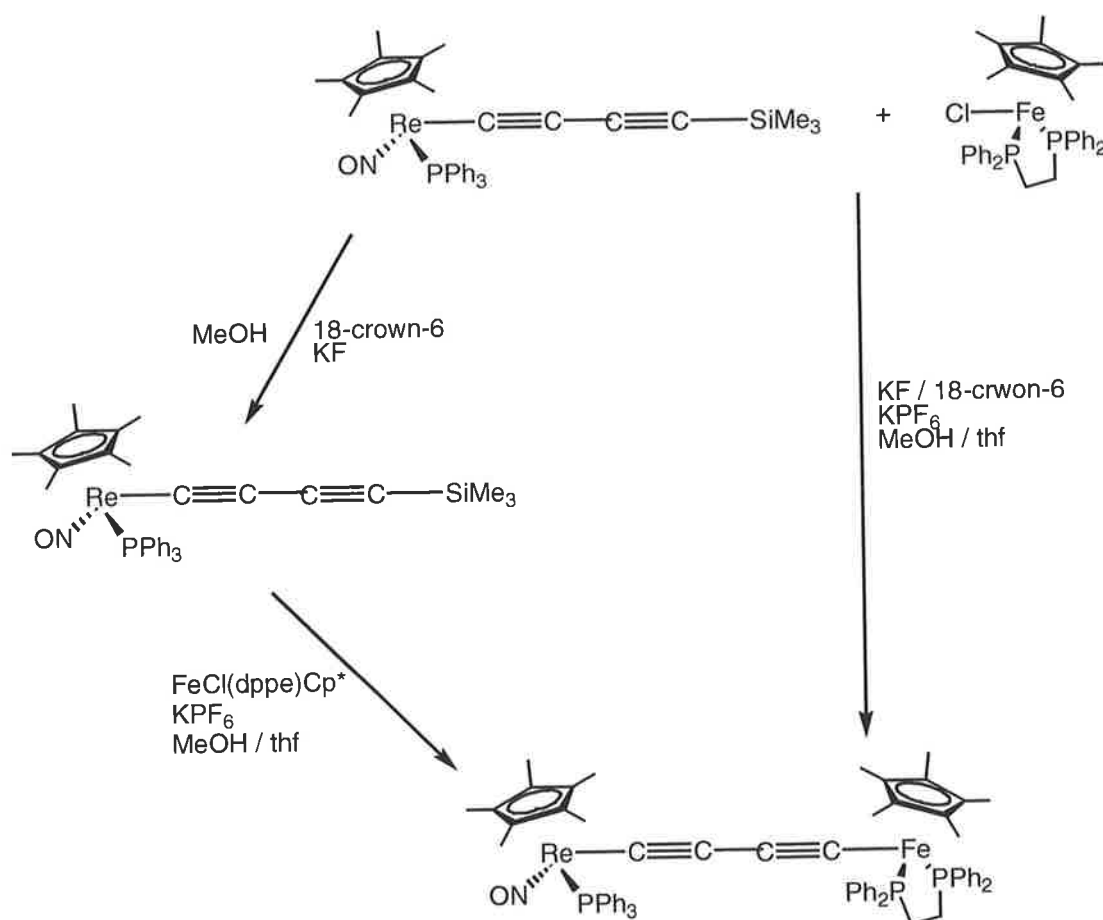
The ESR spectra of $[\mathbf{1.23}][\text{PF}_6]$ was run at 80 K and exhibited three well-separated features corresponding to the three components of the **g** tensor. The resolution of the high-field component into a 1/2/1 triplet was observed, in agreement with a hyperfine coupling with two equivalent ^{31}P nuclei.

A weak and broad band at 1600 nm in the NIR spectra was observed and was assigned to an IVCT. This band was absent in both the neutral and *in situ* generated derivative $[\mathbf{1.23}][\text{PF}_6]_2$.

(iii) $\{\text{Cp}^*(\text{PPh}_3)(\text{NO})\text{Re}\}\text{C}\equiv\text{CC}\equiv\text{C}\{\text{Fe}(\text{dppe})\text{Cp}^*\}$ (**1.24**).

(a) Synthesis

The heterobimetallic complex, $\{\text{Cp}^*(\text{PPh}_3)(\text{NO})\text{Re}\}\text{C}\equiv\text{CC}\equiv\text{C}\{\text{Fe}(\text{dppe})\text{Cp}^*\}$ (**1.24**) is made as shown in Scheme 14.⁸⁷

Scheme 14. Synthesis of **1.24**.

The trimethylsilylbutadiynylrhenium complex was protodesilylated (KF , KPF_6 , 18-crown-6) and then coupled with Fe(dppe)Cp^* to give the mixed rhenium/iron butadiynediyl complex **1.24**. A similar coupling could be effected in a two-pot reaction as shown in Scheme 14 where the trimethylsilyl group is removed before the addition of the FeCl(dppe)Cp^* but the yields were lower.

(b) Structural characterisation

The crystal structure of **1.24** was determined and the relevant bond lengths and angles are compared with those found in the diiron and dirhenium complexes in Table 10.

Table 10. Selected crystallographic data.^a

Complex	M ₁ -M ₂	C≡C	≡C-C≡	M-C≡	M-C≡C	C-C-C	Ref
1.24	7.730	1.209(8)/Fe 1.224(9)/Re	1.370(9)	1.895 (6)/Fe 2.029(6)/Re	176.6(5)/Fe 169.6(6)/Re	177.4(7) 178.3(7)	⁸⁷
1.5	7.828	1.202(7)	1.389(5)	2.037(5)	174.4(5)	176.8(6)	⁶⁹
1.9	7.584	1.22(1)	1.37(1)	1.889(9)	175(1)	177(1)	⁷⁹
		1.22(1)		1.885(8)	179(1)	176(1)	

^aBond lengths in Å, bond distances in °.

General features, such as the formally octahedral geometry at each metal, are in accord with past structures in this series.^{36,69} Most bond lengths and angles fall within previously established ranges. As expected, the Fe-C≡ bond (1.895 Å) is shorter than the Re-C≡ bond (2.209 Å). The C≡C and C-C bond lengths of 1.209/1.224 and 1.370 Å are comparable to those of butadiyne (1.218, 1.384 Å)⁷⁶ and confirm the diyndiyl nature of the C₄ bridge. The Re-C₄-Fe linkage deviates somewhat from linearity. The Re-C≡C angle is most bent (169.6°), followed by the larger Fe-C≡C angle (176.6°). Most {ML_n}C≡CC≡C{ML_n} complexes already discussed feature bond angles of more than 170° (see values in Table 2). Despite the moderate bending, the iron-rhenium separation (7.730 Å) is longer than the iron-iron distances in **1.9** (7.584 Å)⁷⁹ and shorter than the rhenium-rhenium distance in **1.24** (7.828 Å).⁶⁹

(c) Cyclic Voltammetry

The cyclic voltammogram of **1.24** shows two chemically reversible 1-electron oxidations separated by 0.73 V, corresponding to the formation of the mono and dication, respectively. A third oxidation attributed to the trication is observed next to the solvent edge (1.33 V). Comparison of the E° values of **1.24** with the iron and rhenium homometallic analogues shows the iron fragment Fe(dppe)Cp* is more electron releasing than the rhenium fragment Re(NO)(PPh₃)Cp* (Table 11).

Table 11. Electrochemical data.^a

Complex	{ML _n }	E ₁	E ₂	E ₃	1+/2+	2+/3+	Ref
1.24	Re(NO)(PPh ₃)Cp	-0.50	0.23	1.33	0.73	1.10	⁸⁷
	Fe(dppe)Cp*						
1.5	Re(NO)(PPh ₃)Cp*	0.01	0.54		0.53		⁶⁹
1.9	Fe(dppe)Cp*	-0.69	0.03	0.95	0.72	0.92	³⁶

^a0.1 M [NBu₄]PF₆ in CH₂Cl₂ at 20°C; Pt electrodes; scan rate 100 mV/s; V vs SCE; E°([FcH]/[FcH]⁺) = +0.46 V.

The oxidation potentials of **1.24** fall between those of the parent complexes, **1.9**³⁶ and **1.5**.⁶⁹ The first oxidation potential is presumed to have dominant iron character due to the iron fragment being more electron releasing than the rhenium fragment. The oxidation of the iron centre in **1.24** is 0.19 V more difficult than that in **1.9**. This suggests that replacement of one of the iron endgroups in **1.9** by a rhenium endgroup decreases the electron density at iron. Similarly, the second oxidation of **1.24** is 0.31 V more facile than the second oxidation of **1.5**. Thus, from every oxidation state perspective, the iron fragment Fe(dppe)Cp* is more electron releasing than the rhenium fragment Re(NO)(PPh₃)Cp*.

The mono- and di-oxidised complexes, [1.24][PF₆] and [1.24][PF₆]₂ were synthesised by addition of 0.95 and 2.0 equivalents of [FcH][PF₆] respectively.

(d) ⁵⁷Fe Mössbauer Data

The ⁵⁷Fe Mössbauer data for [1.24][PF₆]_n are given in Table 12. At zero field and 80 K, the neutral complex **1.24** gives a doublet typical of a pure iron(II) system (1.983 mm/s).⁸⁸

Table 12. ⁵⁷Fe Mössbauer fitting parameters for [1.24][PF₆]_n (n = 0 – 2).^a

n	IS (mm/s)	QS (mm/s)
0	0.255	1.983
1	0.191	0.995
2	0.138	0.957

^aT = 80 K. QS = quadrupole splitting, IS = isomer shift.

Comparison with the ^{57}Fe Mössbauer data for **1.9** (Table 5) shows that replacement of one of the iron fragments by a rhenium centre reduces the isomer shift (0.255 vs 0.27 mm/s). The QS for the mono-oxidised complex is reduced relative to the neutral complex (0.995 vs 1.983 mm/s). This is characteristic of a 17-electron centre, and unambiguously indicates that the iron centre is best represented by the oxidation state (III). The steady decrease in isomer shift (0.255, 0.191, 0.138 mm/s) is consistent with a decrease in electron density at the iron centre as the complex is oxidised.

(e) Spectroscopy

The ESR spectrum for the mono-oxidised complex showed an isotropic and strongly coupled signal ($g_{\text{iso}} = 2.0346$). The coupling of the unpaired electron to rhenium, which can be approximated as a simple nuclear spin 5/2 system, is apparent in the six-line pattern. The g_{iso} value is close to that of the related iron complex, **1.9** and is consistent with the dominant iron character of the radical.

The di-oxidised complex also gave an ESR signal, which is broader than the signal observed for the mono-oxidised complex. The broadening is due to the two unpaired electrons on the molecule, which greatly reduce the relaxation time. To further probe the electronic structure of the di-oxidised complex, magnetic susceptibility experiments were undertaken. The large negative magnetic coupling constant J (-175 cm^{-1}) indicates the complex has a singlet ground state. However, the energy gap between the $S = 0$ and 1 states is sufficiently small (0.35 kcal/mol) that at ambient temperature the triplet state is appreciably populated (at 300 K: $S/T = 37/63$). Thus, there are two rapidly equilibrating species which explains why the sample, although paramagnetic at room temperature, gives only a slightly shifted ^1H NMR spectrum. As observed previously with mono-oxidised complexes,⁷³ a weak NIR band was observed (2500 nm, ϵ ca. $340 \pm 5 \text{ M}^{-1}\text{cm}^{-1}$, $\Delta\nu_{1/2} = 2150 \text{ cm}^{-1}$). This band is assigned to an IVCT transition and is absent in both the neutral and di-oxidised complexes.

SECTION D

(i) Ferrocene containing $-(C\equiv C)_n-$ complexes

A recent issue of the *Journal of Organometallic Chemistry* was dedicated to ferrocene, celebrating fifty years since its discovery.⁸⁹ Ferrocene acts as a stable, reversible 1-electron redox system, leading to its use as a reference for electrochemistry in organic solvents.⁹⁰

Several groups have investigated ferrocene complexes containing an acetylide moiety and reported their electrochemical behaviour.⁹¹⁻¹⁰⁶ A few examples of these are shown in Figure 5.

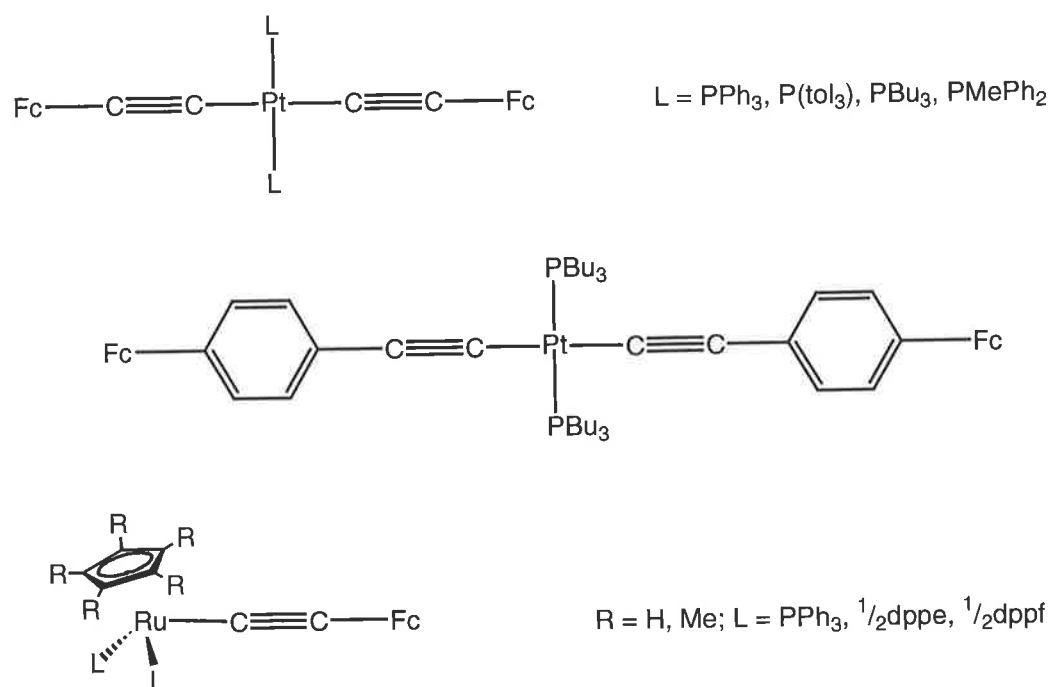


Figure 5.

Fewer complexes have been synthesised and the electrochemical properties reported containing a $(C\equiv C)_n$ moiety with $n \geq 2$.¹⁰⁶⁻¹¹² In most cases there is some electronic interaction between the ferrocenyl groups. Figure 6 shows a few examples of these complexes.

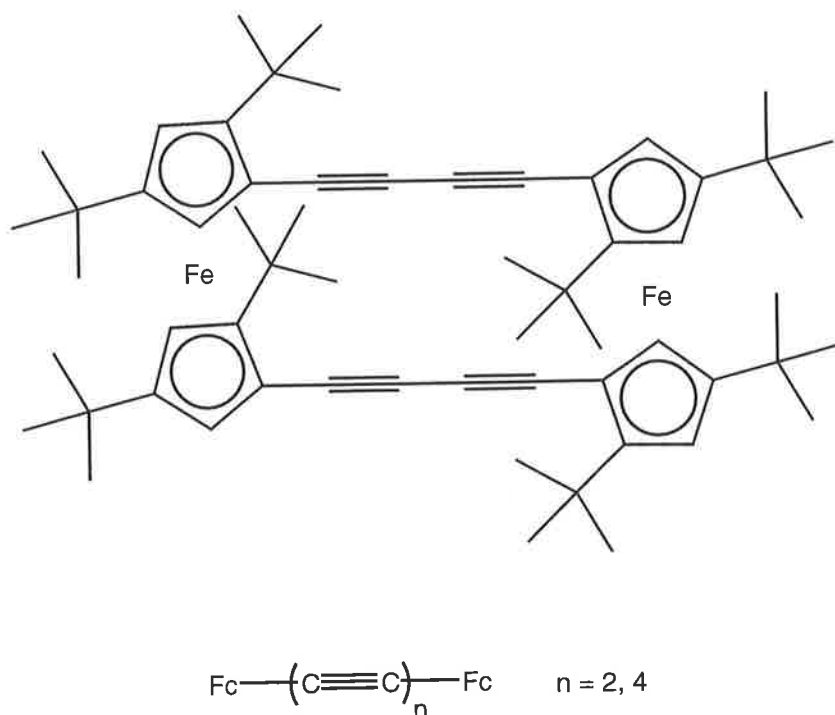


Figure 6.

Many complexes containing two ferrocenyl moieties have been synthesized to investigate the effectiveness of the bridging groups between the redox nuclei for the internuclear interaction.¹¹³ When two ferrocenyl moieties interact electronically with each other, the redox potential splits into two, and the difference between the two can be used to evaluate the magnitude of the interaction.

Of interest are the complexes with two ferrocenyl moieties linked by a carbon chain. The C_4 and C_8 complexes are synthesised by the homocoupling of the ferrocenyl acetylide or butadiynyl complexes respectively (Equation 10).¹¹⁴ The cyclic voltammetry data is listed in Table 13.



Table 13. Electrochemical data for $\text{Fc}(\text{C}\equiv\text{C})_n\text{Fc}^a$.

n	E_1 (V)	E_2 (V)
2	0.62	0.72
4	0.70	

^a CH_2Cl_2 , 298 K; Pt electrodes, $[\text{NBu}_4][\text{BF}_4]$ relative to Pt reference electrode vs $\text{FcH} / [\text{FcH}]^+ = 0.46$ V.

When the two ferrocenyl moieties are linked by a butadiynyl bridge, two oxidation waves are observed. However, these waves are very close together (ΔE° 0.1 V) and close to the limits of cyclic voltammetry in distinguishing the actual potentials. There is some electronic communication between the ferrocenyl endgroups in the butadiynyl case, although the small gap shows this to be minimal. When the chain is lengthened to eight carbons, only a single oxidation wave is observed, due to the simultaneous oxidation of the two ferrocenyl groups.

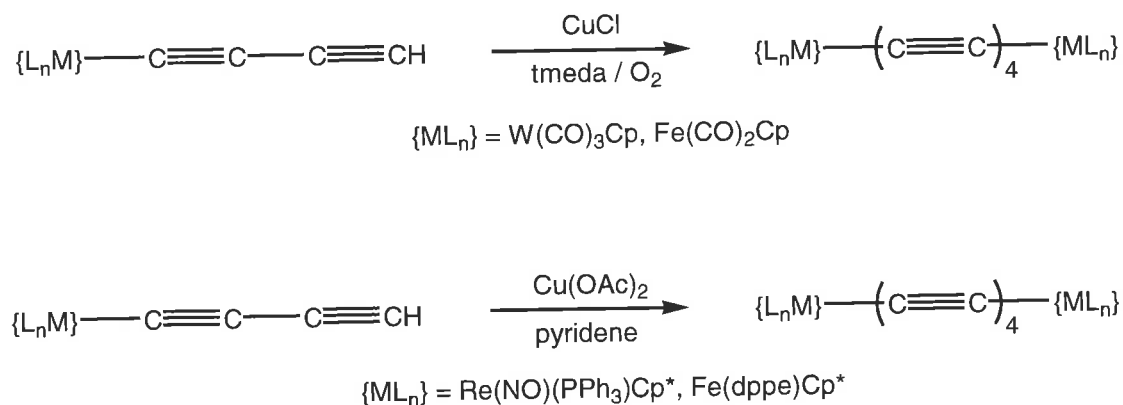
SECTION E

(i) Extended Chains

While complexes containing a four-carbon bridge are now numerous, those with longer chains are less so. This is due to the additional challenges presented by their syntheses. Three different methodologies have been used to realise the syntheses of these longer chain complexes.

(a) $\{\text{ML}_n\}(\text{C}\equiv\text{C})_4\{\text{ML}_n\}$

Like the oxidative coupling of $\{\text{ML}_n\}\text{C}\equiv\text{CH}$ complexes mentioned previously to give the C_4 binuclear complexes, carbon chains eight atoms in length can be conveniently prepared by oxidative coupling of two $\{\text{ML}_n\}\text{C}\equiv\text{CC}\equiv\text{CH}$ units. Again, Hay or Eglinton coupling conditions are used and several complexes of the type $\{\text{ML}_n\}(\text{C}\equiv\text{C})_4\{\text{ML}_n\}$ have been reported (Scheme 15).^{30,115-117}



Scheme 15.

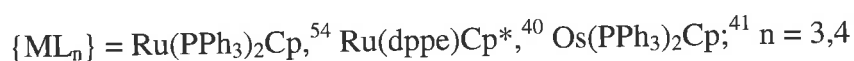
The complex $\{Cp^*(dppe)Fe\}(C\equiv C)_4\{Fe(dppe)Cp^*\}$ was synthesised using an Eglinton coupling (Scheme 15).¹¹⁷ The CV showed two reversible 1-electron oxidations at -0.23 and 0.20 V. The separation between the waves (ΔE° 0.43 V) gives a K_c of 2×10^7 . The first oxidation is thermodynamically more favourable in the C_8 bridged dimer than in the C_4 monomer, $\{Cp^*(dppe)Fe\}C\equiv CC\equiv CH$ ($E^\circ = 0.02$ V).⁷

The mono-oxidised complex, $[\{Cp^*(dppe)Fe\}(C\equiv C)_4\{Fe(dppe)Cp^*\}][PF_6]$ was synthesised by reaction of the neutral complex with 0.97 equiv of $[FcH]PF_6$ at low temperature. The IR spectrum shows a decrease in the $\nu(CC)$ stretching frequencies ($1879, 1784\text{ cm}^{-1}$) when compared to the neutral complex ($2109, 1949\text{ cm}^{-1}$). This indicates the odd electron is fully delocalised between the two iron centres on the very rapid IR time scale (10^{-13} s). This lower $\nu(CC)$ frequency in the mono-oxidised complex indicates the carbon chain adopts a structure intermediate between a polyacetylenic chain containing alternating triple and single bonds and a cumulenic form with double bonds.

Similarly, Eglinton coupling was used to synthesise the rhenium complex, $\{Cp^*(NO)(PPh_3)Re\}(C\equiv C)_4\{Re(NO)(PPh_3)Cp^*\}$ (Scheme 15).¹¹⁶ Like the iron complex, the CV showed two reversible 1-electron oxidations. Again, there was an increase in the first oxidation potentials in comparison to the C_4 analogue (0.24, 0.52 vs 0.01, 0.54 V). While it can be seen that there is little difference between the second oxidation potentials it is the gap between the two oxidation waves that is important here. In the C_4 complex, $\Delta E^\circ = 0.53$ V while in the C_8 complex, $\Delta E^\circ = 0.28$ V. This

decrease in ΔE° implies a decrease in electronic communication between the two metal centres. The corresponding K_c value shows a decrease from 1.1×10^9 to 5.9×10^4 indicating a decrease in the thermodynamic stability of the mono-oxidised complex as shown by Equation 1. For this reason, the oxidised species were not stable enough to be isolated.

Direct reactions of the trimethylsilyl protected polyynes, $\text{Me}_3\text{Si}(\text{C}\equiv\text{C})_n\text{SiMe}_3$ ($n = 3, 4$), in the presence of KF with the corresponding metalhalides gave the dinuclear C_6 and C_8 complexes, $\{\text{ML}_n\}(\text{C}\equiv\text{C})_n\{\text{ML}_n\}$ $\{\text{ML}_n\} = \text{Ru}(\text{PPh}_3)_2\text{Cp}$,⁵⁴ $\text{Ru}(\text{dppe})\text{Cp}^*$,⁴⁰ $\text{Os}(\text{PPh}_3)_2\text{Cp}$;⁴¹ $n = 3, 4$ (Equation 12).



The CVs of these complexes showed four 1-electron oxidations. A comparison of chain length versus electronic communication is shown in Table 14 for several $\{\text{ML}_n\}(\text{C}\equiv\text{C})_n\{\text{ML}_n\}$ ($n = 2 - 4$) series.

As the chain is lengthened the first oxidation potential moves to higher values i.e. the complexes became harder to oxidise. The difference between the first and second potentials is smaller as the chain is lengthened. As mentioned previously, the difference between these two potentials is an indication of the degree of electronic communication between the two metal centres. Thus, as the carbon chain is increased in length, the electronic communication is diminished.

Table 14. Electrochemical data for $\{ML_n\}(C\equiv C)_n\{ML_n\}$.^a

n	$\{ML_n\}$	E ₁	E ₂	E ₃	E ₄	1+/2+	2+/3+	3+/4+	^b K _c	ref
2	Re(NO)(PPh ₃)Cp*	0.01	0.54			0.53			9.2 x 10 ⁸	69
3	Re(NO)(PPh ₃)Cp*	0.10	0.48			0.38			2.7 x 10 ⁶	68
4	Re(NO)(PPh ₃)Cp*	0.24	0.52			0.28			5.4 x 10 ⁴	68
2	Fe(dppe)Cp*	-0.69	0.03	0.95		0.72	0.92		1.5 x 10 ¹²	36
3	Fe(dppe)Cp*	-0.42	0.11			0.63			4.5 x 10 ¹⁰	7
4	Fe(dppe)Cp*	-0.23	0.20			0.43			1.9 x 10 ⁷	117
2	Ru(PPh ₃) ₂ Cp	-0.23	0.41	1.03	1.68	0.64	0.62	0.65	6.6 x 10 ¹⁰	57
3	Ru(PPh ₃) ₂ Cp	0.06	0.52	1.07	1.41	0.46	0.55	0.34	6.0 x 10 ⁷	118
4	Ru(PPh ₃) ₂ Cp	0.24	0.58	1.07	1.31	0.34	0.49	0.24	5.6 x 10 ⁵	118
2	Ru(dppe)Cp*	-0.43	0.23	1.02	1.51	0.66	0.79	0.49	1.4 x 10 ¹¹	40
3	Ru(dppe)Cp*	-0.14	0.32	1.05	1.33	0.46	0.73	0.28	6.0 x 10 ⁷	118
4	Ru(dppe)Cp*	0.03	0.43	1.09	1.28	0.40	0.66	0.19	5.8 x 10 ⁶	118

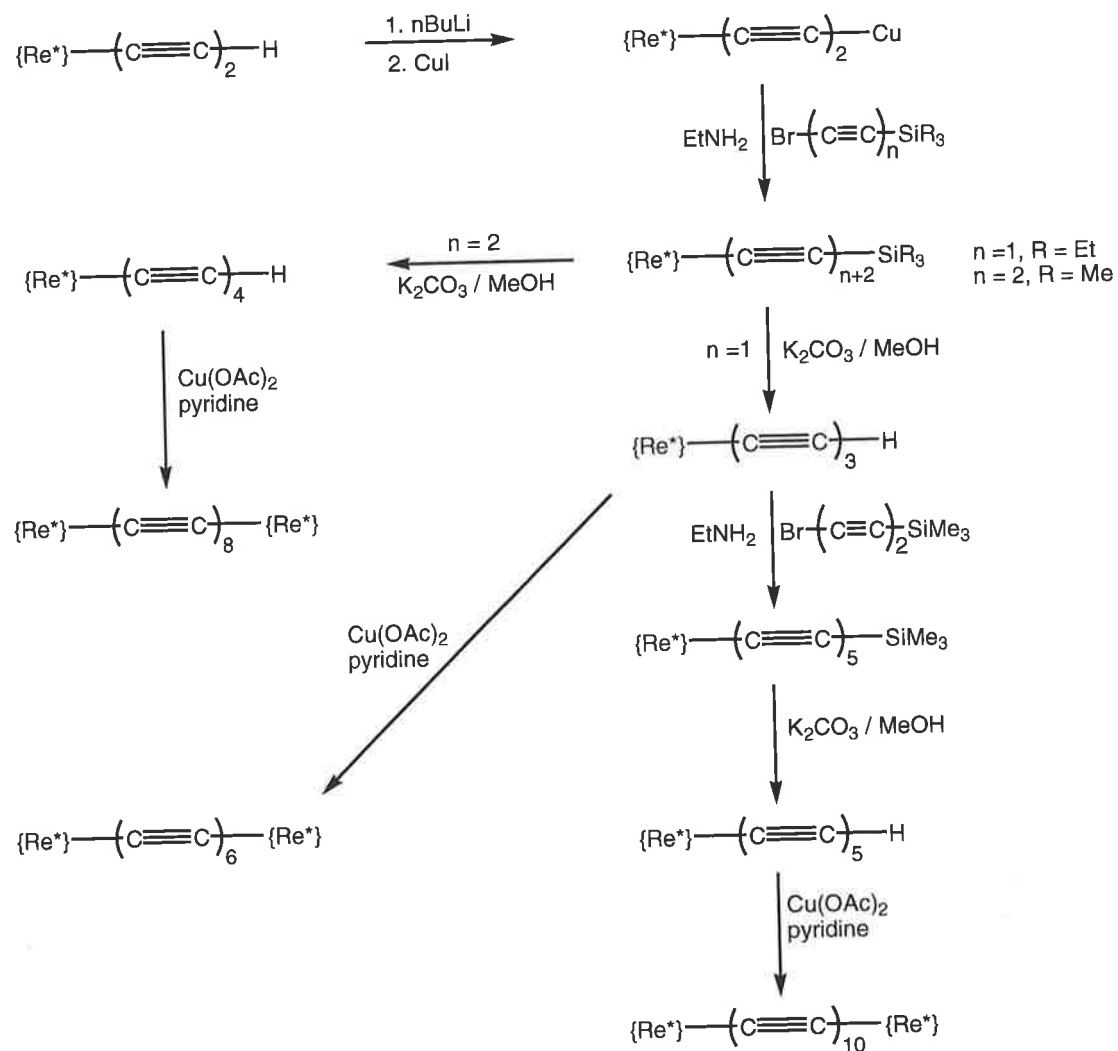
^aSee individual references for details of the electrochemical experiments, potentials given in volts (V). ^bK_c calculated for T = 298 K.

Interestingly, in both the ruthenium series, the value for the third oxidation remains relatively constant despite lengthening of the chain. The fourth oxidation potential moves to lower values reversing the trend in the first and second oxidations. It is not fully understood why this is the case and further work is being done to design complexes whose fourth oxidation potential is lowered enabling the synthesis of the first tetra-cation of a poly-yndiyl complex.

The K_c values are an indication of the stability of the mono-oxidised species. As the chain is lengthened, K_c decreases indicating that the stability of these mono-oxidised complexes also decreases. To date, only Lapinte et al. have isolated a mono-oxidised complex with greater than four carbons in the bridge, that being $\{\text{Cp}^*(\text{dppe})\text{Fe}\}(\text{C}\equiv\text{C})_4\{\text{Fe}(\text{dppe})\text{Cp}^*\}$.

(b) $\{ML_n\}(\text{C}\equiv\text{C})_n\{ML_n\}$, $n > 4$

By far, the longest metal-capped sp-carbon wires reported to date come from the laboratory of Gladysz and co-workers. They have successfully applied Cadiot-Chodkiewicz coupling reactions to metal butadiynyl chemistry and have isolated binuclear complexes of the formula, $\{\text{Cp}^*(\text{NO})(\text{PPh}_3)\text{Re}\}(\text{C}\equiv\text{C})_n\{\text{Re}(\text{NO})(\text{PPh}_3)\text{Cp}^*\}$ with $n = 2, 3, 4, 6, 8$ and 10 . The sequential reactions leading to the formation of $n = 6, 8$ and 10 are shown in Scheme 16.

Scheme 16. $\{Re^*\} = Re(NO)(PPh_3)Cp^*$.

A comparison of the oxidation potentials for the $\{\text{Cp}^*(\text{NO})(\text{PPh}_3)\text{Re}\}(\text{C}\equiv\text{C})_n\{\text{Re}(\text{NO})(\text{PPh}_3)\text{Cp}^*\}$ series is given in Table 15.

Table 15. Redox data for $\{\text{Cp}^*(\text{NO})(\text{PPh}_3)\text{Re}\}(\text{C}\equiv\text{C})_n\{\text{Re}(\text{NO})(\text{PPh}_3)\text{Cp}^*\}$.⁶⁸

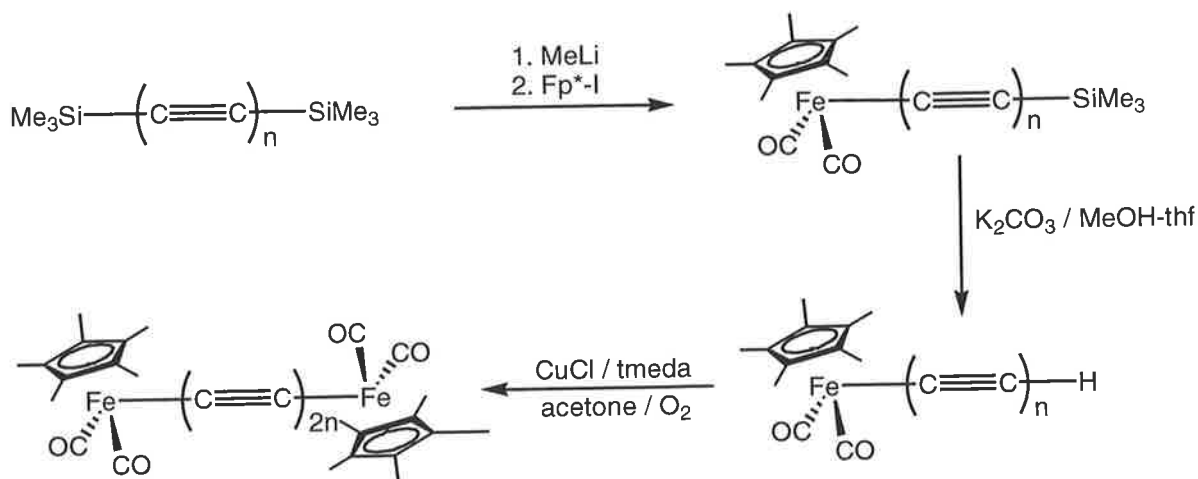
n	E ₁	E ₂	ΔE°	K _c
4	0.01	0.54	0.53	1.1 x 10 ⁹
6	0.10	0.48	0.48	3.0 x 10 ⁶
8	0.24	0.52	0.38	5.9 x 10 ⁴
10	0.43	0.63	0.20	2.6 x 10 ³
12	0.46	0.65	0.19	1.7 x 10 ³
16	0.57	0.66	0.09	34
20	0.64			

Conditions: $(7 - 9) \times 10^{-5}$ M in 0.1 M $[\text{Bu}_4\text{N}]\text{BF}_4$ / CH_2Cl_2 at 22.5 ± 1 °C: Pt working and counter electrodes, potential (V) vs Ag wire pseudo-reference: scan rate, 100 mV/s: $[\text{FcH}]/[\text{FcH}]^+ = 0.46$ V.

As the chain lengthens, the first oxidation potentials become thermodynamically less favourable. The second oxidation potentials are less strongly affected. Consequently, ΔE° decreases as the chain is lengthened and thus, electronic communication decreases. With $n = 20$, only a single presumably 2-electron oxidation is observed. This indicates the chain length at which the two rhenium endgroups start to behave independently, at least in a redox sense. The K_c values also decrease indicating the thermodynamic stability of the mono-oxidised complexes decreases as the chain is lengthened. Attempts to isolate the oxidised complexes with greater than four carbons in the chain have been unsuccessful to date. Recently, Gladysz et al. have changed the PPh₃ ligand for PAr₃ (Ar = 4-C₆H₄CH₃, 4-C₆H₄-*t*-C₄H₉, 4-C₆H₄C₆H₅, *c*-C₆H₁₁)³³ in an attempt to stabilise the mono-oxidised complexes. However, this did not enable the isolation of the mono-oxidised complexes.

Akita and Moro-oka have described the synthesis and characterisation of several polyynediyl complexes using the $\text{Fe}(\text{CO})_2\text{Cp}^*$ fragment (Fp*).^{115,119,120} The syntheses are similar to that used by Gladysz and co-workers,⁶⁸ although the formation of the initial

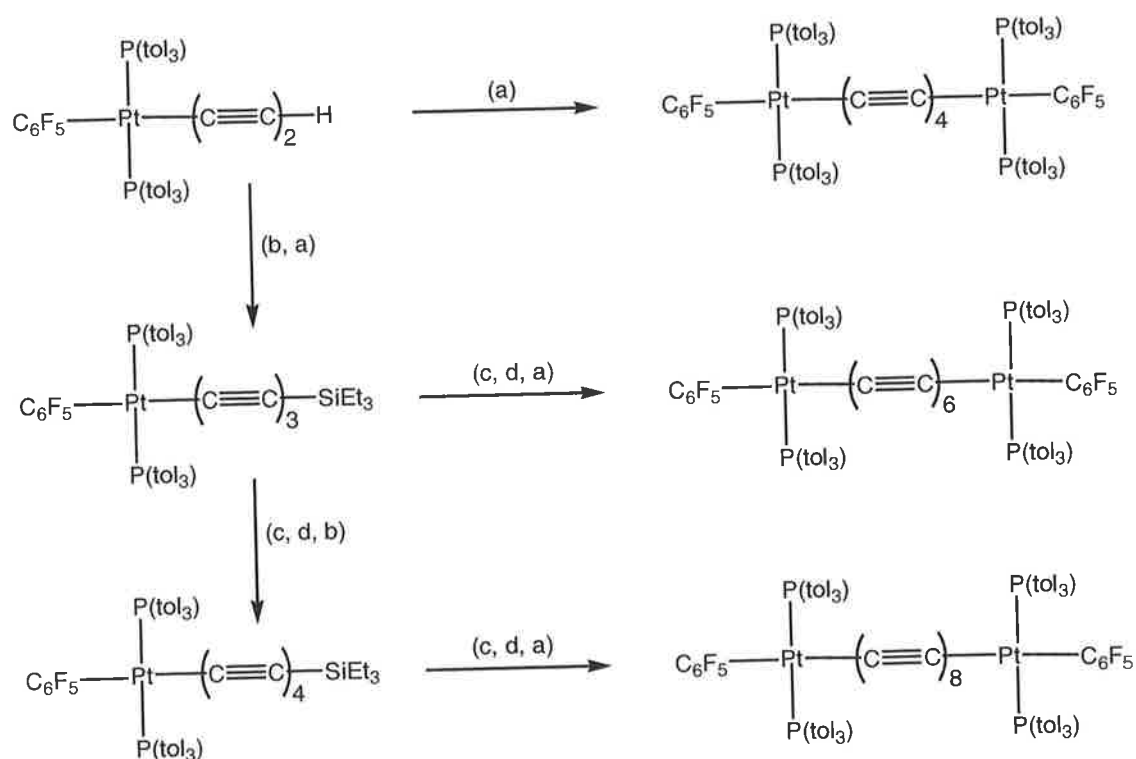
(trimethylsilyl)poly-ynyl complex is via metathesis between the $\text{FeI}(\text{CO})_2\text{Cp}^*$ fragment and ((trimethylsilyl)poly-ynyl)lithium as shown in Scheme 17.



Scheme 17. $n = 2, 3$.

The poly-ynyl complexes were then coupled using the Hay conditions to give poly-ynediyl complexes with 8 and 12 carbons in the chain.^{115,120} While no electrochemical studies were undertaken to ascertain the nature of the carbon bridge and its bonding to the metal centres, spectroscopic and structural data were obtained. A downfield shift was noted for the ^{13}C resonance of C_α as the carbon bridge was lengthened. It was suggested that this is due to the increase in contribution of the vinylidene structure. It is well established that the α -carbon of vinylidene complexes are deshielded and usually appear downfield ca 300 ppm.¹²¹ A shift of the IR $\nu(\text{CO})$ to higher energies is also observed as the carbon chain is lengthened. Both these observations were explained by the increased contribution of the zwitterionic vinylidene structure. This form has the negative charge developed on the carbon rod and may be more effectively stabilised by delocalisation over a longer carbon chain.

With the decreasing stabilities of the longer homologues in the $\{\text{Cp}^*(\text{NO})(\text{PPh}_3)\text{Re}\}\{\text{C}\equiv\text{C}\}_n\{\text{Re}(\text{NO})(\text{PPh}_3)\text{Cp}^*\}$ series,⁶⁸ Gladysz and co-workers turned their attention to the platinum complexes $\{(\text{P}(\text{tol})_3)_2(\text{Ar})\text{Pt}\}(\text{C}\equiv\text{C})_n\{\text{Pt}(\text{Ar})(\text{P}(\text{tol})_3)_2\}$ ($\text{Ar} = \text{tol}$, $n = 8, 12$;¹²² $\text{Ar} = \text{C}_6\text{F}_5$, $n = 8, 12, 16$ ¹²³). To date they have prepared complexes with up to 16 carbon atoms in the chain (Scheme 18) and have structurally characterised all of them.



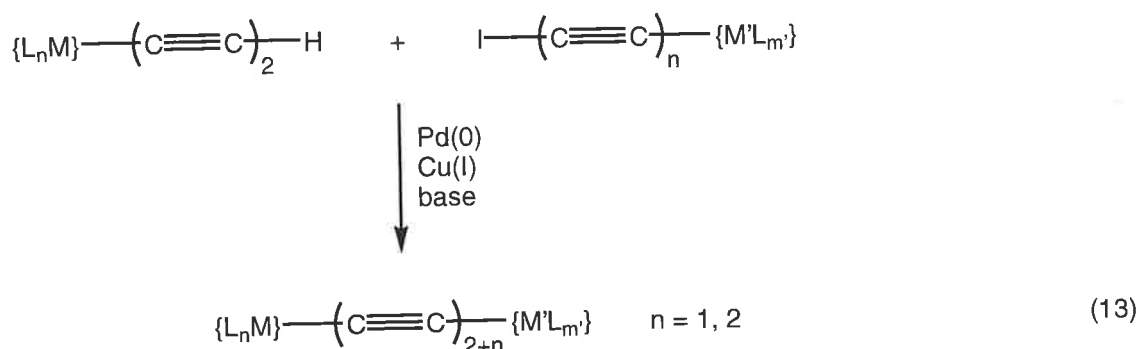
Scheme 18. (a) O_2 , acetone, cat. CuCl/tmeda . (b) $\text{HC}\equiv\text{CSiEt}_3$ (excess). (c) Wet $[\text{Bu}_4\text{N}]\text{F}$, thf. (d) SiClMe_3 .

The hexatriynyl- and octatetraynyl-platinum complexes are not stable enough in the C_6F_5 series to be isolated. Thus, the C_{12} and C_{16} complexes were obtained by in situ desilylation of the triethylsilyl-protected poly-yne followed by coupling under Hay conditions.

There is a distinct bending in the chain when compared to shorter carbon chain complexes. The complex $\{(\text{C}_6\text{F}_5)(\text{P}(\text{tol})_3)_2\text{Pt}\}(\text{C}\equiv\text{C})_6\{\text{Pt}(\text{P}(\text{tol})_3)_2(\text{C}_6\text{F}_5)\}$ shows the highest degree of bending. Unlike the other complexes prepared in this series the bond angles in the carbon chain reinforce each other. That is, the bending is in one direction. Accordingly, the Pt-Pt distance is 5.9 % shorter than the sum of the intervening bond lengths.

The synthesis of the p-tolyl-platinum series was not hampered by the instability of the poly-ynyl complexes. Both the C_8 and C_{12} complexes were structurally characterised, but the bending of the chains was not as noticeable as in the C_6F_5 series described above.

Another possible method for chain extension which has not been utilised is the palladium/copper catalysed coupling of a butadiynyl complex, $[\text{ML}_n]\text{C}\equiv\text{CC}\equiv\text{CH}$, with an iodo-acetylide or iodo-butadiynyl complex, $[\text{ML}_n](\text{C}\equiv\text{C})_n\text{I}$ (Equation 13). No iodo-butadiynyl complexes are known. The few organic iodo-butadiynes reported are thermally unstable and tend to explode upon heating.¹²⁴⁻¹²⁶ Thus, this route has not been used to synthesise poly-yndiyl complexes.



SECTION F

(i) Gold containing complexes

Gold(I) chemistry continues to excite researchers. This stems, in part, from its linear two-coordination¹²⁷⁻¹³¹ and from the property of *aurophilicity*,^{132,133} or the weak intramolecular attractions between gold atoms which are displayed in many of its compounds. The former results in formation of rigid-rod polymeric materials,^{134,135} currently of interest for their unusual photo-emission¹³⁶ and non-linear optical properties,¹³⁷ while *aurophilic* effects have resulted in the construction of systems having a variety of unusual geometries.¹³⁸ It is well known that singly charged heavy metal complex cation AuL^+ (L = neutral ligand) is isolobal with the cation HgR^+ (R = acido ligand).¹³⁹ Both these metals commonly form 14-electron linear complexes QAuL or QHgR (Q = organic ligand). It is also expected that the AuL^+ moiety behaves like a proton.

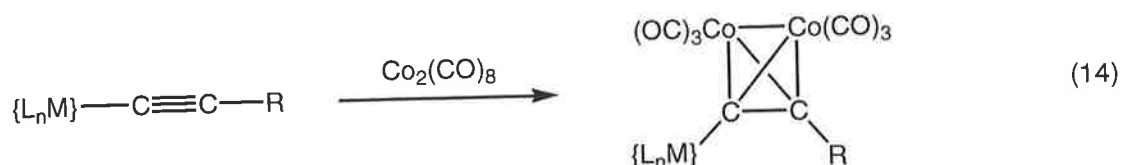
Others have used the linear two-coordinate geometry of gold(I), in particular, to link alkynyl ligands, thereby generating molecular rods, squares, rectangles and sundry other geometries,¹⁴⁰ together with catenanes, all of which form readily by self

assembly.¹⁴¹ Extension to cyclic and polymeric materials containing dialkynylaryl,¹⁴² isocyanide¹⁴³ and alkynylisocyanide ligands^{134,135} as the carbon linkers has also been achieved.

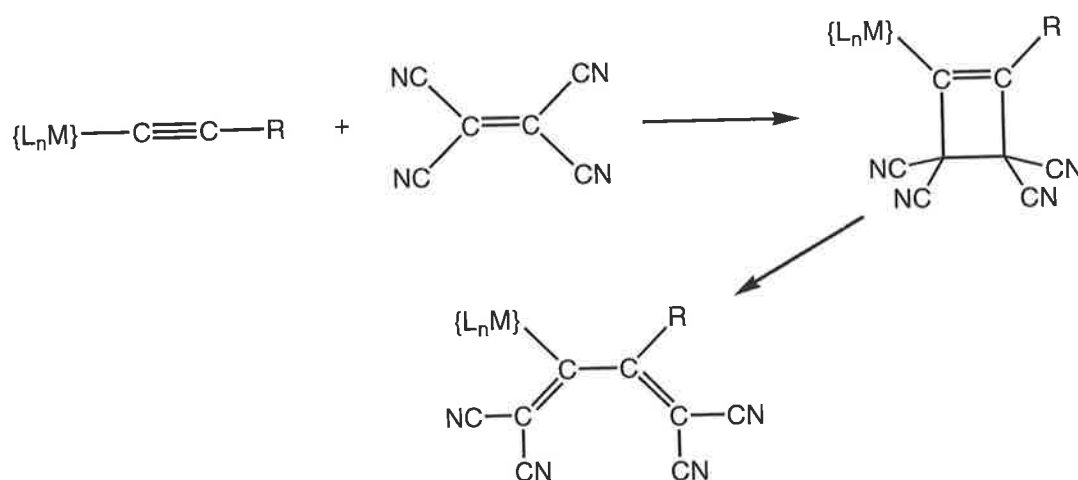
Several gold(I) complexes have been used as precursors for alkynylgold(I) derivatives. These include $\text{AuCl}(\text{L})$ ($\text{L} = \text{PPh}_3, \text{SC}_4\text{H}_8$),^{144,145} $(\text{AuCl})_2(\mu\text{-dppm})$ ¹⁴⁶ and $[\text{ppn}][\text{Au}(\text{acac})_2]$.¹⁴⁷ The dppm complex is notable for the presence of an aurophilic interaction between the two gold atoms, resulting in the two Cl atoms being on the same side of the molecule.¹⁴⁶ A similar structure has been found for $\{\text{Au}(\text{C}\equiv\text{CBu}^t)\}_2(\mu\text{-dppm})$.¹⁴⁸ It was hoped that this feature would generate novel systems in which the two diyne units also occupied sites on the same side of the molecule. Formation of molecular rectangles based on the $\text{Au}_2(\mu\text{-dppm})$ subunit is also possible, complexes such as $\{\text{Au}(\text{C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{C})\}_2(\mu\text{-PPh}_2\text{C}_6\text{H}_4\text{PPh}_2)$ having been described previously.¹³⁷ The lability of the acac ligands in $[\text{Au}(\text{acac})_2]^-$ in reactions of compounds containing acidic CH, NH, PH or SH groups enables an extensive range of neutral and anionic gold(I) complexes to be prepared.¹⁴⁷

Some gold(I) complexes of 1,3-butadiyne have been reported recently by this research group and are summarized in Scheme 19.¹⁴⁹ Reaction of buta-1,3-diyne with $\text{AuCl}(\text{PPh}_3)$ and $(\text{AuCl})_2(\mu\text{-dppm})$ in the presence of base gave the diyne complexes $\text{Au}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{PPh}_3)$ and $\{\text{Au}(\text{C}\equiv\text{CC}\equiv\text{CH})\}_2(\mu\text{-dppm})$, respectively. Similar reaction of $\text{W}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{CO})_3\text{Cp}$ with the two gold(I) complexes gave the heteronuclear diyndiyls $\text{W}\{\text{C}\equiv\text{CC}\equiv\text{C}[\text{Au}(\text{PPh}_3)]\}(\text{CO})_3\text{Cp}$ and $\{\text{Au}(\text{C}\equiv\text{CC}\equiv\text{C}[\text{W}(\text{CO})_3\text{Cp}])\}_2(\mu\text{-dppm})$. Reaction of $[\text{ppn}][\text{Au}(\text{acac})_2]$ with the appropriate diynes afforded $[\text{ppn}][\text{Au}(\text{C}\equiv\text{CC}\equiv\text{CH})_2]$, $[\text{ppn}][\text{Au}\{\text{C}\equiv\text{CC}\equiv\text{C}[\text{W}(\text{CO})_3\text{Cp}]\}_2]$, $[\text{ppn}][\text{Au}\{\text{C}\equiv\text{CC}\equiv\text{C}[\text{Au}(\text{PPh}_3)]\}_2]$ and $[\text{ppn}][\text{Au}(\text{C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CPh})_2]$; the latter anion was also obtained as the very unstable NMe_4 salt. The reaction between $\{\text{Au}(\text{C}\equiv\text{CC}\equiv\text{CH})\}_2(\mu\text{-dppm})$ and $\{\text{Au}(\text{OTf})\}_2(\mu\text{-dppm})$ likely afforded *cyclo*- $\{\text{Au}_2(\mu\text{-C}\equiv\text{CC}\equiv\text{C})(\mu\text{-dppm})\}_2$, although this compound was not structurally characterised.

or confirming the nature of metal complexes containing di- or poly-ynyl ligands (Equation 14). In most cases the $\text{Co}_2(\text{CO})_6$ groups can be removed oxidatively using Ce(IV) to regenerate the original complex.^{54,150}



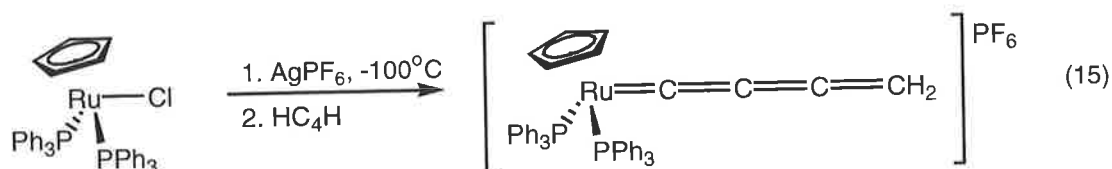
Cycloaddition of tetracyanoethylene (tcne) to $\text{C}\equiv\text{C}$ triple bonds is another characteristic reaction of σ -alkynyl or poly-ynyl ligands on transition metals.¹⁵⁵⁻¹⁶¹ In this case, the di- or poly-ynyl ligands cannot be regenerated from the resulting cyanocarbon ligand, but the reactions offer further confirmation of the presence of the former. In general, the reactions proceed *via* deep green paramagnetic intermediates, to give cyclobutenyl complexes, which may isomerise to the ring opened butadienyl complexes (Scheme 20).



Scheme 20. Cycloaddition of tcne to a metal acetylide.

The addition of nucleophiles or electrophiles to $[\text{ML}_n]\text{C}\equiv\text{CC}\equiv\text{CR}$ or $[\text{ML}_n]\text{C}\equiv\text{CC}\equiv\text{C}[\text{ML}_n]$ complexes has been a relatively uncharted area of research.

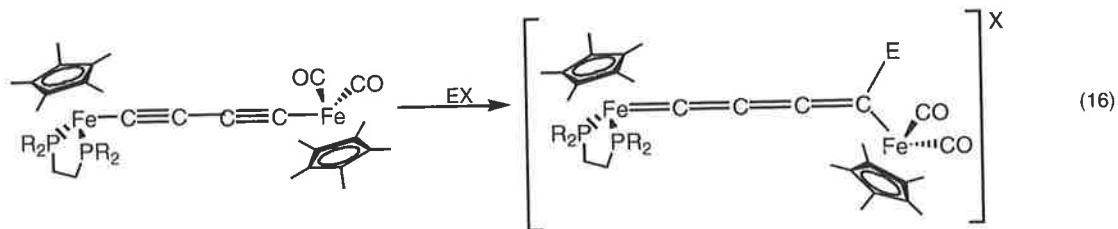
Bruce et al. have described the reactions of an intermediate butatrienylidene complex, $[\text{Ru}(=\text{C}=\text{C}=\text{C}=\text{CH}_2)(\text{PPh}_3)_2\text{Cp}][\text{PF}_6]$ synthesised from the reaction shown in Equation 15.¹⁶²



Formation of a butatrienylidene complex.

This butatrienylidene complex has not been isolated. If left to warm up to r.t it will react with the slightest amount of H₂O to form the known acetylenyl derivative, Ru{C≡C-C(O)Me}(PPh₃)₂Cp.¹⁶³ When prepared in the presence of an amine, the heteroallenylidene [Ru{=C=C=CMe(NR₂)}(PPh₃)₂Cp][PF₆] is formed.¹⁶²

Lapinte et al. have studied the reactions of the donor-acceptor complex, {Cp*(PP)Fe}C≡CC≡C{Fe(CO)₂Cp*} (PP = dppe, dippe) with HBF₄ and MeOTf (Equation 16).¹⁶⁴ This led to the isolation and structural characterisation of the first thermally stable butatrienylidene complexes.



R = Ph, ⁱPr; E = H, Me; X = BF₄, OTf.

No other products were isolated from the reactions where a different carbon of the chain had been attacked. Ab initio calculations have shown that the related ligands :C=CHC≡CH and :C=C=C=CH₂ have almost the same stability,¹⁶⁵ but only the butatrienylidene has been observed experimentally. Thus, it can be concluded from these electrophilic reactions, that the most electron rich carbon is attached to the most electron poor metal centre. It is also thought that there is no steric control over the reaction.

SECTION G

Work described in this thesis

To study changes in the properties and reactivities of complexes as the carbon chain is lengthened stepwise, Chapter 2 describes the synthesis and properties of complexes bearing both $\text{W}(\text{CO})_3\text{Cp}$ and redox-active Fc endgroups with carbon chains of 2, 4, 6 and 8 atoms in length.

A route into heterobimetallic complexes bearing two redox active endgroups, $\text{Ru}(\text{PPh}_3)_2\text{Cp}$ and $\text{Fe}(\text{dppe})\text{Cp}^*$ is described in Chapter 3. A detailed investigation into their spectroscopic and electronic properties is reported. Chemical oxidation allows isolation of the derived complexes. All complexes are compared to the parent homobimetallic complexes as well as to the mixed iron/rhenium butadiyndiyl complex.

The chemistry of butadiynyl complexes containing gold has only recently received attention.¹⁴⁹ Chapter 4 describes the syntheses of several gold butadiynyl and polyynyl complexes bearing phosphine ligands, together with an account of some of their reactions.

Some related complexes are described in Chapter 5 as well as the syntheses of some useful starting materials used in the previous chapters.

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Chapter 2

Complexes Containing Carbon Chains Capped by Ferrocenyl and $W(CO)_3Cp$ Groups

INTRODUCTION

During the fifty years that have passed since the announcements of the discovery of ferrocene^{1,2} the development of its chemistry and subsequent utility have included the recognition of its redox properties and its subsequent employment as a reference compound for electrochemical measurements.³ Due to its high stability and reversible redox characteristics, ferrocene has been extensively used as starting materials in the synthesis of versatile ferrocenyl derivatives.⁴ For example, ferrocenyl derivatives are important electron-transfer systems for molecular electronics owing to their characteristic redox behaviours,⁵ and they could also be expected to play a key role of a chemical probe of the electron-transfer process in biological molecules.⁶ Aromatic heterocyclic systems covalently linked to ferrocenyl fragments have shown interesting electrochemical behaviour, suggesting electronic communication between the ferrocenyl group and another coordinated metal centre through π -conjugated systems.⁷⁻¹⁴

Many complexes containing two ferrocenyl moieties linked by various groups have been synthesised to investigate the effectiveness of internuclear interactions via the bridging groups.¹⁵ When two ferrocenyl moieties interact electronically with each other, the difference between the two potentials can be used to evaluate the magnitude of the interaction. The larger difference between these potentials, the larger the degree of electronic communication between the ferrocenyl groups via the bridge.

Many synthetic and electrochemical investigations of ferrocenyl containing metal complexes have focussed on those with a carbon chain bridging the ferrocenyl moiety and another redox active metal centre.

Sato et al.¹⁶ have focussed on complexes of the type $\text{FcC}\equiv\text{C}\{\text{RuP}_2\text{Cp}'\}$ ($\text{P} = \text{PPh}_3$, $1/2\text{dppe}$; $\text{Cp}' = \text{Cp}, \text{Cp}^*$) and more recently their ruthenocene analogues.^{17,18} Cyclic voltametric data suggest a large electron delocalisation occurs between the iron or ruthenium atom of the metallocene moiety and the ruthenium atom of $\text{RuP}_2\text{Cp}'$ in the one-electron oxidised complexes which occurs across the ethynediyl bridge.

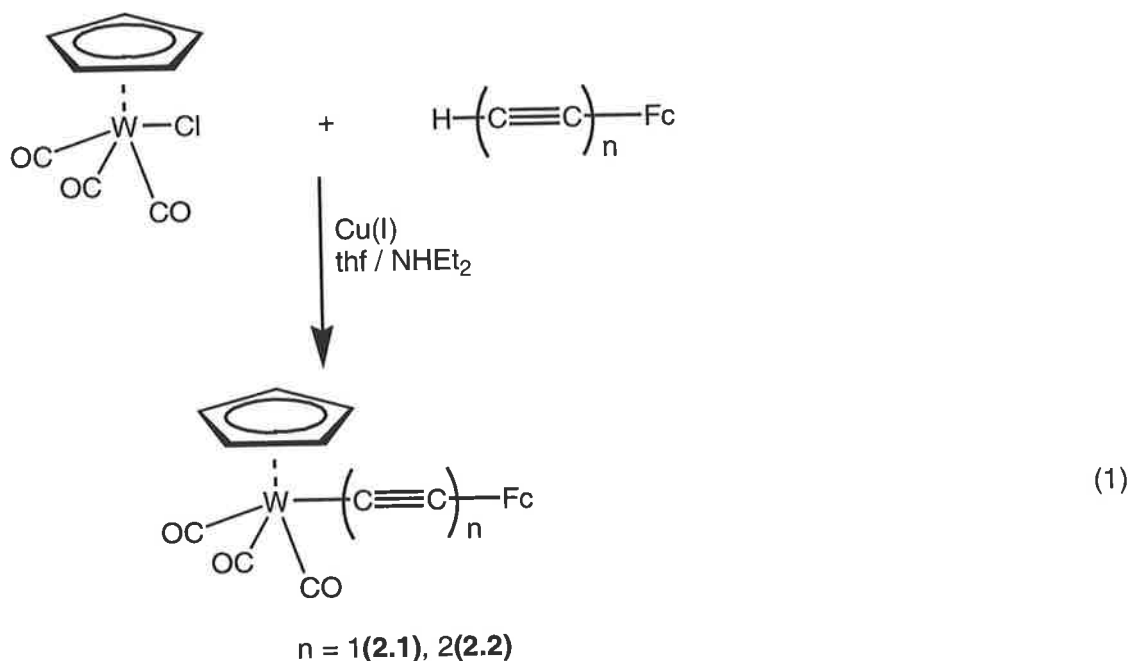
Dixneuf and co-workers^{19,20} have synthesised complexes of the type $\text{FcC}\equiv\text{CRC}\equiv\text{CFc}$ and $\text{FcC}\equiv\text{CRC}\equiv\text{C}[\text{ML}_n]\text{C}\equiv\text{CRC}\equiv\text{CFc}$ ($\text{R} = -\text{C}_6\text{H}_4-$; $\text{ML}_n = \text{trans-Pd}(\text{PBu}_3)_2$). For the former, the cyclic voltammogram showed a single oxidation wave. This was interpreted as being due to two superimposed one-electron oxidation waves rather than a single two-electron oxidation. The palladium bridged complex showed only a two-electron oxidation wave from the two ferrocenyl moieties.

Addition of $\text{Co}_2(\text{CO})_8$, $\text{Co}_2(\text{CO})_6(\mu\text{-dppm})$ and tene to alkynyl and poly-yndiyl complexes has been well established by us and others.²¹⁻²⁹ A recent structural study of $\text{Co}_2(\text{CO})_8$ addition to several ferrocenyl alkynes has been reported.³⁰

This chapter describes the synthesis and properties of several complexes of the type $\text{Fc}(\text{C}\equiv\text{C})_n\{\text{W}(\text{CO})_3\text{Cp}\}$.

RESULTS

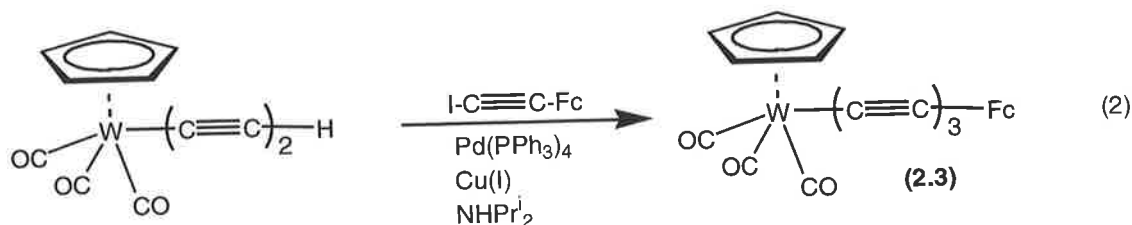
The copper(I)-catalysed reaction between $\text{FcC}\equiv\text{CH}$ and $\text{WCl}(\text{CO})_3\text{Cp}$ was carried out in a mixed thf/diethylamine solvent and afforded orange $\text{W}(\text{C}\equiv\text{CFc})(\text{CO})_3\text{Cp}$ (**2.1**, Equation 1) in 55% yield, which was readily characterised spectroscopically. Thus, its IR $\nu(\text{CO})$ spectrum contained the expected two-band pattern for the $\text{W}(\text{CO})_3\text{Cp}$ group, together with a single weak $\nu(\text{C}\equiv\text{C})$ absorption at 2099 cm^{-1} . Resonances in the ^1H and ^{13}C NMR spectra were readily assigned to the Fc [singlet (δ_{H} 4.14, δ_{C} 69.57) and multiplet resonances (δ_{H} 4.04, 4.25, δ_{C} 65-70) for the Cp and C_5H_4 groups, respectively] and CpW groups (singlets at δ_{H} 5.60, δ_{C} 91.60). The two CO resonances (at δ 229.89 and 211.53) showed 62 and 72 Hz couplings to ^{183}W . These features are common to most of the complexes described in this section. The two carbons of the acetylenic chain resonated at δ 125.81 and 67.90 and are assigned to C_α and C_β , respectively, by comparison to similar complexes,¹⁶⁻¹⁸ neither nucleus showed coupling to tungsten. The electrospray (ES) mass spectrum contained M^+ at m/z 514, which fragmented by loss of CO groups. An X-ray structure determination was carried out and the structure is shown in Figure 1. Important bond lengths and angles are given in Table 1.



Synthesis of $\text{W}(\text{C}\equiv\text{C})_n(\text{CO})_3\text{Cp}$; $n = 1$ **2.1**, **2.2**.

A similar reaction between $\text{FcC}\equiv\text{CC}\equiv\text{CH}$ and $\text{WCl}(\text{CO})_3\text{Cp}$ gave red $\text{W}(\text{C}\equiv\text{CC}\equiv\text{CFc})(\text{CO})_3\text{Cp}$ (**2.2**, Equation 1) in 79% yield, which was characterised by an X-ray structure determination (Figure 2, Table 1). Its spectroscopic properties include the characteristic two-band $\nu(\text{CO})$ pattern and two $\nu(\text{C}\equiv\text{C})$ bands at 2253 and 2186 cm^{-1} in the IR spectrum, and the expected resonances in the ^1H and ^{13}C NMR spectra. Four resonances at δ 111.84 [for C_α] and between δ 65 and 73.3 are due to the four carbons of the diyne chain, but the latter could not be unambiguously assigned. The base peak in the ES mass spectrum is M^+ at m/z 566.

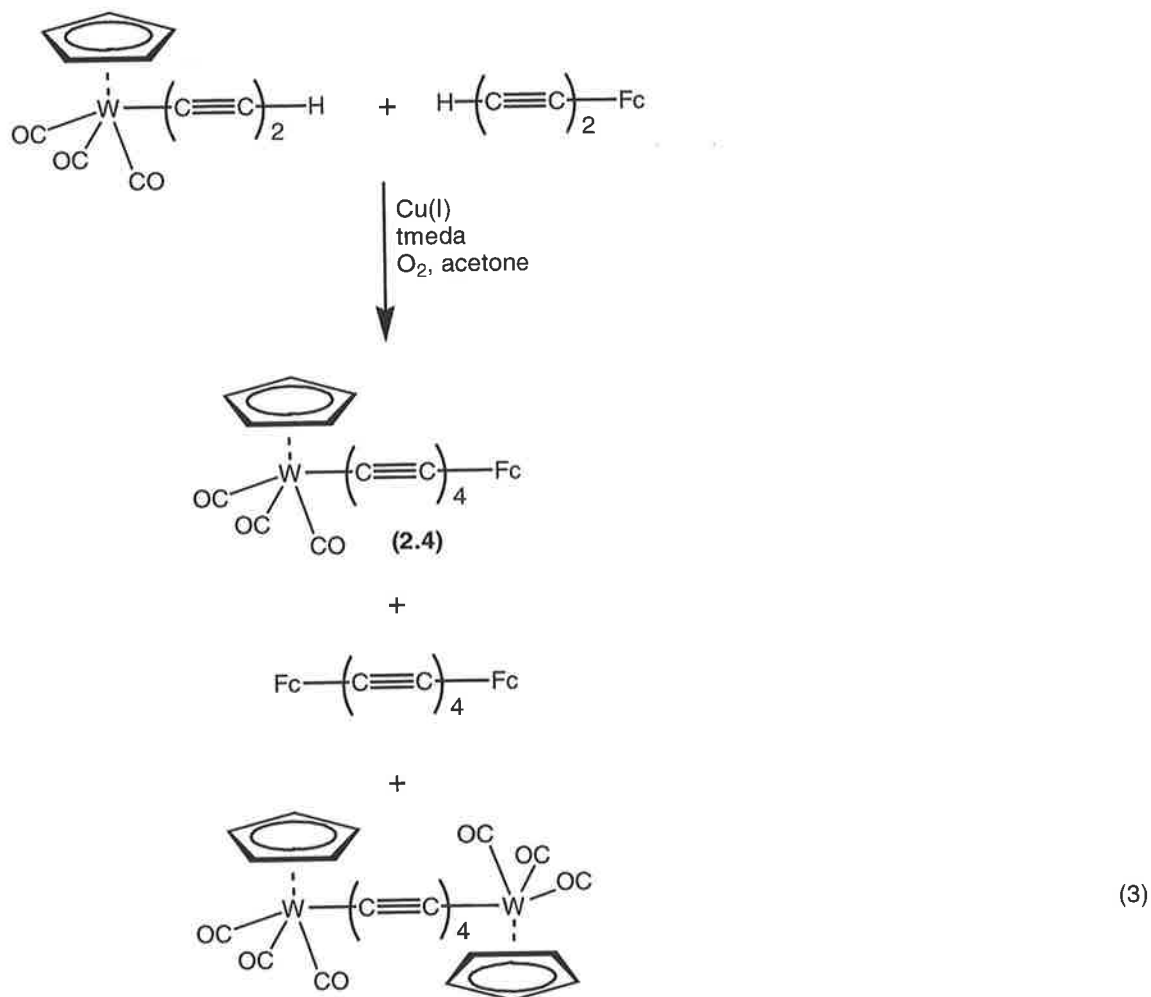
The complex $\text{W}(\text{C}\equiv\text{CC}\equiv\text{CC}\equiv\text{CFc})(\text{CO})_3\text{Cp}$ (**2.3**) was obtained by a copper(I)-palladium(0)-catalysed coupling between $\text{FcC}\equiv\text{CI}$ and $\text{W}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{CO})_3\text{Cp}$ as a bright orange solid in 72% yield (Equation 2). The IR spectrum of **2.3** contained three $\nu(\text{C}\equiv\text{C})$ bands between 2181 and 2040 cm^{-1} , and the usual two-band $\nu(\text{CO})$ pattern. In the ^{13}C NMR spectrum, C_α resonates at δ 112.17, but the five resonances of the other carbons of the triyne chain appearing between δ 71.4 and 60.63 could not assigned with certainty. In the ES mass spectrum, M^+ at m/z 590 is the base peak.



Synthesis of **2.3** via a palladium/copper coupling reaction.

An oxidative coupling reaction between $\text{FcC}\equiv\text{CC}\equiv\text{CH}$ and $\text{W}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{CO})_3\text{Cp}$ was carried out under Hay conditions [Cu(I) -tmeda/acetone, O_2 , r.t.] (Equation 3). The expected mixture of the three possible coupling products was readily separated by preparative t.l.c., giving $\text{Fc}(\text{C}\equiv\text{C})_4\text{W}(\text{CO})_3\text{Cp}$ (**2.4**) in 24% yield, together with known $\text{Fc}(\text{C}\equiv\text{C})_4\text{Fc}$ (22%)^{31,32} and $\{\text{W}(\text{CO})_3\text{Cp}\}_2\text{C}_4$ (24%).³³ The IR spectrum of **2.4** contained several $\nu(\text{C}\equiv\text{C})$ bands between 2184 and 2011 cm^{-1} , together with $\nu(\text{CO})$ absorptions at 2047 and 1961 cm^{-1} . In the ^{13}C NMR spectrum, seven singlets between δ 60.6 and 80.4 arise from the carbons C(2)-C(8) of the tetrayne chain, together with C(1) at δ 112.16. More readily assignable peaks are at δ 91.68 (WCp) and 70.31

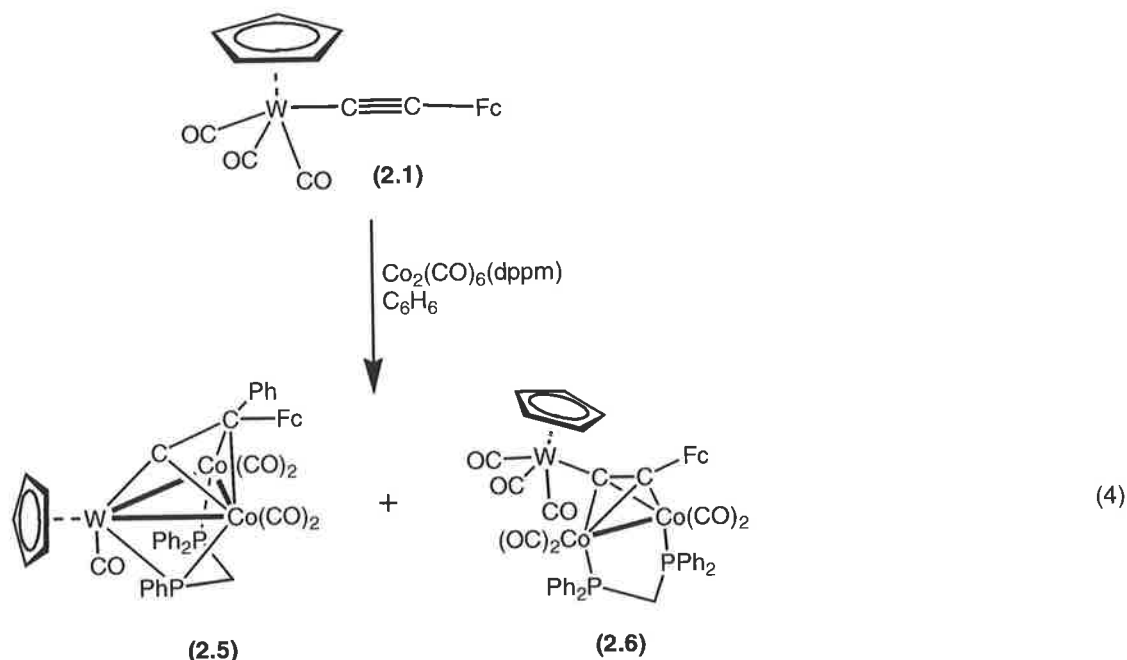
(FeCp). It was necessary to add $[\text{Ag}(\text{NCMe})_4]^+$ as an aid to ionisation in the ES mass spectrum, whereupon ions at m/z 1336 ($[\text{2M} + \text{Ag}]^+$) and 655 ($[\text{M} + \text{MeCN}]^+$) were found.



Oxidative coupling to form **2.4**.

We have previously reported on the utility of simple η^2 -alkyne adducts containing $\text{Co}_2(\text{CO})_6$ or $\text{Co}_2(\mu\text{-dppm})(\text{CO})_4$ fragments in identifying or confirming the nature of metal complexes containing di- or poly-ynyl ligands.^{21,22} In most cases, the $\text{Co}_2(\text{CO})_6$ groups can be removed oxidatively to regenerate the original complex. In view of the difficulties in obtaining structural characterisation of complexes **2.3**, **2.4**, we have examined their reactions with the dicobalt carbonyl precursors.

The reaction between **2.1** and $\text{Co}_2(\mu\text{-dppm})(\text{CO})_6$ was carried out in benzene at 80°C for 16 h (Equation 4). Two complexes were separated from the reaction mixture by preparative t.l.c.



Reaction between **2.1** and $\text{Co}_2(\text{CO})_6(\mu\text{-dppm})$.

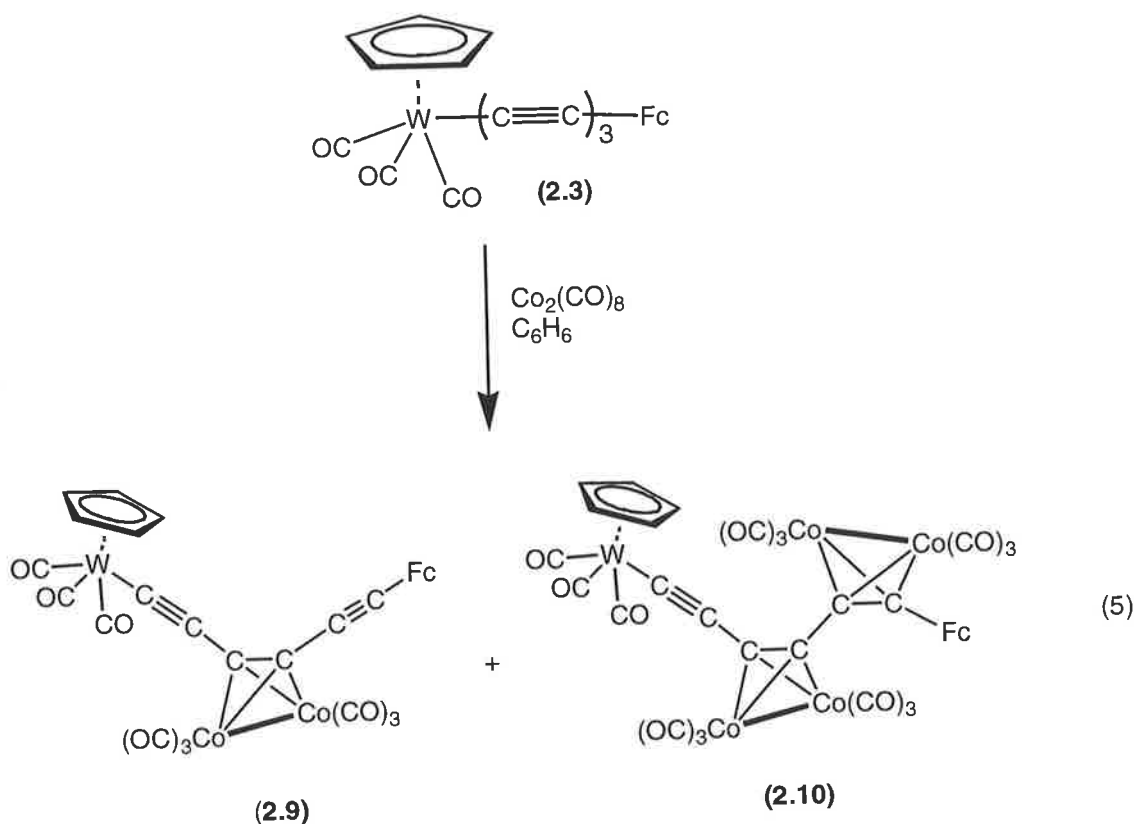
The faster moving band contained a dark red compound, which was characterised by a single-crystal X-ray structure determination (Figure 3, Table 2) as the cluster vinylidene $\text{Co}_2\text{W}(\mu_3\text{-CCPhFc})(\mu_3\text{-PPhCH}_2\text{PPh}_2)(\text{CO})_5\text{Cp}$ (**2.5**, Equation 4). Spectroscopic properties were in accord with the solid-state structure, with several $\nu(\text{CO})$ bands between 2014 and 1899 cm^{-1} in the IR spectrum. In the ^1H NMR spectrum, singlet resonances at δ 5.11 (WCp) and 3.66 (FeCp) were accompanied by multiplets assigned to CH_2 , C_5H_4 and Ph protons. The ^{13}C NMR spectrum contained resonances for vinylidene carbons at δ 103.88 [C(1)] and 70.23 [C(2)], singlet resonances at δ 86.87 (WCp) and 68.92 (FeCp) and the dppm CH_2 resonance at δ 29.7. In the ES mass spectrum of a solution containing NaOMe, the highest mass ions were at m/z 1123 ($[\text{M} + \text{Na}]^+$) and 1016 ($[\text{M} - 3\text{CO}]^+$).

The second complex appears to be the heptacarbonyl precursor of **2.5**, namely $\text{W}\{\eta^1:\eta^2\text{-C}_2\text{Fc}[\text{Co}_2(\mu\text{-dppm})(\text{CO})_4]\}(\text{CO})_3\text{Cp}$ (**2.6**, Equation 5), as indicated by microanalytical and some spectroscopic data. The IR spectrum contains three terminal and one bridging $\nu(\text{CO})$ bands between 1986 and 1812 cm^{-1} , while the ^1H and ^{13}C NMR spectra contain the expected singlets for the WCp and FeCp groups. In the ES mass spectrum, the only significant ions correspond to $[\text{M} - n\text{CO}]^+$ ($n = 5\text{-}7$), between m/z 1016 and 960.

The reaction between **2.2** and $\text{Co}_2(\text{CO})_8$ afforded the simple adduct $\text{W}\{\eta^1:\eta^2\text{-C}\equiv\text{CC}_2\text{Fc}[\text{Co}_2(\text{CO})_6]\}(\text{CO})_3\text{Cp}$ (**2.7**) as black crystals in 60% yield. A single-crystal X-ray structure determination (Figure 4, Table 3) confirmed that the Co_2 fragment is attached to the sterically least-congested $\text{C}\equiv\text{C}$ triple bond, i.e. that carrying the Fc group. Spectroscopic data are in accord with the solid-state structure and deserve no further comment here; the negative ion ES mass spectrum contains $[\text{M} + \text{OMe}]^-$ at m/z 883, which fragments by loss of up to nine CO groups.

Similarly, a dark red solid (**2.8**) was obtained in 42% yield from the reaction between **2.2** and $\text{Co}_2(\mu\text{-dppm})(\text{CO})_6$. An X-ray determination (Figure 5, Table 4) showed this to have a structure analogous to that of **2.7**, as suggested by the elemental analysis and spectroscopic data. In this case, we suggest that resonances at δ 111.74, 95.37, 90.85 and 75.57 can be assigned to C_α , C_β , C_γ and C_δ , respectively. The ES mass spectrum contains the ions $[\text{M} - n\text{CO}]^+$ ($n = 2\text{-}7$).

Two black compounds were obtained from the reaction between **2.3** and $\text{Co}_2(\text{CO})_8$ (Equation 5).



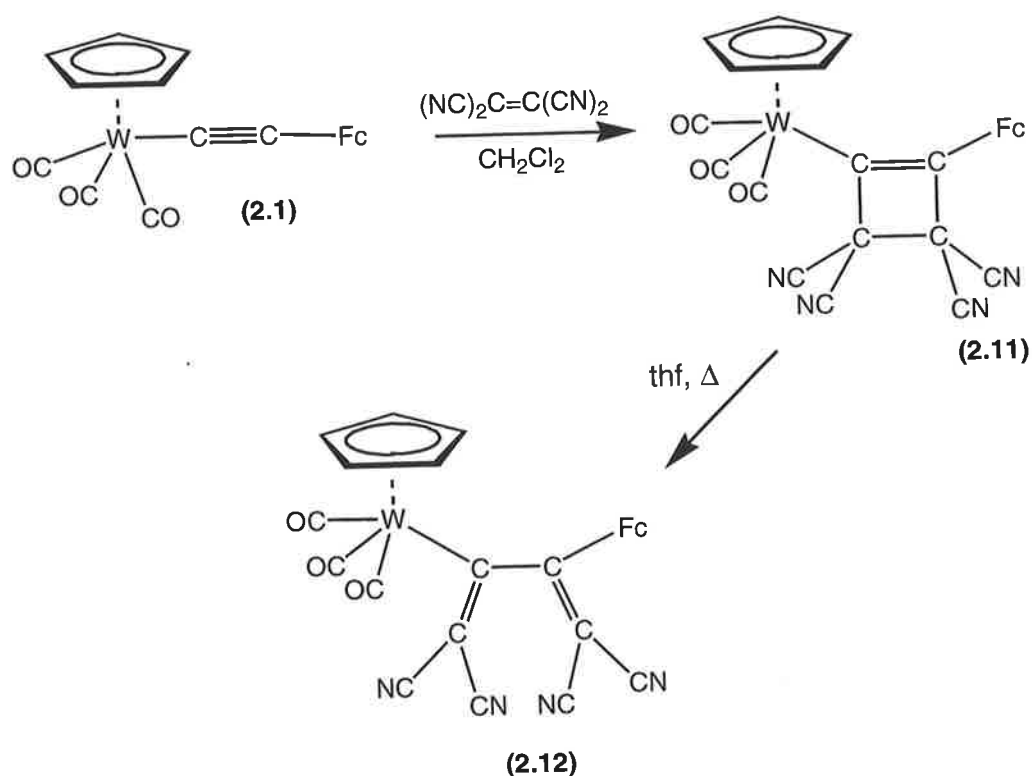
Reaction between **2.3** and $\text{Co}_2(\text{CO})_8$.

Separation by preparative t.l.c. gave the mono-adduct, $\text{W}\{\text{C}\equiv\text{CC}_2[\text{Co}_2(\text{CO})_6]\text{C}\equiv\text{CFc}\}(\text{CO})_3\text{Cp}$ (**2.9**) as the slower-moving band, in 38% yield, and the bis-adduct $\text{W}\{\text{C}\equiv\text{CC}_2[\text{Co}_2(\text{CO})_6]\text{C}_2\text{Fc}[\text{Co}_2(\text{CO})_6]\}(\text{CO})_3\text{Cp}$ (**2.10**) in 21% yield. The latter was characterised by a single-crystal X-ray structure determination as shown in Figure 6. Spectroscopic data are in agreement with the structures proposed or found. For **2.9**, $\nu(\text{C}\equiv\text{C})$ for an uncoordinated $\text{C}\equiv\text{C}$ triple bond was at 2134 cm^{-1} , while the NMR spectra contained singlets at δ_{H} 5.69 and 4.28 and δ_{C} 91.75 and 69.85 for the WCp and FcCp groups, respectively. Several resonances between δ_{C} 69 and 113 are assigned to the carbons of the C_6 chain, although only the resonance at δ 112.46 can be confidently assigned to C(1). A quadrupole-broadened singlet at δ 198.74 arises from the $\text{Co}(\text{CO})$ groups. In the ES mass spectrum, M^+ is found at m/z 876. Compound **2.10** has similar spectroscopic properties, the $\nu(\text{CO})$ region containing two more bands, while there is no $\nu(\text{C}\equiv\text{C})$ absorption for an uncoordinated $\text{C}\equiv\text{C}$ triple bond. In the ^{13}C NMR spectrum, the carbons of the C_6 chain were not resolved, singlets at δ_{C} 91.73 and 69.73 being assigned to the WCp and

FeCp groups, respectively. The Co(CO) groups again resonate as a broad singlet at δ 199.24. The negative ion ES mass spectrum of a solution containing NaOMe contained $[M + \text{OMe}]^-$ at m/z 1192.

Cycloaddition of tetracyanoethene (tcne) to $\text{RC}\equiv\text{CM}$ triple bonds to give cyclobutenyl complexes and subsequent ring-opening to buta-1,3-dien-2-yl complexes are other characteristic reactions of σ -alkynyl or σ -poly-ynyl ligands on transition metals.^{23-27,29,34} In these cases, the di- or poly-ynyl ligands cannot be regenerated from the cyanocarbon ligand, but the reactions offer further confirmation of the presence of the carbon ligands.

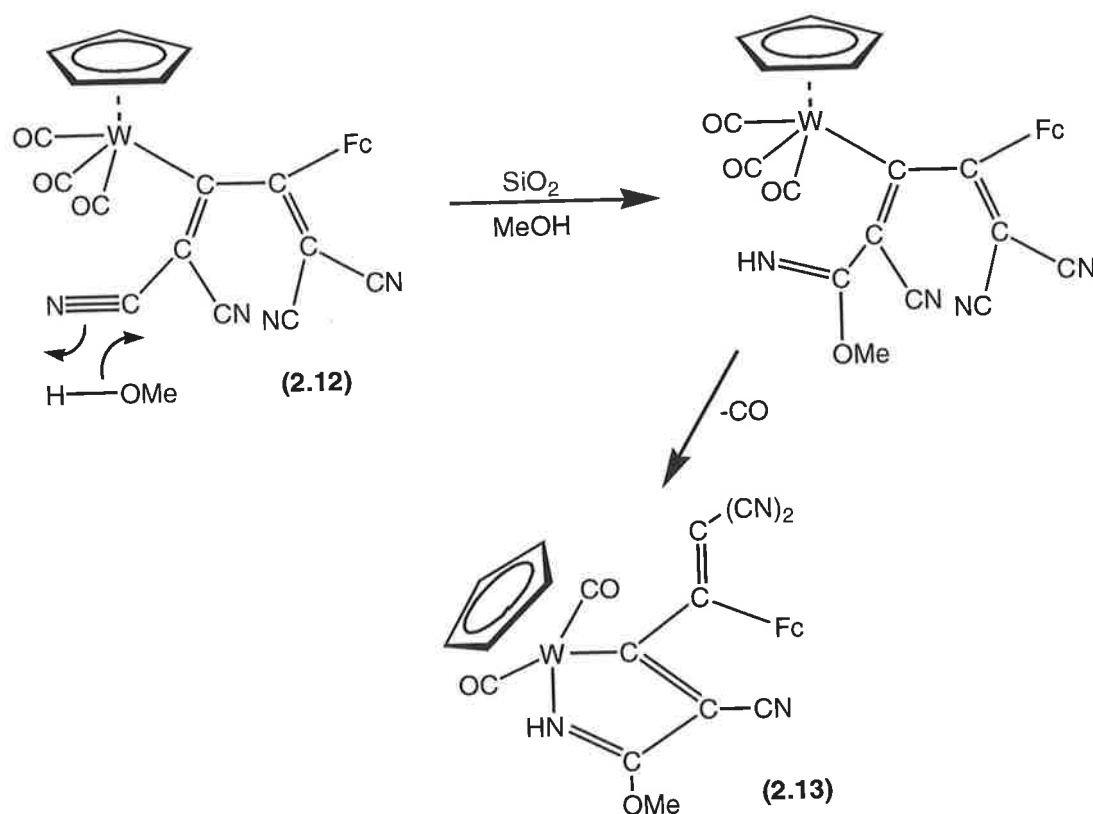
Addition of tcne to **2.1** (Scheme 1) in dichloromethane solution resulted in a change in colour from orange to red after a few minutes. The solution gave an orange solid in 74% yield, which was shown to be the corresponding cyclobutenyl complex $\text{W}\{\text{C}=\text{CFcC}(\text{CN})_2\text{C}(\text{CN})_2\}(\text{CO})_3\text{Cp}$ (**2.11**) by an X-ray structural study (Figure 7, Table 6).



Scheme 1. Cycloaddition of tcne to **2.1**.

Characteristic spectral properties include weak $\nu(\text{CN})$ bands at 2390 and 2338 cm^{-1} , the usual $\nu(\text{CO})$ pattern at 2042 and 1963 cm^{-1} , and singlet resonances for WCp and FeCp groups at δ_{H} 4.29 and 5.83, and δ_{C} 70.54 and 91.88, respectively. The cyclobutenyl ring carbons resonate around δ 68–74, the $\text{C}(\text{CN})_2$ atoms at δ ca 45, and the CN groups at δ ca 110. The ES spectrum of a solution containing NaOMe contained $[\text{M} + \text{Na}]^+$ at m/z 693.

On heating a solution of **2.11** in refluxing thf for 6 h (Scheme 1), the colour deepened, and preparative t.l.c. enabled separation of the blue buta-1,3-dien-2-yl complex $\text{W}\{\text{C}=[\text{C}(\text{CN})_2]\text{CFc}=\text{C}(\text{CN})_2\}(\text{CO})_3\text{Cp}$ (**2.12**), again characterised by a crystallographic study (Figure 8, Table 7). Spectroscopic data include $\nu(\text{CN})$ at 2222 cm^{-1} , $\nu(\text{CO})$ at 2049 and 1960 cm^{-1} and singlet resonances for the FeCp and WCp groups at δ_{H} 4.45 and 5.51, respectively. Butadienyl carbons are found between δ_{C} ca 68 and 75, the CN carbons at δ_{C} ca 114 and the $\text{C}(\text{CN})_2$ carbons at δ_{C} 28.66 and 29.33. The molecular ion is found at m/z 670 in the ES mass spectrum.



Scheme 2. Addition of MeOH to a CN group of **2.12**.

When **2.12** was extracted from t.l.c. silica gel with methanol (Scheme 1), the colour changed to red. Purification and crystallisation gave the methanol adduct $W\{C[=C(CN)_2C(OMe)=NH]CFc=C(CN)_2\}(CO)_2Cp$ (**2.13**), as shown by a single-crystal X-ray structure determination in Figure 9. Addition of methanol to one of the CN groups of the $=C(CN)_2$ unit adjacent to the tungsten has occurred (Scheme 2). Full spectroscopic data were not obtained, the IR spectrum containing $\nu(CN)$ at 2220 cm^{-1} and two strong $\nu(CO)$ bands at 1969 and 1897 cm^{-1} , while the ^1H NMR spectrum contained singlet resonances at δ 4.52 and 5.08 for FeCp and WCp groups, respectively, and at δ 4.05 for the OMe protons. In the ES mass spectrum, M^+ is found at m/z 674.

Dark green crystals of $W\{C\equiv CC[=C(CN)_2]CFc=C(CN)_2\}(CO)_3Cp$ (**2.14**) were obtained in 75% yield from the reaction between **2.2** and tcne. The illustrated structure (Figure 10) was determined by an X-ray study and spectral properties were in accord with it. Two $\nu(CN)$ bands at 2225 and 2165 cm^{-1} , a $\nu(C\equiv C)$ absorption at 2073 cm^{-1} and two $\nu(CO)$ bands at 2026 and 1965 cm^{-1} are present in the IR spectrum, while the singlets for the FeCp and WCp groups occur at δ_H 4.37 and 5.79 and δ_C 72.49 and 92.56, respectively. Other resonances in the ^{13}C NMR spectrum can be assigned to the CN carbons (at δ ca 111-114), dieny carbons (at δ 75.43 and 88.03), acetylenic carbons C(2) and C(6) (δ 147.73 and 170.18) and the $C(CN)_2$ carbons (at δ ca 31). Positive- and negative-ion ES mass spectra of a solution containing NaOMe contained $[M + Na]^+$ and $[M + OMe]^-$ at m/z 717 and 725, respectively.

The red-brown complex obtained in 48% yield from **2.3** and tcne is probably $W\{C\equiv CC[=C(CN)_2]C[=C(CN)_2]C\equiv CFc\}(CO)_3Cp$ (**2.15**) due to the middle triple bond being the least sterically hindered. The IR spectrum contains two $\nu(CN)$ bands (2225 , 2164 cm^{-1}), two $\nu(C\equiv C)$ bands (2130 and 2055 cm^{-1}) and two $\nu(CO)$ bands (2025 and 1967 cm^{-1}). In the NMR spectra, singlets are found for the FeCp and WCp groups (δ_H 4.41 and 5.70; δ_C 72.67 and 92.12, respectively); carbon resonances at δ ca 110-113 (CN), ca 75 [$C(CN)_2$], and between δ ca 71 and 76 (diene carbons) are accompanied by signals at δ 148.53 and 169.66 [for C(2) and C(6)] and at δ 209.27 and 222.85

[W(CO)]. The ES mass spectrum of a solution containing $[\text{Ag}(\text{NCMe})_4]^+$ contained ions at m/z 1544 and 826, corresponding to $[2\text{M} + \text{Ag}]^+$ and $[\text{M} + \text{Ag}]^+$, respectively.

MOLECULAR STRUCTURES

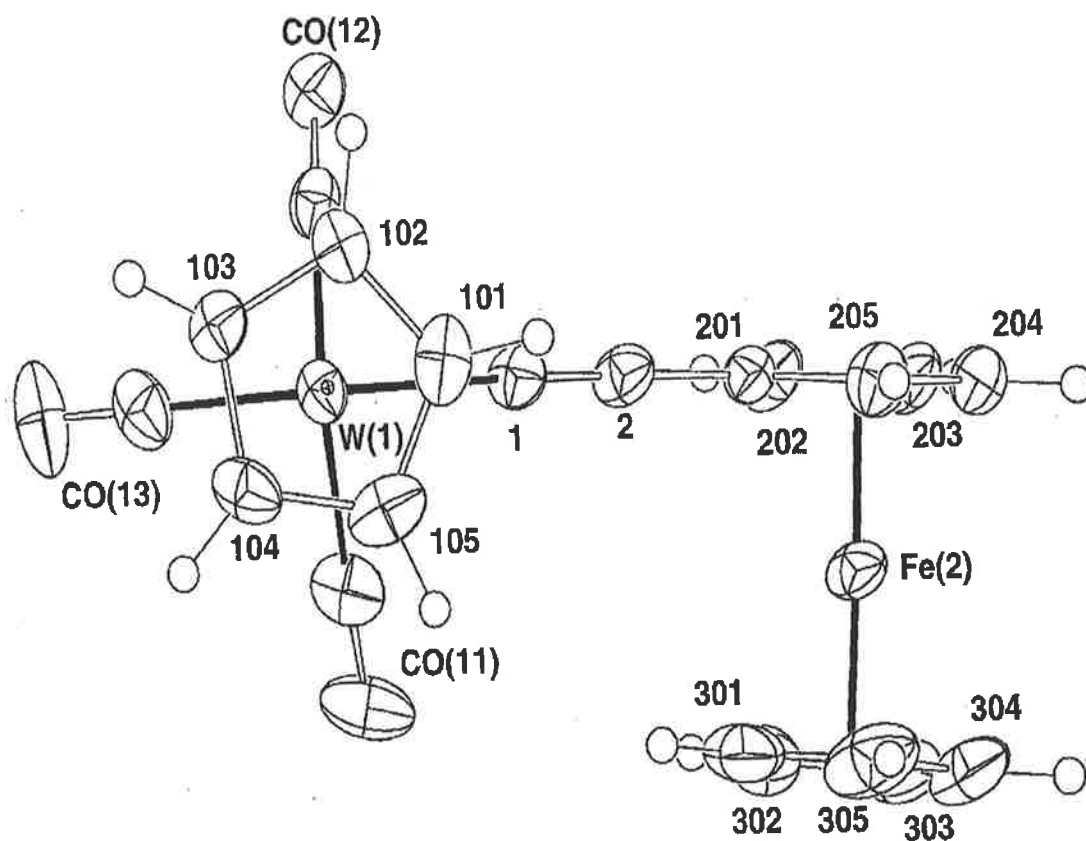


Figure 1. Plot of a molecule of **2.1** showing the atom numbering scheme.

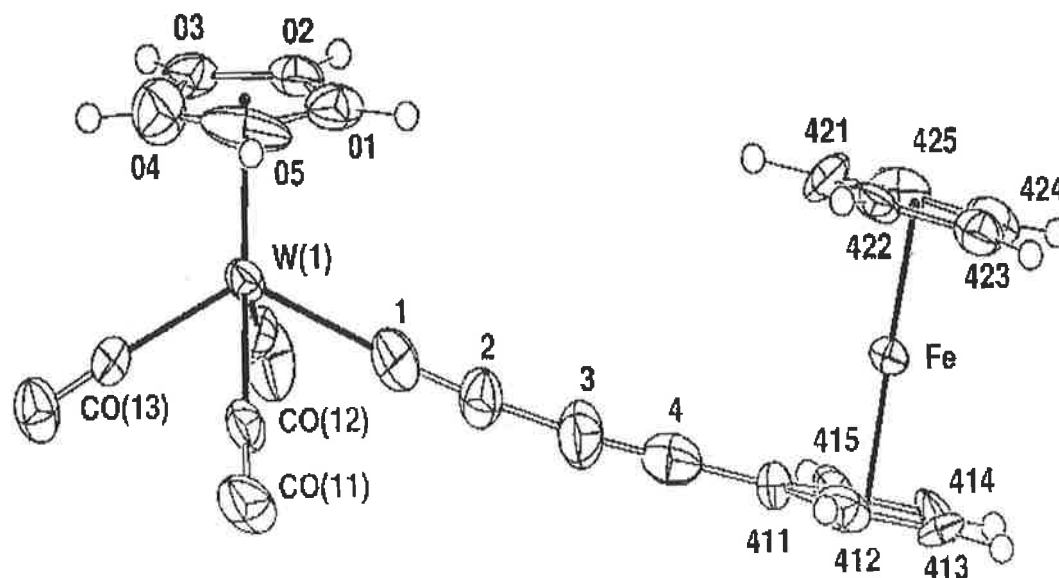


Figure 2. Plot of a molecule of **2.2** showing the atom numbering scheme.

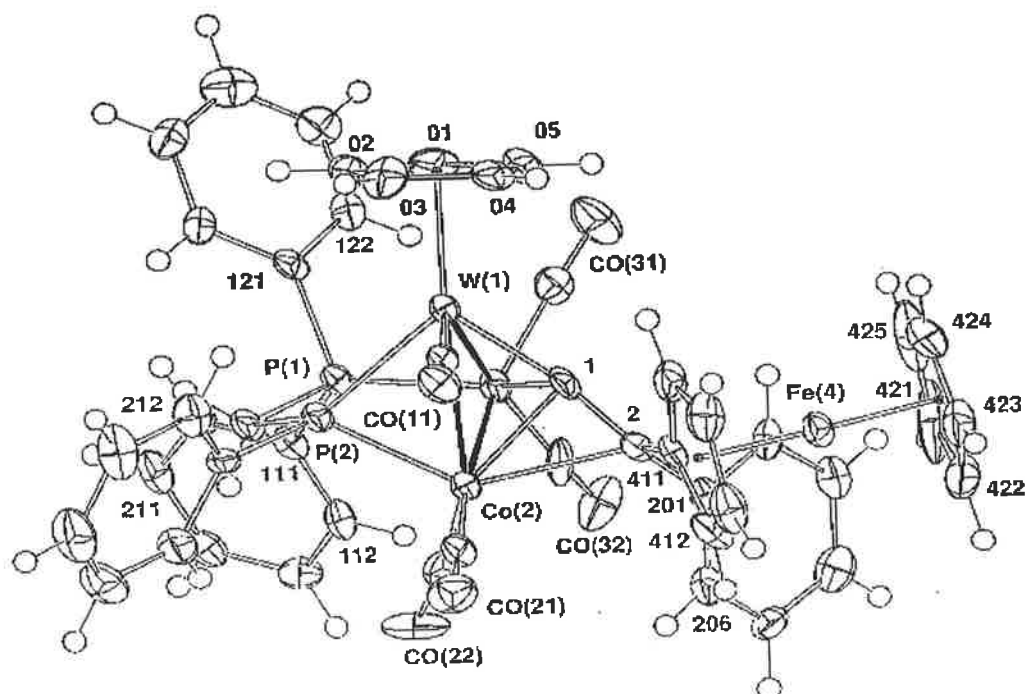


Figure 3. Plot of a molecule of **2.5** showing the atom numbering scheme.

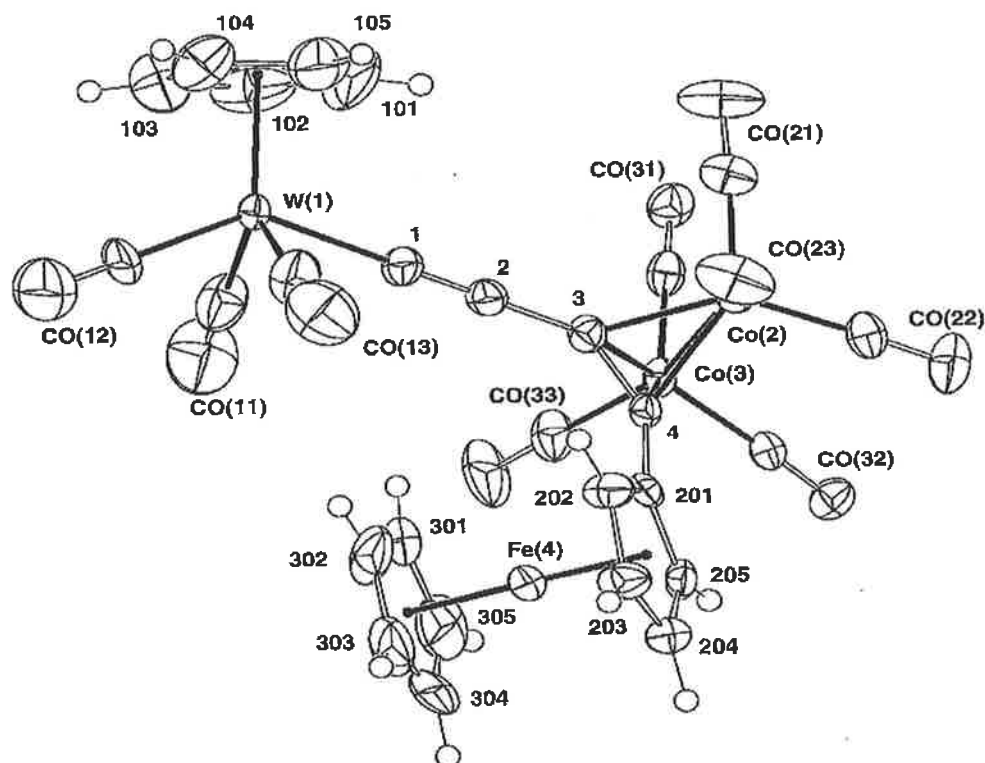


Figure 4. Plot of a molecule of **2.7** showing the atom numbering scheme.

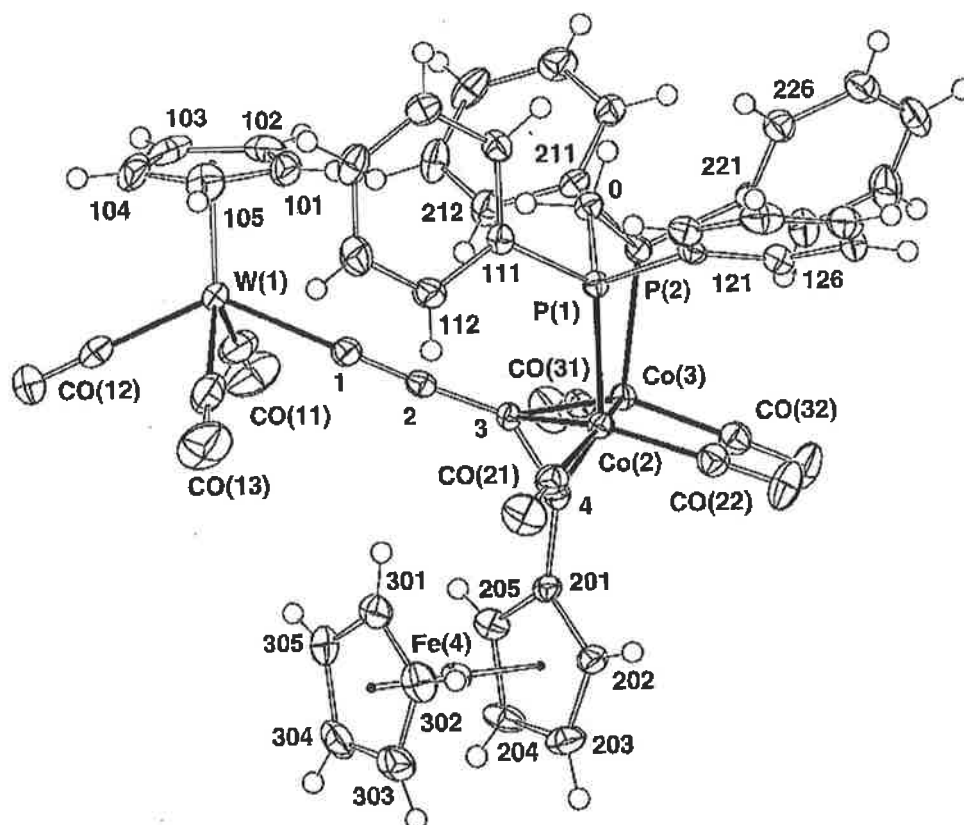


Figure 5. Plot of a molecule of **2.8** showing the atom numbering scheme.

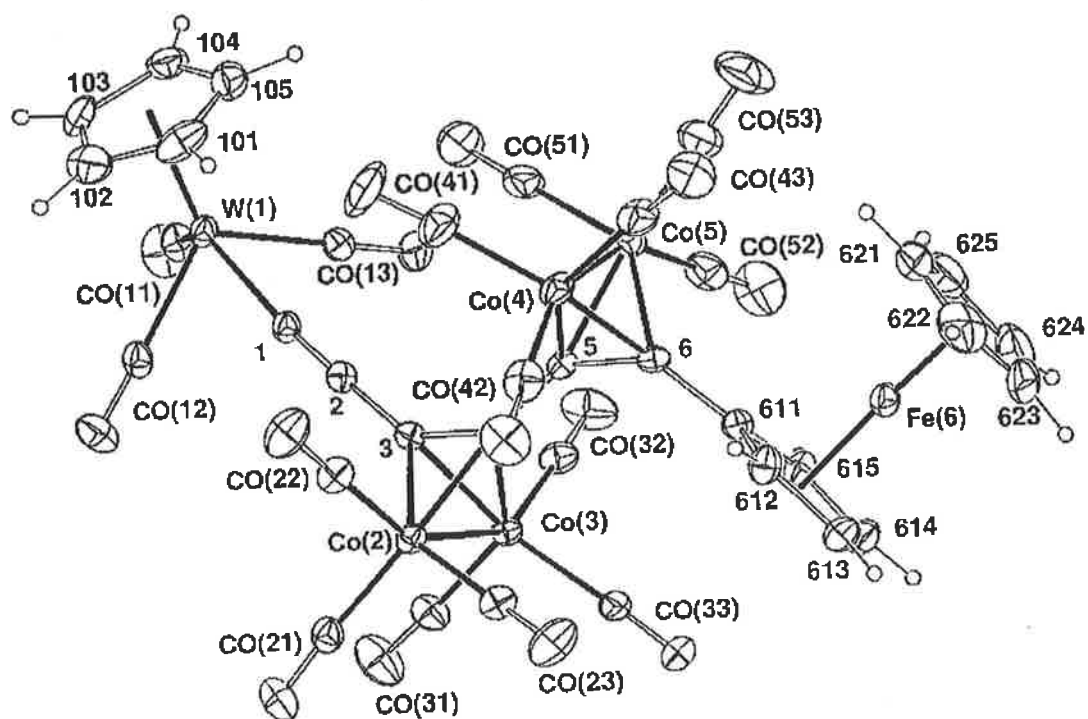


Figure 6. Plot of a molecule of **2.10** showing the atom numbering scheme.

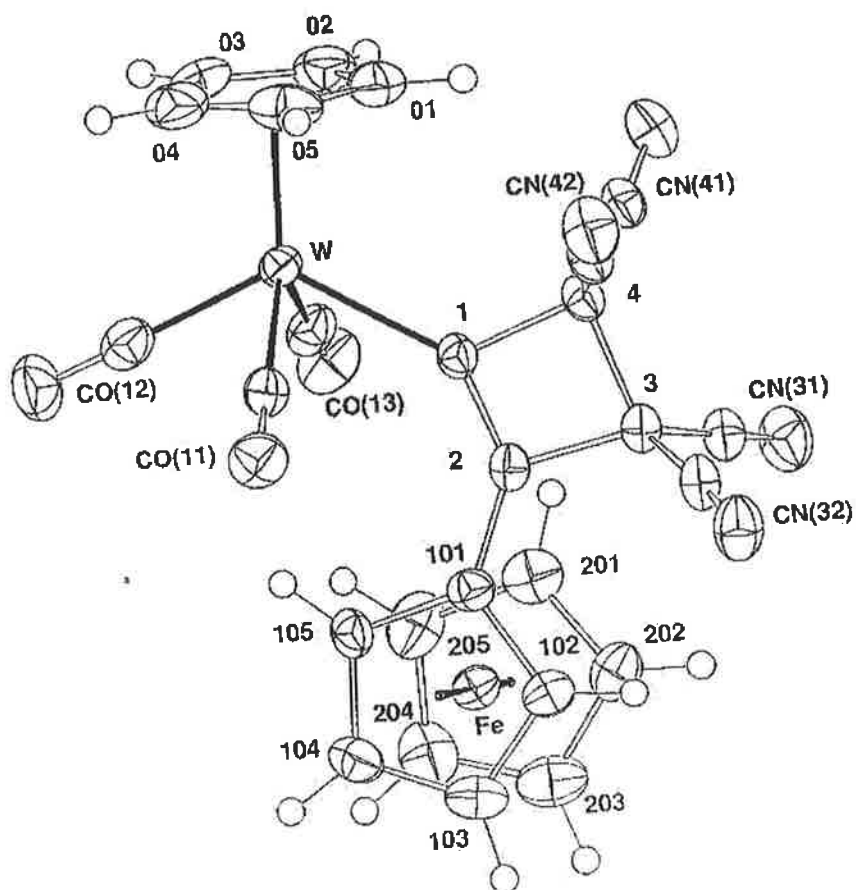


Figure 7. Plot of a molecule of **2.11** showing the atom numbering scheme.

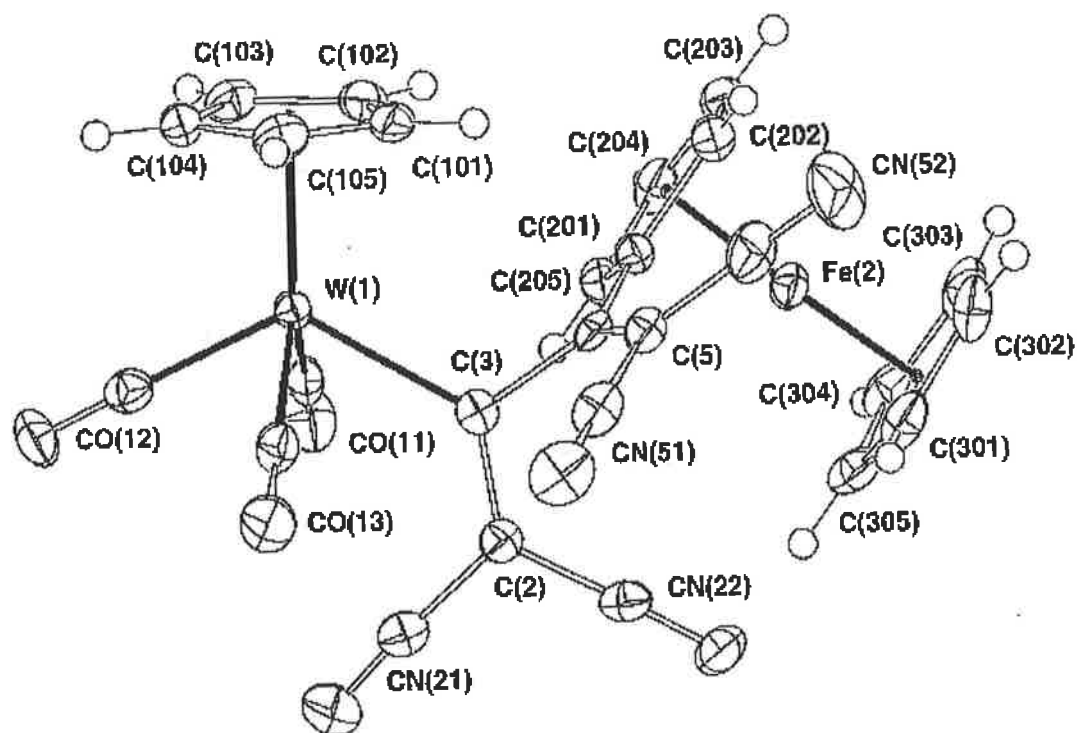


Figure 8. Plot of a molecule of **2.12** showing the atom numbering scheme.

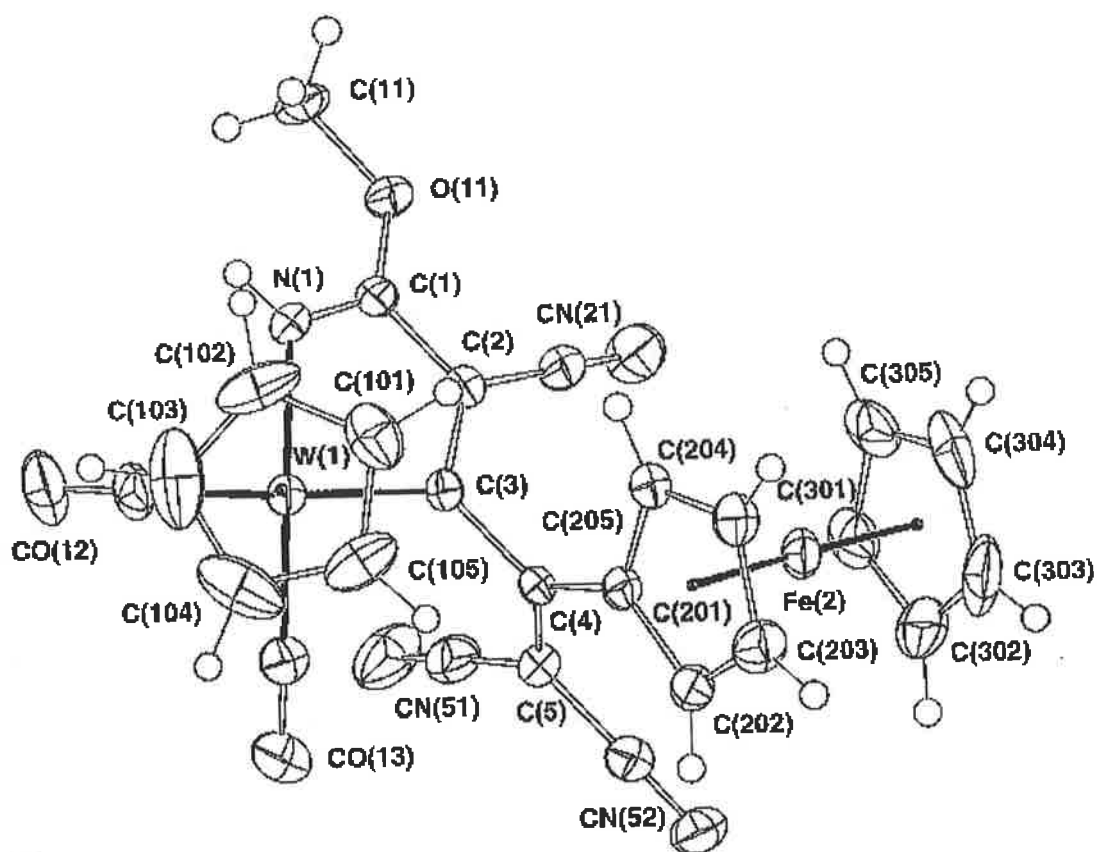


Figure 9. Plot of a molecule of **2.13** showing the atom numbering scheme.

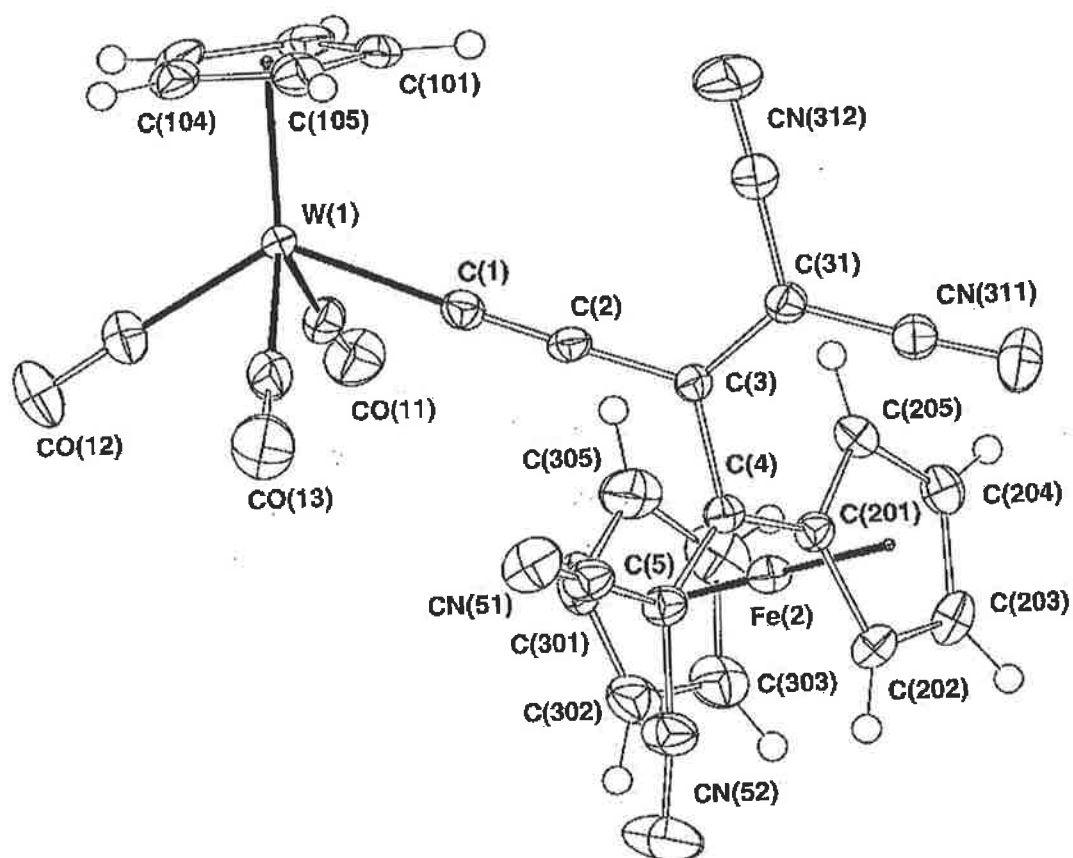


Figure 10. Plot of a molecule of **2.14** showing the atom numbering scheme.

Table 1. Important bond lengths (Å) and angles (°) of **2.1** and **2.2**.

Bond distances	1	2
W-C(Cp)	2.296-2.356(7)	2.30-2.35(1)
(av.)	2.33(4)	2.32(2)
W-CO(12)	2.009(7)	2.00(1)
W-CO(11, 13)	1.979, 2.001(8)	2.01, 2.00(1)
Fe-C(Cp)	2.029-2.054(8)	2.01-2.06(1)
(av)	2.04(8)	2.04(1)
W-C(1)	2.162(7)	2.12(2)
C(1)-C(2)	1.19(1)	1.20(2)
C(2)-C(3)		1.37(2)
C(3)-C(4)		1.24(2)
C(n)-C(201)	1.44(1)	1.39(2)
Bond angles		
C(12)-W-C(11, 13)	77.4, 79.1(3)	77.8, 77.4(5)
C(11)-W-C(13)	112.0(3)	113.8(5)
C(1)-W-C(12)	128.9(3)	128.2(5)
C(1)-W-C(11, 13)	73.8, 74.0(3)	75.6, 73.9(5)
W-C(1)-C(2)	176.9(6)	176(1)
C(1)-C(2)-C(3)		176(1)
C(n-1)-C(n)-C(201)	178.5(8)	177(1)
	n = 2	n = 4

Table 2. Important bond lengths (Å) and angles (°) of **2.5**.

Bond distances			
Co(2)-Co(3)	2.500(2)	W(1)-C(1)	2.021(8)
Co(2)-W(1)	2.660(1)	Co(2)-C(1)	2.004(8)
Co(3)-W(1)	2.717(1)	Co(2)-C(2)	2.336(8)
Co(2)-P(2)	2.219(2)	Co(3)-C(1)	1.973(8)
Co(3)-P(1)	2.266(2)	W(1)-C(Cp)	2.315-2.385(9)
W(1)-P(2)	2.341(2)	(av.)	2.35(3)
W-CO	1.959(8)	Fe-C(Cp)	2.002-2.080(7)
Co(2)-CO	1.800, 1.761(8)	(av.)	2.04(2)
Co(3)-CO	1.752, 1.799(9)		
P-C(0)	1.841, 1.847(8)	C(1)-C(2)	1.41(1)
Bond angles			
Co(2)-P(2)-W(1)	71.29(6)	W(1)-C(1)-C(2)	145.5(6)
P(1)-C(0)-P(2)	105.2(4)	C(1)-C(2)-C(201)	120.3(7)
Co(3)-C(1)-C(2)	122.5(6)	C(1)-C(2)-C(411)	122.4(7)

Table 3. Important bond lengths (Å) and angles (°) of **2.7**.

Bond distances			
Co(2)-Co(3)	2.469(1)	W(1)-C(1)	2.118(7)
W(1)-C(Cp)	2.29-2.40(1)	Co(2)-C(3)	1.962(6)
(av.)	2.34(4)	Co(2)-C(4)	1.988(6)
Fe-C(Cp)	2.018-2.055(6)	Co(3)-C(3)	1.986(7)
(av.)	2.05(1)	Co(3)-C(4)	1.953(6)
W-CO(12)	1.984(7)	C(1)-C(2)	1.222(9)
W-CO(11, 13)	2.005-2.006(7)	C(2)-C(3)	1.406(9)
Co(2)-CO	1.794-1.819(7)	C(3)-C(4)	1.345(8)
Co(3)-CO	1.790-1.816(8)	C(4)-C(201)	1.441(8)
Bond angles			
C(12)-W-C(11, 13)	77.3(3)-82.9(4)	W(1)-C(1)-C(2)	176.5(5)
C(11)-W-C(13)	108.3(3)-108.9(4)	C(1)-C(2)-C(3)	177.5(7)
C(1)-W-C(12)	130.6(3)	C(2)-C(3)-C(4)	141.1(7)
C(1)-W-C(11, 13)	77.5-71.3(3)	C(3)-C(4)-C(201)	140.3

Table 4. Important bond lengths (Å) and angles (°) of **2.8**.

Bond distances			
Co(2)-Co(3)	2.4745(6)	W(1)-C(1)	2.139(3)
W(1)-C(Cp)	2.308-2.369(3)	Co(2)-C(3)	1.981(3)
(av.)	2.34(3)	Co(2)-C(4)	1.937(3)
Fe-C(Cp)	2.030-2.055(3)	Co(3)-C(3)	1.987(3)
(av.)	2.041(9)	Co(3)-C(4)	1.967(3)
W-CO(12)	2.002(4)	C(1)-C(2)	1.217(4)
W-CO(11, 13)	1.996-2.005(4)	C(2)-C(3)	1.404(4)
Co(2)-CO	1.772-1.779(3)	C(3)-C(4)	1.360(4)
Co(3)-CO	1.779-1.801(3)	C(4)-C(201)	1.453(4)
Co(2)-P(1)	2.2118(8)	Co(3)-P(2)	2.2245(8)
Bond angles			
C(12)-W-C(11, 13)	78.2(2), 78.1(1)	W(1)-C(1)-C(2)	178.9(3)
C(11)-W-C(13)	110.4(1)	C(1)-C(2)-C(3)	176.1(3)
C(1)-W-C(12)	131.1(1)	C(2)-C(3)-C(4)	141.2(3)
C(1)-W-C(11, 13)	74.2, 75.0(1)	C(3)-C(4)-C(201)	131.3(3)

Table 5. Important bond lengths (Å) and angles (°) of **2.10**.

Bond distances			
Co(2)-Co(3)	2.4672(9)	Co(2, 3)-C(4)	1.953, 1.976(4)
Co(4)-Co(5)	2.480(1)	Co(4, 5)-C(5)	1.975, 1.962(4)
W(1)-C(Cp)	2.302-2.355(5)	Co(4, 5)-C(6)	1.944, 1.983(4)
(av.)	2.33(2)	C(1)-C(2)	1.207(6)
Fe-C(Cp)	2.00(1)-2.057(5)	C(2)-C(3)	1.405(6)
(av.)	2.03(1)	C(3)-C(4)	1.343(6)
W-CO(12)	2.001(5)	C(4)-C(5)	1.433(6)
W-CO(11, 13)	1.969-1.987(5)	C(5)-C(6)	1.350(6)
W(1)-C(1)	2.128(4)	C(6)-C(611)	1.458(6)
Co(2, 3)-C(3)	1.976, 1.976(4)		
Bond angles			
C(12)-W-C(11, 13)	76.5, 77.3(2)	C(1)-C(2)-C(3)	175.2(5)
C(11)-W-C(13)	107.7(2)	C(2)-C(3)-C(4)	142.8(4)
C(1)-W-C(12)	128.9(2)	C(3)-C(4)-C(5)	142.3(4)
C(1)-W-C(11, 13)	75.7, 71.7(2)	C(4)-C(5)-C(6)	142.4(4)
W(1)-C(1)-C(2)	173.9(4)	(C5)-C(6)-C(611)	137.6(4)

Table 6. Important bond lengths (Å) and angles (°) of **2.11**.

Bond distances			
W-C(Cp)	2.306-2.393(5)	C(1)-C(2)	1.360(5)
(av.)	2.34(4)	C(1)-C(4)	1.563(4)
W-CO(12)	1.987(4)	C(2)-C(3)	1.531(4)
W-CO(11, 13)	2.001, 1.988(4)	C(3)-C(4)	1.596(5)
Fe-C(Cp)	2.035-2.052(4)	C(2)-C(101)	1.448(5)
(av)	2.042(6)	C(3)-CN	1.478-1.480(5)
W-C(1)	2.198(3)	C(4)-CN	1.465-1.481(6)
Bond angles			
C(12)-W-C(11, 13)	78.5-76.7(2)	C(1)-C(2)-C(101)	138.5(3)
C(11)-W-C(13)	115.0(2)	C(1)-C(2)-C(3)	97.0(3)
C(1)-W-C(12)	126.0(1)	C(2)-C(1)-C(4)	91.7(2)
C(1)-W-C(11, 13)	73.8-74.6(1)	C(3)-C(2)-C(101)	124.3(3)
W-C(1)-C(2)	140.6(3)	C(2)-C(3)-C(4)	84.5(2)
W-C(1)-C(4)	127.7(2)	C(1)-C(4)-C(3)	86.7(2)

Table 7. Important bond lengths (Å) and angles (°) of **2.12**.

Bond distances			
W-C(Cp)	2.314-2.373(4)	C(2)-C(3)	1.362(4)
(av.)	2.34(2)	C(3)-C(4)	1.496(5)
W-CO(12)	1.992(4)	C(4)-C(5)	1.366(5)
W-CO(11, 13)	2.029, 1.994(4)	C(4)-C(101)	1.454(4)
Fe-C(Cp)	2.026-2.059(4)	C(2)-CN	1.453, 1.453(5)
(av)	2.04(4)	C(5)-CN	1.434, 1.435(5)
W-C(3)	2.228(3)		
Bond angles			
C(12)-W-C(11, 13)	74.4-77.0(2)	W(1)-C(3)-C(2)	128.1(3)
C(11)-W-C(13)	114.2(1)	W(1)-C(3)-C(4)	117.1(2)
C(3)-W-C(12)	125.8(1)	C(2)-C(3)-C(4)	114.8(3)
C(3)-W-C(11, 13)	75.6, 75.8(1)	C(3)-C(4)-C(201)	115.5(3)

Table 8. Important bond lengths (Å) and angles (°) of **2.13**.

Bond distances			
W-C(Cp)	2.291-2.369(7)	C(1)-C(2)	1.425(6)
(av.)	2.33(3)	C(2)-C(3)	1.388(8)
W-N(1)	2.149(5)	C(3)-C(4)	1.479(6)
W-CO(12,13)	1.979, 1.989(4)	C(4)-C(5)	1.365(6)
Fe-C(Cp)	2.032-2.062(5)	C(4)-C(201)	1.454(4)
(av.)	2.05(5)	C(2)-CN	1.434(7)
W-C(3)	2.140(4)	C(5)-CN	1.432, 1.447(7)
Bond angles			
C(12)-W-C(13)	79.8(2)	W(1)-C(3)-C(2)	117.4(3)
C(12)-W-N(1)	77.4(2)	W(1)-C(3)-C(4)	124.5(4)
C(13)-W-N(1)	132.4(2)	C(1)-C(2)-C(3)	113.9(4)
C(3)-W-N(1)	72.8(2)	C(2)-C(3)-C(4)	118.0(4)
C(3)-W-C(12, 13)	80.4, 115.5(2)	C(3)-C(4)-C(201)	115.8(3)
W-N(1)-C(1)	120.3(3)	C(3)-C(4)-C(5)	120.3(4)

Table 9. Important bond lengths (Å) and angles (°) of **2.14**.

Bond distances			
W-C(Cp)	2.306-2.359(7)	C(1)-C(2)	1.211(5)
(av.)	2.33(2)	C(2)-C(3)	1.404(5)
W-CO(12)	2.007(6)	C(3)-C(31)	1.379(7)
W-CO(11, 13)	1.995, 2.007(6)	C(3)-C(4)	1.508(8)
Fe-C(Cp)	2.034-2.063(4)	C(4)-C(5)	1.367(6)
(av)	2.05(1)	C(4)-C(201)	1.439(5)
W-C(1)	2.107(3)	C(31)-CN	1.427-1.43(1)
		C(5)-CN	1.437-1.449(9)
Bond angles			
C(12)-W-C(11, 13)	77.9(2)-76.3(1)	C(1)-C(2)-C(3)	178.8(4)
C(11)-W-C(13)	110.0(2)	C(2)-C(3)-C(31)	120.9(5)
C(1)-W-C(12)	129.4(2)	C(2)-C(3)-C(4)	118.2(4)
C(1)-W-C(11, 13)	74.2(1)-74.9(2)	C(3)-C(4)-C(5)	116.1(4)
W-C(1)-C(2)	177.6(4)	C(3)-C(4)-C(201)	117.3(4)

The molecular structures of **2.1**, **2.2**, **2.3**, **2.5**, **2.8**, **2.9** and **2.11-2.16** have been determined by single-crystal X-ray diffraction studies. A single molecule, devoid of crystallographic symmetry, comprises the asymmetric unit in each case, with the exception of **2.8**, where two independent molecules are found. A molecule of each is depicted in Figs. 1-10 and significant structural data are collected in Tables 1-9.

All complexes except **2.3**, **2.5**, **2.12** and **2.15** contain $\text{W}(\text{CO})_3\text{Cp}$ groups, which have the usual piano-stool structure, with $\text{CO}(12)$ group being *trans* to the σ -bonded carbon ligand. The structural parameters fall within a narrow range [$\text{W}-\text{C}(\text{Cp})$ 2.291(7)-2.393(5), $\text{W}-\text{CO}$ 1.969-2.029(4) Å; angles at W: $\text{OC}-\text{W}-\text{CO}(\text{cis})$ 71.3-78.5(3), $\text{OC}-\text{W}-\text{CO}(\text{trans})$ 108.3-115.0(2), $\text{C}(1)-\text{W}-\text{CO}(\text{trans})$ 125.8-131.1(2)°]. Similarly, the $\text{Fe}-\text{C}(\text{Cp})$ [2.01(1)-2.063(4) Å] fall within the usual range. Other details worthy of comment follow.

$\text{W}(\text{C}\equiv\text{CFc})(\text{CO})_3\text{Cp}$ (**2.1**). The $\text{W}-\text{C}$ [2.162(7) Å] and $\text{C}-\text{C}$ distance [1.19(1) Å] confirm the acetylide formulation which is essentially linear with $\text{W}-\text{C}(1)-\text{C}(2)$ [176.9(6)°] and $\text{C}(1)-\text{C}(2)-\text{C}(201)$ [178.5(8)].

$\text{W}(\text{C}\equiv\text{CC}\equiv\text{CFc})(\text{CO})_3\text{Cp}$ (**2.2**). The $\text{W}-\text{C}$ [2.12(2) Å] and $\text{C}-\text{C}$ distances [1.20, 1.37, 1.24(2) Å] confirm the diyne nature of the carbon chain, which is slightly bent (by *ca* 4° at each carbon atom).

$\text{W}\{\text{C}\equiv\text{CC}_2\text{Fc}[\text{Co}_2(\text{CO})_6]\}(\text{CO})_3\text{Cp}$ (**2.8**),

$\text{W}\{\text{C}\equiv\text{CC}_2[\text{Co}_2(\text{CO})_6]\text{C}_2\text{Fc}[\text{Co}_2(\text{CO})_6]\}(\text{CO})_3\text{Cp}$ (**2.11**) and $\text{W}\{\text{C}\equiv\text{CC}_2\text{Fc}[\text{Co}_2(\mu\text{-dppm})(\text{CO})_4]\}(\text{CO})_3\text{Cp}$ (**2.9**). The $\text{W}-\text{C}(1)$ distances for these three complexes are similar [2.118(7), 2.128(4), 2.139(3) Å] and the $\text{C}(1)-\text{C}(2)$ distances [1.222(9), 1.207(6), 1.217(4) Å] confirm the presence of the $\text{C}\equiv\text{C}$ triple bond. Complexing to the Co_2 unit lengthens the $\text{C}-\text{C}$ separations to 1.345(8), 1.343(6), 1.360(4) Å and induces bend-back angles of between 141.1(7) and 142.8(4)°. The $\text{Co}-\text{Co}$ separations are 2.467-2.480(1) Å, the presence of the dppm ligand resulting in little change. The pair of Co_2 components in **2.11** lie *transoid* about $\text{C}(4)-\text{C}(5)$.

$\text{Co}_2\text{W}(\mu_3\text{-PPhCH}_2\text{PPh}_2)(\mu_3\text{-CCPhFc})(\text{CO})_5\text{Cp}$ (**2.5**). The X-ray structure determination (Fig. 3 and Table 2) confirms the molecular arrangement, with the Co_2W cluster [Co-Co 2.500(2), Co(2,3)-W 2.660, 2.717(1) Å] supporting the vinylidene ligand, in which the C-C distance is lengthened to 1.41(1) Å as a result of interaction with Co(2). The difference in Co-W distances results from π attachment of both C(1) and C(2) to Co(2), increasing the electron density at this centre and thus shortening the Co(2)-W bond compared with Co(1)-W. Structural parameters for the $\text{PhCH}_2\text{PPh}_2$ ligand are similar to those found in numerous other examples.

$\text{W}\{\text{C}=\text{CFcC}(\text{CN})_2\text{C}(\text{CN})_2\}(\text{CO})_3\text{Cp}$ (**2.11**), $\text{W}\{\text{C}[\text{C}(\text{CN})_2]\text{CFc}=\text{C}(\text{CN})_2\}(\text{CO})_3\text{Cp}$ (**12**) and $\text{W}\{\text{C}\equiv\text{CC}[\text{C}(\text{CN})_2]\text{CFc}=\text{C}(\text{CN})_2\}(\text{CO})_3\text{Cp}$ (**2.14**). The first two structures enable a direct comparison to be made between the cyclobutenyl and butadienyl ligands. In **2.11**, the C(3)-C(4) bond is relatively long [1.596(5) Å] and the torsion angle about this bond is $-1.8(2)^\circ$, suggesting that the conrotatory ring-opening which eventually leads to **2.12** is beginning in this complex. In the butadienyl, a *transoid* conformation is adopted, the C(1)-C(4) and C(2)-C(3) separations clearly showing the presence of C=C double bonds. The W-C(1) distances [2.198(3), 2.228(3) Å for **2.11** and **2.12**, respectively] are ca 0.09, 0.12 Å longer than found for the W-C(sp) bond in **2.14** [2.107(3) Å], and are consistent with the usual lengthening found on going from sp to sp² hybridised carbons. The structural determination of **2.14** confirms the site of addition of the cyano-olefin as the Fc-C $\equiv$ C triple bond of precursor **2.2**, bond parameters being similar to those of **2.14**.

$\text{W}\{\text{C}[\text{C}(\text{CN})\text{C}(\text{OMe})=\text{NH}]\text{CFc}=\text{C}(\text{CN})_2\}(\text{CO})_2\text{Cp}$ (**2.13**). The structure determination (Fig. 9, Table 6) confirms the site of addition of the MeOH molecule to one of the dicyanomethylene CN groups adjacent to the tungsten, thus allowing chelation of the resulting imine group. Structural data are consistent with the formulation, with W-C and W-N distances of 2.140(4) and 2.149(5) Å respectively; the various C-C and C-N separations in the ligand are consistent with the formulation shown in structure **2.13**.

ELECTROCHEMISTRY

Table 13. Selected electrochemical data (V)^a

Complex	E ₁	E ₂
2.1	0.50	1.06 (irr)
2.2	0.56	1.05 (irr)
2.3	0.62	1.04 (irr)
2.4	0.65	1.11 (irr)
2.6	0.29	0.63
2.7	0.49	1.03 (irr)
2.8^b	0.32	0.71
2.11	0.73	1.44 (irr)
2.12	0.76	1.42 (irr)
2.14^c	0.89	1.18 (irr)

^a 0.1 mg ml⁻¹ in CH₂Cl₂, 0.1 M [NBu₄]BF₄, r.t., Pt electrodes ([FcH]/[FcH]⁺ = 0.46 V).

^b Also shows third, irreversible oxidation wave at +1.11 V. ^c Also shows two reversible reduction waves at -0.59, -0.80 V.

Interest in the conduction of electronic effects along the unsaturated carbon chain led us to examine the CVs of these complexes, although as previously described, the tungsten end-cap is not generally redox active in similar compounds. Consequently, the single reversible oxidation wave found for each compound [E° +0.50 (**2.1**), +0.56 (**2.2**), +0.62 (**2.3**), +0.65 V (**2.4**); referenced to FcH/[FcH]⁺ = +0.46 V] (Table 13) is assigned to the one electron oxidation of the ferrocenyl nucleus, which moves to higher potentials as the chain is lengthened. This is consistent with partial electron transfer from the ferrocene nucleus onto the carbon chain. Irreversible oxidations between +1.04 and +1.11 V are assigned to processes occurring at the tungsten centre: there is no obvious correlation between these potentials and chain length.

Addition of the Co₂(CO)₆ fragment to **2.2** to give **2.7** resulted in a decrease in oxidation potential to +0.49 V, with an irreversible oxidation occurring at +1.03 V. More dramatic changes in oxidation potential were found with the adducts **2.6** and **2.8**, which showed two reversible 1-e oxidations at +0.29 and 0.63 V, and +0.32 and 0.71 V, respectively. Only **2.8** showed an irreversible oxidation at higher potential

(+1.11 V). The reduction in oxidation potential of $\text{Co}_2(\mu\text{-dppm})(\text{CO})_4$ adducts of poly-ynyl complexes has been noted before and is ascribed to the increased electron density in the Co_2C_2 core as a result of the presence of the dppm ligand.³⁵⁻³⁷

Alteration of the carbon chain by cycloaddition of tcne and subsequent ring-opening reactions to give tetracyanobutadienyl derivatives results in an increase in the first oxidation potentials to +0.73, 0.76 and 0.89 V for **2.11**, **2.12** and **2.14**, respectively. The first two showed irreversible oxidations at +1.44 and +1.42 V, respectively, while for **2.14**, this second oxidation was found at +1.18 V. Unusually, the latter complex also showed two reduction waves at -0.59 and -0.80 V, which are likely to involve the cyanocarbon groups. These observations are all consistent with the addition of strongly electron-withdrawing groups to the chain, although we have not yet carried out any further characterisation of the oxidation or reduction products.

DISCUSSION

Application of Sonogashira, Hay and oxidative coupling reactions has enabled the preparation of a series of alkynyl and poly-ynyl complexes of tungsten, which additionally contain redox-active ferrocenyl groups. Thus, copper(I)-catalysed reactions of ethynyl- and butadiynyl-ferrocenes with $\text{WCl}(\text{CO})_3\text{Cp}$ gave $\text{W}\{(\text{C}\equiv\text{C})_n\}(\text{CO})_3\text{Cp}$ ($n = 1$ **2.1** and 2 **2.2**, respectively), while Hay coupling of $\text{FcC}\equiv\text{CI}$ with $\text{W}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{CO})_3\text{Cp}$ gave the derivative with $n = 3$ **2.3**. The heterometallic tetrayne **2.4** was obtained with the two homometallic complexes by oxidative coupling of $\text{FcC}\equiv\text{CC}\equiv\text{CH}$ with $\text{W}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{CO})_3\text{Cp}$, all three coupling products being obtained in approximately equal amounts. All complexes **2.1-2.4** were obtained pure as crystalline solids and characterised spectroscopically. Unfortunately, it has not been possible to assign the resonances for the carbon chains unequivocally as couplings to tungsten were not resolved. The possibility of using tertiary phosphine-substituted tungsten groups was not explored. X-ray crystal structure determinations of **2.3** and **2.4** were dogged by difficulties in refinement so that only the structures of **2.1** and **2.2** were satisfactorily obtained.

Subsequent chemistry associated with the poly-yne system was carried out with the dicobalt carbonyl and tetracyanoethylene adducts. With $\text{Co}_2(\text{CO})_8$, **2.2** gave a mono-adduct, shown crystallographically to be the expected isomer with the $\text{Co}_2(\text{CO})_6$ unit attached to the C_2 group adjacent to the Fc group, i.e. the least sterically hindered site. No evidence for the formation of the other isomer with the Co_2 group attached to the $\text{W-C}\equiv\text{C}$ triple bond was obtained. With **2.3**, two adducts were obtained, one bearing a $\text{Co}_2(\text{CO})_6$ fragment attached to the central C_2 unit and the other being the bis-adduct, where the second dicobalt fragment is attached to the C_2 unit next to the Fc group. The formation of mono-adducts in which the Co_2 unit is attached to either the $\text{W-C}\equiv\text{C}$ or the $\text{Fc-C}\equiv\text{C}$ triple bond was not observed, nor were any complexes containing a complexed $\text{W-C}\equiv\text{C}$ triple bond obtained.

Reactions of $\text{Co}_2(\mu\text{-dppm})(\text{CO})_6$ with **2.1** afforded the expected simple adduct **2.4**, together with a rearranged product which was identified crystallographically as the Co_2W cluster **2.5**. Although the latter was obtained from a reaction carried out in

refluxing benzene for 16 h, similar treatment of **2.4** did not result in any transformation to **2.5**. The cluster contains a dephenylated dppm ligand together with a vinylidene bearing both phenyl and ferrocenyl groups, which bridges all three metal atoms. As found previously,³⁵⁻³⁷ the vinylidene is π -bonded to the most electronegative metal centre. It is reasonable to suggest that thermal cleavage of a P-Ph bond liberates a Ph group which is trapped by the ferrocenylethynyl ligand, effectively an electrophilic attack by the phenyl group. Under the reaction conditions, decarbonylation also occurs with concomitant cluster formation, no doubt assisted by the cluster-capping requirements of the two non-carbonyl ligands. It is not possible to say whether any other intermediates are formed, for example, by oxidative addition of the P-Ph bond to either W or Co₂ centres. Coordination of a Co₂(μ -dppm)(CO)₄ fragment to the Fc-C $\equiv$ C triple bond of **2.2** gives **2.8** as the only product isolated, from the reaction between **2.2** and Co₂(μ -dppm)(CO)₆.

Many reactions of tcne with σ -alkynyl-metal complexes have been described.^{23-27,29,34} The generally accepted course of these reactions is via a radical (or diradical) intermediate to give a σ -cyclobutenyl complex, which then more or less rapidly undergoes ring opening to form the corresponding σ -buta-1,3-dien-2-yl derivative. The butadienyl ligand in these complexes may chelate the metal centre to give an η^3 -allylic system if an easily displaced ligand is present.

The present study has examined reactions of tcne with **2.1**, **2.2** and **2.3**. Only with **2.1** has the cyclobutenyl complex **2.11** been isolated; thermolysis of **2.11** afforded butadienyl **2.12**. Both complexes were crystallographically characterised as was an unusual product obtained when **2.12** was extracted from t.l.c. silica gel with methanol. We have subsequently found that this reaction between **2.12** and MeOH occurs only in the presence of the solid support. The product **2.13** is formed by addition of MeOH across one of the CN groups of the tetracyano-dienyl ligand to give the methoxy-imine which chelates the tungsten via the NH group with displacement of CO. A similar product, serendipitously isolated from the reaction between W{C=CPhC(CF₃)₂C(CN)₂}(CO)₃Cp and Me₃NO.2H₂O, and formed by hydrolysis of a CN group was described earlier.²⁷

The product **2.14** obtained from tcne and **2.2** results from addition of the cyano-olefin to the Fc-C $\equiv$ C triple bond, whereas that from **2.3** is formed by addition to the central C $\equiv$ C triple bond. In all cases, the reactions apparently occur under steric control. We have no evidence for the formation of complexes containing more than one molecule of tcne.

CONCLUSIONS

This chapter has described the preparation of a series of poly-ynyl complexes containing ferrocenyl and W(CO)₃Cp end-groups. The redox properties of the ferrocenyl nucleus show a moderate increase in oxidation potential which can be correlated with increasing chain length. The tungsten centre is irreversibly oxidised at higher and relatively constant potentials. Conventional addition reactions occur between the complexes and dicobalt carbonyls, an unexpected product in one case being formed by dephenylation of a dppm ligand and trapping of the released phenyl group by the ferrocenylethynyl group to form a vinylidene ligand. With tcne, the anticipated cyclobutenyl and butadienyl derivatives are formed. Reaction of the tcne adduct **2.12** with MeOH in the presence of silica gel resulted in addition of MeOH to one CN group to form an imine ligand which chelates the tungsten atom.

EXPERIMENTAL

General experimental conditions

All reactions were carried out under dry, high purity nitrogen unless otherwise stated, using standard Schlenk techniques. Common solvents were dried, distilled under nitrogen and degassed before use. Elemental analyses were performed by the Canadian Microanalytical Service, Delta, B.C., Canada. Preparative t.l.c. was carried out on glass plates (20 x 20 cm) coated with silica gel (Merck 60 GF₂₅₄, 0.5 mm thick).

Instrumentation

Infrared spectra were obtained with a Perkin-Elmer 1720X FTIR spectrometer. Solution spectra in CH₂Cl₂ were obtained using a 0.5 mm path length solution cell with NaCl windows. Nujol mull spectra were obtained from samples mounted between NaCl discs. NMR spectra were recorded on a Varian Inova 600 (¹H at 599.873 MHz, ¹³C at 150.85 MHz) or Bruker ACP 300 (¹H at 300.13 MHz, ¹³C at 75.47 MHz) or Varian Gemini 200 (¹H at 199.8 MHz, ¹³C at 50.29 MHz) spectrometers. Samples were dissolved in CDCl₃ (unless otherwise stated) contained in 5 mm sample tubes. ES mass spectra were measured using methanol solutions (unless otherwise stated) which were injected into a Finnigan LCQ mass spectrometer via slow infusion using a syringe pump (250 µL) at a flow rate of 15 µL/minute. Nitrogen was used as the drying and nebulising gas. A capillary voltage of 27 V was used and the spray voltage was 5.4 V. Aids to ionisation were used as indicated³⁸. The cyclic voltammograms were collected on a MacLab xxxxx at r.t from (0.1 mg mL⁻¹) solutions in CH₂Cl₂ containing 0.1 M [NBu₄][BF₄] as the supporting electrolyte, at 200 mV s⁻¹, using a platinum working electrode, pseudo reference electrode and platinum wire counter electrode referenced to [FcH]/[FcH]⁺ = +0.46 V.

Reagents

CuI (Fluka), Co₂(CO)₈ (Strem), CuCl (Ajax), tmeda (Merck) and tcne (Fluka) were used as received. The compounds FcC≡CH,³⁹ WCl(CO)₃Cp,⁴⁰ FcC≡CC≡CH,³² W(C≡CC≡CH)(CO)₃Cp,⁴¹ Pd(PPh₃)₄,⁴² and Co₂(μ-dppm)(CO)₆⁴³ were prepared using the cited methods. FcC≡CI was prepared as described in Chapter 5.

(a) $\text{W}(\text{C}\equiv\text{CFc})(\text{CO})_3\text{Cp}$ (**2.1**).

To a stirred solution of $\text{WCl}(\text{CO})_3\text{Cp}$ (750 mg, 2.04 mmol) in $\text{thf}/\text{NH}_4\text{Et}_2$ (45 mL, 1/2) was added CuI (40 mg) followed by $\text{FcC}\equiv\text{CH}$ (428 mg, 2.04 mmol). After 30 min, the solution was filtered to remove $[\text{NH}_4\text{Et}_2]\text{Cl}$ and the solvent removed. The residue was taken up in CH_2Cl_2 and passed down an alumina column. Elution with hexane produced an orange fraction which yielded orange $\text{W}(\text{C}\equiv\text{CFc})(\text{CO})_3\text{Cp}$ (**2.1**) (604 mg, 55%). Anal. Found: C, 43.89; H, 2.60; $\text{C}_{20}\text{H}_{14}\text{FeO}_3\text{W}$ calcd: C, 44.32; H, 2.60%; M, 542. IR: $\nu(\text{C}\equiv\text{C})$ 2099w; $\nu(\text{CO})$ 2036s, 1951s (br) cm^{-1} . ^1H NMR: δ 4.04, 4.25 (2 x m, 4H, FcC_5H_4), 4.14 (s, 5H, FeCp), 5.60 (s, 5H, WCp). ^{13}C NMR: δ 65.61 (s, C_a), 67.50 (s, C_b), 67.90 (s, C_β), 69.57 (s, FeCp), 70.84 (s, C_c), 91.60 (s, WCp), 125.81 (s, C_α), 211.53 (t, J_{CW} 72 Hz, CO), 229.89 (t, J_{CW} 62 Hz, CO). ES mass spectrum (MeOH, positive ion, m/z): 542, M^+ ; 514, $[\text{M} - \text{CO}]^+$; 458, $[\text{M} - 2\text{CO}]^+$.

(b) $\text{W}(\text{C}\equiv\text{CC}\equiv\text{CFc})(\text{CO})_3\text{Cp}$ (**2.2**).

To a stirred solution of $\text{WCl}(\text{CO})_3\text{Cp}$ (150 mg, 0.41 mmol) in $\text{thf}/\text{NH}_4\text{Et}_2$ (15 mL, 1/2) was added CuI (ca 10 mg) followed by $\text{FcC}\equiv\text{CC}\equiv\text{CH}$ (95 mg, 0.41 mmol). After 15 min the solution was then filtered to remove $[\text{NH}_4\text{Et}_2]\text{Cl}$ and the solvent removed. The residue was taken up in CH_2Cl_2 and passed down an alumina column. Elution with hexane produced a red/orange fraction which yielded red $\text{W}(\text{C}\equiv\text{CC}\equiv\text{CFc})(\text{CO})_3\text{Cp}$ (**2.2**) (184 mg, 79%). Crystals suitable for the X-ray study were grown from CH_2Cl_2 /pentane. Anal. Found: C, 46.04; H, 2.55; $\text{C}_{22}\text{H}_{14}\text{FeO}_3\text{W}$ calcd: C, 46.68; H, 2.49%; M, 566. IR: $\nu(\text{C}\equiv\text{C})$ 2186w, 2054 (sh); $\nu(\text{CO})$ 2036s, 1955s (br) cm^{-1} . ^1H NMR: δ 4.15, 4.25 (2 x m, 4H, FcC_5H_4), 4.20 (s, 5H, FeCp), 5.62 (s, 5H, WCp). ^{13}C NMR: δ 64.94 (s), 67.89 (s), 68.68 (s, C_b), 69.94 (s, FeCp), 71.97 (s, C_c), 72.59 (s), 73.30 (s, C_β), 91.60 (s, WCp), 111.84 (s), 210.65 (t, J_{CW} 61Hz, CO), 228.07 (t, J_{CW} 61Hz, CO). ES mass spectrum (MeOH, positive ion, m/z): 566, M^+ ; 538, $[\text{M} - \text{CO}]^+$.

(c) $\text{W}\{(\text{C}\equiv\text{C})_3\text{Fc}\}(\text{CO})_3\text{Cp}$ (**2.3**).

NHPr_2 (15 ml) in a flame-dried Schlenk tube was rigorously deoxygenated using the freeze/pump/thaw method. $\text{W}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{CO})_3\text{Cp}$ (200 mg, 0.52 mmol), $\text{FcC}\equiv\text{C}\text{I}$ (176 mg, 0.52 mmol), $\text{Pd}(\text{PPh}_3)_4$ (40 mg, 0.034 mmol) and CuI (ca 10 mg) were

added in that order and the resulting orange-red solution was stirred in the dark for 3 h. After this time the orange precipitate which had formed was collected and dissolved in a minimum amount of CH_2Cl_2 . This solution was then passed down an alumina column, eluting with hexane to yield bright orange $\text{W}\{(\text{C}\equiv\text{C})_3\text{Fc}\}(\text{CO})_3\text{Cp}$ (**2.3**) (220 mg, 72%). Anal. Found: C, 48.04; H, 2.46; $\text{C}_{24}\text{H}_{14}\text{FeO}_3\text{W}$ calcd: C, 48.85; H, 2.39%; M, 590. IR: $\nu(\text{C}\equiv\text{C})$ 2178w, 2138m, 2023m; $\nu(\text{CO})$ 2047s, 1959s (br) cm^{-1} . ^1H NMR: δ 4.45, 4.20 (2 x m, 4H, FeC_5H_4), 4.20 (s, 5H, FeCp), 5.62 (s, 5H, WCp). ^{13}C NMR: δ 60.09 (s), 60.95 (s), 63.29 (s, C_a), 63.83 (s), 66.13 (s), 69.23 (s, C_b), 70.20 (s, FeCp), 71.40 (s), 72.44 (s, C_c), 91.67 (s, WCp), 112.17 (s), 210.33 (t, J_{CW} 72Hz, CO), 227.22 (t, J_{CW} 61Hz, CO). (ES mass spectrum (MeOH, positive ion, m/z): 590, M^+ ; 562, $[\text{M} - \text{CO}]^+$).

Preparation of Hay's catalyst

To a suspension of freshly purified CuCl (50 mg, 0.51 mmol) in acetone (5 ml) was added *tmeda* (75 μL , 59 mg, 0.51 mmol). The solution turned blue immediately and was stirred for a further 30 min.

(d) $\text{W}\{(\text{C}\equiv\text{C})_4\text{Fc}\}(\text{CO})_3\text{Cp}$ (**2.4**)

$\text{W}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{CO})_3\text{Cp}$ (150 mg, 0.39 mmol) and $\text{Fc}(\text{C}\equiv\text{CC}\equiv\text{CH})$ (92 mg, 0.39 mmol) were dissolved in acetone (20 ml) and a vigorous stream of oxygen was passed through the orange-red solution. The Hay catalyst was added in portions until the reaction was adjudged complete (t.l.c.). The solvent was removed in vacuo and the residue extracted with CH_2Cl_2 . Preparative t.l.c. (hexane/acetone, 7/3) gave three fractions. The first (R_f 0.7) contained $\text{Fc}_2(\text{C}\equiv\text{C})_4$ (40 mg, 22%). The second band (R_f 0.5) afforded $\text{W}\{(\text{C}\equiv\text{C})_4\text{Fc}\}(\text{CO})_3\text{Cp}$ (**2.4**) (57 mg, 24%). The third band contained $\{\text{W}(\text{CO})_3\text{Cp}\}(\text{C}\equiv\text{C})_4$ (70 mg, 24%). The two known compounds were characterised from their IR and ^1H NMR spectra. Data for $\text{W}\{(\text{C}\equiv\text{C})_4\text{Fc}\}(\text{CO})_3\text{Cp}$ (**2.4**): Anal. Found: C, 49.92; H, 2.63; $\text{C}_{26}\text{H}_{14}\text{FeO}_3\text{W}$ calcd: C, 50.85; H, 2.30%; M, 614. IR: $\nu(\text{C}\equiv\text{C})$ 2184m, 2131w, 2099w, 2011m; $\nu(\text{CO})$ 2047s, 1961s (br) cm^{-1} . ^1H NMR: δ 4.25, 4.49 (2 x m, FeC_5H_4), 4.23 (s, 5H, FeCp), 5.63 (s, 5H, WCp). ^{13}C NMR: δ 60.63(s), 62.12 (s), 62.70 (s), 64.45 (s), 65.67 (C_a), 69.69 (s, C_b), 70.31 (s, FeCp), 70.48 (s), 71.39 (s), 73.02 (s, C_c), 80.38 (s), 91.68 (s, WCp), 112.16 (s), 210.19 (s,

CO). ES mass spectrum (MeCN, positive ion, with $[\text{Ag}(\text{NCMe})_4]\text{BF}_4$, m/z): 1336, $[2\text{M} + \text{Ag}]^+$, 655, $[\text{M} + \text{NCMe}]^+$.

Reactions with dicobalt carbonyl complexes

(e) $\text{W}(\text{C}\equiv\text{CFc})(\text{CO})_3\text{Cp}$ and $\text{Co}_2(\mu\text{-dppm})(\text{CO})_6$.

2.1 (70 mg, 0.13 mmol) and $\text{Co}_2(\mu\text{-dppm})(\text{CO})_6$ (100 mg, 0.15 mmol) were dissolved in C_6H_6 (15 ml) and warmed to 80°C . Stirring was continued for 16 h after which the solvent was removed. Preparative t.l.c. (hexane/ CH_2Cl_2 , 7/3) gave two major bands.

The dark red-brown band (R_f 0.5) contained dark red $\text{Co}_2\text{W}(\mu_3\text{-CCPhFc})(\mu_3\text{-PPhCH}_2\text{PPh}_2)(\text{CO})_5\text{Cp}$ (**2.5**) (20 mg, 14%). Crystals suitable for the structure determination were grown from CH_2Cl_2 /pentane. Anal. Found: C, 48.55; H, 3.38; $\text{C}_{47}\text{H}_{36}\text{Co}_2\text{FeO}_5\text{P}_2\text{W}\cdot\text{CH}_2\text{Cl}_2$ calcd: C, 48.64; H, 3.23%; M, 1100. IR: $\nu(\text{CO})$ 2014m, 1991s, 1956s (br), 1899m (br) cm^{-1} . ^1H NMR: δ 3.66 (s, 5H, FeCp), 4.21, 4.41, (2 x m, 4H, FeC_5H_4), 5.11 (s, 5H, WCp), 7.2-7.8 (m, 20H, Ph). ^{13}C NMR: δ 29.70 (m, CH_2P), 68.21 (s, C_β), 68.92 (s, FeCp), 69.44 (s, C_α), 70.23 (s, C_β), 86.87 (s, WCp), 103.88 (s, C_α), 125.69-131.92 (m, Ph). ES mass spectrum (MeOH, positive ion, NaOMe added, m/z): 1123, $[\text{M} + \text{Na}]^+$; 1016, $[\text{M} - 3\text{CO}]^+$; 988, $[\text{M} - 5\text{CO}]^+$; 960, $[\text{M} - 4\text{CO} - \text{Ph}]^+$.

The black band (R_f 0.35) yielded black $\text{W}\{\eta^1:\eta^2\text{-C}_2\text{Fc}[\text{Co}_2(\mu\text{-dppm})(\text{CO})_4]\}(\text{CO})_3\text{Cp}$ (**2.6**) (30 mg, 20%). Anal. Found: C, 49.84; H, 3.74; $\text{C}_{49}\text{H}_{36}\text{Co}_2\text{FeO}_7\text{P}_2\text{W}$ calcd: C, 50.90; H, 3.14%; M, 1156. IR: $\nu(\text{CO})$ 1986s, 1954s, 1928 (sh), 1812m (br) cm^{-1} . ^1H NMR: δ 3.91 (m, 2H, P- CH_2), 4.20 (s, 5H, FeCp), 4.49, 4.90 (2 x m, 4H, FeC_5H_4), 4.72 (s, 5H, WCp), 7.15-7.62 (m, 20H, PPh₂). ^{13}C NMR: δ 92.81 (s, WCp), 126.33-137.22 (m, Ph). ES mass spectrum (CH_2Cl_2 /MeOH, positive ion, m/z): 1016, $[\text{M} - 5\text{CO}]^+$; 988, $[\text{M} - 6\text{CO}]^+$; 960, $[\text{M} - 7\text{CO}]^+$.

(f) $\text{W}\{\eta^1:\eta^2\text{-C}\equiv\text{CC}_2\text{Fc}[\text{Co}_2(\text{CO})_6]\}(\text{CO})_3\text{Cp}$ (**2.7**).

2.2 (50 mg, 0.09 mmol) and $\text{Co}_2(\text{CO})_8$ (41 mg, 0.12 mmol) were dissolved in benzene (10 ml) and stirred for 16 h. The black solution was evaporated and the residue purified by preparative t.l.c. (hexane/ CH_2Cl_2 , 3/1). The black band (R_f 0.4) contained

$W\{\eta^1:\eta^2-C\equiv CC_2Fc[Co_2(CO)_6]\}(CO)_3Cp$ (**2.7**) (46 mg, 60%). Crystals suitable for the X-ray determination were grown from CH_2Cl_2 /pentane. Anal. Found: C, 38.54; H, 1.82; $C_{28}H_{14}Co_2FeO_9W.0.5CH_2Cl_2$ calcd: C, 38.27; H, 1.69%; M, 852. IR: $\nu(C\equiv C)$ 2085m; $\nu(CO)$ 2048s, 2033s, 2021s, 1953s (br) cm^{-1} . ^1H NMR: δ 4.29 (s, 5H, FeCp), 4.29, 4.42 (2 x m, 4H, FeC_5H_4), 5.68 (s, 5H, WCp). ^{13}C NMR: δ 69.67 (s, FeCp), 69.91 (s, C_b), 69.94 (s, C_c), 85.69 (s), 91.76 (s, WCp), 93.21 (s), 124.82 (s), 210.34 (s, WCO), 228.41 (s, WCO). ES mass spectrum (MeOH, negative ion, NaOMe added, m/z): 883, $[M + OMe]^-$; 799-631, $[M + OMe - nCO]^-$ ($n = 3 - 9$).

(g) $W\{\eta^1:\eta^2-C\equiv CC_2Fc[Co_2(\mu-dppm)(CO)_4]\}(CO)_3Cp$ (**2.8**).

2.2 (68 mg, 0.12 mmol) and $Co_2(\mu-dppm)(CO)_6$ (100 mg, 0.15 mmol) were heated in refluxing C_6H_6 (10 ml) for 1 h. The solvent was removed in vacuo and the black residue extracted with CH_2Cl_2 . Preparative t.l.c. (hexane/ CH_2Cl_2 , 7/3) produced a dark red band (R_f 0.35) from which dark red $W\{\eta^1:\eta^2-C\equiv CC_2Fc[Co_2(\mu-dppm)(CO)_4]\}(CO)_3Cp$ (**2.8**) (60 mg, 42%) was obtained. X-ray quality crystals were grown from CH_2Cl_2 /pentane. Anal. Found: C, 52.84; H, 3.54; $C_{51}H_{36}Co_2FeOP_2$ calcd: C, 51.90; H, 3.07%; M, 1180. IR: $\nu(C\equiv C)$ 2033m; $\nu(CO)$ 2016m, 1992s (br), 1962 (sh), 1951s (br) cm^{-1} . ^1H NMR: δ 3.25, 3.80 (2 x m, 2H, PCH_2), 4.26, 4.50 (2 x m, 4H, FeC_5H_4), 4.33 (s, 5H, FeCp), 5.59 (s, 5H, WCp), 7.12-7.61 (m, 20H, Ph). ^{13}C NMR: δ 29.62 (s, CH_2P), 67.87 (s, C_a), 69.19 (s, FeCp), 69.64 (s, C_b), 69.82 (s, C_c), 75.57 (s), 91.63 (s, WCp), 90.85 (s), 95.37 (s), 111.74 (s), 127.80-133.51 (m, Ph), 210.84 (s, WCO), 218.44 (s, WCO). ES mass spectrum (MeOH, positive ion, m/z): 1124 - 984, $[M - nCO]^+$ ($n = 2 - 7$).

(h) **2.3** + $Co_2(CO)_8$.

2.3 (150 mg, 0.25 mmol) and $Co_2(CO)_8$ (87 mg, 0.25 mmol) were dissolved in benzene (30 ml) and stirred in the dark for 16 h. The solvent was then removed in vacuo. The resulting oil was dissolved in CH_2Cl_2 . Preparative t.l.c. (hexane/ CH_2Cl_2 , 3/1) gave two black bands.

The first (R_f 0.3) gave $W\{C\equiv CC_2[Co_2(CO)_6]C\equiv CFc\}(CO)_3Cp$ (**2.9**) (85 mg, 38%). Anal. Found: C, 41.63; H, 2.20; $C_{30}H_{14}Co_2FeO_9W$ calcd: C, 41.13; H, 1.61%; M, 876. IR: $\nu(C\equiv C)$ 2134m, 2089w; $\nu(CO)$ 2054s, 2030s, 1956s (br) cm^{-1} . ^1H NMR: δ 4.28 (s,

5H, FeCp), 4.45, 4.34 (2 x m, 4H, FeC₅H₄), 5.69 (s, 5H, WCp). ¹³C NMR: δ 69.17 (s, FeCp), 69.85 (s, C_b), 70.02 (s, C_c), 72.50 (s), 72.55 (s), 84.34 (s), 85.31 (s), 87.72 (s), 91.75 (s, WCp), 112.46 (s), 198.74 (br, CoCO), 210.35 (s, WCO), 227.21 (s, WCO). ES mass spectrum (MeOH, positive ion, *m/z*): 876, M⁺; 848-764, [M - nCO]⁺, (n = 1 - 4).

The second band (*R_f* 0.4) contained W{C≡CC₂[Co₂(CO)₆]C₂Fe[Co₂(CO)₆]}(CO)₃Cp (**2.10**) (31 mg, 21%). Crystals suitable for the X-ray structure determination were grown from CH₂Cl₂/MeOH. Anal. Found: C, 36.90; H, 1.86; C₃₆H₁₄Co₄FeO₁₅W calcd: C, 37.21; H, 1.21%; M, 1162. IR: ν(C≡C) 2095m; ν(CO) 2076s, 2057vs, 2031s, 2020s, 1954s (br) cm⁻¹. ¹H NMR: δ 4.24 (s, 5H, FeCp), 4.33, 4.56 (2 x m, 4H, FeC₅H₄), 5.60 (s, 5H, WCp). ¹³C NMR: δ 68.72 (s, C_b), 69.73 (s, FeCp), 70.95 (s, C_c), 91.73 (s, WCp), 112.45 (s, C_α), 199.24 (br, CoCO), 210.06 (s, WCO), 228.41 (s, WCO). ES mass spectrum (MeOH, negative ion, NaOMe added, *m/z*): 1192, [M + OMe]⁻; 1108-742, [M + OMe - nCO]⁻ (n = 3 - 15).

Reactions with tetracyanoethene

(i) W{C=CFcC(CN)₂C(CN)₂}(CO)₃Cp (**2.11**).

2.1 (200 mg, 0.37 mmol) and tcne (51 mg, 0.40 mmol) were dissolved in CH₂Cl₂ (20 ml). The initial orange solution turned red after a few min. After 1 h the volume was reduced to ca 1-2 ml and dropped into rapidly stirred hexane. The light orange-brown precipitate was purified by preparative t.l.c. (hexane/ CH₂Cl₂, 1/1) to give orange W{C=CFcC(CN)₂C(CN)₂}(CO)₃Cp (**2.11**) (183 mg, 74%). Crystals were grown from CH₂Cl₂/pentane. Anal. Found: C, 46.90; H, 2.20; N, 8.36; C₂₆H₁₄FeN₄O₃W calcd: C, 46.60; H, 2.11; N, 8.27%; M, 670. IR: ν(CN) 2390w, 2338w; ν(CO) 2042s, 1963s, 1944 (sh) cm⁻¹. ¹H NMR: δ 4.29 (s, 5H, FeCp), 4.46, 4.52 (2 x m, 4H, FeC₅H₄), 5.83 (s, 5H, WCp). ¹³C NMR: δ 46.88, 44.35 (2 x s, 2 x C(CN)₂), 67.82 (s, C_a), 70.54 (s, FeCp), 70.83 (s, C_b), 73.84 (s, C_c), 91.88 (s, WCp), 110.61, 111.28 (2 x s, 2 x CN), 155.15 (s, C_β), 212.83 (s, WCO), 221.78 (s, C_α), 228.40 (s, WCO). ES mass spectrum (MeOH, positive ion, NaOMe added, *m/z*): 693, [M + Na]⁺.

(j) Pyrolysis of $W\{C=CFcC(CN)_2C(CN)_2\}(CO)_3Cp$ (**2.12**).

2.11 (100 mg, 0.15 mmol) was heated in refluxing thf (15 ml) for 6 h. The solvent was removed and the residue chromatographed on preparative t.l.c. plates developing with CH_2Cl_2 . The blue band (R_f 0.6) contained $W\{C[=C(CN)_2]=CFc=C(CN)_2\}(CO)_3Cp$ (**2.12**) (33 mg, 33%) (from CH_2Cl_2 /hexane). Anal. Found: C, 46.31; H, 2.48; N, 7.89; $C_{26}H_{14}FeN_4O_3W$ calcd: C, 46.60; H, 2.11; N, 8.36%; M, 670. IR: $\nu(CN)$ 2222w; $\nu(CO)$ 2049s, 1960s, (br) cm^{-1} . ^1H NMR: δ 4.45 (s, 5H, FeCp), 4.73, 4.92 (2 x m, 4H, FeC_5H_4), 5.51 (s, 5H, WCp). ^{13}C NMR: δ 28.66, 29.33 (2 x s, 2 x $C(CN)_2$), 29.67 (s, C_β), 67.81 (s, C_α), 71.09 (s, C_a), 72.69 (s, FeCp), 73.03 (s, C_b), 74.71 (s, C_c), 93.95 (s, WCp), 113.68, 115.09 (2 x s, 2 x CN), 216.39 (s, WCO), 221.22 (s, WCO). ES mass spectrum (MeOH, positive ion, m/z): 670, M^+ .

When **2.12** is extracted from silica gel with MeOH, a new red product is formed. Purification (t.l.c., $CHCl_3$) gave a red band (R_f 0.3). Extraction and precipitation from CH_2Cl_2 /hexane gave $W\{C[=C(CN)C(OMe)=NH]CFc=C(CN)_2\}(CO)_2Cp$ (**2.13**). Crystals suitable for X-ray analysis were grown from CH_2Cl_2 /MeOH. Anal. Found: C, 45.69; H, 2.33; N, 8.31; $C_{27}H_{18}FeN_4O_4W$ calcd: C, 46.32; H, 2.69; N, 8.31%; M, 674. IR (CH_2Cl_2): $\nu(CN)$ 2220w, $\nu(CO)$ 2046w, 2033w, 1969s, 1897s cm^{-1} . ^1H NMR: δ 4.05 (s, 3H, OMe), 4.52 (s, 5H, FeCp), 4.73, 4.83 (2 x m, 4H, FeC_5H_4), 5.08 (s, 5H, WCp). ES mass spectrum (MeOH, positive ion, m/z): 674, M^+ .

(k) $W\{C\equiv CC[=C(CN)_2]CFc=C(CN)_2\}(CO)_3Cp$ (**2.14**).

2.2 (50 mg, 0.09 mmol) and tcne (13 mg, 0.10 mmol) were dissolved in CH_2Cl_2 (10 ml). The orange solution turned dark green after 5 min. Stirring was continued for a further 1 h. The solvent was removed in vacuo and the residue extracted with CH_2Cl_2 . Preparative t.l.c. (hexane/ CH_2Cl_2 , 2/3) gave a dark green band which was crystallised (CH_2Cl_2 /pentane) to give dark green $W\{C\equiv CC[=C(CN)_2]CFc=C(CN)_2\}(CO)_3Cp$ (**2.14**) (47mg, 75%). Crystals suitable for X-ray analysis were grown from $CHCl_3$ /MeOH. Anal. Found: C, 48.45; H, 2.03; N, 8.07; $C_{28}H_{14}FeN_4O_3W$ calcd: C, 48.73; H, 2.54; N, 7.79%; M, 694. IR: $\nu(CN)$ 2225w, 2166w; $\nu(C\equiv C)$ 2073w; $\nu(CO)$ 2026s, 1965s (br) cm^{-1} . ^1H NMR: δ 4.37 (s, 5H, FeCp), 4.90, 4.96, 5.35 (3 x m, 4H, FeC_5H_4), 5.79 (s, 5H, WCp). ^{13}C NMR: δ 31.89, 31.54 (2 x s, 2 x $C(CN)_2$), 71.01 (s, C_a), 72.49 (s, FeCp), 73.37 (s, C_b), 75.43 (s, C_c), 88.03 (s, C_β), 92.56 (s, WCp),

111.36, 112.89, 113.11, 114.23 (4 x s, 4 x CN), 147.73 (s, C_δ), 170.18 (s, C_γ), 210.20 (s, WCO), 221.21 (s, WCO). ES mass spectrum (MeOH, positive ion, NaOMe added, *m/z*): 717, [M + Na]⁺, (negative ion): 725, [M + OMe]⁻; 697, [M + OMe - CO]⁻; 669, [M + OMe - 2CO]⁻; 641, [M + OMe - 3CO]⁻; 615, [M + OMe - 3CO - CN]⁻.

(l) W{C≡CC[=C(CN)₂]C[=C(CN)₂]C≡CFc}(CO)₃Cp (**2.15**).

2.3 (45 mg, 0.08 mmol) and tcne (11 mg, 0.09 mmol) were stirred in CH₂Cl₂ (10 ml) for 1 h. The solvent was removed and the residue extracted with CH₂Cl₂. Preparative t.l.c. (hexane/CH₂Cl₂, 1/3) gave one major red-brown band which yielded W{C≡CC[=C(CN)₂]C[=C(CN)₂]C≡CFc}(CO)₃Cp (**2.15**) (26 mg, 48%). Anal. Found: C, 49.90; H, 2.07; N, 7.73%; C₃₀H₁₄FeN₄O₃W_{calcd}: C, 50.17; H, 1.96; N, 7.80%; M, 718. IR: ν(CN) 2225w, 2164w; ν(C≡C) 2130s, 2055m; ν(CO) 2025s, 1967s (br) cm⁻¹. ¹H NMR: δ 4.41 (s, 5H, FeCp), 4.89, 4.97, 5.32 (3 x m, 4H, FeC₅H₄), 5.70 (s, 5H, WCp). ¹³C NMR: δ 70.93 (s, C_a), 71.53 (s), 72.67 (s, FeCp), 72.84 (s, C_b), 73.70 (s, C_c), 76.14, 75.84 (2 x s, 2 x C(CN)₂), 92.12 (s, WCp), 105.26 (s, C_α), 110.92, 111.48, 112.87, 113.42 (4 x s, 4 x CN), 148.53 (s, C_δ), 169.66 (s, C_γ), 209.27 (s, WCO), 222.85 (s, WCO). ES mass spectrum (MeOH, positive ion, [Ag(NCMe)₄]BF₄ added, *m/z*): 1544, [2M + Ag]⁺; 826, [M + Ag]⁺; 798, [M + Ag - CO]⁺.

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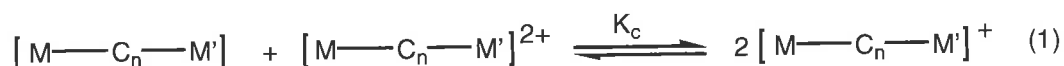
Chapter 3

Syntheses, electrochemistry and properties of mixed ruthenium/iron butadiynediyl complexes.

INTRODUCTION

The construction of complexes capable of mediating electronic effects are under investigation as potential molecular wires which are required for use in the assembly of nanoscale electronic devices.¹⁻⁴ Complexes based on linear polycarbon chains, $-(C\equiv C)_n-$, have emerged as some of the most efficient 'wires' examined to date.⁵⁻⁷

For complexes of the type $M-C_n-M'$, the degree of electronic delocalisation between two equivalent termini, $M = M'$, is gauged by the comproportionation constant, K_c , for the equilibrium shown in Equation 1.



K_c can be calculated from the electrode potentials $E_{1/2}(2+/1+)$ and $E_{1/2}(1+/0)$ ^{8,9} from Equation 2.

$$K_c = (\exp\{F[E_{1/2}(2+/1+)-E_{1/2}(1+/0)]/RT\}) \quad (2)$$

The separation of the oxidation waves ΔE° , also gives an indication of the degree of electronic communication between the metal centres along the C_n bridge. A molecular wire should be a Class III material i.e. delocalised with well separated waves in the CV.

At the beginning of this work, four groups were researching this topic, each using different redox active termini.

Table 1. Electrochemical data for $\{ML_n\}C\equiv CC\equiv C\{ML_n\}^a$.

Complex	$\{ML_n\}$	E_1	E_2	E_3	E_4	1+/2+	2+/3+	3+/4+	$^bK_c \times 10^8$	$^cK_c \times 10^8$	Ref
3.1	Mn(dmpe) ₂ I	^d	^d			0.63			540	450	¹⁰
3.2	Re(NO)(PPh ₃)Cp*	0.01	0.54			0.53			11	9.2	¹¹
3.3	Re(NO)(P(tol) ₃)Cp*	-0.22	0.31			0.53			11	9.2	¹²
3.4	Fe(dppe)Cp*	-0.69	0.03	0.95		0.72	0.92		16000	15000	¹³
3.5	Fe(dippe)Cp*	-0.97	-0.18	0.81		0.79	0.99		n/r	230000	¹⁴
3.6	Ru(PPh ₃) ₂ Cp	-0.23	0.41	1.03	1.68	0.64	0.62	0.65	1500	660	¹⁵
3.7	Ru(PPh ₃)(PMe ₃)Cp	-0.26	0.33	0.97	1.46	0.59	0.64	0.49	2100	950	¹⁵
3.8	Ru(dppe)Cp*	-0.43	0.23	1.02	1.51	0.66	0.79	0.49		1400	¹⁶
3.9	Os(dppe)Cp*	-0.61	0.15	0.80	1.20	0.76	0.55	0.40		71000	¹⁷

^aSee individual references for details of the electrochemical experiments, potentials given in volts (V). ^b K_c reported. ^c K_c re-calculated for $T = 298$ K using Equation 2. ^dThe separation of the two oxidation waves is given (0.63 V) but the actual potentials are yet to be reported.
n/r = not reported

Berke et al. have described complexes containing the manganese endgroup, $\text{Mn}(\text{dmpe})_2\text{I}$. The corresponding butadiynyl complex, **3.1** undergoes two 1-electron oxidation processes.¹⁰ Interestingly, **3.1** is paramagnetic and has a triplet ground state with two electrons with parallel spins occupying practically degenerate, orthogonal π -molecular orbitals which extend over the C_4 chain and the manganese centres. This is confirmed by DFT calculations on the model complex, $\{\text{I}(\text{PH}_3)_4\text{Mn}\}\text{C}\equiv\text{CC}\equiv\text{C}\{\text{Mn}(\text{PH}_3)_4\text{I}\}$. The NMR spectra are paramagnetically shifted. The oxidation products have also been isolated. The mono-oxidised complex has only one unpaired electron and thus the NMR spectrum is less paramagnetically shifted. The di-oxidised complex has no unpaired electrons and gives a diamagnetic NMR spectrum. Structural and IR data indicate that the triplet ground state of **3.1** has alternating C-C and $\text{C}\equiv\text{C}$ bonds, and the diamagnetic singlet dication is cumulenyl.

The chiral rhenium centre $\text{Re}(\text{NO})(\text{PPh}_3)\text{Cp}^*$, has been used by Gladysz et al. The butadiynyl complex **3.2**¹¹ undergoes two reversible 1-electron oxidation processes, shown by cyclic voltammetry. Both the mono- and di-oxidised complexes have been synthesised. The di-oxidised complex has a cumulenyl structure.

Lapinte et al. have concentrated their research on the $\text{Fe}(\text{dppe})\text{Cp}^*$ building block. The diyndyl complex **3.4**¹³ has been synthesised and the oxidation chemistry explored. The complex undergoes three reversible 1-electron oxidation processes, as evidenced by cyclic voltammetry. The mono- and di-oxidised species have been synthesised by chemical oxidation and their properties studied. Unlike the rhenium analogue, the di-oxidised complex has a butadiynyl structure and triplet ground state.

More recently, both Lapinte and Gladysz have modified their respective endgroups in a bid to increase the electron density at the metal centre thereby making the oxidations easier and thus the higher oxidation states more accessible chemically.

Replacement of the dppe moiety in **3.4** for the more electron releasing dippe ligand¹⁴ decreased the oxidation potentials by between 0.14 – 0.29 V in **3.5**. This then enabled the isolation of the first tri-cationic butadiynyl complex, $[\text{3.5}][\text{PF}_6]_3$.

Gladysz et al. looked at replacing the PPh_3 group by $\text{P}(\text{tol})_3$ and also observed a decrease (0.23 V) in both oxidation potentials.¹²

Bruce et al. have chosen to study the ruthenium metal centre, $\text{Ru}(\text{PPh}_3)_2\text{Cp}$. More recently, studies on the more electron-rich $\text{Ru}(\text{dppe})\text{Cp}^*$ group have occurred. The butadiynyl complexes **3.6**^{15,18,19} and **3.8**¹⁶ have been synthesised and show an unprecedented series of four one-electron oxidation processes, again assayed by cyclic voltammetry.

Theoretical calculations indicate that oxidation affects both the metal centres and the carbon atoms of the C_4 bridge, since this process corresponds to the removal of electrons housed in MOs delocalised over all atoms of the $\text{Ru-C}_4\text{-Ru}$ chain.

To date, no molecular wire complex has been reported using osmium endgroups. Accordingly, Bruce and co-workers synthesised the osmium butadiyndiyl complex, **3.9**¹⁷ and have found the oxidation potentials are substantially lower for the osmium complexes when compared to the ruthenium analogue, **3.8**. This research is still in its infancy but indicates that the higher oxidation states should be chemically accessible.

A comparison can be made between these molecular wire complexes on the basis of their oxidation potentials in the CV. These are listed in Table 1.

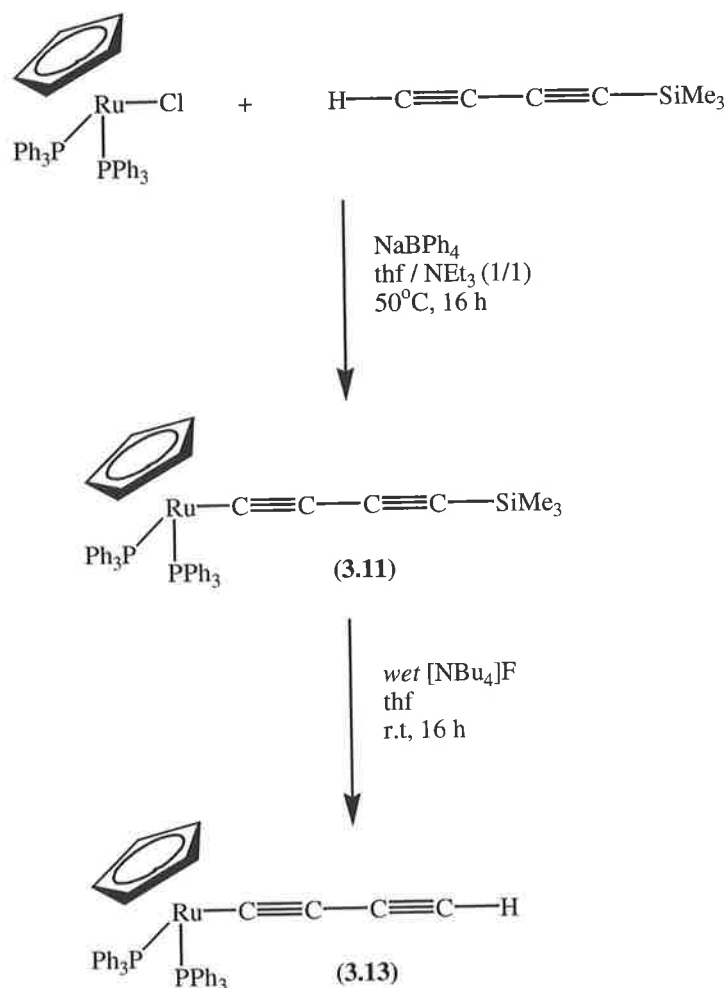
From Table 1 it can be seen that the iron systems (**3.4**, **3.5**) of Lapinte are the most easily oxidised. The rhenium system (**3.2**) is the most difficult to oxidise and only two waves are observed in the CV. While the ruthenium systems are not quite as easily as oxidised as the iron systems, they do have the advantage in that four oxidation waves are observed in the CV. This gives the opportunity of studying the higher oxidation states, +3 and +4, to ascertain the nature of the C_4 bridge. The osmium complex, **3.9** has oxidation potentials very close to those of the iron analogue. Interestingly, the third oxidation potential is the lowest reported and is currently being investigated with the aim of isolating the tri-cationic complex. The data for the manganese system have not yet been published, although a communication has reported the separation of the two observed oxidation waves (0.63 V).¹⁰

The separation of the first two oxidation waves is representative of the degree of electronic delocalisation. The K_c values for each complex can be calculated although these values are extremely sensitive to the temperature at which the CV is measured. Thus, a true comparison cannot be made unless all the complexes listed in Table 1 are examined at the same temperature and under identical conditions. The K_c values recalculated for $T = 298$ K allows a comparison to be made and shows that **[3.5][PF₆]** has the highest value indicating that this complex has the highest thermodynamic stability. Interestingly, the K_c for **[3.9][PF₆]** is similar to that of **[3.5][PF₆]**.

While most of this research has focused on the homobimetallic complexes, one paper has recently appeared describing the properties of the heterobimetallic butadiynediyl complex, $\{\text{Cp}^*(\text{dppe})\text{Fe}\}\text{C}\equiv\text{CC}\equiv\text{C}\{\text{Re}(\text{NO})(\text{PPh}_3)\text{Cp}^*\}$ (**3.10**).²⁰ Three reversible 1-electron oxidations were observed (-0.50, +0.23 and +1.33 V). A comparison between the heterobimetallic complex and the analogous homobimetallic parent complexes (**3.2**, **3.4**) shows that there is still strong communication between the iron and rhenium centres as the oxidation potentials fall between those of the homobimetallic parent complexes.

This chapter focuses on a new heterobimetallic complex with iron and ruthenium endgroups. It was hoped that the increased electron density at the ruthenium centre when compared to rhenium, and the accessible Ru(IV) oxidation state would repay study. The synthesis of these complexes is detailed and the spectroscopic data analysed. In addition to the usual spectroscopic data, UV-Vis, NIR, Mössbauer and ESR spectroscopic techniques have been employed to probe the nature of the complex in each of the isolated oxidation states. Their properties are carefully compared with the parent complexes **3.6**¹⁵ and **3.4**¹³ as well as the heterobimetallic complex **3.10**.²⁰

RESULTS

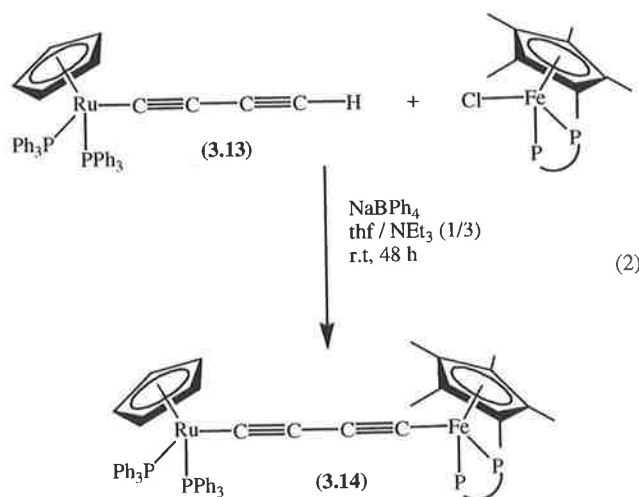
Synthesis and Characterisation

Scheme 1. Syntheses of the new ruthenium butadiynyl complexes **3.11** and **3.13**.

The reaction between $\text{RuCl(PPh}_3)_2\text{Cp}$ and $\text{HC}\equiv\text{CC}\equiv\text{CSiMe}_3$ in a mixed thf/NEt_3 solvent in the presence of NaBPh_4 gave orange-brown $\text{Ru(C}\equiv\text{CC}\equiv\text{CSiMe}_3\text{)(PPh}_3)_2\text{Cp}$ (**3.11**) in 94% yield (Scheme 1). This method is similar to that employed for the synthesis of the iron butadiynyl complex, $\text{Fe(C}\equiv\text{CC}\equiv\text{CSiMe}_3\text{)(dppe)Cp}^*$ (**3.12**)²¹ except that thf was used to aid solvation of $\text{RuCl(PPh}_3)_2\text{Cp}$. Heating was also required to break the Ru-Cl bond which is stronger than the Fe-Cl bond. No reaction was observed after stirring for 24 hours, but after stirring at 50°C for 16 hours the desired product **3.11** was obtained in almost quantitative yield.

The IR spectrum contained three $\nu(\text{C}\equiv\text{C})$ bands at 2166, 2103 and 1997 cm^{-1} . The ^1H NMR and ^{13}C NMR spectra contained singlet resonances at δ_{H} 4.30 and δ_{C} 85.59 for the Cp ligand and multiplets between δ_{H} 7.58 – 6.92 and δ_{C} 138.90 – 125.55 assigned to the PPh_3 ligands. A triplet at δ 120.67 ($^2J_{\text{PC}} = 24\text{Hz}$) and three singlets at δ 96.29, 94.37 and 67.22 were assigned to C_α , C_β , C_γ and C_δ respectively, by comparison with similar complexes.²² The methyl groups of the SiMe_3 moiety were found at δ_{H} 0.26 and δ_{C} 0.93. The ^{31}P NMR spectra showed a singlet resonance at δ 50.65 due to the PPh_3 ligands. Two irreversible 1-electron oxidation waves were observed in the cyclic voltammogram at +0.58 and +0.98 V. By comparison, **3.12** shows one reversible oxidation at 0.00 V indicating the iron system is more electron releasing than the ruthenium endgroup.

Proto-desilylation of **3.11** with $[\text{NBu}_4]\text{F}$ in wet thf gave $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{PPh}_3)_2\text{Cp}$ (**3.13**) in 74% yield (Scheme 1). The IR spectrum of **3.13** showed two $\nu(\text{C}\equiv\text{C})$ bands at 2107 and 1970 cm^{-1} and $\nu(\equiv\text{CH})$ at 3298 cm^{-1} . The ^1H NMR spectrum showed a multiplet at δ 7.42 – 7.06 for the PPh_3 ligands and singlets at δ 4.29 and 1.42 for the Cp and $\text{C}\equiv\text{CH}$ protons respectively. The four carbons of the chain ($\alpha - \delta$) resonated at δ_{C} 116.51, 94.34, 73.87 and 51.54 with the former a triplet showing coupling to ^{31}P ($^2J_{\text{PC}} = 24\text{Hz}$). These were assigned by comparison with similar complexes.²² A singlet in the ^{31}P NMR spectrum at δ 50.98 was assigned to the PPh_3 ligands. Two irreversible 1-electron oxidations were observed in the cyclic voltammogram at +0.52 and +0.93 V. This shows that the butadiynyl complex is easier to oxidise than the trimethylsilyl-protected derivative by ca 0.06 V. As previously discussed, oxidation of $\text{M}(\text{C}\equiv\text{CH})(\text{dppe})\text{Cp}^*$ with $[\text{FcH}][\text{PF}_6]$ gives the bis-vinylidene, $[\{\text{Cp}^*(\text{dppe})\text{M}\}=\text{C}=\text{CHCH}=\text{C}=\{\text{M}(\text{dppe})\text{Cp}^*\}][\text{PF}_6]_2$ ($\text{M} = \text{Fe}^{13}, \text{Ru}^{16}, \text{Os}^{17}$). It is possible that the first oxidation wave in the CV of both **3.11** and **3.13** corresponds to the formation of a similar product, which is further oxidised as evidenced by the second wave in the CV. This agrees with the non-reversibility of both the oxidation waves.



Synthesis of the heterobimetallic butadiyndiyl complex **3.14**.

The reaction between **3.13** and FeCl(dppe)Cp^* under similar conditions used for the preparation of **3.11** gave the new heterobimetallic complex, $\{\text{Cp}(\text{PPh}_3)_2\text{Ru}\}\text{C}\equiv\text{CC}\equiv\text{C}\{\text{Fe(dppe)Cp}^*\}$ (**3.14**) in good yield (Equation 2). Crystals suitable for an X-ray structure determination were grown by the slow diffusion of pentane into a concentrated CH_2Cl_2 solution. The IR spectrum contained two $\nu(\text{C}\equiv\text{C})$ bands at 2037 and 1959 cm^{-1} . The ^1H and ^{13}C NMR resonances were severely broadened at r.t while no signals could be obtained for the ^{31}P nuclei. Fast electron exchange with traces of a paramagnetic compound oxidised is probably the reason as has been observed in similar complexes.²³ Deoxygenation of the solution and cooling to -80°C allowed collection of spectra. Thus, the ^{31}P NMR spectrum showed two signals in a 1:1 ratio at δ 101.77 and 52.43 from the dppe and PPh_3 ligands, respectively. The Cp ligand gave singlets at δ_{H} 4.40 and δ_{C} 85.68 while the Cp^* ligand showed a singlets at δ_{H} 1.66 and at δ_{C} 81.98 and 10.45 ppm. The Ph groups of the PPh_3 and dppe moieties gave rise to multiplets between δ_{H} 7.15 – 8.41 and δ_{C} 127.41 – 142.16. Two multiplets due to the methylene protons of the dppe ligand were observed at δ_{H} 1.98 and 3.01 while a singlet resonance was observed at δ 30.02 in the ^{13}C NMR spectrum. The carbons of the butadiynyl bridge were not observed as was also found for **3.10**.²⁰

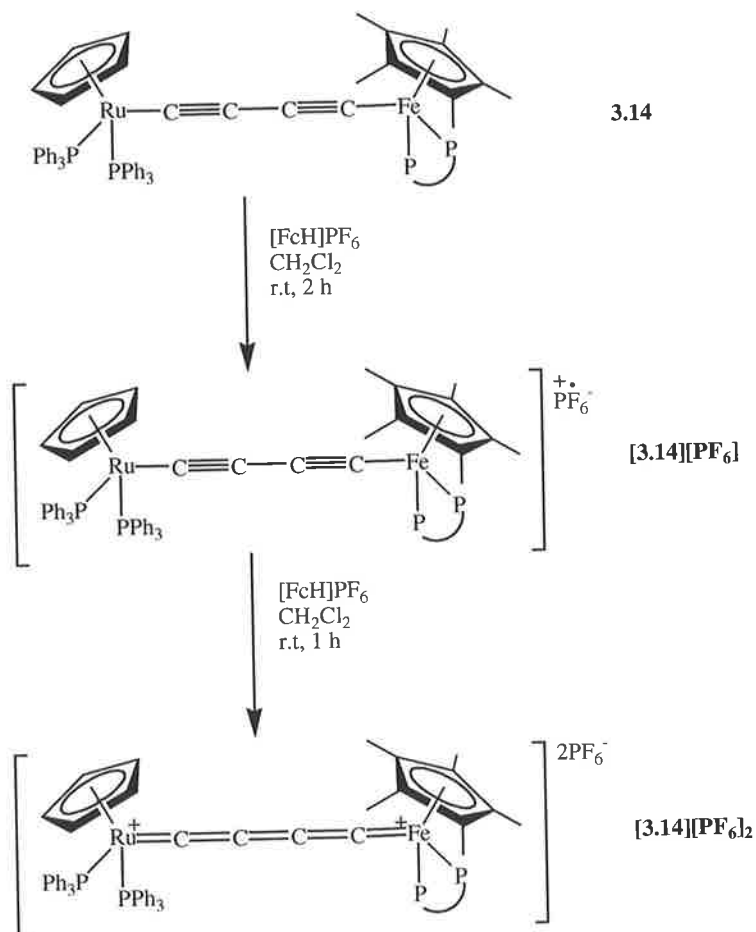
The CV of **3.14** showed three reversible 1-electron oxidation waves (-0.51, 0.30 and 1.00 V). As described in Chapter 1, the oxidation potentials and their separation provides a measure of the electronic communication between the iron and ruthenium centres. In addition, the oxidation potentials guide the choice of oxidising reagent which must be used to prepare bulk samples of the related cationic complexes. This will be discussed in detail later.

Table 2 shows selected ^1H NMR chemical shifts of **3.14** and some related complexes. Comparing the Cp and Cp* ^1H resonances of **3.14** and the trimethylsilyl-protected iron and ruthenium butadiynyl complexes **3.11**, **3.12**, it can be seen that these signals have been shifted downfield by ca. 0.1 – 0.27 ppm in **3.14**. This indicates that the iron and ruthenium endgroups are more electron releasing than trimethylsilyl.

Table 2. Selected ^1H NMR chemical shifts (ppm) for C_4 complexes with ruthenium and/or iron endgroups

Complex	Cp	Cp*	C_6H_5	Solvent	ref
3.11	4.30		7.58 - 6.92	CDCl_3	^a
3.12		1.39	7.93 - 6.99	C_6D_6	²²
3.14	4.40	1.66	8.41 - 7.15	C_6D_6	^a
[3.14][PF₆]₂	5.05	-0.86	7.98 - 6.65	CD_2Cl_2	^a
3.6	4.17		7.64 - 7.03	CDCl_3	¹⁵
[3.6][PF₆]₂	5.03		7.70 - 7.07	CDCl_3	¹⁵
3.4		1.55	8.16 - 7.00	C_6D_6	¹³
[3.4][PF₆]₂		-6.03	9.60 - 6.20	CD_2Cl_2	¹³

^aThis work.

Scheme 2. Oxidation of **3.14**.

Guided by the CV of **3.14** the ferrocenium cation was chosen as the oxidising reagent²⁴ in the preparation of the 1- and 2-electron oxidised complexes. A stronger oxidising agent such as Ag⁺ would be required in the preparation of the 3-electron oxidised product. However, attempts to isolate the tri-cation were unsuccessful as the complex decomposed rapidly at even -78°C.

Addition of [FcH]PF₆ to a solution of **3.14** in CH₂Cl₂ resulted in an immediate colour change from orange-brown to dark brown. Workup gave the dark green-brown monocation as its PF₆ salt in 96 % yield (Scheme 2). The IR spectrum showed two ν(CC) bands at 2035 and 1961 cm⁻¹. Only broad resonances were observed in the NMR spectra due to the paramagnetic nature of the complex.

Treatment of **[3.14][PF₆]** with an equivalent of [FcH]PF₆ in CH₂Cl₂ gave dark blue **[3.14][PF₆]₂** in 93 % yield (Scheme 2). Two IR $\nu(\text{CC})$ bands were found at 1961 and 1890 cm⁻¹. The ¹H NMR spectra showed the Cp singlet resonances at δ_{H} 5.05 and δ_{C} 90.95. The Cp* ligand showed a singlet at δ_{H} -0.86 and two singlets at δ_{C} 1.00 (C₅Me₅) and 88.26 (C₅Me₅). The ³¹P NMR spectrum showed two singlets at δ 86.25 and 42.91 assigned to the dppe and PPh₃ ligands, respectively, and a septet at δ -143.47 due to the PF₆ anion.

Table 2 shows the ¹H NMR comparison between the di-oxidised complexes of **3.14** and the homobimetallic analogues **[3.4][PF₆]₂** and **[3.6][PF₆]₂**. Most notable is the upfield shift of the Cp* ligand relative to **3.14**. This shift is observed in the parent iron complex but to a much greater extent. The Cp ligand bound to ruthenium is shifted downfield relative to **3.14** as was observed for the parent ruthenium butadiyndiyl complex. The ¹³C NMR spectrum again shows a large upfield shift of the Cp* resonance and downfield shift of the Cp resonance in **[3.14][PF₆]₂** relative to **3.14**. The ³¹P signals follow this trend too, with the dppe ligand bound to iron shifted downfield in **[3.14][PF₆]₂** relative to **3.14** and the PPh₃ ligands bound to ruthenium shifted upfield in **[3.14][PF₆]₂** compared to **3.14**. While **[3.4][PF₆]₂** is paramagnetic (as evidenced by magnetic susceptibility measurements and variable temperature ¹H NMR spectroscopy),¹³ the analogous ruthenium complex **[3.6][PF₆]₂** is diamagnetic.¹⁵ The structure of the carbon ligand in these two complexes is very different with the iron complex having a butadiynyl bridge and the ruthenium having a cumulenyl bridge. In the context of this study, it appears the carbon bridge in **[3.14][PF₆]₂** has a structure between butadiyndiyl and cumulenyl. This is further supported by the IR data which is discussed below.

Table 3. IR data for **[3.14][PF₆]_n** and related compounds.

Complex	Medium	$\nu(\text{CC})$ (cm ⁻¹)	ref
3.14	nujol	2037w, 1959br	a
[3.14][PF₆]	nujol	2035w, 1961br	a
[3.14][PF₆]₂	nujol	1961br, 1890br	a
3.11	nujol	2166m, 2103s, 1997m	a
3.13	nujol	2107s, 1970br	22
3.12	nujol	2165m, 2090vs, 1980m	22
3.15	nujol	2099s, 1958w	13
3.4	CH ₂ Cl ₂	1955, 1880	13
[3.4][PF₆]	CH ₂ Cl ₂	1973, 1880	13
[3.4][PF₆]₂	CH ₂ Cl ₂	2160, 1950	15
3.6	nujol	1970m	15
[3.6][PF₆]	nujol	1861s	15
[3.6][PF₆]₂	nujol	1766s	15

^aThis work.

The IR data for the **[3.14][PF₆]_n** series compare well with those of the related homobimetallic complexes (Table 3).

Both **3.11** and **3.12** show three $\nu(\text{C}\equiv\text{C})$ bands. These could possibly result from the coupling of one of the normal modes with another oscillator such as the SiMe₃ moiety.^{25,26} The $\nu(\text{C}\equiv\text{C})$ frequencies decrease when the SiMe₃ moiety is replaced by H suggesting an increase in electron density on the carbon chain. When the butadiynyl proton is replaced by the Fe(dppe)Cp* endgroup the $\nu(\text{C}\equiv\text{C})$ frequencies drop by 70 cm⁻¹, which is due to the Fe(dppe)Cp* fragment being more electron releasing than H.

The neutral and mono-oxidised complexes derived from both **3.14** and the iron analogue **3.4** show very little change in $\nu(\text{C}\equiv\text{C})$ on removal of an electron from the system. This suggests very little change in the butadiynyl nature of the bridge. However, removal of another electron gives very different $\nu(\text{CC})$ frequencies for **[3.14][PF₆]₂** and the homobimetallic analogues. There is a decrease in the $\nu(\text{CC})$ frequency of ca. 70 cm⁻¹ in **[3.14][PF₆]₂**. In the case of **[3.6][PF₆]₂** there is decrease of ca. 100 cm⁻¹ which suggests there isn't as large a change in the bonding across the chain in **[3.14][PF₆]₂**. The IR $\nu(\text{CC})$ spectra of **[3.4]ⁿ⁺** ($n = 0$, 1955, 1880; $n = 1$, 1973, 1880; $n = 2$, 2160, 1950 cm⁻¹) on the other hand, show a shift toward the higher energy ($n = 0 < 1 < 2$). This indicates that on oxidation there is an increase in CC

bond order. This result was unexpected and indicates that there is no contribution from the cumulenic resonance structure. Along with the paramagnetic nature of the di-oxidised species, the carbon bridge is best described by a diyndyl structure. Thus, the structure of **[3.14][PF₆]₂** is between butadiyndiyl and cumulenic in nature and is reinforced by the NMR data discussed earlier.

Crystal Structures

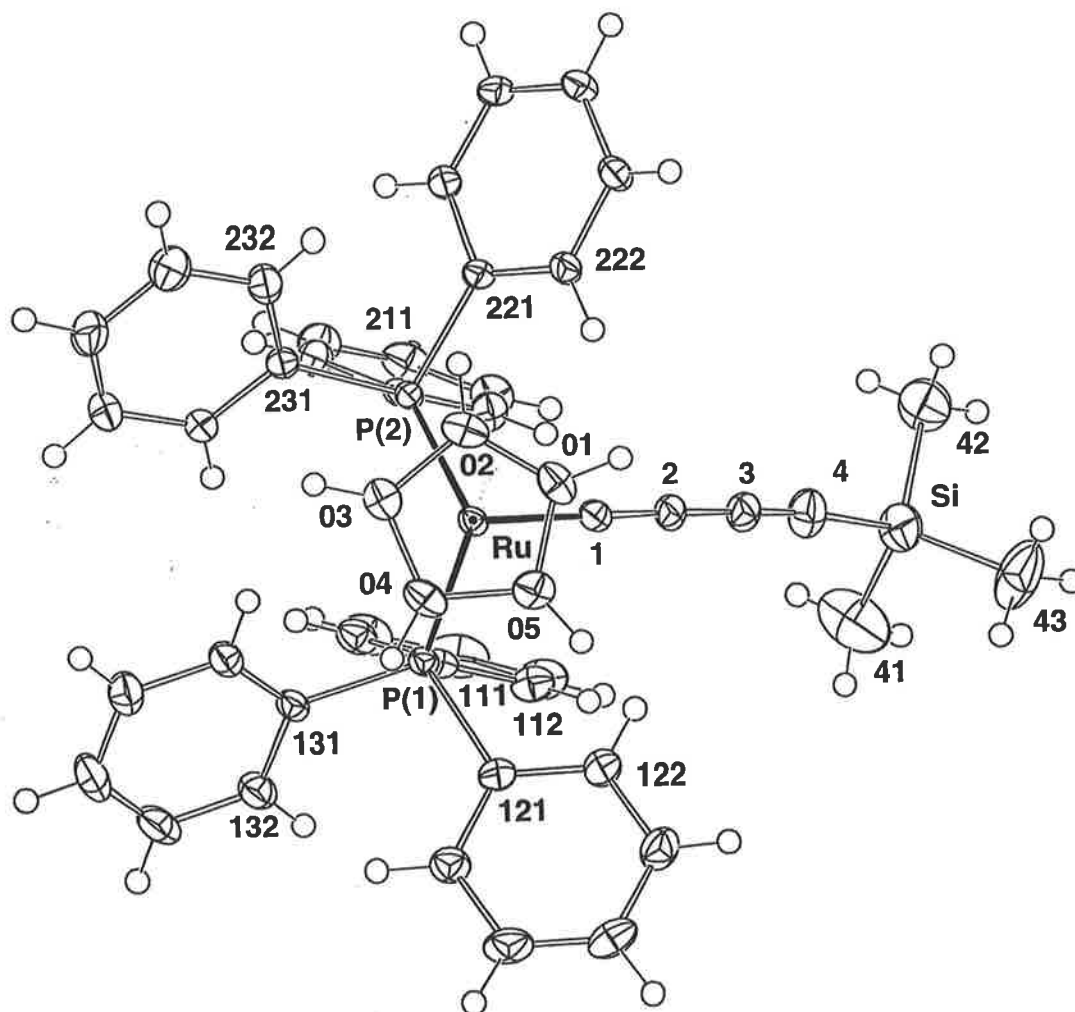


Figure 1. ORTEP plot of a molecule of **3.11**.

Table 4. Important bond lengths (Å) and angles (°) in **3.11**.

Bond distances			
Ru-C(Cp)	2.238-2.256(2)	C(1)-C(2)	1.225(2)
(av.)	2.24(1)	C(2)-C(3)	1.375(2)
Ru-P	2.2975-2.2980(5)	C(3)-C(4)	1.213(3)
Ru-C(1)	1.988(2)	C(4)-Si	1.824(2)
Bond angles			
P-Ru-P	101.01(2)	C(1)-C(2)-C(3)	171.1(2)
P-Ru-C(1)	86.63(5)-87.15(5)	C(2)-C(3)-C(4)	178.0(2)
Ru-C(1)-C(2)	179.6(1)	C(3)-C(4)-Si	174.6(2)

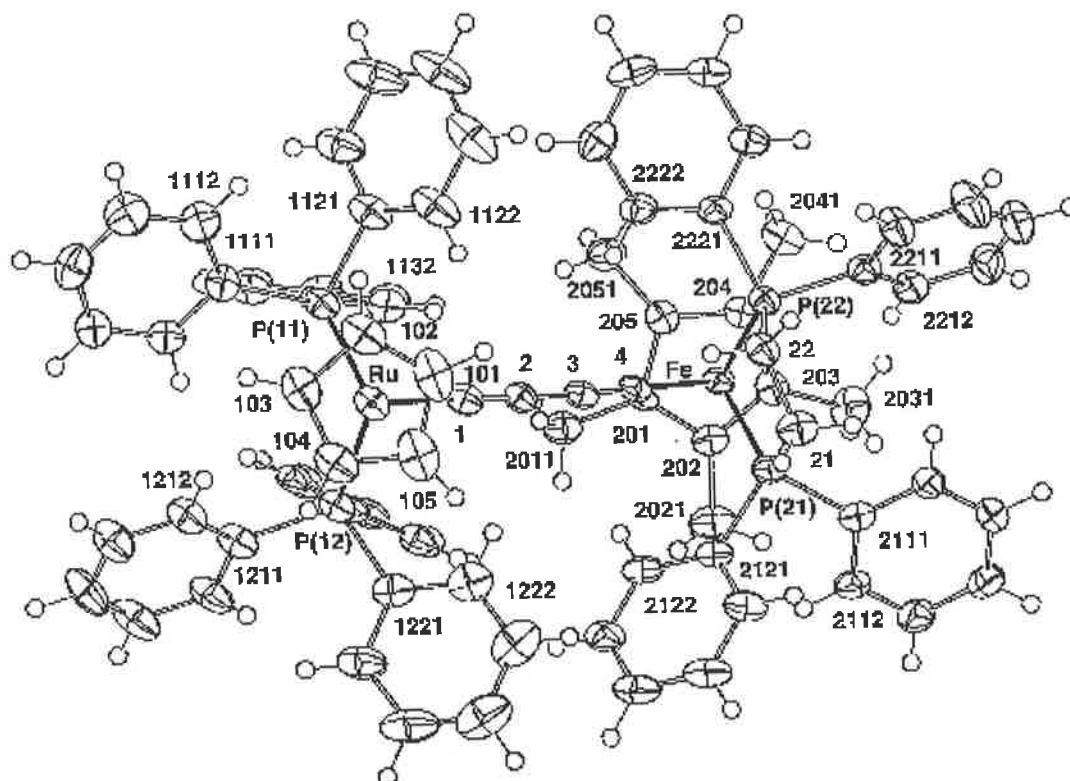
Figure 2. ORTEP plot of a molecule of **3.14**.

Table 5. Important bond lengths (Å) and angles (°) in **3.14**.

Bond distances			
Ru-C(Cp)	2.224-2.254(8)	Fe-P	2.168-2.175(2)
(av.)	2.24(3)	Fe-C(4)	1.898(5)
Ru-P	2.288-2.289(2)	C(1)-C(2)	1.226(7)
Ru-C(1)	2.019(5)	C(2)-C(3)	1.392(7)
Fe-C(Cp*)	2.100-2.144(6)	C(3)-C(4)	1.238(7)
(av)	2.12(3)		
Bond angles			
P(11)-Ru-P(12)	101.49(6)	Ru-C(1)-C(2)	178.3(5)
P-Ru-C(1)	85.5(2)-78.6(2)	C(1)-C(2)-C(3)	177.4(7)
P(21)-Fe-P(22)	85.77(7)	C(2)-C(3)-C(4)	177.3(6)
P-Fe-C(4)	84.1(2)-84.6(2)	C(3)-C(4)-Fe	179.4(5)

Plots of single molecules of **3.11** and **3.14** are shown in Figures 1 and 2 and significant bond parameters are given in Tables 4 and 5.

The structure of the monomeric ruthenium complex **3.11** confirms the butadiynyl nature of the carbon chain (Figure 1). The alternating CC bond distances along the chain of 1.225(2), 1.375(3) and 1.213(3) Å compare well with those of similar complexes.²⁷ The chain has a cumulative bend at the carbon atoms of ca 16°, as can be seen from the plot in Figure 1, with angles at carbon Ru-C(1)-C(2) 179.6°, C(1)-C(2)-C(3) 171.1°, C(2)-C(3)-C(4) 178.0° and C(3)-C(4)-Si 174.6°.

Comparisons with other related C₄ complexes are shown in Table 6. General features, such as the formally octahedral geometry at each metal, are in accord with related structures.^{13,18,20,28}

Table 6. Selected structural data.

Complex	M ₁ -M ₂	C≡C	≡C-C≡	M-C≡	M-C≡C	C-C-C	ref
3.14	7.773	1.226/Ru	1.392	2.019/Ru	178.3/Ru	177.4	^a
		1.238/Fe		1.898/Fe	179.4/Fe	177.3	
3.4	7.584	1.22	1.37	1.889	177	177	29
[3.4][PF₆]	7.431	1.236	1.36	1.830	167.0	177	13
<i>cis</i> - 3.6	7.81	1.20	1.38	2.00	177	178	18
<i>trans</i> - 3.6	7.806	1.217	1.370	2.001	178.9	177.2	18
3.10	7.730	1.209/Fe	1.370	1.895/Fe	176.6/Fe	177.4	20
		1.224/Re		2.029/Re	169.6/Re	178.3	

^aThis work.

Figure 2 shows the RuC₄Fe linkage is essentially linear with Ru-C(1)-C(2) at 178.3° and Fe-C(4)-C(3) at 179.5°. Tables 5 and 6 show the important bond lengths and angles. As expected, the Fe-C≡ bond (1.898 Å) is shorter than the Ru-C≡ bond (2.019 Å) due to the difference in atomic radii (Fe = 1.26, Ru = 1.34 Å).³⁰ The C≡C and C-C distances are somewhat distorted with a lengthening of the C≡C bonds and a shortening of the C-C bond. This can be rationalised by a small contribution from the cumulenenic tautomer. The related iron/rhenium butadiyndiyl complex **3.10** has a much larger bending in the chain with bond angles at carbon of 169.6 and 176.6°.

⁵⁷Fe Mössbauer Data

Mössbauer spectroscopy is a very sensitive probe for identifying the electronic environment of iron.⁵ Quadrupole splittings (QS) and isomer shifts (IS) can provide insight into the nature of the bonds to iron. Thus, ⁵⁷Fe Mössbauer spectra of the series **[3.14][PF₆]_n** (*n* = 0 – 2) were measured at 80 K. At zero field, the spectra of these complexes show doublets and the fitting parameters are summarised in Table 7 and compared with the values obtained for related complexes.

The neutral complex **3.14** gives a doublet (QS = 1.966 mm/s) which compares well with those of other pure iron(II) systems listed Table 7. The QS value is slightly lower than that of the rhenium analogue **3.10** and significantly lower than that of the parent iron complex **3.4**. The IS value is slightly larger for the ruthenium complex when compared to the rhenium complex. This indicates the ruthenium fragment is more electron releasing than the rhenium endgroup. The IS values of all the neutral mixed-metal complexes listed in Table 7 are very similar and slightly smaller than in the diiron derivative **3.4**. As the IS value is related to the electronic density at the iron nucleus, it can be assumed that the electronic density on the iron centre is similar for all three mixed-metal complexes. This is corroborated by the redox potentials. Indeed, the first redox potentials, *E*₁ of the mixed metal complexes are quite close and they decrease by only 0.090 V going from **3.10** to **3.14**.

The mono-cation **[3.14][PF₆]** has a QS value (0.983 mm/s) characteristic of a low spin 17-electron centre, which indicates the iron centre is best represented by the oxidation state Fe(III). The decrease (Δ IS = 0.35 mm/s) in the IS value compared to **3.14** further suggests a decrease in electron density at the iron centre, although it is much less pronounced than the diiron analogue (Δ IS = 0.60 mm/s). Surprisingly, the IS value for **[3.14][PF₆]** is larger than that of the diiron complex **3.4** suggesting the electron density at the iron centre is larger in **[3.14][PF₆]** than in the diiron complex. Also, the IS value for **[3.14][PF₆]** is larger than in the Ru(dppe)Cp* containing complex **3.16**.

Table 7. ^{57}Fe Mössbauer Fitting Parameters ($T = 80\text{K}$).

Complex	IS (mm/s)	QS (mm/s)	ref
3.4	0.270	2.075	13
[3.4][PF₆]	0.210	1.320	13
[3.4][PF₆]₂	0.180	1.045	13
3.10	0.255	1.983	20
[3.10][PF₆]	0.191	0.995	20
[3.10][PF₆]₂	0.138	0.957	20
3.14	0.260	1.966	a
[3.14][PF₆]	0.225	0.983	a
[3.14][PF₆]₂	0.167	0.931	a
3.16	0.252	2.006	31
[3.16][PF₆]	0.211	1.147	31
[3.16][PF₆]₂	0.155	1.112	31

^aThis work

As a counter-intuitive consequence, in this series of mono-oxidised complexes the $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{C})(\text{PPh}_3)_2\text{Cp}$ fragment appears to be more electron releasing than the $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{C})(\text{dppe})\text{Cp}^*$ fragment toward the $\text{Fe}(\text{III})$ centre. This behaviour suggests a change in bonding of the carbon bridge. This again suggests a large degree of electronic communication across the carbon bridge between the iron and ruthenium centres. Interestingly, the decrease in isomer shift for the iron-ruthenium analogues is the same as that of the diiron complex **3.4**. This suggests that there is a larger degree of electronic communication/delocalisation for the iron-ruthenium complex when compared purely by ^{57}Fe Mössbauer spectroscopy.

There is a slight decrease in the QS value for the di-oxidised species **[3.14][PF₆]₂** compared to **[3.14][PF₆]**. This is due to a further decrease in electron density at the iron centre and follows the trend for all the complexes listed in Table 7. The value is consistent with the $\text{Fe}(\text{III})$ formulation, but the decrease in the IS value is less than that of the diiron complexes (ΔIS 0.58 vs 0.30 mm/s). This again suggests a large

degree of electronic communication between the iron and ruthenium centres across the carbon bridge.

Cyclic Voltammetry

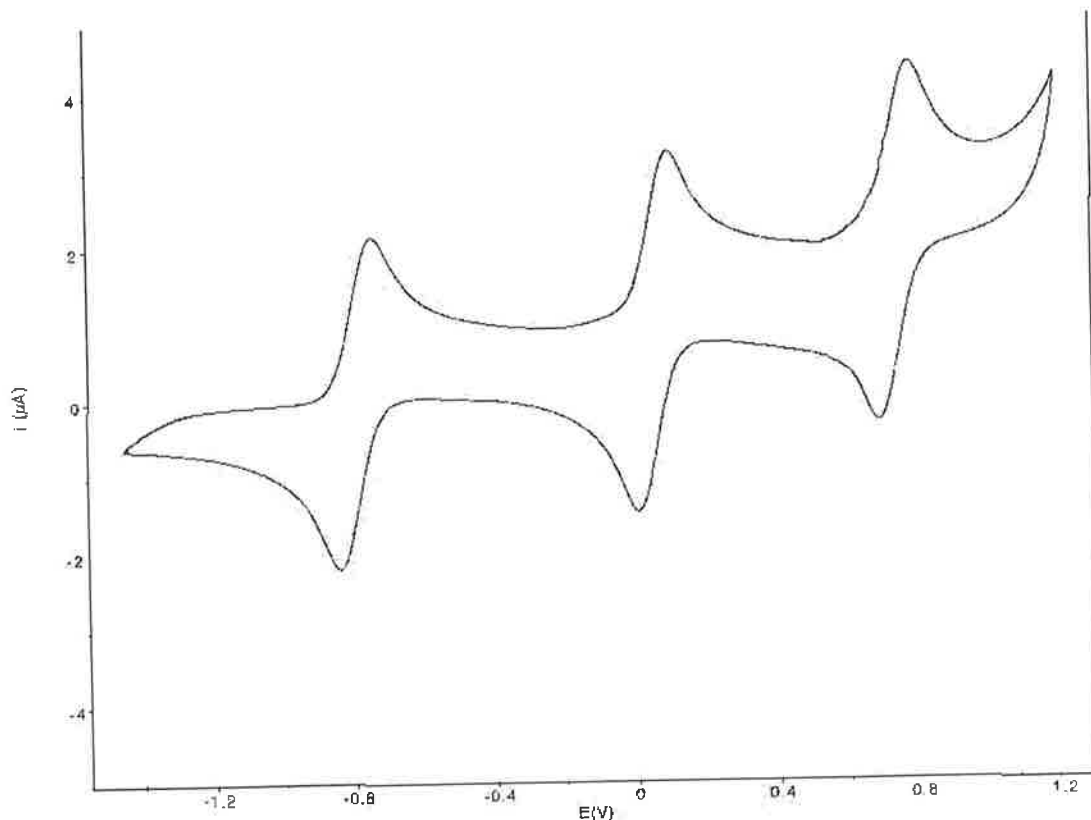


Figure 3. Cyclic voltammogram of **3.14**. Conditions - 0.1 M $[\text{NBu}_4]\text{PF}_6/\text{CH}_2\text{Cl}_2$ at 20°C ; Pt electrode; scan rate 100mV/s; V vs SCE; $E^\circ(\text{ferrocene}) = 0.46 \text{ V}$.

As illustrated in Figure 3, the cyclic voltammogram of **3.14** showed three reversible 1-electron oxidations (-0.51, +0.30 and +1.00 V) separated by 0.81 and 0.70 V representing 0/1+, 1+/2+ and 2+/3+, respectively. Cyclic voltammograms of the related monomeric ruthenium, **3.11**, and iron complexes, **3.12**, were measured under identical conditions (Table 8). The iron complex gave one reversible oxidation while the ruthenium complex gave two irreversible oxidations. The iron complex **3.12** is thermodynamically easier to oxidise by 0.58 V.

Table 8 Electrochemical data.^a

Complex	E ₁	E ₂	E ₃	E ₄	1+/2+	2+/3+	3+/4+	ref
3.14	-0.51	0.30	1.00		0.81	0.70		^b
3.6	-0.23	0.41	1.03	1.68	0.64	0.62	0.65	15
3.4	-0.69	0.03	0.95		0.72	0.92		13
3.10	-0.50	0.23	1.33		0.73	1.10		20
3.11	0.58	0.98			0.40			^b
3.12	0.00							22

^a0.1 M n-Bu₄NPF₆/CH₂Cl₂ at 20°C; Pt electrode; scan rate 100mV/s; V vs SCE; E°(ferrocene) = 0.46 V. ^bThis work.

The large separation of the first two oxidation waves in **3.14** ($\Delta E = 0.81$ V) suggests a large degree of electronic delocalisation across the carbon bridge. In fact, ΔE is larger for **3.14** than either of the homobimetallic analogues ($\Delta E = 0.64$; **3.6**, 0.72; **3.4** V) and also the iron-rhenium butadiyndiyl complex, **3.10** ($\Delta E = 0.73$ V). The comproportionation constant K_c (8.6×10^{13}) of **3.14** is the largest found to date.

Figure 4 shows a graphical representation of the oxidation potentials of **3.14** and the related homobimetallic complexes **3.4** and **3.6**. As can be seen, the graph has the same slope as the parent complexes and the potentials fall between those of the parent complexes. While this is to be expected, the slopes and the separations between the potentials show that there is a large degree of electronic communication between the iron and ruthenium centres.

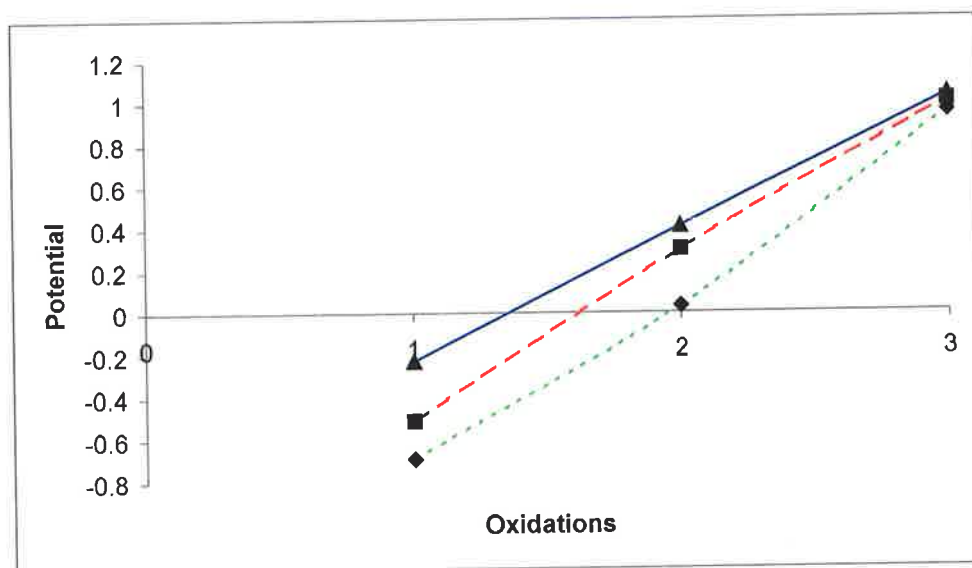


Figure 4. Oxidation potentials of **3.6** (solid line), **3.4** (dotted line) and **3.14** (dashed line).

ESR spectroscopy

The X-band ESR spectrum of **[3.14][PF₆]** was recorded at 80 K in a CH₂Cl₂/C₂H₄Cl₂ (1:1 v/v) glass. The spectrum displays three features corresponding to the three components of the *g* tensor as expected for d⁵ low-spin Fe(III) with pseudo-octahedral geometry.³² The *g* values extracted from the spectrum are recorded in Table 9 together with those of related complexes. As previously noted for homobimetallic iron mono-cations, hyperfine coupling with the phosphorus nuclei was not observed. Direct determination of the isotropic *g* (*g*_{iso}) values was not possible since the complex is not ESR-active at temperatures above the melting points of the solvents. However, calculated *g*_{iso} values for **[3.14][PF₆]** are close to those obtained for the other complexes listed in Table 9. This value is consistent with the dominant iron character of the radical. It is worth noting that the *g*_{iso} value for **[3.14][PF₆]** is higher than that for the diiron complex **[3.4][PF₆]**, suggesting that from a molecular orbital argument, there is a large metal character in the HOMO extending over the six-atom chain. This is in keeping with the Mössbauer data which indicates the iron centre is best represented by the oxidation state (III).

Table 9. ESR parameters determined at 80 K in CH₂Cl₂/C₂H₄Cl₂ (1:1) glass.

Complex	g_x	g_y	g_z	g_{iso}	Δg	ref
[3.4][PF ₆]	2.139	2.089	2.079	2.102	0.060	13
[3.14][PF ₆]	2.2820	2.0542	1.9890	2.108	0.293	^a
[3.16][PF ₆]	2.1865	2.0820	1.9995	2.089	0.187	31
[3.10][PF ₆]	2.2356	2.0075	1.9292	2.054	0.315	20

^aThis work.*UV-Visible and NIR Spectroscopy*

The UV-visible (Fig. 5) and near-IR spectra (Fig. 6) of [3.14][PF₆]_n are summarised in Table 10. The visible bands of [3.14][PF₆] (970 nm; ϵ 7500 L M⁻¹ cm⁻¹) and [3.14][PF₆]₂ (640 nm, ϵ 22000 L M⁻¹ cm⁻¹) are similar to those observed in [3.10]ⁿ⁺ (n = 1; 868 nm, ϵ 5700 L M⁻¹ cm⁻¹, n = 2; 601 nm, ϵ 28700 L M⁻¹ cm⁻¹).²⁰

Table 10. UV-visible and NIR parameters.

Complex	λ_{max} (nm)	ν_{max} (cm ⁻¹)	ϵ (L M ⁻¹ cm ⁻¹)	$\Delta\nu_{1/2}$ (cm ⁻¹)	V_{AB} (cm ⁻¹)	$\Delta G^{\ddagger}$ (cm ⁻¹)
[3.14][PF ₆]	970	10300	7500			1120
	1347	7420	275	2400	188	
[3.14][PF ₆] ₂	640		22000			

To further assess the extent of the electronic interaction between the coupled Cp*(dppe)Fe and Cp(PPh₃)₂Ru units, the intervalence charge transfer bands (IVCT) were examined. As shown in Figure 6, [3.14][PF₆] exhibits a very broad and weak NIR band centred at 1347 nm. This band is absent in both 3.14 and [3.14][PF₆]₂. The NIR bands were fitted to a Gaussian shape, and key parameters were extracted and summarised in Table 10.

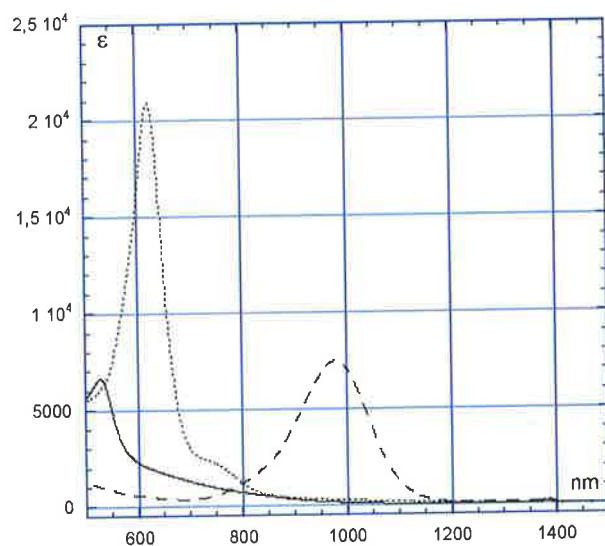


Figure 5. UV-Visible Spectra of $[3.14][PF_6]_n$ - $n = 0$, plain line; $n = 1$, dashed line; $n = 2$, dotted line.

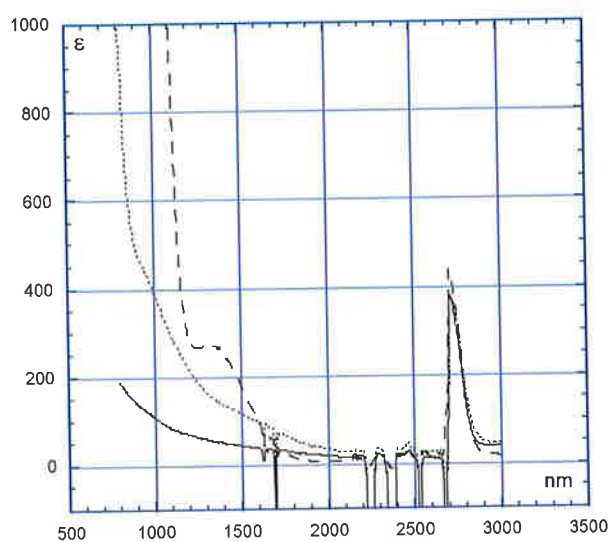
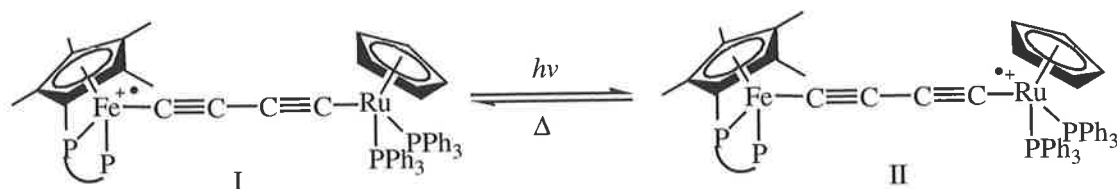


Figure 6. NIR Spectra of $[3.14][PF_6]_n$ - $n = 0$, plain line; $n = 1$, dashed line; $n = 2$, dotted line.

In the case of Class II materials, the IVCT band corresponds to the photo-induced electron transfer from one metal centre to the other as depicted in Scheme 3.



Scheme 3. Redox isomers of **[3.14][PF₆]**.

In the case of Class III materials, it has been recently suggested that this NIR transition is more accurately described as a Non-Valence Transition (NVT).¹⁶ In the case of the diyndiyl complexes **3.6** and **3.8**, the HOMO is orthogonal to the SOMO, and the NVT arises from a transition from a lower filled, predominantly metal-centred orbital which corresponds to the electronic transitions from the HOMO to the SUMO.

The electronic coupling parameter V_{AB} can be calculated for **[3.14][PF₆]** from Equation 3, where $R_{MM'}$ is the through-space metal-metal distance (Å). This formula yields a value of 188 cm⁻¹ for the electronic coupling. This value is high for Class II complexes and higher than the value obtained for **3.10** (152 cm⁻¹).²⁰

Table 11. Electronic coupling parameter, V_{AB} , for **[3.14][PF₆]** and related complexes.

Complex	V_{AB} (cm ⁻¹)	^a Class	ref
[3.14][PF₆]	188	II	^b
[3.2][PF₆]	5646	III	11
[3.4][PF₆]	3791	III	13
[3.8][PF₆]	5727	III	16
[3.10][PF₆]	169	II	20
[3.17][PF₆]	152	II	22

^aRobin and Day Classifications.³³ ^bThis work.

Table 11 shows V_{AB} for some related complexes. In the case of the homobimetallic complexes, **[3.2][PF₆]**, **[3.4][PF₆]** and **[3.8][PF₆]**, V_{AB} is large and the complexes are Class III materials. For the heterobimetallic complexes, **[3.10][PF₆]** and **[{Cp*(dppe)Fe}C≡CC≡C{Fe(CO)₂Cp*}][PF₆]** (**[3.17][PF₆]**), V_{AB} is approximately 10 times smaller and these complexes are Class II materials.

$$V_{AB} = 0.0205 (\epsilon_{\max} V_{\max} \Delta v_{1/2})^{1/2} / R_{MM} \quad (3)$$

$$(\Delta v_{1/2})_{\text{theo}} = [2300(v_{\max} - \Delta G_0)]^{1/2} \quad (4)$$

$$\Delta G^\ddagger = (\lambda - 2V_{ab})^2 / 4\lambda \quad (5)$$

The free energy difference (ΔG_0) between the two redox isomers (Scheme 3) can be approximated by the difference in oxidation potentials between the mononuclear iron and ruthenium complexes, **3.12** and **3.11** ($\Delta G_0 = 2660 \text{ cm}^{-1}$). Equation 4 can then be used to calculate the theoretical bandwidth. The value obtained is higher than that observed ($3300 \text{ vs } 2400 \text{ cm}^{-1}$) and is indicative of a Class II system.³³

Spectro-electrochemistry

Spectro-electrochemistry has been used by Bruce et al. to study the series **[3.6]ⁿ⁺** ($n = 0 - 4$) without the necessity of isolating the tri- and tetra-oxidised complexes, as this is not possible.¹⁵

Figures 7 and 8 show the UV-vis spectro-electrochemical results for the series **[3.14]ⁿ⁺** ($n = 0 - 2$). A clean isosbestic point (Figure 8) marking the interconversion **3.14⁺/3.14²⁺** is observed. These spectra illustrate the stability of the oxidised complexes.

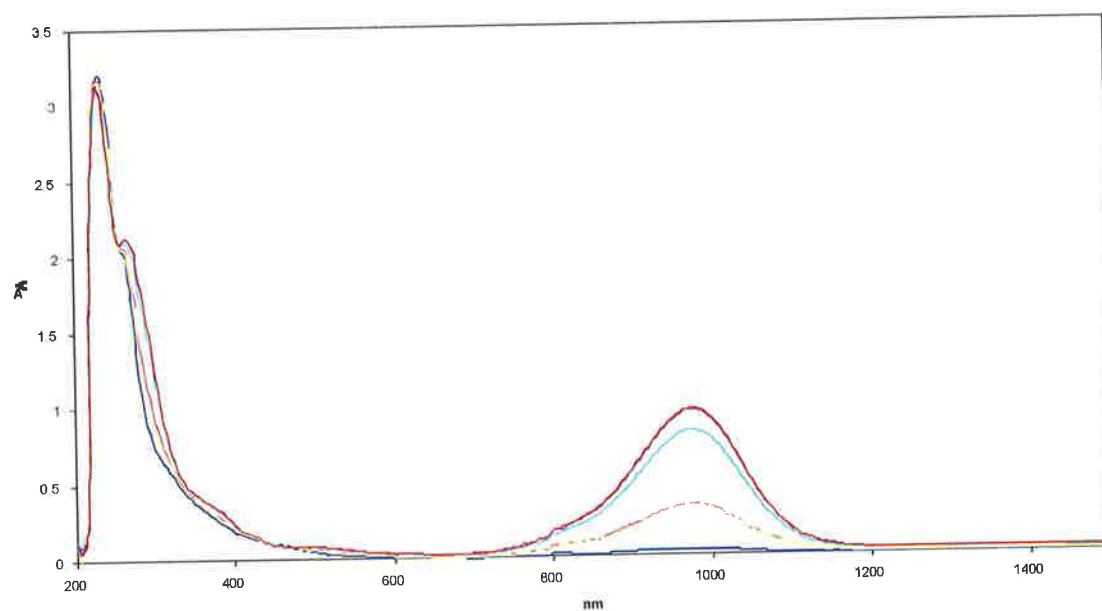


Figure 7. Electroconversion of **3.14** to **[3.14][PF₆]** – UV-Visible region.

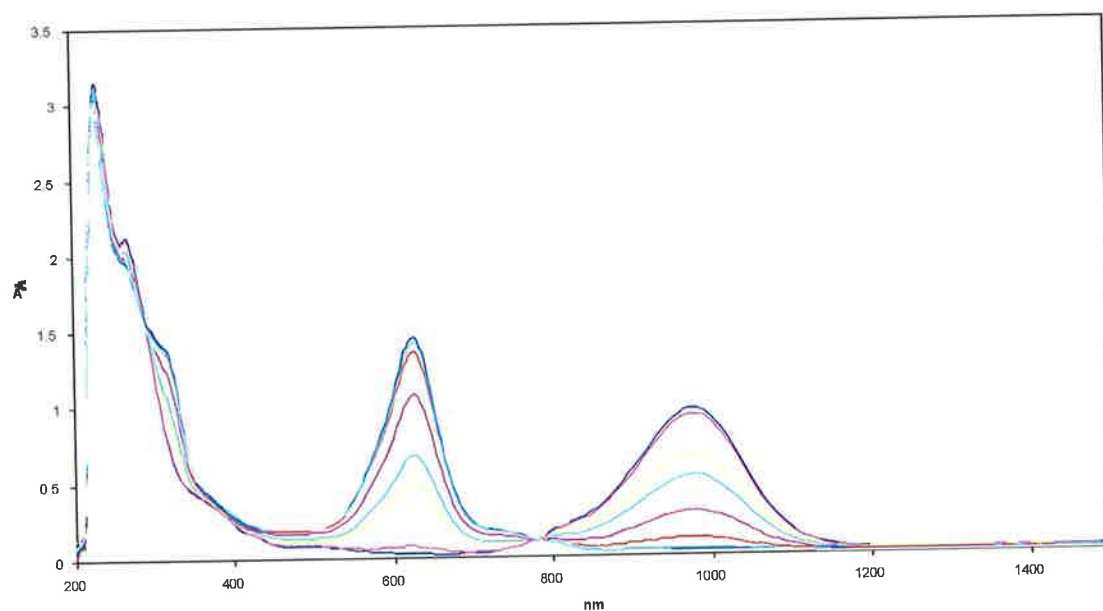


Figure 8. Electroconversion of **[3.14][PF₆]** to **[3.14][PF₆]₂** – UV-Visible region.

DISCUSSION

The synthesis of the trimethylsilyl-protected ruthenium butadiynyl complex **3.11** and its subsequent proto-desilylation is a high yielding route into the ruthenium butadiynyl complex **3.13**. These two complexes closely resemble their iron analogues. Coupling of the butadiynyl complex **3.13** to the iron endgroup, Fe(dppe)Cp*, gave the new heterobimetallic complex {Cp(Ph₃P)₂Ru}C≡CC≡C{Fe(dppe)Cp*} **3.14**, in good yield. The cyclic voltammogram of **3.14** shows three chemically reversible one-electron oxidation waves. Stepwise chemical oxidation with [FcH][PF₆] gave the mono and dications, [3.14][PF₆] and [3.14][PF₆]₂.

The structural, spectroscopic and electronic data have been carefully examined for the series [3.14][PF₆]_n (n = 0 – 2). The X-ray structural data for the neutral complex **3.14** confirm the butadiynyl nature of the bridge. The C≡C and C-C distances are somewhat distorted with a lengthening of the C≡C bond and a shortening of the C-C bond relative to the ruthenium and iron homobimetallic analogues. The RuC₄Fe linkage is essentially linear with angles at carbon of 178.3 and 179.5°. The Mössbauer spectrum shows a single doublet typical of a pure Fe(II) system.

The electronic structure of the mono-oxidised complex, [3.14][PF₆], was probed by ⁵⁷Fe Mössbauer, ESR, IR, UV-vis and NIR spectroscopy. The Mössbauer spectrum is consistent with the iron centre having the oxidation state (III). The g_{iso} value calculated from the ESR spectrum is very close to that of the diiron butadiyndiyl complex indicating the radical has dominant iron character. The IR spectrum is not significantly different from **3.15** indicating there is little change in the diynyl nature of the carbon bridge. The NIR spectrum shows a band at ~1350 nm (ε = 275 L M⁻¹ cm⁻¹) which is also observed in the mixed iron-rhenium complex [3.10][PF₆]. In this case, it was assigned to an IVCT representing a photo-induced electron transfer from iron to ruthenium.

Both ⁵⁷Fe Mössbauer and ESR are relatively slow spectroscopic techniques (10⁻⁸ - 10⁻⁹ s) when compared to IR and NIR (10⁻¹³ - 10⁻¹⁵ s). The unpaired electron in [3.14][PF₆] is somewhat localised on the Mössbauer/ESR time scale but appears to be

delocalised by the other spectroscopic techniques (NMR, IR, NIR). In terms of mixed-valence arguments, this complex can be described as a Class II system.³³ The NIR transition is typical of complexes in this class. From MO point of view, the molecular orbital which extends over the six-atom chain has a large contribution from the iron d-orbitals which suggests the unpaired electron is more localised on the iron terminus. This is unlike the iron and ruthenium homometallic analogues which are Class III complexes and show no localisation.

The di-oxidised complex **[3.14][PF₆]₂** most likely has a structure intermediate between butadiyndiyl and cumulenyl with a singlet ground state. No signal is observed in the ESR spectra at even liquid helium temperatures. The IR spectrum shows a decrease in the $\nu(\text{CC})$ frequency. Unfortunately the resonances of the C₄ chain were not observed. These observations more closely resemble the diruthenium analogue rather than the diiron complex.

EXPERIMENTAL

General experimental conditions

All reactions were carried out under dry, high purity argon using standard Schlenk techniques. Common solvents were dried, distilled under argon and degassed before use.

Instrumentation

Infrared spectra were obtained on a Bruker IFS28 FT-IR spectrometer. Spectra in CH_2Cl_2 were obtained using a 0.5 mm path-length solution cell with NaCl windows. Nujol mull spectra were obtained from samples mounted between NaCl discs. NMR spectra were recorded on Bruker AM300WB or ACP300 (^1H at 300.13 MHz, ^{13}C at 75.47 MHz, ^{31}P at 121.503 MHz) instruments. Samples were dissolved in CDCl_3 , unless otherwise stated, contained in 5 mm sample tubes. Chemical shifts are given in ppm relative to internal tetramethylsilane for ^1H and ^{13}C NMR spectra and external H_3PO_4 for ^{31}P NMR spectra. Cyclic voltammograms were recorded as described in Table 8 using a PAR model 263 apparatus, a saturated calomel electrode, and ferrocene as internal calibrant ($[\text{FcH}]/[\text{FcH}]^+ = 0.46 \text{ V}$). X-Band ESR spectra were recorded on a Bruker ESP-300E spectrometer. Mössbauer spectra were recorded with a $2.5 \times 10^{-2} \text{ Ci}$ ($9.25 \times 10^8 \text{ Bq}$) ^{57}Co source using a triangular sweep mode.³⁴ Elemental analyses were performed at the Centre pour Microanalyses du CNRS, Vernaison, France. UV-vis spectra were recorded on a Varian Cary 5 UV-Vis/NIR spectrometer. Samples (1 mM) were dissolved in CH_2Cl_2 (with 0.5 M $[\text{NBu}_4]\text{BF}_4$ as supporting electrolyte for the spectroelectrochemical experiments). The OTTLE cell was as described³⁵. A 1 mm path length cell was used with a Pt-mesh working electrode, Pt wire counter and pseudo-reference electrodes.

Reagents

NaBPh_4 (Aldrich), and $[\text{NBu}_4]\text{F}$ (Aldrich) were used as received. The compounds $\text{RuCl}(\text{PPh}_3)_2\text{Cp}$,³⁶ $\text{FeCl}(\text{dppe})\text{Cp}^*$,²³ $[\text{FcH}]\text{PF}_6$ ²⁴ and $\text{HC}\equiv\text{CC}\equiv\text{CSiMe}_3$ ³⁷ were prepared using the cited methods.

(a) $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CSiMe}_3)(\text{PPh}_3)_2\text{Cp}$ (**3.11**).

A Schlenk flask was charged with $\text{RuCl}(\text{PPh}_3)_2\text{Cp}$ (2.0 g, 2.76 mmol), NaBPh_4 (1.04 g, 3.00 mmol) and thf/NEt_3 (1/1, 60 mL) at r.t and $\text{HC}\equiv\text{CC}\equiv\text{CSiMe}_3$ (0.70 g, 5.70 mmol) in THF (5 mL) was added. The orange suspension was then warmed to 50°C and stirred for 16 h. The solvent was then removed *in vacuo* and the residue extracted with Et_2O (3 x 15 mL). The Et_2O was then removed *in vacuo* and the resulting orange-brown solid was dried *in vacuo* to give $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CSiMe}_3)(\text{PPh}_3)_2\text{Cp}$ (**3.12**) (2.11 g, 94 %). Anal. Found: C, 70.71; H, 5.31. Calc. For $\text{C}_{48}\text{H}_{44}\text{P}_2\text{RuSi}$: C, 71.00; H, 5.46%. *M*, 812. IR (Nujol): $\nu(\text{C}\equiv\text{C})$ 2166m, 2103s, 1997m cm^{-1} . ^1H NMR (CDCl_3): δ 0.26 (s, 9H, SiMe_3), 4.30 (s, 5H, Cp), 6.92-7.58 (m, 30H, Ph). ^{13}C NMR (CDCl_3): δ 0.93 (s, SiMe_3), 67.22 (s, C_δ), 85.59 (s, Cp), 94.37 (s, C_γ), 96.29 (s, C_β), 120.67 (t, $^2J_{\text{PC}} = 24$ Hz, C_α), 138.90-125.55 (m, Ph). ^{31}P NMR (CDCl_3): δ 50.65 (s).

(b) $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{PPh}_3)_2\text{Cp}$ (**3.13**).

A Schlenk flask was charged with **3.11** (1.0 g, 1.23 mmol) and thf (40 mL). $[\text{NBu}_4]\text{F}$ (0.62 mL, 0.62 mmol of a 1.0 M solution in thf) was added and the resulting dark red-brown solution stirred at r.t for 24 h. The solvent was then removed *in vacuo*. Washing with cold MeCN (2 x 10 mL) and Et_2O (2 x 10 mL) and drying under oil-pump vacuum gave mustard yellow $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{PPh}_3)_2\text{Cp}$ (**3.13**) (670 mg, 74 %). Anal. Found: C, 73.11; H, 5.06. Calc. For $\text{C}_{45}\text{H}_{36}\text{P}_2\text{Ru}$: C, 73.06; H, 4.90%. *M*, 740. IR (Nujol): $\nu(\equiv\text{CH})$ 3298m, $\nu(\text{C}\equiv\text{C})$ 2107s, 1970br cm^{-1} . ^1H NMR (CDCl_3): δ 1.42 (s, 1H, $\equiv\text{CH}$), 4.29 (s, 5H, Cp), 7.42-7.06 (m, 30H, Ph). ^{13}C NMR (CDCl_3): δ 51.54 (s, C_δ), 73.87 (s, C_γ), 85.59 (s, Cp), 94.34 (s, C_β), 116.51 (t, $^2J_{\text{PC}} = 24$ Hz, C_α), 138.63-125.59 (m, Ph). ^{31}P NMR (CDCl_3): δ 50.98 (s).

(c) $\{\text{Cp}(\text{Ph}_3\text{P})_2\text{Ru}\}\text{C}\equiv\text{CC}\equiv\text{C}\{\text{Fe}(\text{dppe})\text{Cp}^*\}$ (**3.14**).

A Schlenk flask was charged with **3.13** (500 mg, 0.675 mmol), $\text{FeCl}(\text{dppe})\text{Cp}^*$ (415 mg, 0.665 mmol), NaBPh_4 (275 mg, 0.805 mmol) and thf/NEt_3 (1/3, 60 mL). The resulting dark red-brown solution was stirred at r.t for 48 h. The solution was filtered and the residue washed with Et_2O (2 x 5 mL). The solvents were removed *in vacuo* to give a dark brown solid. This solid was washed with MeOH (2 x 10 mL) and pentane (2 x 10 mL) and dried under oil-pump vacuum to give burnt orange $\{\text{Cp}(\text{Ph}_3\text{P})_2\text{Ru}\}\text{C}\equiv\text{CC}\equiv\text{C}\{\text{Fe}(\text{dppe})\text{Cp}^*\}$ (**3.14**) (410 mg, 50 %). Anal. Found: C,

72.69; H, 5.89. Calc. For $C_{81}H_{74}FeP_4Ru$: C, 73.24; H, 5.62%. *M*, 1328. IR (Nujol): $\nu(C\equiv C)$ 2037w, 1959br cm^{-1} . ^1H NMR (C_6D_6): δ 1.66 (br, 15H, $FeCp^*$), 3.01, 1.98 (2 x m, 2 x 2H, 2 x CH_2P), 4.40 (s, 5H, $RuCp$), 8.41–7.15 (m, 50H, Ph). ^{13}C NMR (C_6D_6): δ 10.45 (s, FeC_5Me_5), 30.02 (s, PCH_2), 81.98 (s, FeC_5Me_5), 85.68 (s, RuC_5H_5), 142.16–127.41 (m, Ph). ^{31}P NMR ($C_6D_5CD_3$): δ 52.43 (s, PPh_3), 101.77 (s, dppe).

(d) $[\{ Cp(Ph_3P)_2Ru \} C\equiv CC\equiv C \{ Fe(dppe)Cp^* \}] [PF_6]$ (**[3.14][PF₆]**).

A Schlenk flask was charged with **3.14** (500 mg, 0.376 mmol), $[FcH][PF_6]$ (118 mg, 0.356 mmol) and CH_2Cl_2 (25 mL). The resulting brown solution was stirred at r.t for 1.5 h and then concentrated to ca. 5 mL and pentane (100 mL) added. The resulting dark green-brown precipitate was collected and washed with toluene (2 x 5 mL), Et_2O (2 x 5 mL) and pentane (2 x 10 mL) and dried under oil-pump vacuum to give $[\{ Cp(Ph_3P)_2Ru \} C\equiv CC\equiv C \{ Fe(dppe)Cp^* \}] [PF_6]$ (**[3.14][PF₆]**) (505 mg, 96%). Anal. Found: C, 66.13; H, 5.42. Calc. For $C_{81}H_{74}F_6FeP_5Ru$: C, 66.04; H, 5.06%. *M*, 1328. IR (Nujol): $\nu(C\equiv C)$ 2035w, 1961br cm^{-1} .

(e) $[\{ Cp(Ph_3P)_2Ru \} C\equiv CC\equiv C \{ Fe(dppe)Cp^* \}] [PF_6]_2$ (**[3.14][PF₆]₂**).

A Schlenk flask was charged with **[3.14][PF₆]** (300 mg, 0.20 mmol), $[FcH][PF_6]$ (67.4 mg, 0.20 mmol) and CH_2Cl_2 (20 mL). The solution turned deep blue immediately. Stirring was continued at r.t for a further 1 h and then the solution concentrated to ca. 5 mL and pentane (100 mL) added. The resulting blue precipitate was collected and washed with Et_2O (2 x 5 mL) and pentane (2 x 10 mL) and dried under oil-pump vacuum to give deep blue $[\{ Cp(Ph_3P)_2Ru \} C\equiv CC\equiv C \{ Fe(dppe)Cp^* \}] [PF_6]_2$ (**[3.14][PF₆]₂**) (300 mg, 93 %). Anal. Found: C, 55.75; H, 4.21. Calc. For $C_{81}H_{74}F_{12}FeP_6Ru \cdot 2CH_2Cl_2$: C, 55.75; H, 4.40%. *M*, 1328. IR (Nujol): $\nu(CC)$ 1961br, 1890br cm^{-1} . ^1H NMR (CD_2Cl_2): δ -0.86 (s, 15H, $FeCp^*$), 3.21, 1.61 (2 x m, 2 x 2H, 2 x CH_2P), 5.05 (s, 5H, $RuCp$), 7.98–6.65 (m, 50H, Ph). ^{13}C NMR (CD_2Cl_2): δ 1.00 (s, C_5Me_5), 10.26 (m, PCH_2), 88.26 (s, C_5Me_5), 90.95 (s, $RuCp$), 136.73–128.11 (m, Ph). ^{31}P NMR (CD_2Cl_2): δ -143.47 (septet, PF_6), 42.91 (s, PPh_3), 86.25 (s, dppe).

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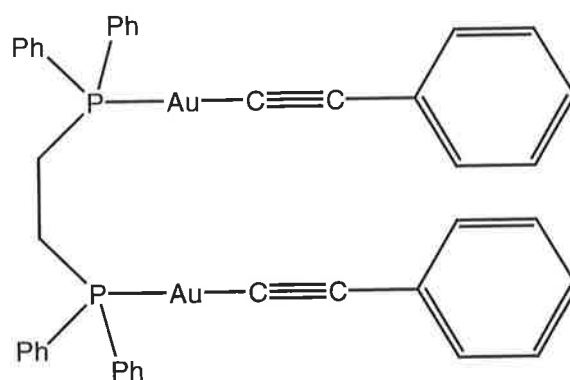
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Chapter 4

Some Gold(I) Complexes of 1,3-Diynes

INTRODUCTION

Two-coordinate linear gold(I) complexes have sparked interest due to the possibility of luminescent properties being discovered.¹⁻¹⁹ The first reported gold(I) alkynyl to show luminescence was described in 1993, when the emissive behaviour of $\text{Au}_2(\mu\text{-dppe})(\text{C}\equiv\text{CPh})_2$ (**4.1**) was recorded.⁹



(4.1)

The preference of gold(I) for a linear coordination geometry and the linearity of alkynyl ligands, make alkynylgold(I) complexes attractive candidates for the design of linear-chain metal-containing polymers with extended electronic conjugation in the backbone.²⁰ Although a few of the reported alkynylgold(I) complexes are anionic or cationic,^{9,10,21,22} most are neutral and the majority correspond to the type $\{\text{Au}(\text{C}\equiv\text{CR})(\text{L})\}$ ($\text{R} = \text{Ph}, ^t\text{Bu}, \text{CF}_3, \text{C}_6\text{H}_{10}\text{OH}$; $\text{L} = \text{tertiary phosphine}$)²³⁻²⁹ or $\{\text{Au}_2(\mu\text{-C}\equiv\text{C})\text{L}_2\}$ ($\text{L} = \text{phosphines}$ or $\text{L}_2 = \text{diphosphines}$).^{9,12-15,18,30-33}

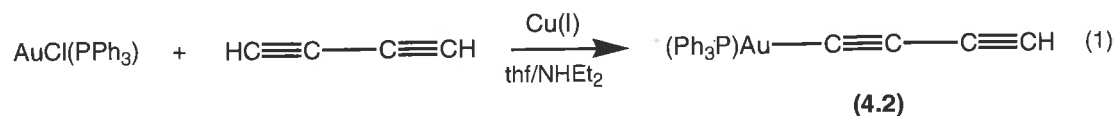
Several gold(I) complexes have been used as precursors for alkynylgold(I) derivatives. These include AuCl(L) ($\text{L} = \text{PPh}_3, \text{SC}_4\text{H}_8$),^{34,35} $(\text{AuCl})_2(\mu\text{-dppm})$ ³⁶ and $[\text{ppn}][\text{Au}(\text{acac})_2]$.³⁷ The dppm complex is notable for the presence of an aurophilic interaction between the two gold atoms, resulting in the two Cl atoms being on the same side of the molecule.³⁶ A similar structure has been found for $\{\text{Au}(\text{C}\equiv\text{CBu}^t)\}_2(\mu\text{-dppm})$.³² It was hoped that this feature would generate novel systems in which two diyne units also occupied sites on the same side of the molecule. Formation of molecular rectangles based on the $\text{Au}_2(\mu\text{-dppm})$ subunit is also possible, complexes such as $\{\text{Au}(\text{C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{C})\}_2(\mu\text{-dppm})$ having been described previously.³³ The lability of the acac ligands in $[\text{Au}(\text{acac})_2]^-$ in reactions of compounds containing acidic CH, NH, PH or SH groups enables an extensive range of neutral and anionic gold(I) complexes to be prepared.³⁷

Some gold(I) complexes of 1,3-butadiyne have been reported recently by this research group and are summarized in Scheme 1.³⁸ Reaction of buta-1,3-diyne with $\text{AuCl(PPh}_3)$ and $(\text{AuCl})_2(\mu\text{-dppm})$ in the presence of base gave the diyne complexes $\text{Au}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{PPh}_3)$ and $\{\text{Au}(\text{C}\equiv\text{CC}\equiv\text{CH})\}_2(\mu\text{-dppm})$, respectively. Similar reaction of $\text{W}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{CO})_3\text{Cp}$ with the two gold(I) complexes gave the heteronuclear diyndiyls $\text{W}\{\text{C}\equiv\text{CC}\equiv\text{C}[\text{Au}(\text{PPh}_3)](\text{CO})_3\text{Cp}$ and $\{\text{Au}(\text{C}\equiv\text{CC}\equiv\text{C}[\text{W}(\text{CO})_3\text{Cp}])\}_2(\mu\text{-dppm})$. Reaction of $[\text{ppn}][\text{Au}(\text{acac})_2]$ with the appropriate diynes afforded $[\text{ppn}][\text{Au}(\text{C}\equiv\text{CC}\equiv\text{CH})_2]$, $[\text{ppn}][\text{Au}\{\text{C}\equiv\text{CC}\equiv\text{C}[\text{W}(\text{CO})_3\text{Cp}]\}_2]$, $[\text{ppn}][\text{Au}\{\text{C}\equiv\text{CC}\equiv\text{C}[\text{Au}(\text{PPh}_3)]\}_2]$ and $[\text{ppn}][\text{Au}(\text{C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CPh})_2]$; the latter anion was also obtained as the very unstable NMe_4 salt. The reaction between $\{\text{Au}(\text{C}\equiv\text{CC}\equiv\text{CH})\}_2(\mu\text{-dppm})$ and $\{\text{Au}(\text{OTf})\}_2(\mu\text{-dppm})$ likely afforded *cyclo*- $\{\text{Au}_2(\mu\text{-C}\equiv\text{CC}\equiv\text{C})(\mu\text{-dppm})\}_2$, although this compound was not structurally characterised.

This Chapter reports the synthesis and characterisation of several gold(I) poly-ynyl and poly-yndiyl complexes that continues our research into the formation of complexes with interesting molecular geometries.

RESULTS

Copper-catalysed coupling of $\text{AuCl}(\text{PPh}_3)$ and buta-1,3-diyne under Cadiot-Chodkiewicz conditions resulted in the formation of $\text{Au}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{PPh}_3)$ (**4.2**) (Equation 1) in 75% yield.



This compound was identified from IR, ^1H , ^{13}C NMR and ES mass spectrometry, elemental analysis and, ultimately, by X-ray crystallography albeit with some co-crystallised material modelled as the iodide. The IR spectrum contained $\nu(\equiv\text{CH})$ (3283) and $\nu(\text{C}\equiv\text{C})$ bands (2148 and 2081 cm^{-1}). The ^1H NMR spectrum contained a singlet for the diyne hydrogen at δ 1.76, while the ^{13}C NMR spectrum contained resonances at δ 60.39, 69.43, 85.79 and 128.54 (d, $^2J_{\text{CP}} = 124\text{ Hz}$) for C_δ , C_γ , C_β and C_α , respectively, assigned by comparison with other buta-1,3-diyne compounds described previously.^{39,40} The ES mass spectrum contained a molecular ion at m/z 508, with an ion at m/z 459 corresponding to $[\text{Au}(\text{PPh}_3)]^+$.

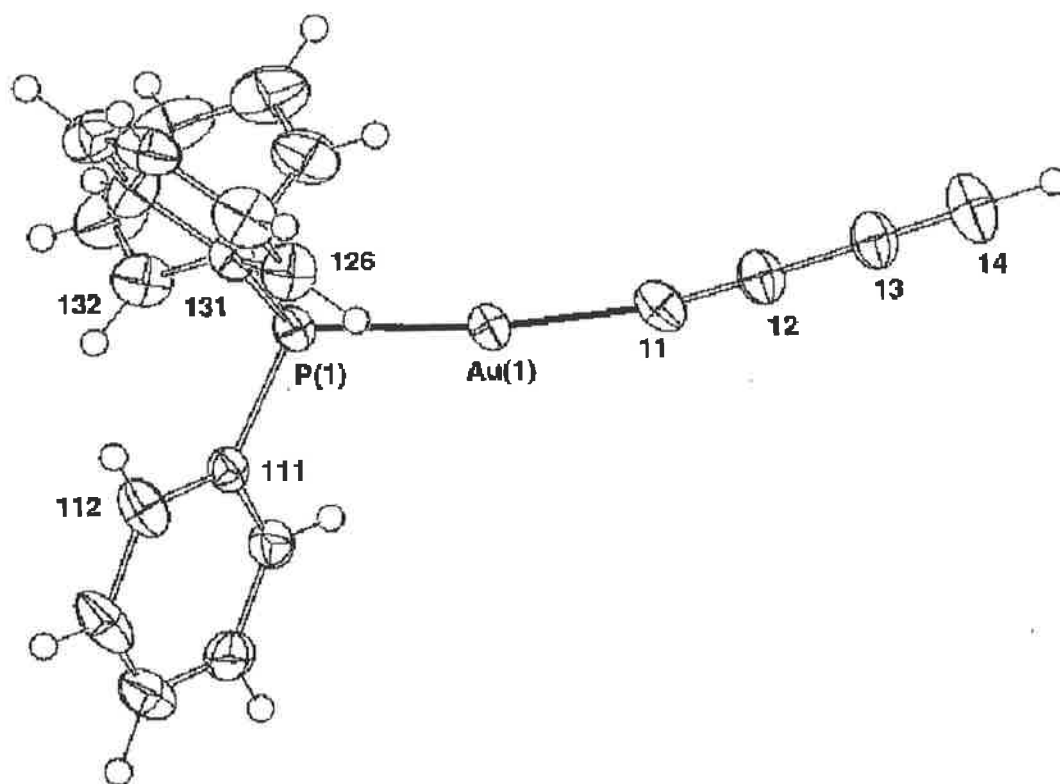


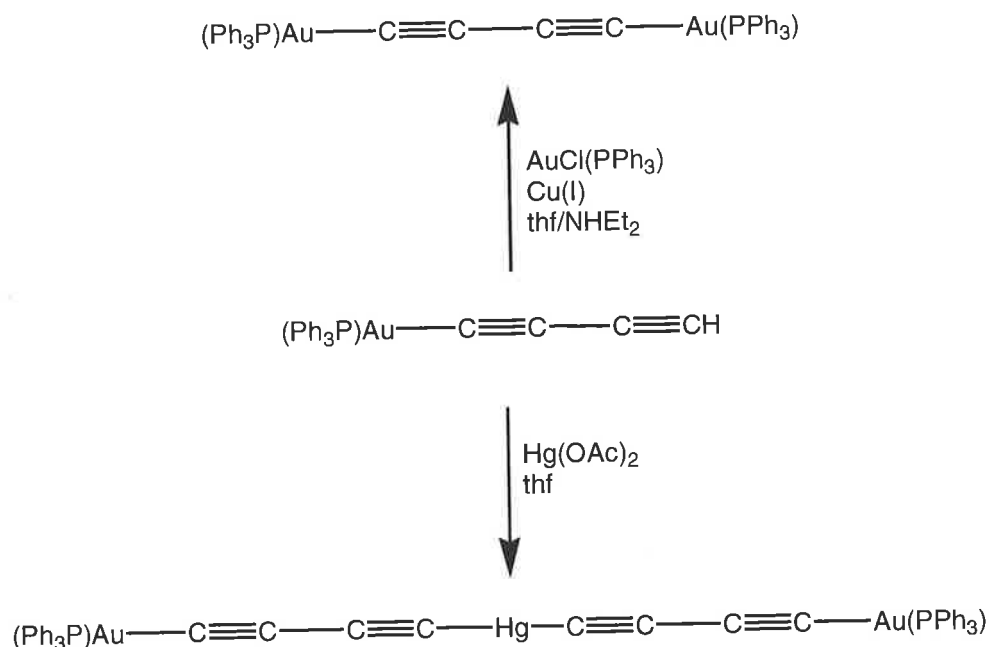
Figure 1. Plot of a molecule of **4.2** showing the atom numbering scheme.

Table 1. Important bond lengths (Å) and angles (°) in **4.2**.

Bond distances (Å)	molecules 1, 2	Bond angles (°)	molecules 1, 2
Au-P	2.276, 2.273(1)	P-Au-C(1)	173.2(1), 172.7(2)
Au-C(1)	2.001, 1.970(5)	Au-C(1)-C(2)	170.6(4), 172.2(6)
C(1)-C(2)	1.204, 1.226(7)	C(1)-C(2)-C(3)	177.7(5), 176.9(7)
C(2)-C(3)	1.379(7), 1.374(8)	C(2)-C(3)-C(4)	178.0(6), 176.5(7)
C(3)-C(4)	1.190(8), 1.188(9)		
P-C(11)	1.813, 1.819(4)	Au-P-C(11)	115.1, 115.6(1)
P-C(12)	1.820(5), 1.805(4)	Au-P-C(12)	111.8(1), 112.7(2)
P-C(13)	1.815, 1.808(5)	Au-P-C(13)	110.9, 110.0(2)
Au-T	2.59(1), 2.659(4)	T-Au-P	175.5(3), 176.24(9)

Although seemingly pure by other criteria, the only usefully crystalline sample of **4.2** obtained for structural work was found to have a co-crystallised contaminant most sensibly modelled as AuI(PPh₃). Two independent molecules of **4.2** comprise the asymmetric unit of the structure, each site having some 'iodide' residue in association with the C₄H ligand, that in company with molecule 1 having occupancy 0.043(2) and that with molecule 2, 0.097(2), C₄H occupancies being modelled as the complements. Despite this perturbation and these differences, associated geometries as presented in Table 1 are plausible. A plot of molecule 1 is given in Fig. 1. The PAuC₄H fragment is essentially linear, with angles at Au and C atoms of between 170.6(4) and 178.0(6)° (molecule 1), 172.6(6) and 172.7(2)° (molecule 2). The Au-P and Au-C(1) distances are 2.276(1), 2.001(5) (molecule 1), 2.273(1), 1.970(5) Å (molecule 2), respectively, while the carbon chains show alternating short/long/short arrangements of the C-C separations [1.204(7), 1.379(7), 1.190(8) (molecule 1), 1.226(7), 1.374(8), 1.188(9) Å (molecule 2)] corresponding to the conjugated 1,3-diyne (-C≡C-C≡C-) formulation. These values may be compared with those found in the electron diffraction study of buta-1,3-diyne itself [1.217(1), 1.383(1) Å; strictly linear]⁴¹, replacement of one H atom by the isolobal Au(PPh₃) group having no significant effect on the geometry.

Addition of **4.2** to AuCl(PPh₃) under similar conditions used in the formation of **4.2** yielded a white precipitate of {(Ph₃P)Au}C≡CC≡C{Au(PPh₃)} (**4.3**) in 83 % yield (Scheme 2). Poor solubility prevented the detailed characterisation of **4.3** but elemental analysis and spectroscopic data agree with the proposed formulation. Thus, one ν(C≡C) band at 2102 cm⁻¹ was found in the IR spectrum. The only resonances observed in the ¹H and ¹³C NMR spectrum were due to the phenyl groups of the PPh₃ ligands. Extended accumulation times and a five second delay between pulses did not enable observation of the butadiyndiyl carbons. A singlet at δ 42.71 in the ³¹P NMR was assigned to the two equivalent phosphorus nuclei.



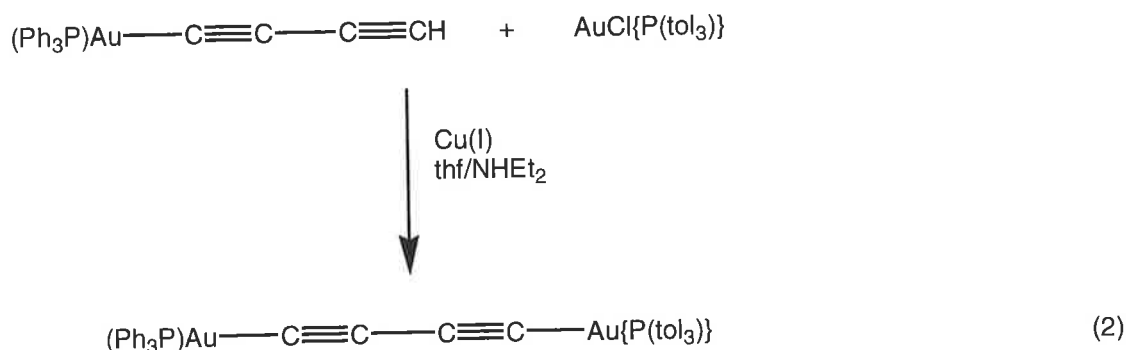
Scheme 2. Reactions of **4.2** with group 11/12 complexes.

The reaction between **4.2** and 0.5 equivalents of $\text{Hg}(\text{OAc})_2$ in refluxing thf gave $\text{Hg}\{\text{C}\equiv\text{CC}\equiv\text{C}[\text{Au}(\text{PPh}_3)]\}_2$ (**4.4**) as a grey-white precipitate in moderate yield (Scheme 2). Like **4.3**, the poor solubility of **4.4** did not allow the resonances of the carbon chain to be observed in the ^{13}C NMR spectrum. Two $\nu(\text{C}\equiv\text{C})$ bands were observed in the IR spectrum at 2100 and 2014 cm^{-1} . The phenyl groups of the PPh_3 ligands gave multiplets at δ_{H} 7.52 – 7.34 and δ_{C} 134.46 – 128.99 and a singlet was observed at δ 42.68 in the ^{31}P NMR spectrum.

The solubility problems for the binuclear complexes made characterisation difficult so the PPh_3 ligand was replaced by $\text{P}(\text{tol}_3)$.

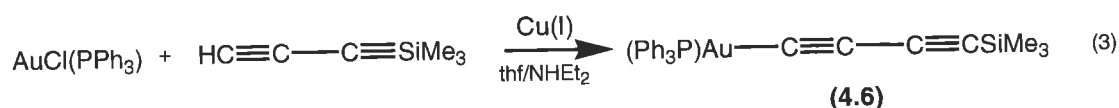
Identical conditions used in the formation of **4.3** gave $\{(\text{Ph}_3\text{P})\text{Au}\}\text{C}\equiv\text{CC}\equiv\text{C}\{\text{Au}[\text{P}(\text{tol}_3)]\}$ (**4.5**) as a pale yellow solid (Equation 2). The solubility of **4.4** was much greater than **4.2**, which greatly aided spectroscopic characterisation. Thus, the IR spectrum gave one $\nu(\text{C}\equiv\text{C})$ band at 2153 cm^{-1} . Two singlets were observed in the ^{31}P NMR spectrum at δ 40.24 and 42.60 in a 1:1 ratio. The downfield signal was assigned to PPh_3 by comparison with $\text{Au}(\text{PPh}_3)$ containing complexes. Singlets at δ_{H} 2.35 and δ_{C} 21.44 were assigned to the methyl groups of

P(tol₃). All four carbons of the chain were observed (δ 85.78, 88.23, 125.80, 126.96) but could not be unequivocally assigned. Comparison with similar complexes however, suggests that δ 126.96 is due to (Ph₃P)Au-C $\equiv$ and δ 125.80 to $\equiv$ C-Au[P(tol₃)].



Synthesis of the mixed phosphine bis-gold butadiyndiyl complex **4.5**.

The trimethylsilyl-protected butadiyne, HC $\equiv$ CC $\equiv$ CSiMe₃, was coupled to AuCl(PPh₃) under Cadiot-Chodkiewicz conditions to give Au(C $\equiv$ CC $\equiv$ CSiMe₃)(PPh₃) (**4.6**) in excellent yield. The IR spectrum contained three $\nu(\text{C}\equiv\text{C})$ bands at 2184, 2129 and 2038 cm⁻¹. In the NMR spectra the SiMe₃ moiety gave singlets at δ_{H} 0.14 and δ_{C} -0.12. Three carbons of the chain were observed at δ 89.52 (C $_{\beta}$), 86.67 (C $_{\gamma}$) and 78.71 (C $_{\delta}$). A singlet at δ 42.41 was observed in the ³¹P NMR spectrum.



Treatment of AuCl{P(tol₃)} with butadiyne in identical conditions used for **4.2** gave Au(C $\equiv$ CC $\equiv$ CH){P(tol₃)} (**4.7**) in good yield. A singlet at δ 40.30 in the ³¹P NMR spectrum was assigned to the P(tol₃) ligand. The methyl groups of P(tol₃) gave sharp singlets at δ_{H} 2.38 and δ_{C} 22.17. The carbons of the chain were observed at δ 60.14, 69.55 and 85.49 and assigned to C $_{\delta}$ - C $_{\beta}$ respectively. The diynyl hydrogen gave a singlet at δ 1.66 in the ¹H NMR spectrum. Its X-ray structure was determined and is shown in Figure 2. Table 2 shows the important bond lengths and angles. As for **4.2**, the PAuC₄H fragment in **4.7** is essentially linear with angles from 171 - 179°. The

carbon chain shows alternating short/long/short arrangements of the C-C separations [1.19(2), 1.38(2), 1.19(3) Å] corresponding to the conjugated 1,3-diyne ($\text{-C}\equiv\text{C-C}\equiv\text{C-}$) formulation. The Au-P distance of 2.272(3) Å is experimentally identical to that of **4.2** [2.276(1)] as is the Au-C(1) distance of 1.99(1) [4.2, 2.001(5)].

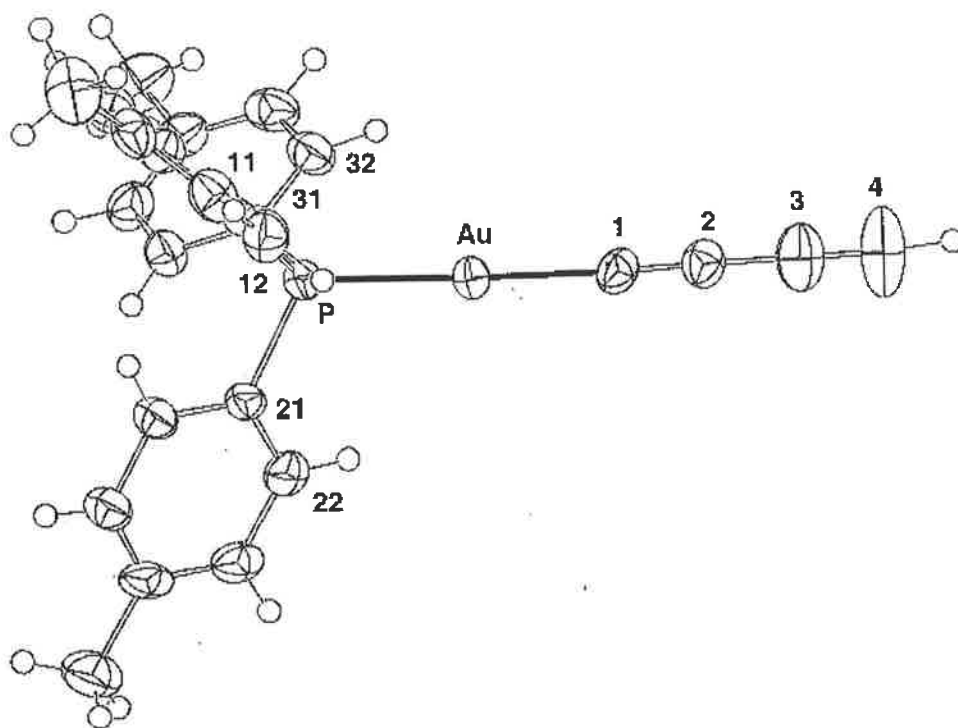


Figure 2. Plot of a molecule of **4.7** showing the atom numbering scheme.

Table 2. Important bond lengths (Å) and angles (°) in **4.7**.

Bond distances (Å)		Bond angles (°)	
Au-P	2.272(3)	P-Au-C(1)	172.5(3)
Au-C(1)	1.99(1)	Au-C(1)-C(2)	171(1)
C(1)-C(2)	1.19(2)	C(1)-C(2)-C(3)	177(1)
C(2)-C(3)	1.38(2)	C(2)-C(3)-C(4)	179(2)
C(3)-C(4)	1.19(3)		
P-C(11)	1.79(1)	Au-P-C(11)	117.5(5)
P-C(12)	1.82(1)	Au-P-C(12)	116.3(4)
P-C(13)	1.83(1)	Au-P-C(13)	109.4(4)

Similarly, addition of $\text{HC}\equiv\text{CC}\equiv\text{CSiMe}_3$ to $\text{AuCl}\{\text{P}(\text{tol}_3)\}$ in thf/NHEt_2 in the presence of CuI gave $\text{Au}(\text{C}\equiv\text{CC}\equiv\text{CSiMe}_3)(\text{Ptol}_3)$ (**4.8**) in excellent yield. The IR spectrum showed three $\nu(\text{C}\equiv\text{C})$ bands at 2183, 2131, and 2036 cm^{-1} . The ^1H NMR spectrum contained two singlets at δ 0.13 and 2.37 due to the SiMe_3 and tolyl groups respectively. The ^{13}C NMR spectrum showed only three of the four carbon atoms of the chain at δ 89.62, 87.02 and 78.89. Comparison with other Au-butadiynyl complexes enabled the assignment of these to C_β , C_γ and C_δ respectively. The methyl carbons of the $\text{P}(\text{tol}_3)$ ligand gave a singlet at δ 21.41 while the SiMe_3 group gave a singlet at δ -0.14. The ^{31}P NMR spectrum contained a singlet at δ 40.25.

A structure determination confirmed the structure proposed and is shown in Figure 3. The structural data for **4.8** is similar to **4.2** and **4.7**. The PAuC_4Si angles are almost linear with angles at carbon ranging between $174.9(2)$ and $177.7(4)^\circ$. The Au-P and Au-C(1) distances of 2.2779(9) and 1.993(6) are identical to that of **4.2** and **4.7**. Again, the separations of the atoms of the carbon chain [$1.163(9)$, $1.418(8)$ and $1.229(7)\text{ \AA}$] support the $\text{C}\equiv\text{C}-\text{C}\equiv\text{C}$ formulation. The C(1)-C(2) separation is slightly shorter and the C(3)-C(4) is slightly longer than those in **4.2** and **4.7**.

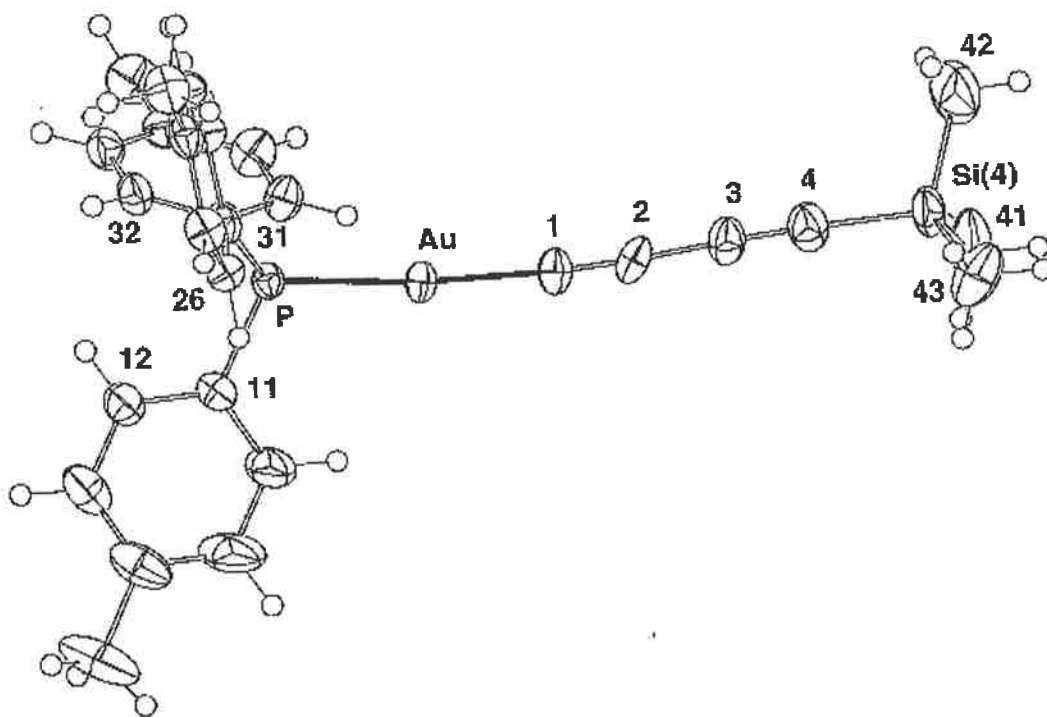
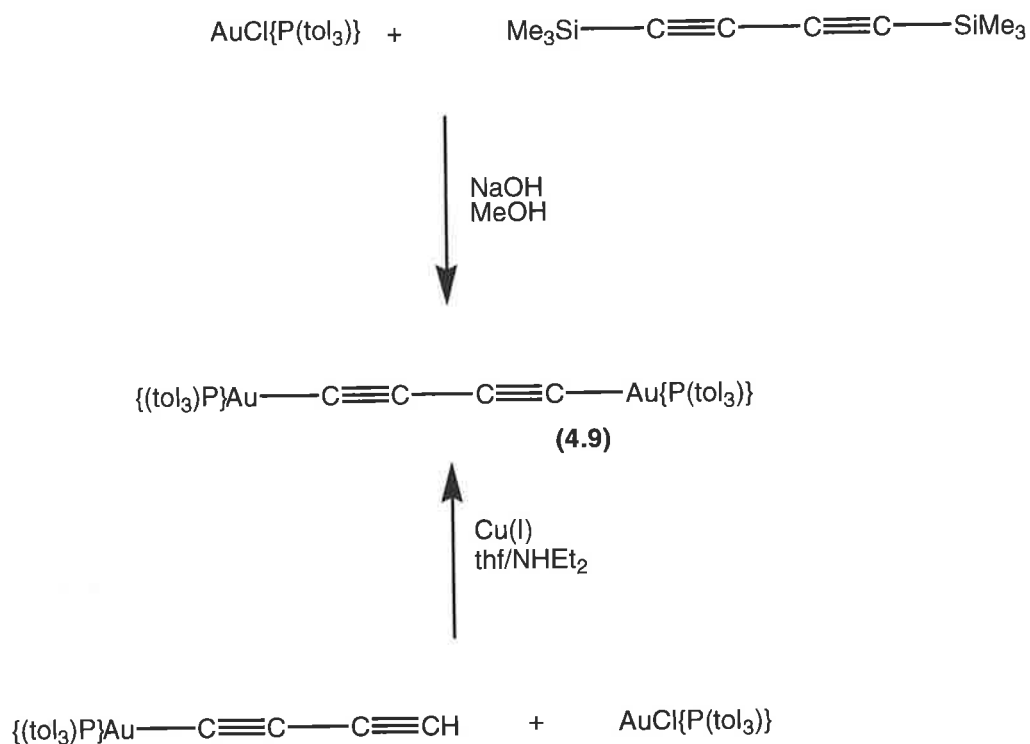


Figure 3. Plot of a molecule of **4.8** showing the atom numbering scheme.

Table 3. Important bond lengths (Å) and angles (°) in **4.8**.

Bond distances (Å)		Bond angles (°)	
Au-P	2.2779(9)	P-Au-C(1)	174.9(2)
Au-C(1)	1.993(6)	Au-C(1)-C(2)	176.3(6)
C(1)-C(2)	1.163(9)	C(1)-C(2)-C(3)	176.6(6)
C(2)-C(3)	1.418(8)	C(2)-C(3)-C(4)	177.1(6)
C(3)-C(4)	1.229(7)	C(3)-C(4)-Si	177.7(4)
P-C(11)	1.803(4)	Au-P-C(11)	114.6(1)
P-C(12)	1.816(3)	Au-P-C(12)	110.4(1)
P-C(13)	1.809(3)	Au-P-C(13)	110.9(1)
Au-‘I’		P-Au-‘I’	177.85(6)

Scheme 3. Synthesis of **4.9** using two different methodologies.

The silyl-protected butadiyne, $\text{Me}_3\text{SiC}\equiv\text{CC}\equiv\text{CSiMe}_3$, is a crystalline solid and a synthon for $\text{HC}\equiv\text{CC}\equiv\text{CH}$. Desilylation *in situ* with NaOH gives, presumably, $\text{NaC}\equiv\text{CC}\equiv\text{CNa}$ which reacts readily with $\text{AuCl}\{\text{P}(\text{tol}_3)\}$ to give

$\{[(\text{tol}_3)\text{P}]\text{Au}\}\text{C}\equiv\text{CC}\equiv\text{C}\{\text{Au}[\text{P}\{\text{tol}_3\}]\}$ (**4.9**) as an off-white solid (Scheme 3). An X-ray structure determination confirmed the addition of two $\text{Au}(\text{P}(\text{tol}_3))$ groups to the C_4 chain and is shown in Figure 4. Important bond lengths and angles are given in Table 4.

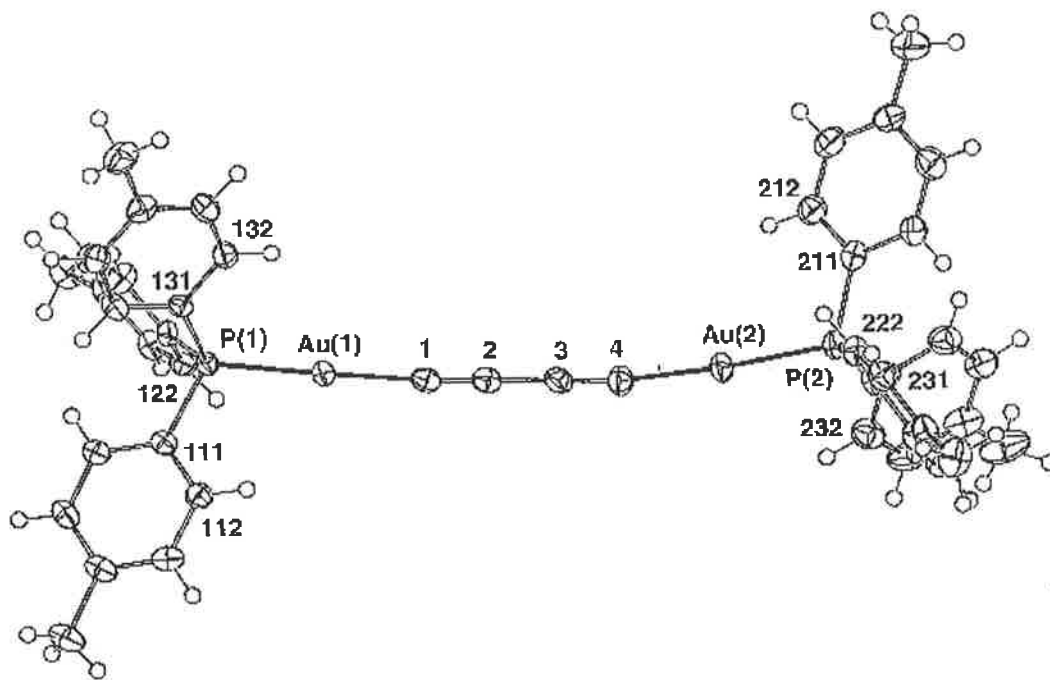


Figure 4. Plot of a molecule of **4.9** showing the atom numbering scheme.

Table 4. Important bond lengths (Å) and angles (°) in **4.9**.

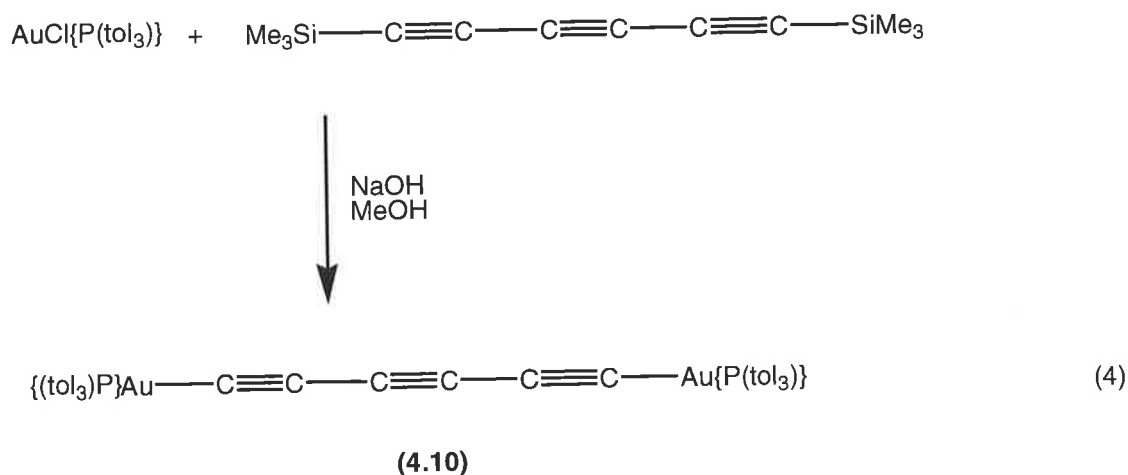
Bond distances (Å)		Bond angles (°)	
Au(1, 2)-P(1, 2)	2.275, 2.273(1)	P(1)-Au(1)-C(1)	178.7(2)
Au(1, 2)-C(1, 4)	1.996, 1.996(5)	P(2)-Au(2)-C(4)	176.2(2)
C(1)-C(2)	1.196(6)	Au(1)-C(1)-C(2)	176.3(6)
C(2)-C(3)	1.390(6)	C(1)-C(2)-C(3)	178.6(6)
C(3)-C(4)	1.215(6)	C(2)-C(3)-C(4)	178.8(5)
P(1, 2)-C(111, 211)	1.817, 1.803(7)	C(3)-C(4)-Au(2)	169.2(6)
P(1, 2)-C(112, 212)	1.814, 1.817(5)		
P(1, 2)-C(113, 213)	1.804, 1.808(6)		

The geometry about the gold atom in **4.9** is similar to both **4.7** and **4.8**. Thus the Au-P [2.275, 2.273(1) Å] and Au-C [1.996(5) Å] distances are experimentally the same in all three complexes. The PAuC₄AuP linkage is not linear with angles at carbon between 169.2(6) and 178.8(5)°. The bending is most noticeable in the C(3)-C(4)-Au(2) value of 169.2(6)° and is probably due to crystal packing forces. The C≡C and C-C distances of 1.196(6)/1.215(6) and 1.390(6) Å are very close to those in butadiyne [1.218(2), 1.384(2) Å]⁴¹ and confirm the butadiyndiyl formulation.

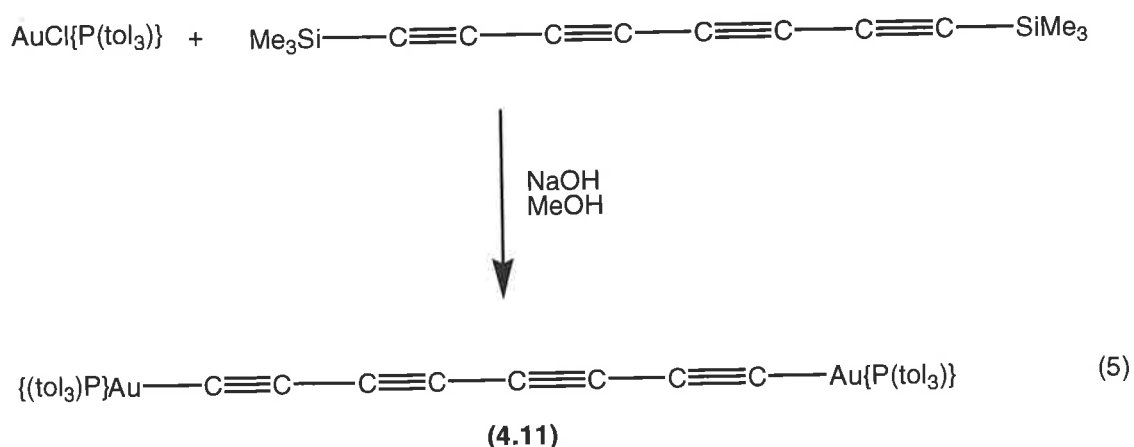
The reaction between **4.7** and AuCl{P(tol₃)} gave **4.9** in a slightly lower yield (Scheme 3). This complex is far more soluble than the PPh₃ analogue **4.3**. The spectroscopic data agree with the structure found. Thus, the IR spectrum showed one ν(C≡C) band at 2157 cm⁻¹. The tolyl moieties gave singlets at δ_H 2.29 and δ_C 21.39. The carbons of the chains were clearly observed at δ_C 119.89 and 88.11, the former a doublet with ²J_{CP} = 140 Hz and are assigned to C_α and C_β respectively. A singlet at δ 40.57 was observed in the ³¹P NMR spectrum.

During the course of this work, Che et al. reported the synthesis and ³(ππ*) emission of a series of gold(I) complexes of the formula {(Cy₃P)Au}(C≡C)_n{Au(PCy₃)} (n = 1 – 4).^{42,43} The synthetic methodology is similar to the one used in the preparation of **4.9** – **4.11**.

Utilising the stability of TMS-capped poly-ynes as precursors to metal complexes containing longer carbon chains, the C₆ analogue of Me₃SiC≡CC≡CSiMe₃ was synthesised.⁴⁴ Under the same conditions used in the preparation of **4.9**, {[(tol₃)P]Au}(C≡C)₃{Au[P(tol₃)]} (**4.10**) was formed in good yield (76%) (Equation 4).

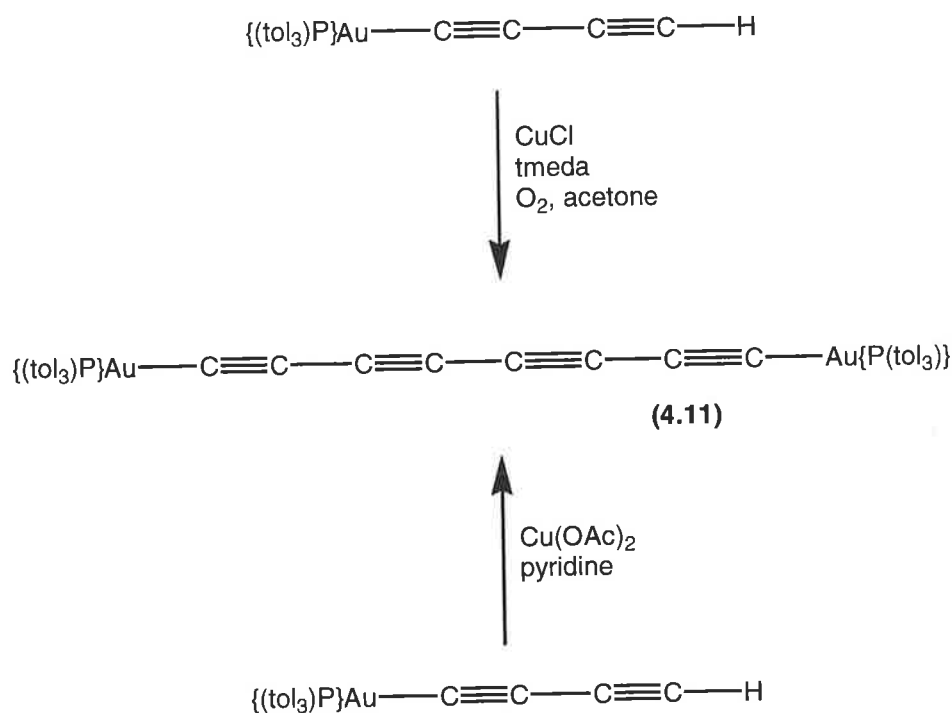


Two $\nu(\text{C}\equiv\text{C})$ bands were observed at 2115 cm^{-1} with a shoulder at 2139 cm^{-1} . The ^1H NMR spectrum contained only resonances due to aromatic protons and a singlet at δ 2.38 due to the methyl protons of the tolyl groups. A singlet at δ 21.42 in the ^{13}C NMR spectrum was assigned to the methyl carbons, the carbons of the chain resonated at δ 127.94, 88.13 and 81.63 assigned to C_α , C_β and C_γ respectively. A singlet was observed in the ^{31}P NMR spectrum at δ 40.26.



The reaction between $\text{Me}_3\text{Si}(\text{C}\equiv\text{C})_4\text{SiMe}_3$ and $\text{AuCl}(\text{Ptol}_3)$ gave the C_8 complex, $\{[(\text{tol}_3)\text{P}]\text{Au}\}(\text{C}\equiv\text{C})_4\{\text{Au}[\text{P}(\text{tol}_3)]\}$ (4.11) in poor yield (Equation 5). Presumably, this is due to the instability of the intermediate NaC_8Na when compared to the C_4 and C_6 analogues. This poor yield and the instability of the organic precursor led us to devise two alternative routes to 4.11.

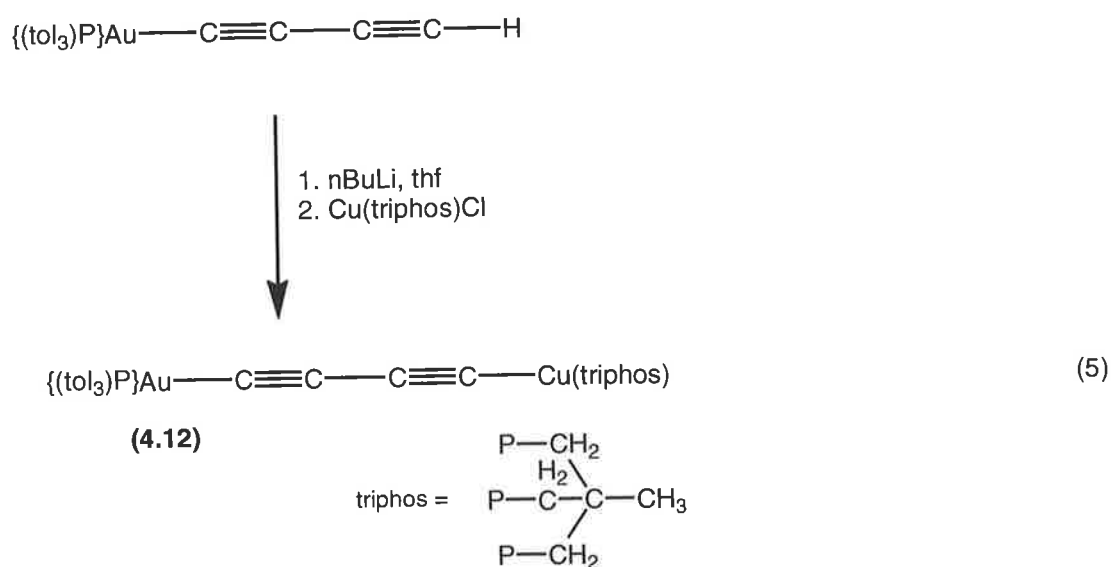
Homocoupling of $\{\text{ML}_n\}\text{C}\equiv\text{CC}\equiv\text{CH}$ complexes to give the C_8 complexes, $\{\text{ML}_n\}(\text{C}\equiv\text{C})_4\{\text{ML}_n\}$ has been investigated previously.^{39,45-47} Within this group, the Hay conditions are preferred owing to their mild nature. Thus, bubbling O_2 through an acetone solution of **4.7** in the presence of the Hay catalyst (CuCl / *tmeda*) gave **4.11** in a slightly better yield (Scheme 4). Glaser type coupling has been successfully used in the preparation of both $\{\text{Cp}^*(\text{NO})(\text{PPh}_3)\text{Re}\}(\text{C}\equiv\text{C})_n\{\text{Re}(\text{NO})(\text{PPh}_3)\text{Cp}^*\}$ ($n = 2, 4, 12, 16, 20$)⁴⁸ and $\{\text{Cp}^*(\text{dppe})\text{Fe}\}(\text{C}\equiv\text{C})_4\{\text{Fe}(\text{dppe})\text{Cp}^*\}$.⁴⁷ Under these conditions, the yield of **4.10** was significantly increased (Scheme 4).



Scheme 4. Alternative syntheses of **(4.11)**.

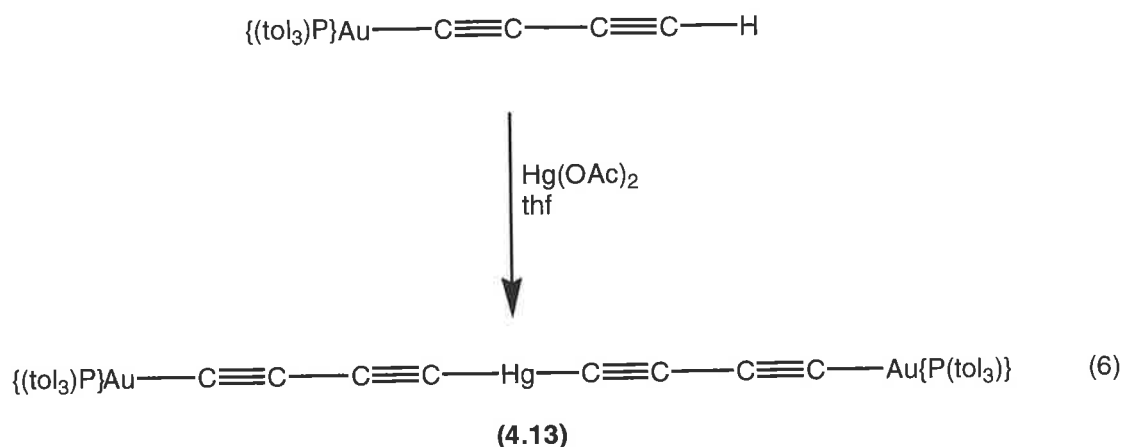
The spectroscopic data agrees well with the proposed formulation. Thus, the IR spectrum showed two $\nu(\text{C}\equiv\text{C})$ bands at 2167 and 2134 cm^{-1} . The ^1H NMR spectrum contains a singlet at δ 2.36 due to the methyl protons and a multiplet due to the aromatic protons of the tolyl groups. The ^{13}C NMR contained the expected resonances for the methyl carbons (singlet, δ 21.42) and the four carbons of the chain at δ 131.29, 86.94, 67.23 and 60.91 due to $\text{C}_\alpha - \text{C}_\delta$ respectively. A singlet was observed at δ 40.26 in the ^{31}P NMR spectrum.

Lithiation of **4.7** followed by addition of CuCl(triphos) gave the first known molecular wire complex capped by σ -bonded gold and copper groups, $\{[(\text{tol}_3)\text{P}]\text{Au}\}\text{C}\equiv\text{CC}\equiv\text{C}\{\text{Cu}(\text{triphos})\}$ (**4.12**) in good yield (Equation 6). The IR spectrum contained two $\nu(\text{C}\equiv\text{C})$ bands at 2158 and 2127 cm^{-1} . The triphos ligand gave two broad singlets in the ^1H NMR spectrum at δ 1.44 and 2.28, the former due to the methyl group and the latter due to the six methylene protons. The tolyl moiety showed a singlet at δ_{H} 2.36. The ^{13}C NMR spectra contained peaks due to the tolyl moieties; a singlet at δ 21.43 and a multiplet between δ 125.27 – 142.31. The triphos ligand gave rise to multiplets at δ 36.47 and 39.93 due to the quaternary and methylene carbons respectively and a singlet at δ 37.53 due to the methyl group. The ^{31}P NMR contained two singlets at δ 45.20 and -25.08 due to $\text{P}(\text{tol}_3)$ and triphos respectively.

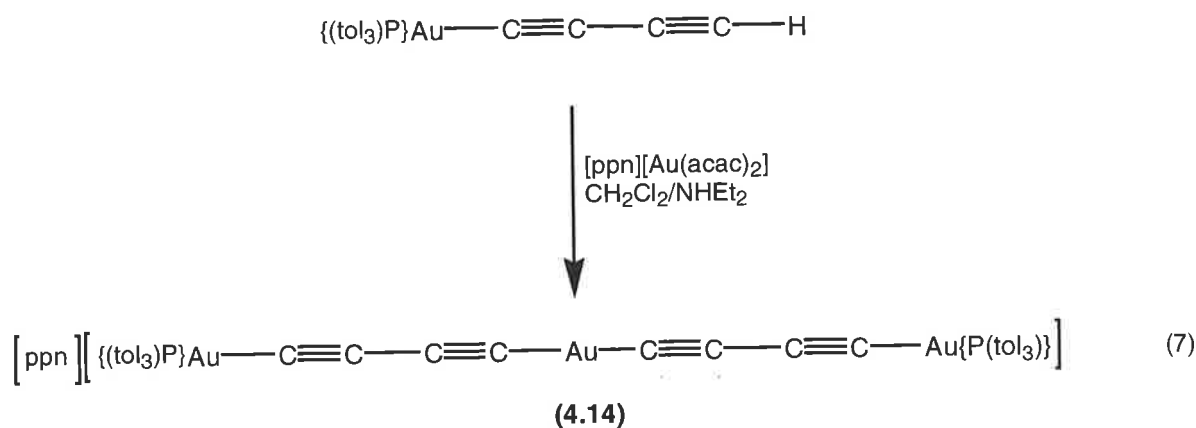


The reaction between **4.7** and $\text{Hg}(\text{OAc})_2$ gave an off-white solid identified as $\text{Hg}\{\text{C}\equiv\text{CC}\equiv\text{CAu}[\text{P}(\text{tol}_3)]\}_2$ (**4.13**) in good yield (Equation 6). Unlike the PPh_3 analogue, this complex was reasonably soluble in common organic solvents. The IR spectrum contained two $\nu(\text{C}\equiv\text{C})$ bands at 2166 and 2052 cm^{-1} . The ^1H NMR spectra contained a singlet at δ 2.35 due to the methyl groups of the tolyl ligands and a multiplet between δ 7.18 – 7.39 due to the aromatic protons of the tolyl ligands. Three carbons of the C_4 bridge were observed in this case with a doublet at δ 88.17 ($^2J_{\text{PC}} = 29$ Hz) and singlets at δ 102.52 and 72.52. No definitive assignment can be made

although the doublet at δ 88.17 is quite possibly $\text{Au-C}\equiv\text{C}$ by comparison with previous complexes. In the ^{13}C NMR spectrum the tolyl phosphines gave rise to a singlet at δ 21.43 and a multiplet between δ 141.70 – 126.80 due to the methyl and aromatic carbons respectively. A singlet in the ^{31}P NMR spectra at δ 40.62 is assigned to the $\text{P}(\text{tol}_3)$.



Complex **4.13** contains a thirteen-atom chain with a mercury atom in the centre. A similar complex can be made which has a gold atom in place of the mercury. The reaction between **4.7** and $[\text{ppn}][\text{Au}(\text{acac})_2]$ gave the desired complex, $[\text{ppn}][\text{Au}\{\text{C}\equiv\text{CC}\equiv\text{C}[\text{Au}(\text{Ptol}_3)]\}_2]$ (**4.14**) in a moderate yield as a sparingly soluble white solid. The IR spectrum contained only one $\nu(\text{C}\equiv\text{C})$ band at 2145 cm^{-1} . The ^1H NMR spectrum showed a singlet at δ 2.29 due to the methyl groups of the $\text{P}(\text{tol}_3)$ ligands and a multiplet between δ 7.15 – 7.62 due to the aromatic protons of the $\text{P}(\text{tol}_3)$ ligands and the PPh_3 groups of the counter ion. The ^{13}C NMR spectrum did not show the carbons of the C_4 bridge. The only signals observed were a singlet at δ 21.36 due to the methyl groups of the $\text{P}(\text{tol}_3)$ ligands and a multiplet between δ 125.54 – 141.81 due to $\text{P}(\text{tol}_3)$ and the PPh_3 groups of the ppn cation. Two singlets were observed in the ^{31}P NMR spectra at δ 39.62 and 22.21 due to $\text{P}(\text{tol}_3)$ and PPh_3 respectively.



DISCUSSION

This chapter has detailed the synthesis and characterisation of several gold(I) complexes with varying geometries and shows that alkynylgold(I) chemistry is readily extended to derivatives of 1,3-diynes, including the parent buta-1,3-diyne. It is possible to attach several common gold(I) fragments, including $\text{Au}(\text{PPh}_3)$ and $\text{Au}\{\text{P}(\text{tol}_3)\}$, to the diyne, replacing the $\text{C} \equiv \text{CH}$ proton. In addition, reaction of the $[\text{Au}(\text{acac})_2]^-$ anion readily proceeds with loss of the labile β -diketonate ligands. From the simplest mononuclear complexes, **4.2**, **4.6**, **4.7** and **4.8** in which the coupling of $\text{AuCl}(\text{PR}_3)$ ($\text{R} = \text{Ph}, \text{tol}$) with either butadiyne or the mono-trimethylsilyl protected species using Cadiot-Chodkiewicz conditions, to the linear rods in which two PAuC_4 units were linked by either a mercury or gold atom (**4.4**, **4.13** and **4.14**). The syntheses that have been established and routinely used in this research group have been successfully applied to gold(I) alkynyl chemistry.

In many cases the carbons of the diyne chain have been observed in the ^{13}C NMR spectra. It has been reported previously^{42,43} that coupling to the phosphorous ligand results in the signals being observed as doublets with $^2J_{\text{CP}}$ and $^3J_{\text{CP}}$ coupling. Table 5 summarises the ^{13}C spectra of the carbon chains.

Table 5. Selected ^{13}C NMR data.

Complex	C_α ($^2J_{\text{CP}}$)	C_β	C_γ	C_δ
4.2	128.54 (124 Hz)	85.79	69.45	60.45
4.6	n/o	89.52	86.67	78.71
4.7	n/o	85.49	69.45	60.14
4.8	n/o	89.62	87.02	78.89
4.5	125.80	85.78	88.23	126.96
4.9	119.89 (140 Hz)	88.11		
4.10	127.94	88.13	81.63	
4.11	131.29	86.94	67.23	60.91

n/o = not observed.

Unfortunately, due to the phenyl or tolyl phosphines ligands, C_α was not observed in all cases. As Table 5 shows, the ^{13}C resonances for the carbons of the chain fall within a well defined range. In two instances, the coupling to ^{31}P was observed for C_α (**4.2**, **4.9**). The extended accumulation and relaxation times did not allow the resolution of the signal assigned to C_β which was observed as a broad singlet in all cases.

The X-ray structures of the mononuclear butadiynyl complexes, **4.2**, **4.7** and **4.8** and the binuclear butadiyndiyl complex, **4.9** have been determined. In all cases the $\text{C}\equiv\text{C}$ (1.163 – 1.229 Å) and C-C (1.379 – 1.418 Å) bond distances compare well with those of butadiyne (1.218, 1.384 Å).⁴¹ The angles at carbon range between ca 169.2 – 178.8°. This bending of the chain is due to crystal packing forces.

Further elaboration of these interesting architectures continues within this research team in a bid to structurally characterise some of these linear rod-like complexes.

EXPERIMENTAL

General experimental conditions and Instrumentation – see Chapter 2.

Reagents

CuI (Fluka), CuCl (Ajax), tmeda (Merck), Hg(OAc)₂ (Aldrich), Cu(OAc)₂ (BDH) and nBuLi (Aldrich), were used as received. The compounds HC≡CC≡CH,⁴⁹ AuCl(PPh₃),⁵⁰ AuCl{P(tol)₃},⁵⁰ [ppn][Au(acac)₂],⁵¹ HC≡CC≡CSiMe₃,⁵² Me₃SiC≡CC≡CSiMe₃,⁵³ Me₃Si(C≡C)₃SiMe₃,⁴⁴ Me₃Si(C≡C)₄SiMe₃,⁵⁴ CuCl(triphos)⁵⁵ were prepared using the cited methods.

(a) Au(C≡CC≡CH)(PPh₃) (**4.2**).

To a suspension of AuCl(PPh₃) (1.17 g, 2.37 mmol) in thf/NHEt₂ (45 mL, 1/2) containing CuI (46 mg, 0.24 mmol) was added HC≡CC≡CH (23 mL of a 1.34 M solution in thf, 31 mmol) and the mixture was stirred at r.t. for 15 min. Solvent was removed and the residue extracted with CH₂Cl₂ and loaded onto a squat column. The product was eluted with CH₂Cl₂, addition of hexane and reduction of solvent volume resulting in precipitation of pale yellow Au(C≡CC≡CH)(PPh₃) (**4.2**) (908 mg, 75%). Anal. Found: C, 49.75; H, 3.26. C₂₂H₁₆AuP·0.5CH₂Cl₂ requires: C, 49.09; H, 3.12; *M*, 508. IR (CH₂Cl₂): ν(≡CH) 3301; ν(C≡C) 2159 cm⁻¹. ¹H NMR: δ 1.76 (s, 1H, C≡CH), 7.30-7.63 (m, 15H, Ph). ¹³C NMR: δ 60.45 (s, C_δ), 69.45 (s, C_γ), 85.79 (br, C_β), 128.54 (d, ²J_{CP} = 124 Hz, C_α), 128.79-133.80 (m, Ph). ³¹P NMR: δ 42.34. ES mass spectrum (CH₂Cl₂ / MeOH, *m/z*): 508, M⁺; 459, [M - C₄H]⁺.

(b) {(Ph₃P)Au}C≡CC≡C{Au(PPh₃)} (**4.3**).

To a suspension of **4.2** (200 mg, 0.39 mmol) and AuCl(PPh₃) (194 mg, 0.39 mmol) in thf/NHEt₂ (25 mL, 1/3) was added CuI (ca 10 mg). The suspension cleared leaving a yellow solution which deposited a white precipitate after 5 min. The precipitate was collected and washed with H₂O, EtOH, MeOH and Et₂O and air-dried to give {(Ph₃P)Au}C≡CC≡C{Au(PPh₃)} (**4.3**) (314 mg, 83 %). Anal. Found: C, 49.63; H, 3.08. C₄₀H₃₀Au₂P₂ requires: C, 49.71; H, 3.13; *M*, 967. IR (nujol): ν(C≡C) 2102w cm⁻¹. ¹H NMR: δ 7.53-7.41 (m, Ph). ¹³C NMR δ 134.42-128.99 (m, Ph). ³¹P NMR: δ 42.71.

(c) $\text{Hg}\{\text{C}\equiv\text{CC}\equiv\text{C}[\text{Au}(\text{PPh}_3)]\}_2$ (**4.4**).

A solution of **4.2** (200 mg, 0.39 mmol) and $\text{Hg}(\text{OAc})_2$ (62 mg, 0.19 mmol) in thf (15 mL) was refluxed for 1h. After allowing to cool to r.t a grey/white precipitate had formed which was collected and washed with H_2O , EtOH, MeOH and Et_2O and air-dried to give $\text{Hg}\{\text{C}\equiv\text{CC}\equiv\text{C}[\text{Au}(\text{PPh}_3)]\}_2$ (**4.4**) (114 mg, 49 %). Anal. Found: C, 43.61; H, 2.27. $\text{C}_{44}\text{H}_{30}\text{Au}_2\text{Hg}_2\text{P}_2$ requires: C, 43.49; H, 2.49; *M*, 967. IR (nujol): $\nu(\text{C}\equiv\text{C})$ 2100w, 2014w cm^{-1} . ^1H NMR: δ 7.52-7.34 (m, Ph). ^{13}C NMR δ 134.46-128.99 (m, Ph). ^{31}P NMR: δ 42.68 (s).

(d) $\{(\text{Ph}_3\text{P})\text{Au}\}\text{C}\equiv\text{CC}\equiv\text{C}\{\text{Au}[\text{P}(\text{tol}_3)]\}$ (**4.5**).

To a solution of **4.2** (250 mg, 0.49 mmol) and $\text{AuCl}\{\text{P}(\text{tol}_3)\}$ (264 mg, 0.49 mmol) in thf/ NH_4Et_2 (30 mL, 1/3) was added CuI (ca 5 mg) and the resulting yellow solution stirred for 1h. A yellow-brown precipitate had formed in this time and was collected and washed with H_2O , EtOH, MeOH and Et_2O and air-dried to give $\{(\text{Ph}_3\text{P})\text{Au}\}\text{C}\equiv\text{CC}\equiv\text{C}\{\text{Au}[\text{P}(\text{tol}_3)]\}$ (**4.5**) (250 mg, 51 %). Anal. Found: C, 51.09; H, 3.45. $\text{C}_{43}\text{H}_{36}\text{Au}_2\text{P}_2$ requires: C, 51.20; H, 3.60; *M*, 1009. IR (CH_2Cl_2): $\nu(\text{C}\equiv\text{C})$ 2153 cm^{-1} . ^1H NMR: δ 2.35 (s, 9H, Me), 7.17-7.54 (m, 27H, tol). ^{13}C NMR: δ 21.44 (s, Me), 85.78 (br, C_β), 88.23 (br, C_γ), 125.80 (br, C_α), 126.96 (br, C_δ), 129.00-142.38 (m, tol). ^{31}P NMR: δ 40.24 [s, $\text{P}(\text{tol}_3)$], 42.60 (s, PPh_3).

(e) $\text{Au}(\text{C}\equiv\text{CC}\equiv\text{CSiMe}_3)(\text{PPh}_3)$ (**4.6**).

To a suspension of $\text{AuCl}(\text{PPh}_3)$ (500 mg, 1.01 mmol) in thf/ NH_4Et_2 (30 mL, 1/2) containing CuI (20 mg, 0.105 mmol) was added $\text{HC}\equiv\text{CC}\equiv\text{CSiMe}_3$ (185 mg, 1.52 mmol) and the mixture was stirred at r.t. for 1h. The solvent was removed and the residue extracted with CH_2Cl_2 and loaded onto a SiO_2 column. The product was eluted with hexane. Reduction of solvent volume resulted in precipitation of pale yellow $\text{Au}(\text{C}\equiv\text{CC}\equiv\text{CSiMe}_3)(\text{PPh}_3)$ (**4.6**) (450 mg, 77%). Anal. Found: C, 49.78; H, 3.38. $\text{C}_{25}\text{H}_{24}\text{AuPSi} \cdot 0.5\text{CH}_2\text{Cl}_2$ requires: C, 49.16; H, 4.05; *M*, 580. IR (nujol): $\nu(\text{C}\equiv\text{C})$ 2184m, 2129m, 2038m cm^{-1} . ^1H NMR: δ 0.14 (s, 9H, SiMe_3), 7.51-7.42 (m, 15H, Ph). ^{13}C NMR δ -0.12 (s, SiMe_3), 78.71 (s, C_δ), 86.67 (s, C_γ), 89.52 (br, C_β), 134.31-129.08 (m, Ph). ^{31}P NMR: δ 42.41.

(f) $\text{Au}(\text{C}\equiv\text{CC}\equiv\text{CH})\{\text{P}(\text{tol}_3)\}$ (**4.7**).

To a solution of $\text{AuCl}\{\text{P}(\text{tol}_3)\}$ (2.0 g, 3.73 mmol) in $\text{thf}/\text{NH}_4\text{Et}_2$ (60 mL, 1/3) was added CuI (71 mg, 0.37 mmol) followed by $\text{HC}\equiv\text{CC}\equiv\text{CH}$ (6.9 mL of a 2.7 M solution in thf , 18.6 mmol) and the mixture was stirred at r.t. for 30 min. The solvent was removed and the residue extracted with CH_2Cl_2 and loaded onto a SiO_2 column. The product was eluted with CH_2Cl_2 , addition of hexane and reduction of solvent volume resulting in precipitation of pale yellow $\text{Au}(\text{C}\equiv\text{CC}\equiv\text{CH})\{\text{P}(\text{tol}_3)\}$ (**4.7**) (1.3 g, 63%). Anal. Found: C, 54.51; H, 4.01. $\text{C}_{25}\text{H}_{22}\text{AuP}$ requires: C, 54.56; H, 4.03; *M*, 550. IR (CH_2Cl_2): $\nu(\equiv\text{CH})$ 3300; $\nu(\text{C}\equiv\text{C})$ 2157 cm^{-1} . ^1H NMR: δ 1.66 (s, 1H, $\text{C}\equiv\text{CH}$), 2.38 (s, 9H, Me), 7.20-7.43 (m, 12H, tol). ^{13}C NMR: δ 22.17 (s, Me), 60.14 (s, C_δ), 69.55 (s, C_γ), 85.49 (br, C_β), 125.75-141.97 (m, tol). ^{31}P NMR: δ 40.30.

(g) $\text{Au}(\text{C}\equiv\text{CC}\equiv\text{CSiMe}_3)\{\text{P}(\text{tol}_3)\}$ (**4.8**).

To a solution of $\text{AuCl}\{\text{P}(\text{tol}_3)\}$ (250 mg, 0.47 mmol) in $\text{thf}/\text{NH}_4\text{Et}_2$ (15 mL, 1/3) was added CuI (ca 5 mg) followed by $\text{HC}\equiv\text{CC}\equiv\text{CSiMe}_3$ (114 mg, 0.94 mmol). The yellow solution was stirred for 1 h in the dark and the solvent removed. Extraction with CH_2Cl_2 and passage through a SiO_2 column eluting with hexane yielded a pale yellow band which gave pale yellow solid $\text{Au}(\text{C}\equiv\text{CC}\equiv\text{CSiMe}_3)\{\text{P}(\text{tol}_3)\}$ (**4.8**) (195 mg, 67%). Anal. Found: C, 53.98; H, 4.83. $\text{C}_{28}\text{H}_{30}\text{AuPSi}$ requires: C, 54.02; H, 4.86; *M*, 623. IR (CH_2Cl_2): $\nu(\text{C}\equiv\text{C})$ 2183m, 2131m, 2036m cm^{-1} . ^1H NMR: δ 0.13 (s, 9H, SiMe_3), 2.37 (s, 9H, Me), 7.19-7.42 (m, 12H, tol). ^{13}C NMR: δ -0.14 (s, SiMe_3), 21.41 (s, Me), 78.89 (s, C_δ), 87.02 (s, C_γ), 89.62 (br, C_β), 125.82-142.00 (m, tol). ^{31}P NMR: δ 40.25.

(h) $\{[(\text{tol}_3)\text{P}]\text{Au}\}\text{C}\equiv\text{CC}\equiv\text{C}\{\text{Au}[\text{P}(\text{tol}_3)]\}$ (**4.9**).1. From $\text{Me}_3\text{SiC}\equiv\text{CC}\equiv\text{CSiMe}_3$.

Dissolved $\text{Me}_3\text{SiC}\equiv\text{CC}\equiv\text{CSiMe}_3$ (50 mg, 0.26 mmol) and NaOH (206 mg, 5.20 mmol) in MeOH (25 mL) and stirred for 30 min. Added $\text{AuCl}\{\text{P}(\text{tol}_3)\}$ (276 mg, 0.52 mmol) and stirred a further 1.5 h. A pale yellow precipitate had formed and was collected and washed with MeOH , Et_2O and pentane and air-dried to give $\{[(\text{tol}_3)\text{P}]\text{Au}\}\text{C}\equiv\text{CC}\equiv\text{C}\{\text{Au}[\text{P}(\text{tol}_3)]\}$ (**4.9**) (230 mg, 85 %). Anal. Found: C, 52.43; H, 3.96. $\text{C}_{46}\text{H}_{42}\text{Au}_2\text{P}_2$ requires: C, 52.58; H, 4.03; *M*, 1051. IR (CH_2Cl_2): $\nu(\text{C}\equiv\text{C})$ 2157 cm^{-1} . ^1H NMR: δ 2.29 (s, 9H, Me), 7.12-7.32 (m, 12H, tol). ^{13}C NMR: δ 21.39 (s,

Me), 88.11 (br, C_β), 119.89 (d, ²J_{CP} = 140 Hz, C_α), 126.67-141.69 (m, tol). ³¹P NMR: δ 40.57 (s).

2. From **4.7** and AuCl{P(tol₃)}.

A Schlenk flask was charged with **4.7** (100 mg, 0.18 mmol), AuCl{P(tol₃)} (97 mg, 0.18 mmol), CuI (ca 5 mg) and thf/NHEt₂ (20 mL, 1/2). The suspension cleared to give a yellow solution that was stirred for 1 h at r.t. The solution was filtered and the solvent removed. Extraction with CH₂Cl₂ and passage through a SiO₂ column eluting with CH₂Cl₂/hexane (1/1) gave pale yellow {[(tol₃)P]Au}C≡CC≡C{Au[P(tol₃)]} (**4.9**) (148 mg, 78 %).

(i) {[(tol₃)P]Au}(C≡C)₃{Au[P(tol₃)]} (**4.10**).

Dissolved Me₃Si(C≡C)₃SiMe₃ (50 mg, 0.23 mmol) and NaOH (184 mg, 4.60 mmol) in MeOH (25 mL) and stirred for 30 min. Added AuCl{P(tol₃)} (246 mg, 0.46 mmol) and stirred a further 1.5 h. A pale yellow precipitate had formed and was collected and washed with MeOH, Et₂O and pentane and air-dried to give {[(tol₃)P]Au}(C≡C)₃{Au[P(tol₃)]} (**4.10**) (188 mg, 76 %). Anal. Found: C, 53.66; H, 3.87. C₄₈H₄₂Au₂P₂ requires: C, 53.64; H, 3.94; *M*, 1075. IR (CH₂Cl₂): ν(C≡C) 2139sh, 2115m cm⁻¹. ¹H NMR: δ 2.38 (s, 9H, Me), 7.20-7.40 (m, 12H, tol). ¹³C NMR: δ 21.42 (s, Me), 81.63 (s, C_γ), 88.13 (br, C_β), 127.94 (br, C_α), 129.77-142.06 (m, tol). ³¹P NMR: δ 40.26 (s).

(j) {[(tol₃)P]Au}(C≡C)₄{Au[P(tol₃)]} (**4.11**).

1. From AuCl(Ptol₃) and Me₃Si(C≡C)₄SiMe₃.

Dissolved Me₃Si(C≡C)₄SiMe₃ (75 mg, 0.31 mmol) and NaOH (248 mg, 6.20 mmol) in MeOH (25 mL) and stirred for 30 min. Added AuCl{P(tol₃)} (302 mg, 0.56 mmol) and stirred a further 1.5 h. A pale yellow precipitate had formed and was collected and washed with MeOH, Et₂O and pentane and air-dried to give {[(tol₃)P]Au}(C≡C)₄{Au[P(tol₃)]} (**4.11**) (60 mg, 20 %). Anal. Found: C, 54.59; H, 3.77. C₅₀H₄₂Au₂P₂ requires: C, 54.66; H, 3.85; *M*, 1099. IR (nujol): ν(C≡C) 2167w, 2134m cm⁻¹. ¹H NMR: δ 2.36 (s, 9H, Me), 7.20-7.38 (m, 12H, tol). ¹³C NMR: δ 21.42

(s, Me), 60.91 (s, C_δ), 67.23 (s, C_γ), 86.94 (br, C_β), 131.29 (br, C_α), 126.15-142.02 (m, tol). ³¹P NMR: δ 40.26 (s).

2. From Au(C≡CC≡CH){P(tol₃)} + CuCl/tmeda

Hay catalyst – CuCl (100 mg, 1.01 mmol) was dissolved in acetone (5 mL). tmeda (0.15 mL, 0.3 mmol) was added dropwise and the resulting blue solution stirred a further 30 min.

Dioxygen was bubbled through a solution of **4.7** (300 mg, 0.55 mmol) in acetone (25 mL). The Hay catalyst was added in 1 mL portions over 1 h after which the reaction was adjudged complete (t.l.c). The solvent was removed and the residue chromatographed on a SiO₂ column eluting with hexane/CH₂Cl₂ (1/1) and a bright yellow fraction collected. Removal of the solvent yielded {[(tol₃)P]Au}(C≡C)₄{Au[P(tol₃)]} (**4.11**) (100 mg, 33 %).

3. From Au(C≡CC≡CH){P(tol₃)} and Cu(OAc)₂/pyridine.

To a solution of **4.7** (100 mg, 0.18 mmol) in pyridine (3 mL) was added Cu(OAc)₂·H₂O (55 mg, 0.27 mmol) and the resulting yellow solution stirred at 80°C for 2 h. The solvent was removed and the dark brown residue passed down a SiO₂ column eluting with CH₂Cl₂. A bright yellow fraction was collected and hexane (10 mL) added. Removal of the solvent gave yellow {[(tol₃)P]Au}(C≡C)₄{Au[P(tol₃)]} (**4.11**) (56 mg, 57 %).

(k) {[(tol₃)P]Au}C≡CC≡C{Cu(triphos)} (**4.12**).

To a solution of **4.7** (100 mg, 0.18 mmol) in thf (30 mL) at -100°C was added nBuLi (73 μL, 0.18 mmol of a 2.5 M solution in hexane). Stirring was continued for 15 mins. CuCl(triphos) (123 mg, 0.17 mmol) was added and the yellow solution turned into a cream coloured suspension. The suspension was allowed to warm to r.t and slowly cleared to a yellow solution. After stirring for 3.5 h at r.t the solvent was removed. The residue was extracted with CH₂Cl₂ (min) and then filtered into cold hexane. A cream-white precipitate was collected and washed with Et₂O (2 x 5 mL) and n-pentane (2 x 5 mL) and air-dried to give {[(tol₃)P]Au}C≡CC≡C{Cu(triphos)} (**4.12**) (130 mg, 62 %). Anal. Found: C, 63.62; H, 5.07. C₆₆H₆₀AuP₄Cu requires: C, 64.05; H,

4.89; *M*, 1238. IR (nujol): $\nu(\text{C}\equiv\text{C})$ 2158m, 2127w cm^{-1} . ^1H NMR: δ 1.44 (s, 3H, CH_3), 2.28 (s, 6H, CH_2), 2.36 (s, 9H, Me), 6.82-7.46 (m, 42H, Ph, tol). ^{13}C NMR: δ 21.43 (s, Me), 36.47 (m, $\text{C}-\text{CH}_3$), 37.53 (s, $\text{C}-\text{CH}_3$), 39.93 (m, $\text{P}-\text{CH}_2$), 125.27-142.31 (m, Ph, tol). ^{31}P NMR: δ -25.08 (triphos), 45.20 [s, $\text{P}(\text{tol}_3)$].

(l) $\text{Hg}\{\text{C}\equiv\text{CC}\equiv\text{CAu}[\text{P}(\text{tol}_3)]\}_2$ (**4.13**).

A solution of **4.7** (200 mg, 0.36 mmol) and $\text{Hg}(\text{OAc})_2$ (57 mg, 0.18 mmol) in thf (15 mL) was warmed to 45°C and stirred for 2 h. Filtering the solution and addition of hexane (150 mL) produced a milky-white precipitate which was collected and washed with Et_2O (2 x 10 mL) and *n*-pentane (20 mL) and air-dried to give $\text{Hg}\{\text{C}\equiv\text{CC}\equiv\text{CAu}[\text{P}(\text{tol}_3)]\}_2$ (**4.13**) (126 mg, 54 %). Anal. Found: C, 46.35; H, 3.35. $\text{C}_{50}\text{H}_{42}\text{Au}_2\text{HgP}_2$ requires: C, 46.22; H, 3.26; *M*, 1299. IR (nujol): $\nu(\text{C}\equiv\text{C})$ 2166w, 2052w cm^{-1} . ^1H NMR: δ 2.35 (s, 18H, Me), 7.18-7.39 (m, 24H, tol). ^{13}C NMR: δ 21.43 (s, Me), 72.52, 88.15 (d, $^3J_{\text{PC}} = 29$ Hz), 102.52, 126.80-141.70 (m, tol). ^{31}P NMR: δ 40.62 [s, $\text{P}(\text{tol}_3)$].

(m) $[\text{ppn}][\text{Au}\{\text{C}\equiv\text{CC}\equiv\text{CAu}[\text{P}(\text{tol}_3)]\}_2]$ (**4.14**).

A solution of **4.7** (110 mg, 0.2 mmol) and $[\text{ppn}][\text{Au}(\text{acac})_2]$ (92 mg, 0.1 mmol) in $\text{CH}_2\text{Cl}_2/\text{NH}_4\text{Et}_2$ (10 mL, 10/1) was stirred at r.t for 2h. The solvent was then removed and the residue extracted with CH_2Cl_2 and filtered into cold hexane. A cream-white precipitate formed which was collected and washed with Et_2O (2 x 10 mL) and *n*-pentane (20 mL) and air-dried to give $[\text{ppn}][\text{Au}\{\text{C}\equiv\text{CC}\equiv\text{CAu}[\text{P}(\text{tol}_3)]\}_2]$ (**4.14**) (72 mg, 39 %). Anal. Found: C, 56.49; H, 4.06. $\text{C}_{86}\text{H}_{72}\text{Au}_3\text{NP}_4$ requires: C, 56.31; H, 3.96; *M*, 1296. IR (nujol): $\nu(\text{C}\equiv\text{C})$ 2145w cm^{-1} . ^1H NMR: δ 2.29 (s, 18H, Me), 7.15-7.62 (m, 54H, Ph, tol). ^{13}C NMR: δ 21.36 (s, Me), 125.54-141.81 (m, Ph, tol). ^{31}P NMR: δ 22.21 (s, ppn), 39.62 [s, $\text{P}(\text{tol}_3)$].

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Chapter 5

Novel complexes with carbon chains

INTRODUCTION

This chapter reports the synthesis and, in several cases, the X-ray structures of some novel complexes. Some of these complexes have been used as starting materials for chemistry described in previous chapters, while others were envisaged as intermediates into some new heterobimetallic butadiynyl complexes. Although such complexes were not obtained from them, their syntheses and properties are interesting nonetheless. CV data is also reported where appropriate and compared with similar complexes.

RESULTS AND DISCUSSION

(a) Synthesis of $\text{FcC}\equiv\text{CI}$ and its reaction with $\text{Co}_2(\text{CO})_8$.

Iodoethynylferrocene, $\text{FcC}\equiv\text{CI}$ (**5.1**), was synthesised via the iodo-morpholine complex in good yield (75%).¹ The structure is shown in Figure 1 and Table 1 gives the important bond lengths and angles. The IR spectrum contained a $\nu(\text{C}\equiv\text{C})$ absorption at 2175 cm^{-1} . In the ^1H NMR spectrum, multiplets at δ 4.44 and 4.18 were assigned to the protons of the $\text{C}_5\text{H}_4\text{C}\equiv\text{CI}$ ring and the singlet at δ 4.22 to the unsubstituted Cp ring. The ^{13}C NMR spectrum contained resonances for the ethynyl carbons δ 92.04 and 67.88. The carbons of the Cp group gave a singlet resonance at δ 69.95, while the three carbons of the $\text{C}_5\text{H}_4\text{I}$ group appeared at δ 65.56, 68.69 and 71.70. The ES mass spectrum showed the molecular ion at m/z 336.

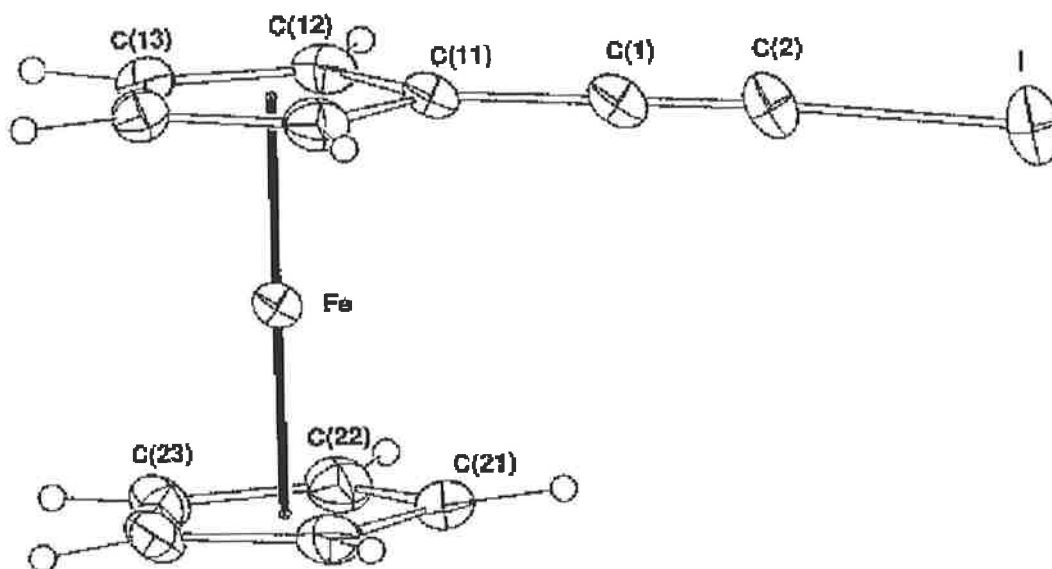


Figure 1. Plot of a molecule of **5.1** showing the atom numbering scheme.

Table 1. Important bond lengths (Å) and angles in **5.1**.

Bond distances			
C(11)-C(1)	1.448(8)	C(2)-I	2.000(6)
C(1)-C(2)	1.162(8)	Fe-C(cp)	2.019(6)-2.050(4)
		(av.)	2.03(6)
Bond angles			
I-C(2)-C(1)	177.4(5)	C(11)-C(1)-C(2)	179.8(6)

Single crystals suitable for the X-ray structure determination were obtained from CH_2Cl_2 /pentane and Fig. 1 is a plot of a molecule of **5.1**; Table 1 contains significant structural parameters. Fig. 2, projected normal to the crystallographic mirror plane which partitions the molecule, shows the packing of molecules in the unit.

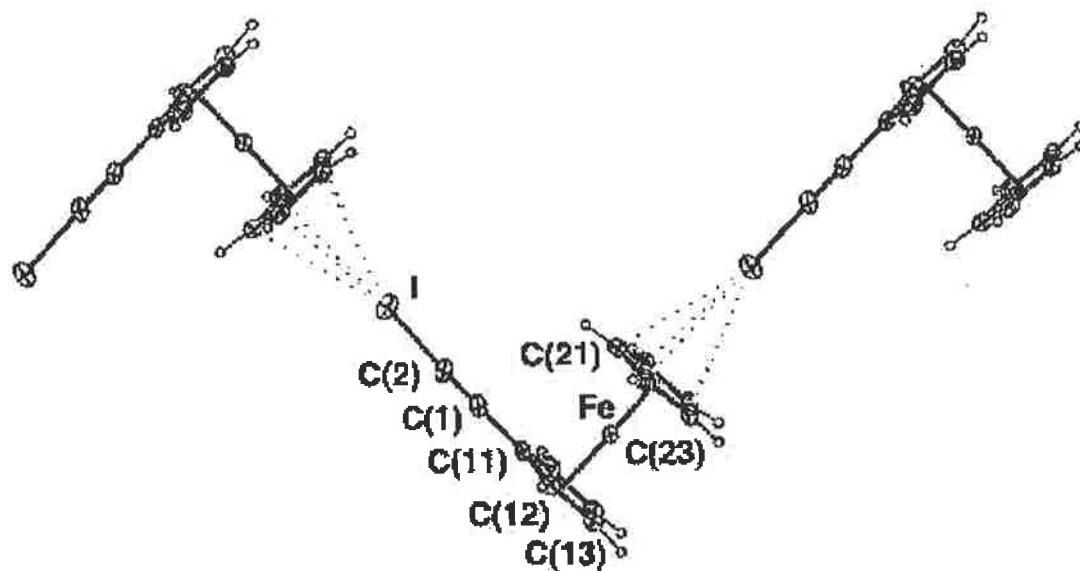
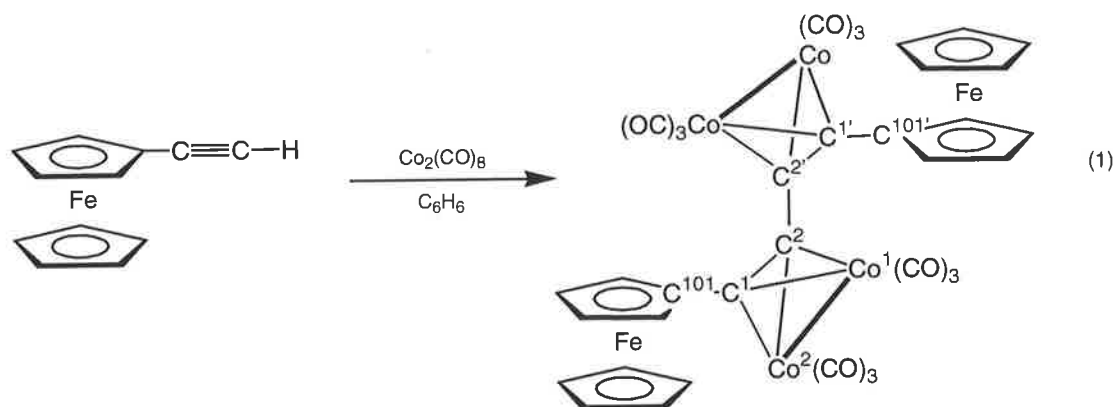


Figure 2. Plot of the unit cell of **5.1** showing the interaction between the unsubstituted Cp ring and the iodine atom of an adjacent molecule.

The major point of interest is the iodoalkynyl group, in which the $\text{C}\equiv\text{C}$ bond distance of $1.162(8) \text{ \AA}$ is typical. The $\text{C}(2)\text{-I}$ distance of $2.000(6) \text{ \AA}$ determined here may be compared with earlier values found in C_2I_2 ($1.99 \text{ \AA}$),² its complexes with 1,4-cyclohexanedione ($1.98 \text{ \AA}$)³ and dioxan ($1.88 \text{ \AA}$),⁴ and the complex anion in $[\text{PPh}_4][\text{I}(\text{IC}\equiv\text{Cl})_2]$ [$2.01(3) \text{ \AA}$],⁵ $\text{IC}\equiv\text{CC}\equiv\text{N}$ ($1.79 \text{ \AA}$),⁶ noting also the $\text{PhC}\equiv\text{Cl}$ complex with morpholine (no value given),⁷ and the complex anions in $[\text{PMePh}_3][\text{Cl}(\text{IC}\equiv\text{CPh})_2]$ [$2.031(5) \text{ \AA}$]⁸ and $[\text{PPh}_4][\text{X}(\text{IC}\equiv\text{CPh})_4]$ ($\text{X} = \text{Cl}$ [$2.023(4)$], Br [$2.028(5)$], I [$2.041(4) \text{ \AA}$]).⁹ Similar distances are found in the alkynyliodonium cations $[\text{PhI}(\text{C}\equiv\text{CX})]^+$ ($\text{X} = \text{CN}$ [$2.00(1)$],¹⁰ Ph [$1.97(3) \text{ \AA}$]¹¹) and $[\text{I}(\text{C}\equiv\text{CSiPr}_3)_2]^+$ [$2.01, 2.02(1) \text{ \AA}$]¹² and in π -complexed iodoalkynes in $\text{WCl}_4(\text{thf})(\eta^2\text{-PhC}_2\text{I})$ [$2.03(2) \text{ \AA}$]¹³ and the anions $[\text{WX}_5(\eta^2\text{-C}_2\text{I}_2)]^-$ ($\text{X} = \text{F}$ [$2.09, 2.12(4) \text{ \AA}$],¹⁴ Cl [$2.00, 2.02(2) \text{ \AA}$]¹⁵). While the $\text{C}(11)\text{-C}(1)\text{-C}(2)$ angle is linear within experimental precision [$179.8(6)^\circ$], the $\text{I-C}(2)\text{-C}(1)$ moiety is slightly bent [$177.4(5)^\circ$], probably due to crystal packing effects. The bond lengths and angles about the ferrocenyl group are similar to those found for many other examples, with $\text{Fe-C}(\text{Cp})$ $2.019\text{--}2.050(6)$, $\text{C-C}(\text{ring})$ $1.411\text{--}1.430(5) \text{ \AA}$ and inter-ring angles of $107.2\text{--}108.6(4)^\circ$.

Figure 2 shows the distance between the Cp ring and the iodo moiety is a relatively short 3.6 Å. The arrangements of the molecules in the lattice are such that each iodo group is pointed directly at the centre of a neighbouring Cp ring of an adjacent molecule. This non-covalent interaction is most likely influencing the packing of the molecules in the unit cell. Similar observation have been reported for charge-transfer complexes of tcne,¹⁶ fluorinated organic compounds¹⁷ and aromatic azines.¹⁸

The reaction between **5.1** and $\text{Co}_2(\text{CO})_8$ was carried out in benzene for 24 h (Equation 1). Work-up of the black reaction mixture afforded black crystals which were shown to be $\{\text{Co}_2(\text{CO})_6\}_2(\mu:\mu\text{-FcC}_2\text{C}_2\text{Fc})$ (**5.2**) by a single-crystal X-ray structure determination (Figure 3, Table 2).



Reaction between **5.1** and $\text{Co}_2(\text{CO})_8$.

The maximum yield of **5.2** was obtained when three equivalents of $\text{Co}_2(\text{CO})_8$ were used in the reaction. The analytical and spectroscopic properties of **5.2** are in accord with the solid-state structure. Thus, there is no $\nu(\text{C}\equiv\text{C})$ band in the IR spectrum, but five terminal $\nu(\text{CO})$ absorptions are found between 2095 and 2019 cm^{-1} . The ^1H NMR spectrum contains only resonances from the ferrocenyl groups at δ 4.24 (singlet, C_5H_5) and two multiplets at δ 4.32 and 4.41 (C_5H_4). The ES mass spectrum was obtained with a solution containing NaOMe and showed an $[\text{M} + \text{OMe}]^+$ ion at m/z 1020, together with twelve fragment ions formed by stepwise loss of the CO groups from this ion.

Table 2. Important bond lengths (Å) and angles (°) in **5.2**.

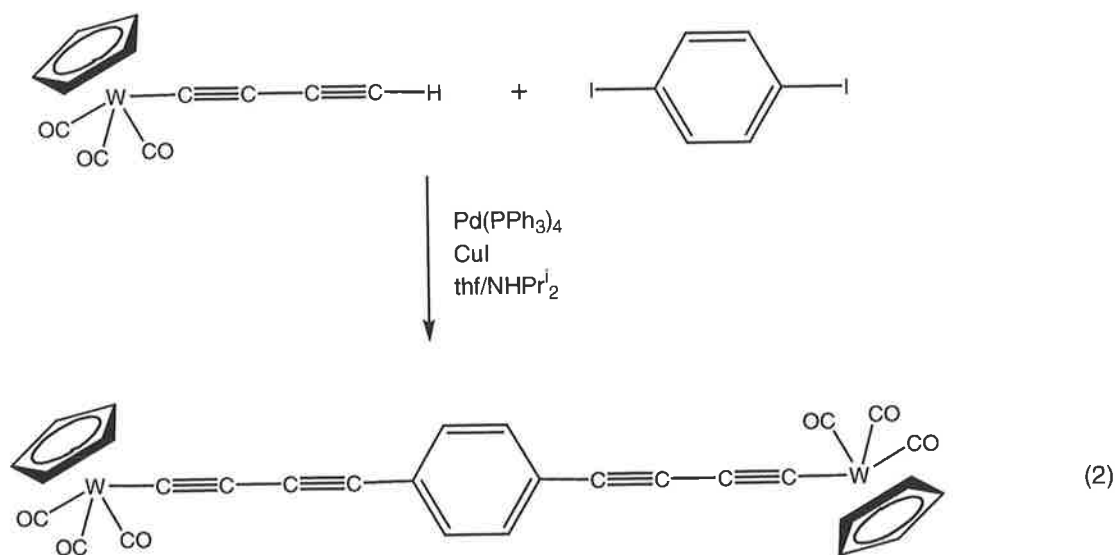
Bond distances			
Co(1)-Co(2)	2.4735(5)	C(1)-C(2)	1.351(2)
Fe-C(cp)	2.030-2.060(3)	C(2)-C(2')	1.420(2)
(av.)	2.04	Co(1)-C(1)	1.952(2)
Co(1)-CO	1.788-1.831(3)	Co(1)-C(2)	1.987(2)
Co(2)-CO	1.788-1.836(3)	Co(2)-C(1)	1.994(2)
C(101)-C(1)	1.455(3)	Co(2)-C(2)	1.967(1)
Bond angles			
C(101)-C(1)-C(2)	137.1(2)	C(1)-C(2)-C(2')	143.4(2)

A plot of a molecule of **5.2** is shown in Fig. 3 and significant structural parameters are collected in Table 2. As can be seen, the centrosymmetric molecule consists of a 1,4-diferrocenylbuta-1,3-diyne molecule to each $\text{C}\equiv\text{C}$ triple bond of which is attached a $\text{Co}_2(\text{CO})_6$ fragment. As a result, the $\text{C}(101)\text{-C}(1)\text{-C}(2)\text{-C}(2')\text{-C}(1')\text{-C}(101')$ chain is considerably distorted from the linear arrangement found in the parent diyne, with angles at C(1) and C(2) of 137.1(2) and 143.4(2)°. The C-C distances along this carbon chain are 1.455(3), 1.351(2) and 1.420(2) Å, the acetylenic C-C bonds being lengthened by complexation to the $\text{Co}_2(\text{CO})_6$ moiety. Within the latter, the Co(1)-Co(2) separation is 2.4735(5) Å and the Co-C distances are between 1.952 and 1.994(2) Å, again within the ranges found in the many alkyne- $\text{Co}_2(\text{CO})_6$ adducts already reported. The ferrocenyl group geometries are similar to those found in **5.1**, with Fe-C(cp) distances between 2.030 and 2.060(2) Å, ring C-C distances between 1.372 and 1.435(4) Å and inter-ring angles between 106.5 and 109.3(3)°.

The molecular structure of $\text{FcC}\equiv\text{CC}\equiv\text{CFc}$ has been reported previously.^{19,20} Comparison with that of **5.2** shows that the Fc groups are similar (within experimental precision), but, as expected, there are considerable changes in the C_4 chain as a result of attachment of the $\text{Co}_2(\text{CO})_6$ fragments. The C(cp)-C(sp), $\text{C}\equiv\text{C}$ and C(sp)-C(sp) bonds are respectively 1.422(3), 1.198(4) and 1.373(3) Å in the centrosymmetric molecule of the free diyne, with angles at the two independent carbon atoms in the chain being 179.8(3) and 178.1(3)°.²⁰

(b) $1,4\text{-}\{\text{Cp}(\text{CO})_3\text{W}\}\text{C}\equiv\text{CC}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CC}\equiv\text{C}\{\text{W}(\text{CO})_3\text{Cp}\}$.

The chemistry of $\text{W}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{CO})_3\text{Cp}$ has been well established including the coupling of aromatic groups to the end of the chain.^{21,22} However, no complexes had previously been isolated with two WC_4 groups linked by an aromatic moiety. Palladium/copper catalysed coupling of two equivalents of $\text{W}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{CO})_3\text{Cp}$ to 1,4-diiodobenzene gave $1,4\text{-}\{\text{Cp}(\text{CO})_3\text{W}\}\text{C}\equiv\text{CC}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CC}\equiv\text{C}\{\text{W}(\text{CO})_3\text{Cp}\}$ (**5.3**) as a sparingly soluble, bright-yellow complex in excellent yield (Equation 2), characterised from elemental analysis and spectroscopy.



Palladium/copper catalysed coupling to form **5.3**.

Two $\nu(\text{C}\equiv\text{C})$ bands at 2181 and 2056 cm^{-1} , together with $\nu(\text{CO})$ bands at 2038 and 1956 cm^{-1} , were observed in the IR spectrum. A Cp singlet at δ 5.64 and an A_2B_2 multiplet at δ 7.28 for the C_6H_4 protons were present in the ^1H NMR spectrum, while singlet resonances at δ 92.91 and 132.17, assigned to the Cp and C_6H_4 carbons respectively, appeared in the ^{13}C NMR spectrum. Singlet resonances for the W-CO ligands were found at δ 214.1 and 228.17, while the C_4 carbons resonate at δ 110.42, 83.75, 79.31 and 72.66, assigned to $\text{C}_{\alpha-\delta}$ respectively by comparison with $\text{W}(\text{C}\equiv\text{CC}\equiv\text{CPh})(\text{CO})_3\text{Cp}$.²¹ None of these signals showed any coupling to tungsten. The ES mass spectrum obtained with a solution containing NaOMe contained the ions $[\text{M} + \text{OMe} - n\text{CO}]^-$ ($n = 0, 2, 4$) at m/z 869, 813 and 757, respectively.

(c) $\text{W}(\text{C}\equiv\text{CC}\equiv\text{CSiMe}_3)(\text{CO})_2(\text{dppm-}P)\text{Cp}$

The substitution chemistry at the tungsten centre was examined, only to find that the W-CO bonds are broken with difficulty. In the reaction with dppm, carried out to generate a more electron-rich tungsten centre in the anticipated monocarbonyl product, the only tractable product isolated was $\text{W}(\text{C}\equiv\text{CC}\equiv\text{CSiMe}_3)(\text{CO})_2(\text{dppm-}P)\text{Cp}$ (**5.4**), containing monodentate dppm, as shown finally by a single crystal X-ray structure determination (Figure 4).

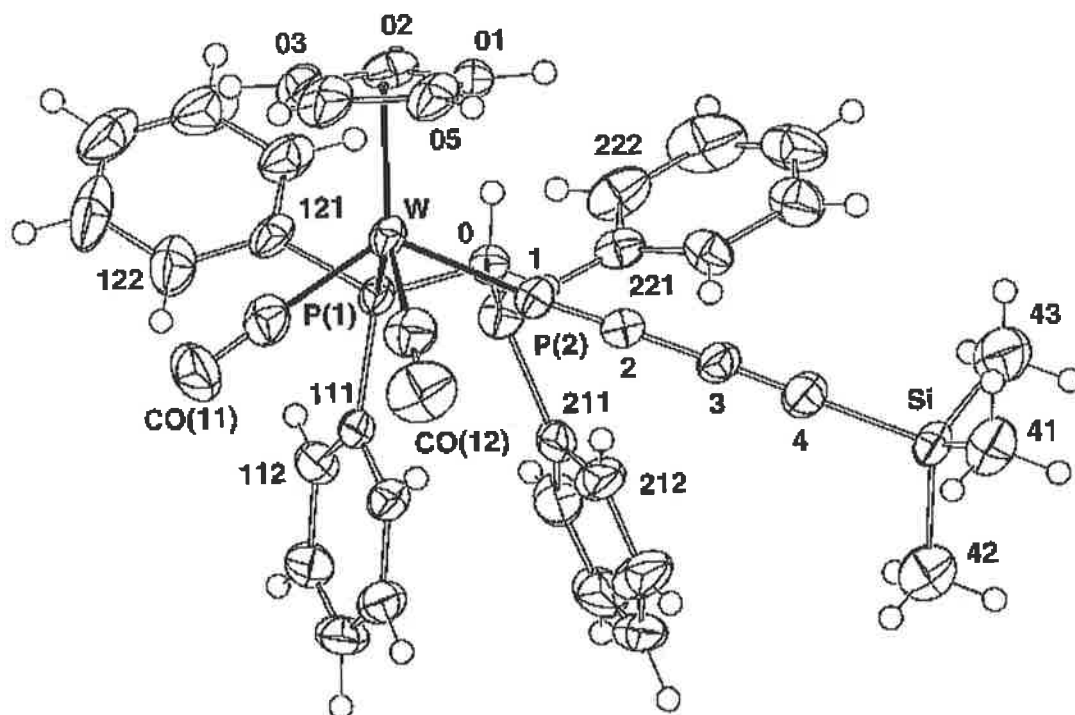


Figure 4. Plot of a molecule of **5.4** showing the atom numbering scheme.

Table 4. Important bond lengths (Å) and angles (°) of **5.4**.

Bond distances			
W-C(Cp)	2.299-2.37(1)	C(1)-C(2)	1.22(1)
(av.)	2.34(4)	C(2)-C(3)	1.37(1)
W-P	2.486(2)	C(3)-C(4)	1.22(1)
W-CO(11,12)	1.95, 1.955(9)	C(4)-Si	1.823(8)
W-C(1)	2.116(7)		
Bond angles			
P-W-CO(11,12)	78.7, 120.3(3)	W-C(1)-C(2)	176.1(7)
P-W-C(1)	77.8(3)	C(1)-C(2)-C(3)	177(1)
C(11)-W-C(12)	74.2(4)	C(2)-C(3)-C(4)	178.4(9)
C(11,12)-W-C(1)	122.0, 73.6(4)	C(3)-C(4)-Si	177(1)

The geometry about the tungsten atom is similar to those previously described for $\text{W(CO)}_3\text{Cp}$ containing complexes.^{22,23} Thus, the average value for W-C(Cp) is 2.34(4) Å. The substitution of dppm for one of the CO groups has a noticeable change on the W-CO bond distances. In the tricarbonyl precursor, the W-CO distances are between 2.01 – 2.103(7) Å compared to 1.95 – 1.955(9) for **5.4**. This compares well for the PPh_3 substituted complex, *cis*- $\text{W(C}\equiv\text{CPh)(CO)}_2(\text{PPh}_3)\text{Cp}$ (W-CO, 1.937 – 1.975(8) Å).²² The W-P distance of 2.486(2) Å is experimentally the same as that found in *cis*- $\text{W(C}\equiv\text{CPh)(CO)}_2(\text{PPh}_3)\text{Cp}$ (2.491(2) Å).²² The W-C $\equiv$ bond distance of 2.116(7) Å is the same as in the tricarbonyl precursor, [2.124(8) Å] as are the C $\equiv$ C and C-C bond distances [1.22(1), 1.37(1) in **5.4** vs. 1.22(1), 1.36(1) Å]. As well as those reported²⁴ for the electron diffraction study of $\text{Me}_3\text{SiC}\equiv\text{CC}\equiv\text{CSiMe}_3$ (1.235(2), 1.375(3) Å). The Si-C $\equiv$ distance (1.823(8) Å) in **5.4** is similar to the bond distance reported for $\text{Me}_3\text{SiC}\equiv\text{CC}\equiv\text{CSiMe}_3$ (1.830(2) Å). The C_4 chain is not perfectly linear but again compares well with the tricarbonyl precursor with angles at carbon ranging between 176.1(7) – 178.4(9) and 177(1) – 179(1)° respectively.

The spectral properties are in accord with this formulation, with two $\nu(\text{C}\equiv\text{C})$ absorptions at 2165 and 2117, and two (CO) bands at 1951 and 1869 cm^{-1} , respectively. In the ^1H NMR spectrum, singlets at δ 0.15 and 5.32 arise from the

SiMe₃ and Cp protons, with dppm CH₂ and Ph multiplets at δ 3.32 and 3.98, and between 7.06-7.71. In the ¹³C NMR spectrum, resonances at δ 227.06 (singlet) and 243.45 (doublet) are assigned to the CO groups, and the singlet at δ 91.02 to the Cp group. The four carbons of the C₄ chain give singlets at δ 113.57, 91.41, 88.43 and 79.66, while the SiMe₃ resonance is found as a singlet at δ 0.34. No observable coupling of these resonances with ³¹P or ¹⁸³W was found. Resonances at δ 12.00 and -25.00 in the ³¹P NMR spectrum are assigned to the coordinated and free P atoms, respectively, on account of the coupling of the former to ¹⁸³W (120 Hz). The two phosphorus nuclei are coupled to each other (60 Hz). In the ES mass spectrum, the molecular ion at *m/z* 810 fragments by stepwise loss of the two CO groups.

(d) Ru(C≡CC≡CSiMe₃)(CO)₂Cp

The copper catalysed coupling reaction between RuCl(CO)₂Cp and HC≡CC≡CSiMe₃ in thf/NHEt₂ gave Ru(C≡CC≡CSiMe₃)(CO)₂Cp (**5.5**) in good yield. Crystals suitable for an X-ray study were grown from CHCl₃/pentane and the structure is shown in Figure 5.

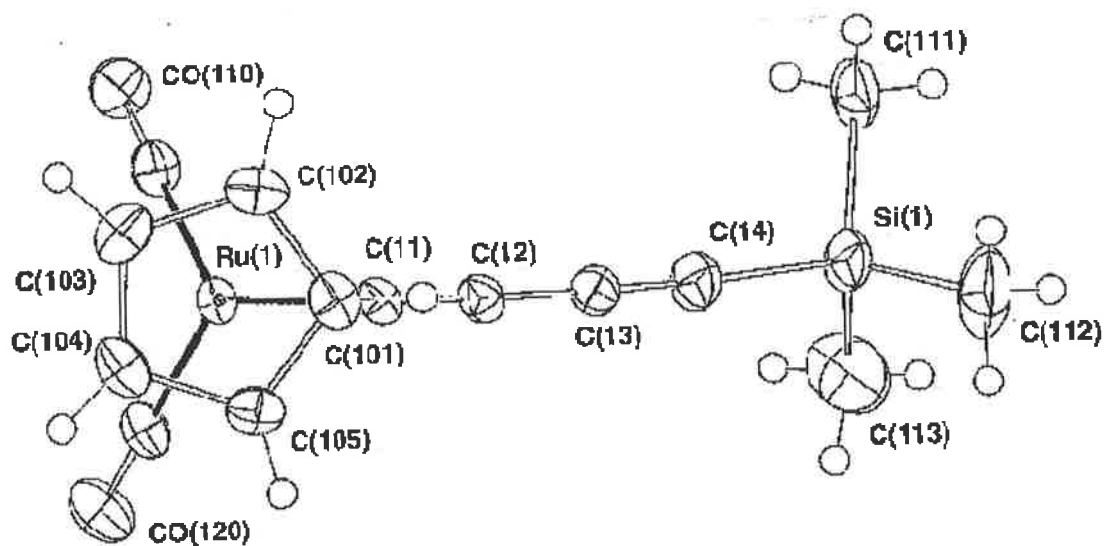


Figure 5. Plot of a molecule of **5.5** showing the atom numbering scheme.

Table 5. Important bond lengths (Å) and angles (°) of **5.5**.

Bond distances			
Ru-C(Cp)	2.235-2.260(3)	C(11)-C(12)	1.216(4)
(av.)	2.24(2)	C(12)-C(13)	1.384(5)
Ru-CO(110,120)	1.888-1.893(4)	C(13)-C(14)	1.207(5)
Ru-C(11)	2.010(3)	C(14)-Si	1.841(4)
Bond angles			
C(110)-Ru-C(120)	92.1(2)	C(11)-C(12)-C(13)	177.8(4)
C(110,120)-Ru-C(1)	87.9, 90.6(1)	C(12)-C(13)-C(14)	178.6(4)
Ru-C(11)-C(12)	177.3(3)	C(13)-C(14)-Si	177.7(4)

The X-ray structure confirms the butadiynyl nature of the carbon chain. The Ru(CO)₂Cp fragment has distances and angles similar to those of similar structures reported^{25,26}. The carbon chain has C≡C and C-C [1.216(4) and 1.384(5) Å] experimentally the same as those found in HC≡CC≡CH (1.217(1) and 1.383(1) Å).²⁷ The chain is not quite linear with angles between 177.3 – 178.6(4)° and is due to crystal packing effects.

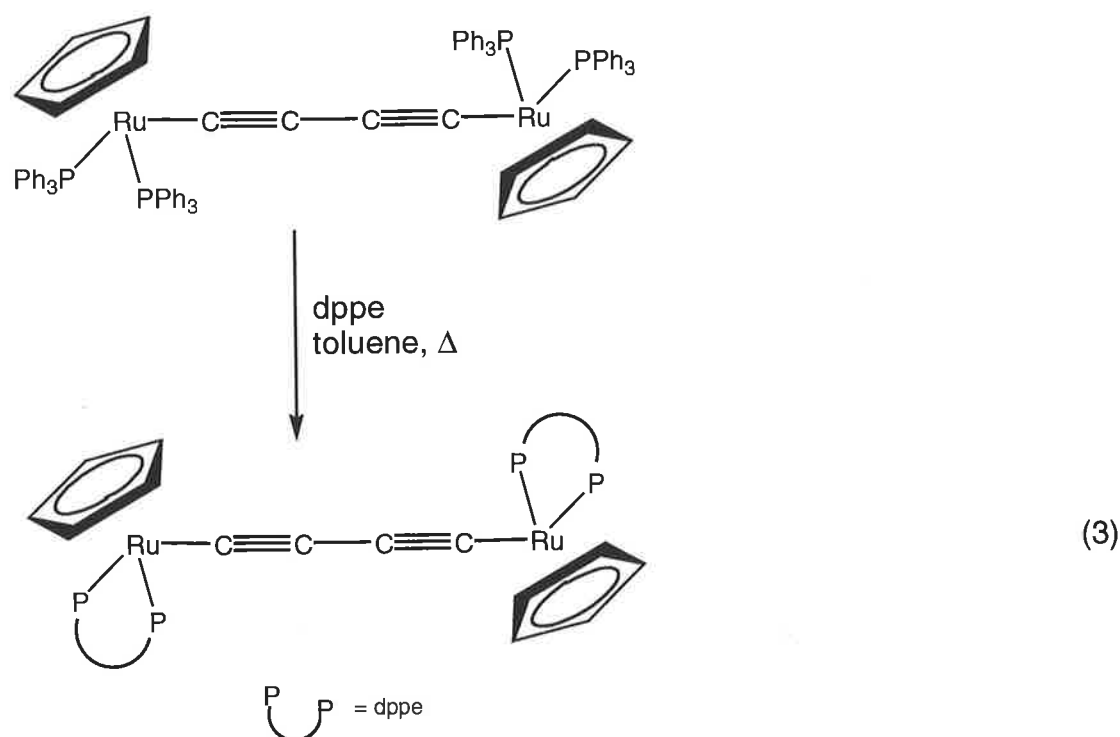
The IR spectrum shows three $\nu(\text{C}\equiv\text{C})$ stretches as was observed for Ru(C≡CC≡CSiMe₃)(PPh₃)₂Cp **3.12** and Fe(C≡CC≡CSiMe₃)(dppe)Cp* **3.13**²⁸ at 2181, 2128 and 2114 cm⁻¹ and two $\nu(\text{CO})$ stretches at 2056 and 2002 cm⁻¹. Singlets due to the SiMe₃ moiety were observed at δ_{H} 0.12 and δ_{C} 0.01 ppm. The Cp resonances were observed at δ_{H} 5.41 and δ_{C} 87.84 ppm while the carbons of the chain gave singlets at δ_{C} 92.55, 90.84, 84.23 and 72.74 due to C $_{\alpha-\delta}$ respectively. A singlet at δ_{C} 195.90 was assigned to the CO ligands.

(e) $\{\text{Cp}(\text{PP})\text{Ru}\}\text{C}\equiv\text{CC}\equiv\text{C}\{\text{Ru}(\text{dppe})\text{Cp}'\}$ ($\text{PP} = 2\text{PPh}_3$, dppe ; $\text{Cp}' = \text{Cp}$, Cp^*)

(i) *Synthesis and Characterisation*

As discussed in Chapter 3, very few heterobimetallic butadiyndiyl complexes are known with both metals being redox-active. The variety of ruthenium-phosphine containing metal fragments available and used by this research group enabled the synthesis of new $\{\text{RuL}_n\}\text{C}\equiv\text{CC}\equiv\text{C}\{\text{Ru}'\text{L}_n'\}$ complexes to be achieved.

The exchange of the phosphine ligands in the sparingly soluble $\{\text{Cp}(\text{PPh}_3)_2\text{Ru}\}\text{C}\equiv\text{CC}\equiv\text{C}\{\text{Ru}(\text{PPh}_3)_2\text{Cp}\}$ was investigated previously using PMe_3 .²⁹ It was found, however, that only two of the PPh_3 ligands were replaced by two PMe_3 ligands even with an excess of PMe_3 . A similar reaction was performed using the bidentate ligand, dppe . Heating $\{\text{Cp}(\text{PPh}_3)_2\text{Ru}\}\text{C}\equiv\text{CC}\equiv\text{C}\{\text{Ru}(\text{PPh}_3)_2\text{Cp}\}$ in refluxing toluene with two equivalents of dppe followed by trituration with hexane gave yellow-orange $\{\text{Cp}(\text{dppe})\text{Ru}\}\text{C}\equiv\text{CC}\equiv\text{C}\{\text{Ru}(\text{dppe})\text{Cp}\}$ (**5.6**) in excellent yield (Equation 3). Single crystals suitable for the X-ray structure determination were obtained and the structure is shown in Figure 3.



Formation of **5.6** via ligand exchange.

The solubility of the diruthenium- C_4 complex is greatly increased by replacement of PPh_3 by dppe such that a low temperature ^{31}P NMR could be obtained. A singlet was observed at δ 86.70. The IR spectrum showed a single $\nu(C\equiv C)$ stretch at 1970 cm^{-1} . A singlet in the ^1H NMR spectrum at δ 4.60 was assigned to the Cp protons. This is shifted 0.40 ppm downfield compared with the PPh_3 analogue, as the dppe ligand is more electron-releasing than PPh_3 . Two multiplets at δ 2.35 and 2.01 are assigned to the CH_2CH_2 group of the dppe ligand. In the ^{13}C NMR spectrum, the carbons of the chain were not observed. The Cp carbons resonate at δ 82.23 and the methylene carbons of the dppe ligand give a multiplet at δ 29.01.

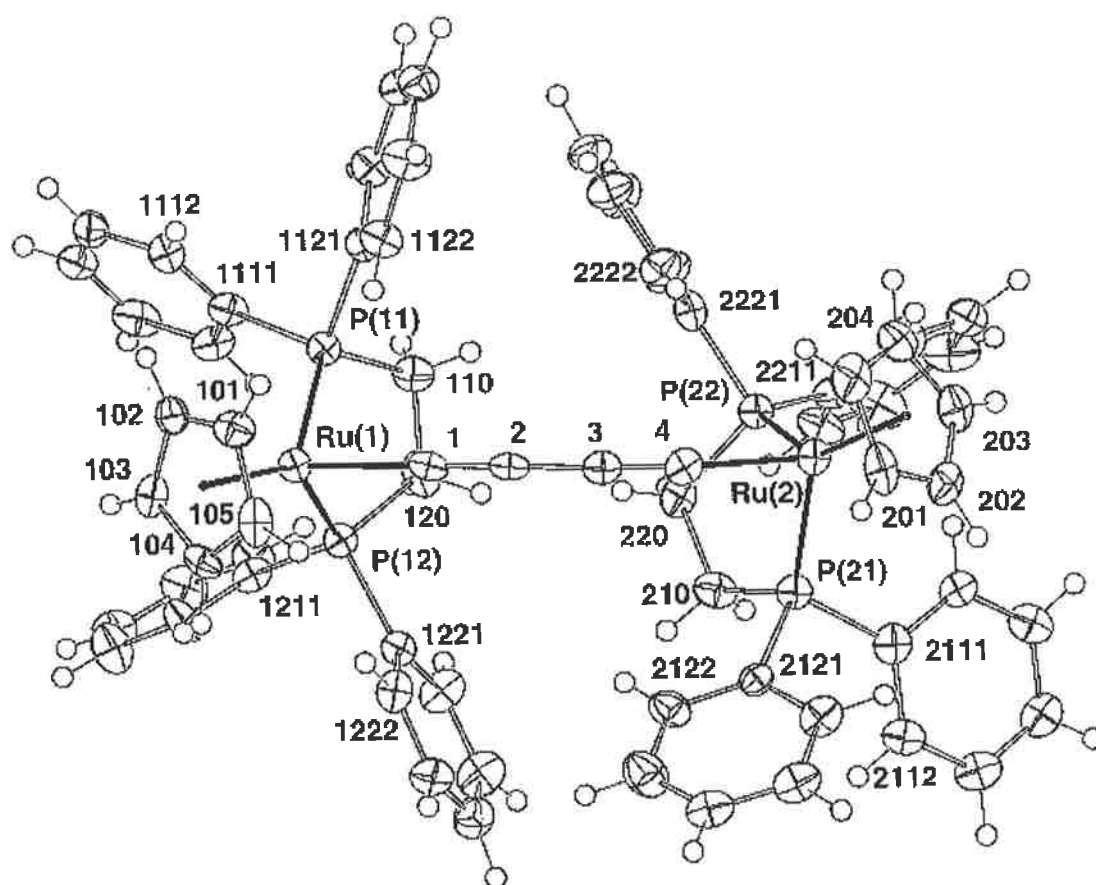


Figure 3. Plot of a molecule of **5.6** showing the atom numbering scheme.

Table 3. Important bond lengths (Å) and angles (°) of **5.6**.

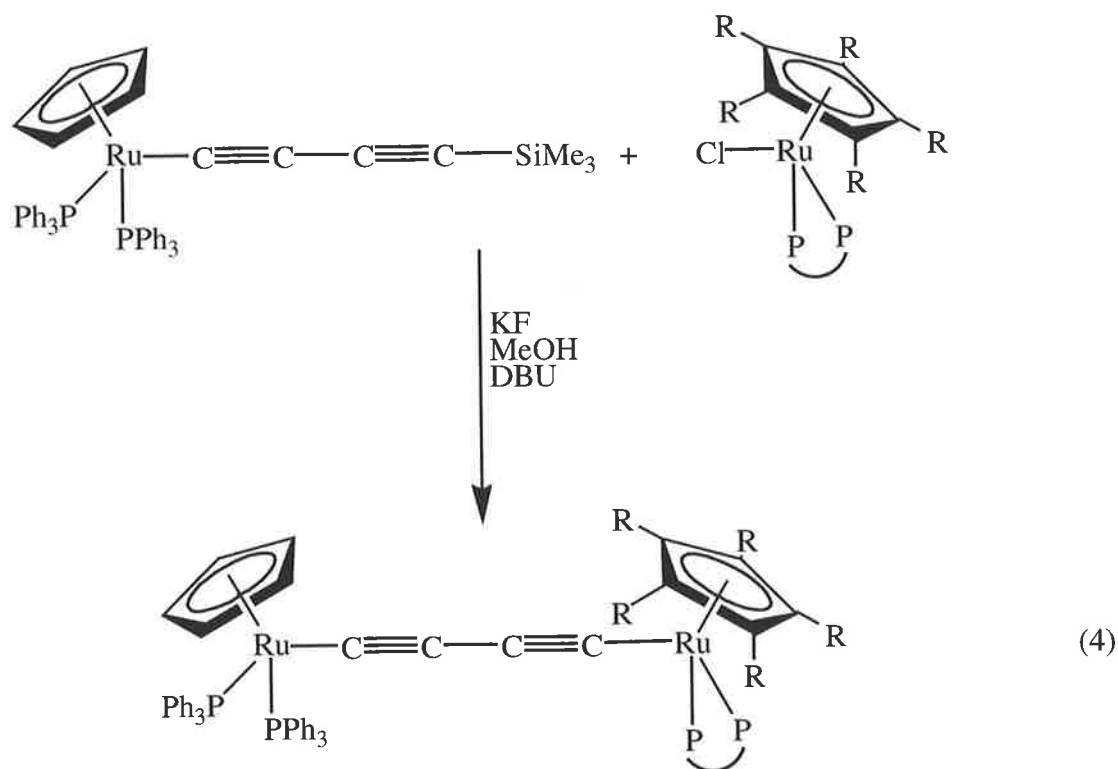
Bond distances			
Ru-C(Cp)	2.23-2.26(1)	C(1)-C(2)	1.22(1)
(av.)	2.24(1)	C(2)-C(3)	1.40(1)
Ru-P	2.228-2.258(3)	C(3)-C(4)	1.22(1)
Ru(1)-C(1)	2.016(7)	C(4)-Ru(2)	2.007(8)
Bond angles			
P-Ru(1,2)-P	82.0, 82.3(1)	C(1)-C(2)-C(3)	176(1)
P-Ru(1)-C(1)	81.2, 85.0(3)	C(2)-C(3)-C(4)	172(1)
P-Ru(2)-C(4)	81.5, 84.3(3)	C(3)-C(4)-Ru(2)	171.4(9)
Ru(1)-C(1)-C(2)	177.1(9)		

The molecular structures of both the *cis* and *trans* isomers of $\{\text{Cp}(\text{PPh}_3)_2\text{Ru}\}\text{C}\equiv\text{CC}\equiv\text{C}\{\text{Ru}(\text{PPh}_3)_2\text{Cp}\}$ have been reported previously.^{30,31} Their bond parameters are similar, with Ru-C(Cp) distances between 2.23 – 2.26(1) (av) 2.24 Å in 6 [Ru-C(Cp), *cis*; 2.16 – 2.31(3) (av) 2.23 Å, *trans*; 2.220 – 2.2241(3) (av) 2.228 Å]. The Ru-P distances are longer in the *cis* and *trans* isomers of $\{\text{Cp}(\text{PPh}_3)_2\text{Ru}\}\text{C}\equiv\text{CC}\equiv\text{C}\{\text{Ru}(\text{PPh}_3)_2\text{Cp}\}$ as the phosphines are different. Replacement of one of the phenyl groups by a methylene group has the effect of shortening the Ru-P bond in the dppe-containing complex **5.6** [2.25 – 2.28(3) Å in 6 vs 2.285 – 2.29(1) Å]. The bidentate phosphine, dppe, gives a much smaller cone angle when compared to the PPh₃ analogues [P-Ru-P 82.0 - 82.3(1)° in 6 vs 102.8(4)°]. A comparison of the geometries about the metal centre can be made with the known complex, Ru(C≡CPh)(dppe)Cp.³² The Ru-P distances in **5.6** range between 2.28 – 2.258(3) Å and compare well with those in Ru(C≡CPh)(dppe)Cp [Ru-P 2.240 – 2.250(1) Å].³²

The most interesting feature of the structure relates to the coordination of the C₄ fragment. The Ru-C distance of 2.106(7) Å is similar to those in the PPh₃ analogues [Ru-C, *cis*; 2.01(3) Å, *trans*; 2.001(3) Å].³⁰ Other values for Ru-C(sp) bonds have been found between 2.009 – 2.017 Å.³² Within the C₄ chain, the C-C distances are 1.22(1) and 1.40(1) Å and are comparable to those in the *trans* isomer of $\{\text{Cp}(\text{PPh}_3)_2\text{Ru}\}\text{C}\equiv\text{CC}\equiv\text{C}\{\text{Ru}(\text{PPh}_3)_2\text{Cp}\}$ [C-C 1.217(4), 1.370(6) Å]. The *cis* isomer

has similar C-C distances [1.24(4) and 1.31(4) Å]. The ruthenium/iron C₄ complex described in Chapter 3 has similar C-C distances also [1.226(7), 1.392(7) Å]. The gas-phase values in free 1,3-butadiyne are C≡C 1.217, C-C 1.383 Å.²⁷ The C₄ chain in **5.6** is not strictly linear with angles at carbon of 177.1(9), 176(1), 172(1) and 171.4(9) Å from Ru(1) to Ru(2) respectively. The *cis* isomer of {Cp(PPh₃)₂Ru}C≡CC≡C{Ru(PPh₃)₂Cp} has a similar deviation from linearity with angles at carbon of 174(2) and 176(3) Å while the *trans* isomer is relatively linear with angles at carbon of 178.9(2) and 177.2(3) Å.

The in situ deprotection of trimethylsilyl-protected alkynes has been previously reported.³¹ Using this methodology, and the new trimethylsilyl-protected ruthenium butadiynyl complex, Ru(C≡CC≡CSiMe₃)(PPh₃)₂Cp **3.12**, the syntheses of two new heterobimetallic complexes of the formula {Cp(PPh₃)₂Ru}C≡CC≡C{Ru(dppe)(C₅R₅)} were achieved (R = H **5.7**, Me **5.8**) (Equation 4).



Synthesis of {Cp(PPh₃)₂Ru}C≡CC≡C{Ru(dppe)(C₅R₅)} (R = H **5.7**, Me **5.8**)

The reaction between $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CSiMe}_3)(\text{PPh}_3)_2\text{Cp}$ and $\text{RuCl}(\text{dppe})\text{Cp}$ in the presence of KF and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) gave $\{\text{Cp}(\text{PPh}_3)_2\text{Ru}\}\text{C}\equiv\text{CC}\equiv\text{C}\{\text{Ru}(\text{dppe})\text{Cp}\}$ (**5.7**) as a yellow solid after recrystallisation in good yield (Equation 4). Spectroscopic data were similar to those of both the homobimetallic complexes. The IR spectra contained a single $\nu(\text{C}\equiv\text{C})$ stretch at 1966 cm^{-1} . The ^1H NMR spectra contained two singlets due to Cp resonances at δ 4.77 and 4.42, the downfield signal being assigned to the $\text{Ru}(\text{dppe})\text{Cp}$ fragment by comparison with **5.6**. The singlet at δ 4.42 was therefore assigned to the $\text{Ru}(\text{PPh}_3)_2\text{Cp}$ fragment. The phenyl region contained a multiplet from δ 8.16 to 6.83 while the CH_2CH_2 group of the dppe moiety gave two multiplets at δ 3.02 and 2.18. The ^{13}C NMR spectra contained two singlets due to Cp groups at δ 82.06 and 85.57 assigned to the $\text{Ru}(\text{dppe})\text{Cp}$ and $\text{Ru}(\text{PPh}_3)_2\text{Cp}$ fragments respectively by comparison with the **5.6**. The CH_2CH_2 group of the dppe ligand gave rise to a multiplet at δ 29.12 while signals between 128.17 – 139.86 were assigned to the phenyl carbons of the phosphine ligands. Two singlets in a 1:1 ratio were observed in the ^{31}P NMR spectrum at δ 86.09 and 51.41 and were assigned to the dppe and PPh_3 ligands respectively.

The Cp^* analogue was synthesised similarly using $\text{RuCl}(\text{dppe})\text{Cp}^*$ instead of $\text{RuCl}(\text{dppe})\text{Cp}$ (Equation 4). The yellow complex $\{\text{Cp}(\text{PPh}_3)_2\text{Ru}\}\text{C}\equiv\text{CC}\equiv\text{C}\{\text{Ru}(\text{dppe})\text{Cp}^*\}$ (**5.8**) has spectroscopic data similar to those of the analogous homobimetallic complexes. Thus, the IR spectrum contained one $\nu(\text{C}\equiv\text{C})$ stretch at 1965 cm^{-1} . Two singlets due to the Cp and Cp^* ligands were observed in the ^1H NMR spectrum at δ 4.32 and 1.73, respectively. The CH_2CH_2 group of the dppe ligand gave two multiplets at δ_{H} 2.92 and 2.03. The ^{31}P NMR spectrum showed two singlets at δ 82.01 and 51.49 due to the dppe and PPh_3 ligands, respectively. In the ^{13}C NMR spectrum singlets at δ 10.71 and 93.05 were assigned to the methyl and ring carbons of the Cp^* ligand respectively. A singlet at δ 85.94 was assigned to the Cp ligand while the CH_2CH_2 group of the dppe ligand gave rise to a multiplet at δ 30.19. The phenyl carbons showed resonances between δ 127.36 – 140.02.

(ii) Cyclic Voltammetry

The CV of both the above complexes showed four 1-electron oxidation waves like their homobimetallic analogues. The first three were reversible while the fourth was irreversible. Table 6 summarises these data and also lists the CV data for several related $\{\text{RuL}_n\}\text{C}\equiv\text{CC}\equiv\text{C}\{\text{RuL}'_n\}$ complexes for comparison.

As can be seen from Table 6, the substitution of one $\text{Ru}(\text{PPh}_3)_2\text{Cp}$ fragment for a $\text{Ru}(\text{dppe})\text{Cp}$ has no major effect on the oxidation potentials. The first and second oxidations are at slightly higher potentials than both the homobimetallic analogues. As is observed for all the complexes in the Table, the third oxidation is found at relatively constant potential. The first oxidation is midway between the two homobimetallic analogues. Substitution of one $\text{Ru}(\text{PPh}_3)_2\text{Cp}$ fragment for a $\text{Ru}(\text{dppe})\text{Cp}^*$ group has a much more dramatic effect on the oxidation potentials. The first, second and fourth oxidation potentials fall midway between the two homobimetallic analogues, while the third is again relatively unchanged.

The separation of the first two oxidation potentials is a useful way of assessing the degree of electronic communication between the two ruthenium centres. Table 6 also lists ΔE° values for all the homo- and hetero-bimetallic ruthenium butadiyndiyl complexes we have studied.

As table 6 shows, the separation of the first two oxidation potentials is between 0.59 and 0.67 V for all complexes. Comparing these ΔE° values with the known homobimetallic butadiyndiyl complexes of Lapinte (0.73 V),³³ Gladysz (0.53 V)³⁴ and Berke (0.63 V)³⁵ shows that there is strong electronic communication between the ruthenium centres for all the complexes listed in Table 6. Thus, replacement of one ruthenium fragment for another does not diminish the electronic communication between the two metal centres.

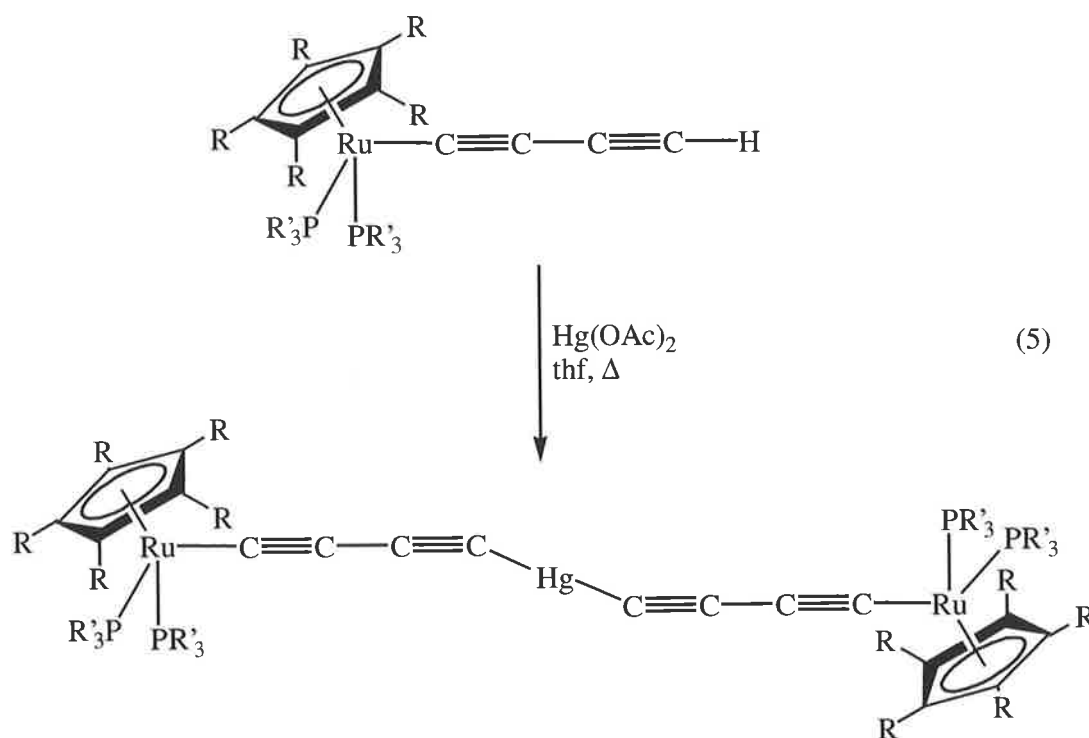
Table 6. Electrochemical data for $\{\text{RuL}_n\}\text{C}\equiv\text{CC}\equiv\text{C}\{\text{RuL}'_n\}$.^a

$\{\text{RuL}_n\}$	$\{\text{RuL}'_n\}$	E_1 (V)	E_2 (V)	E_3 (V)	E_4 (V)	1+/2+	2+/3+	3+/4+	ref
$\text{Ru}(\text{PPh}_3)_2\text{Cp}$	$\text{Ru}(\text{PPh}_3)_2\text{Cp}$	-0.23	0.41	1.03	1.68	0.64	0.58	0.65	²⁹
$\text{Ru}(\text{PPh}_3)(\text{PMe}_3)\text{Cp}$	$\text{Ru}(\text{PPh}_3)(\text{PMe}_3)\text{Cp}$	-0.26	0.33	0.97	1.46	0.59	0.64	0.49	²⁹
$\text{Ru}(\text{dppe})\text{Cp}^*$	$\text{Ru}(\text{dppe})\text{Cp}^*$	-0.43	0.23	1.02	1.51	0.66	0.79	0.49	³⁶
$\text{Ru}(\text{dppm})\text{Cp}^*$	$\text{Ru}(\text{dppm})\text{Cp}^*$	-0.50	0.13	1.02	1.41	0.63	0.89	0.39	³⁶
$\text{Ru}(\text{dppe})\text{Cp}$	$\text{Ru}(\text{dppe})\text{Cp}$	-0.24	0.35	1.08	1.44	0.59	0.73	0.36	^b
$\text{Ru}(\text{PPh}_3)_2\text{Cp}$	$\text{Ru}(\text{dppe})\text{Cp}$	-0.22	0.42	1.07	1.52	0.64	0.65	0.45	^b
$\text{Ru}(\text{PPh}_3)_2\text{Cp}$	$\text{Ru}(\text{dppe})\text{Cp}^*$	-0.33	0.34	1.04	1.55	0.67	0.70	0.51	^b

^a CH_2Cl_2 , 298 K; Pt electrodes, 0.1 M $[\text{NBu}_4][\text{BF}_4]$ relative to Pt reference electrode, vs. $\text{FcH} / [\text{FcH}]^+ = 0.46$ V. ^bThis work.

(f) $\text{Hg}\{\text{C}\equiv\text{CC}\equiv\text{C}[\text{RuL}_2\text{Cp}']\}_2$ ($\text{L}_2 = 2\text{PPh}_3$, dppe, $\text{Cp}' = \text{Cp}$, Cp^*).

Of the several examples of complexes containing two $\{\text{ML}_n\}\text{C}\equiv\text{CC}\equiv\text{C}-$ chains linked by a third metal centre^{37,38} the electrochemistry of only two have been studied, namely $\{[\text{Cp}^*(\text{PPh}_3)(\text{NO})\text{Re}](\text{C}\equiv\text{C})_n\}_2\text{Pd}(\text{PEt}_3)_2$ ($n = 1, 2$). In these instances, the ESR spectra of the mono-oxidised cations showed that the unpaired electron is localised on the rhenium atom, i.e. there is no communication between the metal centres.³⁷ This research group has been interested in the similar behaviour of complexes in which two $-\text{C}\equiv\text{CC}\equiv\text{C}\{\text{ML}_n\}$ fragments are linked by a Group 11 or 12 metal, such as $\text{Au}(\text{I})$ ³⁸ or $\text{Hg}(\text{II})$ ²¹. While the synthesis of these materials is relatively easy, there have been few structural studies carried out, on account of their very low solubility and the resulting difficulty in growing crystals suitable for X-ray diffraction studies. We recall that it is only relatively recently that the structures of some mercury(II) alkynyls have been reported, with the interesting result that evidence for some mercuriphilic (analogous to aurophilic interactions) interactions has been obtained.³⁹



Synthesis of **5.9** and **5.10**.

Reactions between $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{PR}_3)_2\text{Cp}'$ [$(\text{PR}_3)_2 = \text{dppe}$, $\text{Cp}' = \text{Cp}^*$; $\text{PR}_3 = \text{PPh}_3$, $\text{Cp}' = \text{Cp}$] and $\text{Hg}(\text{OAc})_2$ were carried out in refluxing thf overnight (Equation 5). Unusually for mercury(II) derivatives of this type, solutions were obtained, which afforded yellow precipitates when hexane was added. These materials were characterised as the complexes $\text{Hg}\{\text{C}\equiv\text{CC}\equiv\text{C}[\text{Ru}(\text{PR}_3)_2\text{Cp}']\}_2$ [$(\text{PR}_3)_2 = \text{dppe}$, $\text{Cp}' = \text{Cp}^*$ **5.9**, **X**; $\text{PR}_3 = \text{PPh}_3$, $\text{Cp}' = \text{Cp}$, **5.10**] by elemental analyses, their general spectroscopic features and finally, by a single-crystal X-ray structure determination carried out on a crystalline sample of **5.9** obtained from benzene.

The compounds have limited solubility in common organic solvents, partial decomposition of **5.9** occurring in CDCl_3 . The IR spectrum of **5.9** contained three $\nu(\text{C}\equiv\text{C})$ bands between 2160 and 1992 cm^{-1} , some 50 cm^{-1} to lower energy when compared with the ruthenium precursor. In the ^1H NMR spectrum, resonances for the Me, CH_2 and Ph groups were found at δ 1.49, 2.07 and 2.64, and between δ 7.10 and 7.65, while signals at δ 9.67 (Me), 29.46 (CH_2), 93.41 (Cp^* ring) and δ between 127.42 and 138.27 (Ph) appeared in the ^{13}C NMR spectrum. The resonances of the C_4 chain were not detected. The ES mass spectrum was obtained from solutions in MeOH, but only ions assigned to $[\text{Ru}(\text{C}_4)(\text{MeOH})(\text{dppe})\text{Cp}^*]^+$ (m/z 717) and $[\text{Ru}(\text{dppe})\text{Cp}^*]^+$ (m/z 635) were present; no ions containing mercury were found.

A few rod-like crystals of **5.9** suitable for an X-ray study were obtained by layering a solution in benzene with hexane. Figure 4 is a plot of a single molecule which, with three solvate benzenes disposed about the origin, forms the unit cell. The molecule is centrosymmetric, thus requiring strict linearity for the $\text{C}(4)\text{-Hg-C}(4')$ fragment. The geometry of the ruthenium fragment is similar to those of many that have been reported before, the closest analogues being $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{dppe})\text{Cp}^*$ with a distorted octahedral arrangement about the metal atom. The $\text{Ru-C}(\text{Cp}^*)$ [2.221 – 2.267(3) Å, av. 2.25₂ Å] and Ru-P distances [2.2703, 2.2711(7) Å] are similar to those found for $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{dppe})\text{Cp}^{*36}$ [$\text{Ru-C}(\text{Cp}^*)$ 2.216 – 2.281(3) Å, av. 2.25₀ Å; Ru-P 2.256, 2.279(1) Å], while the P-Ru-X angles [$\text{X} = \text{P}$ 82.48(2), $\text{X} = \text{C}$ 82.66, 85.38(7)°] are somewhat less than the usual values of *ca* 90°, probably as a result of the presence of the bulky Cp^* group [cf. values for $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{dppe})\text{Cp}^*$, $\text{X} = \text{P}$ 83.43(4), $\text{X} = \text{C}$ 84.2, 85.5(1)°].

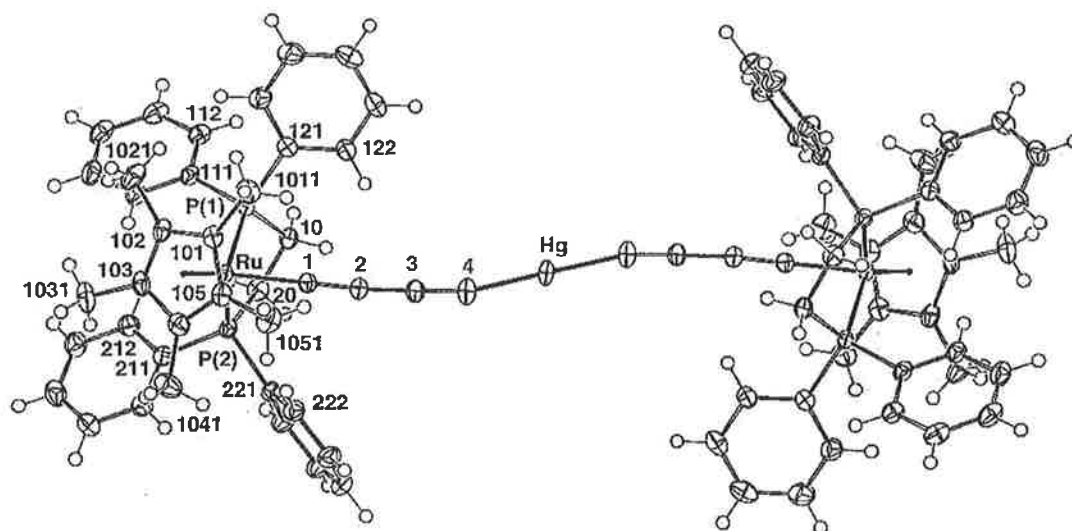


Figure 4. Plot of a molecule of **5.9** showing the atom numbering scheme.

Table 8. Important bond lengths (Å) and angles (°) of **5.9**.

Bond distances			
Ru-C(Cp*)	2.221-2.267(3)	C(1)-C(2)	1.224(3)
(av.)	2.25(2)	C(2)-C(3)	1.367(3)
Ru-P	2.2703-2.2711(7)	C(3)-C(4)	1.217(3)
Ru-C(1)	1.974(2)	C(4)-Hg	1.981(2)
Bond angles			
P-Ru-P	82.48(2)	C(1)-C(2)-C(3)	174.8(3)
P-Ru-C(1)	82.66, 85.38(7)	C(2)-C(3)-C(4)	177.7(3)
Ru(1)-C(1)-C(2)	178.7(3)	C(3)-C(4)-Hg	166.5(3)

The Ru-C₄-Hg-C₄-Ru portion forms an eleven-atom chain, the central mercury atom linking the two C₄ chains [Hg-C(4) 1.981(2) Å]. The Ru-C(1) distance is 1.974(2) Å [cf. 2.015(4) Å in Ru(C≡CC≡CH)(dppe)Cp*] while the C-C distances [1.224, 1.367, 1.217(3) Å] preserve the conjugated 1,3-diyne structure found in buta-1,3-diyne itself [1.217(1), 1.383(2) Å, by electron diffraction²⁷ and Ru(C≡CC≡CH)(dppe)Cp* [1.186, 1.387, 1.193(6) Å].³⁶ Angles at the chain atoms C(1-4), Hg are respectively 178.7, 174.8, 177.7 and 166.5(3)°, the first three being within the ranges previously noted for complexes of this type.

Whilst the geometry about the mercury(II) atoms conforms to strict sp hybridisation, the degree of bending at C(4) appears to be unusual for complexes of this type. It is of interest that where long (C₈-C₁₆) chains are present, the cumulative bending at the carbon atoms sometimes results in extreme conformations of the M-C_x-M chain, but individual angles at carbon generally fall in the range 172-180°. ⁴⁰⁻⁴² In the previous examples of Hg(C≡CR)₂ that have been studied, nearly linear RC≡CHgC≡CR arrays have been found for R = SiMe₃ (C-Hg-C 170.8-178.1°), Ph (174.3-178.6°) ³⁹ and C(NMe₂)=[W(CO)₅] (180°). ⁴³ In the polymeric 4-pyridinylethynyl derivative, where the Hg is also coordinated to a pyridyl nitrogen of a second molecule, the C-Hg-C angle is 172(1)° ⁴⁴ while in Hg(C≡CR)₂(phen) (R = CH₂Cl, Ph), a *cis* orientation is found, with C-Hg-C angles of 165, 168(1) and 165.6(4)°. ^{45,46} The Hg-C(1)-C(2) angles on these complexes range from 165 to 179°, the extremes being found in Hg(C≡CR)₂ (R = Ph and SiMe₃, respectively).

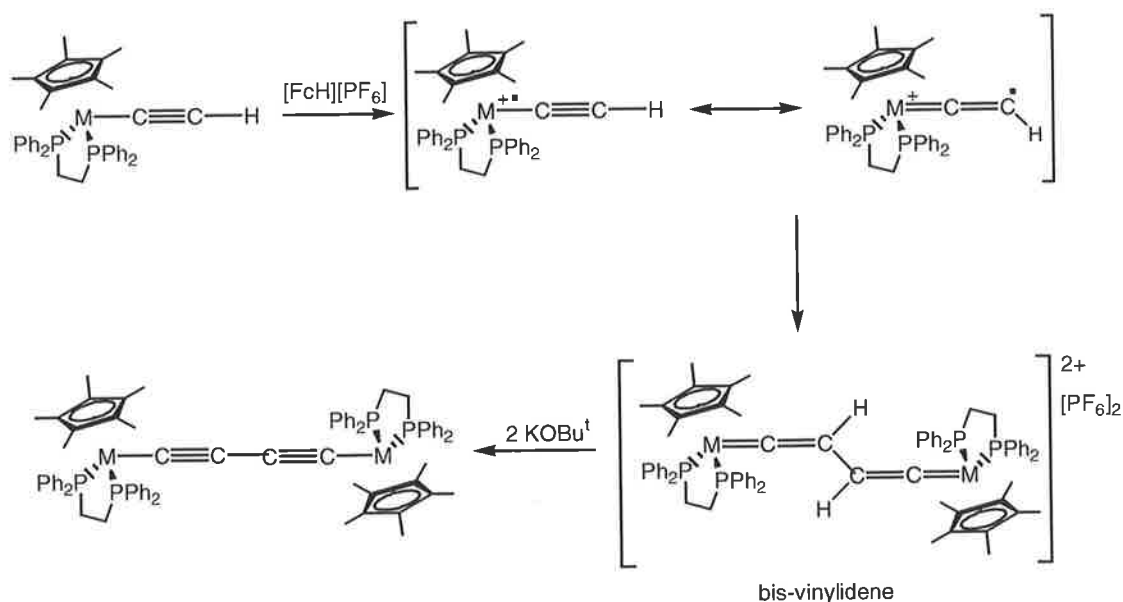
A theoretical study ⁴⁷ of Hg{C≡CC≡C[Ru(dppe)Cp*]}₂, which shows an unusual bending of the C-C-Hg fragment, suggests that there is no electronic source of this feature and that it is caused by lattice forces.

The spectroscopic features of **5.10** are similar to those of **5.9**. Thus, the IR spectrum contained two $\nu(\text{C}\equiv\text{C})$ stretches at 2108 and 1955 cm⁻¹. The ¹H NMR spectrum contained a singlet at δ 4.29 due to the Cp singlet and phenyl resonances between 7.08 and 7.41. The ¹³C NMR spectrum showed a singlet at δ 85.88 due to the Cp ligand and many signals between δ 127.36 and 138.07 due to the phenyl carbons. Again, no resonances of the C₄ chain were detected. The ³¹P spectrum gave a singlet at δ 50.26 due to the PPh₃ ligands. The ES mass spectrum did not show any ions containing mercury, however an ion was observed at m/z 429 due to [Ru(PPh₃)₂Cp]⁺. Interestingly, this complex gave two semi-reversible oxidation waves in its CV at 0.26 and 0.60 V. The magnitude of these oxidation waves (1- or 2-electron) is not clear and no attempt to synthesise the electron deficient complexes chemically has been made. As the waves are not fully reversible, it is possible that the Hg-C bonds are broken upon oxidation and the resulting RuC₄ fragments are coupled to give the known C₈ complex, {Cp(PPh₃)₂Ru}C≡CC≡CC≡CC≡C{Ru(PPh₃)₂Cp}. ³¹

(g) Protonation of $\{\text{Cp}(\text{PPh}_3)_2\}\text{C}\equiv\text{CC}\equiv\text{C}\{\text{Ru}(\text{PPh}_3)_2\text{Cp}\}$ and $\{\text{Cp}(\text{PPh}_3)_2\text{Ru}\}\text{C}\equiv\text{CC}\equiv\text{C}\{\text{Fe}(\text{dppe})\text{Cp}^*\}$.

There are many reports on the synthesis and reactions of metal-acetylides.^{30,48,49} Addition of electrophiles to these complexes results in the formation of vinylidene complexes, deprotonation of which results in the formation of neutral acetylide complexes

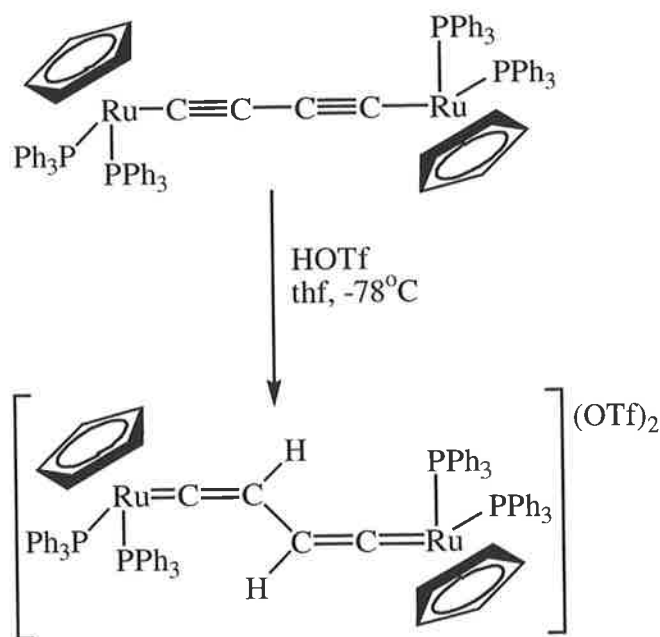
The formation of bis-vinylidenes is not new. Both this^{36,50} and Lapinte's³³ research team has utilised bis-vinylidenes as intermediates in the formation of some $\{\text{ML}_n\}\text{C}\equiv\text{CC}\equiv\text{C}\{\text{ML}_n\}$ complexes via oxidative coupling of metal acetylides (Scheme 1).



Scheme 1. $\text{M} = \text{Fe, Ru, Os}$.

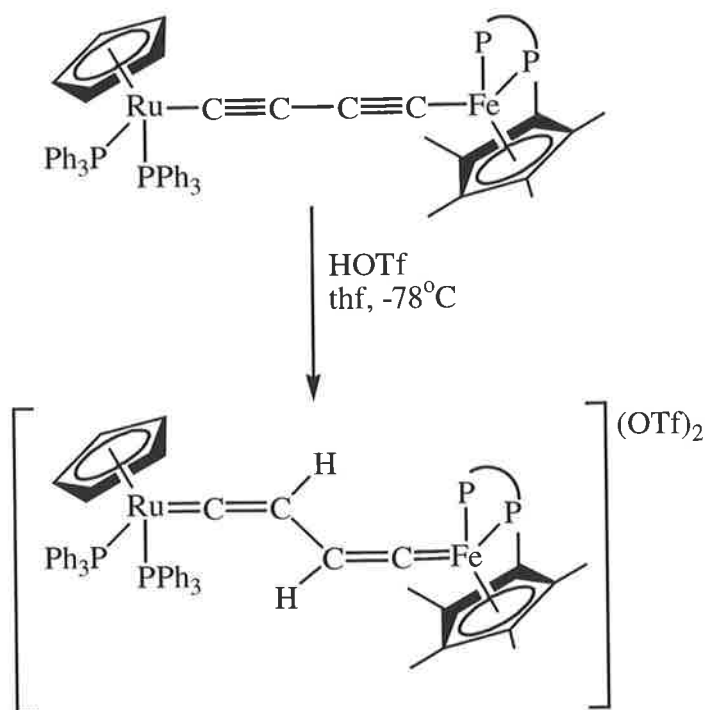
However, it has not been shown that the final step in the above scheme is reversible. The addition of electrophiles to a butadiyndiyl complex has been reported recently⁵¹, although only mono-addition was investigated.

Addition of 2.2 equivalents of trifluoromethanesulphonic acid (HOTf) to $\{\text{Cp}(\text{PPh}_3)_2\text{Ru}\}\text{C}\equiv\text{CC}\equiv\text{C}\{\text{Ru}(\text{PPh}_3)_2\text{Cp}\}$ gave the bis-vinylidene $[\{\text{Cp}(\text{PPh}_3)_2\text{Ru}\}=\text{C}=\text{CHCH}=\text{C}=\{\text{Ru}(\text{PPh}_3)_2\text{Cp}\}][\text{OTf}]_2$ (**5.11**) in excellent yield. The IR spectrum shows a $\nu(\text{CC})$ band at 1613 cm^{-1} characteristic of the bis-vinylidenes reported previously.³³ In the ^1H NMR spectrum the vinylidene protons were observed as an unresolved multiplet at δ 5.50. The Cp signal has been shifted downfield to δ 5.48 when compared to the precursor complex (δ 4.30). A triplet ($^2J_{\text{PC}} = 32\text{ Hz}$) was observed in the ^{13}C NMR spectrum at δ 352.02 and was assigned to C_α by comparison with similar complexes. The downfield shift is characteristic of these systems.⁴⁹ A singlet at δ 101.98 was assigned to C_β while the Cp signal is again shifted downfield to δ 95.97 from δ 85.4 in the precursor complex.³⁰ A singlet in the ^{31}P NMR spectrum at δ 43.86 is due to the PPh_3 ligands. The downfield shifts observed in the ^1H and ^{13}C NMR spectra for the Cp ligands are due to the change in bonding between the ruthenium atom and C_α going from $\text{Ru}-\text{C}$ to $\text{Ru}=\text{C}$ and have been observed previously.⁴⁹



Equation 6. Electrophilic addition of H^+ to $\{\text{Cp}(\text{PPh}_3)_2\text{Ru}\}\text{C}\equiv\text{CC}\equiv\text{C}\{\text{Ru}(\text{PPh}_3)_2\text{Cp}\}$.

A similar reaction between $\{\text{Cp}(\text{PPh}_3)_2\text{Ru}\}\text{C}\equiv\text{CC}\equiv\text{C}\{\text{Fe}(\text{dppe})\text{Cp}^*\}$ and HOTf gave the new mixed ruthenium/iron bis-vinylidene, $[\{\text{Cp}(\text{PPh}_3)_2\text{Ru}\}=\text{C}=\text{CHCH}=\text{C}=\{\text{Fe}(\text{dppe})\text{Cp}^*\}][\text{OTf}]_2$ (**5.12**) in excellent yield (Equation 6). The IR spectra showed two $\nu(\text{C}=\text{C})$ stretches at 1620 and 1593 cm^{-1} . In the ^1H NMR spectrum, the vinylidene protons were again observed as an unresolved multiplet at δ 5.62. The Cp and Cp* ligands gave rise to singlets at δ 5.35 and 1.63 respectively. The methylene protons of the dppe ligand gave two multiplets at δ 3.14 and 2.69. The phenyl region contained a multiplet from δ 7.80 to 6.75. The ^{13}C NMR spectra contained two triplets at δ 356.28 ($^2J_{\text{PC}} = 68$ Hz) and 353.51 ($^2J_{\text{PC}} = 32$ Hz) due to $\text{Fe}=\text{C}=\text{C}$ and $\text{Ru}=\text{C}=\text{C}$ respectively, assigned by comparison with similar complexes.^{33,49} Singlets at δ 106.03 and 102.22 were assigned to $\text{Fe}=\text{C}=\text{C}$ and $\text{Ru}=\text{C}=\text{C}$, respectively. The Cp ligand gave rise to a singlet at δ 96.02 while the Cp* ligand gave singlets at δ 101.24 (C_5Me_5) and 10.20 (C_5Me_5). Two singlets in the ^{31}P NMR spectra at δ 88.07 and 44.41 in a 1:1 ratio were assigned to the dppe and PPh_3 ligands respectively.



Equation 7. Electrophilic addition of H^+ to $\{\text{Cp}(\text{PPh}_3)_2\text{Ru}\}\text{C}\equiv\text{CC}\equiv\text{C}\{\text{Fe}(\text{dppe})\text{Cp}^*\}$.

As mentioned above, the reason for the synthesis of the bis-vinylidene complexes, **5.11** and **5.12**, was to test the reversibility of the last step of Scheme 1. With this now proven, the deprotonation of these complexes was undertaken to prove this reaction was also reversible. Thus, addition of 2.2 equivalents of KOBut to **5.11** and **5.12** gave the neutral butadiyndiyl complexes in near quantitative yield.

EXPERIMENTAL

General experimental conditions and instrumentation – see Chapter 2.

Reagents

I₂ (Merck), Co₂(CO)₈ (Strem), 1,4-diiodobenzene (Aldrich), CuI (Fluka), dppm (Aldrich), dppe (Fluka), KF (BDH), DBU (Aldrich), Hg(OAc)₂ (Aldrich), trifluoromethanesulphonic acid (3M) were used as received, tmno (Aldrich) was freshly sublimed before use. W(C≡CC≡CH)(CO)₃Cp,²¹ W(C≡CC≡CSiMe₃)(CO)₃Cp,²¹ RuCl(dppe)Cp,⁵² RuCl(dppe)Cp*,³⁶ {Cp(PPh₃)₂Ru}C≡CC≡C{Ru(PPh₃)₂Cp},⁵³ Pd(PPh₃)₄,⁵⁴ Ru(C≡CC≡CH)(dppe)Cp*,³⁶ HC≡CC≡CSiMe₃⁵⁵ were prepared using the cited methods. Ru(C≡CC≡CSiMe₃)(PPh₃)₂Cp and Ru(C≡CC≡CH)(PPh₃)₂Cp were prepared as described in Chapter 3.

(a) FcC≡CI (**5.1**).

Morpholine (2 mL) in C₆H₆ (5 mL) was added dropwise to a solution of I₂ (1.14 g, 4.5 mmol) in C₆H₆ (50 mL) at 50°C. The solution turned a cloudy red and was stirred for a further 20 min. FcC≡CH (633 mg, 3 mmol) was then added and the red solution stirred at 50°C for a further 24 h. The solution was then filtered and washed with Et₂O. The solvent was then removed and the residue taken up in CH₂Cl₂. Chromatography on alumina and elution with hexane yielded an orange fraction which gave orange-red solid FcC≡CI (**5.1**) (754 mg, 75%) on removal of solvent. Crystals suitable for X-ray structure determination were grown from CH₂Cl₂/hexane, m.p. 94–96°C. Anal: Found: C, 42.98; H, 2.73; C₁₂H₉FeI calcd: C, 42.90; H, 2.70; *M*, 336. IR (nujol): 2175 cm⁻¹, ν(C≡C). ¹H NMR (CDCl₃): δ 4.18 (m, 2H, C₅H₄), 4.22 (s, 5H, Cp), 4.44 (m, 2H, C₅H₄). ¹³C NMR (CDCl₃): δ 65.56 (s, C_a), 67.88 (s, ≡CFc), 68.59 (s, C_b), 69.95 (s, Cp), 71.70 (s, C_c), 92.04 (s, ≡CI). ES MS (MeOH, +ve): *m/z* 336, M⁺.

(b) $\{\text{Co}_2(\text{CO})_6\}_2(\mu:\mu\text{-FcC}_2\text{C}_2\text{Fc})$ (**5.2**).

A solution of **5.1** (75 mg, 0.22 mmol) and $\text{Co}_2(\text{CO})_8$ (228 mg, 0.66 mmol) in benzene (25 mL) was stirred for 24 hr. The solvent was then removed in vacuo and the residue taken up in CH_2Cl_2 . Preparative t.l.c. eluting with hexane/ CH_2Cl_2 (3/1) gave a black band (R_f 0.7) which yielded black solid $\{\text{Co}_2(\text{CO})_6\}_2(\mu:\mu\text{-FcC}_2\text{C}_2\text{Fc})$ (**5.2**) (62 mg, 57%). Crystals suitable for X-ray structure determination were grown from $\text{CH}_2\text{Cl}_2/\text{MeOH}$. Anal. Found: C, 43.72; H, 2.11; $\text{C}_{36}\text{H}_{18}\text{Co}_4\text{Fe}_2\text{O}_{12}$ calcd: C, 43.67; H, 1.83; M , 990. IR (CH_2Cl_2): 2095m, 2076s, 2056vs, 2029 (sh), 2019s cm^{-1} . ^1H NMR (CDCl_3): δ 4.24 (s, 5H, Cp), 4.32 (m, 2H, C_5H_4), 4.41 (m, 2H, C_5H_4). ^{13}C NMR (CDCl_3): δ 67.92 (s, C_a), 69.17 (s, C_b), 69.87 (s, Cp), 70.43 (s, C_c), 74.08 (s, C_β), 75.19 (s, C_α). ES MS (MeOH , -ve, + NaOMe): m/z 1020, $[\text{M} + \text{OMe}]^-$; 992 - 684, $[\text{M} + \text{OMe} - n\text{CO}]^-$ ($n = 1 - 12$).

(c) $1,4\text{-}\{\text{Cp}(\text{CO})_3\text{W}\}\text{C}\equiv\text{CC}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CC}\equiv\text{C}\{\text{W}(\text{CO})_3\text{Cp}\}$ (**5.3**).

To a flame-dried Schlenk flask was added $\text{thf}/\text{NHPr}^i_2$ (1/1, 20 ml). The solution was rigorously degassed using the freeze/pump/thaw method. $\text{W}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{CO})_3\text{Cp}$ (200 mg, 0.52 mmol), 1,4-diiodobenzene (99 mg, 0.30 mmol), $\text{Pd}(\text{PPh}_3)_4$ (60 mg, 0.052 mmol) and CuI (ca. 5mg) were added in that order. The resulting yellow suspension was stirred for 16 h in the dark. After this time the solution had turned a dark orange and an orange-yellow precipitate had formed. The precipitate was collected and washed with hexane (2 x 10 mL), Et_2O (2 x 10 mL) and taken up in the minimum amount of CH_2Cl_2 . Dropwise addition of this solution to cold hexane gave an orange-yellow precipitate which was washed with hexane and air-dried to give $1,4\text{-}\{\text{Cp}(\text{CO})_3\text{W}\}\text{C}\equiv\text{CC}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CC}\equiv\text{C}\{\text{W}(\text{CO})_3\text{Cp}\}$ (**5.3**) (195 mg, 89%). Anal. Found: C, 42.17; H, 1.83 calcd for $\text{C}_{30}\text{H}_{14}\text{O}_6\text{W}_2$. $0.5\text{CH}_2\text{Cl}_2$: C, 42.24; H, 2.03; M , 784. IR (CH_2Cl_2): $\nu(\text{C}\equiv\text{C})$ 2181w, 2056w; $\nu(\text{CO})$ 2038s, 1956(br) cm^{-1} . ^1H NMR: δ 5.64 (s, 10H, 2 x Cp), 7.28 (s, 4H, Ph). ^{13}C NMR ($\text{dmsO}-d_6$): δ 72.66 (s, C_δ), 79.31 (s, C_γ), 83.75 (s, C_β), 92.91 (s, Cp), 110.42 (s, C_α), 122.10 (s, $i\text{-C}$), 132.17 (s, Ph), 214.10, 228.17 (2 x s, 2 x CO). ES mass spectrum ($\text{CH}_2\text{Cl}_2/\text{MeOH}$ containing NaOMe, m/z): 871, $[\text{M} + \text{OMe}]^-$; 815, $[\text{M} + \text{OMe} - 2\text{CO}]^-$; 759, $[\text{M} + \text{OMe} - 4\text{CO}]^-$; 703, $[\text{M} + \text{OMe} - 6\text{CO}]^-$.

(d) $\text{W}(\text{C}\equiv\text{CC}\equiv\text{CSiMe}_3)(\text{CO})_2(\text{dppm-P})\text{Cp}$ (**5.4**).

A Schlenk flask was charged with $\text{W}(\text{C}\equiv\text{CC}\equiv\text{CSiMe}_3)(\text{CO})_3\text{Cp}$ (100 mg, 0.22 mmol), dppm (86 mg, 0.22 mmol), tmno (24 mg, 0.32 mmol) and MeCN (20ml). The yellow solution was stirred for 30 min after which time the colour had changed to orange. The solvent was removed and the red-orange residue purified by preparative t.l.c. (hexane/acetone, 7/3). The major yellow-orange band (R_f 0.45) contained $\text{W}(\text{C}\equiv\text{CC}\equiv\text{CSiMe}_3)(\text{CO})_2(\text{dppm-P})\text{Cp}$ (**5.4**) (125mg, 70%). Crystals suitable for X-ray analysis were grown from $\text{CHCl}_3/\text{MeOH}$. Anal. Found: C, 50.90; H, 4.0. calcd for $\text{C}_{39}\text{H}_{36}\text{O}_2\text{P}_2\text{WSi}\cdot\text{CHCl}_3$: C, 51.66; H, 4.01%. IR (CH_2Cl_2): $\nu(\text{C}\equiv\text{C})$ 2165w, 2117w; $\nu(\text{CO})$ 1951s, 1869s cm^{-1} . ^1H NMR: δ 0.15 (s, 9H, SiMe_3), 3.32, 3.98 (2 x m, 2 x 1H, P- CH_2), 5.32 (s, 5H, Cp), 7.06-7.71 (m, 20H, Ph). ^{13}C NMR: δ 0.34 (s, SiMe_3), 27.96 [t, $J(\text{CP})$ 23, P- CH_2], 79.66 (s, C_δ), 88.43 (s, C_γ), 91.02 (s, Cp), 91.41 (s, C_β), 113.57 (s, C_α), 124.72-139.35 (m, Ph), 227.06 (s, W-CO), 243.45 [d, $J(\text{CP})$ 22, W-CO]. ^{31}P NMR: δ -25.00 [d, $J(\text{PP})$ 60, free P- CH_2], 12.00 [dt, $J(\text{PP})$ 60, $J(\text{PW})$ 120, W-P]. ES mass spectrum (MeOH, m/z): 810, M^+ ; 782, $[\text{M} - \text{CO}]^+$; 754, $[\text{M} - 2\text{CO}]^+$.

(e) $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CSiMe}_3)(\text{CO})_2\text{Cp}$ (**5.5**).

To a solution of $\text{RuBr}(\text{CO})_2\text{Cp}$ (400 mg, 1.32 mmol) in thf/ NH_4Et_2 (1/2, 40 mL) was added CuI (25 mg, 0.13 mmol) followed immediately by $\text{HC}\equiv\text{CC}\equiv\text{CSiMe}_3$ (430 mg, 3.50 mmol). The solution was stirred in the dark for 45 min, filtered and the solvent removed. Passage down a basic Al_2O_3 column eluting with Et_2O /pentane (1/1) yielded an orange-yellow band which was crystallised from CH_2Cl_2 /hexane to give $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CSiMe}_3)(\text{CO})_2\text{Cp}$ (**5.5**) as a pale yellow solid (325 mg, 72 %). Anal. Found: C, 50.90; H, 4.02. Calcd for $\text{C}_{15}\text{H}_{14}\text{O}_2\text{RuSi}\cdot\text{CHCl}_3$: C, 51.66; H, 4.01%. M , 344. IR (CH_2Cl_2): $\nu(\text{C}\equiv\text{C})$ 2181m, 2128m, 2114sh; $\nu(\text{CO})$ 2056s, 2002s cm^{-1} . ^1H NMR: δ 0.12 (s, 9H, SiMe_3), 5.41 (s, 5H, Cp). ^{13}C NMR: δ 0.01 (s, SiMe_3), 72.74 (s, C_δ), 84.23 (s, C_γ), 87.84 (s, Cp), 90.84 (s, C_β), 92.55 (s, C_α), 195.50 (s, CO). ES mass spectrum (MeOH, m/z): 344, M^+ ; 316, $[\text{M} - \text{CO}]^+$.

(f) $\{\text{Cp}(\text{dppe})\text{Ru}\}\text{C}\equiv\text{CC}\equiv\text{C}\{\text{Ru}(\text{dppe})\text{Cp}\}$ (**5.6**).

A Schlenk flask was charged with $\{\text{Cp}(\text{PPh}_3)_2\text{Ru}\}\text{C}\equiv\text{CC}\equiv\text{C}\{\text{Ru}(\text{PPh}_3)_2\text{Cp}\}$ (1.0 g, 0.70 mmol), dppe (580 mg, 1.46 mmol) and toluene (120 mL). The resulting orange solution was refluxed for 3 days after which time the colour had deepened to an orange-red. Evaporation of the solvent and trituration with hot hexane (3 x 25 mL) gave $\{\text{Cp}(\text{dppe})\text{Ru}\}\text{C}\equiv\text{CC}\equiv\text{C}\{\text{Ru}(\text{dppe})\text{Cp}\}$ (**5.6**) as a bright orange solid (705 mg, 86 %). Anal. Found: C, 67.29; H, 4.94. Calc. For $\text{C}_{66}\text{H}_{58}\text{P}_4\text{Ru}_2$: C, 67.34; H, 4.97%. *M*, 1177. IR (CH_2Cl_2): $\nu(\text{C}\equiv\text{C})$ 1970 cm^{-1} . ^1H NMR (CDCl_3): δ 2.01, 2.35 (2 x m, 2 x 2H, 2 x CH_2P), 4.60 (s, 10H, Cp), 7.03 - 7.71 (m, 40H, Ph). ^{13}C NMR (CDCl_3): δ 29.01 (m, CH_2P), 82.23 (s, Cp), 127.21 - 143.06 (m, Ph). ^{31}P NMR (CD_2Cl_2): δ 86.70 (s, dppe).

(g) $\{\text{Cp}(\text{PPh}_3)_2\text{Ru}\}\text{C}\equiv\text{CC}\equiv\text{C}\{\text{Ru}(\text{dppe})\text{Cp}\}$ (**5.7**).

To a solution of $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CSiMe}_3)(\text{PPh}_3)_2\text{Cp}$ (200 mg, 0.246 mmol), $\text{RuCl}(\text{dppe})\text{Cp}$ (138 mg, 0.230 mmol) and KF (16 mg, 0.275 mmol) in MeOH (30 mL) was added DBU (5 drops). The resulting orange/brown suspension was refluxed for 16 h. After this time the solution had darkened and an olive green precipitate had formed. The precipitate was collected and washed with hexane and air-dried. Recrystallisation from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ gave yellow $\{\text{Cp}(\text{PPh}_3)_2\text{Ru}\}\text{C}\equiv\text{CC}\equiv\text{C}\{\text{Ru}(\text{dppe})\text{Cp}\}$ (**5.7**) (130 mg, 42 %). Anal. Found: C, 66.40; H, 4.53. Calcd for $\text{C}_{76}\text{H}_{64}\text{P}_4\text{Ru}_2\cdot\text{CH}_2\text{Cl}_2$: C, 66.33; H, 4.83%. *M*, 1303. IR (CH_2Cl_2): $\nu(\text{C}\equiv\text{C})$ 1966 cm^{-1} . ^1H NMR (C_6D_6): δ 2.18, 3.02 (2 x 2H, P- CH_2CH_2 -P), 4.42 (s, 5H, Cp), 4.77 (s, 5H, Cp), 8.16 - 6.83 (m, 50H, Ph). ^{13}C NMR: δ 29.12 (m, P- CH_2CH_2 -P), 82.06 (s, $\text{Ru}(\text{dppe})\text{Cp}$), 85.57 (s, $\text{Ru}(\text{PPh}_3)_2\text{Cp}$), 128.17 - 139.86 (m, Ph). ^{31}P NMR (C_6D_6): δ 51.41 (s, PPh_3), 86.09 (s, dppe).

(h) $\{\text{Cp}(\text{PPh}_3)_2\text{Ru}\}\text{C}\equiv\text{CC}\equiv\text{C}\{\text{Ru}(\text{dppe})\text{Cp}^*\}$ (**5.8**).

To a solution of $\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{CSiMe}_3)(\text{PPh}_3)_2\text{Cp}$ (100 mg, 0.123 mmol), $\text{RuCl}(\text{dppe})\text{Cp}^*$ (83 mg, 0.123 mmol) and KF (9 mg, 0.155 mmol) in MeOH (15 mL) was added DBU (3 drops). The resulting orange/brown suspension was refluxed for 16 h. After this time the solution had darkened and an olive green precipitate had formed. The precipitate was collected and washed with hexane and air-dried. Recrystallisation from $\text{CHCl}_3/\text{MeOH}$ gave yellow $\{\text{Cp}(\text{PPh}_3)_2\text{Ru}\}\text{C}\equiv\text{CC}\equiv\text{C}\{\text{Ru}(\text{dppe})\text{Cp}^*\}$ (**5.8**) (76 mg, 45 %). Anal. Found: C, 70.74;

H, 5.46 calcd for $C_{81}H_{74}P_4Ru_2$: C, 70.83; H, 5.43%. *M*, 1375. IR (CH_2Cl_2): $\nu(C\equiv C)$ 1965 cm^{-1} . ^1H NMR (C_6D_6): δ 1.73 (s, 15H, Cp^*), 2.03, 2.92 (2 x m, 2 x 2H, P- CH_2CH_2 -P), 4.32 (s, Cp), 7.00 – 8.09 (m, 50H, Ph). ^{13}C NMR: δ 10.71 (s, C_5Me_5), 30.19 (m, P- CH_2CH_2 -P), 85.94 (s, Cp), 93.05 (s, C_5Me_5), 127.36 – 140.02 (m, Ph). ^{31}P NMR ($CDCl_3$): δ 51.49 (s, PPh_3), 82.01 (s, dppe).

(i) $Hg\{C\equiv CC\equiv C[Ru((dppe)Cp^*)]\}_2$ (**5.9**).

A mixture of $Ru(C\equiv CC\equiv CH)(dppe)Cp^*$ (68.4 mg, 0.1 mmol) and $Hg(OAc)_2$ (15.9 mg, 0.05 mmol) was heated in refluxing thf (20 mL) overnight. The yellow solution was concentrated to ca 2 mL and dropped into rapidly stirring hexane (50 mL) at r.t. The yellow precipitate of $Hg\{C\equiv CC\equiv C[Ru((dppe)Cp^*)]\}_2$ (**5.9**) (63 mg, 81 %) which separated was filtered, washed with hexane and air-dried. Anal. Found: C, 61.31; H, 4.96. Calc. For $C_{80}H_{78}P_4Ru_2Hg$: C, 61.35; H, 5.02%. *M*, 1566. IR (CH_2Cl_2): $\nu(C\equiv C)$ 2156m, 2095m, 1992 cm^{-1} . ^1H NMR ($CDCl_3$): δ 1.49 (s, 30H, Cp^*), 2.07, 2.64 (2 x m, 2 x 2H, CH_2), 7.10 – 7.65 (m, 40H, Ph). ^{13}C NMR ($CDCl_3$): δ 9.67 (s, C_5Me_5), 29.46 (m, CH_2), 93.41 (s, C_5Me_5), 127.42 – 138.27 (m, Ph). ^{31}P NMR ($CDCl_3$): δ 81.39 (s). ES mass spectrum (MeOH, *m/z*): 717 $[Ru(C_4)(MeOH)(dppe)Cp^*]^+$; 635 $[Ru(dppe)Cp^*]^+$.

(j) $Hg\{C\equiv CC\equiv C[Ru(PPh_3)_2Cp]\}_2$ (**5.10**).

A mixture of $Ru(C\equiv CC\equiv CH)(PPh_3)_2Cp$ (150 mg, 0.20 mmol) and $Hg(OAc)_2$ (35 mg, 0.11 mmol) was heated in refluxing thf (20 mL) overnight. The resulting green/brown solution was evaporated to dryness. The residue was extracted with CH_2Cl_2 (min) and dropped into cold hexane. The olive/green precipitate was collected and washed with Et_2O (2 x 5 mL) and pentane (2 x 5 mL) and air-dried to give $Hg\{C\equiv CC\equiv C[Ru(PPh_3)_2Cp]\}_2$ (**5.10**) (123 mg, 73 %). Anal. Found: C, 64.37; H, 4.32. Calc. For $C_{90}H_{70}P_4Ru_2Hg$: C, 64.42; H, 4.20%. *M*, 1678. IR (CH_2Cl_2): $\nu(C\equiv C)$ 2108m, 1955 cm^{-1} . ^1H NMR ($CDCl_3$): δ 4.29 (s, 10H, Cp), 7.08 – 7.41 (m, 60H, Ph). ^{13}C NMR ($CDCl_3$): δ 85.88 (s, Cp), 127.36 – 138.07 (m, Ph). ^{31}P NMR ($CDCl_3$): δ 50.26 (s). ES mass spectrum (MeOH, positive ion, *m/z*): 429 $[Ru(PPh_3)Cp]^+$.

(k) $[\{\text{Cp}(\text{PPh}_3)_2\text{Ru}\}=\text{C}=\text{C}(\text{H})\text{C}(\text{H})=\text{C}=\{\text{Ru}(\text{PPh}_3)_2\text{Cp}\}][\text{OTf}]_2$ (**5.11**).

To a solution of $\{\text{Cp}(\text{PPh}_3)_2\text{Ru}\}\text{C}\equiv\text{CC}\equiv\text{C}\{\text{Ru}(\text{PPh}_3)_2\text{Cp}\}$ (100 mg, 0.07 mmol) in thf (15 mL) at -78°C was added dropwise a solution of HOTf (23 mg, 0.15 mmol) in thf (0.5 mL). The colour changed from orange through wine-red to deep purple immediately. Stirring was continued for 5 mins at -78°C and then pentane (100 mL, -78°C) added. The orange-brown precipitate was collected and washed with Et_2O (2 x 5 mL) and pentane (2 x 10 mL) and dried under oil-pump vacuum to give light red $[\text{Cp}(\text{PPh}_3)_2\text{Ru}(=\text{C}=\text{C}(\text{H})\text{C}(\text{H})=\text{C}=\text{Ru}(\text{PPh}_3)_2\text{Cp})][\text{OTf}]_2$ (**5.11**) (89 mg, 74%). Anal. Found: C, 60.97; H, 4.30. Calc. For $\text{C}_{88}\text{H}_{72}\text{O}_6\text{P}_4\text{S}_2\text{F}_6\text{Ru}_2$: C, 61.11; H, 4.20%. *M*, 1730. IR (Nujol): $\nu(\text{C}\equiv\text{C})$ 1613br cm^{-1} . ^1H NMR (CD_3COCD_3): δ 5.48 (s, 10H, Cp), 5.50 (m, 2H, $=\text{C}(\text{H})-$), 7.47 - 7.12 (m, 60H, Ph). ^{13}C NMR (CD_3COCD_3): δ 95.97 (s, Cp), 101.98 (s, C_β), 128.84 - 135.74 (m, Ph), 352.02 (t, $^2J_{\text{PC}}$ 32Hz, C_α). ^{31}P NMR (CD_3COCD_3): δ 43.86 (s, PPh_3).

(l) $[\{\text{Cp}(\text{PPh}_3)_2\text{Ru}\}=\text{C}=\text{C}(\text{H})\text{C}(\text{H})=\text{C}=\{\text{Fe}(\text{dppe})\text{Cp}^*\}][\text{OTf}]_2$ (**5.12**).

To a solution of $\{\text{Cp}(\text{PPh}_3)_2\text{Ru}\}\text{C}\equiv\text{CC}\equiv\text{C}\{\text{Fe}(\text{dppe})\text{Cp}^*\}$ (100 mg, 0.07 mmol) in thf (15 mL) at -80°C was added dropwise a solution of HOTf (25 mg, 0.17 mmol) in thf (0.5 mL). The colour changed from orange to wine-red immediately. Stirring was continued for 5 mins at -80°C and then pentane (100 mL) added. The orange-brown precipitate was collected and washed with Et_2O (2 x 5 mL) and pentane (2 x 10 mL) and dried under oil-pump vacuum to give deep red $[\{\text{Cp}(\text{PPh}_3)_2\text{Ru}\}=\text{C}=\text{C}(\text{H})\text{C}(\text{H})=\text{C}=\{\text{Fe}(\text{dppe})\text{Cp}^*\}][\text{OTf}]_2$ (**12**) (92 mg, 81%). Anal. Found: C, 61.12; H, 4.65. Calc. For $\text{C}_{83}\text{H}_{76}\text{O}_6\text{P}_4\text{S}_2\text{F}_6\text{RuFe}$: C, 61.22; H, 4.70%. *M*, 1629. IR (CH_2Cl_2): $\nu(\text{C}\equiv\text{C})$ 1620m, 1593m cm^{-1} . ^1H NMR (CD_3COCD_3): δ 1.63 (s, 15H, FeCp^*), 3.14, 2.69 (2 x m, 2 x 2H, 2 x CH_2P), 5.35 (s, RuCp), 5.62 (m, 2H, $=\text{C}(\text{H})-$), 6.75 - 7.80 (m, 50H, Ph). ^{13}C NMR (CD_3COCD_3): δ 10.20 (s, FeC_5Me_5), 96.02 (s, Cp), 101.24 (s, FeC_5Me_5), 102.22 (s, $\text{Ru}=\text{C}=\text{CH}$), 106.03 (s, $\text{Fe}=\text{C}=\text{CH}$), 125.64 - 136.76 (m, Ph), 353.51 (t, $^2J_{\text{PC}}$ 32Hz, $\text{Ru}=\text{C}=\text{CH}$), 356.28 (t, $^2J_{\text{PC}}$ 68Hz, $\text{Fe}=\text{C}=\text{CH}$). ^{31}P NMR (CD_3COCD_3): δ 44.41 (s, PPh_3), 88.07 (s, dppe).

(m) Deprotonation of **5.11**.

To a solution of **5.11** (50 mg, 0.29 mmol) in thf (10 mL) was added KOBu^t (7 mg, 0.062 mmol). The resulting brown solution was stirred for 15 min and evaporated to dryness. The crude residue was then washed with MeOH (2 x 5 mL), Et₂O (2 x 5 mL) and pentane (2 x 5 mL) and air-dried to give {Cp(PPh₃)₂Ru}C≡CC≡C{Ru(PPh₃)₂Cp} (39 mg, 94 %) and identified by comparison with an authentic sample.

(n) Deprotonation of **5.12**.

To a solution of **5.12** (50 mg, 0.031 mmol) in thf (10 mL) was added KOBu^t (7.5 mg, 0.067 mmol). The resulting brown solution was stirred for 15 min and evaporated to dryness. The crude residue was extracted with Et₂O (3 x 5 mL) and the solvent removed *in vacuo*. The orange-brown solid was then washed with MeOH (2 x 5 mL), and pentane (2 x 5 mL) and dried *in vacuo* to give {Cp(PPh₃)₂Ru}C≡CC≡C{Fe(dppe)Cp*} (37 mg, 95 %) and identified by comparison with an authentic sample.

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Appendix

Publications by the Author arising from this Work

1. Syntheses of complexes containing substituted 4-ethynylquinolines or 1-azabuta-1,3-dienes by addition of imines to a cationic butatrienyldiene-ruthenium complex, *J. Organomet. Chem.*, **1999**, 590, 184-201 (with M. I. Bruce, M. Ke, B. D. Kelly, P. J. Low, B. W. Skelton and A. H. White).
2. Preparation and molecular structure of $\text{FcC}\equiv\text{CI}$ and $\{\text{Co}_2(\text{CO})_6\}_2(\mu:\mu\text{-FcC}_2\text{C}_2\text{Fc})$ [Fc = Ferrocenyl, $(\eta\text{-C}_5\text{H}_4)\text{Fe}(\eta\text{-C}_5\text{H}_5)$], *Aust. J. Chem.*, **1999**, 52, 431-435 (with M. I. Bruce, B. W. Skelton and A. H. White).
3. Heterometallic complexes containing C_4 chains. X-ray structures of $\{\text{Cp}(\text{OC})_3\text{W}\}\text{C}\equiv\text{CC}\equiv\text{C}\{\text{Ir}(\text{CO})(\text{PPh}_3)_2(\text{O}_2)\}$ and $\text{cis-Pt}\{\text{C}\equiv\text{CC}\equiv\text{C}[\text{W}(\text{CO})_3\text{Cp}]\}_2(\text{PEt}_3)_2$, *Inorg. Chim. Acta*, **2000**, 300-302, 633-644 (with M. I. Bruce, B. C. Hall, P. J. Low, B. W. Skelton and A. H. White).
4. Syntheses and some reactions of complexes containing carbon chains capped by ferrocenyl and $\text{W}(\text{CO})_3\text{Cp}$ Groups, *J. Organomet. Chem.*, **2001**, 637-639, 484-499. Ferrocene Anniversary Issue (with M. I. Bruce, B. W. Skelton and A. H. White).
5. Some chemistry of diynyl-tungsten complexes, *Aust. J. Chem.*, **2001**, 54(7), 453-460 (with M. I. Bruce, P. J. Low, M. Ke, B. D. Kelly, B. W. Skelton, A. H. White and N. B. Witton).
6. Some molecular rods: Gold(I) complexes of 1,3-diynes. Crystal structures of $\text{Au}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{PPh}_3)$ and $\{\text{Cu}_3(\mu\text{-dppm})_3\}(\mu_3\text{-I})(\mu_3\text{-C}\equiv\text{CC}\equiv\text{CAuC}\equiv\text{CC}\equiv\text{CH})$, *J. Chem. Soc. Dalton. Trans.*, **2002**, 995-1001 (with M. I. Bruce, B. C. Hall, B. W. Skelton and A. H. White).

7. Preparation and Molecular Structure of $\text{Hg}\{\text{C}\equiv\text{CC}\equiv\text{C}[\text{Ru}(\text{dppe})\text{Cp}^*]\}_2$ - Non-linearity in a Molecular Rod, *Inorg. Chim. Acta*, **2002**, in press (with M. I. Bruce, J-F. Halet, B. Le Guennic, B. W. Skelton and A. H. White).

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Journal of Organometallic Chemistry, v. 590 (2), pp. 184-201.

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Bruce, M.I., Skelton, B.W., Smith, M.E., and White, A.H., (1999) Preparation and Molecular Structures of $\text{FcC} \equiv \text{Cl}$ and $\{\text{Co}_2(\text{CO})_6\}_2(\mu:\mu\text{-FcC}_2\text{C}_2\text{Fc})$ [Fc = Ferrocenyl, $(\text{h-C}_5\text{H}_4)\text{Fe}(\text{h-C}_5\text{H}_5)$].
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Bruce, M.I., Hall, B.C., Low, P.J., Smith, M.E., Skelton, B.W., and White, A.H., (2000) Heterometallic complexes containing C₄ chains. X-ray structures of {Cp(OC)₃W}CCCC{Ir(CO)(PPh₃)₂(O₂)} and cis-Pt{CCCC[W(CO)₃Cp]}₂(PEt₃)₂. *Inorganica Chimica Acta*, v. 300-302, pp. 633-644.

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Journal of Organometallic Chemistry, v. 637-639, pp. 484-499.

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Bruce, M.I., Low, P.J., Ke, M., Kelly, B.D., Skelton, B.W., Smith, M.E., (et al.)
(2001) Some chemistry of diynyl-tungsten complexes.
Australian Journal of Chemistry, v. 54 (7), pp. 453-460.

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Bruce, M.I., Hall, B.C., Skelton, B.W., Smith, M.E., and White, A.H., (2002) Some molecular rods: gold(I) complexes of 1,3-diynes. Crystal structures of $\text{Au}(\text{C}\equiv\text{CC}\equiv\text{CH})(\text{PPh}_3)$ and $\{\text{Cu}_3(\mu\text{-dppm})_3\}(\mu_3\text{-I})(\mu_3\text{-C}\equiv\text{CC}\equiv\text{CAu}\text{C}\equiv\text{CC}\equiv\text{CH})$. *Journal of the Chemical Society, Dalton Transactions*, v. 6, pp. 995-1001.

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<http://dx.doi.org/10.1039/B107446F>

'ERRATA'

Abstract,
p2, line 11: en route

Acknowledgments

Abbreviations: pentamethylcyclopentadienyl
1,2-bis(dimethylphosphino)ethane
tetramethylethylenediamine
saturated calomel electrode
intervalence charge transfer
reciprocal centimetres
optical transparent thin-layer electrochemical

p1: line -6: dependent
p3: line 8: voltammetric
p12: Heading: Miscellaneous
p14: line 2: Eglinton
p15: Scheme 8: The last step has the reactant FeCl(dippe)Cp* missing
p16: Figure 2: FMO refers to the frontier molecular orbital
p17: line -3: 298 K
p21: line -1: naphthalenide
p29: line 4: phosphorus
p33: Table 7: pentaphenylcyclopentadienyl
p36: Table 8: Electrochemical data
p37: line -11: spectrum
p38: Scheme 14: leftmost complex should have a C≡CC≡CH ligand.
p38: Scheme 14: right-hand side - crown
p45: Scheme 15: pyridine
p65: refs 144, 147: Vicente
p66: ref 152: McAdam, C. J and Robinson, B. H
p69: Equation 1: $W(C\equiv C)_nFc(CO)_3Cp$
p70: line -5: $\{W(CO)_3Cp\}_2(C\equiv C)_4$
p74: line -3: $\nu(C\equiv C)$ is hidden behind the $\nu(CO)$ bands of the Co_2 units
p94: line 8: $PPh_2CH_2PPh_2$
p100: line -10: MacLab(4e) supplied by AD Instruments
p101: line 12: 458, $[M - 3CO]^+$
p102: line -7: $\{W(CO)_3Cp\}_2$
p103: for 2.5: 988, $[M - 4Co]^+$: 960, $[M - 5CO]^+$.
p106: line 1: 2.11 not 2.12
p111: line 1: Delete 'The construction of'
p113: line -7: di-oxidised
p132: Table 9: [3.10][PF₆]
p138: line 3: From the MO....
p139: line 13: tetramethylsilane
p151: equation 3: $HC\equiv C-C\equiv CSiMe_3$
p158: line 8: 4.11 not 4.10
p158: line -7: agree

p159: equation 5: triphos should have 2 Phs on each P
p159: line -4: contained a singlet at
p161: line 14: phosphorus
p166: lines -12, -1: integrals due to 18H and 24H respectively
p170: refs 20, 34, 37: Vicente
p171: ref 51: Vicente
p173: line -1: unit cell plot
p174: ref 7: Acta Cryst. **2000**, 252, C 56. C-I (2.053 Å)
p175: line -3: [M + OMe]⁻
p180: line -9: , as well as those....
p185: lines 4, 8, 10: replace 6 with **5.6**
p185: line 8: 2.228-2.258(3) not 2.25-2.28(3)
p185: line 12: 2.228-2.258(3) not 2.28-2.258(3)
p193: line -7: *m/z* 429 due to [Ru(PPh₃)Cp]⁺
p194: line 1: {Cp(PPh₃)₂Ru}
p196: line 3: Equation 7
p199: line -2: 869 not 871, 813 not 815, 757 not 759
p199: line -1: 701 not 703
p202: line 14: 2 x 4H
p208: ref 1: this publication stems from work preceding this thesis.