Some Organometallic Complexes Containing All-Carbon Ligands

by

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Some Chemistry of the Allenylidene and Butatrienylidene Ligands

Appendix 1

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Errata

General points :
C_{70} has been coordinated to metal centres - see J.R. Bowser, *Adv. Organomet. Chem.*, 1994, **36**, 73; the coupling to W should be described as a singlet, with ^{183}W (ca. 15% natural abundance) satellites. In the cases where coupling to W has been reported as a triplet, the true coupling constant is twice the value quoted; the *cis* isomers of complexes **41** and **42** may be the kinetic products, rather than a result of steric interactions; values of C(2)-C(3) in ruthenium acetylide complexes fall in the range 1.370(2) - 1.54(5)Å, while Ru-C(sp) bonds fall in the range 1.906(9) - 2.120(5) (I.R. Whittal, M.G. Humphrey, D.C.R. Hockless, B.W. Skelton and A.H. White, *Organometallics*, 1995, **14**, 3970).

Typographical errors:
Abstract, line 2: containing not containg, derived not derivived; line 18 unprecedented not unprecendented; line 31 nucleophilic not nuclephilic.
Abbreviations : Angstroms not Angstoms, fluoride not flouride;
include Fc ferrocene, TBA tetrabutylammonium, tmno trimethylamine *N*-oxide; for Spectroelectrochemistry absorption not absorbtion.
pg 6, line 6: ...referred to an...
pg 8, line 7: ...should be extraordinarily...
pg 9, Figure 6 caption: planar not planer.
pg 11, line 18: reactions not reations; line 19: heterogeneous not heterogenous; line 24: $Ru_{10}(\mu_6$-... not $Ru(\mu_6$...; line 23: categories not catagories.
pg 16, line 1: ...reaction was extended...; oligomeric not oligermeric.
pg 20, line 1: ...presence of strong...; line 3: ...$C{\equiv}CCPh_2(OSiMe_3)$...; line 7: nucleophiles not nuclephiles.
pg 23, line 8: pyridine not pyridene; line 10: $[Cp^*(PPh_3)Re](C{\equiv}C)_m[Re(PPh_3)Cp^*]$ not $[31](C{\equiv}C)[31]$.
pg 26, line 4: ...manipulation of highly...; line 11: ...have been...
pg 29, line 1: readily not readliy; line 4: thought not though.
pg 30, line 6: ...ligands were obtained from...; line 11: ...contain a...
pg 33, Figure 7 caption, line 3: arbitrary not arbitary.
pg 40, line 12: ...under conditions ranging from...; line 17: successful not succesful.
pg 51, line 7: ...$C{\equiv}CCPh_2(OSiMe_3)$...; line 11: ketenyl not ketene; line 23: ...behave like acetylide...
pg 52, line 2: ...that there have...; reports not report.
pg 55, line 4: Equation 3 not Equation 4.
pg 57, Scheme 7: replace "$+F^-$" with "KF/MeOH" over second and penultimate arrows.
pg 70, line 19: ...characterised by two strong...
pg 71, line 4: renders not render.
pg 73, line 16: adequately not adequetly; line 20: ...of **31** was...;line 24: sensitive not senstive.
pg 75, line 5: possess not posses.
pg 75, line 8: ...obscured by solvent resonances...
pg 79, line 1: ...the ES mass spectrum...
pg 83, line 13: *Preparation of Complexes*...
pg 86, line 5: ...presence of donor ligands...
pg 92, line 3: ...shows that two...
pg 89, line 9: [M] not $[ML_m]$ (twice).
pg 90, line 10: ...hindered carbon-carbon...
pg 92, line 7: ...in a manner...
pg 96, line 20: ...gave both $[M + Na]^+$ and $[M]^+$ ions.
pg 98, line 15: ...bond length [1.19(1) Å] indicates...

pg 99, Figure 16 caption: omitted not ommitted.
pg 102, line 10: received not recieved (also pg 161, line 5).
pg 103, line 14: dissolved not disolved; line 18: 0.82 g not 0.82 mg.
pg 105, line 13: condenser not condensor (also line 14); line 16: paraffin not parafin.

pg 106, line 7: ...in a mixture; line 12: ...onto a column...

pg 107, line 8, 16: volatiles not volitiles (also pg 110, line 23).
pg 107, line 19: ...concentrated to ca. 5 ml...

pg 108, line 6: ...to give $\{Cp(CO)_3W\}C{\equiv}CC{\equiv}C\{W(CO)_3Cp\}$...

pg 111, line 7: $[M]^+$ not $[M+H]^+$; line 11: buta not but; line 14: ...the mixture stirred..., a solution not asolution; line 22: lithiumdiisopropylamide not lithiumdiisopropylamine (also pg 112, lines 12, 25).
pg 112, line 27: ...addition of a...
pg 116, line 25: chromatography not chrmatography, Elution not Eluation.
pg 120, line 12: crystallised not crytallised; line 21: ...carried out in a ..., essentially not essentailly.

pg 125, Equation 20: $\underline{2}\ [\{M(n)\}(\mu\text{-}L)\{M'(n+1)\}]^{(m+1)+}$; line 7: indicates not indicate.
pg 125, 126: **51.[PF$_6$]** not **51.PF$_6$** and **52.[PF$_6$]** not **52.PF$_6$** throughout.
pg 128, line 14: ...ion was...
pg 131, line 3: ...gave weak...; line 15: ...of the...
pg 132, Table 3: electrolysis not electroylisis; TBA not $[NBu_4]$.
pg 133, line 1: description not discription.
pg 134, line 5: suggesting not suggest.
pg 137, line 2: diyndiyl not diyndiyk.

pg 141, Figure 22 caption: ...$RuCl_2(P^iPr_2CH_2CH_2OMe)_2$...
pg 142, line 17: trifluoracetate not triflate.
pg 145, line 9: fragments not fragment.
pg 150, line 1: complementary not complimentary; line 4: ...made to leave.
pg 151, line 11: C(1)-C(2) [1.36 Å] not C(2)-C(3) [1.36 Å].
pg 156: note that butadiyne and diacetylene both refer to buta-1,3-diyne.
pg 157, line 10: substituents not substituents; line 15: a not A.
pg 163, line 2: precipitated not preciptated; line 13 immediately not immediatel, solvent not solven; line 20: ...J_{CP} = 24 Hz...
pg 165, line 5: ...parameters are...
pg 167, Figure A1: exchange (a) and (b) headings.
pg 174, reference 51: Weinheim not Weinham; reference 52 (first entry) *Angew. Chem.* not *Angew. Chem., Int. Ed. Engl.*.
pg 176, reference 80: Martinengo not Martinego.
pg 180, reference 150: B.K. Nicholson not B.K.N. Nicholson.
pg 183, reference 183 *Acetylenic* not *Acetyleneic*.

- Abstract -

This thesis details the synthesis, characterisation and reactions of some transition metal complexes containg ligands dervived from the diacetylenes 1,4-bis(trimethylsilyl)buta-1,3-diyne and buta-1,3-diyne. Some related chemistry of $[Ru(C{=}C{=}CPh_2)(PPh_3)_2Cp]PF_6$ and $[Ru(C{=}C{=}C{=}CH_2)(PPh_3)_2Cp]PF_6$ is also described.

A brief review of the literature dealing with metal complexes of all-carbon ligands is given in Chapter 1.

A number of metal complexes derived from 1,4-bis(trimethylsilyl)buta-1,3-diyne are reported in Chapter 2. Further reactions afford mixed metal complexes in which the heterometallic fragments are linked by a C_4 chain.

The preparation of diynyl ($[L_mM]C{\equiv}CC{\equiv}CR$) and diyndiyl ($[L_mM]C{\equiv}CC{\equiv}C[ML_m]$) complexes are described in Chapter 3. Elaboration of the diynyl ligand has been achieved. Co-ordination to the C≡C triple bonds and incorporation of the terminal C atoms into clusters results in electron rearrangement along the C_4 chain. The bis-metallated tetra-yne complexes $\{Cp(CO)_3M\}C{\equiv}CC{\equiv}CC{\equiv}CC{\equiv}C\{M'(CO)_3Cp\}$ (M, M' = Mo, W) have been prepared by oxidative coupling of the appropriate diynyl precursors.

In Chapter 4 the binuclear ruthenium complexes $[Ru]_2(\mu\text{-}C{\equiv}CC{\equiv}C)$ ([Ru] = $Ru(PPh_3)_2Cp$ or $Ru(PMe_3)(PPh_3)Cp$) are shown to undergo an unprecendented series of four, one-electron oxidation processes. The nature of the electronic structure of the carbon bridge in these oxidised complexes has been probed using spectroelectrochemical techniques. Three of the $Ru(PPh_3)_2Cp$ series have been prepared by chemical oxidation and isolated.

The final Chapter begins with a description of the reactions between various nucleophiles and the allenylidene complex $[Ru(C{=}C{=}CPh_2)(PPh_3)_2Cp]PF_6$. In all cases attack occurs at the exposed C_γ, and the acetylide complexes $Ru(C{\equiv}CCPh_2R)(PPh_3)_2Cp$ {R = Me, OMe, CN, C_5H_5, $CH(CO_2Me)_2$} have been obtained. With $NHMe_2$, the cationic acetylide $[Ru\{C{\equiv}CCPh_2(NHMe_2)\}(PPh_3)_2Cp]PF_6$ was formed. The trienylidene ligand in $[Ru(C{=}C{=}C{=}CH_2)(PPh_3)_2Cp]PF_6$ reacts with various nucleophiles to give compounds containing allenylidene, vinyl acetylide, ethynylquinoline or azabuta-1,3-diene ligands. These observations have been rationalised in terms of initial attack at C_γ and the nature of the nuclephilic reagent.

- 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 photocopying and loan.

Paul J. Low

- Acknowledgements -

I wish to express my gratitude to my supervisor, mentor and friend Professor Michael I. Bruce for his outstanding guidance during the course of this research. He always seemed to know exactly when to take an active role in directing the project and when to let me simply go and play in the lab. He was always there when needed for advice or encouragement, and knew exactly when to deliver the odd well-aimed rocket! I think the best way to describe Michael's approach to supervision is to recount a conversation we had in the very early days of my candidature. Michael asked me "Why are you here?". Somewhat taken aback, I replied that I was here to gain a PhD degree. With a shake of his head he replied "No. You're here to learn how to think." Well Prof, the lesson has been well taught, and for that alone I owe you a great deal. It remains to be seen how well I have learnt that lesson.

Thanks must go to the other members of the Bruce group that I have been fortunate enough to work with during the last four years. The support and advice of Drs. Jonathon Hinchliffe, Mingzhe Ke, Michael Schulz, Anja Werth and especially Natasha Zaitseva is gratefully acknowledged.

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An Australian Postgraduate Award is gratefully acknowledged.

To all my friends in the Department of Chemistry, past and present - Thanks for the good times guys.

These ackowledgements would not be complete without a mention of the Adelaide University Cricket Club. The support and good humour of my Club mates is something I will really miss when the time comes for me to finally pack my kit away.

To the ladies in my life, Kathy, Gayle, Gerri, Anni and Kym, thanks for being, each in your own very special way, such great friends. Even when things were not going so well at the bench, I always knew where to go to find a smile.

The support I have had from my family during my time at University is not something a few words can describe. I shall simply let it be said that they have always allowed me to follow my own path, and have done everything possible to make that path a smooth one. For that, and everything else, I thank you.

- Abbreviations -

in general

Å	angstoms
av.	average
b.p.	boiling point
Bu	butyl
n-Bu	normal butyl
sec-Bu	secondary butyl
^{t}Bu	tertiary butyl
ca	circa
Cp	cyclopentadienyl
Cp*	pentamethylcyclopentadienyl
d	days
dbu	1,8-diazabicyclo[5.4.0]undec-7-ene
dppe	1,2-bis(diphenylphosphino)ethane
dppm	bis(diphenylphosphino)methane
e.g.	for example
Et	ethyl
g	grams
h	hours
HOMO	highest occupied molecular orbital
Hz	hertz
K	Kelvin
kV	kilovolts
L	ligand or litre
$[L_mM]$	general metal-ligand fragment
M	metal or molarity
Me	methyl
mg	milligrams
MHz	megahertz
min	minutes
ml	millilitres
mmol	millimoles
MO	molecular orbital
OAc	acetate

Ph	phenyl
^{i}Pr	iso-propyl
r.t.	room temperature
R_f	retardation factor (TLC)
tbaf	tetrabutylammonium flouride
tcne	tetracyanoethylene
thf	tetrahydrofuran
TLC	thin layer chromatography
X	anion

for Cyclic Voltammetry

E^{o}	formal electrode potential
$E_{p.a.}$	anodic peak potential
$E_{p.c.}$	cathodic peak potential
SCE	standard calomel electrode

for Electronic Absorption Spectroscopy (UV / Vis)

λ	wavelength
ε	extinction coefficient

for Infrared Spectroscopy (IR)

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

for Mass Spectrometry (MS)

ES MS	electrospray mass spectra
FAB MS	fast atom bombardment mass spectra
[M]	molecular ion

m/z	mass per unit charge

for Nuclear Magnetic Resonance Spectroscopy (NMR)

δ	chemical shift (ppm)
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

IRRAS	infrared reflection absorbtion spectroscopy
OTTLE	optically transparent thin layer electrode

The Night to Make Crystals

(J.F. Hansen, in "The Chemical Bond", St. Louis Section ACS, December 1978.)

'Twas the night to make crystals, and all through the hood,
Compounds were reacting; I'd hoped that they would.
The hood door I'd closed with greatest of care,
To keep noxious vapours from fouling the air.
The reflux condensor was hooked to the tap,
And the high vacuum pump had a freshly filled trap.
I patiently waited to finish my task,
While boiling chips merrily danced in the flask.
Then from the pump there arose such a clatter
That I sprang from my chair to see what was the matter.
Away to the fume hood! Up with the door!
And half of my product foamed out on the floor.
Then what to my watering eyes should appear,
But a viscous black oil which had once been so clear.
I turned off the pump in a terrible rush,
And the oil that sucked back filled the line up with mush.
The ether boiled out of the flask with a splash,
And hitting the mantle went off with a flash.
My nose turned quite ruddy, my eyebrows went bare,
The blast had singed off nearly half of my hair.
I shut the hood door with a violent wrench,
As acid ate holes in the floor and the bench.
I flushed it with water, and to my dismay,
Found sodium hydride had spilled in the fray.
And then e'er the fire got way out of hand,
I managed to quench it with buckets of sand.
With aqueous base I diluted the crud,
Then shovelled up seven big buckets of mud.
I extracted the slurry again and again
With ether and then with dichloromethane.
Chromatographic techniques were applied
Several times 'til the product had been purified.
I finally viewed with a satisfied smile,
One half a gram in a shiny new vial.
I mailed the yield report to my boss,
Ninety percent (allowing for loss)
"Good work, " said the boss in the answering mail,
"Use same conditions on preparative scale."

- CHAPTER 1 -

Introduction

Carbon exists in many allotropic forms. The structurally well characterised examples of these allotropes are restricted to three main types: diamond, graphite and the fullerenes. While graphite and diamond have been known since antiquity the study of the fullerenes is a far more modern pursuit. The physical properties of the carbon allotropes are attributable to the different bonding of the carbon atoms in each case, and it is this structure-property relationship which has caused so much interest in the chemistry of compounds comprised solely of carbon.

Diamond consists of an infinite three-dimensional array of tetrahedral (sp^3) carbon in which each carbon atom is bonded to four tetrahedrally located others. Diamond is the hardest substance known, one of the best electrical insulators known, and yet surpasses most metals in its thermal conductivity. Consequently, diamond is used extensively in many different industrial processes.

The carbon atoms in graphite are sp^2-hybridised, and arranged in vast two-dimensional sheets. Each sheet is comprised of a planar array of fused six-membered rings. There is considerable delocalisation of the π-electrons through the carbon network, and as a result graphite is able to conduct electricity. The relatively weak van der Waals forces that exist between the sheets allows them to slide past each other, and graphite is often used as a lubricant.

Unlike diamond and graphite, the fullerenes (C_{60}, C_{70}, etc) are discrete, all-carbon *molecules*. Since the detection of C_{60} in the mass-spectrum of laser-vaporised graphite in 1985, and its isolation in 1990, there has been a extraordinary surge of interest in these all-carbon molecules. C_{60} has a cage-like structure rather like a hollow ball, and is very stable. Various uses for fullerenes have been proposed, from lubricants to molecular "capsules" which will allow the transport of sensitive drugs about the body, and many applications of these compounds are being explored [1].

There is evidence for other carbon allotropes, and the early theoretical and experimental work in this area has been reviewed [2]. While the study of new carbon networks continues to attract the attention of many workers [3], one of the simplest, most interesting, and yet more poorly characterised carbon allotropes is choaite, sometimes called karbin. The structure of chaoite is thought to contain one-dimensional cumulene (Figure 1, **A** or **C**) or alkyne (Figure 1, **B** or **D**) rods [4, 5]. Acetylenic carbon chains terminated by delocalised electrons are extremely unstable under normal conditions, and hydrogen-capped polyynes are usually only stable below room temperature [6]. It is said that end-groups bulkier than hydrogen, such as $SiEt_3$ [7], CF_3 and ^tBu [4] stabilise long chains of acetylenic carbon by hindering the close approach of the carbon chains. Whether or not these long chains of acetylenic carbon which are capped by groups containing elements other than carbon should be regarded as new allotropes of carbon is a matter for debate, but it should be remembered that both the surface of diamond and the edges of graphitic sheets are terminated by hydrogen, hydroxyl and oxide groups [8].

Modern spectroscopic techniques have detected small, reactive all-carbon molecules in various environments from hydrocarbon flames [9] to the circumstellar gas envelopes surrounding carbon-rich stars [10, 11]. Advanced computational methods have been used to predict the geometry, ionisation energy and vibrational frequencies of these all-carbon compounds [12, 13] and it appears that, in general, all-carbon molecules C_n with values of $n < 10$ adopt linear structures, while cyclic structures dominate for $n \geq 10$ [12].

The linear C_n carbon molecules may be represented by the simple structures illustrated in Figure 1. For even values of n, the simplest electronic form may be represented by either a dicarbene-cumulene **A**, or a diradical-polyyne **B**. Molecules with odd values of n may be represented by either structure **C** or the carbyne-polyyne structure **D**. There appears to be agreement that the lowest energy form of odd-numbered carbon chains ($n \leq 9$) is based on the linear cumulenic structure **C** [12, 13].

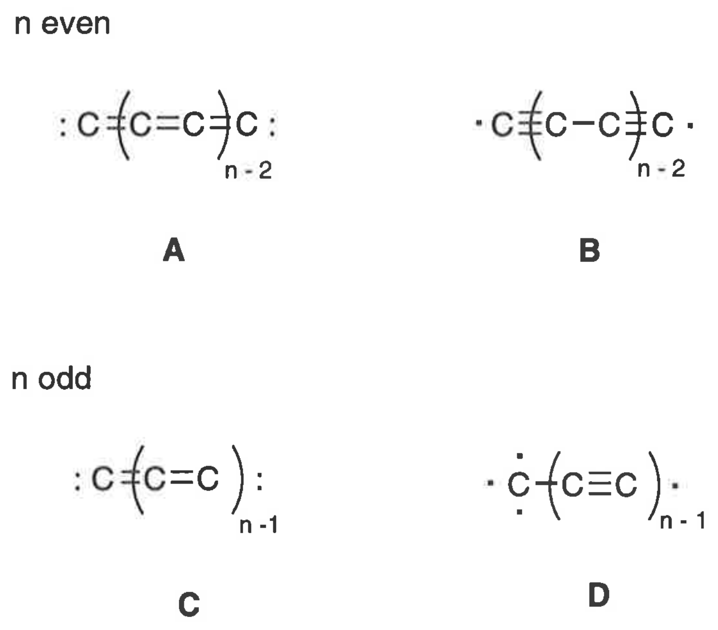


Figure 1: Electronic structures of linear C_n molecules.

The lowest energy structures of the small ($n \leq 10$), even-numbered C_n molecules are still uncertain. For example, depending on the method of calculation employed, various low energy structures have been predicted for C_4 [12, 13]. Some of these are illustrated in Figure 2. At least one study has concluded that the cumulenic $^3\Sigma_g^-$ structure **E** is essentially isoenergetic with the rhombic ^1A_g structure **G** [14]. The structures of C_6, C_8 and C_{10} are similarly uncertain [12, 13].

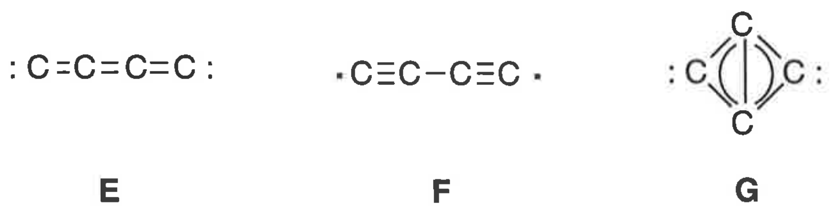
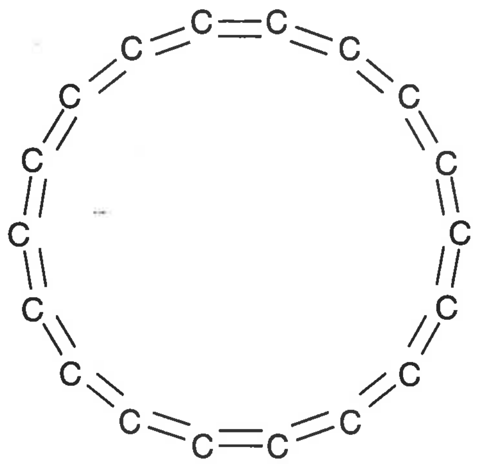


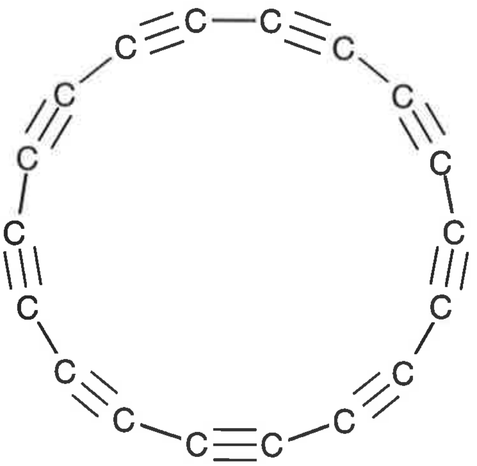
Figure 2 : Some low energy isomers of C_4.

A great deal of theoretical and experimental effort has been invested in clarifying the structures and properties of *n*-membered, monocyclic rings of carbon as these cyclo[*n*]carbons appear to play an important role in the formation of fullerenes [15-19]. The electronic properties of these compounds are also of considerable interest, as they contain two perpendicular systems of conjugated π-orbitals.

Two extreme electronic structures may be written for the cyclo[*n*]carbons. These are illustrated in Figure 3 for cyclo-C_{18}, which is the most extensively studied of these compounds to date. Cyclo-C_{18} contains a (4n + 2) electron system, and might therefore be expected to be aromatic and adopt the cumulenic structure **H**. However, there is a tendency for large conjugated systems to adopt a localised-electron structure [20]. It appears that the stability gained by aromaticity is exceeded by the tendency for electron-localisation in the cyclo[*n*]carbons for large n. The cross over point occurs near C_{14}, and consequently cyclo-C_{18} adopts the localised-electron (polyyne) structure **I**. The synthetic routes to these cyclic compounds, and the theoretical predictions of the structures they adopt, have been reviewed [5, 12, 21].



H



I

Figure 3 : Two structural isomers of cyclo-C_{18}.

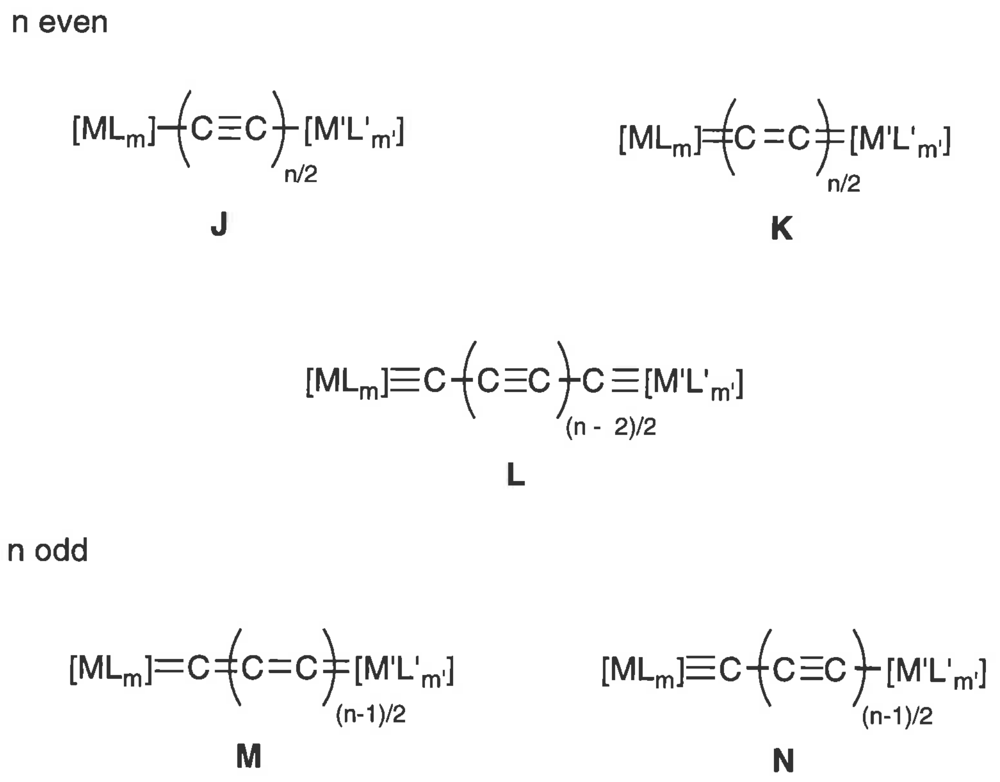
Bimetallic Complexes with All-Carbon Ligands.

The study of metal complexes containing ligands comprised solely of carbon has become an area of intense interest in recent years [22-25]. It is thought that unusual allotropes of carbon may be stabilised as metal complexes not only as a result of the steric protection afforded by the bulky metal fragment, but also through interactions between molecular orbitals from the carbon fragment with metal-based orbitals of the appropriate symmetry. In addition to the intrinsic fascination with these complexes, metal complexes containing ligands comprised solely of carbon are being actively pursued as precursors to useful new materials. For example, the presence of charge-transfer bands in the UV and visible regions of the spectrum, which are common for transition metal species, are often associated with compounds which display large second-order non-linear optical effects [26].

Binuclear complexes in which the metal centres are linked by a μ-C_n ligand may be represented by the structures shown in Figure 4. The complexes containing bridges with an even number of carbon atoms in the bridge may exist in one of several forms **J** - **L**. The odd-numbered bridges occur as either **M** (cumulene-like) or **N** (carbyne-like).

Bimetallic Complexes of C_1.

Organometallic complexes in which a single carbon atom bridges two metal atoms have been investigated as model complexes for surface-bound carbides [27]. The bonding in these complexes may be represented by a dicarbene structure (**M**), as in $\{(tpp)Fe\}=C=\{Fe(CO)_4\}$ (tpp = tetraphenylporphyrinate) [22], or by a metallo-carbyne (**N**), as in $\{(^tBuO)_3W\}\equiv C-\{Ru(CO)_2Cp\}$ [28].



$[ML_m]\text{–}(C{\equiv}C)_{n/2}\text{–}[M'L'_{m'}]$ **J**

$[ML_m]{=}(C{=}C)_{n/2}{=}[M'L'_{m'}]$ **K**

$[ML_m]{\equiv}C\text{–}(C{\equiv}C)_{(n-2)/2}\text{–}C{\equiv}[M'L'_{m'}]$ **L**

$[ML_m]{=}C{=}(C{=}C)_{(n-1)/2}{=}[M'L'_{m'}]$ **M**

$[ML_m]{\equiv}C\text{–}(C{\equiv}C)_{(n-1)/2}\text{–}[M'L'_{m'}]$ **N**

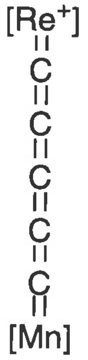
Figure 4 : Electronic structures of bimetallic complexes with bridging C_n ligands.

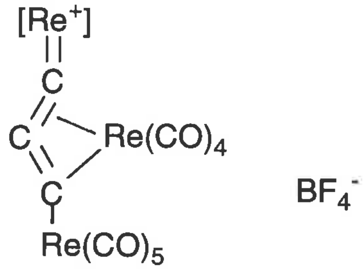
Metal Complexes of C_2.

Three valence bond descriptions may be used to describe the μ-η^1:η^1-dicarbon bridge (see Figure 4). While the most common is the acetylenic form **J** [22], complexes such as $\{(^tBu_3SiO)_3Ti\}{=}C{=}C{=}\{Ti(OSi^tBu_3)_3\}$ [29] and $\{(^tBuO)_3W\}{\equiv}C\text{-}C{\equiv}\{W(O^tBu)_3\}$ [30], containing examples of the cumulenic (**K**) and dicarbyne (**L**) structures respectively, are known. For lead references to binuclear complexes of C_2, the reader is referred an excellent review article by Beck, Niemer and Wieser [22]. A recent theoretical study has examined the factors influencing the electronic arrangement of the dicarbon μ-C_2 ligand in some binuclear complexes [31].

Metal Complexes of C_3 and C_5.

The mixed rhenium / manganese complexes $[\{Cp^*(PPh_3)(NO)Re\}{=}C{=}(C{=}C)_n{=}\{Mn(CO)_2(\eta\text{-}C_5H_{5\text{-}x}Cl_x)\}][BF_4]$ (n = 1, x = 0 [32], 5 [33]; n = 2, x = 5 [33]) are rare examples of complexes in which a C_3 or C_5 ligand spans the metal termini. The spectral properties of these compounds suggests that the carbon bridge is best described by the cumulenic structure **M** (Figure 4). The trimetallic complex $[\{Cp^*(PPh_3)(NO)Re\}(\mu\text{-}\eta^1{:}\eta^3{:}\eta^1C_3)\{Re(CO)_4\}\{Re(CO)_5\}][BF_4]$ contains a bent C_3 ligand [34].





$[Re^+] = Re(NO)(PPh_3)Cp^*$

$[Mn] = Mn(CO)_2(\eta\text{-}C_5Cl_5)$

Metal Complexes of C_4.

The earliest report of a transition metal complex containing a bridging C_4 ligand, $K_8[\{(NC)_5Fe\}C{\equiv}CC{\equiv}C\{Fe(CN)_5\}]$, was made by Nast and Urban in 1957 [35]. While there have been several more recent accounts of the synthesis of complexes bearing the C_4 ligand [36-47], remarkably few of these contain carbon chains capped by two different metal atoms or metal-ligand fragments [48-50]. In the vast majority of these C_4 complexes the carbon ligand has considerable diacetylenic character (Figure 4, **J**). The synthetic approaches to these diyndiyl complexes are summarised below. A notable conversion between the structural types **A** and **B** has been observed following oxidation of the complex $\{Cp^*(PPh_3)(NO)Re\}C{\equiv}CC{\equiv}C\{Re(NO)(PPh_3)Cp^*\}$ to the dication $[\{Cp^*(PPh_3)(NO)Re\}{=}C{=}C{=}C{=}C{=}\{Re(NO)(PPh_3)Cp^*\}]^{2+}$ [45].

Metal Complexes of Diacetylenes - Diynyl and Diyndiyl Complexes.

Metal complexes bearing polyacetylide complexes are attractive synthetic targets. In addition to the obvious application of these complexes as precursors to complexes of all-carbon molecules C_n, these complexes are a source of interest in their own right. Given the extensive reactivity that has been demonstrated for the C≡C and C≡CR functional groups in organic and organometallic chemistry [51], transition metal polyacetylide complexes should extraordinarily reactive species. These complexes also promise to display unusual electrochemical properties, and the C_4 bridge has been shown to allow strong electronic coupling between redox active centres [43, 52, 53].

In the search for materials which display useful physical properties several groups have examined the preparation of *trans*-bis(polyacetylide) complexes [54-57]. However, complexes in which alkynyl ligands are disposed at angles other than 180° to each other also offer intriguing possibilities for further development. The compounds may be employed as molecular "tweezers" to stabilise various mono-nuclear fragments, in a manner reminiscent of more traditional host-guest chemistry (Figure 5). Several workers are actively pursuing this aspect of the chemistry of diynyl complexes [58-60].

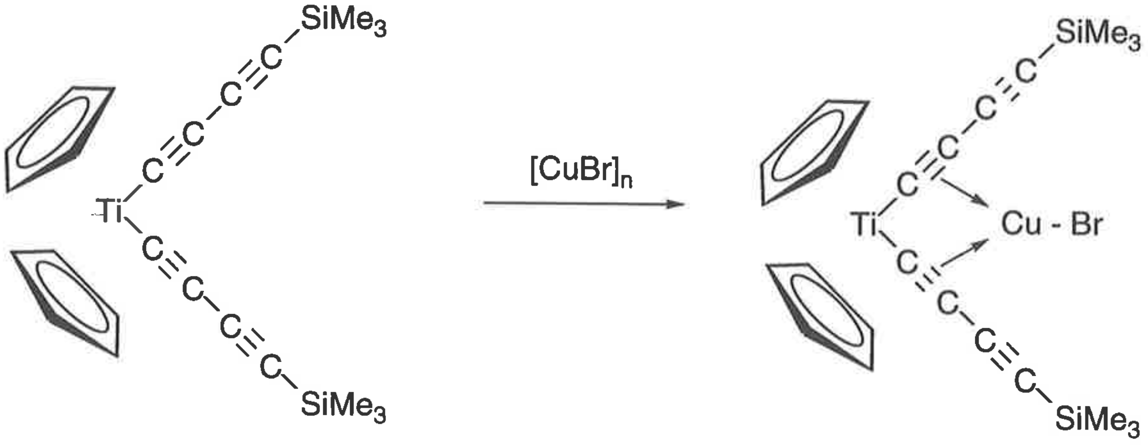


Figure 5 : A Pair of "Molecular Tweezers" [58].

In the design of macromolecules with novel molecular architectures square planar complexes with *cis*-{bis(diynyl)} ligands are useful building blocks with the ability to form the corner pieces of molecular squares and rectangles (Figure 6). The cavities of these large macrocyclic complexes would be lined with regions of π-electrons and as a result may well display unusual coordination and inclusion chemistry.

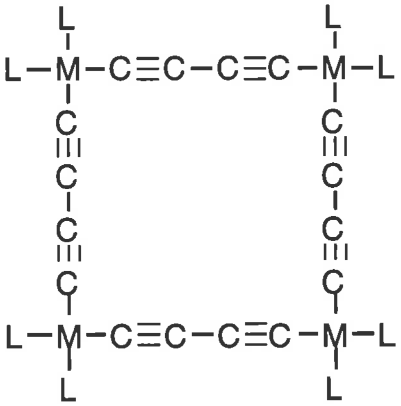


Figure 6 : A "molecular square" assembled from square planer metal fragments and C_4 ligands

Metal Complexes of C_n ($n \geq 4$).

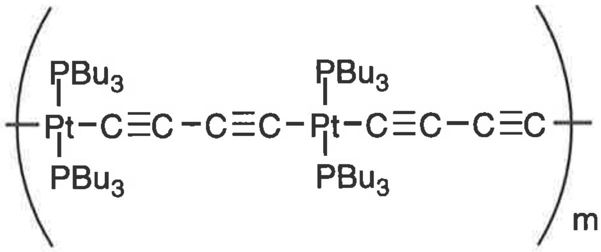
Copper mediated oxidative coupling reactions of the metal complexes $[ML_m]\{(C{\equiv}C)_xC{\equiv}CH\}$ (ML_m = $Ni(PPh_3)Cp$ [37], $Re(NO)(PPh_3)Cp^*$ [36, 52], $Fe(dppe)Cp^*$ [61]) have yielded bimetallic complexes containing (even-numbered) polycarbon chains up to C_{20}. This approach to the synthesis of long acetylenic carbon chains which are capped by transition metals is completely analogous to the synthesis of purely organic acyclic polyynes.

$$[L_mM]\!\left(C{\equiv}C\right)_x C{\equiv}CH \xrightarrow{\text{oxidative coupling}} [L_mM]{-}C{\equiv}C\left(C{\equiv}C\right)_{2x}C{\equiv}C{-}[ML_m]$$

A number of different metal complexes containing coordinated fullerene (C_{60}) ligands have been prepared. While these complexes contain examples of the largest all-carbon ligands isolated to date [62-66], various mass spectrometric studies have detected much larger M_yC_n species [67].

Polymeric Metal Complexes of C_n.

Polymeric materials containing transition metal centres incorporated into a polyacetylenic backbone have been extensively investigated in recent times as a result of the potentially useful liquid crystalline [68] and magnetic properties they display [69], and the possible application of these compounds in the preparation of materials which display large third-order non-linear optical effects [26, 70-72]. To date, the backbones of most of these metal-polyyne polymers have been based upon diynyl monomers of general form *trans*-[{$M(PR_3)_2$}C≡CC≡C-] (M = Pd, Pt). A typical example [73, 74] is illustrated below.



Electrochemistry of C_n-Bridged Bimetallic Complexes.

Several studies have been directed to the study of the redox properties of some C_n ligands terminated by various redox-active end-caps, including porphyrins [53] and metal clusters [75-77]. However, it is not yet clear to what extent these oxidation processes, and the resulting effects on the bridging ligand, are governed by the nature of the metal centre and other supporting ligands.

The redox active bis-metal polyacetylide complexes [Fe](C≡C)$_m$[Fe] ([Fe] = Fe(dppe)Cp*, m = 2 [43], 4 [61]) and [Re](C≡C)$_m$ [Re] ([Re] = Re(NO)(PPh$_3$)Cp*, m = 2 [36, 45], 3 [36], 4 [36], 6 [52], 8 [52], 10 [52]) have recently been prepared by Lapinte and Gladysz and their respective co-workers. As the length of the chain spanning the metal termini increases, the degree of electronic interaction steadily decreases, until the metal centres become equivalent, as in the deca-yne {Cp*(PPh$_3$)(NO)Re}(C≡C)$_{10}${Re(NO)(PPh$_3$)Cp*} [52]. The interactions between the metal centres are therefore strongest in the diyndiyl (C_4) complexes.

Transition Metal Clusters with C_n Ligands.

Small carbon molecules have also been stabilised by multi-site attachment to metal clusters. These carbido clusters may be grouped into two broad classes: those in which the carbon atom(s) are fully encapsulated by the metal framework; and those in which the carbon ligand is exposed on one face of the cluster. The encapsulated carbon ligands, while of interest from a structure and bonding point of view, are generally unreactive as they are buried deep in the cluster core. On the other hand, the reactions of exposed carbon ligands are remarkable for their diversity. In adddition to the intrinsic fascination these compounds hold, transition metal clusters with exposed carbon ligands are interesting models for the carbon fragments which are involved during reations of carbon monoxide and acetylenes on heterogenous catalyst surfaces.

Compounds containing an encapsulated, or partially encapsulated, carbide (C_1) ligands have been known for many years, with the first example $Fe_5C(CO)_{15}$ being isolated by Dahl and co-workers in 1962 [78]. Several dicarbide clusters are known, and these fall into three catagories, those with two separated C_1 ligands, such as the anionic cluster $[Ru(\mu_6\text{-}C)_2(\mu\text{-}CO)_4(CO)_{20}]^{2-}$ [79], those with a fully-encapsulated C_2 ligand, as in $[Rh_{12}(C_2)(CO)_{24}]^{2-}$ [80], and those in which the dicarbon ligand is exposed on one face of the cluster, as in the pentanuclear ruthenium cluster $Ru_5(\mu_5\text{-}C_2)(\mu\text{-}PPh_2)_2(\mu\text{-}SMe)_2(CO)_{11}$ [81].

Several complexes in which metal cluster fragments are linked by a C_n ligand are also known, although the reactivity of these all-carbon bridges remains essentially unexplored [82].

The chemistry of these carbon-containing clusters has been reviewed several times [83].

Preparation of Complexes with Diynyl, Diyndiyl and Other Polyacetylide Ligands.

Metal complexes containing σ-bonded polyacetylide ligands have been prepared using many different synthetic approaches. As an aid to the discussion, these synthetic methods have been summarised under the categories:

A. Syntheses from diacetylide anions and metal-halide complexes.
B. Cu(I) catalysed reactions of 1,3-diynes with metal-halide complexes.
C. Oxidative addition of terminal diynes to suitable electron deficient metal centres.
D. Reactions between metal halides and organostannanes.
E. Deprotonation of vinylidene-like intermediates and complexes
F. Coupling reactions of $[ML_m](C{\equiv}C)_nH$ complexes.

A brief description of each method follows.

A. Syntheses from diacetylide anions and metal-halide complexes

The acetylenic hydrogens of 1,3-diynes are as acidic as 1-alkynes and therefore readily form alkali metal salts and organomagnesium derivatives [84]. Thus, careful treatment of $HC{\equiv}CC{\equiv}CR$ (R = H, alkyl, trialkylsilyl, aryl) with one equivalent of EtMgBr or BuLi affords $BrMgC{\equiv}CC{\equiv}CR$ or $LiC{\equiv}CC{\equiv}CR$, respectively. This approach suffers from the difficulties associated with preparing the highly sensitive, and potentially explosive, 1,3-diynes. The mono-sodium and lithium salts of buta-1,3-diyne also have a tendency to disproportionate to give insoluble dianions, and reactions involving these species are therefore exceptionally sensitive to the conditions employed.

Alternative syntheses of diacetylide anions include treatment of *cis*-$HC{\equiv}CCH{=}CH(OMe)$ with two equivalents of BuLi to give $LiC{\equiv}CC{\equiv}CH$ and LiOMe [85], and the preparation of the trimethylsilyl derivative $LiC{\equiv}CC{\equiv}CSiMe_3$ by monodesilylation of 1,4-bis(trimethylsilyl)buta-1,3-diyne with MeLi.LiBr [86].

The dialkynyl carbanions are sufficiently nucleophilic to displace halide ligands from a variety of transition metal complexes to give metal diynyl compounds. Examples of complexes prepared in this manner include $Ni(C{\equiv}CC{\equiv}CH)(PPh_3)Cp$ (from $NiCl(PPh_3)Cp$ and $BrMgC{\equiv}CC{\equiv}CH$) [37], $Fe(C{\equiv}CC{\equiv}CSiMe_3)(CO)_2Cp$ [from $FeCl(CO)_2Cp$ and $LiC{\equiv}CC{\equiv}CSiMe_3$; Equation 1] [49] and $Ti(C{\equiv}CC{\equiv}CEt)_2(\eta^5\text{-}C_5H_4SiMe_3)_2$ [from $TiCl_2(\eta^5\text{-}C_5H_4SiMe_3)_2$ and $LiC{\equiv}CC{\equiv}CEt$] [58].

$$[L_mM]\text{-}X + LiC{\equiv}C{-}C{\equiv}CR \xrightarrow{-\,LiX} [L_mM]C{\equiv}C{-}C{\equiv}CR$$

for example $[L_mM]\text{-}X = FeCl(CO)_2Cp$
$R = SiMe_3$

Equation 1.

The reactivity of the η^1-diynyl ligand also closely resembles that of the purely organic analogue and complexes bearing $C{\equiv}CC{\equiv}CSiMe_3$ ligands are readily desilylated under standard conditions to give the corresponding terminal diynyl complexes [48, 49, 57, 61]. Thus treatment of $Fe(C{\equiv}CC{\equiv}CSiMe_3)(CO)_2Cp$ with fluoride gave $Fe(C{\equiv}CC{\equiv}CH)(CO)_2Cp$ [49].

The diynyl protons in $Fe(C{\equiv}CC{\equiv}CH)(CO)(L)Cp$ (L = CO, PPh_3) [49] and $Re(C{\equiv}CC{\equiv}CH)(NO)(PPh_3)Cp^*$ [48] are sufficiently acidic to be removed by strong bases, such as BuLi. The resulting $[ML_n]C{\equiv}CC{\equiv}CLi$ species have been trapped by reaction with a variety of organic and organometallic reagents containing electrophilic centres to give substituted derivatives. Examples of compounds prepared in this manner include the simple methyl derivative $Re(C{\equiv}CC{\equiv}CMe)(NO)(PPh_3)Cp^*$ [48], bimetallic species such as $\{Cp(CO)_2Fe\}C{\equiv}CC{\equiv}C\{W(CO)_3Cp\}$ [49] (Equation 2), $\{$*trans*-$(PEt_3)_2ClPd\}C{\equiv}CC{\equiv}C\{Re(NO)(PPh_3)Cp^*\}$ and *trans*-$\{Cp^*(PPh_3)(NO)Re\}C{\equiv}CC{\equiv}C\{Pd(PEt_3)_2\}C{\equiv}CC{\equiv}C\{Re(NO)(PPh_3)Cp^*\}$, and the Fischer carbene complex $Cp^*(PPh_3)(NO)ReC{\equiv}CC{\equiv}CC(OMe){=}\{Mn(CO)_2(\eta^5\text{-}C_5Cl_5)\}$ [33].

$$[L_mM]C{\equiv}C{-}C{\equiv}CH \xrightarrow[\text{2) } [L'_{m'}M']\text{-}X]{\text{1) Base}} [L_mM]C{\equiv}C{-}C{\equiv}C[M'L'_{m'}]$$

for example $[L_mM] = Fe(CO)_2Cp$

$[L'_{m'}M']\text{-}X = WCl(CO)_3Cp$

Equation 2.

The dianionic diacetylide reagent $LiC{\equiv}CC{\equiv}CLi$ has been used recently to prepare the bis(transition metal) complexes $\{Cp(CO)_2Fe\}C{\equiv}CC{\equiv}C\{Fe(CO)_2Cp\}$ [49] and $\{Cp(PPh_3)_2Ru\}C{\equiv}CC{\equiv}C\{Ru(PPh_3)_2Cp\}$ [41] from reactions with $FeCl(CO)_2Cp$ [49] or $[Ru(thf)(PPh_3)_2Cp]PF_6$ [41] respectively (Equation 3).

$$2\,[L_mM]\text{-}X + LiC{\equiv}C{-}C{\equiv}CLi \longrightarrow [L_mM]C{\equiv}C{-}C{\equiv}C[ML_m]$$

$[L_mM] = Fe(CO)_2Cp$, $X = Cl$

$[L_mM] = Ru^+(PPh_3)_2Cp$, $X = thf$

Equation 3.

B. Cu(I) catalysed reactions of 1,3-diynes with metal-halide complexes.

In transition metal chemistry, the use of CuI to catalyse the reaction between metal halide species and 1-alkynes has considerable precedence [87, 88] (Equation 4).

$$PtX_2L_2 \quad + \quad HC{\equiv}CR \xrightarrow[NH_{3-n}R'_n]{CuI} Pt(C{\equiv}CR)_2L_2$$

$X = Cl, Br$

$L = PEt_3, PBu_3, PPh_3$

$R = H, Ph, C_2H, CH_2OH$, etc

$$[L_mM]\text{-}Cl \quad + \quad HC{\equiv}CPh \xrightarrow[NH_{3-n}R'_n]{CuI} [L_mM]C{\equiv}CPh$$

$[L_mM] = W(CO)_3Cp;\ Fe(CO)_2Cp;\ Ni(PPh_3)Cp$

Equation 4.

While the mechanism of these reactions has not been investigated in detail, it is likely that an intermediate copper(I) acetylide is formed, which undergoes a halide exchange reaction with the $[L_mM]$-X species, resulting in the formation of the transition metal σ-acetylide complex and a Cu(I) halide, which completes the catalytic cycle.

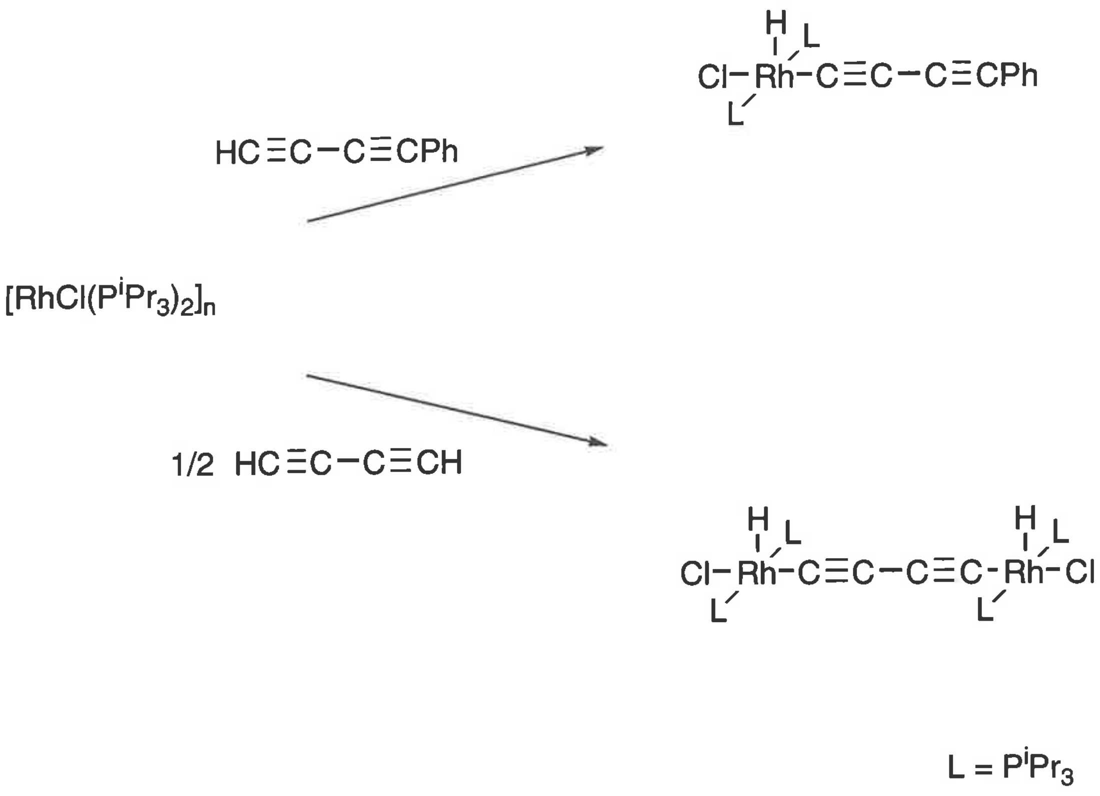
The synthesis of bis-dialkynyl complexes of Pt(II) using this approach was initially explored by the Hagihara group in the course of pioneering studies directed towards the synthesis of polymers containing Group 10 metals in the polymer backbone [50, 73, 74, 89]. For example, reaction of *trans*-$PtCl_2(PBu_3)_2$ with buta-1,3-diyne in the presence of Cu(I) afforded the bis-butadiynyl complex *trans*-$Pt(C{\equiv}CC{\equiv}CH)_2(PBu_3)_2$ in 82% yield (Equation 4, $R = C_2H$) [88].

The reaction was has been extended to the preparation of oligermeric complexes, and *trans*-$\{(PBu_3)_2ClPd\}C\equiv CC\equiv C\{Pt(PBu_3)_2\}C\equiv CC\equiv C\{PdCl(PBu_3)_2\}$ was readily obtained following treatment of $Pt(C\equiv CC\equiv CH)_2(PBu_3)_2$ with two equivalents of $PdCl_2(PBu_3)_2$ in the presence of a catalytic amount of CuI [50]. High molecular weight polymers were prepared in similar fashion from the reaction of equimolar amounts of the bis(diynyl) complex with equimolar amounts of the dihalide.

The nickel bis-dialkynyl complex *trans*-$Ni(C\equiv CC\equiv CH)_2(PBu_3)_2$ has been prepared by Cu(I)-catalysed alkynyl ligand exchange between the complex *trans*-$Ni(C\equiv CH)_2(PBu_3)_2$ and buta-1,3-diyne [54].

C. Oxidative Addition of 1,3-Diynes to Suitable Electron Deficient Metal Centres.

The Werner group has developed the chemistry of the labile Rh(I) complexes $RhL(P^iPr_3)_2$ [$L = \eta^2\text{-}O_2CCH_3$, $\eta^3\text{-}CH_2Ph$] and the halide-bridged polymeric species $\{RhCl(P^iPr_3)_2\}_n$ with $HC\equiv CC\equiv CR$ (R = H, Ph) [47, 90]. Oxidative addition of the diyne C-H bond to the metal centre readily afforded rhodium diynyl complexes. For example, the polymeric rhodium(I) complex $[RhCl(P^iPr_3)_2]_n$ reacted with $HC\equiv CC\equiv CPh$ to give the Rh(III)-diynyl compound $RhHCl(C\equiv CC\equiv CPh)(P^iPr_3)_2$ (Equation 5), while the acetato complex $Rh(\eta^2\text{-}O_2CCH_3)(P^iPr_3)_2$ reacted with two equivalents of phenylbutadiyne in the presence of Na_2CO_3 to afford the five-coordinate bis-phenylbutadiynylhydridorhodium(III) complex $RhH(C\equiv CC\equiv CPh)_2(P^iPr_3)_2$ [47]. The bimetallic complexes $\{(P^iPr_3)_2ClHRh\}C\equiv CC\equiv C\{RhHCl(P^iPr_3)_2\}$ and $[\{RhH(PMe_3)_4\}C\equiv CC\equiv C\{RhH(PMe_3)_4\}]Cl_2$ were prepared in a similar manner from the oxidative addition of both $C\equiv CH$ moieties of buta-1,3-diyne to $\{RhCl(P^iPr_3)_2\}_n$ [46] (Equation 5) or $[Rh(PMe_3)_4]Cl$ [38] respectively.



Equation 5 : Examples of Oxidative Addition Reactions of 1,3-Diynes [46, 90].

D. *Syntheses from Organostannanes.*

The Stille reaction, in which an aryl-, alkenyl or alkylstannane is cross-coupled with an aryl or vinyl halide, pseudo-halides or arenediazonium salt in the presence of a Pd(0) catalyst, has become a common method for the preparation of new carbon-carbon bonds (Equation 6) [91-93].

$$\text{R-X} + \text{R'SnR''}_3 \xrightarrow{\text{"Pd(0)"}} \text{R-R'} + \text{X-SnR''}_3$$

Equation 6 : The Stille Reaction.

Different groups on the tin centre are transferred at different rates. A simple alkyl group has the lowest transfer rate. It is therefore usual to use trimethyl or butyl tin derivatives to couple alkynyl, alkenyl, benzyl or allyl groups with aryl, alkenyl, alkynyl or benzyl halides. It has been demonstrated recently that a similar approach may be used to form new metal-carbon bonds. Treatment of $FeI(CO)_2Cp$ with one equivalent of $Me_3SnC{\equiv}CC{\equiv}CH$ in the presence of $PdCl_2(NCMe)_2$, from which the catalytically active Pd(0) species was generated *in situ*, gave the σ-diacetylide complex $Fe(C{\equiv}CC{\equiv}CH)(CO)_2Cp$ (Equation 7). The diyndiyl complex $\{Cp(CO)_2Fe\}C{\equiv}CC{\equiv}C\{Fe(CO)_2Cp\}$ was obtained in similar fashion from $FeI(CO)_2Cp$ and one-half equivalent of $Me_3SnC{\equiv}CC{\equiv}CSnMe_3$ [40].

$$[Pd(II)L_2]Cl_2 \xrightarrow[-\ 2\ Me_3SnCl]{+\ 2\ Me_3SnC{\equiv}CR} RC{\equiv}C{-}[Pd(II)]{-}C{\equiv}CR$$

$$\Big\downarrow\ -\ RC{\equiv}C{-}C{\equiv}CR$$

$$[Pd(0)L_2]$$

$R = C{\equiv}CH$

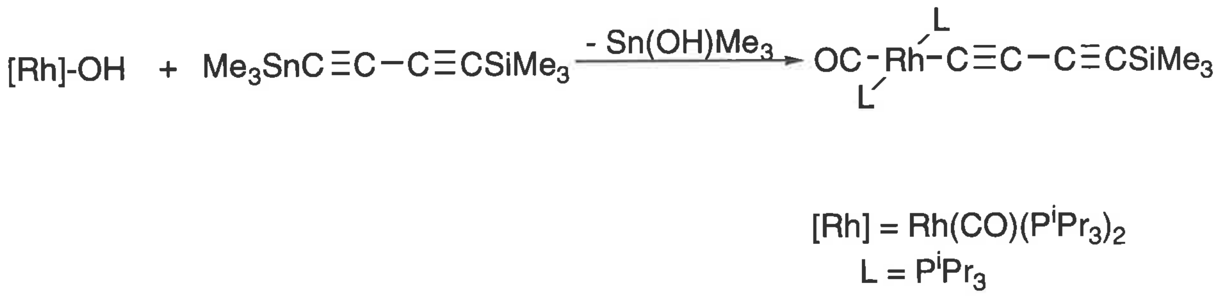
$L = NCMe, PPh_3$

$$[Fe]\text{-}I \ + \ Me_3SnC{\equiv}C{-}C{\equiv}CH \xrightarrow{\text{"Pd(0)"}} [Fe]C{\equiv}C{-}C{\equiv}CH$$

$[Fe] = Fe(CO)_2Cp$

Equation 7.

Organostannanes have been used by several groups in other one-pot preparations of diynyl complexes. For example, treatment of the labile (hydroxy)rhodium(I) complex *trans*-$Rh(OH)(CO)(P^iPr_3)_2$ with $Ph_3SnC{\equiv}CC{\equiv}CSiMe_3$ gave *trans*-$Rh(C{\equiv}CC{\equiv}CSiMe_3)(CO)(P^iPr_3)_2$. There was no requirement for a catalyst, and the reaction was presumably driven by the elimination of $Sn(OH)Ph_3$, [47] (Equation 8). Dixneuf and coworkers have reported that the reaction of $RuCl_2(dppm)_2$ with $Bu_3SnC{\equiv}CC{\equiv}CCPh_2(OSiMe_3)$ in the presence of $NaPF_6$ resulted in the elimination of $SnClBu_3$ and the formation of *trans*-$RuCl\{C{\equiv}CC{\equiv}CCPh_2(OSiMe_3)\}(dppm)_2$ in moderate yield (30%) [94].



Equation 8.

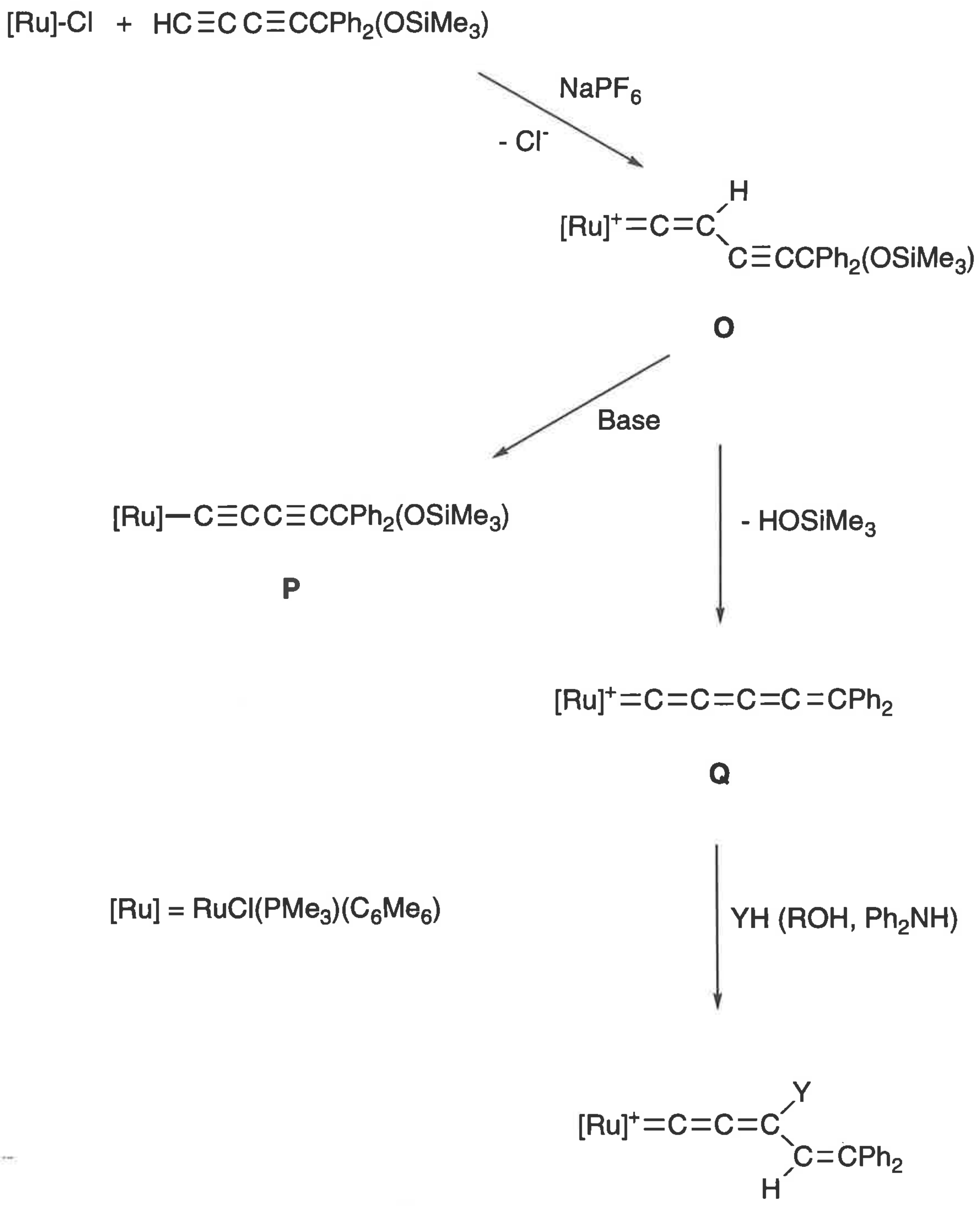
Similar reactions of the reagents $Me_3SnC{\equiv}C(C{\equiv}C)_mSnMe_3$ with the platinum di-chloride complexes $PtCl_2(YBu_3)_2$ (Y = P, As) have been employed by the Lewis group to prepare high molecular weight polymers of general form $\{Pt(YBu_3)_2\text{-}C{\equiv}C(C{\equiv}C)_m\text{-}\}_n$ [56].

E. Deprotonation of Vinylidene-like Intermediates and Complexes.

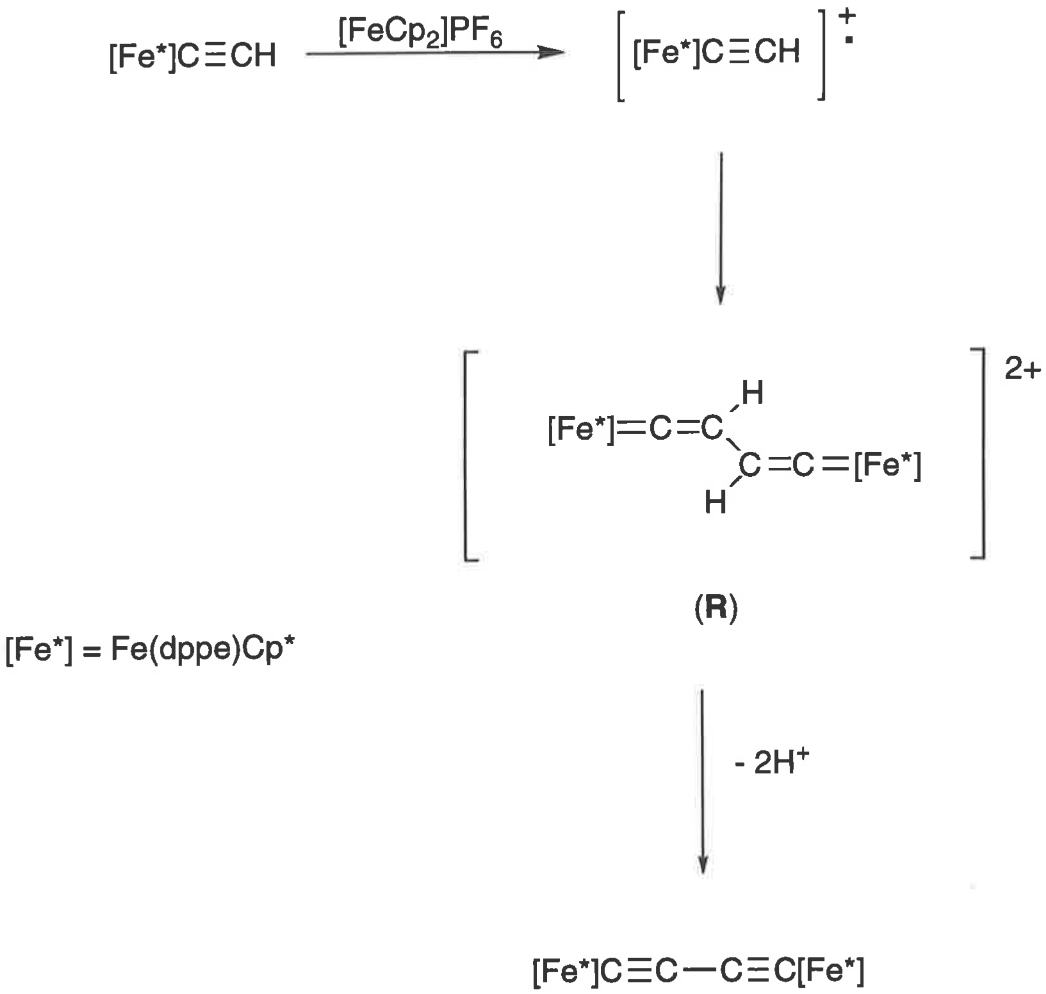
The deprotonation of vinylidene complexes is one of the most general methods of preparing transition metal acetylide complexes [95]. Vinylidene complexes are conveniently obtained from the reaction of 1-alkynes with a wide variety of transition metal complexes *via* a 1,2-H shift [96]. Similar reactions of the 1,3-diyne $HC{\equiv}CC{\equiv}CCPh_2(OSiMe_3)$ with $RuCl_2(PMe_3)(C_6Me_6)$ have been examined by Dixneuf and co-workers. The reactions are thought to proceed *via* the ethynylvinylidene intermediate (**O**) indicated in Scheme 1. In the presence of a strong, non-nucleophilic bases such as NEt_3 or NH^iPr_2, the diynyl complex Ru{C≡CC≡CC(OSiMe$_3$)}Cl(PMe$_3$)(C$_6$Me$_6$) (**P**) was formed. Similar reactions have been used to prepare [Ru{C≡CC≡CCPh$_2$(OSiMe$_3$)}$_2$(dppm)$_2$] [94] and RuCl{C≡CC≡CCPh$_2$(OSiMe$_3$)}(L)(η^6-C$_6$Me$_6$) (L = PMe$_3$, PMePh$_2$) [97].

In the absence of the base elimination of Si(OH)Me$_3$ occurs to give the pentatrienylidene complex **Q**, which readily adds nuclephiles at C_γ. For example, the alkenylallenylidenes [RuCl{C=C=C(OR)CH=CPh$_2$}(L)(C$_6$Me$_6$)]PF$_6$ (R = Et, Pr^i; L = PMe$_3$, PMePh$_2$) were obtained from the reaction of HC≡CC≡CCPh$_2$(OSiMe$_3$) with RuCl$_2$(L)(C$_6$Me$_6$) in the presence of NaPF$_6$ and the appropriate alcohols. Similarly, the reaction of RuCl$_2$(dppm)$_2$ with HC≡CC≡CCPh$_2$(OSiMe$_3$) and NaPF$_6$ in MeOH gave [RuCl{C=C=C(OMe)CH=CPh$_2$}(dppm)$_2$]PF$_6$. This chemistry has recently been reviewed by Le Bozec and Dixneuf [98].

The complex {Cp*(dppe)Fe}C≡CC≡C{Fe(dppe)Cp*} has been prepared by a two-step reaction [42, 43]. Oxidation of Fe(C≡CH)(dppe)Cp* with [FcH]PF$_6$ gave the 17-electron species [Fe(C≡CH)(dppe)Cp*][PF$_6$]. Usually, 17-electron metal species dimerise through metal-metal interactions [99, 100], but in the case of the [Fe(C≡CH)(dppe)Cp*]$^+$ cation, the extreme steric crowding about the metal centre prevents the metal centres from approaching close enough for any significant interaction to occur. Instead, coupling occurs between the acetylide ligands to yield the bis(vinylidene) compound [{Cp*(dppe)Fe}=C=C(H)C(H)=C={Fe(dppe)Cp*}][PF$_6$]$_2$ (**R**), which upon treatment with KO^{t}Bu gave the desired diacetylide complex (Scheme 2)



Scheme 1: A Ruthenium Diynyl Complex Prepared *via* a Vinylidene Intermediate [98].



[Fe*] = Fe(dppe)Cp*

Scheme 2 : Synthesis of {Cp*(dppe)Fe}C≡CC≡C{Fe(dppe)Cp*} [43].

F. Coupling reactions of [ML$_n$]C≡CH complexes.

The preparation of symmetrically substituted diynes is usually accomplished by oxidative coupling reactions of 1-alkynes. Whilst many different reaction conditions have been established for the homo-coupling of terminal organic alkynes [101], there are few examples of coupling reactions of C≡CH units in the metal coordination sphere.

As mentioned previously, the first example of a complex containing a $\mu,\eta^1:\eta^1$-C≡CC≡C ligand, $K_8[\{Fe(CN)_5\}C{\equiv}CC{\equiv}C\{Fe(CN)_5\}]$, was isolated by Nast and Urban after treating a solution of $K_4[Fe(C{\equiv}CH)(CN)_5]$ with NH_2NO [35]. Some years later, the Hagihara group used the Hay conditions (CuCl / tmeda, O_2) [102] to prepare a number of polyyne complexes including $[ML_n]C{\equiv}CC{\equiv}C[ML_n]$ [ML_n = $Ni(PPh_3)Cp$, $Fe(CO)_2Cp$] by oxidative coupling of $[ML_n]C{\equiv}CH$ complexes (Equation 9) [37].

$$2\ [L_mM]{-}C{\equiv}C{-}H \xrightarrow[Me_2NCH_2CH_2NMe_2]{CuCl\ /\ O_2} [L_mM]{-}C{\equiv}C{-}C{\equiv}C{-}[ML_m]$$

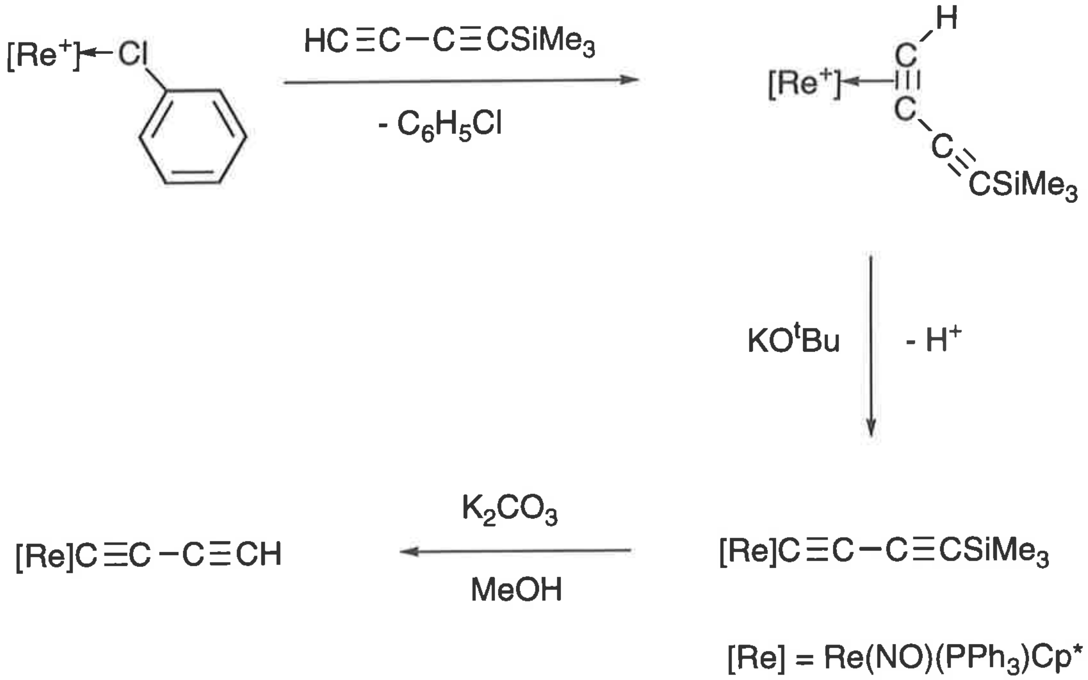
$$[L_mM] = Ni(PPh_3)Cp,\ \ Fe(CO)_2Cp$$

Equation 9 : Hay Coupling of Metal Acetylides [37].

The related rhenium complex $\{Cp^*(PPh_3)(NO)Re\}C{\equiv}CC{\equiv}C\{Re(NO)(PPh_3)Cp^*\}$ was prepared by Eglinton coupling [$Cu(OCOMe)_2$ / pyridene] [103] of the metal alkynyl complex $Re(C{\equiv}CH)(NO)(PPh_3)Cp^*$ [36, 45]. Similar conditions have also been used to prepare $[31](C{\equiv}C)_m[31]$ (m = 3 - 10) [52] and $\{Cp^*(dppe)Fe\}(C{\equiv}C)_4\{Fe(dppe)Cp^*\}$ [61] from the appropriate terminal polyacetylide precursors.

G. Miscellaneous Preparations.

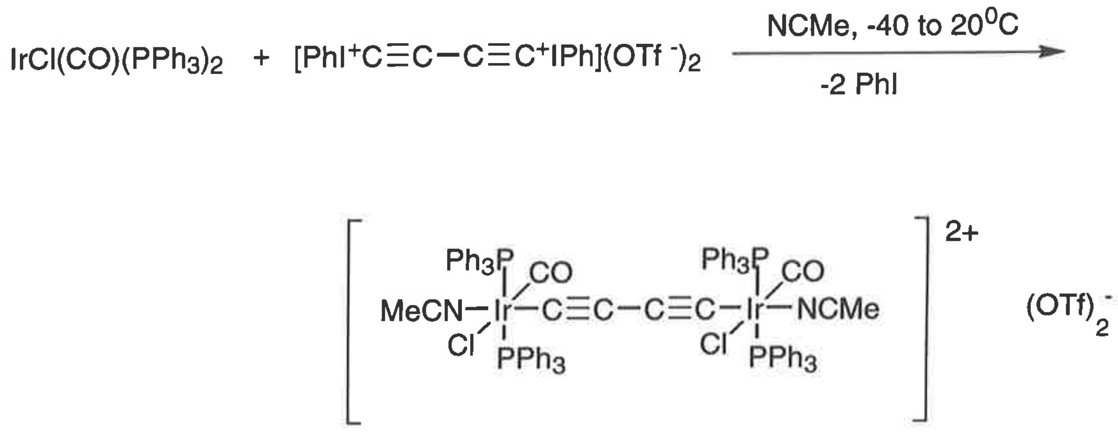
Gladysz and coworkers have prepared the complex $Re(C{\equiv}CC{\equiv}CSiMe_3)(NO)(PPh_3)Cp^*$ by the multi-step synthesis illustrated in Scheme 3. The key step in this approach is the preparation and subsequent deprotonation of the η^2-alkyne complex $[Re(\eta^2\text{-}HC_2C{\equiv}CSiMe_3)(NO)(PPh_3)Cp^*]^+$ [48]. The $SiMe_3$ protecting group was readily removed in methanolic K_2CO_3 to give the terminal diynyl complex Re(C≡CC≡CH)(NO)(PPh_3)Cp* (Scheme 4).



Scheme 4 : Synthesis of Re(CCCCH)(NO)(PPh_3)Cp* [48].

Werner's group has shown that treatment of the reactive Ir complex $IrH_2Cl(PPr^i_3)_2$with HC≡CC≡CCPh_2(OH) yields the five coordinate species *trans*-IrHCl{C≡CC≡CCPh_2(OH)}(PPr^i_3)$_2$ in a reaction accompanied by the elimination of H_2 [104].

Many of the synthetic methods described above involve the use of nucleophilic $RC≡C^-$ reagents or synthons. Stang and Tykwinski have described the use of the electrophilic acetylenic reagents, $[PhI^+C≡CC≡CI^+Ph](OTf^-)_2$, in the preparation of complexes of rhodium and iridium [39]. The preparation of [{(PPh_3)$_2$(CO)(NCMe)ClIr}C≡CC≡C{IrCl(NCMe)(CO)(PPh_3)$_2$}](OTf)$_2$ is shown in Equation 10.



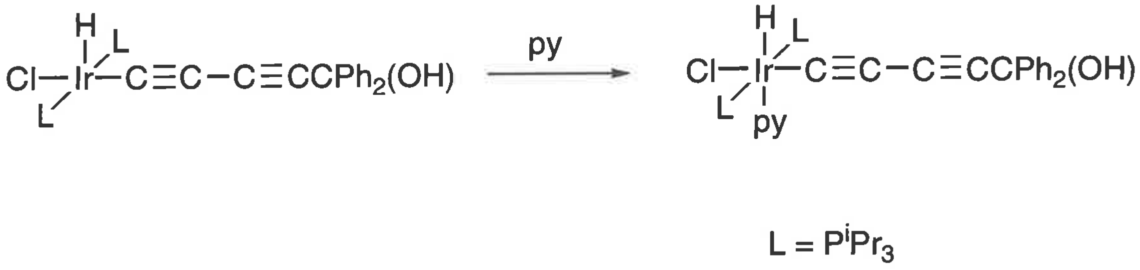
Equation 10.

The presence of the η^1-diynyl ligand appears to have little effect on the normal reactivity associated with the metal fragment. Thus, the carbonyl ligands of the iron complexes $\mathrm{Fe(C{\equiv}CC{\equiv}CSiMe_3)(CO)_2Cp'}$ (Cp' = Cp, Cp*) undergo thermal or photochemical exchange reactions with phosphines to give $\mathrm{Fe(C{\equiv}CC{\equiv}CSiMe_3)(L_2)Cp'}$ (Cp' = Cp, L_2 = $\mathrm{(CO)(PPh_3)}$ [49]; Cp' = Cp*, L_2 = dppe (Equation 11) [42, 43]).

$$\mathrm{Cp^*(CO)_2FeC{\equiv}C{-}C{\equiv}CSiMe_3} \xrightarrow[h\nu]{\text{dppe}} \mathrm{Cp^*(dppe)FeC{\equiv}C{-}C{\equiv}CSiMe_3}$$

Equation 11.

The five-coordinate diynyl complex *trans*-$\mathrm{IrHCl\{C{\equiv}CC{\equiv}CCPh_2(OH)\}(PPr^i{}_3)_2}$ was smoothly converted to $\mathrm{IrHCl\{C{\equiv}CC{\equiv}CCPh_2(OH)\}(py)(PPr^i{}_3)_2}$ upon treatment with pyridine [104], while $\mathrm{RhH(C{\equiv}CC{\equiv}CPh)_2(PPr^i{}_3)_2}$ reacts with both pyridine and CO to give the six-coordinate species $\mathrm{RhH(C{\equiv}CC{\equiv}CPh)_2(L')(PPr^i{}_3)_2}$ (L' = py , CO) [90].



Equation 12.

Work described in this Thesis.

While the syntheses of complexes bearing diynyl and diyndiyl, or C_4, ligands described above are simple in principle, they are not necessarily straight-forward in practice. The preparation of many of these compounds requires the manipulation of the highly sensitive reagents, or the introduction of several protection / deprotection steps.

This thesis describes the development of some more generally applicable routes to transition metal diynyl and diyndiyl complexes. Both buta-1,3-diyne, HC≡CC≡CH, and 1,4-bis(trimethylsilyl)buta-1,3-diyne, $Me_3SiC{\equiv}CC{\equiv}CSiMe_3$, have been examined as precursors to both diynyl complexes, $[L_mM]C{\equiv}CC{\equiv}CR$, and complexes of the all-carbon ligand C_4. The redox properties of the bis(ruthenium)diyndiyl complexes $\{Cp(PPh_3)(PR_3)Ru\}C{\equiv}CC{\equiv}C\{Ru(PR_3)(PPh_3)Cp\}$ (R = Ph, Me) has been examined using cyclic voltammetry, and the complexes have been shown to undergo an unprecedented series of four one-electron oxidation processes. A spectroelectrochemical study has established that during these oxidation processes the electronic nature of the C_4 bridge in these complexes varies from a diacetylenic C≡CC≡C structure (**J**) through a cumulated C=C=C=C (**K**) form to an acetylene-bridged dicarbyne ≡C-C≡C-C≡ (**L**). The odd-electron in the intermediate complexes is delocalised over the six-atom Ru-C_4-Ru chain. A convenient, one-pot synthesis of diynyl complexes $[ML_m]C{\equiv}CC{\equiv}CH$ $\{[ML_m] = Mo(CO)_3Cp$, $W(CO)_3Cp$, $Fe(CO)_2Cp$, $Pt(C{\equiv}CC{\equiv}CH)(dppe)\}$ has been developed. The reactivity of the parent diynyl ligand C≡CC≡CH in

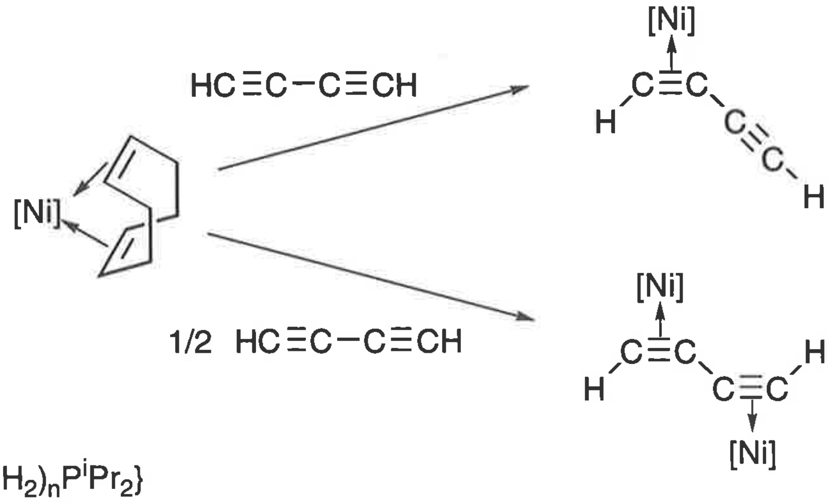
W(C≡CC≡CH)$(CO)_3$Cp and some related complexes has been examined, and synthetic methods for the preparation of a range of other diynyl and diyndiyl complexes are described. Some related chemistry of the unsaturated carbene complexes [Ru(C=C=CPh_2)$(PPh_3)_2$Cp]PF_6 and [Ru(C=C=C=CH_2)$(PPh_3)_2$Cp]PF_6 has also been explored.

- CHAPTER 2 -

Complexes Derived from 1,4-Bis(trimethylsilyl)buta-1,3-diyne

INTRODUCTION.

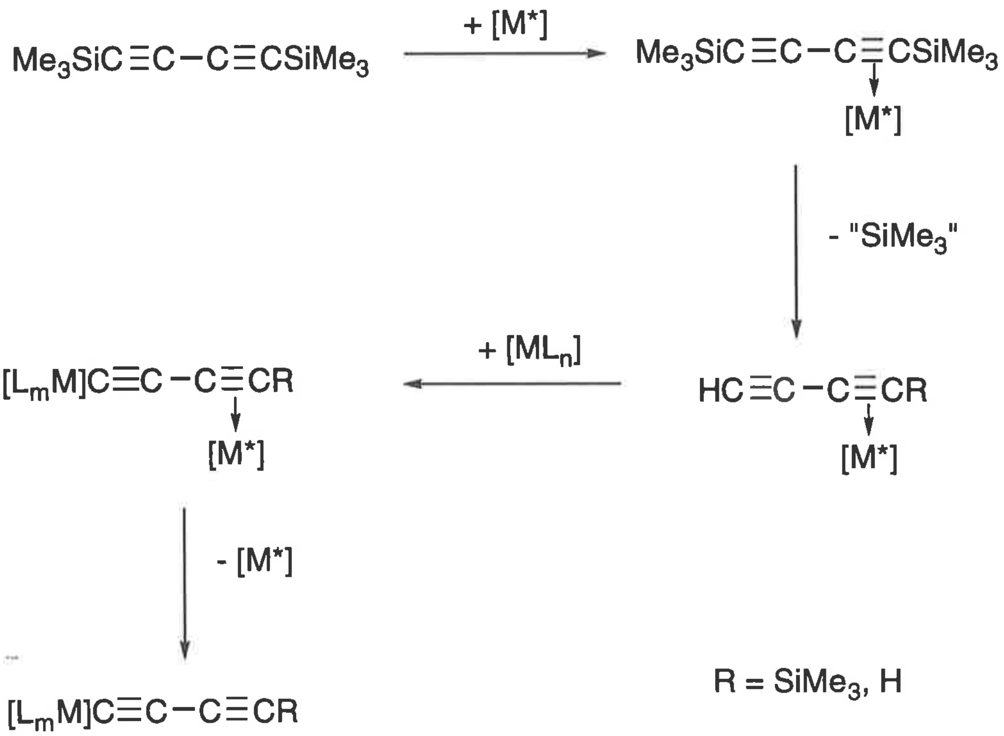
Coordination of metal fragments to the π-system of 1,3-diynes has given stable complexes which are completely analogous to the complexes of mono-alkynes. Examples include: $\{Co_2(CO)_6\}_2(\mu{:}\mu\text{-}\eta^2{:}\eta^2\text{-}HC_2C_2H)$, prepared from the photochemical reaction of $Hg\{Co(CO)_4\}_2$ with 1,3-butadiyne [105]; $(NiL_2)_n(\eta^2\text{-}HC_2C_2H)$ [n = 1, 2; $L_2 = {}^iPr_2P(CH_2)_mP^iPr_2$, m = 2, 3], which were isolated from the stoichiometric reactions of the labile $Ni(cod)L_2$ complexes with buta-1,3-diyne [106] (Scheme 5); and $Co_2(\mu, \eta^2\text{-}RC_2C{\equiv}CH)(\mu\text{-dppm})(CO)_4$ (R = $SiMe_3$, H), prepared by desilylating the corresponding bis(trimethylsilyl) complex [107, 108]. Coordination of the first C≡C triple bond apparently has little effect on the ability of the second alkynyl moiety to react with a metal fragment. Curiously though, there are remarkably few complexes in which different metals are coordinated to each C≡C triple bond [109].



[Ni] = $Ni\{{}^iPr_2P(CH_2)_nP^iPr_2\}$
n = 2,3

Scheme 5 : Some Nickel Complexes of Buta-1,3-Diyne.

1,4-Bis(trimethylsilyl)buta-1,3-diyne, $Me_3SiC{\equiv}CC{\equiv}CSiMe_3$, is a readliy available, air-stable, crystalline synthon of buta-1,3-diyne. The silyl protecting groups are easily removed by simply exposing the reagent to a source of fluoride, or another mild nucleophile. It was though that coordination of one of the C≡C triple bonds in this diyne, followed by removal of the silyl groups would afford metal protected 1,3-diynes. Metallation of the uncomplexed C≡CH fragment would then afford metal-protected diynyl complexes. The approach is summarised in Scheme 6.

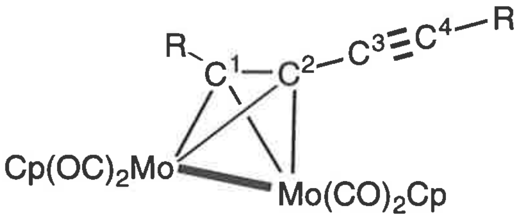


Scheme 6 : The Preparation of Diynyl Complexes *via* a Metal Protected 1,3-Diyne.

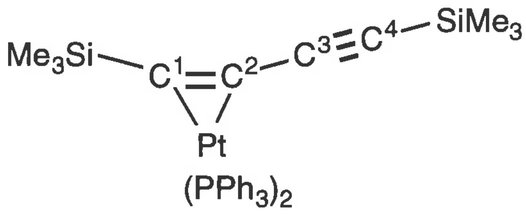
RESULTS AND DISCUSSION.

Reactions of 1,4-bis(trimethylsilyl)buta-1,3-diyne.

1,4-Bis(trimethylsilyl)buta-1,3-diyne reacts with $\{Mo(CO)_2Cp\}_2$ and $Pt(\eta\text{-}C_2H_4)(PPh_3)_2$, affording the expected complexes $Mo_2(\mu\text{-}\eta^2\text{-}Me_3SiC_2C{\equiv}CSiMe_3)(CO)_4Cp_2$ (**1**) [110] and $Pt(\eta^2\text{-}Me_3SiC_2C{\equiv}CSiMe_3)(PPh_3)_2$ (**2**) respectively. Similar binuclear molybdenum complexes with bridging $4\text{-}RH_4C_6C{\equiv}CC{\equiv}CC_6H_4R\text{-}4'$ (R = H, F) ligands complexes were obtained by from the thermolysis of $Mo(C{\equiv}CC_6H_4R)(CO)_3Cp$ at 110 to 115 °C [111]. The pale yellow platinum complex **2** is analogous to the R_2C_4 complexes (R = Me, Ph) described by Heyns and Stone some years ago [112].



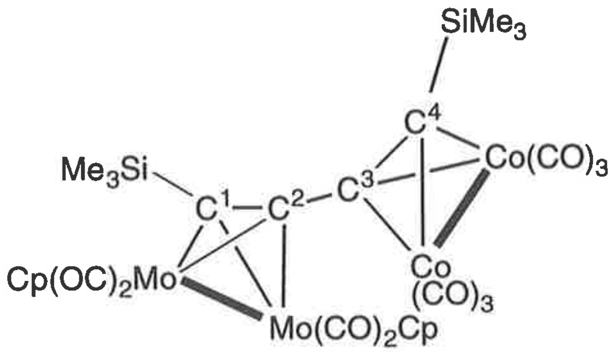
(**1**) R = $SiMe_3$
(**4**) R = H



(**2**)

The new complexes **1** and **2** were readily characterised by the usual methods, details of which are given in the Experimental section of this Chapter. These complexes contain an non-coordinated C≡C triple bond, which gives a ν(CC) absorption at 2125 (**1**) or 2132 and 2094 cm^{-1} (**2**), and two distinct $SiMe_3$ groups, which give well-resolved resonances in the ^1H and ^{13}C NMR spectra. The FAB MS of **1** contained a molecular ion, which fragmented by loss of upto three CO ligands. The ES MS of **2** contains an intense $[M + H]^+$ ion, which fragments by loss of $SiMe_3$, C_6H_6, and $C_4(SiMe_3)_2$ groups.

Further complexation of metal-ligand groups to the free C≡C triple bond can be achieved readily. Reaction between $Mo_2(\mu\text{-}\eta^2\text{-}Me_3SiC_2C{\equiv}CSiMe_3)(CO)_4Cp_2$ and $Co_2(CO)_8$ gave deep green crystals of the mixed molybdenum / cobalt complex $\{Mo_2(CO)_4Cp_2\}\{Co_2(CO)_6\}(\mu\text{:}\mu\text{-}\eta^2\text{:}\eta^2\text{-}Me_3SiC_2C_2SiMe_3)$ (**3**). A small amount (6%) of $\{Co_2(CO)_6\}_2(\mu\text{:}\mu\text{-}\eta^2\text{:}\eta^2\text{-}Me_3SiC_2C_2SiMe_3)$ was also isolated from the reaction mixture, and identified by comparison with an authentic sample [113]. The identity of **3** was deduced from analytical and spectroscopic data and confirmed by a single crystal X-ray structure determination (see below). The ν(CO) spectrum contained ten absorptions; overall, the pattern approximates a superposition of the component ν(CO) spectra, i.e. there is little or no electronic interaction between the two metal carbonyl groups. No absorptions were found in the ν(CC) region. In the ^{13}C NMR spectrum, two signals at δ 201 and 231.5 are assigned to the CO groups on Co and Mo respectively (*cf.* corresponding resonances at δ 227.68 and 230.0 in **1**). The simplicity of the spectrum in this region indicates that there are CO-exchange processes, which are fast on the NMR time scale at room temperature, localised on each metal centre. The diyne C resonances were not observed, even with long pulse delays in the ^{13}C NMR experiment, suggesting a lack of efficient relaxation processes for these carbon nuclei.



(3)

Under mild oxidative conditions, $Co_2(\mu\text{-}\eta^2\text{-}RC_2R')(CO)_6$ complexes often decompose to liberate the alkyne [114]. Exposure of **3** to atmospheric oxygen on silica for several minutes was sufficient to remove the coordinated $Co_2(CO)_6$ group and regenerate **1**. This effect at least partly accounts for the moderate yield of **3** when isolated by preparative TLC (33%).

The molecular structure of **3** has been determined, and a picture of a molecule is given in Figure 7. Some significant bond parameters are given in the caption. It can be seen that each C≡C triple bond is coordinated to a dimetal system, C(1)-C(2) to Mo(1)-Mo(2) and C(3)-C(4) to Co(1)-Co(2). The metal-metal distances are similar to those found in $Co_2(\mu\text{-}\eta^2\text{-}C_2R_2)(CO)_6$ (2.460(1) (R = Bu^t) [115]; 2.476(1) Å (R = Ph) [116]) and $Mo_2\{\mu\text{-}\eta^2\text{-}C_2(SiMe_3)_2\}(CO)_4Cp_2$ (2.952(1) Å [117]). The metal-carbon distances are within the ranges found for the similar Mo_2- or Co_2-η^2- alkyne complexes mentioned above. The C(1)-C(2) and C(3)-C(4) distances show the expected lengthening on coordination. The total deviation from linearity as defined by summation of the angles along the Si-C_4-Si chain is 123.1°. Coordination about the respective metal centres also shows no significant differences from the parameters found in the related Mo_2 and Co_2 complexes indicated above.

Desilylation reactions.

Desilylation of **1** with tetrabutylammonium fluoride (tbaf) proceeded readily. In moist thf, the complex $Mo_2(\mu\text{-}\eta^2\text{-}HC_2C\equiv CH)(CO)_4Cp_2$ (**4**) was isolated in 22% yield. Desilylation of the analogous cobalt complex $Co_2(\mu\text{-}\eta^2\text{-}Me_3SiC_2C\equiv CSiMe_3)(CO)_6$ (**5**) [113] was performed with KF in methanol to give $Co_2(\mu\text{-}\eta^2\text{-}HC_2C\equiv CH)(CO)_6$ (**6**). These 1,3-butadiyne complexes were readily characterised from their spectroscopic properties, which included resonances in the ^1H NMR spectra for the two types of HC≡ protons around 2.73 and 5.63 (**4**) or 3.73 and 6.20 (**6**), assigned to protons on the free and coordinated C≡C systems, respectively. These assignments were made by comparison with the chemical shifts of terminal acetylenes and $Co_2(\mu\text{-}\eta^2\text{-}HC_2R)(CO)_6$ complexes [118]. The FAB mass spectrum of **4** contained the expected molecular ions and fragment ions formed by loss of CO groups. Complex **6** is remarkably volatile, codistilling with MeOH at 1 mm; it decomposed rapidly at -20 °C under dry nitrogen and

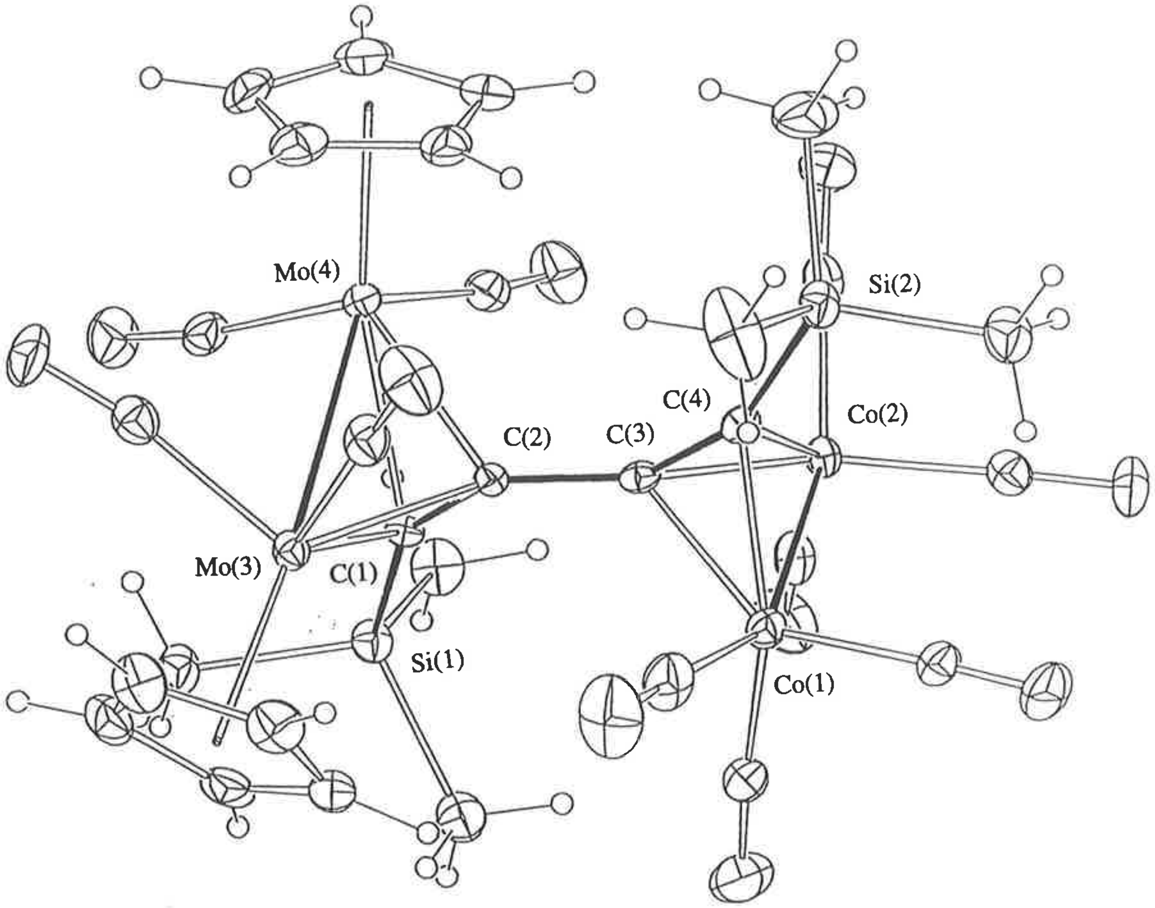
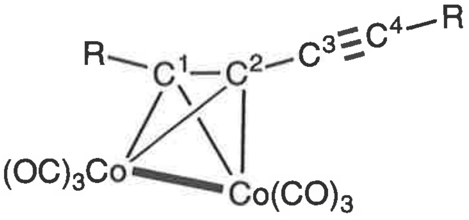
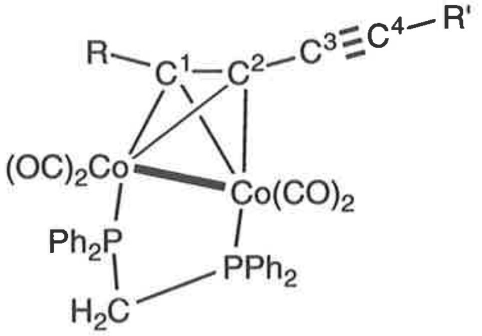


Figure 7 : Plot of a molecule of **3** showing the atom numbering scheme. In this and subsequent Figures non-hydrogen atoms are shown with 20% thermal envelopes; hydrogen atoms have arbitary radii of 0.1 Å. Important bond distances (Å) and angles (°): Co(1)-Co(2) 2.470(1); Mo(3)-Mo(4) 2.958(1); Mo(3,4)-C(1) 2.185(6), 2.244(6); Mo(3,4)-C(2) 2.208(6), 2.220(6); Co(1,2)-C(3) 2.029(6), 2.009(6); Co(1,2)-C(4) 1.979(6), 2.008(6); C(1)-C(2) 1.358(8), C(3)-C(4) 1.345(8); Si(1)-C(1)-C(2) 151.6(5), C(1)-C(2)-C(3) 140.5(5), C(2)-C(3)-C(4) 147.3(5), C(3)-C(4)-Si(2) 157.5(5) (by B.W. Skelton and A.H. White).

thus proved to be unsuitable as a reagent for further metallation reactions. A much more stable complex was obtained by replacing two CO ligands in **5** by bis(diphenylphosphino)methane prior to desilylation, as reported by Diederich and co-workers [107, 108]. The product, $Co_2(\mu\text{-}\eta^2\text{-}Me_3SiC_2C{\equiv}CSiMe_3)(\mu\text{-dppm})(CO)_4$ (**7**), undergoes stepwise desilylation to give the stable crystalline derivatives $Co_2(\mu\text{-}\eta^2\text{-}Me_3SiC_2C{\equiv}CH)(\mu\text{-dppm})(CO)_4$ (**8**) and $Co_2(\mu\text{-}\eta^2\text{-}HC_2C{\equiv}CH)(\mu\text{-dppm})(CO)_4$ (**9**) [107, 108].



(**5**) R = $SiMe_3$
(**6**) R = H

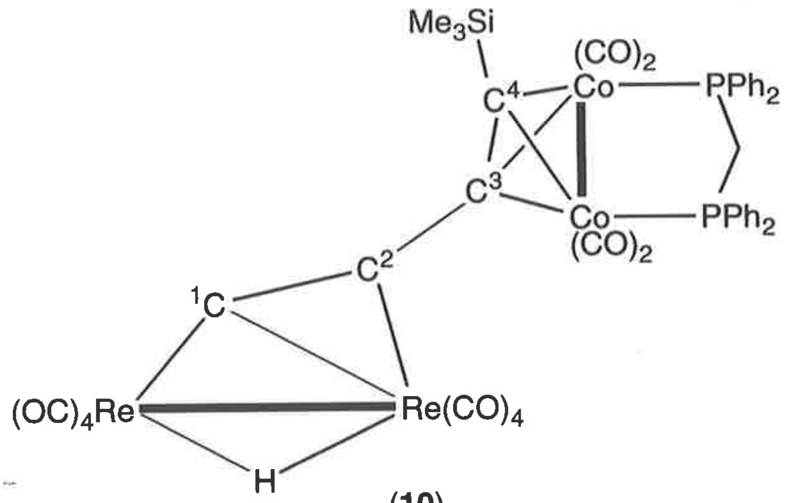


(**7**) R = R' = $SiMe_3$
(**8**) R = $SiMe_3$, R' = H
(**9**) R = R' = H

Reactions of $Co_2(\mu\text{-}\eta^2\text{-}RC_2C{\equiv}CH)(\mu\text{-dppm})(CO)_4$.

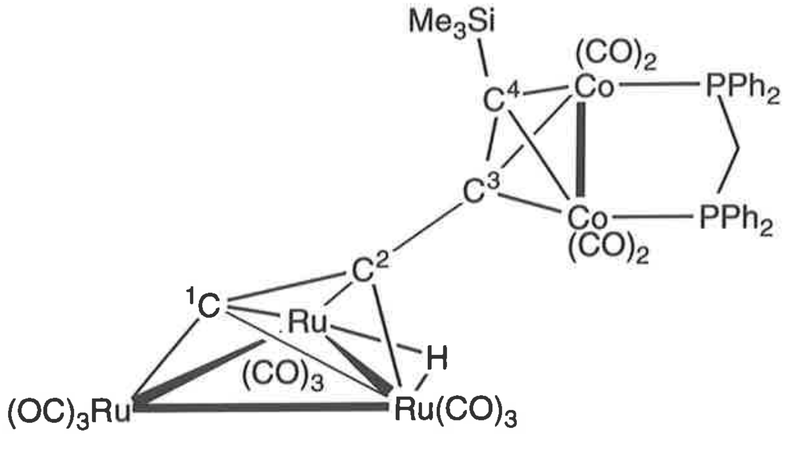
We were able to use the uncoordinated -C≡CH portion of the complex **8** to form mixed Co_2Re_2 and Co_2Ru_3 complexes by oxidative addition of the C-H bond across the Re-Re bond in $Re_2(CO)_8(NCMe)_2$ or an Ru-Ru bond in $Ru_3(CO)_{12}$. Both complexes, namely $Re_2(\mu\text{-H})\{\mu\text{-}\eta^1\text{:}\eta^2\text{;}\mu\text{-}\eta^2\text{-}C_2C_2SiMe_3[Co_2(\mu\text{-dppm})(CO)_4]\}(CO)_8$ (**10**) and $Ru_3(\mu\text{-H})\{\mu_3\text{-}\eta^1,\eta^2\text{;}\mu\text{-}\eta^2\text{-}C_2C_2[Co_2(\mu\text{-dppm})(CO)_4]\}(CO)_9$ (**11**) were fully characterised by single-crystal X-ray structures: other spectroscopic data were in accord with the solid-state structures.

The former product, obtained in 85% yield, contained a characteristic Re-H resonance at δ -12.88 in the ^{1}H NMR spectrum. The analogous octacarbonyl complex $Re_2(\mu\text{-}H)(\mu\text{-}\eta^1\text{:}\eta^2\text{-}C_2Ph)(CO)_8$ has been prepared from either $Re_2(CO)_{10}$ or $Re_2(\mu\text{-}H)(\mu\text{-}\eta^1\text{:}\eta^2\text{-}$*trans*$\text{-}CH{=}CHCH_3)(CO)_8$ and phenylacetylene [119, 120]. Similar reactions of $Re_2(CO)_8(NCMe)_2$ with phenylacetylene or α-ethynylestradiol gave acetonitrile-substituted derivatives of general formula $Re_2(\mu\text{-}H)(\mu\text{-}\eta^1\text{:}\eta^2\text{-}C_2R)(CO)_7(NCMe)$ [121]. In these cases, it was suggested that the incorporation of NCMe into these products was due to thermal substitution of one of the axial CO ligands of an undetected octacarbonyl intermediate by the MeCN liberated from the dirhenium precursor during the course of reaction. Curiously, however, **10** retains all eight carbonyl ligands on the di-rhenium core.



(10)

The reaction involving $Ru_3(CO)_{12}$ is notable for the very high yield (96%) of **11** obtained in the reaction with unactivated $Ru_3(CO)_{12}$. This product is similar to those reported earlier from 1-alkynes and $Ru_3(CO)_{12}$ or $Ru_3(CO)_{10}(NCMe)_2$ [122, 123], and is characterised by an Ru-H resonance at δ -19.99.



(11)

Figure 8 shows a plot of a molecule of **10** and selected bond parameters are given in the caption. The molecule consists of an $Re_2(CO)_8$ fragment which is bridged by a hydrogen (not detected in the X-ray study) and C(1)-C(2) of the $Co_2(\mu\text{-}\eta^2\text{-}Me_3SiC_2C_2)(\mu\text{-dppm})(CO)_4$ fragment in the η^1,η^2- mode. These parameters are similar to those found in of $Re_2(\mu\text{-}H)(\mu\text{-}\eta^1,\eta^2\text{-}C_2Ph)(CO)_7(NCMe)$ [121]. The geometry of the $Co_2(\mu\text{-dppm})(CO)_4$ unit is also normal [107, 108, 124]. Not surprisingly, the latter part of the molecule is placed so that there is minimum steric interference between the two parts of the molecule. The torsion angles C(1)-C(2)/C(3)-C(4) and Co(1)-Co(2)/Re(3)-Re(4) are 153(4) and 66.1°, respectively.

Two independent molecules of **11** were found in the unit cell. The molecular structure of one of these molecules is depicted in Figure 9 and some structural parameters are listed in the caption. The triangular Ru_3 cluster is capped by the $C_2C_2SiMe_3\{Co(\mu\text{-dppm})(CO)_4\}$ moiety in the usual η^1,η^2-mode with the putative μ-H atom bridging Ru(1)-Ru(2). Again we find that the geometry of the two parts of the molecule are in accord with previously reported examples [107, 108, 124, 125], with the $Co_2(\mu\text{-dppm})(CO)_4$ fragment disposed as far away from the Ru_3 cluster as possible. The torsion angles C(1)-C(2)/C(3)-C(4) and Co(4)-Co(5)/Ru(1)-Ru(2) are -179(4), 176(4) and 1.7, 3.2°,

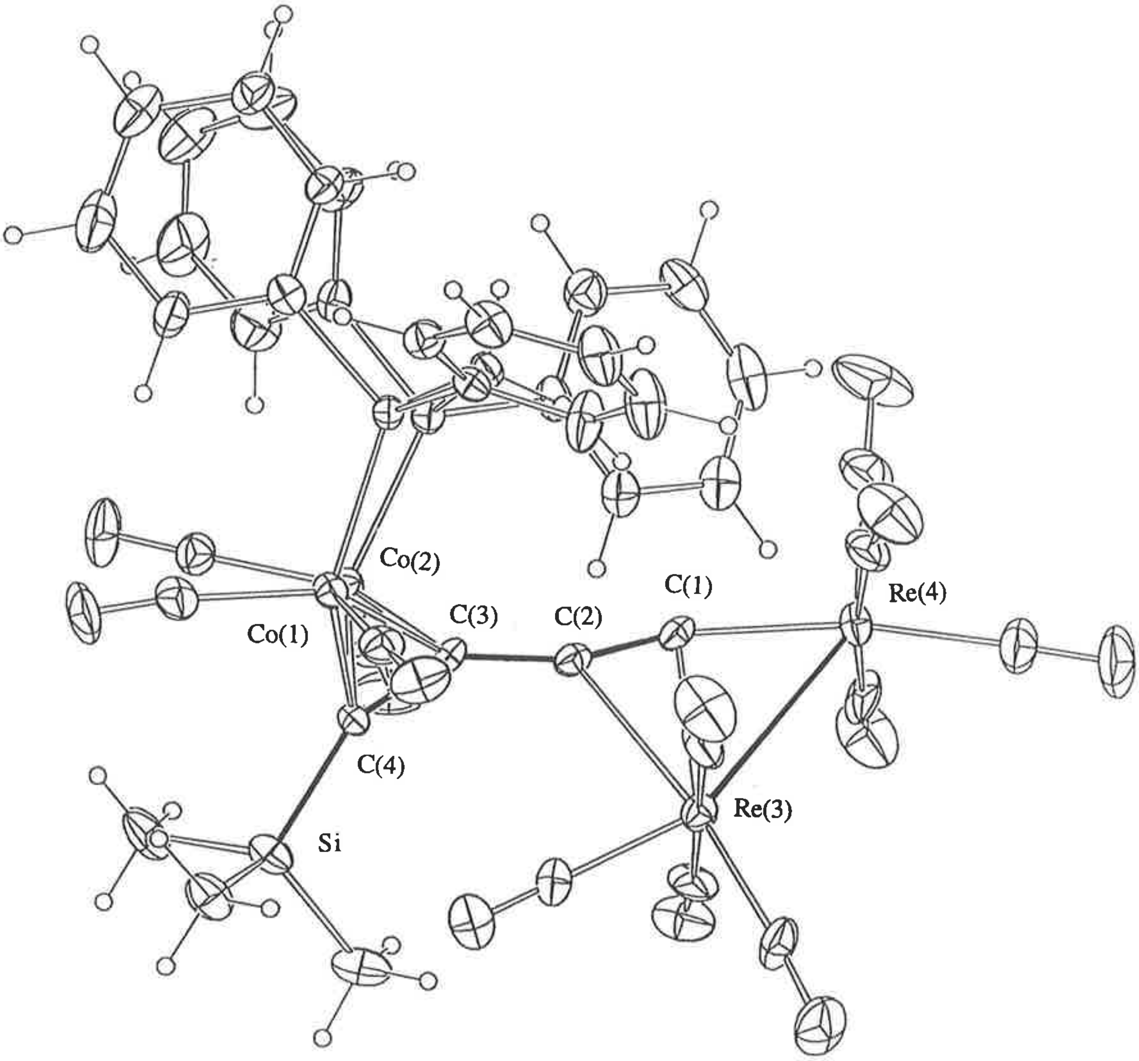


Figure 8 : Plot of a molecule of **10** showing the atom numbering scheme. Significant bond length (Å) and angles (°): Co(1)-Co(2) 2.472(3); Re(3)-Re(4) 3.0651(9); Re(3)-C(1,2) 2.35(1), 2.50(1); Re(4)-C(1) 2.11(1); C(1)-C(2) 1.24(2); C(1)-C(2) 1.24(2); C(2)-C(3) 1.43(2); C(3)-C(4) 1.36(2); C(4)-Si 1.85(1); Re(4)-C(1)-C(2) 168(1); C(1)-C(2)-C(3) 161(1); C(2)-C(3)-C(4) 144(1) (by B.W. Skelton and A.H. White).

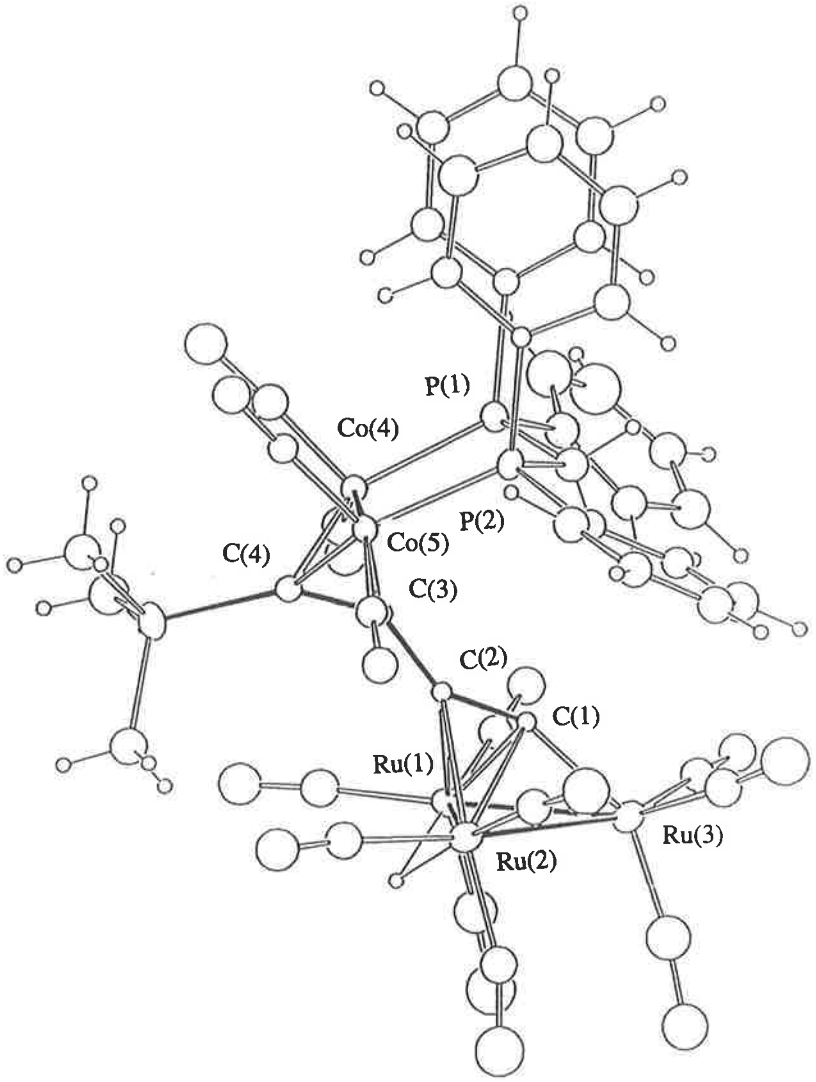


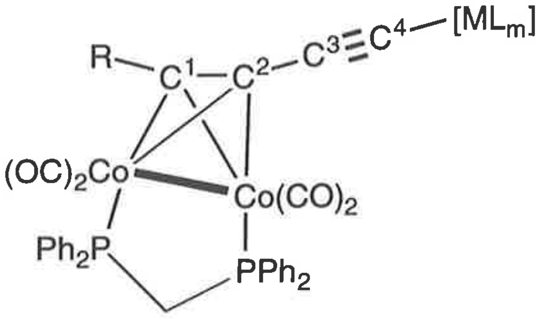
Figure 9 : Plot of one molecule of **11** showing the atom numbering scheme. Important bond lengths (Å) and angles (°): Co(4)-Co(5) 2.478(5); Co(4)-C(3) 1.97(2); C(4)-C(4) 1.94(2); Co(5)-C(3) 1.98(2); Co(5)-C(4) 1.94(2); Co(4)-P(1) 2.225(9); Co(5)-P(2) 2.256(8); C(3)-C(4) 1.32(3); Ru(1)-Ru(2) 2.790(4); Ru(1)-Ru(3) 2.800(4); Ru(2)-Ru(3) 2.775(4); Ru(1)-C(1,2) 2.17(2), 2.31(2); Ru(2)-C(1,2) 2.15(3), 2.28(3); Ru(3)-C(1) 1.97(3); Si-C(4) 1.90(2); C(1)-C(2) 1.26(4); C(2)-C(3) 1.45(3); C(3)-C(4) 1.32(3); Ru(3)-C(1)-C(2) 159(2); C(1)-C(2)-C(3) 148(2); C(2)-C(3)-C(4) 147(2); C(3)-C(4)-Si 151(2); dihedral angle Co(4)-Co(5)/Ru(1,2,3) plane 88.36(8) (by B.W. Skelton and A.H. White).

respectively, i.e. the two metal-metal bonds are essentially parallel. In this complex, the total deviation of the C_4 chain from linearity is 94°.

Formation of a σ-bonded acetylide was found in the copper-catalysed reaction between **8** and $WCl(CO)_3Cp$ run in $NHEt_2$. Deep-red needles of $Co_2\{\mu\text{-}\eta^2\text{-}Me_3SiC_2C{\equiv}C[W(CO)_3Cp]\}(\mu\text{-dppm})(CO)_4$ (**12**) were obtained in 70% yield. A similar reaction with **9** afforded brick-red $Co_2\{\mu\text{-}\eta^2\text{-}HC_2C{\equiv}C[W(CO)_3Cp]\}(\mu\text{-dppm})(CO)_4$ (**13**) in 50% yield. In the ^{13}C NMR spectrum, broad Co-CO resonances were at δ 202.7 and 207.5 (**12**), 203.2 and 206.2 (**13**); sharp singlets at δ 210.9 and 230.2 (**12**) or 210.9 and 229.8 (**13**) were assigned to the W-CO groups. Similarly, in **12** the C_2 unit coordinated to Co (triplets at δ 84.4 and 86.8 by coupling to the dppm ^{31}P nuclei) could be distinguished from the singlets for the C_2 σ-bonded to W (δ 95.8 and 109.0). The acetylenic proton in **13** resonated at δ 6.04 in the ^1H NMR spectrum.

The reaction between **9** and $AuCl(PPh_3)$ in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (dbu) resulted in replacement of only the acetylenic H atom of the uncomplexed C≡CH moiety by the isolobal $Au(PPh_3)$ group. The resulting complex, $Co_2\{\mu\text{-}\eta^2\text{-}HC_2C{\equiv}C[Au(PPh_3)]\}(\mu\text{-dppm})(CO)_4$ (**14**), was obtained in 48% yield as deep-red needles. The acetylenic proton resonance was found at δ 5.98 (^1H NMR); only the carbons attached to Co could be located in the ^{13}C NMR spectrum at δ 70.63 and 78.74.

Complexes **12**, **13** and **14** may be regarded as $Co_2(CO)_4(dppm)$ complexes of the diynyl complexes $W(C{\equiv}CC{\equiv}CSiMe_3)(CO)_3Cp$, $W(C{\equiv}CC{\equiv}CH)(CO)_3Cp$ and $Au(C{\equiv}CC{\equiv}CH)(PPh_3)$. For a more detailed discussion of the chemistry of the tungsten complexes, the reader is referred to Chapter 4.



[ML_m] = $W(CO)_3Cp$; R = $SiMe_3$ (**12**), H (**13**)

[ML_m] = $Au(PPh_3)$, R = H (**14**)

Attempted Removal of the $Co_2(\mu\text{-dppm})(CO)_4$ Protecting Group.

Several oxidising agents, such as Ce(IV), Fe(III) or amine N-oxides, have been used to remove the $Co_2(CO)_6$ moiety from various $Co_2(\mu\text{-}\eta^2\text{-}RC_2R')(CO)_6$ cobalt-alkyne complexes [126-128]. The introduction of the bridging dppm strengthens the cobalt-alkyne bond by increasing the electron density in the d-orbitals, which favours increased back-bonding into the alkyne π^*-orbitals [118]. In addition, the steric influence of the bulky Ph groups must also hinder the approach of reagents to the cobalt centres. However, attempts to remove the $Co_2(\mu\text{-dppm})(CO)_4$ fragment from $Co_2(\mu\text{-}\eta^2\text{-}RC_2R')(\mu\text{-dppm})(CO)_4$ complexes have met with occasional success [124].

Unfortunately, reactions of the protected diynyl complexes **12**, **13** or **14** with the oxidising reagents O_2, $[NH_4]_2Ce(SO_4)_3$ or $Fe(NO_3)_3$ in thf, acetone, methanol or toluene under conditions from ranging from room temperature to *ca.* 100°C failed to yield the free diynyl complexes. The starting materials were either extensively decomposed, or recovered unchanged.

CONCLUSION.

The reactions of 1,4-bis(trimethylsilyl)buta-1,3-diyne with metal reagents were partially succesful as a route to diynyl complexes and compounds containing the all-carbon ligand C_4. Complexes **3**, **10** and **11** contain heterometallic fragments linked by a C_4 chain.

Reactions of the protected 1,3-diynes **8** and **9** have given the $Co_2(\mu\text{-dppm})(CO)_4$-protected diynyl complexes **12**, **13**, and **14**. Conditions suitable for removal of the $Co_2(\mu\text{-dppm})(CO)_4$ are yet to be established.

The next Chapter describes a more generally applicable method of preparing diynyl and C_4 complexes, and details some chemistry of these compounds.

- Experimental -

General reaction conditions. All reactions were carried out under dry, high purity nitrogen using standard Schlenk techniques. Solvents were dried, distilled and degassed before use. Light petroleum refers to a fraction of b.p. 60 - 80 °C. Elemental analyses were by the Canadian Microanalytical Service, Delta, B.C.. Preparative TLC was carried out on glass plates (20 x 20 cm) coated with silica gel (Merck 60 GF_{254}, 0.5 mm thick).

Instrumental conditions. Infrared: Perkin Elmer 1700X FT-IR. Solution spectra were obtained using a 0.5 mm path length solution cell fitted with NaCl or CaF_2 windows. Nujol mull spectra were collected from samples mounted between NaCl discs. NMR: Samples were dissolved in $CDCl_3$ (Cambridge Isotope Laboratories), and spectra were recorded in standard 5 mm sample tubes using either a Bruker ACP300 (^1H at 300.13 MHz, ^{13}C at 75.47 MHz) or Varian Gemini 200 (^1H at 199.98 MHz, ^{13}C at 50.29 MHz) spectrometer. FAB mass spectra: Spectra were measured with a VG ZAB 2HF spectrometer, using 3-nitrobenzyl alcohol as matrix, exciting gas Ar, FAB gun voltage 7.5 kV, current 1 mA, accelerating potential 7 kV. ES mass spectra: The samples were dissolved in acetonitrile / water (1 / 1), unless otherwise indicated, and injected into a 10 µl injection loop attached to a VG Platform II mass spectrometer. Nitrogen was used as the drying and nebulising gas. Samples were examined over a range of cone voltages (20 - 90 V) to find the best conditions. Chemical aids to ionisation are indicated where required.

Reagents. The compounds $Me_3SiC{\equiv}CC{\equiv}CSiMe_3$ [129], $\{Mo(CO)_2Cp\}_2$ [130], $Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2$ [112], $Re_2(CO)_8(NCMe)_2$ [131], $Ru_3(\mu\text{-dppm})(CO)_{10}$ [132], $WCl(CO)_3Cp$ [133] and $AuCl(PPh_3)$ [134] were prepared by literature methods.

$Co_2(CO)_8$ (Strem), tetrabutylammonium fluoride (1M solution in thf), dppm and dbu were purchased (Aldrich) and used as received.

Minor modifications of published methods were used for the syntheses of the complexes $Co_2(\mu\text{-}\eta^2\text{-}Me_3SiC_2C{\equiv}CSiMe_3)(\mu\text{-dppm})_n(CO)_{6-2n}$ (n = 0 (**5**) [113]), 1 (**7**) [107, 108]], $Co_2(\mu\text{-}\eta^2\text{-}Me_3SiC_2C{\equiv}CH)(\mu\text{-dppm})(CO)_4$ (**8**) [107, 108], and $Co_2(\mu\text{-}\eta^2\text{-}HC_2C{\equiv}CH)(\mu\text{-dppm})(CO)_4$ (**9**) [107, 108], as detailed below:

(5). $Co_2(CO)_8$ (1.75 g, 5.12 mmol) and $Me_3SiC_2C_2SiMe_3$ (1 g, 5.12 mmol) were stirred in light petroleum (100 ml) for 1 h. The solvent was removed *in vacuo* and the red-brown residue was purified by column chromatography on Al_2O_3. Light petroleum eluted a red-brown band, which yielded **5** (1.86 g, 75%) as a red oil.

(7). Complex **5** (1 g, 2 mmol) and dppm (800 mg, 2 mmol) were dissolved in benzene (50 ml) and heated to reflux point for 12 h. Evaporation and recrystallisation (CH_2Cl_2 / MeOH) gave deep red crystals of **7** (1.54 g, 91%).

(8). Complex **7** (1.3 g, 1.77 mmol) was dissolved in thf (100 ml containing 2% MeOH) and tbaf (20 μl of a 1M thf solution) was added. The reaction solution was allowed to stir until TLC analysis indicated complete conversion (1 - 2 h). The solvent was removed and the red residue obtained was dissolved in MeOH (15 ml). Upon standing crystallization began giving deep red crystals of (**8**) (0.95 g, 80%).

(9). This complex was prepared and isolated in the same manner as **8** except that the reaction solvent contained 10% MeOH. If the reaction failed to go to completion, a further 20 μL of the tbaf solution was added. (0.88 g, 75%).

Reactions of $Me_3SiC_2C_2SiMe_3$.

$Mo_2(\mu\text{-}\eta^2\text{-}Me_3SiC_2C{\equiv}CSiMe_3)(CO)_4Cp_2$ *(1)*. $\{CpMo(CO)_2\}_2$ (520 mg, 1.2 mmol) and $Me_3SiC_2C_2SiMe_3$ (233 mg, 1.2 mmol) were heated in refluxing toluene (50 ml). After 2.5 h the solvent was removed to give a deep red residue which was extracted with pentane, filtered, and concentrated to give $Mo_2(\mu\text{-}\eta^2\text{-}Me_3SiC_2C{\equiv}CSiMe_3)(CO)_4Cp_2$ (**1**) as a deep red microcrystalline solid (620 mg, 82%). Found: C, 45.68; H, 4.45%. $C_{24}H_{28}O_4Si_2Mo_2$ requires: C, 45.87; H, 4.46%. IR (cyclohexane) ν(C≡C) 2125w, ν(CO) 2001s, 1949s, 1934s, 1851s cm^{-1}; δ_H 5.32 (5H, s, Cp), 0.23 (9H, s, $SiMe_3$), 0.17 (9H, s, $SiMe_3$); δ_C 230.00 (s, CO), 227.68 (s, CO), 108.93 [s, C(2)], 97.59 [s, C(1)], 92.22 (s, Cp), 87.93 [s, C(3)], 85.93 [s, C(4)], -0.15 (s, $SiMe_3$), -0.53 (s, $SiMe_3$); FAB MS (*m/z*) 628 [M]$^+$, 571 - 515 [M - nCO]$^+$ (n = 1 - 3).

$Pt(\eta^2\text{-}Me_3SiC_2C{\equiv}CSiMe_3)(PPh_3)_2$ *(2)*. 1,4-Bis(trimethylsilyl)buta-1,3-diyne (100 mg, 0.52 mmol) was added to a suspension of $Pt(\eta\text{-}C_2H_4)(PPh_3)_2$ (385 mg, 0.52 mmol) in light petroleum (40 ml) and stirred at r.t. for 18 h. The suspension was filtered to remove the unreacted $Pt(C_2H_4)(PPh_3)_2$ (90 mg, 23%), and the filtrate evaporated to dryness. The sticky residue obtained was triturated with MeOH (3 x 5 ml) to give $Pt(\eta^2\text{-}Me_3SiC_2C{\equiv}CSiMe_3)(PPh_3)_2$ (**2**) as a pale yellow powder (305 mg, 86% based on Pt consumed). Found: C, 60.90; H, 6.30%. $C_{46}H_{48}P_2Si_2Pt$ requires: C, 60.46; H, 5.25%. IR (nujol) ν(C≡C) 2132m, 2094s, ν(C=C) 1663s cm^{-1}; δ_H 7.38 - 7.11 (30H, m, Ph), 0.09 (9H, s, $SiMe_3$), -0.16 (9H, s, $SiMe_3$); δ_C 137.68 - 127.68 (m, Ph), 88.26, 86.19 [2 x s, C≡C (uncoordinated)], 0.12 (s, $SiMe_3$), -0.26 (s, $SiMe_3$); ES MS (*m/z*) 914 [M + H]$^+$, 840 [M - $SiMe_3$]$^+$, 761 [M - $SiMe_3$ - C_6H_6]$^+$, 720 [$Pt(PPh_3)_2$ + H]$^+$.

$\{Mo_2(CO)_4Cp_2\}\{Co_2(CO)_6\}(\mu{:}\mu\text{-}\eta^2{:}\eta^2\text{-}Me_3SiC_2C_2SiMe_3)$ *(3)*. $Co_2(CO)_8$ (103 mg, 0.30 mmol) was added in portions to a solution of $Mo_2(\eta^2\text{-}Me_3SiC_2C_2SiMe_3)(CO)_4Cp_2$ (**1**) (100 mg, 0.24 mmol) in light petroleum (15 ml) and allowed to stir. The reaction was stopped when all the starting material had been consumed (IR). After removal of solvent, recrystallisation of the residue (CH_2Cl_2 / MeOH) gave deep green crystals of $\{Mo_2(CO)_4Cp_2\}\{Co_2(CO)_6\}(\mu{:}\mu\text{-}\eta^2{:}\eta^2\text{-}Me_3SiC_2C_2SiMe_3)$ (**3**) (110 mg, 50%). Attempted purification of the reaction mixture by preparative TLC (light petroleum / acetone 9 / 1) gave three bands after repeated development. The first band was identified as $\{Co_2(CO)_6\}_2(\mu{:}\mu\text{-}\eta^2{:}\eta^2\text{-}Me_3SiC_2C_2SiMe_3)$ (5 mg, 6%) by comparison with an authentic sample. The second band contained **1** (20 mg, 20%). The third broad, deep green band contained **3** (55 mg, 33%). Prolonged exposure of the reaction mixture on the TLC plates to air before or after development resulted in the conversion of deep green **3** back to red **1**. Found: C, 39.17; H, 3.11%. $C_{30}H_{28}O_{10}Si_2Co_2Mo_2$ requires: C, 39.40; H, 3.06%. IR (cyclohexane) ν(CO) 2076vs, 2040vs, 2015vs, 2009vs, 1998m, 1989s, 1959m, 1930s, 1925m, 1847s cm^{-1}; δ_H 5.36 (5H, s, Cp), 0.49 (9H, br, $SiMe_3$); δ_C 231.45 (s, MoCO), 200.99 (s, CoCO), 92.48 (s, Cp), 5.63 (s, $SiMe_3$), 3.32 (s, $SiMe_3$); FAB MS (*m/z*): 830 - 634 $[M - nCO]^+$ (n = 3 - 10).

Desilylation of $Me_3SiC_2C_2SiMe_3$ *complexes.*

$Mo_2(\mu\text{-}\eta^2\text{-}HC_2C{\equiv}CH)(CO)_4Cp_2$ *(**4**)*. Methanol (1 ml) and tbaf (0.24 mmol as 1M thf solution) were added to a solution of **1** (150 mg, 0.24 mmol) in thf (10 ml). After 4 h the solvent was removed and the residue purified by TLC (light petroleum / acetone 8 / 2). The major red band yielded $Mo_2(\mu\text{-}\eta^2\text{-}HC_2C{\equiv}CH)(CO)_4Cp_2$ (**4**) (25 mg, 22%) after crystallization (toluene / pentane). Found: C, 44.93; H, 2.55%; $C_{18}H_{12}O_4Mo_2$ requires: C, 44.64; H 2.48%. IR (cyclohexane) ν(C≡C) 2078w; ν(CO) 2002vs, 1948vs, 1941(sh), 1853vs cm^{-1}; δ_H 5.63 [1H, s, $\mu\text{-}\eta^2\text{-}HC_2$], 5.39 (5H, s, Cp), 2.73 (1H, s, C≡CH); δ_C 230.28, 226.66 (2 x s, CO), 92.30 (s, Cp), 90.77 [s, C(3)], 88.45 [s, C(4)], 79.41 [s, C(2)], 74.89 [s, ≡C(1)H]; FAB MS (*m/z*): 485 $[M]^+$, 428 - 378 $[M - nCO]^+$ (n = 2 - 4).

*$Co_2(\mu\text{-}\eta^2\text{-}HC_2C{\equiv}CH)(CO)_6$ (**6**).* Complex **5** (250 mg, 0.52 mmol) and KF (60 mg, 1.04 mmol) were dissolved in methanol (15 ml) and the solution warmed to 35-40 ^{0}C. After 30 minutes the solvent was removed at room temperature on a rotary evaporator and the resulting dark oil purified by flash chromatography on alumina (light petroleum eluant) to give $Co_2(\mu\text{-}\eta^2\text{-}HC_2C{\equiv}CH)(CO)_6$ (**6**) as a bright red oil (70-80%) which decomposed over several hours at -20 °C under nitrogen to a brown intractable polymer. IR (thf) ν(C≡C) 2113w; ν(CO) 2024s, 2000vs, 1973vs; δ_H 6.20 [1H, s, $HC_2(Co_2)$], 3.73 (1H, s, C≡CH).

*Reactions of $Co_2(\mu\text{-}\eta^2\text{-}Me_3SiC_2C{\equiv}CH)(\mu\text{-}dppm)(CO)_4$ (**8**).*

*$Re_2(\mu\text{-}H)[\mu\text{-}\eta^1{:}\eta^2;\mu\text{-}\eta^2\text{-}C_2C_2SiMe_3\{Co_2(\mu\text{-}dppm)(CO)_4\}](CO)_8$ (**10**).* $Re_2(CO)_8(NCMe)_2$ (100 mg, 0.15 mmol) and **8** (108 mg, 0.15 mmol) were heated in refluxing light petroleum (15 ml). After 3 h all the $Re_2(CO)_8(NCMe)_2$ had been consumed although a significant amount of the Co-diyne was still present (TLC). Another equivalent of $Re_2(CO)_8(NCMe)_2$ was added and reflux continued. The remaining Co-diyne was rapidly consumed. The solution was cooled, filtered and purified by preparative TLC (light petroleum / acetone 8 / 2). Two major bands were isolated. The top brown band (R_f 0.8) gave deep red $Re_2(\mu\text{-}H)[\mu\text{-}\eta^1{:}\eta^2;\mu\text{-}\eta^2\text{-}C_2C_2SiMe_3\{Co_2(\mu\text{-}dppm)(CO)_4\}](CO)_8$ (**10**) (60 mg, 30%) after recrystallization (CH_2Cl_2 / MeOH). Found: C, 39.58; H, 2.44%. $C_{44}H_{32}O_{12}SiP_2Co_2Re_2$ requires: C, 39.51; H 2.69%. IR (cyclohexane) ν(CO) 2115m, 2089m, 2026vs, 2022vs, 2006s, 2001s, 1995s, 1982m, 1972vs, 1959m, 1937w cm^{-1}; δ_H 7.50 - 7.02 (20H, m, Ph), 4.09 (1H, m, CH_2P_2), 3.63 (1H, m, CH_2P_2), 0.54 (9H, s, $SiMe_3$), -12.88 (1H, s, μ-H); δ_C 206.59, 202.35 (s, CoCO), 184.78, 182.06, 181.33 (s, ReCO), 137.2 - 127.9 (m, Ph), 96.86 [s, C(1)], 94.37 [s, C(2)], 86.77 [br, C(3)], 80.01 [br, C(4)], 31.81 (t, CH_2P_2, J_{CP} = 19 Hz), 2.09 (s, $SiMe_3$); FAB MS (*m/z*): 1248 - 1080, $[M - nCO]^+$ (n = 3 - 9). The purple band (R_f 0.5) gave an unidentified compound [IR (cyclohexane) ν(CO) 2096m, 2036s, 2020s, 2001vs, 1994vs, 1982m, 1970s, 1968s, 1962s, 1954m,

1945m, 1939m, 1933m, 1930m cm^{-1}] which isomerized to **10** (110 mg, 55%) during crystallization (CH_2Cl_2 / iso-butanol). The combined yield of **10** was 170 mg, 85%.

*$Ru_3(\mu\text{-}H)[\mu_3\text{-}\eta^1,\eta^2;\mu\text{-}\eta^2\text{-}C_2C_2SiMe_3\{Co_2(\mu\text{-}dppm)(CO)_4\}](CO)_9$ (**11**).* A mixture of complex **8** (50 mg, 0.068 mmol) and $Ru_3(CO)_{12}$ (40 mg, 0.06 mmol) was heated in refluxing thf (10 ml). The reaction was followed by the disappearence of the 2061 cm^{-1} band in the IR spectrum and TLC. After 2 h the solvent was removed and the residue taken up in CH_2Cl_2 (10 ml). Methanol (5 ml) was added and the solution concentrated to give $Ru_3(\mu\text{-}H)[\mu_3\text{-}\eta^1,\eta^2;\mu\text{-}\eta^2\text{-}C_2C_2SiMe_3\{Co_2(\mu\text{-}dppm)(CO)_4\}](CO)_9$ (**11**) as flakey, red-brown crystals. The mother liquor was evaporated and the residue purified by TLC (light petroleum / acetone 8 / 2) to give a further 27 mg of the product. Total yield 70 mg, 96%. Crystals suitable for X-ray analysis were grown by slow evaporation of a CH_2Cl_2/MeOH solution. Found: C, 41.39; H, 2.61%. $C_{45}H_{32}O_{13}P_2SiCo_2Ru_3$ requires: C, 41.73; H, 2.48%. I R (cyclohexane) ν(CO) 2095m, 2073vs, 2061m, 2048vs, 2024vs, 2016m, 2010(sh), 1998s, 1986w, 1974s, 1958w cm^{-1}; δ_H 7.58 - 6.84 (20H, m, Ph), 4.48 (1H, m, CH_2P_2), 3.64 (1H, m, CH_2P_2), 0.48 (9H, s, $SiMe_3$), -19.99 (1H, s, μ-H); δ_C 206.74, 202.92 (s, RuCO), 188.95, 186.16 (s, CoCO), 165.10 [s, C(2)], 138.09 - 127.75 (m, Ph), 92.78 [s, C(1)], 30.70 (t, CH_2P_2, J_{CP} = 20 Hz), 2.94 (s, $SiMe_3$); FAB MS (*m/z*) 1178 [M - 4CO]$^+$, 1122 - 926 [M - nCO]$^+$ (n = 6 - 13).

*$Co_2[\mu\text{-}\eta^2\text{-}Me_3SiC_2C{\equiv}C\{W(CO)_3Cp\}](\mu\text{-}dppm)(CO)_4$ (**12**).* $WCl(CO)_3Cp$ [50 mg, 0.136 mmol] and **8** (100 mg, 0.136 mmol) were stirred in dry, degassed $NHEt_2$ (15 ml) with a catalytic amount of CuI (5 mg). After 18 h the solvent was removed and the residue purified by preparative TLC (light petroleum / acetone 8 / 2). The only significant bands were a brown baseline and a deep red band (R_f 0.3). Crystallization of the red band gave $Co_2[\mu\text{-}\eta^2\text{-}Me_3SiC_2C{\equiv}C\{W(CO)_3Cp\}](\mu\text{-}dppm)(CO)_4$ (**12**) as deep red needles [101 mg, 70%]. Found: C, 48.53; H, 3.32%. $C_{44}H_{36}O_7P_2SiCo_2W$ requires: C, 49.53; H, 3.38%. IR (cyclohexane) ν(CO) 2038m, 2021s, 1998s(br),

1971s, 1958s, 1943s cm^{-1}; δ_H 7.54 - 7.05 (20H, m, Ph), 5.55 (5H, s, Cp), 4.04 (1H, m, CH_2P_2), 3.40 (1H, m, CH_2P_2), 0.41 (s, 9H, $SiMe_3$); δ_C 230.21, 210.86 (s, WCO), 207.53, 202.70 (br, CoCO), 139.4 - 127.8 (m, Ph), 108.97 [s, C(2)], 95.77 [s, C(1)], 91.76 (s, Cp), 86.80 [t, J_{CP} = 10 Hz, C(3)], 84.43 [t, J_{CP} = 8 Hz, C(4)], 35.58 (t, J_{CP} = 21 Hz, CH_2P_2), 0.48 (s, $SiMe_3$); FAB MS (*m/z*) 1068 [M]$^+$; 1040 - 872, [M - nCO]$^+$ (n = 1 - 7).

Reactions of $Co_2(\mu$-η^2-$HC_2C{\equiv}CH)(\mu$-dppm$)(CO)_4$ (9).

$Co_2[\mu$-η^2-$HC_2C{\equiv}C\{W(CO)_3Cp\}](\mu$-dppm$)(CO)_4$ *(13)*. $WCl(CO)_3Cp$ (55 mg, 0.15 mmol) and **9** (100 mg, 0.15 mmol) were stirred in degassed $NHEt_2$ (15 ml) with CuI (5 mg, cat.) for 10 h. Preparative TLC (light petroleum / acetone 7 / 3) gave one major deep red band (R_f 0.4). Trituration of the residue gave $Co_2[\mu$-η^2-$HC_2C{\equiv}C\{W(CO)_3Cp\}](\mu$-dppm$)(CO)_4$ (**13**) as a brick red powder (70 mg, 50%)which was recrystallized (CH_2Cl_2 / hexane). Found: C, 49.22; H, 2.87%. $C_{41}H_{28}O_7P_2Co_2W$ requires: C, 49.41; H 2.81%. IR (cyclohexane) ν(CO) 2038s, 2025vs, 2002vs, 1975vs, 1958br, 1943vs cm^{-1}; δ_H 7.56 - 7.06 (20H, m, Ph), 6.04 (1H, s, μ-η^2-HC_2), 5.59 (5H, s, Cp), 3.79 (1H, m, CH_2P_2), 3.40 (1H, m, CH_2P_2); δ_C 229.84, 210.92 (s, WCO), 206.24, 203.15 (br, CoCO), 138.7 - 127.9 (m, Ph), 35.35 (t, J_{CP} = 21 Hz, CH_2P_2); FAB MS (*m/z*) 912 - 798 [M - nCO]$^+$ (n = 3 - 7).

$Co_2(\mu$-dppm$)[\mu$-η^2-$HC_2C{\equiv}C\{Au(PPh_3)\}](CO)_4$ (14). $AuCl(PPh_3)$ (100 mg, 0.20 mmol) and **9** (135 mg, 0.20 mmol) were dissolved in thf (10 ml) with an excess of dbu (2 drops). The red solution was allowed to stir at room temperature overnight. The solvent was then removed and the red residue obtained purified by preparative TLC (light petroleum / acetone 7 / 3). The major band (R_f 0.5) was collected and recrystallized (CH_2Cl_2/hexane) to give $Co_2(\mu$-dppm$)[\mu$-η^2-$HC_2C{\equiv}C\{Au(PPh_3)\}](CO)_4$ (**14**) as deep red needles (107 mg, 48%). Found: C, 54.75; H, 3.87%. $C_{51}H_{38}O_4P_3Co_2Au$ requires: C, 54.55; H, 3.40%; IR (thf) ν(CO) 2021s, 1997s(br), 1967s(br), 1948sh

cm^{-1}; δ_H 7.61 - 7.12 (35 H, m, Ph), 5.98 (1H, s, μ-η^2-HC$_2$), 3.82, 3.39 (2 x 1H, 2 x m, CH$_2$P$_2$); δ_C 204.87, 203.43 (br, CoCO), 134.16 - 127.62 (m, Ph), 78.74 [br, C(3)], 70.63 [br, C(4)], 36.77 (t, J_{CP} =19 Hz, CH$_2$P$_2$); FAB MS (*m/z*) 1581 [M + Au(PPh$_3$)]$^+$, 1066 - 1010 [M - nCO]$^+$ (n = 2 - 4).

- CHAPTER 3 -

Synthesis and Reactivity of Some Diynyl and Diyndiyl Complexes

INTRODUCTION.

Many different synthetic approaches have been devised which allow complexes bearing diynyl and diyndiyl ligands to be synthesised, as summarised in Chapter 1. However, the further development of the chemistry of these complexes still suffers from the limited range of complexes that are available by simple, reliable methods. Diynyl complexes with $C{\equiv}CC{\equiv}CH$ ligands, which are readily amenable to derivatisation, should be especially prized.

The reactivity of the terminal $C{\equiv}CH$ alkyne moiety of 1,3-diynes is often found to closely resemble that of simple, non-conjugated 1-alkynes. For example, both types of compound are deprotonated by strong bases [84], enter into Cu(I)-catalysed coupling reactions with Group 10 di-halides [88], undergo oxidative addition reactions with low-valent metal centres [46] and are susceptible to copper-assisted coupling reactions with halo-alkynes (Cadiot-Chodkiewicz coupling) [6].

It is therefore reasonable to suppose that diynyl and diyndiyl complexes may be prepared from 1,3-diynes *via* methods similar to those used to prepare metal-acetylide complexes from 1-alkynes. The most common route to acetylide complexes of the type $Ru(C{\equiv}CR)(PPh_3)_2Cp$ involves the deprotonation of intermediate vinylidene cations $[Ru(C{=}CHR)(PPh_3)_2Cp]^+$ [95]. The vinylidene cations are usually prepared from reactions of 1-alkynes with $[L_mM]X$ complexes in the presence of a suitable halide abstracting agent [96, 135]. However, attempts to prepare the dicationic bis-vinylidene $[\{Cp(PPh_3)_2Ru\}{=}C{=}CHCH{=}C{=}\{Ru(PPh_3)_2Cp\}]^{2+}$ by sequential treatment of

$RuCl(PPh_3)_2Cp$ with $AgPF_6$ and HC≡CC≡CH were unsuccessful. Instead the reaction described resulted in the formation of the highly reactive butatrienylidene complex $[Ru(C{=}C{=}C{=}CH_2)(PPh_3)_2Cp][PF_6]$, which was susceptible to rapid addition of nucleophiles at C_γ (see Chapter 5).

At the commencement of the studies that form this thesis, structurally characterised diynyl and diyndiyl complexes were exceptionally rare. The first example of such a structural study appears to be $RuCl\{C{\equiv}CC{\equiv}CC(OSiMe_3)\}(PMe_3)(C_6Me_6)$, which was reported in 1990 by Dixneuf and co-workers [97]. In the context of the work described in this Chapter it is also worth noting that structurally characterised acetylide complexes of $W(CO)_{3-n}(L)_nCp$ are rare. The cyclopropyl complex $W(C{\equiv}CC_3H_5)(CO)_2(PMe_3)Cp$ was prepared by reduction of the ketene moiety in $W\{C(C_3H_5){=}C{=}O\}(CO)_2(PMe_3)Cp$ under a CO atmosphere [136]. The thermolysis of $W(C{\equiv}CPh)(CO)_3Cp$ and PPh_3 gave $W(C{\equiv}CPh)(CO)_2(PPh_3)Cp$, although the results of the structure determination were not fully reported [111]. The ionic binuclear complex $[Cp(CO)_3W(\mu,\eta^1,\eta^2\text{-}C_2Ph)W\{\eta^2\text{-}HC_2Ph\}(CO)Cp]BF_4$ was prepared by treating $W(C{\equiv}CPh)(CO)_3Cp$ with HBF_4. The σ-acetylide ligand of the $W(C{\equiv}CPh)(CO)_3Cp$ fragment is coordinated in η^2-fashion to the second tungsten centre.

Diynyl complexes contain several potentially reactive sites: the two C≡C moieties, one of which is adjacent to the metal centre, the other of which may be regarded as "terminal"; the metal centre and other (non-diynyl) ligands; and the C-H moiety in the case of diynyl complexes with C≡CC≡CH ligands. The presence of these functional groups raises several questions, such as do the C≡C carbon-carbon triple bonds: behave as typical organic alkynes; behave like a metal acetylide ligands; or react in a unique manner. It is equally valid to question whether the presence of the diynyl ligand affects the usual chemistry of the metal centre.

Given the vast potential of diynyl complexes to be used in the preparation of new materials, it is rather surprising that have been only a few report detailing the reactivity of the diynyl ligand. The desilylation and deprotonation reactions of $C{\equiv}CC{\equiv}CSiMe_3$ and $C{\equiv}CC{\equiv}CH$ ligands have been indicated in Chapter 1, but few reactions involving these species have been described. It has been demonstrated that $Re(C{\equiv}CC{\equiv}CH)(NO)(PPh_3)Cp^*$ and $Fe(C{\equiv}CC{\equiv}CH)(CO)(PPh_3)Cp$ are deprotonated by ^nBuLi, and the resulting anion has been trapped by MeI and metal halide complexes to give substituted products in good yield [48, 49].

During the course of these studies, Gladysz and coworkers reported the applicability of the Cadiot-Chodkiewicz conditions [103] for the preparation of metal complexes containing σ-bound polyyne chains [36, 52]. In contrast to the method described in this thesis, in which the Cu-alkynyl species was generated catalytically, the Gladysz group prepared copper species of general form $Re\{C{\equiv}C(C{\equiv}C)_nCu\}(NO)(PPh_3)Cp^*$ by stoichiometric reactions of $Re\{C{\equiv}C(C{\equiv}C)_nH\}(NO)(PPh_3)Cp^*$ with n-BuLi and CuI. These copper complexes were then reacted with silyl-protected bromo-alkynes $BrC{\equiv}CSiEt_3$ or $BrC{\equiv}CC{\equiv}CSiMe_3$ in NH_2Et to give the coupled products containing extended polyyne ligands. The groups of both Gladysz and Lapinte have applied traditional Cu(I)-catalysed alkynyl coupling techniques to $[ML_n]C{\equiv}CC{\equiv}CH$ species (ML_n = Fe(dppe)Cp* [61], $Re(NO)(PPh_3)Cp^*$ [36, 52]) to give bimetallic complexes containing longer polyyne ligands capped at each end by a transition metal.

Phenyl isocyanide has been inserted into one of the metal-carbon bonds of the bimetallic palladium complex $\{(PBu_3)_2ClPd\}C{\equiv}CC{\equiv}C\{PdCl(PBu_3)_2\}$ to give $\{(PBu_3)_2ClPd\}\{C{\equiv}CC{\equiv}CC({=}NPh)\}\{PdCl(PBu_3)_2\}]$ [137]. More recently, several cluster compounds have been obtained from the reactions of $Ru_3(CO)_{12}$ derivatives with some tungsten diynyl complexes [138, 139].

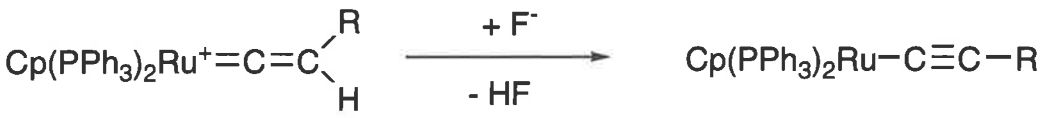
This Chapter details the synthesis of several diynyl and diyndiyl complexes using 1,4-bis(trimethylsilyl)buta-1,3-diyne or buta-1,3-diyne itself as the only source of the carbon ligands. A novel route to the diyndiyl complex $\{Cp(PPh_3)_2Ru\}C\equiv CC\equiv C\{Ru(PPh_3)_2Cp\}$ has been developed following the observation that fluoride is sufficiently strong a base to remove the vinylidene hydrogen from $[Ru(C=CHR)(PPh_3)_2Cp]^+$ (R = Ph, ^tBu). Copper(I)-catalysed reactions of buta-1,3-diyne have proved to be excellent sources of diynyl complexes containing a range of different metals. These one-pot reactions proceed rapidly, with reaction times typically in the range of 5 to 20 minutes for *ca.* 2g of halide reagent, and are clean and simple to work-up.

The reactivity of the diynyl ligand has been probed through an examination of the reactions of the remarkably versatile terminal diynyl complex $W(C\equiv CC\equiv CH)(CO)_3Cp$. The diynyl ligand may be metallated or coupled with aryl- and alkynyl-iodides, as well as itself. Both diynyl and diyndiyl ligands react with tetracyanoethylene and are readily coordinated by $Co_2(CO)_8$.

RESULTS AND DISCUSSION.

Synthesis of $\{Cp(PPh_3)_2Ru\}C\equiv CC\equiv C\{Ru(PPh_3)_2Cp\}$.

A rather serendipitous experiment lead to the observation that addition of fluoride {pK_a (HF) = 3.17 [140]}, either as the potassium or tetrabutylammonium salt, to a methanolic solution of $[Ru(C=CHR)(PPh_3)_2Cp]Cl$ (R = Ph, ^tBu) resulted in an immediate colour change of the solution from red to yellow, and the deposition of yellow crystals of the acetylide complex $Ru(C\equiv CR)(PPh_3)_2Cp$ (Equation 12).



Equation 12.

The fluoride ion is also a common reagent for the removal of trialkylsilyl protecting groups. As silylated diynes are stable, readily available compounds the reaction of these compounds with $RuCl(PPh_3)_2Cp$ in the presence of fluoride was examined as a potential route to diynyl or diyndiyl complexes.

In a trial reaction, a methanolic suspension of $RuCl(PPh_3)_2Cp$, $PhC{\equiv}CSiMe_3$ and KF was heated at reflux point for several hours. Filtration of the reaction mixture afforded $Ru(C{\equiv}CPh)(PPh_3)_2Cp$ (Equation 13) [141]. The complex $Ru(C{\equiv}CC_6H_4C{\equiv}CSiMe_3)(PPh_3)_2Cp$ (**15**) was obtained as a bright yellow crystalline solid from the analogous reaction between equimolar amounts of the metal chloride complex and *p*-$Me_3SiC{\equiv}CC_6H_4C{\equiv}CSiMe_3$. The IR spectrum of **15** was characterised by two distinct $C{\equiv}C$ triple bond absorptions, which were observed at 2153 and 2070 cm^{-1}. By comparison with the spectra of $Me_3SiC{\equiv}CC_6H_4C{\equiv}CSiMe_3$ [$\nu(C{\equiv}C)$ 2156 cm^{-1}] and $Ru(C{\equiv}CPh)(PPh_3)_2Cp$ [$\nu(C{\equiv}C)$ 2068 cm^{-1}] these bands are assigned to silyl and ruthenium substituted alkyne moieties, respectively. The ^1H NMR spectrum displayed a resonance due to the $SiMe_3$ group at δ 0.26, while the Cp signal was observed at δ 4.35. In the ^{13}C NMR spectrum, a triplet at δ 123.46 was assigned to Ru-*C*≡C, while singlet resonances at δ 116.71, 115.10 and 106.48 were assigned to the other alkynyl carbons. The carbon nuclei of the $SiMe_3$ group were observed as a sharp singlet at δ 0.13. The ES MS contained only the molecular ion. The monosubstituted complex is sufficiently insoluble in methanol to precipitate from the reaction mixture before removal of the second silyl group.

$$[Ru]{-}Cl \quad + \quad Me_3Si{-}C{\equiv}C{-}R \quad \xrightarrow[\substack{-\ SiFMe_3 \\ -Cl^-}]{+\ F^-} \quad [Ru]{-}C{\equiv}C{-}R$$

$[Ru] = Ru(PPh_3)_2Cp$
$R = Ph, Bu^t, C_6H_4C{\equiv}CSiMe_3$ (**15**)

Equation 13.

The bis(ruthenium) diacetylide complex $\{Cp(PPh_3)_2Ru\}C{\equiv}CC{\equiv}C\{Ru(PPh_3)_2Cp\}$ (**16**) has been obtained previously from the reaction of the lightly stabilised complex $[Ru(thf)(PPh_3)_2Cp][PF_6]$, prepared by treating a thf solution of the corresponding chloride compound with $AgPF_6$, with half an equivalent of $LiC{\equiv}CC{\equiv}CLi$ (Equation 4) [41]. The reaction between two equivalents of $RuCl(PPh_3)_2Cp$ and KF with $Me_3SiC{\equiv}CC{\equiv}CSiMe_3$ gave **16** as a pale orange microcrystalline solid in good yield (Equation 14).

$$2\ [Ru]{-}Cl \quad \xrightarrow[Me_3Si{-}C{\equiv}C{-}C{\equiv}C{-}SiMe_3]{2\ F^-} \quad \underset{\mathbf{16}}{[Ru]{-}C{\equiv}C{-}C{\equiv}C{-}[Ru]}$$

Equation 14.

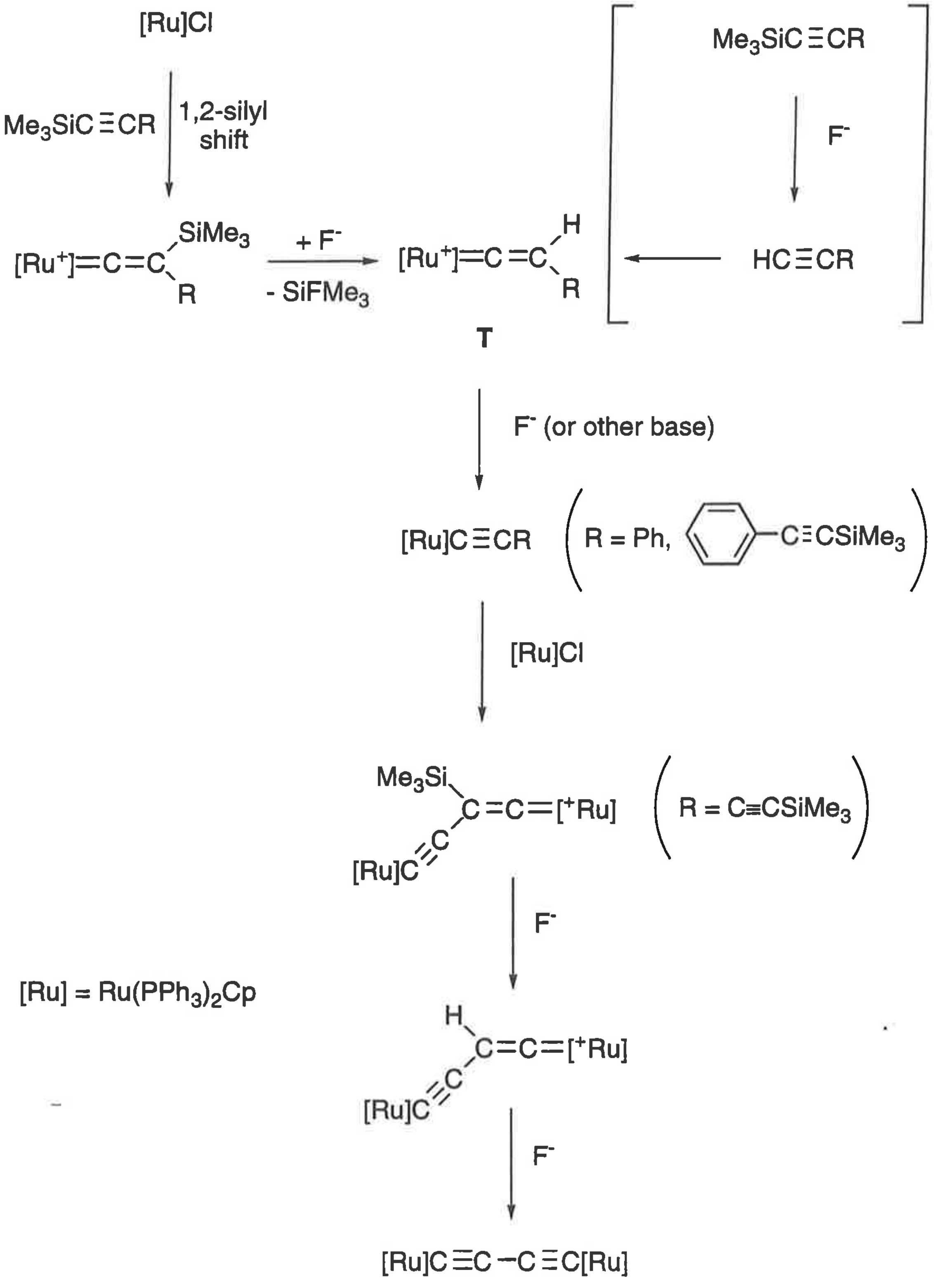
Adjusting the stoichiometry had no effect on the product of the reaction. Thus attempts to prepare the diynyl complexes $Ru(C{\equiv}CC{\equiv}CR)(PPh_3)_2Cp$ (R = $SiMe_3$, H) by reaction of the ruthenium chloride reagent and an excess of $Me_3SiC{\equiv}CC{\equiv}CSiMe_3$ resulted only in the isolation of **16** and the stoichiometric amount of $RuCl(PPh_3)_2Cp$. This indicates that the metallation of $Ru(C{\equiv}CC{\equiv}CR)(PPh_3)_2Cp$ is more facile than the metallation of the diyne precursor $Me_3SiC{\equiv}CC{\equiv}CSiMe_3$ under the conditions described.

Scheme 7 accounts for the formation of these acetylide complexes *via* the key vinylidene intermediate **T**, which is deprotonated by fluoride. The reaction is driven by the precipitation of the acetylide products. On the basis of the experiments described above it is not possible to distinguish between the suggested mechanism, which involves a 1,2-silyl shift [46, 142], from an alternate mechanism whereby the silyl group is removed to give a 1-alkyne, or 1,3-diyne, prior to reaction with the metal centre. The intermediate vinylidene complex **T** may then be formed in the usual manner by a 1,2-H shift [96].

However, in light of the thermal instability of 1,3-diynes, and the results described in Chapter 5 where buta-1,3-diyne is shown to react with the $Ru(PPh_3)_2Cp$ fragment *via* a 1,4 H-shift, Scheme 7 describes the more likely pathway.

The reaction requires the addition of only one equivalent of fluoride for each silyl group to be metallated. While the protonolysis of fluorosilanes is a slow process [143] the presence of a significant concentration of F^- ions is maintained throughout the reaction by the equilibria illustrated in Scheme 8.

The yield of **17** increased from *ca.* 50% to *ca.* 70% when the reaction solution contained an additional equivalent of a hindered base such as ethyldicyclohexylamine, which supports the intermediacy of **T**.



[Ru] = $Ru(PPh_3)_2Cp$

16

Scheme 7.

$$\mathrm{R{-}C{\equiv}C{-}SiMe_3} + \mathrm{F^-} \rightleftharpoons \mathrm{R{-}C{\equiv}C{-}H} + \mathrm{SiFMe_3}$$

$$\mathrm{SiFMe_3} + \mathrm{MeOH} \rightleftharpoons \mathrm{Si(OMe)Me_3} + \mathrm{HF}$$

$$\mathrm{HF} \rightleftharpoons \mathrm{H^+} + \mathrm{F^-}$$

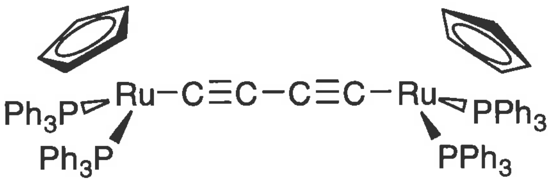
$$\mathrm{R{-}C{\equiv}C{-}H} + \mathrm{RuCl(PPh_3)_2Cp} \rightleftharpoons \mathrm{[Ru(C{=}CHR)(PPh_3)_2Cp]^+} + \mathrm{Cl^-}$$

$$\mathrm{[Ru(C{=}CHR)(PPh_3)_2Cp]^+} + \mathrm{F^-} \rightleftharpoons \mathrm{Ru(C{\equiv}CR)(PPh_3)_2Cp} + \mathrm{HF}$$

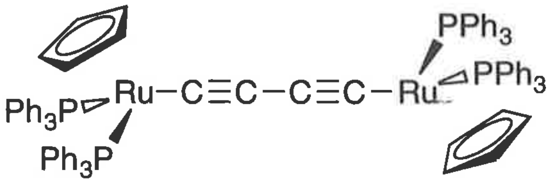
Scheme 8

*Interconversion of cis and trans {Cp(PPh$_3$)$_2$Ru}C≡CC≡C{Ru(PPh$_3$)$_2$Cp} (**16**).*

A previous study of **16** identified two rotamers in which the Cp rings were disposed in either *cis* or *trans* fashion about the C_4 ligand, although no details of the selective preparation of these isomers, their interconversion or distinguishing spectral properties were reported [41].



cis-**16**



trans-**16**

Vapour diffusion of diethyl ether into a thf solution of {Cp(PPh$_3$)$_2$Ru}C≡CC≡C{Ru(PPh$_3$)$_2$Cp} yielded crystals of one isomer, **16a**, as a di-thf solvate, which was characterised by a single ν(CC) band in the IR spectrum at 1970 cm^{-1}. A single crystal X-ray structure determination established the *cis* orientation of the

Cp ligands in this form. A molecule of **16a** is shown in Figure 10, and important parameters are given in the caption.

The structure shows two $Ru(PPh_3)_2Cp$ fragments linked by a four-carbon chain. The two metal fragments are oriented in such a way that the Cp ligands are found *cis* to each other. The coordination about the Ru centres is essentially octahedral, and the bond parameters of these groups are similar to those described for other complexes containing this moiety [144]. The bond distances in the carbon chain suggest a degree of electron delocalisation throughout the ligand. The Ru(1)-C(1) and Ru(2)-C(4) distances [2.00(1), 2.01(1) Å] are comparable with other Ru-C(sp) bonds, which fall in the range 2.009 - 2.017 Å [145]. The C(2)-C(3) single bond [1.38(2) Å] is shortened from the normal value of *ca.* 1.48 Å. However, the low precision of the structure determination precludes a meaningful detailed analysis. Overall, the structure is very similar to that reported earlier for a non-solvated sample [41]. The disposition of the Cp* ligands in the rhenium complex (*SS,RR*)-$\{Cp^*(PPh_3)(NO)Re\}C{\equiv}CC{\equiv}C\{Re(NO)(PPh_3)Cp^*\}$ is similar to that of the Cp ligands in **16a**. It is worth noting that the IR spectrum of the rhenium diyndiyl complex also contains only a single ν(C≡C) band [45].

Heating a thf solution of **16a** at reflux point for 10 minutes, followed by precipitation of the complex with pentane, gave orange microcrystals of a second isomer, **16b**, with ν(C≡C) bands (nujol) at 1990w and 1976m cm^{-1}. The iron complexes [Fe]C≡CC≡C[Fe], {[Fe]C≡CC≡C[Fe]}PF_6 and {[Fe]C≡CC≡C[Fe]}$[PF_6]_2$ ([Fe] = Fe(dppe)Cp*) also have two ν(C≡C) bands in their IR spectra [43]. A single crystal X-ray study of the mono-cation established the *trans* configuration of the Cp* ligands in these compounds [43]. By analogy, we suggest **16b** to be the *trans* rotamer of $\{Cp(PPh_3)_2Ru\}C{\equiv}CC{\equiv}C\{Ru(PPh_3)_2Cp\}$.

The solution IR spectra of both isomers **16a** and **16b** in CH_2Cl_2 were identical in the ν(C≡C) region [1969 cm^{-1}]. Crystallisation of **16b** from CH_2Cl_2 gave **16a** with no loss

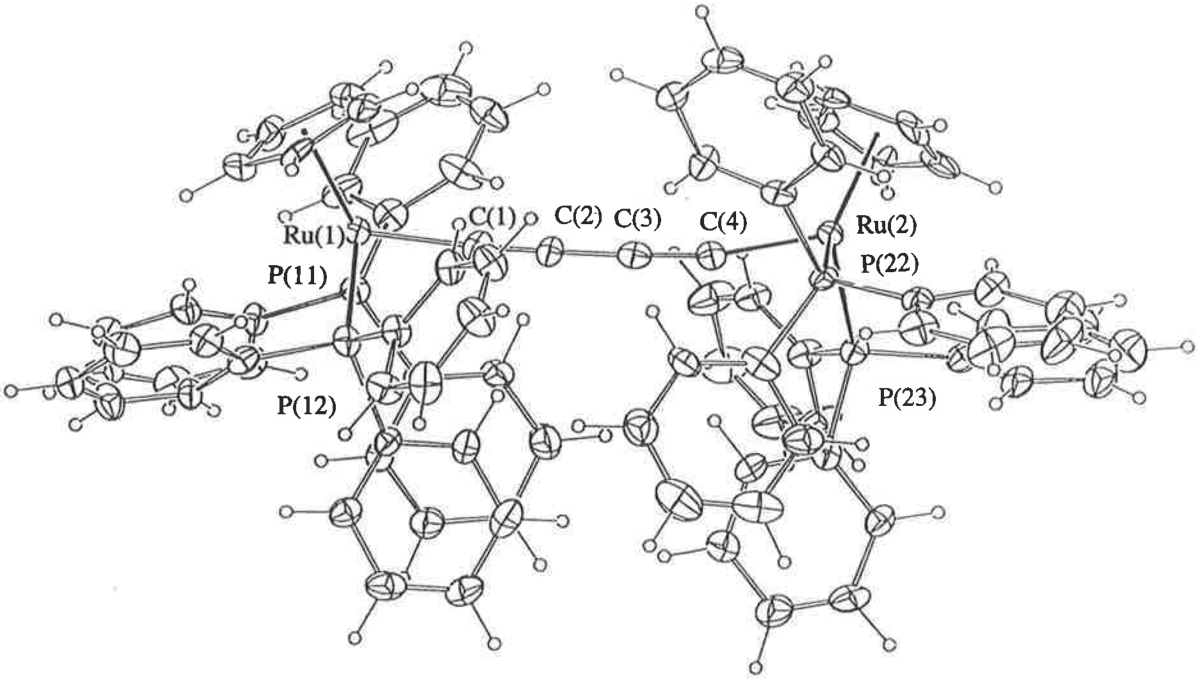


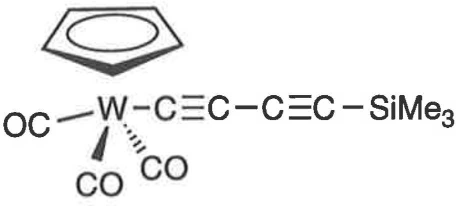
Figure 10 : Plot of a molecule of **16a** showing the atom numbering scheme. Important bond lengths (Å) and angles (°): Ru(1)-P(11) 2.304(3); Ru(1)-P(12) 2.276(5); Ru(1)-C(1) 2.00(1); C(1)-C(2) 1.20(2); C(2)-C(3) 1.38(2); C(3)-C(4) 1.25(2); C(4)-Ru(2) 2.01(1); Ru(2)-P(21) 2.289(3); Ru(2)-P(22) 2.284(4); P(11)-Ru(1)-P(12) 101.7(1); P(11)-Ru(1)-C(1) 86.7(3); P(12)-Ru(1)-C(1) 89.0(5); Ru(1)-C(1)-C(2) 177(1); C(1)-C(2)-C(3) 178(2); C(2)-C(3)-C(4) 175(1); C(3)-C(4)-Ru(2) 170(1); C(4)-Ru(2)-P(21) 90.8(3); C(4)-Ru(2)-P(22) 85.8(4); P(21)-Ru(2)-P(22) 102.7(1) (by B.W. Skelton and A.H. White).

of material. An examination of the crystal structures of **16a** indicates that interactions between the phenyl groups of the PPh_3 ligands are responsible for the isolation of the *cis* and *trans* isomers [41].

Preparation of 1,3-Diynyl Complexes.

Treatment of the 1,3-butadiyne synthon $Me_3SiC{\equiv}CC{\equiv}CSiMe_3$ with one equivalent of MeLi.LiBr results in the formation of $LiC{\equiv}CC{\equiv}CSiMe_3$ [86]. Several diynyl complexes have been prepared by reaction of this reagent with suitable metal species containing readily displaced halide ligands [49, 57, 61]. Unfortunately, all efforts to prepare $Ru(C{\equiv}CC{\equiv}CSiMe_3)(PPh_3)_2Cp$ from $LiC{\equiv}CC{\equiv}CSiMe_3$ and $RuCl(PPh_3)_2Cp$ or $[Ru(S)(PPh_3)_2Cp]PF_6$ (S = NCMe, thf) were unsuccessful. On one occasion, the reaction with $RuCl(PPh_3)_2Cp$ gave $RuBr(PPh_3)_2Cp$, presumably as a result of halide exchange with the LiBr present in the $LiC{\equiv}CC{\equiv}CSiMe_3$ solution. The structure of $RuBr(PPh_3)_2Cp$ was determined, and is included in Appendix 1. A green complex, probably $Ni(C{\equiv}CC{\equiv}CSiMe_3)(PPh_3)Cp$, was detected in the reaction mixture after addition of $LiC{\equiv}CC{\equiv}CSiMe_3$ to a solution of $NiBr(PPh_3)Cp$, but it could not be isolated.

A more satisfactory result was obtained from the reaction of $WCl(CO)_3Cp$ with $LiC{\equiv}CC{\equiv}CSiMe_3$. The diynyl complex $W(C{\equiv}CC{\equiv}CSiMe_3)(CO)_3Cp$ (**17**) was isolated as a yellow crystalline solid from the reaction mixture in moderate yield. The complex was characterised by elemental microanalysis, spectroscopic and crystallographic methods. The IR spectrum contained two weak $\nu(C{\equiv}C)$ bands and $\nu(CO)$ carbonyl absorptions characteristic of the $W(CO)_3Cp$ fragment. The ^1H NMR spectrum contained well-resolved singlet resonances for the Cp ligand and $SiMe_3$ groups while in the ^{13}C NMR spectrum the four carbon centres of the diynyl ligand were observed at δ 111.74 (C_α), 110.86 (C_β), 90.04 (C_γ) and 73.59 (C_δ). The resonances of the diynyl $C{\equiv}C$ carbons are shifted to progressively lower fields the closer the carbon centres are to the metal nucleus. In **17**, and the other W diynyl complexes described below, C_α showed coupling to ^{183}W (J_{CW} typically 60-70 Hz). The FAB mass spectrum was relatively simple, containing the molecular ion, which fragments by loss of CO.



17

A single crystal structure determination confirmed the presence of the tungsten bound η^1-C≡CC≡CSiMe$_3$ ligand. A molecule of **17** is shown in Figure 11, along with selected parameters. The methyl groups of the SiMe$_3$ part of the molecule were found to be disordered over two sets of sites. The disposition of the CO and Cp ligands about the metal centre in the W(CO)$_3$Cp fragment is similar to that observed in other WX(CO)$_3$Cp complexes (X = Cl [146], C≡CC{=C(CN)$_2$}C{=C(CN)$_2$}H (see below)), and will not be discussed further. The most interesting feature of the structure is the six-atom W-C(1)-C(2)-C(3)-C(4)-Si chain. There is little deviation from linearity along the chain as evidenced by the angles W-C(1)-C(2) [179.0(8) Å] and C(2)-C(3)-C(4) [177(1) Å]. The C(1)-C(2) and C(3)-C(4) bond lengths are experimentally identical at 1.22(1) Å, while the C(2)-C(3) bond length is considerably longer at 1.36(1) Å. These dimensions are comparable to those observed for the diynyl ligand in the ruthenium complex *trans*-Ru(C≡CC≡CSiMe$_3$)$_2$(CO)$_2$(PEt$_3$)$_2$ (C(1)-C(2) 1.226(2), C(2)-C(3) 1.370(2), C(3)-C(4) 1.209(2) Å [57]).

The C≡C triple bonds C(1)-C(2) and C(3)-C(4) bonds in **17** are longer than the analogous C(1)-C(2) distance in W(C≡CPh)(CO)$_2$(PPh$_3$)Cp (**38**) [1.19(1) Å] (see below). This may be attributed to electron delocalisation along the W-C≡CC≡C-Si chain. It has been proposed that alkylsilyl groups facilitate delocalisation along metal-polyyne

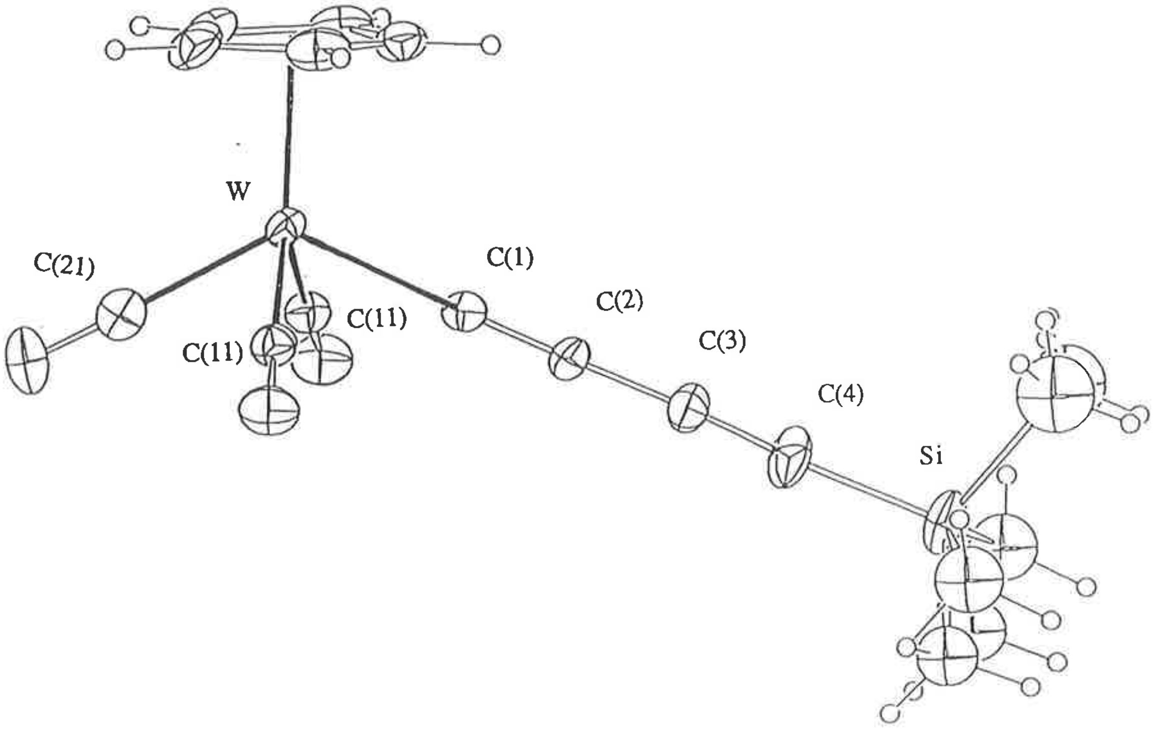


Figure 11 : Plot of a molecule of **17** showing the atom numbering scheme. Selected bond lengths (Å) and angles (°): W-C(0) 1.996(-); W-C(11) 2.013(7); W-C(21) 2.01(1); W-C(1) 2.124(8); C(1)-C(2) 1.22(1); C(2)-C(3) 1.36(1); C(3)-C(4) 1.22(1); C(4)-Si 1.82(1); C(11)-W-C(0) 122.8(-); C(11)-W-C(21) 76.7(2); C(11)-W-C(1) 75.3(2); C(21)-W-C(1) 127.1(4); W-C(1)-C(2) 179(1); C(1)-C(2)-C(3) 179(1); C(2)-C(3)-C(4) 177(1); C(3)-C(4)-Si 177(1). C(0) is the centroid of the Cp ring (by B.W. Skelton and A.H. White).

chains through $d_{\pi}(Si)$-$d_{\pi}(C_{sp})$-$d_{\pi}(M)$ conjugation or $\sigma(Si$-$C_{sp})$-$p_{\pi}(C_{sp})$-$d_{\pi}(M)$ hyperconjugation [57]. As expected for the larger W centre, the W-C(1) bond [2.124(8) Å] is longer than the analogous Ru-C bond [2.057(2) Å] [57].

Despite repeated efforts, it was not possible to increase the yield of **17** significantly. After these rather disappointing results, an alternative synthetic strategy was explored.

Cu(I)-Catalysed Syntheses of η^1*-Diynyl Complexes.*

Addition of a five-fold excess of buta-1,3-diyne, as a 3 M solution in thf, to a solution of $WCl(CO)_3Cp$ containing $NHEt_2$ in the presence of CuI resulted in a rapid colour change from red to bright yellow, and the precipitation of $[NH_2Et_2]Cl$ (Equation 15). The complex $W(C{\equiv}CC{\equiv}CH)(CO)_3Cp$ (**18**) was isolated as a bright yellow, light-sensitive powder (90%) after column chromatography on Al_2O_3.

$$[L_mM]Cl + \quad HC{\equiv}C{-}C{\equiv}CH \quad \xrightarrow[NHEt_2]{CuI} [L_mM]C{\equiv}C{-}C{\equiv}CH$$

$[L_mM]$ = $W(CO)_3Cp$ (**18**); $Mo(CO)_3Cp$ (**19**); $Fe(CO)_2Cp$ (**20**)

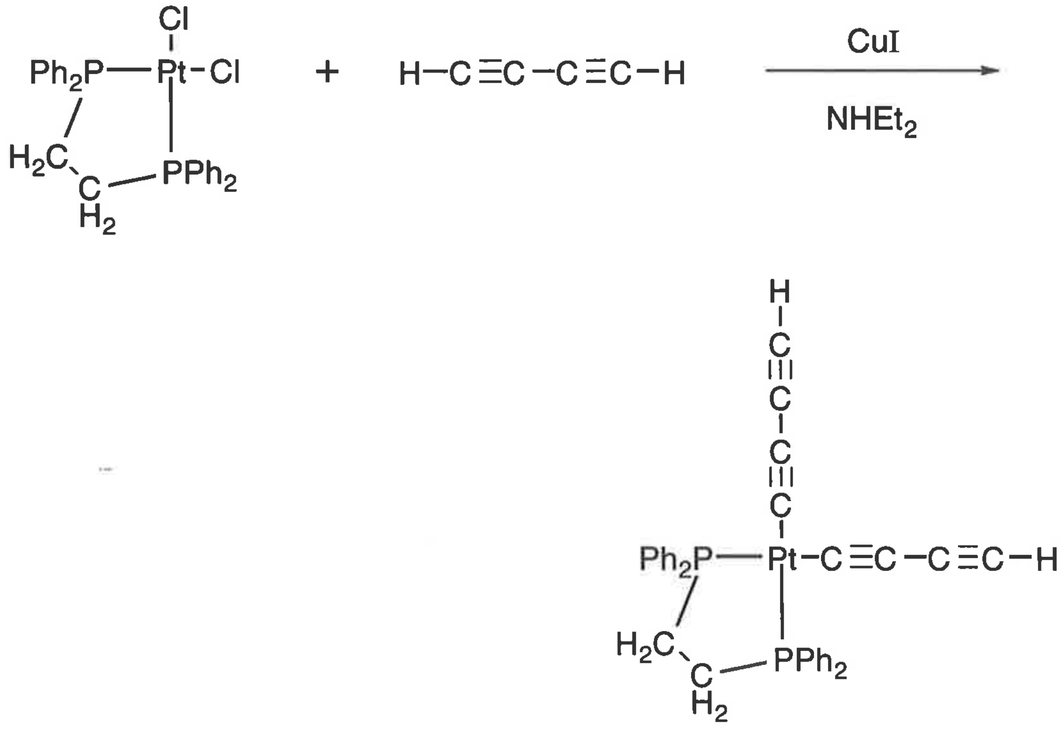
Equation 15.

The IR spectrum of **18** contained strong ν(CO) absorption bands at 2044 and 1958 cm^{-1}, characteristic of the $W(CO)_3Cp$ fragment. The terminal C≡C triple bond gave rise to a much weaker band at 2145 cm^{-1}. The absorption arising from the alkyne moiety σ-bonded to the metal centre was obscured by the ν(CO) bands and could not be observed. The C-H stretch was found at 3260 cm^{-1}. In the ^1H NMR spectrum, the terminal C≡CH proton gave rise to a singlet resonance near δ 2, which is within the range found for the corresponding signal in purely organic 1-alkynes and 1,3-diynes [6, 147]. The Cp resonances were observed at δ 5.66 and 91.51 in the ^{1}H and ^{13}C NMR spectra respectively. The carbon nuclei of the diynyl ligand gave weak resonances in the ^{13}C NMR spectrum at δ 110.52 (C_α), 71.60 (C_β), 70.13 (C_γ) and 63.30 (C_δ). In addition to C_α, the C_β and C_γ carbons of **18** also displayed a weaker coupling to ^{183}W, which assisted in their assignment. It was assumed that the magnitude of the coupling constants J_{CW} follows the trend previously observed for J_{CP} in the iron diynyl complexes $Fe(C{\equiv}CC{\equiv}CR)(dppe)Cp^*$ (R = $SiMe_3$, H) and the $^4J_{CW}$ coupling to C_γ is larger than $^3J_{CW}$ to C_β [61]. The ES MS of a solution of **18** in MeCN / H_2O at low cone voltages showed three ions at *m/z* 396, 368 and 355 derived from **18** by loss of carbonyl ligands. Two of these fragment ions were stabilised by a molecule of NCMe. The observation of $[M + solvent]^+$ ions is common with this technique [148]. At higher cone voltages more complete fragmentation occurred, and only the $[M + H - 3CO]^+$ ion was observed.

The analogous dark yellow molybdenum compound $Mo(C{\equiv}CC{\equiv}CH)(CO)_3Cp$ (**19**) was similarly prepared from $MoX(CO)_3Cp$ (X = Cl, I) and buta-1,3-diyne. This compound was more light sensitive than the tungsten compound **18**, becoming brown after only a few minutes exposure to fluorescent laboratory lighting. The spectral properties of **19** were not significantly different from those of **18**. The absence of a spin-active metal nucleus resulted in the observation of four sharp singlets in the ^{13}C NMR spectrum for the carbon nuclei of the diynyl ligand.

The iron-diynyl compound $Fe(C{\equiv}CC{\equiv}CH)(CO)_2Cp$ (**20**) was also obtained directly from buta-1,3-diyne and $FeCl(CO)_2Cp$ in the presence of Cu(I). Complex **20** has also been obtained by treating $Fe(C{\equiv}CC{\equiv}CSiMe_3)(CO)_2Cp$ with fluoride (Equation 1) [49]. Complex **20** has also been isolated from the Pd(0)-catalysed coupling reaction between $Me_3SnC{\equiv}CC{\equiv}CH$ and $FeI(CO)_2Cp$ (Equation 7) [40]. The spectral data obtained for **20** prepared by the Cu(I)-catalysed reaction was in good agreement with that given by Crescenzi and Lo Sterzo [40].

The preparation of $Pt(C\equiv CC\equiv CH)_2(dppe)$ (**21**) using the Cu(I) method described above was straight forward (Equation 16). The chelating bis(diphenylphosphino)ethane (dppe) ligand imposes a rigid *cis* geometry on the complex. In the IR spectrum, acetylenic ν(CH) and ν(C≡C) bands were observed at 3288 and 2147 cm^{-1} respectively. The butadiynyl ligands were equivalent in solution, and only one ^{1}H resonance for the acetylenic C≡CH protons were observed at δ 1.82. This signal was flanked by ^{195}Pt satellite signals. In the ^{13}C NMR spectrum, the resonances of the diynyl ligands were observed at δ 93.7 (C_α), 77.21 (C_β, s), 71.75 (C_γ, s), 61.74 (C_δ, s). The ^{31}P NMR spectrum contained only a single resonance, which also showed coupling to ^{195}Pt. The FAB MS of **21** showed the molecular ion at *m/z* 692, and fragment ions from the sequential loss of the diynyl ligands at *m/z* 642 and 593.



21

Equation 16.

A single crystal X-ray study of **21**, as a bis-CH_2Cl_2 solvate, confirmed the proposed structure. A molecule of **21** is illustrated in Figure 12, and selected bond lengths and angles are listed in the caption. The arrangement of the ligands about the Pt centre was distorted from ideal square planar geometry [C(1)-Pt-C(1*) 93.2°] because of the limited bite angle of the chelating bis-phosphine ligand [P-Pt-P* 86.2°]. There is little evidence for electronic delocalisation between the Pt centre and the diynyl ligands. The C≡C triple bonds C(1)-C(2) and C(3)-C(4) are rather short at 1.17(2) and 1.16(2) Å respectively. The diynyl ligands are twisted above and below the P-Pt-P plane, presumably as a result of crystal packing forces.

Formation of Diyndiyl Complexes via Cu(I)-Catalysed Coupling Reactions.

Complex **18** and the related compounds described above are convenient precursors to a variety of bimetallic diynyl complexes. For example, addition of an equimolar amount of $WCl(CO)_3Cp$ to a solution of **18** in thf / $NHEt_2$ containing a catalytic amount of CuI resulted in the formation of the bimetallic diyndiyl complex $\{Cp(CO)_3W\}C\equiv CC\equiv C\{W(CO)_3Cp\}$ (**22**) (80%) as a sparingly soluble yellow powder (Equation 17).

$$[L_mM]C\equiv C-C\equiv CH \quad + \quad [L'_{m'}M']Cl \xrightarrow[NHEt_2]{CuI} [L_mM]C\equiv C-C\equiv C[M'L'_{m'}]$$

$[L_mM]$ = $W(CO)_3Cp$; $[M'L'_{m'}]$ = $W(CO)_3Cp$ (**22**), $Mo(CO)_3Cp$ (**23**); $Fe(CO)_2Cp$ (**24**)

Equation 17.

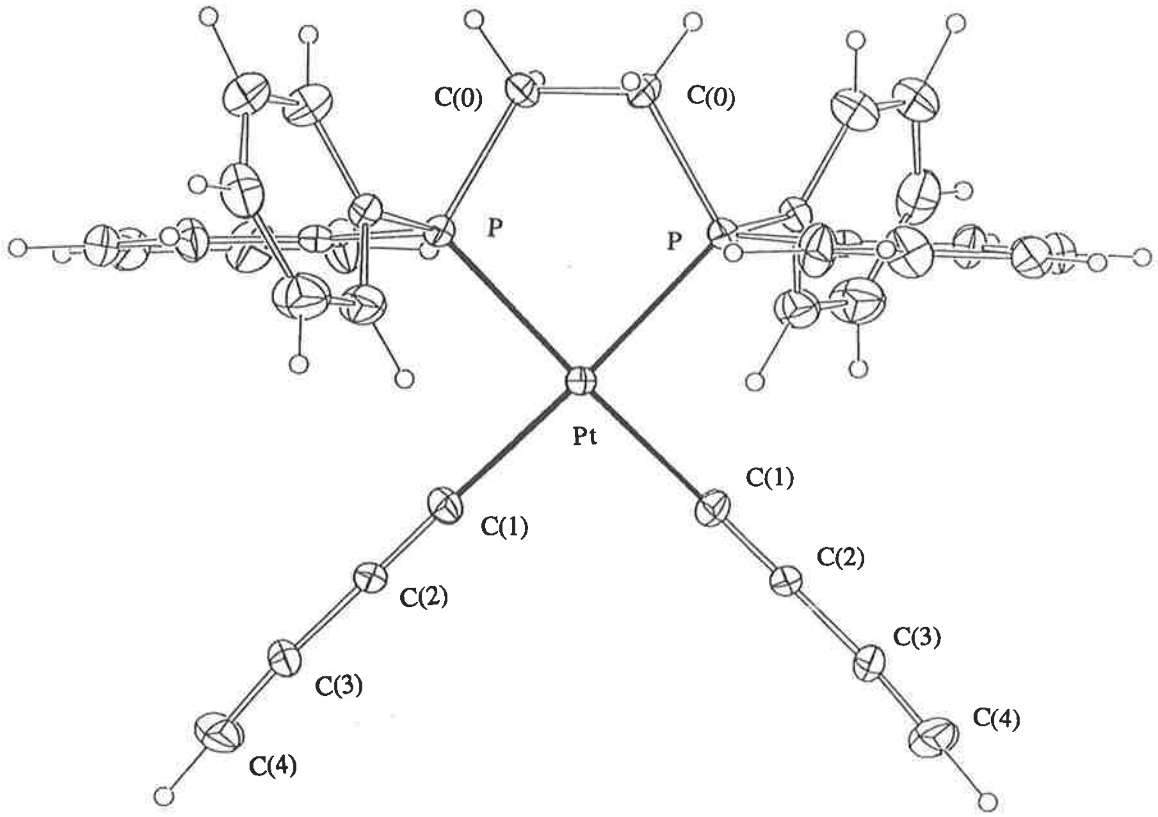


Figure 12 : A plot of a molecule of **21** showing the atom numbering scheme. Important bond lengths (Å) and angles (°): Pt-P 2.269(3); Pt-C(1) 2.02(1); C(1)-C(2) 1.17(2); C(2)-C(3) 1.36(2); C(3)-C(4) 1.16(2); C(1)-Pt-P 90.5(3); C(1)-Pt-P* 173.7(3); P-Pt-P* 86.2(1); Pt-C(1)-C(2) 171.7(9); C(1)-C(2)-C(3) 176(1); C(2)-C(3)-C(4) 175(1). [* symmetry operation: 1-x,y,(3/2)-z] (by B.W. Skelton and A.H. White).

Complex **22** was identified from its microanalytical and spectral data. The IR spectrum of the diyndiyl complex **22** was very similar to that of the diynyl compound **18**. A weak ν(C≡C) band was observed in a dilute CH_2Cl_2 solution at 2145 cm^{-1}, while the carbonyl ligands of the $W(CO)_3Cp$ fragments gave rise to two very closely spaced bands at 2043 and 2037 cm^{-1} and a broad absorption at 1955 cm^{-1}. The Cp ligands gave rise to a single resonance at δ 5.81 in the ^1H NMR spectrum. The low solubility of **22** prevented the measurement of a satisfactory ^{13}C NMR spectrum . The ES MS spectrum at low cone voltage contained a single peak at *m/z* 687 which was assigned to the $[M - CO + H]^+$ ion. At higher cone voltages, more extensive fragmentation occurred, and ions corresponding to the loss of up to six carbonyl ligands from **22** were observed. In addition a small ion was found at *m/z* 718. This ion was assigned the formula $[M - 2CO + NCMe + H_2O + H]^+$ on the basis of correlation between the observed and calculated isotope patterns.

The di-molybdenum analogue $\{Cp(CO)_3Mo\}C{\equiv}CC{\equiv}C\{Mo(CO)_3Cp\}$(**23**) was prepared similarly from **19** and $MoCl(CO)_3Cp$, while the mixed-metal complex $\{Cp(CO)_3W\}C{\equiv}CC{\equiv}C\{Mo(CO)_3Cp\}$ (**24**) was obtained from both the reaction of **18** with $MoCl(CO)_3Cp$ and **19** with $WCl(CO)_3Cp$. Again, the poor solubility of these bimetallic complexes prevented the recording of their ^{13}C NMR spectra. The Cp resonances in the ^1H NMR spectrum of the molybdenum complex **23** was observed at δ 5.53, while for **24**, two discrete signals were found at δ 5.67 and 5.55. These were assigned to the ligands on tungsten and molybdenum, respectively, by comparison with the chemical shifts of the Cp ligands in **18** (δ 5.66) and **19** (δ 5.58). In order to obtain a clean ES mass spectrum of **23** it was necessary to add a small amount of NaOMe to the sample solution [149]. In addition to a peak at *m/z* 510 from the $[M - CO + H]^+$ ion, peaks at *m/z* 1099 $[2M + Na]^+$ and 560 $[M + Na]^+$ were also observed. The nature of these alkali-metal containing ions is currently being investigated in greater detail [150]. It should be noted that similar aggregate ions containing alkali metals were formed with a number of the alkynyl and diynyl complexes reported in this work.

The mixed tungsten-iron complex $\{Cp(CO)_3W\}C{\equiv}CC{\equiv}C\{Fe(CO)_2Cp\}$ (**25**) was isolated from the Cu(I)-catalysed reaction between $FeCl(CO)_2Cp$ and **18**; the related ruthenium complex $\{Cp(CO)_3W\}C{\equiv}CC{\equiv}C\{Ru(CO)_2Cp\}$ (**26**) was obtained from a similar reaction of **18** and $RuCl(CO)_2Cp$. Complex **25** has also been obtained by treating $Fe(C{\equiv}CC{\equiv}CH)(CO)_2Cp$ sequentially with *sec*-BuLi and $WCl(CO)_3Cp$ [49].

The profile of the ν(CO) bands in the IR spectrum of **25** approximates to a superposition of those of **18** and **20**. The frequency of these bands were reduced by 5 to 10 cm^{-1}, which indicates that there is a limited degree of electronic interaction between the metal centres through the diyndiyl ligand. Wong and coworkers have reported a somewhat greater decrease (*ca.* 40 cm^{-1}) in the ν(CO) frequencies of $\{Cp(PPh_3)(CO)Fe\}C{\equiv}CC{\equiv}C\{Fe(CO)_2Cp\}$ when compared with those of $\{Cp(CO)_2Fe\}C{\equiv}CC{\equiv}C\{Fe(CO)_2Cp\}$ [49]. Several electrochemical studies of butadiynediyl complexes have indicated substantial electronic interaction between metal centres linked by this ligand (see Chapter 4).

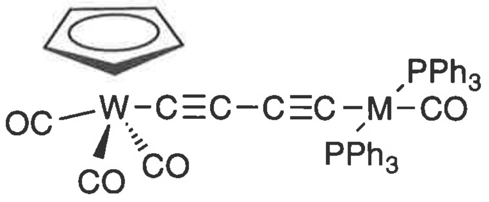
The spectral data of **26** were essentially identical to those of the iron analogue **25**. The complex was very sensitive to light , and an accurate microanalysis was not obtained.

The complex $\{Cp(CO)_3W\}C{\equiv}CC{\equiv}C\{Ir(CO)(PPh_3)_2\}$ (**27**) was obtained from a similar reaction between **18** and Vaska's compound $IrCl(CO)(PPh_3)_2$ in the presence of Cu(I). The compound was characterised by a two strong ν(CO) bands in the IR spectrum, the Ir ν(CO) being coincident with the 1952 cm^{-1} ν(CO) band of the $W(CO)_3Cp$ fragment. The ^1H and ^{13}C NMR spectra contained resonances associated with the Cp ligand on tungsten and PPh_3 ligands on iridium. It was not possible to observe the resonances from the carbons of the bridging C_4 ligand. The FAB mass spectrum showed the molecular ion and the $[M - CO]^+$ and $[Ir(CO)(PPh_3)_2]^+$ fragment ions. During recrystallisation, the complex formed the di-oxygen adduct

$\{Cp(CO)_3W\}C{\equiv}CC{\equiv}C\{Ir(O_2)(CO)(PPh_3)_2\}$. The presence of the O_2 ligand was determined by single-crystal X-ray diffraction study [151]. While the atom connectivity in the complex has been established, the low precision of the structure determination, resulting from the poor quality of the crystal used in the data collection, render the result unpublishable.

The oxidative addition of small molecules like molecular oxygen, CO, HCl, CH_3I, benzyl chloride, etc. to Vaska's compound is text-book chemistry and the oxygen adduct of $Ir(C{\equiv}CPh)(CO)(PPh_3)_2$ is known [152]. The ready addition of O_2 to **27**, while not surprising, suggests that **27** is a reagent deserving a much more detailed examination than has been possible during the course of this study. A satisfactory microanalysis could not be obtained, presumably through a combination of the light-sensitivity of **27** and the presence of some of the O_2 adduct in the microanalytical sample.

The rhodium analogue $\{Cp(CO)_3W\}C{\equiv}CC{\equiv}C\{Rh(CO)(PPh_3)_2\}$ (**28**) was prepared and characterised in a similar fashion. The all-*trans* geometry is imposed upon the Group 9 metal by the steric bulk of the PPh_3 ligands.

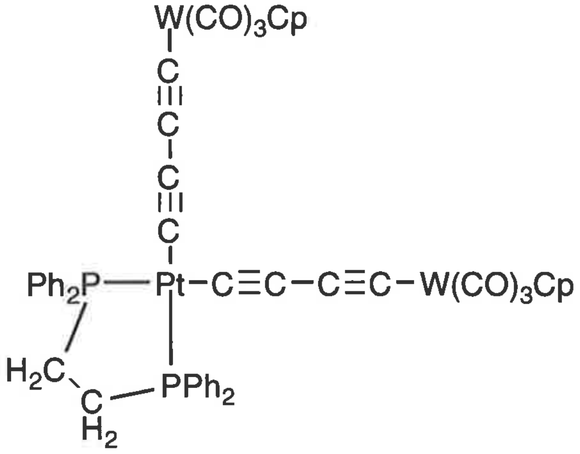


M = Ir (**27**), Rh (**28**)

Both diynyl ligands of $Pt(C{\equiv}CC{\equiv}CH)_2(dppe)$ (**21**) were metallated by $WCl(CO)_3Cp$ in the presence of Cu(I) to give $Pt[C{\equiv}CC{\equiv}C\{W(CO)_3Cp\}]_2(dppe)$ (**29**). No $\nu(C{\equiv}C)$ bands were observed in the IR spectrum of this tri-metallic complex, and the spectrum was dominated by the intense $\nu(CO)$ bands of the $W(CO)_3Cp$ fragment. The

$W(CO)_3Cp$ fragments were equivalent in solution, the Cp ligands giving rise to sharp singlet resonances at δ 5.56 and 91.68 in the ^1H and ^{13}C NMR spectra respectively. The C≡C and CO carbon signals were not observed in the ^{13}C NMR experiment due to the low solubility of **29** and the relatively slow relaxation rates of these nuclei.

The ES MS of **29** in NCMe containing formic acid was simple with ions $[M + H]^+$, $[M + H + NCMe - CO]^+$ and $[M + H - CO]^+$ found. However, in the presence of $AgNO_3$ two unusual dicationic aggregates were observed at *m/z* 1566 and 1464 [153]. The dicationic nature of these species was evidenced by the separation of the isotope peaks by 0.5 amu. These ions are assigned as $[(M + H + Ag + NO_3 + NCMe)_2]^{2+}$ and $[(M + Ag)_2]^{2+}$ respectively, although the incomplete resolution of the isotope pattern makes such assignments tentative at best. Again, the light sensitivity of the complex hampered efforts to obtain a sufficiently pure sample for elemental microanalysis.



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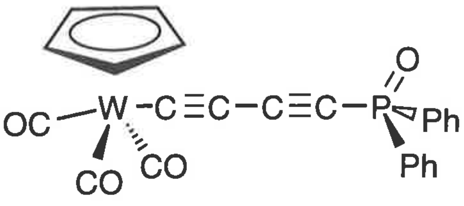
Derivatives resulting from the deprotonation of W(C≡CC≡CH)(CO)₃Cp (18).

Attempts to react **18** with n-BuLi resulted in extensive decomposition of the diynyl reagent. However, **18** was cleanly deprotonated by the bulky base lithium diisopropylamide (LDA) to give the lithiated intermediate $W(C{\equiv}CC{\equiv}CLi)(CO)_3Cp$ (**30**) which has proved to be a useful intermediate in the synthesis of both main-group and transition metal derivatives of **18**. For example, treatment of **18** with LDA at low temperature followed by $SiClMe_3$ gave $W(C{\equiv}CC{\equiv}CSiMe_3)(CO)_3Cp$ (**17**) in good yield (80%). This preparation of **17** was a considerable improvement on the reaction between $WCl(CO)_3Cp$ and $LiC{\equiv}CC{\equiv}CSiMe_3$ (see above). Similar reactions with $PClPh_2$ or $MnBr(CO)_5$ gave $W\{C{\equiv}CC{\equiv}CP(O)Ph_2\}(CO)_3Cp$ (**31**) (25%) or $\{Cp(CO)_3W\}C{\equiv}CC{\equiv}C\{Mn(CO)_5\}$ (**32**) (20%), respectively.

The bis(carbonyl) complex $Fe(C{\equiv}CC{\equiv}CH)(CO)_2Cp$ (**20**) also reacted sluggishly with ^nBuLi, and cleaner results were obtained from reactions with the bulkier reagent sec-BuLi [49]. It seems likely that the reactions of these carbonyl complexes with ^nBuLi are complicated by nucleophilic attack of the lithiated reagent at the carbonyl ligands, although no Fischer carbene complexes could be isolated after sequential reaction of **18** with ^nBuLi and MeI or MeOTf.

The attempted preparation of the phosphine complex $W(C{\equiv}CC{\equiv}CPPh_2)(CO)_3Cp$ by reaction of $PClPh_2$ with **30** gave a large amount of a black, presumably polymeric, compound which could not be adequetely characterised. After extensive chromatography, a yellow solid was isolated in low yield, which was identified as the phosphine-oxide $W\{C{\equiv}CC{\equiv}CP(O)Ph_2\}(CO)_3Cp$ (**31**) from the microanalytical and spectroscopic data. In addition to the usual ν(C≡C) and ν(CO) bands associated with the tungsten-diynyl fragment, the IR spectrum of the **31** was characterised by a strong ν(PO) band at 1199 cm^{-1}. The ^{31}P spectrum contained a well resolved resonance at δ 5.61. The ^{13}C spectrum contained the usual CO and Cp resonances, but only the C_α and C_β carbons of the diynyl chain were observed.

The heterobimetallic complex **32** was obtained as a highly light senstive yellow needle-like crystals. The IR spectrum contained two weak ν(C≡C) and four stronger ν(CO) bands. Four weak resonances in the ^{13}C spectrum were attributed to the carbon nuclei of



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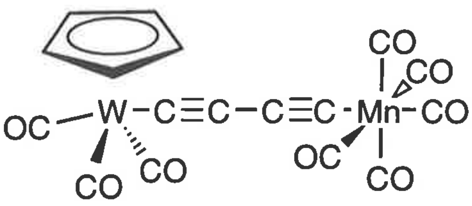
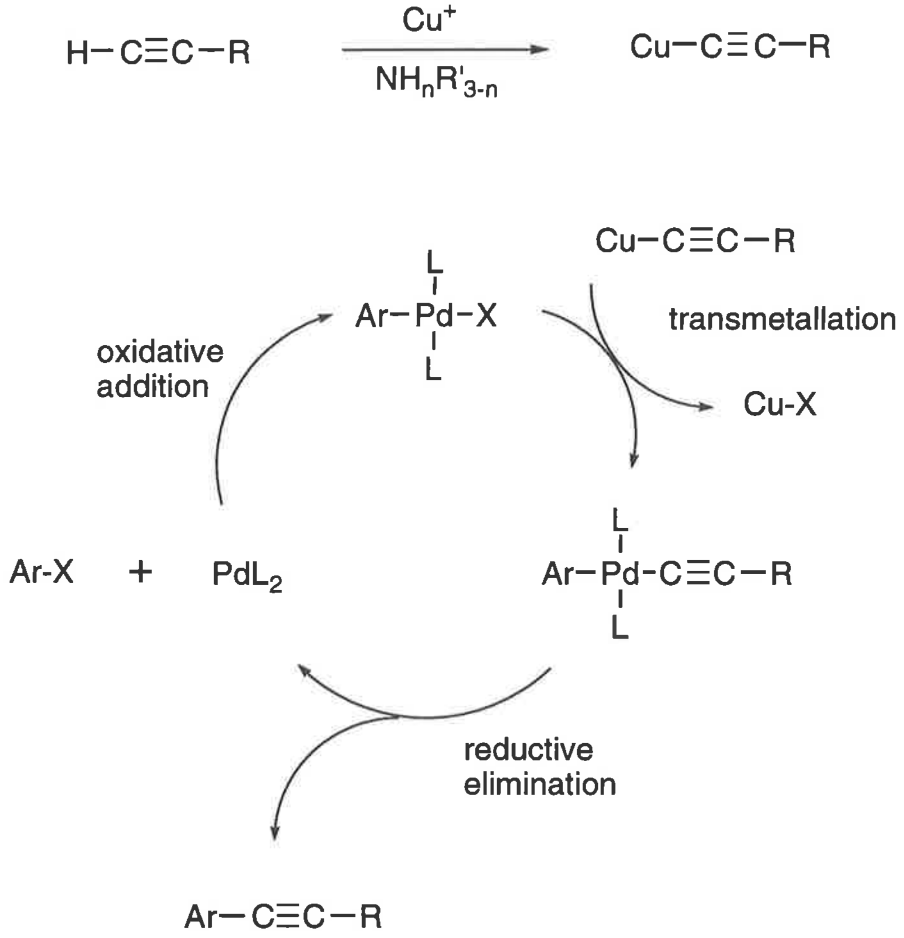


32

the diynyl bridge. The FAB MS of **32** was characterised by a molecular ion, and several fragment ions resulting from loss of carbonyl and cyclopentadienyl ligands.

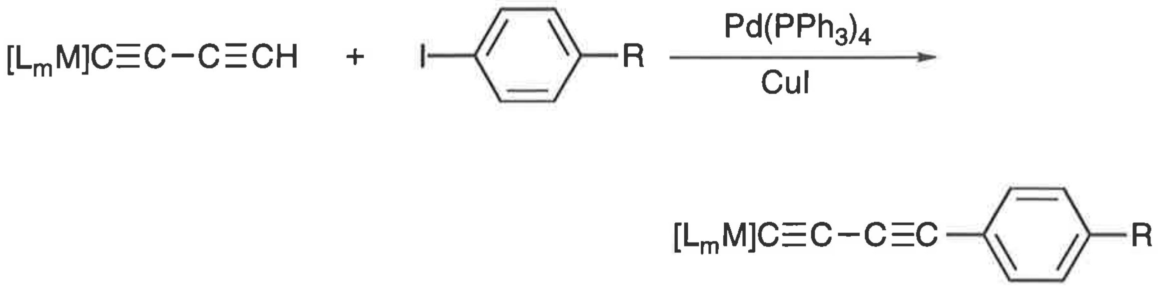
Palladium(0) / Copper(I) Catalysed Coupling Reactions with Aryl- and Alkynyl-Halides.

Palladium catalysts have been used with great effect in the formation of new C-C bonds in organic synthesis [154]. For example, 1-alkynes undergo facile cross-coupling reactions with aryl- and vinyl-halides in the presence of basic amines and a catalyst comprised of a source of Cu(I) and a palladium(0) species, which may either be introduced as $Pd(PPh_3)_4$ or generated *in situ* [155, 156]. A general outline of the accepted mechanism is given in Scheme 9. It is thought that oxidative addition of the halide to the active Pd(0) catalyst generates an intermediate Pd(II) species, which undergoes a transmetallation reaction with a Cu(I) acetylide formed *in situ* to give a palladium complex containing both fragments to be coupled. Reductive elimination of the aryl and alkynyl fragments produces the coupled product and regenerates the Pd(0) catalyst.



Scheme 9 : Palladium(0) / Copper (I) Catalysed Coupling of an Aryl-Halide with a 1-Alkyne.

This procedure has been applied to the C≡CH moiety of the coordinated diynyl ligand in **18** and **19**. Thus $M(C{\equiv}CC{\equiv}CPh)(CO)_3Cp$ (M = W **33**; Mo **34**) were prepared by treating a diisopropylamine solution of the diynyl reagent with a 1.5 fold excess of iodobenzene in the presence of catalytic amounts of $Pd(PPh_3)_4$ and CuI (Equation 18). Both complexes posses very similar spectral properties. Of most interest were the ^{13}C NMR spectra, which contained resonances for the four distinct carbon nuclei of the phenyl fragment. The C_β resonance was not observed in either **33** or **34**. This signal may have been obscured by the residual non-deuterated solvent resonances.



$[ML_m] = W(CO)_3Cp$; R = H (**33**), OMe, Me, CO_2Me

$[ML_m] = Mo(CO)_3Cp$; R = H (**34**)

Equation 18.

Other aryl-iodides may also be coupled with **18** using these conditions. Thus, reaction of **18** with *p*-iodoanisole, *p*-iodotoluene or methyl *p*-iodobenzoate in the presence of the mixed catalyst gave the substituted derivatives in 35-90% yields [157]. Attempts to couple **18** with bromo-alkynes, such as 1-bromo-2-phenylacetylene, were unsuccessful. However, 1-iodo-2-phenylacetylene entered into a Pd(0) / Cu(I) catalysed coupling to yield the triynyl complex $W(C{\equiv}CC{\equiv}CC{\equiv}CPh)(CO)_3Cp$ in good yield [157].

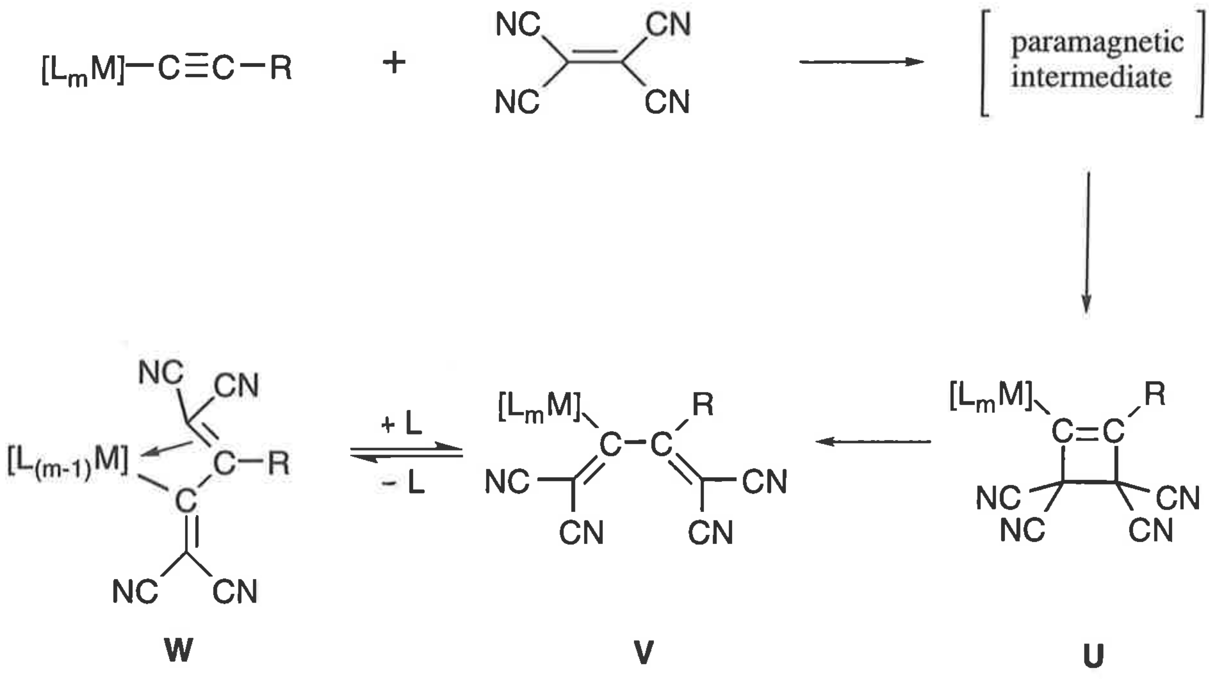
These reactions are believed to be the first applications of this palladium / copper catalysed chemistry in the metal coordination sphere. It is worth noting that the only other examples of complexes bearing phenyldiynyl ligands were prepared directly from phenyldiacetylene, either by oxidative addition of the 1-alkynyl C≡CH moiety to a Rh(I) species [90], or by Cu(I)-catalysed coupling of the diyne with $WCl(CO)_3Cp^*$ [139, 158]. The diynyl ligands in **33**, **34** and the substituted derivatives are all derived from buta-1,3-diyne.

Reactions with tetracyanoethylene (tcne).

The reactions of tetracyanoethylene (tcne), and the related fluorocarbon 1,1-dicyano-2,2-bis(trifluoromethyl)ethene (dcfe), with half-sandwich acetylide complexes of tungsten $W(C{\equiv}CPh)(CO)_3Cp$ and ruthenium $Ru(C{\equiv}CMe)(PPh_3)_2Cp$ or $Ru(C{\equiv}CPh)(L_2)Cp$ [$L_2 = (PPh_3)_2$, dppe, $(P(OMe)_3)(PPh_3)$, $(CO)(PPh_3)$] have been studied in some detail [159-162] and are summarised in Scheme 10. In general, the reactions proceed *via* deep green paramagnetic intermediates, to give cyclobutenyl complexes **U**, which may isomerise to the ring opened butadienyl complexes. Displacement of one ligand L from the butadienyl complexes **V**, either thermally or photochemically, and coordination of an olefinic moiety in the cyano-carbon ligand to the metal centre gives complexes with η^3-allyl ligands **W**.

For example, the bis-phosphine complexes $Ru(C{\equiv}CR)(PPh_3)_2Cp$ (R = Me, Ph) react with tcne in refluxing benzene to give η^3-allyl complexes $Ru[\eta^3\text{-}C(CN)_2CRC{=}C(CN)_2](PPh_3)Cp$ [159]. The ready loss of one PPh_3 ligand from the metal ligand sphere is a feature of the chemistry of $RuX(PPh_3)_2Cp$, and is usually attributed to steric factors [163]. The reactions of $W(C{\equiv}CPh)(CO)_3Cp$ with tcne proceed in a similar fashion. The initially formed complex $W[C{=}CPhC(CN)_2C(CN)_2](CO)_3Cp$ undergoes a ring opening process over 2 days in CH_2Cl_2 to give the butadienyl complex $W\{C[{=}C(CN)_2]CPh{=}C(CN)_2\}(CO)_3Cp$, which loses a CO ligand on UV irradiation to yield $W[\eta^3\text{-}C(CN)_2CPhC{=}C(CN)_2](CO)_2Cp$ [161].

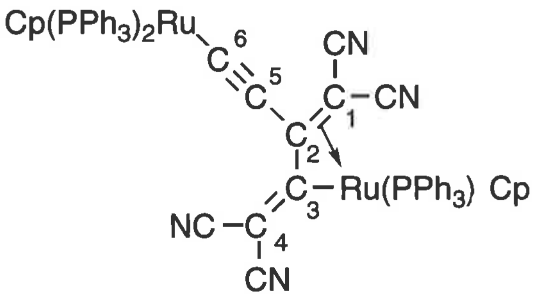
Treatment of the allylic complex $Ru[\eta^3\text{-}C(CN)_2CPhC{=}C(CN)_2](PPh_3)Cp$ with CN^tBu gave the butadienyl complex $Ru\{C[{=}C(CN)_2]CPh{=}C(CN)_2\}(CN^tBu)(L)Cp$ [L = PPh_3, CN^tBu]. It is therefore possible to interconvert complexes with structural features **V** and **W**.



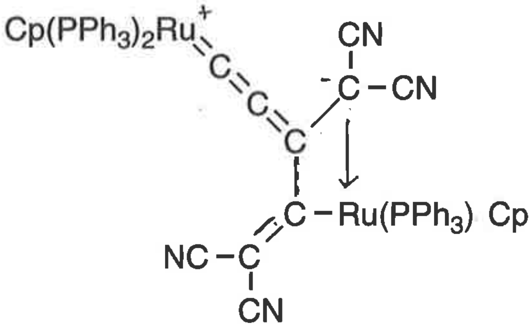
Scheme 10 : The Reactions of Metal Acetylides with TCNE.

*Reaction of tetracyanoethylene with {Cp(PPh$_3$)$_2$Ru}C≡CC≡C{Ru(PPh$_3$)$_2$Cp} (**16**).* Addition of one equivalent of tcne to **16** in CH_2Cl_2 at room temperature resulted in an immediate change in colour of the solution from orange to deep green then blood-red over five minutes. After this time the reaction was complete, as judged by ^{1}H NMR spectroscopy, and the allylic complex Ru[η^3-C(CN)$_2$C{C≡C[Ru(PPh$_3$)$_2$Cp]} C=C(CN)$_2$](PPh$_3$)Cp (**35**) was isolated as a dark-red powder by precipitation with hexane.

The spectral properties of **35** are similar to those reported for the related compounds **W** derived from Ru(C≡CR)(PPh$_3$)$_2$Cp (R = Ph, Me) [160]. The ^{1}H NMR spectrum contained resonances associated with the Cp ligands at δ 4.51 and 4.39. The ^{13}C NMR spectrum contained the usual signals for the PPh$_3$ and Cp ligands, and resonances characteristic of the four carbons of the allylic fragment at δ 224.7, 81.58, 60.21 and 14.09 assigned to C(3), C(1), C(4) and C(2) respectively. The carbon atoms are labelled so as to be consistent with the literature. The ES MS spectrum obtained in the presence of NaOMe gave an intense $[M + Na]^+$ ion at *m/z* 1318. The IR spectrum contained a strong ν(CN) band (2210 cm^{-1}), a strong ν(C=C) band (1585 cm^{-1}) and a very intense absorption at 1933 cm^{-1}. The position and intensity of this band more closely resembles the ν(C=C=C) bands of allenylidene complexes (see Chapter 5) than the ν(C≡C) bands of metal acetylide complexes. The electron-withdrawing cyano groups are conjugated with the C≡C triple bond in **35**, and the complex may perhaps be better represented by the electron-delocalised structure **35b** than the localised structure **35a**.



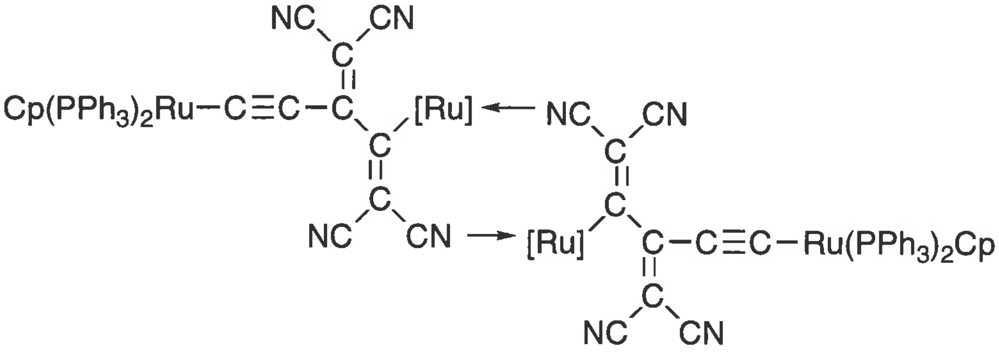
35a



35b

In solution **35** exists in equilibrium with the yellow tetranuclear compound $[Ru\{C[=C(CN)_2]C\{C{\equiv}C[Ru(PPh_3)_2Cp]\}C(CN)_2\}(PPh_3)Cp]_2$ (**36**), which was detected by ^1H NMR spectroscopy (see below). Attempts to purify **35** by preparative TLC on silica gel resulted in conversion of the sample to the tetranuclear complex **36** which yielded a pure sample after recrystallisation. The IR spectrum of **36** was very similar to that of **35**, and strong ν(CN) and ν(C≡C) [or ν(C=C=C)] bands were observed at 2202 and 1976 cm^{-1} respectively, and two very weak ν(C=C) bands were observed at 1586 and 1571 cm^{-1}. The ^1H NMR spectrum of **36** contained characteristic resonances for the Cp ligands at δ 4.59 and 4.26. The ^{13}C NMR spectrum only contained resonances associated with the PPh_3, Cp (δ 87.09 and 81.59) and CN (δ 118.06, 115.23 and 113.27) ligands; the other carbon atoms of the cyano-carbon ligand were not observed. The dimeric compound was cleaved under the conditions of the FAB MS experiment, and the base peak at *m/z* 1296 was assigned to the $[M / 2]^+$ ion. Fragment ions were observed at *m/z* 1034 ($[M/2 - PPh_3]^+$) and 772 ($[M/2 - 2PPh_3]^+$).

As the spectral data were not unambiguous a single crystal X-ray study of **36** was undertaken. The structure is still in the latter stages of refinement, and cannot be discussed in detail here, but the atom connectivity has been established [151].



[Ru] = Ru(PPh$_3$)Cp

36

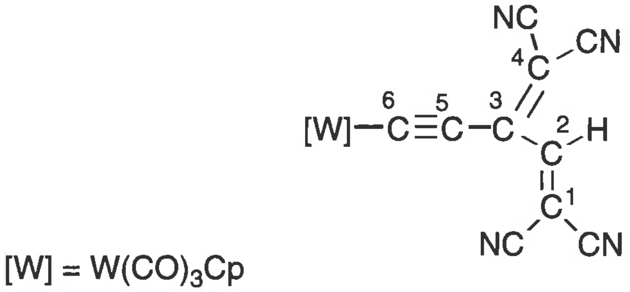
The formation of the dimeric complex **36** from the allylic complex **36** is closely related to the synthesis of the butadienyl complexes $[ML_n]\{C[=C(CN)_2]CPh=C(CN)_2\}$ from the reaction of the allylic precursors $[ML_{n-1}][\eta^3\text{-}C(CN)_2CPhC=C(CN)_2]$ with CN^tBu indicated above.

*Interconversion of **35** and **36**.*

The equilibration of **35** and **36** was conveniently monitored by ^1H NMR spectroscopy. A freshly prepared solution of **35** in $CDCl_3$ was allowed to stand, and the ^1H NMR spectrum recorded periodically. After 3 days, equilibrium had been reached and the solution contained *ca.* 10% **36**, estimated from the integration of the Cp resonances. Similarly, a solution of **36** reached equilibrium after *ca.* 7 days.

*Reaction of tetracyanoethylene with W(C≡CC≡CH)(CO)₃Cp (**18**).*

The reaction of **18** with tcne in CH_2Cl_2 proceeds via a short-lived, deep green intermediate to give a deep purple solution, from which W{C≡CC[=C(CN)$_2$]C[=C(CN)$_2$]H}(CO)$_3$Cp (**37**) was isolated (84%) as a dark purple crystalline solid which has been fully characterised by X-ray crystallography.



37

The IR spectrum of **37** contained the expected ν(CN), ν(C≡C) and two ν(CO) bands at 2221, 2078 and 2030 and 1970 cm^{-1} respectively. The observation of a low field resonance (δ 7.63) in the ^{1}H NMR spectrum, attributed to the butadienyl H nucleus suggested that reaction had occurred at the outer C≡C triple bond and this was confirmed by a single-crystal X-ray diffraction study. The ^{13}C NMR spectrum contained singlet resonances at δ 221.05, 148.70, 94.41 and 91.90 assigned to the carbon atoms C(3), C(2), C(4) and C(1) of the butadienyl ligand by comparison with the spectrum of W{C[=C(CN)$_2$]CPh=C(CN)$_2$}(CO)$_3$Cp [160].

A molecule of **37** is shown in Figure 13. The most significant feature of the structure is the geometry of the cyano-carbon ligand. The ligand is essentially planar, bisecting the C(12)-W-C(13) angle, and is therefore coplanar with the plane defined by C(11), W and the centroid of the Cp ligand. This observation,

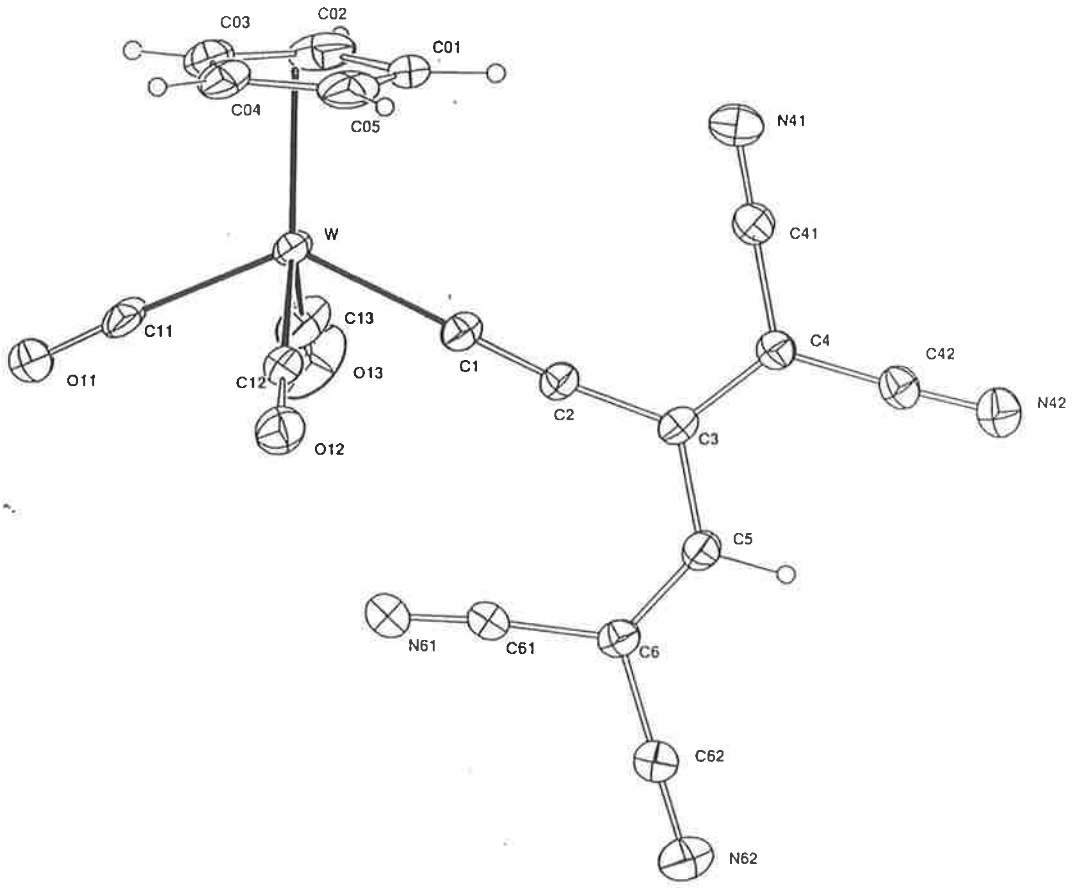


Figure 13 : A plot of a molecule of **37** showing the atom numbering scheme. Important bond lengths (Å) and angles (°): W-C(1) 2.102(7); C(1)-C(2) 1.21(1); C(2)-C(3) 1.397(9); C(3)-C(4) 1.380(9); C(3)-C(5) 1.44(1); C(5)-C(6) 1.35(1); C(4)-C(41, 42) 1.44(1), 1.43(1); C(6)-C(61, 62) 1.44(1), 1.43(1); C-N (av.) 1.12; W-C(11, 12, 13) 2.006(8), 1.966(8), 1.99(1); C-O (av.) 1.14; C(11)-W-C(12) 77.6(3); C(11)-W-C(13) 77.2(4); C(11)-W-C(1) 129.8(3); C(12)-W-C(1) 75.3(3); W-C(1)-C(2) 177.5(6); C(1)-C(2)-C(3) 173.7(7); C(2)-C(3)-C(4) 120.5(6); C(2)-C(3)-C(5) 121.5(6); C(4)-C(5)-C(6) 118.0(6); C(3)-C(4)-C(41) 118.2(6); C(3)-C(4)-C(42) 124.4(6); C(3)-C(5)-C(6) 127.1(6); C(5)-C(6)-C(61) 125.0(7); C(5)-C(6)-C(62) 114.1(6) (by B.W. Skelton and A.H. White).

taken together with the contraction of the W-C(1) [2.102(7) Å] and C(2)-C(3) [1.397(9) Å] bonds and lengthening of the C(1)-C(2) [1.21(1) Å] and C(3)-C(4) [1.380(9) Å] bonds, and the fact that reaction occurred at the C≡C triple bond removed from the metal centre indicates a degree of electron delocalisation throughout the ligand.

Attempts to add a second equivalent of tcne to the remaining C≡C triple bond in **35** or **37** were unsuccessful. As tcne readily adds to the triple bonds in $Ru(C{\equiv}CPh)(PPh_3)_2Cp$ and $W(C{\equiv}CPh)(CO)_3Cp$ it seems unlikely that steric factors are involved. Instead, it is more probable that the electron-withdrawing cyano groups, which are conjugated with the "free" C≡C triple bond in these complexes, deactivate these sites and prevent the [2+2] cycloaddition. The influence of the cyano groups on the electronic nature of the C≡C has already been alluded to in the discussion of the IR spectrum of **35** and the solid-state structure of **37**.

Preparation Complexes with Longer Polyyne Ligands.

Recently, the dimetallated tetra-ynes $\{Re(PPh_3)(NO)(\eta^5\text{-}C_5Me_5)\}_2(\mu\text{-}C_8)$ [36] and $\{Fe(dppe)(\eta^5\text{-}C_5Me_5)\}_2(\mu\text{-}C_8)$ [61] were prepared by oxidative coupling of the appropriate diynyl precursors using $Cu(OAc)_2$ in pyridine at elevated temperatures (Eglinton coupling). Similar attempts to prepare $\{Cp(CO)_3W\}_2(\mu\text{-}C_8)$ (**38**) resulted only in extensive decomposition of the diynyl reagent. However, under the milder Hay conditions (Cu_2Cl_2 / tmeda, O_2 purge, acetone, r.t.) [102], homo-coupling of the diynyl ligand proceeded smoothly to give the dimetallated tetra-yne **38** (85%) as a deep orange powder. The analogous Mo compound $\{Cp(CO)_3Mo\}_2(\mu\text{-}C_8)$ (**39**) was prepared similarly, and isolated as a highly light-sensitive burnt orange powder in moderate to good yield (Equation 19).

The IR spectra of these tetra-yne complexes contained strong ν(CO) bands from the $M(CO)_3Cp$ fragments and much weaker ν(C≡C) bands near 2150 cm^{-1}. The ^{13}C NMR spectra contained typical resonances for the CO and Cp ligands. The four magnetically

$$[L_mM]C{\equiv}C{-}C{\equiv}CH \xrightarrow[\text{[Cu(tmeda)]}^+]{O_2} [L_mM]C{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{-}C{\equiv}C\{ML_m]$$

$$[L_mM] = W(CO)_3Cp\ (\mathbf{38}),\ Mo(CO)_3Cp\ (\mathbf{39})$$

Equation 19.

inequivalent carbon nuclei in the C_8 bridge of the tungsten compound **38** were found as well resolved, if rather weak, resonances at δ 112.39 (C_α), 91.60 (C_β), 63.70 (C_γ) and 60.91 (C_δ). Only the C_α resonance showed coupling to ^{183}W. The C≡C carbons in the molybdenum analogue **39** gave resonances with similar chemical shifts. It is worth noting that the ^{13}C chemical shifts of acetylenic carbons in the purely organic polyynes that have been studied also appear to approach a limiting lower value near 60 ppm [6].

At low cone voltage in the presence of a small amount of $AgNO_3$ [153], the ES MS of **38** contained peaks at higher molecular weights, corresponding to the dimeric Ag^+-bridged species $[\{W_2(\mu\text{-}C_8)(CO)_6Cp_2\}_2(\mu\text{-}Ag)]^+$ and the $[Ag(NCMe)]^+$-coordinated species $[\{W_2(\mu\text{-}C_8)(CO)_6Cp_2\}Ag(NCMe)]^+$. At higher cone voltages several fragment ions formed by the successive loss of CO ligands were observed. The ES-MS of **39** at low cone voltages contained a comparable $[M + Ag + NCMe]^+$ ion, but no larger aggregate ions were observed.

Phosphine Exchange Reactions.

*Preparation of $\{Cp(PPh_3)(PMe_3)Ru\}C{\equiv}CC{\equiv}C\{Ru(PPh_3)(PMe_3)Cp\}$ (**40**).*

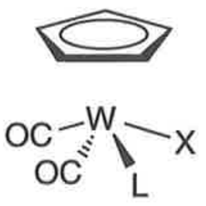
Exchange reactions of the PPh_3 ligands in $Ru(PPh_3)_2Cp$ complexes are well documented [163]. It was therefore not surprising that reaction of **16** with PMe_3 in refluxing toluene resulted in the formation of $\{Cp(PPh_3)(PMe_3)Ru\}C{\equiv}CC{\equiv}C\{Ru(PPh_3)(PMe_3)Cp\}$ (**40**). The mixed phosphine complex was characterised by a single ν(C≡C) band in the IR spectrum at 1974 cm^{-1} and a parent ion at *m/z* 1056 in the ES mass spectrum. The fragmentation ions were consistent with the proposed structure, including one ion at *m/z* 505 assigned to $[Ru(PMe_3)(PPh_3)Cp]^+$. Well resolved resonances in the ^1H NMR spectrum at δ 4.43 and 1.17 for the Cp and PMe_3 ligands respectively confirmed that substitution had occurred at each of the metal centres.

In contrast to **16**, it was not possible to observe distinct rotamers of **40**. The decreased steric bulk about each metal centre results in a much smaller degree of interaction between the ligand spheres. Whilst both metal centres in **40** are optically active, we have been unable to resolve, or detect, the diastereomers and this complex has been studied as a mixture of diastereomers.

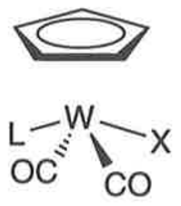
Exchange reactions with alkynyl, diynyl and diyndiyl complexes of $W(CO)_3Cp$.

Substitution reactions of the carbonyl ligands in $WX(CO)_3Cp'$ (X = H, halide, alkyl; Cp' = Cp, Cp*) complexes have been examined using a variety of thermal, photochemical and chemical methods [164-170]. Both *cis*- and *trans* isomers are known and in some instances the reactions produce a mixture of isomers, the proportions of which depend on the nature of X, the incoming ligand, and the preparative method employed. The *cis-trans* isomerisation process has been studied for the case of $MH(CO)_2LCp$ (M = Mo, W; L = PMe_3, PEt_3, PPh_3; not all combinations) [168]. Although the factors controlling the relative stabilities of the isomers are not always clear, it has been suggested that the position of the equilibrium may be a delicate balance between the trans influence of the ligands and the steric interactions between the ligands L and X [171].

Both isomers of $WX(CO)_2LCp$ give similar two band ν(CO) patterns in the IR region, although the spectra of the *trans* isomers typically show less intense symmetric and more intense antisymmetric ν(CO) bands than the *cis* isomers [167, 168]. The ^{13}C carbonyl resonances provide the simplest method of distinguishing the two isomers. The *trans* isomers contain only a single ^{13}C CO resonance, while for *cis* isomers the inequivalent carbonyl ligands give rise to two resonances [165].



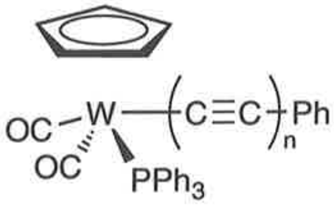
cis-WX(L)(CO)$_2$Cp



trans-WX(L)(CO)$_2$Cp

Trimethylamine *N*-oxide (tmno) has become established as a convenient reagent for oxidative decarbonylation of a wide range of metal-carbonyl species. These reactions are usually performed in the presence of a donor ligands, such as NCMe or phosphines, and give the substituted products in moderate to good yield .

In a model reaction a solution of W(C≡CPh)(CO)$_3$Cp and PPh$_3$ was treated with tmno to give *cis*-W(C≡CPh)(CO)$_2$(PPh$_3$)Cp (**41**) in moderate yield. The complexes M(C≡CPh)(CO)$_2$(PPh$_3$)Cp (M = Mo, W) were previously obtained by thermolysis of M(C≡CPh)(CO)$_3$Cp in the presence of PPh$_3$, but full details of their characterisation were not reported [111]. The IR spectrum of **41** contained a weak ν(C≡C) band at 2089 cm^{-1} and two ν(CO) bands, the stronger at 1949 (symmetric) and the weaker at 1863 (antisymmetric) cm^{-1}, suggesting *cis* geometry. The *cis* geometry was further indicated by the observation of two CO resonances in the ^{13}C spectrum at δ 244.54 and 228.79 and confirmed by a single crystal X-ray diffraction study (see below). The ES MS of this complex in methanol contained an intense molecular ion, as a result of oxidation of **41** on the ES probe tip. Such processes are rare for carbonyl complexes using this technique. The formation of the [M]$^+$ ion in the absence of an oxidising agent, such as Ag$^+$, suggests that **41** is quite electron rich.



n = 1 (**41**), 2 (**42**)

A molecule of **41** is shown in Figure 14, and important bond lengths and angles are summarised in the caption. It can be seen that the bulky PPh_3 ligand occupies a position *cis* to the linear C≡CPh ligand, which minimises the steric interactions with the CO ligands. There is little evidence for π-backbonding between the W centre and the C≡C ligand in the structure. In fact, despite the presence of the electron-donating PPh_3 ligand, the W-C(1) [2.141(8) Å] bond appears to be longer, and the C(1)-C(2) bond [1.19(1) Å] bond shorter, than those in the complexes $W(C{\equiv}CR)(CO)_3Cp$ [W-(C1) / C(1)-C(2) Å: R = $C{\equiv}CSiMe_3$ (**17**) 2.124(8) / 1.22(1); $C[=C(CN)_2]CH=C(CN)_2$ (**37**) 2.102(7) / 1.21(1)].

The analogous diynyl complex *cis*-$W(C{\equiv}CC{\equiv}CPh)(PPh_3)(CO)_2Cp$ (**42**) was prepared from a similar reaction between **18** and PPh_3 with tmno. The *cis* geometry of **42**, suggested by a ν(CO) band profile similar to that of the mono-acetylide complex **41**, was confirmed by the observation of two CO resonances in the ^{13}C NMR spectrum at δ 243.15 and 222.63. Two ν(C≡C) bands were observed at 2039 and 2172 cm^{-1}. The ES MS, recorded in the presence of NaOMe, contained both $[M + Na]^+$ and M^+ ions.

The tmno assisted reaction between the diyndiyl complex $\{Cp(CO)_3W\}C{\equiv}CC{\equiv}C\{W(CO)_3Cp\}$ (**22**) and PPh_3 or PMe_3 did not proceed cleanly, and a large number of uncharacterised products were formed. Prolonged thermolysis of the diyndiyl precursor **22** with PMe_3 gave the complex *trans,trans*-$\{Cp(PMe_3)(CO)_2W\}C{\equiv}CC{\equiv}C\{W(CO)_2(PMe_3)Cp\}$ (**43**) in low yield, which was identified by the usual spectroscopic methods. The ES MS of **43** in the presence of NaOEt gave aggregate ions with sodium consistent with substitution of two carbonyl ligands. The simple, two-band ν(CO)

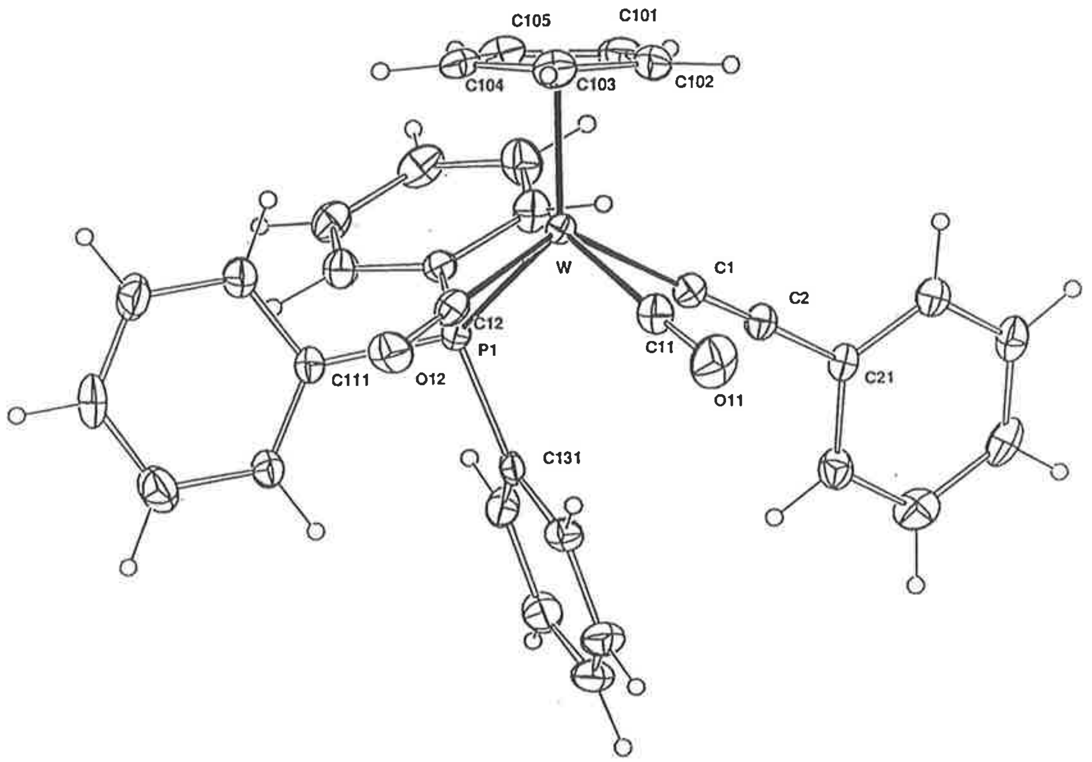
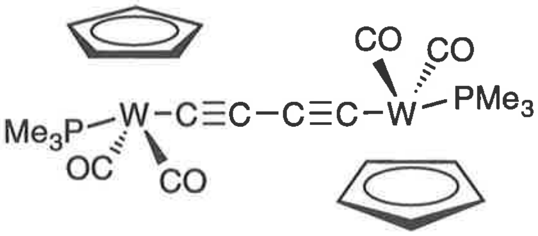


Figure 14 : A plot of a molecule of **41**. Important bond lengths (Å) and angles (°): W-P(1) 2.491(2); W-C(11) 1.937(9); W-C(12) 1.975(8); W-C(1) 2.141(8); C(1)-C(2) 1.19(1); C(2)-C(21) 1.43(1); C(11)-W-C(12) 75.7(3); C(11)-W-C(1) 76.9(3); C(12)-W-C(1) 129.9(3); P(1)-W-C(11) 115.8(3); P(1)-W-C(12) 80.2(2); P(1)-W-C(1) 75.1(2); C(11)-W-C(1) 76.9(3); C(12)-W-C(1) 129.9(3); W-C(1)-C(2) 178.1(7); C(1)-C(2)-C(21) 177.3(8) (by B.W. Skelton and A.H. White).

pattern in the IR spectrum and the presence of only one Cp resonance and one PMe_3 resonance in the ^1H and ^{13}C NMR spectra indicated that substitution had occurred at each metal centre. The *trans,trans* geometry of the product was indicated by the greater intensity of the antisymmetric carbonyl absorption and the presence of a single CO resonance in the ^{13}C spectrum. Given the reaction conditions employed in the synthesis of **43** (ca. 110°C, 10d.), the *trans,trans* isomer is likely to be the thermodynamic product.



43

Reactions of Some Diynyl and Diyndiyl Complexes with $Co_2(CO)_8$.

Reactions between $Co_2(CO)_8$ and $[L_mM](C{\equiv}CC{\equiv}CH)(CO)_3Cp$ $\{[ML_m] = W$ (**18**), Mo (**19**)$\}$ or $\{Cp(CO)_3W\}C{\equiv}CC{\equiv}C\{Fe(CO)_2Cp\}$ (**25**) occurred at the less sterically-hindered C≡C triple bonds to yield the derivatives $Co_2\{\mu\text{-}RC_2C{\equiv}C[ML_m]\}(CO)_6$ [$ML_m = W(CO)_3Cp$, R = H (**44**) or $Fe(CO)_2Cp$ (**45**); $ML_m = Mo(CO)_3Cp$, R = H (**46**)]. The related compounds $Co_2\{\mu\text{-}RC_2C{\equiv}C[W(CO)_3Cp]\}(\mu\text{-dppm})(CO)_4$ (R = H and $SiMe_3$) were described in Chapter 2. In addition to the usual Cp resonance at δ 5.67, the ^1H NMR spectrum of **44** is characterised by a low field resonance at δ 6.04 assigned to the coordinated alkynyl $Co_2(\mu\text{-}C_2H)(CO)_6$ fragment. The ν(CO) spectrum of **44** approximates to a superposition of the usual $W(CO)_3Cp$ and $Co_2(\mu\text{-}RC_2R')(CO)_6$

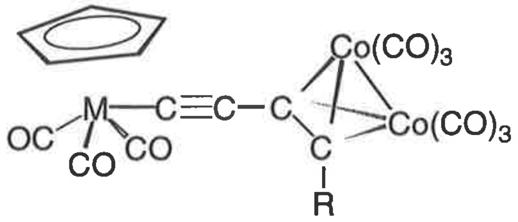
spectra. Other spectroscopic data were in accord with the proposed structure. The Mo analogue **46** was characterised similarly.

Coordination of the $Co_2(CO)_6$ fragment in **45** to the alkyne moiety adjacent to the Fe centre was established by the NMR data. In the ^1H and ^{13}C NMR spectra of **45** Cp resonances were observed at δ 5.67 and 5.16, and δ91.85 and 86.68, respectively. By comparison with the resonances observed for the Cp ligands in the precursor **25**, [(^1H, ^{13}C) WCp δ 5.62, 91.56; FeCp δ 5.03, 85.28] it can be concluded that a greater change in environment has occurred near the $Fe(CO)_2Cp$ fragment as opposed to the $W(CO)_3Cp$ fragment. These observations are consistent with addition of the dicobalt fragment to the less sterically hindered C≡C carbon-carbon triple bond.

The ^{13}C NMR spectrum contained distinct resonances from the CO ligands bound to the different metals, indicating there is no significant exchange of CO between the W, Fe or Co centres on the NMR time scale. The Co(CO) resonance was broad, probably as a result of both Co_2-localised CO exchange process and broadening due to the ^{59}Co quadrupole.

Even in the presence of excess $Co_2(CO)_8$ the alkyne moiety adjacent to the $W(CO)_3Cp$ fragment in **44**, **45** and **46** remained uncoordinated, presumably as a result of steric crowding. The uncoordinated C≡C triple bond in $\{Co_3(CO)_9(\mu_3C)\}C{\equiv}CC_2[Co_2(CO)_6]\text{-}\{(\mu_3\text{-}C)Co_3(CO)_9\}$ is similarly inert to reaction with $Co_2(CO)_8$ [172].

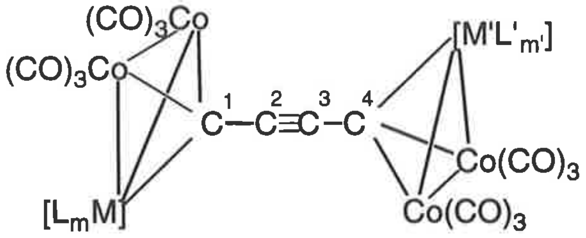
Treatment of the diyndiyl complexes $\{Cp(CO)_3M\}C{\equiv}CC{\equiv}C\{M'(CO)_3Cp\}$ [M = M' = W (**22**), Mo (**23**); M = W, M' = Mo (**24**)] in which both ends of the diynyl chain are terminated by bulky $M(CO)_3Cp$ groups with $Co_2(CO)_8$ gave the $MCo_2(\mu_3\text{-}C)$ cluster-capped acetylenes $\{Co_2M(\mu_3\text{-}C)(CO)_8Cp\}C{\equiv}C\{Co_2M'(\mu_3\text{-}C)(CO)_8Cp\}$ [M = M' = W (**47a**), Mo (**47b**); M = W, M' = Mo (**47c**)] in 20 to 40% yield. Related $Co_2Mo(\mu_3\text{-}C)$ complexes have been obtained from $Co_3(\mu_3\text{-}C)$ clusters by replacement of $Co(CO)_3$ by



M = W, R = H (**44**), Fe$(CO)_2$Cp (**45**)

M = Mo, R = H (**46**)

Mo$(CO)_2$Cp [173, 174]. The analogous cobalt complex $\{Co_3(\mu_3\text{-}C)(CO)_9\}C{\equiv}C\{Co_3(\mu_3\text{-}C)(CO)_9\}$ (**48**) has been obtained as one product from the dehalogenation of $Co_3(\mu_3\text{-}CX)(CO)_9$ (X = Cl, Br) in various arene solvents [175].



47a $[ML_m] = [M'L'_{m'}]$ = W$(CO)_2$Cp

47b $[ML_m] = [M'L'_{m'}]$ = Mo$(CO)_2$Cp

47c $[ML_m]$ = W$(CO)_2$Cp, $[M'L'_{m'}]$ = Mo$(CO)_2$Cp

48 $[ML_m] = [M'L'_{m'}] = Co(CO)_3$

A molecule of **47b** is shown in Figure 15. The other compounds **47** have similar structures. The important bond lengths and angles for each structure are summarised in Tables 1 and 2, along with the comparable data for $\{Co_3(\mu_3\text{-}C)(CO)_9\}C{\equiv}C\{Co_3(\mu_3\text{-}C)(CO)_9\}$ [175]. The mixed molybdenum / tungsten complex **47c** was disordered with each Group 6 metal site being half occupied by Mo and W. In the refinements W(1), Mo(1) and W(4), Mo(4) were constrained to occupy the same coordinates.

The structure shows two $MCo_2(\mu_3\text{-}C)$ clusters are linked through a two-carbon bridge. One of the more interesting features is the short C(2)-C(3) bonds [**47a** 1.18(1) Å; **47b** 1.216(6) Å; **47c** 1.216(8) Å], which are comparable with the C≡C bond length in acetylene [1.2088 Å]. The C(1) and C(4) carbons are found capping the metal triangles in manner analogous to the μ_3-carbyne ligands in the many known $M_3(\mu_3\text{-}C)$ clusters [172-177]. Thus, the bridging diacetylide ligand originally present in **22**, **23** and **24** has isomerised to an acetylene-bridged dicarbyne. Similar behaviour is observed during the electrochemical oxidation of the binuclear diacetylide complexes $\{Cp(PPh_3)(PMe_3)Ru\}C{\equiv}CC{\equiv}C\{Ru(PR_3)(PPh_3)Cp\}$ (see Chapter 4).

An earlier analysis of the solid state structure of **48** indicated a rather long bridging C≡C fragment [C(2)-C(3) 1.24 Å] as a result of some delocalisation of electron density between the cluster cores through the C_4 bridge [175]. A examination of the bond lengths in the C_4 bridges of the complexes **47** indicates a trend towards a shorter central C≡C bond suggesting more limited interactions between the mixed-metal cluster cores.

While the IR spectra of all three complexes showed evidence of a semi-bridging CO ligand in solution [$\nu(\mu\text{-CO})$ cm^{-1} : **47a** 1891; **47b** 1897; **47c** 1894 cm^{-1}], only terminal carbonyl ligands were observed in the solid state structures.

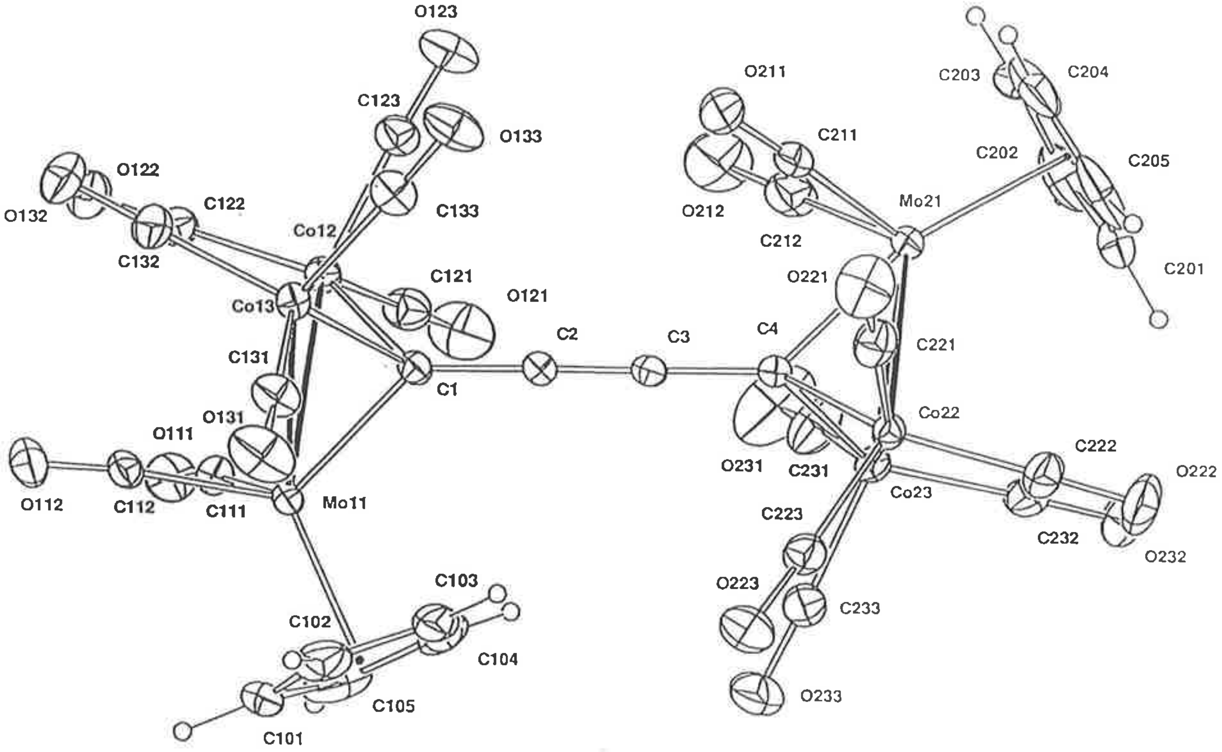


Figure 15 : A plot of a molecule of **47b** indicating the atom numbering scheme (by B.W. Skelton and A.H. White).

Table 1 : Important bond lengths (Å) for complexes **47** and **48**.

	47a M(11) = M(21) = W	**47b** M(11) = M(21) = Mo	**47c** M(11) = W/Mo; M(21) = W/Mo	**48** [175] M(11) = M(21) = Co
M(11)-Co(12)	2.913(1)	2.7674(7)	2.723(1)	2.465(5)
M(11)-Co(13)	2.467(2)	2.7247(9)	2.7642(9)	2.485(4)
Co(12)-Co(13)	2.776(2)	2.5109(9)	2.510(1)	2.462(4)
M(11)-C(1)	1.900(9)	2.076(5)	2.055(6)	1.91(1)
Co(12)-C(1)	2.08(1)	1.934(4)	1.940(6)	1.92(1)
Co(13)-C(1)	2.01(1)	1.950(4)	1.932(5)	1.93(1)
C(1)-C(2)	1.36(1)	1.385(6)	1.396(8)	1.37(1)
C(2)-C(3)	1.18(1)	1.216(6)	1.216(8)	1.24(2)
C(3)-C(4)	1.39(1)	1.380(6)	1.386(7)	1.37(1)
M(21)-Co(22)	2.937(1)	2.6708(6)	2.6658(8)	2.465(5)
M(21)-Co(23)	2.441(2)	2.698(1)	2.689(1)	2.485(4)
Co(22)-Co(23)	2.573(3)	2.498(1)	2.499(1)	2.462(4)
M(21)-C(4)	2.089(8)	2.107(4)	2.104(5)	1.91(1)
Co(22)-C(4)	1.99(1)	1.932(4)	1.931(6)	1.92(1)
Co(23)-C(4)	1.95(1)	1.937(4)	1.938(6)	1.93(1)

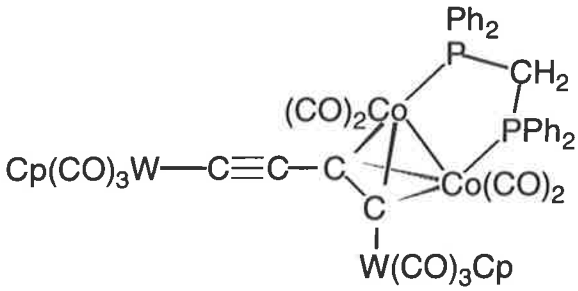
Table 2 : Important bond angles (°) for complexes **47** and **48**.

	47a	**47b**	**47c**	**48** [175]
	M(11) = M(21) = W	M(11) = M(21) = Mo	M(11) = W/Mo; M(21) = W/Mo	M(11) = M(21) = Co
M(11)-Co(12)-Co(13)	51.33(4)	61.93(2)	63.63(3)	60.6(1)
M(11)-Co(13)-Co(12)	67.21(5)	63.67(3)	61.94(3)	59.8(1)
M(11)-C(1)-Co(12)	93.9(4)	87.2(2)	85.9(2)	80.2(4)
M(11)-C(1)-Co(13)	78.2(3)	85.1(2)	87.7(3)	80.6(3)
Co(12)-C(1)-Co(13)	85.5(3)	80.6(2)	80.8(2)	79.5(3)
C(1)-C(2)-C(3)	175(1)	175.7(5)	176.1(7)	178(1)
C(2)-C(3)-C(4)	178(1)	176.9(4)	177.0(5)	178(1)
M(21)-Co(22)-Co(23)	52.10(4)	62.83(2)	62.65(3)	60.6(1)
M(21)-Co(23)-Co(22)	71.65(6)	61.72(2)	61.71(3)	59.8(1)
M(21)-C(4)-Co(22)	92.2(4)	82.7(2)	82.6(2)	80.2(4)
M(21)-C(4)-Co(23)	74.2(3)	83.6(1)	83.3(2)	80.6(3)
Co(22)-C(4)-C(23)	81.6(3)	80.4(2)	80.5(2)	79.5(3)

The solid state structures show some flexing in the four-carbon bridge, but this is most likely to be a result of crystal packing effects. In solution **47a** and **47b** are symmetrical, and only single Cp and μ_3-C resonances are observed in the ^{13}C NMR spectra. In **47c**, the Cp ligands attached to Mo and W were observed as discrete signals at δ 93.56 and 91.21 respectively. The μ_3-C atoms on each cluster gave rise to distinct resonances at δ 127.65 and 124.76. These assignments were made by comparison with the data obtained from **47a** and **47b**.

The complexes **47** form as a result of steric interaction between the carbonyl ligands of the $M(CO)_3$ and $Co_2(CO)_6$ fragments, possibly via an intermediate $Cp(CO)_3MC_2[Co_2(CO)_6]C_2[Co_2(CO)_6]M(CO)_3Cp$ complex. As one of the CO ligands bound to the Group 6 metal is displaced, new metal-metal bonds form to meet the electronic requirements of the Group 6 metal with a consequent redistribution of electron density through the carbon ligand.

Attempts to form simple dicobalthexacarbonyl complexes $\{Cp(CO)_3M\}C{\equiv}CC_2[Co_2(CO)_6]\{M(CO)_3Cp\}$ (M = Mo, W) of **22**, **23** or **24** through reaction of these compounds with less than one equivalent of $Co_2(CO)_8$ only resulted in the formation of smaller amounts of **47**. However, heating a solution of **22** and $Co_2(\mu\text{-dppm})(CO)_6$ in refluxing benzene gave $\{Cp(CO)_3W\}C{\equiv}CC_2[Co_2(\mu\text{-dppm})(CO)_4]\{W(CO)_3Cp\}$ (**49**) in good yield (72%). The ES MS of **49** in the presence of NaOMe gave both $[M + Na]^+$ and $[M + H]^+$ ions. At higher cone voltages fragment ions formed by the successive loss of CO ligands were observed. The ^{1}H NMR spectrum contained two distinct Cp resonances at δ 5.85 and 5.50 and two doublet of triplet resonances characteristic of the methylene protons of the dppm ligand. Other spectroscopic and microanalytical data were in accord with the proposed structure.



49

Reaction of W(C≡CC≡CH)(CO)$_3$Cp with Ru$_3$(μ-dppm)(CO)$_{10}$.

In a manner completely analogous to the reactions of simple organic 1-alkynes, facile oxidative addition reactions of **18** with metal clusters such as $Ru_3(CO)_{10}L_2$ (L = NCMe [138], L_2 = μ-dppm) gave complexes containing μ_3-η^1,η^2 bonded alkynyl ligands in high yield. Thus, the reaction between Ru_3(μ-dppm)$(CO)_{10}$ and 1.5 equivalents of **18** afforded Ru_3(μ-H){μ_3-η^1,η^2-C_2C≡C[W$(CO)_3$Cp]}(μ-dppm)$(CO)_7$ (**50**) (92%).

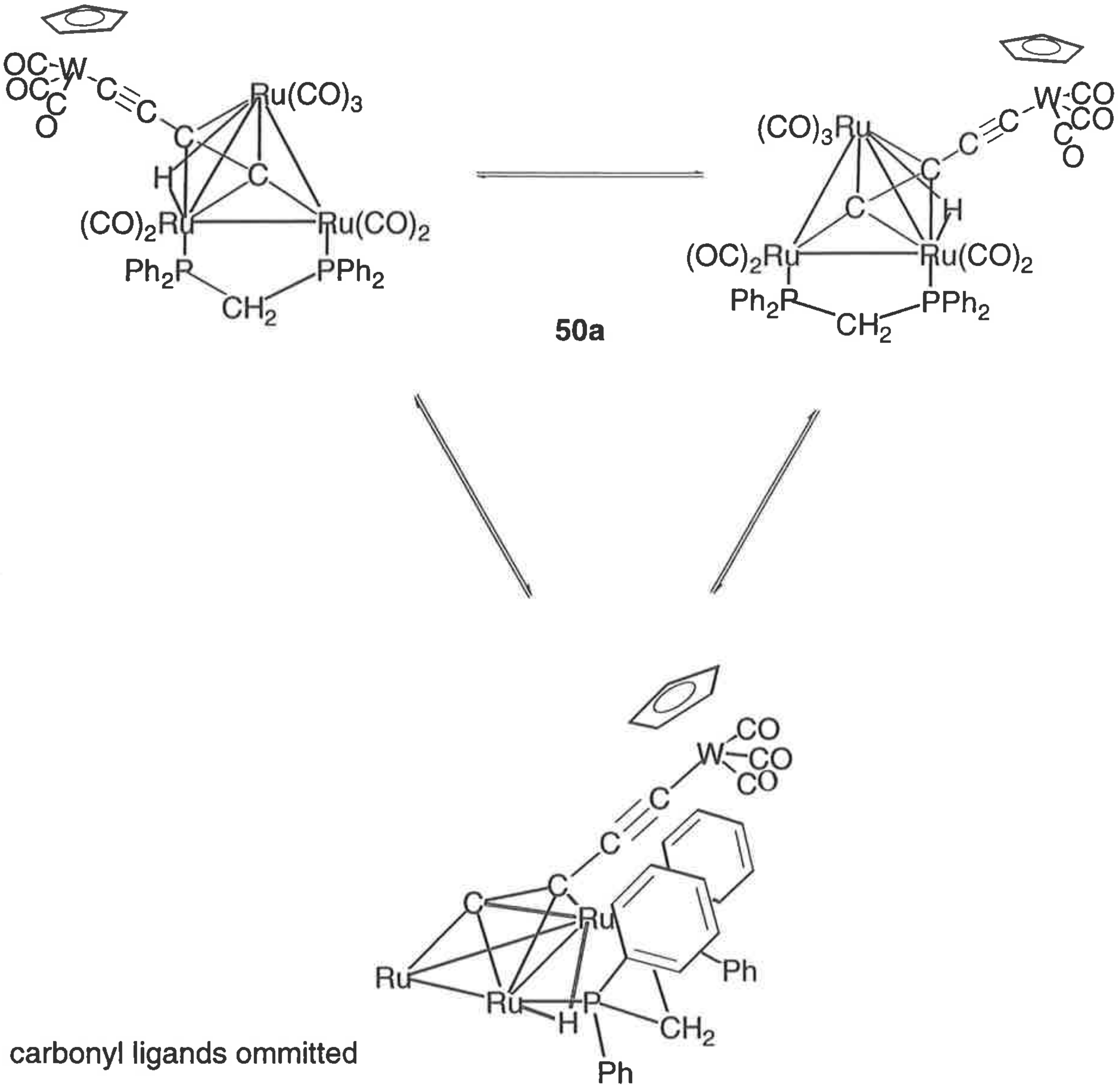
The ES MS of **50** with NaOMe contained both $[M + Na]^+$ and $[M + Na - CO]^+$ cations. In the negative ion spectrum both the methoxide adduct $[M + OMe]^-$ and the deprotonated anion $[M - H]^-$ were observed. In solution at r.t. this complex exists as an interconvertible mixture of isomers (*ca.* 2:1), the major component (**50a**) showing the usual "windscreen-wiper" motion found for cluster-bound acetylide ligands [178]. The ^1H NMR spectra of **50a** at various temperatures are essentially identical to the spectra of Ru_3(μ-H)(μ_3-η^1,η^2-C≡C^{t}Bu)(μ-dppm)$(CO)_7$ recorded under similar conditions [178].

A triplet resonance in the hydride region of the ^1H NMR spectrum (δ -19.82, J_{HP} = 15 Hz), attributable to the minor isomer (**50b**), indicates that the ^{31}P nuclei are equivalent. Thus the μ-H ligand and μ-diynyl ligands must be bridging the Ru-Ru bond also bridged by the dppm ligand. The diynyl group in **50b** therefore lies between the phenyl rings of the dppm ligand in a manner similar to that found crystallographically in Ru_3(μ-H)(μ_3-

η^1,η^2-$C_2C{\equiv}CSiMe_3)(\mu$-dppm$)_2(CO)_5$ [179]. There was no significant change in this signal upon lowering the temperature to 193K.

At temperatures above 313K, the hydride resonances began to collapse, and at 333K the resonances from the hydride ligand of **50a** and **50b** had coalesced into a single broad signal, indicating rapid conversion of all isomers. The results are summarised in Figure 16.

The solid-state structure of **50** was determined crystallographically, and a molecule is shown in Figure 17, with selected bond lengths and angles given in the caption. The geometry of the $Ru_3(\mu$-$H)(\mu$-$C_2)(\mu$-dppm$)(CO)_7$ fragments is similar to those found in related complexes [180] while the structure of the $W(CO)_3Cp$ moiety is analogous to the other examples reported in this thesis, and will not be discussed further. The most interesting feature of the structure is the location of the diynyl and hydride ligands across the Ru(1)-Ru(3) vector, which is the longest in the complex. The solid state structure is therefore that of the major isomer observed in solution **50a**. The short C(1)-C(2) bond length [1.19(1) Å] which indicates that there is little delocalisation of electron density between the Ru_3 cluster and the W centre through the C_4 ligand.



50a

carbonyl ligands ommitted

50b

Figure 16.

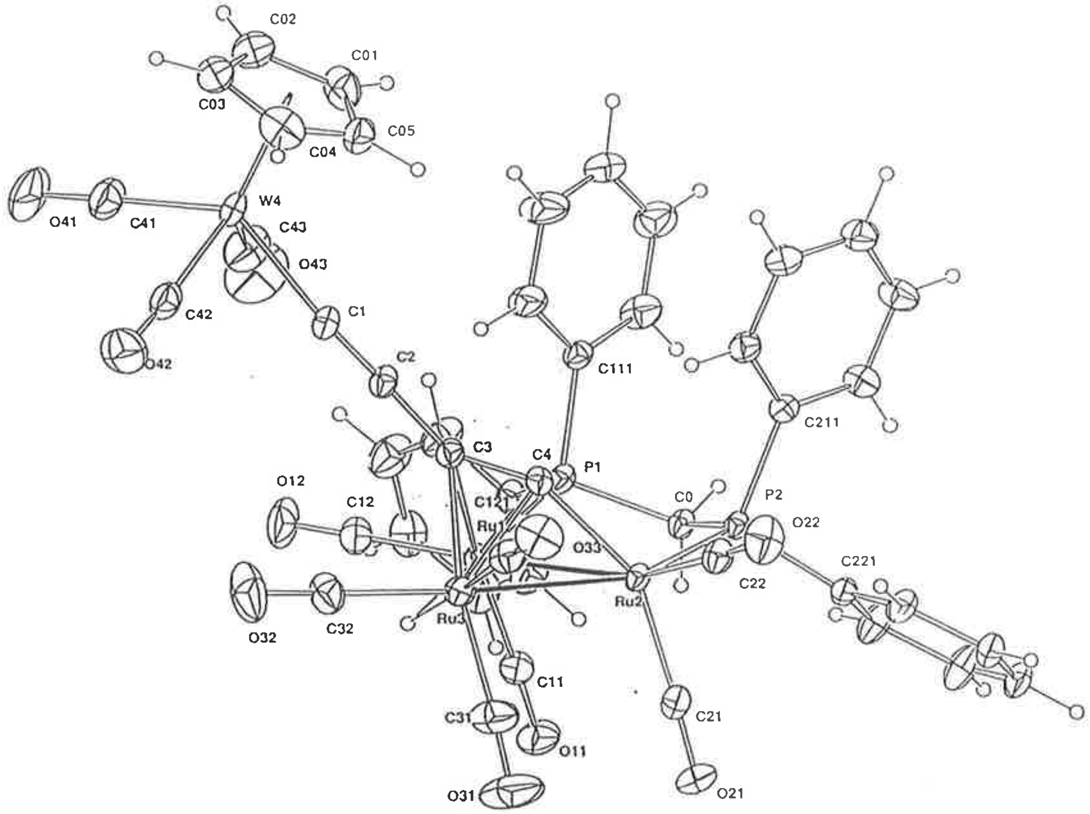


Figure 17 : A plot of a molecule of **50a** showing the atom numbering scheme. Important bond lengths (Å) and angles (°): Ru(1)-Ru(2) 2.777(3); Ru(1)-Ru(3) 2.801(2); Ru(2)-Ru(3) 2.796(2); Ru(1)-P(1) 2.328(2); P(1)-C(0) 1.838(7); C(0)-P(2) 1.834(7); Ru(1)-H 1.84(7); Ru(3)-H 1.73(7); Ru(1)-C(4) 2.200(6); Ru(2)-C(4) 1.980(7); Ru(3)-C(4) 2.226(7); Ru(1)-C(3) 2.801(2); Ru(3)-C(3) 2.276(7); C(3)-C(4) 1.32(1); C(3)-C(2) 1.39(1); C(2)-C(1) 1.19(1); C(1)-W 2.135(7); Ru(2)-Ru(1)-P(1) 91.45(6), Ru(1)-Ru(2)-P(2) 94.12(7); P(1)-C(0)-P(2) 111.1(4); Ru(1)-H-Ru(3) 103(3); Ru(2)-C(4)-C(3) 75.0(4); C(4)-C(3)-C(2) 149.6(7); C(3)-C(2)-C(1) 178.3(7); C(2)-C(1)-W 174.6(6). Intraring angles at Ru(1, 2, 3) are 60.17(4), 60.33(6), 59.49(5)° (by B.W. Skelton and A.H. White).

CONCLUSION.

A number of new diynyl and diyndiyl complexes have been prepared from simple reactions using 1,4-bis(trimethylsilyl)buta-1,3-diyne or buta-1,3-diyne as the only source of the C_4 ligand. The diynyl ligand C≡CC≡CH is readily metallated using Cu(I)-catalysed reactions with various metal-halide complexes. The reactivity of the C≡CH moiety resembles that of organic 1-alkynes, and the diynyl ligand is deprotonated by strong bases, coupled with iodo-alkynes using a mixed palladium(0)-copper(I) catalyst to give complexes with substituted diynyl ligands and undergoes oxidative addition reactions with $Ru_3(\mu\text{-dppm})(CO)_{10}$. Carbonyl-phosphine exchange reactions with diynyl or diyndiyl complexes of $W(CO)_3Cp$ may be performed either thermally or in the presence of trimethylamine-*N*-oxide. Tetracyanoethylene forms adducts with diynyl and diyndiyl ligands which are similar to the complexes formed with acetylide complexes. Dicobalt octacarbonyl readily forms complexes with diynyl and diyndiyl compounds to give either simple $Co_2(CO)_6$ adducts, or C_4-bridged mixed metal clusters.

- Experimental -

Standard conditions, as detailed in Chapter 2, were employed throughout.

Reagents. The compounds $PhC{\equiv}CSiMe_3$ [181], $Me_3SiC{\equiv}CH$ [182], 1,4-dichlorobut-2-yne [183], $MoI(CO)_3Cp$ [184], $MoCl(CO)_3Cp$ [185], $FeCl(CO)_2Cp$ [186], $RuCl(CO)_2Cp$ [187], $RuCl(PPh_3)_2Cp$ [188], $PtCl_2(dppe)$ [189], $IrCl(CO)(PPh_3)_2$ [190], $RhCl(CO)(PPh_3)_2$ [191], LDA [192], MeLi.LiBr [193], $MnI(CO)_5$ [194], $Ru_3(CO)_{10}(dppm)$ [132], $Co_2(CO)_6(\mu\text{-dppm})$ [195], PMe_3 [196], $Pd(PPh_3)_4$ [197] were prepared by literature methods.

Cuprous chloride (Ajax), CuI (Ajax), KF (BDH), PPh_3 (Strem), $SiClMe_3$ (Aldrich), KOH (BDH) and $NEt(chex)_2$ (Willow Brook Labs Inc.) were purchased and used as recieved.

Tetramethylethylenediamine (Merck), 1,4-dibromobenzene (Ajax), $HC{\equiv}CPh$, $HC{\equiv}C^tBu$, C_6H_5I (Aldrich), trimethylamine-*N*-oxide (Aldrich) and $PClPh_2$ (Aldrich) were purchased and purified by standard methods prior to use.

Minor modifications of the published method, as detailed below, were used for the synthesis of *p*-$Me_3SiC{\equiv}CC_6H_4C{\equiv}CSiMe_3$ [198] and buta-1,3-diyne [183].

Acetylide complexes $Ru(C{\equiv}CR)(PPh_3)_2Cp$.

from $PhC{\equiv}CH$: $RuCl(PPh_3)_2Cp$ (200 mg, 0.276 mmol), phenylacetylene (0.5 ml, excess) and KF (17 mg, 0.29 mmol) were warmed together in MeOH (20 ml). The orange suspension rapidly became bright yellow. After 5 min the solution was cooled in ice, and the suspension filtered. $Ru(C_2Ph)(PPh_3)_2Cp$ was isolated as a bright yellow powder (195 mg, 90%) and identified by comparison with an authentic sample.

from $^tBuC{\equiv}CH$: $RuCl(PPh_3)_2Cp$ (100 mg, 0.138 mmol), 3,3-dimethylbut-1-yne (0.5 ml, excess) and KF (8 mg, 0.138 mmol) were warmed in MeOH (10 ml). The suspension cleared, followed by rapid deposition of a bright yellow precipitate of $Ru(C_2{}^tBu)(PPh_3)_2Cp$ (65 mg, 61%). IR (nujol) ν(C≡C) 2083 cm^{-1}; δ_H 7.58 - 7.06 (30H, m, PPh_3), 4.19 (5H, s, Cp), 1.22 (9H, s, CMe_3); FAB MS (*m/z*) 773 $[M]^+$, 691 $[M - C_2{}^tBu]^+$, 428 $[M - C_2{}^tBu - PPh_3]^+$.

from $PhC{\equiv}CSiMe_3$. $RuCl(PPh_3)_2Cp$ (200 mg, 0.276 mmol), PhC_2SiMe_3 (60 µl, 30 mmol) and KF (17 mg, 0.29mmol]) were heated in refluxing MeOH (20 ml) for 18 h. The solution was cooled in ice, and the precipitated $Ru(C_2Ph)(PPh_3)_2Cp$ collected (130 mg, 60%).

p-$Me_3SiC{\equiv}CC_6H_4C{\equiv}CSiMe_3$: 1,4-dibromobenzene (0.75 g, 3.18 mmol) and $Me_3SiC{\equiv}CH$ (1.0 g, 10.6 mmol) were disolved in degassed NEt_3 (100 ml) and treated with $Pd(PPh_3)_4$ (0.35 g, 0.30 mmol) and CuI (0.06 g, 0.3mmol). The reaction mixture was heated in an oil bath at 100 °C for ca. 24 h. After this time, the solution was filtered, the solvent removed, and the pale brown residue recrystallised (MeOH) to give *p*-$Me_3SiC{\equiv}CC_6H_4C{\equiv}CSiMe_3$ (0.82 mg, 96%).

*$Ru(C{\equiv}CC_6H_4C{\equiv}CSiMe_3)(PPh_3)_2Cp$ (**15**)*: A suspension of $RuCl(PPh_3)_2Cp$ (250 mg, 0.34 mmol) in MeOH (20 ml) was treated with *p*-$Me_3SiC{\equiv}CC_6H_4C{\equiv}CSiMe_3$ (93 mg, 0.34mmol) and KF (20 mg, 0.34 mmol) and heated at reflux point for 4h. After this time, the solution was cooled and the yellow precipitate of $Ru(C{\equiv}CC_6H_4C{\equiv}CSiMe_3)(PPh_3)_2Cp$ (**15**) collected, washed with cold MeOH [3 x 5 ml] and air dried (256 mg, 76%). Found: C 72.43; H 5.39%; $C_{54}H_{48}SiP_2Ru$ requires: C, 72.97; H 5.40%. IR (nujol) ν(C≡CSiMe₃) 2153, ν(C≡CRu) 2070 cm^{-1}; δ_H 7.50 -

7.00 [34H, m, Ph and C_6H_4], 4.35 [5H, s, Cp], 0.26 [9H, s, $SiMe_3$]; δ_C 138.96 - 127.54 [m, Ph and C_6H_4], 123.46 [t, J_{CP} 25 Hz, Ru-*C*≡C], 116.71, 115.10, 106.48 [3 x s, Ru-C≡*C* and C≡CSi], 85.21 [s, Cp], 0.13 [s, $SiMe_3$], ES MS (*m/z*): 888 $[M]^+$.

{Cp(PPh₃)₂Ru}C≡CC≡C{Ru(PPh₃)₂Cp} (16). $RuCl(PPh_3)_2Cp$ (2 g, 2.76 mmol) was suspended in methanol (150 ml). $Me_3SiC{\equiv}CC{\equiv}CSiMe_3$ (268 mg, 1.38 mmol), KF (160 mg, 2.76mmol) and $NEt(chex)_2$ (600 μl, 3.3 mmol) were added, and the solution heated at reflux point for 18 h. After this time the solution was deep blue over a pale yellow-orange precipitate. The precipitate was removed by filtration, and washed with several portions of cold methanol. The solid was purified by flash chromatography on alumina (30 x 200 mm). Concentration of the orange eluant (light petroleum / acetone 7 / 3) gave $\{Cp(PPh_3)_2Ru\}C{\equiv}CC{\equiv}C\{Ru(PPh_3)_2Cp\}$ (**16**) as a pale orange, microcrystalline powder [1.3 g, 66%]. IR (Nujol) ν(CC) 1970m cm^{-1}; δ_H 7.64 - 7.03 (m, 30H, PPh_3), 4.17 (s, 5H, Cp); ES MS (*m/z*) 1430 $[M]^+$, 715 $[M]^{2+}$, 692 $[Ru(PPh_3)_2Cp]^+$.

NOTE: It is important that the diacetylide be removed from the column as quickly as possible to minimize oxidation of the product. After elution of **16**, any oxidized material may be eluted as a deep green band with a CH_2Cl_2 / MeOH gradient. Addition of NH_4PF_6, followed by concentration on a rotary evaporator gives **16.PF₆** as a deep green powder (Chapter 4).

Diynyl and Diyndiyl Complexes derived from Cu(I)-Catalysed Reactions.

Diynyl Complexes.

PRECAUTIONARY WARNING:

While no problems were experienced in the preparation, manipulation and reactions of buta-1,3-diyne, this compound must be handled with the necessary degree of respect at all times, especially in the presence of Cu(I). Neat HC≡CC≡CH should never be isolated. As a matter of routine precaution solutions of this reagent (2 - 3 M) were kept cold (ca. -78°C), under dry nitrogen, and used within 5 days of preparation. All manipulations of this compound were performed behind an explosion-proof shield.

HC≡CC≡CH. A 250 ml flask was fitted with a large magnetic stirrer bar, thermometer, 100 ml pressure equalising dropping funnel, nitrogen purge and B14 liebig condensor. The top of the condensor was connected via a short length of plastic tubing to a drying tube loosely filled with $CaCl_2$. The drying tube was in turn connected in series to two cold traps (-80 °C), each of which contained 40 ml of peroxide-free thf, and a parafin bubbler. The delivery arms of the cold traps protruded no more than 5 mm below the surface of the thf.

The flask was charged with KOH (20 g, 0.356 mol), water (100 ml) and DMSO (20 ml). The apparatus was purged of air by passing a stream of nitrogen through the water / DMSO mixture for several minutes. A water bath was used to bring the temperature of the reaction mixture to 65 °C. The nitrogen purge was maintained while 1,4-dichlorobut-

2-yne (20 g, 0.163 mol) was added in small portions over 30 min to the vigorously stirred solution. During this time the temperature was maintained between 65 and 75 °C. After the addition was complete, the temperature of the reaction was increased to 90 - 100 °C for 45 min. The traps were removed under nitrogen. The first trap contained approximately 6 g (74%) of buta-1,3-diyne as a 3 mol dm^{-3} solution in thf, while the second trap was essentially free of the diacetylene.

W(C≡CC≡CH)(CO)$_3$Cp (18). WCl(CO)$_3$Cp (2.5 g, 6.79 mmol) was dissolved in mixture of thf (20 ml) and NHEt$_2$ (50 ml). To this solution CuI (150 mg, 0.79 mmol) was added, followed immediately and rapidly by buta-1,3-diyne (7 ml of a 3M solution in thf). The reaction mixture rapidly changed colour from red to yellow-orange, and a white precipitate of [NH$_2$Et$_2$]Cl formed. After 5 min the solution was filtered and the solvent removed. The residue was extracted (CH$_2$Cl$_2$) and loaded onto an column of alumina. Elution with light petroleum / acetone (7 / 3) gave a bright yellow band. Concentration of the eluant (ca. 10 ml) resulted in the precipitation of W(C≡CC≡CH)(CO)$_3$Cp (**18**) (2.3 g, 89 %) as a bright yellow powder, which was collected, washed with cold hexane and air dried. The compound was best stored in the dark at -18°C. Found: C 37.38; H 1.54%. $C_{12}H_6O_3W$ requires: C 37.72; H 1.57%. IR (CH$_2$Cl$_2$) ν(C≡C) 2145 m, ν(CO) 2044 s, 1958 br cm^{-1}; δ_H 5.66 (5H, s, Cp); 2.03 (1H, s, C≡CH); δ_C 227.41 (t, J_{CW} = 70 Hz, CO), 210.87 (t, J_{CW} = 70 Hz, CO), 110.52 (br, C_α), 91.51 (s, Cp), 71.60 (t, J_{CW} = 44 Hz, C_β), 70.13 (t, J_{CW} = 47 Hz, C_γ), 63.30 (s, C_δ); ES MS (low cone voltage) (*m/z*) 396 [M - CO + NCMe + H]$^+$, 368 [M - 2CO + NCMe + H]$^+$, 355 [M - CO + H]$^+$; (high cone voltage) (*m/z*) 299 [M - 3CO + H]$^+$.

Mo(C≡CC≡CH)(CO)$_3$Cp (19). In a reaction similar to that described for the tungsten analogue, dark yellow Mo(C≡CC≡CH)(CO)$_3$Cp (**19**) was isolated in 60% yield (0.95 g) from MoI(CO)$_3$Cp (2 g, 5.4 mmol) and buta-1,3-diyne. The compound was eluted with light petroleum / acetone (9 / 1). Found: C 49.02; H 2.63%. $C_{12}H_6O_3Mo$: C 48.69; H

2.03%. IR (CH_2Cl_2) ν(C≡C) 2145 m, ν(CO) 2050 s, 1970 br cm^{-1}; δ_H 5.58 (5H, s, Cp), 2.04 (1H, s, C≡CH); δ_C 237.39 (s, CO), 221.86 (s, CO), 110.46 (s, C_α), 92.94 (s, Cp), 87.25 (s, C_β), 70.27 (s, C_γ), 62.10 (s, C_δ); FAB MS (*m/z*) 293 [M]$^+$, 266 - 210 [M - nCO]$^+$ (n = 1 - 3).

*Fe(C≡CC≡CH)(CO)$_2$Cp (**20**).* A solution of FeCl(CO)$_2$Cp (200 mg, 0.83 mmol) in $NHEt_2$ (20 ml) was treated with a catalytic amount of CuI, followed by diacetylene (4 mmol as a thf solution). The deep red solution turned dark and was allowed to stir for five minutes before being filtered though Celite. The volitiles were removed and the residue purified by preparative TLC (light petroleum / acetone 7 / 3). The first band (R_f 0.8) was maroon in colour and yielded a trace amount of {Fe(CO)$_2$Cp}$_2$. The major band (R_f 0.6) was yellow and gave Fe(C≡CC≡CH)(CO)$_2$Cp (**20**) (67 mg, 32 %). IR (CH_2Cl_2) ν(C≡C) 2149m, ν(CO) 2050s, 2003s cm^{-1}; δ_H 5.07 (5H, s, Cp), 1.47 (1H, s, C≡CH).

*Pt(C≡CC≡CH)$_2$(dppe) (**21**).*To a solution of PtCl$_2$(dppe) (1.0 g, 1.5 mmol) in dmf (45 ml) / $NHEt_2$ (15 ml), CuI (30 mg, 0.15mmol) and diacetylene (15 mmol as a thf solution) were added in that order and allowed to stir 15 min. The volitiles were removed in vacuo and the residue treated with water (20 ml) and stirred. The crude material obtained was washed with several portions of water, methanol, Et_2O and then extracted with CH_2Cl_2. The extracts were concentrated to a ca. 5 ml and filtered slowly into rapidly stirred hexane. The resulting white precipitate was collected, washed with cold hexane and air dried to give Pt(C≡CC≡CH)$_2$(dppe) (**21**) (1.0 g, 96%) . Crystals suitable for X-ray study were grown from CH_2Cl_2 / hexane by slow diffusion . Found: C 59.25; H 3.76%. $C_{34}H_{26}P_2Pt$ requires: C 59.09; H 3.76%. IR (nujol) ν(C≡CH) 3288 w, ν(C≡C) 2147 s cm^{-1}; δ_H 7.44 - 7.89 (10H, m, PPh$_2$), 2.42 (2H, m, P(CH$_2$)$_2$P), 1.82 (1H, t, J_{HPt} = 4 Hz, C≡CH); δ_C 133.53 - 128.41 (m, Ph), 93.7 (m, C_α), 77.21 (s, C_β), 71.75 (s, C_γ), 61.74 (s, C_δ), 27.80 (unresolved dd, CH$_2$P); δ_P 38.54 (t, J_{PtP} = 2300 Hz); FAB MS (*m/z*) 692 [M + H]$^+$, 642 [M - C$_4$H + H]$^+$, 593 [M - 2C$_4$H]$^+$.

Diyndiyl Complexes

{Cp(CO)$_3$W}C≡CC≡C{W(CO)$_3$Cp} (22). A solution of WCl(CO)$_3$Cp (280mg, 0.76 mmol) and CuI (ca. 5 mg, cat.) in thf (7 ml) / NHEt$_2$ (10 ml) was treated with W(C≡CC≡CH)(CO)$_3$Cp (300 mg, 0.78 mmol) and stirred 10 min. The bright yellow precipitate was collected, and washed with several portions of water, methanol, ethanol and diethyl ether to give gave {Cp(CO)$_3$W}C≡CC≡C{W(CO)$_3$Cp} (**22**) as a bright yellow powder (420 mg, 77%). Found: C 33.43; H 1.47%. $C_{20}H_{10}O_6W_2$ requires: C 33.64; H 1.40%. IR (CH$_2$Cl$_2$) ν(C≡C) 2145w, 2043s,2037s, 1955br cm^{-1}; δ_H 5.81 (s, Cp); ES MS (*m/z*) (low cone voltage) 687 $[M - CO + H]^+$; (high cone voltage) 718 $[M - 2CO + NCMe + H_2O + H]^+$, 687 - 547 $[M - nCO + H]^+$ (n = 1 - 6).

{Cp(CO)$_3$Mo}C≡CC≡C{Mo(CO)$_3$Cp} (23). A solution of MoCl(CO)$_3$Cp (1.0 g, 3.57 mmol) in thf (10 ml) / NHEt$_2$ (30 ml) was treated sequentially with CuI (70 mg, 0.36 mmol) and Mo(C≡CC≡CH)(CO)$_3$Cp (1.05 g, 3.57 mmol). The solution rapidly deposited a yellow precipitate which was collected and washed with several portions of water, methanol, ethanol, diethyl ether and air dried to give {Cp(CO)$_3$Mo}C≡CC≡C{Mo(CO)$_3$Cp} (**23**) as a bright yellow powder (1.44 g, 75%). Found: C 44.11; H 1.97%. $C_{20}H_{10}O_6Mo_2$ requires: C 44.62; H 1.86%. IR (CH$_2$Cl$_2$) 2043 m, 1967 vs cm^{-1}; δ_H 5.53 (s, Cp); ES MS (*m/z*) (with NaOMe) 1099 $[2M + Na]^+$, 560 $[M + Na]^+$, 510 $[M - CO]^+$.

{Cp(CO)$_3$W}C≡CC≡C{Mo(CO)$_3$Cp} (24). A rapidly stirred solution of MoCl(CO)$_3$Cp (1 g, 3.57 mmol) in NHEt$_2$ (50ml) was treated sequentially with CuI (190 mg, 0.357 mmol) and W(C≡CC≡CH)(CO)$_3$Cp (1.36 g, 3.57 mmol). The solution immediately deposited a bright yellow precipitate. The solution was allowed to stir 5 min then filtered. The bright yellow powder obtained was washed with several portions of water, methanol, ethanol, diethyl ether and air dried to give

$\{Cp(CO)_3W\}C\equiv CC\equiv C\{Mo(CO)_3Cp\}$ (**24**) (2.14 g, 95%). Found: C 37.94; H 1.85%. $C_{20}H_{10}O_6MoW$ requires: C 38.37; H 1.60%. IR (CH_2Cl_2) ν(C≡C) 2145 w, 2045 s, 2038 s, 1957 br cm^{-1}; δ_H 5.67 (5H, s, WCp), 5.55 (5H, s, MoCp); ES MS (low cone voltage) (*m/z*) 599 $[M - CO + H]^+$; (high cone voltage) 599 $[M - CO + H]^+$, 571 $[M - 2CO + H]^+$, 515 $[M - 4CO + H]^+$.

$\{Cp(CO)_3W\}C\equiv CC\equiv C\{Fe(CO)_2Cp\}$ (25). To a solution of $W(C\equiv CC\equiv CH)(CO)_3Cp$ (500 mg, 1.31 mmol) in $NHEt_2$ (40 ml) CuI (30 mg, 0.16 mmol) was added, followed by $FeCl(CO)_2Cp$ (280 mg, 1.31 mmol). The solution was allowed to stir for 1h in the dark. The solvent was removed from the dark orange suspension and the residue purified by column chromatography on Al_2O_3. Elution with light petroleum / acetone (7 / 3) gave a yellow-orange band which upon concentration yielded $\{Cp(CO)_3W\}C\equiv CC\equiv C\{Fe(CO)_2Cp\}$ (**25**) as an orange powder (475 mg, 65%). IR (CH_2Cl_2) ν(C≡C) 2135w,br, ν(CO) 2045s, 2038vs, 1997s, 1950br cm^{-1}; δ_H 5.62 (5H, s, WCp), 5.03 (5H, s, FeCp); δ_C 230.71 (t, J_{CW} = 65 Hz, WCO); 211.66 (br, WCO), 210.88 {s, FeCO), 115.45 (br, C_α), 101.00 (s, C_δ), 91.56 (s, WCp), 85.28 (s, FeCp), 63.32 (s, C_β), 42.32 (s, C_γ); FAB MS (*m/z*) 530 - 474 $[M - nCO]^+$ (n = 1 - 3).

$\{Cp(CO)_3W\}C\equiv CC\equiv C\{Ru(CO)_2Cp\}$ (26). A solution of $RuCl(CO)_2Cp$ (101 mg, 0.39 mmol) in thf (5 ml) / $NHEt_2$ (10 ml) was treated sequentially with CuI (ca. 5 mg, cat.) and $W(C\equiv CC\equiv CH)(CO)_3Cp$ (150 mg, 0.39 mmol) and allowed to stir in the dark 12 h. The cloudy solution was taken to dryness, and the residue purified by column chromatography on Al_2O_3. Elution with a light petroleum / acetone gradient gave $[Ru(CO)_2Cp]_2$, followed by a mixed orange-yellow fraction. This mixed fraction was taken to dryness, and washed with hexane until the washings were colourless to remove any traces of $[Ru(CO)_2Cp]_2$. The resulting yellow solid was identified as $\{Cp(CO)_3W\}C\equiv CC\equiv C\{Ru(CO)_2Cp\}$ (**26**) (120mg, 51%). IR (CH_2Cl_2) ν(C≡C) 2142w, ν(CO) 2051m, 2038s, 1999 s, 1950br cm^{-1}; δ_H 5.62 (5H, s, WCp), 5.44 (5H, s, RuCp); ES MS (*m/z*) 604 $[M + H]^+$, 576 $[M + H - CO]^+$.

{Cp(CO)$_3$W}C≡CC≡C{Ir(CO)(PPh$_3$)$_2$} (27). A solution of W(C≡CC≡CH)(CO)$_3$Cp (100 mg, 0.26 mmol) and IrCl(CO)(PPh$_3$)$_2$ (202 mg, 0.26 mmol) in NHEt$_2$ (15 ml) / thf (5ml) was treated with CuI (ca. 5 mg, cat.) and stirred in the dark for 1h. The yellow-orange precipitate was purified by column chromatography on Al$_2$O$_3$. A light petroleum / acetone gradient gave a bright yellow band, which afforded {Cp(CO)$_3$W}C≡CC≡C{Ir(CO)(PPh$_3$)$_2$} (**27**) (240 mg, 82%) upon concentration. IR (CH$_2$Cl$_2$) ν(CO) 2037s, 1952vs cm^{-1}; δ_H 7.75 - 7.39 (m, 30H, Ph), 5.55 (s, 5H, Cp); δ_C 240.25 (s, IrCO), 231.62 (br, WCO), 211.89 (s, WCO), 134.92 - 128.13 (m, Ph), 91.59 (s, Cp); FAB-MS (*m/z*) 1126 [M]$^+$, 1098 [M - CO]$^+$, 745 [Ir(CO)(PPh$_3$)$_2$]$^+$.

{Cp(CO)$_3$W}C≡CC≡C{Rh(CO)(PPh$_3$)$_2$} (28). A solution of W(C≡CC≡CH)(CO)$_3$Cp (100 mg, 0.26 mmol) and *trans*-RhCl(CO)(PPh$_3$)$_2$ (202 mg, 0.26 mmol) in NHEt$_2$ (15 ml) / thf (5 ml) was treated with CuI (ca. 5 mg, cat.) and stirred in the dark for 30 min. The yellow-orange precipitate was purified by column chromatography on Al$_2$O$_3$. A light petroleum / acetone gradient gave a bright yellow band, which afforded {Cp(CO)$_3$W}C≡CC≡C{Rh(CO)(PPh$_3$)$_2$} (**28**) (200 mg, 74%). IR (CH$_2$Cl$_2$) ν(CO) 2037s, 1973vs, 1952vs cm^{-1}; δ_H 7.75, 7.40 (m, 30H, Ph), 5.47 (s, 5H, Cp); δ_C 239.82 (s, RhCO), 231.68 (br, WCO), 210.83 (s, WCO), 134.82 - 128.20 (m, Ph), 91.55 (s, Cp); ES MS (*m/z*) (with NaOMe) (positive ion mode) 1059 [M + Na]$^+$, (negative ion mode) 1067 [M + OMe]$^-$.

Pt(C≡CC≡C[W(CO)$_3$Cp])$_2$(dppe) (29). A solution of PtCl$_2$(dppe) (150 mg, 0.23mmol) in dmf (4 ml) / NHEt$_2$ (6 ml) was treated sequentially with CuI (ca. 5 mg) and W(C≡CC≡CH)(CO)$_3$Cp (175 mg, 0.46 mmol), and the resulting dark yellow mixture allowed to stir in the dark 15 min. The volitiles were removed in vacuo, and the oily residue purified by column chromatography on Al$_2$O$_3$. A yellow band was eluted with a light petroleum / acetone gradient. The eluant was evaporated, extracted with CH$_2$Cl$_2$ (ca. 5 ml) and the filtered extracts added dropwise to rapidly stirred methanol

(20 ml). The suspension was allowed to stir overnight in the dark. The resulting precipitate was collected, washed with several portions of cold diethyl ether, and dried to give $Pt(C{\equiv}CC{\equiv}C[W(CO)_3Cp])_2(dppe)$ (**29**) (230 mg, 73%) as a pale yellow powder which was crystallised (benzene / hexane). Found C 44.44, H 2.60%. $C_{50}H_{34}O_6P_2W_2Pt$ requires: C 44.25, H 2.51%. IR (CH_2Cl_2) ν(CO) 2038s, 1952vs cm^{-1}. δ_H 8.03 - 7.38 (20H, m, Ph), 5.56 (5H, s, Cp), 2.31 (4H, m, $P(CH_2)_2P$); δ_C 133.67 - 128.56 (m, Ph), 91.68 (s, Cp); ES MS (with formic acid) (*m/z*) 1356 $[M + H]^+$, 1342 $[M + H + NCMe - CO]^+$, 1329 $[M + H - CO]^+$; (with $AgNO_3$) 1566 $[(M + H + Ag + NO_3 + NCMe)_2]^{2+}$, 1464 $[(M + Ag)_2]^{2+}$.

*Preparation and Reactions of $W(C{\equiv}CC{\equiv}CLi)(CO)_3Cp$ (**30**).*

$W(C{\equiv}CC{\equiv}CSiMe_3)(CO)_3Cp$ (**17**). *via $LiC{\equiv}CC{\equiv}CSiMe_3$*: 1,4-bis(trimethylsilyl)but-1,3-diyne (250 mg, 1.23 mmol) in thf (10 ml) at -78 °C was treated dropwise with MeLi.LiBr (1.5M solution in Et_2O, 0.860 ml, 1.23 mmol). The cold bath was removed and the stirred for 2h to give asolution of $LiC{\equiv}CC{\equiv}CSiMe_3$ (0.12 M).
A solution of $WCl(CO)_3Cp$ (200 mg, 0.54 mmol) in thf (10 ml) was cooled to -78°C and treated dropwise with $LiC{\equiv}CC{\equiv}CSiMe_3$ (0.12 M, 5 ml, 0.6 mmol). After warming to room temperature over 1h preparative TLC (light petroleum / acetone 7/3) afforded $W(C{\equiv}CC{\equiv}CSiMe_3)(CO)_3Cp$ (**17**) (yellow band, R_f 0.7, 88mg, 36% after crystallisation from min. volume CH_2Cl_2 / hexane at -20 °C) and unchanged $WCl(CO)_3Cp$ (orange band, R_f 0.6, 50mg, 25%).

via $W(C{\equiv}CC{\equiv}CLi)(CO)_3Cp$: A solution of $W(C{\equiv}CC{\equiv}CH)(CO)_3Cp$ (**18**) (200 mg, 0.52 mmol) in thf (15 ml) was cooled to -78 °C and lithiumdiisopropylamine (0.5 M solution in thf/hexane, 1.04 ml, 0.52 mmol) was added dropwise to the stirred solution. The solution became orange and was allowed to stir for 5 min before $SiClMe_3$ (66μl, 57mg, 0.52mmol) was added. The solution was allowed to warm to room temperature over 20 minutes. The solvent was removed and the residue extracted with CH_2Cl_2. The filtered

(Celite) extracts were concentrated (ca. 10ml) and diluted with a similar volume of *n*-hexane. Further concentration resulted in the precipitation of $W(C{\equiv}CC{\equiv}CSiMe_3)(CO)_3Cp$ (**17**) as a pale yellow powder which was washed with several portions of cold hexane and air dried (190mg, 80%). Found: C 39.18; H 3.11%. $C_{15}H_{14}O_3SiW$ requires: C 39.68; H 3.08%. IR (CH_2Cl_2) ν(C≡C) 2174w, 2127w, ν(CO) 2045vs, 2026m, 1957br cm^{-1}; δ_H 5.66 (s, 5H, Cp), 0.20 (s, 9H, $SiMe_3$); δ_C 227.53 (s, CO), 210.56 (t, J_{CW} = 77 Hz, CO), 111.74 (br, C_α), 110.86 (s, C_β), 91.53 (s, Cp), 90.04 (s, C_γ), 73.59 (s, C_δ); FAB MS (*m/z*) 454 $[M]^+$, 426 $[M - CO]^+$, 370 $[M - 3CO]^+$.

W{C≡CC≡CP(O)Ph₂}(CO)₃Cp (31). A cold (-78 °C) solution of $W(C{\equiv}CC{\equiv}CH)(CO)_3Cp$ (1.0 g, 2.60 mmol) in thf (100 ml) was treated dropwise with lithiumdiisopropylamine (0.5 M solution in thf/hexane, 5.5 ml, 2.8 mmol) and stirred for 10 min. Freshly distilled $PClPh_2$ (0.5 ml, 2.8 mmol) was added slowly, and the solution allowed to warm to r.t. over 2 hours. The solvent was removed, and the residue taken up in CH_2Cl_2 and loaded onto a squat Al_2O_3 column. The column was washed initially with CH_2Cl_2 to remove any unchanged $W(C{\equiv}CC{\equiv}CH)(CO)_3Cp$, then with acetone to give crude $W(C{\equiv}CC{\equiv}CP(O)Ph_2)(CO)_3Cp$ (**31**), which was purified further by preparative TLC (light petroleum / acetone 6 / 4) and crystallisation (CH_2Cl_2 / hexane) (250 mg, 16%). Found C 49.11, H 2.63%. $C_{24}H_{15}O_4PW$ requires: C 49.40, H 2.57%; IR (CH_2Cl_2) ν(C≡C) 2138m, ν(CO) 2051s, 2031m, 1962br, [nujol ν(PO) 1199] cm^{-1}; δ_H 7.89-7.47 (m, 10H, PPh_2), 5.69 (s, 5H, Cp); δ_C 225.43 (s, CO); 210.23 (t, J_{CW} = 71 Hz, CO), 134.33-128.45 (Ph); 110.57 (t, J_{CW} = 8 Hz, C_α); 91.64 (s, Cp); 91.32 (s, C_β); FAB-MS (*m/z*) 583 $[M]^+$, 555 $[M - CO]^+$, 498 $[M - 3CO]^+$.

{Cp(CO)₃W}C≡CC≡C{Mn(CO)₅} (32). Treatment of a cold (-78°C) solution of $W(C{\equiv}CC{\equiv}CH)(CO)_3Cp$ (200 mg, 0.52 mmol) in thf (15 ml) with lithiumdiisopropylamine (0.5 M solution in thf / hexane, 1.04 ml, 0.52 mmol) gave an orange solution which was stirred cold for 10 min. Dropwise addition a solution of

$MnI(CO)_5$ (165 mg, 0.51 mmol) in thf (10 ml) resulted in a colour change to dark yellow. The solvent was removed and the residue purified initially by column chromatography on Al_2O_3 (light petroleum / acetone 1 / 1) then preparative TLC (light petroleum/acetone 6/4). The major band (yellow-orange, R_f 0.50) was collected and crystallised (CH_2Cl_2 / hexane) to give yellow needles of $\{Cp(CO)_3W\}C{\equiv}CC{\equiv}C\{Mn(CO)_5\}$ (**32**) (55 mg, 18%). IR (cyclohexane) ν(C≡C) 2150w, 2128w, ν(CO) 2047s, 2004m, 1968vs, 1955vs cm^{-1}. δ_H 5.65 (s, Cp); δ_C 229.70 (t, J_{CW} = 61 Hz, WCO), 210.88 (t, J_{CW} = 71 Hz, WCO), 206.98 (s, MnCO), 205.96 (s, MnCO), 114.88 (t, J_{CW} = 11 Hz, C_α), 101.49, 80.83, 55.65 (3 x s, C_β, C_γ, C_δ), 91.56 (s, Cp). FAB-MS (*m/z*) 576 $[M]^+$, 548 $[M - CO]^+$, 520 $[M - 2CO]^+$, 511 $[M - Cp]^+$.

W(C≡CC≡CPh)(CO)₃Cp (33). Dry diisopropylamine (50 ml) was introduced into a flame-dried schlenk flask and rigorously deoxygenated by using a freeze, pump, thaw sequence three times. Solid $W(C{\equiv}CC{\equiv}CH)(CO)_3Cp$ (1.0 g, 2.62 mmol) was added followed by freshly distilled iodobenzene (801 mg, 3.93 mmol), $Pd(PPh_3)_4$ (151 mg, 0.13 mmol) and CuI (50 mg, 0.26 mmol) in that order. The solution was stirred in the dark for 16h. The yellow precipitate obtained was washed with several portions of cold hexane, dissolved in the minimum volume of CH_2Cl_2 and purified on a squat column of Al_2O_3 (30 x 50mm). Elution with light petroleum/acetone (7 / 3) gave a bright yellow fraction which was concentrated to give $W(C{\equiv}CC{\equiv}CPh)(CO)_3Cp$ (**33**) as a bright yellow microcrystalline powder (650 mg). Similar treatment of the filtrate from the reaction mixture on a longer Al_2O_3 column gave a further 140 mg of **33**. The overall yield was 790 mg, 66%. The microanalytical sample was recrystallised from acetone/hexane. Found C 46.80, H 2.29%. $C_{18}H_{10}O_3W$ requires: C 47.20, H 2.18%. IR (CH_2Cl_2) ν(C≡C) 2183m, 2059m, ν(CO) 2038vs, 1956br cm^{-1}; δ_H 7.27 - 7.46 (5H, m, Ph), 5.68 (5H, s, Cp); δ_C 227.60 (t, J_{CW} = 60 Hz, CO), 210.64 (t, J_{CW} = 71 Hz, CO), 132.38 (s, *o*-C), 128.16 (s, *m*-C), 127.97 (s, *p*-C), 123.05 (s, *i*-C), 111.03

(t, J_{CW} = 11 Hz, C_α), 91.62 (s, Cp), 76.19, 73.78 (2 x s, C_γ/ C_δ). FAB MS (*m/z*) 458 $[M]^+$, 430 $[M - CO]^+$.

Mo(C≡CC≡CPh)(CO)$_3$Cp (34). Using conditions similar to those described for the preparation of the tungsten analogue **33**, a solution of Mo(C≡CC≡CH)(CO)$_3$Cp (100 mg, 0.34 mmol) in dry, degassed diisopropylamine was treated with iodobenzene (100 mg, 0.50 mmol), Pd(PPh$_3$)$_4$ (20 mg, 0.017 mmol) and CuI (7 mg, 0.03 mmol), and stirred for 16h in the dark. Preparative TLC (light petroleum / acetone 7/3) separated 15 compounds. A bright yellow band (R_f = 0.57) yielded very light-sensitive Mo(C≡CC≡CPh)(CO)$_3$Cp (**34**) (50 mg, 40%) after crystallisation (CH_2Cl_2/hexane). The other bands were not pursued. Found: C 57.70; H 2.73%. $C_{18}H_{10}O_3Mo$ requires: C 58.38; H 2.70%. IR (CH_2Cl_2) ν(C≡C) 2183 m, ν(CO) 2059 m, 2042 vs, 1970br cm^{-1}; δ_H 7.46 - 7.27(5H, m, Ph), 5.58 (5H, s, Cp); δ_C 237.50 (s, CO), 221.77 (s, CO), 132.31 (s, *o*-C), 128.15 (s, *m*-C), 127.92 (s, *p*-C), 123.15 (s, *i*-C), 110.92 (s, C_α), 93.02 (s, Cp), 76.42 (s, C_δ), 72.59 (s, C_γ); ES-MS (added NaOMe) (low cone voltage) (*m/z*) 402 $[M+OMe]^-$.

Reactions with tetracyanoethylene.

Ru[η^3-C(CN)$_2$C{C≡C[Ru(PPh$_3$)$_2$Cp]}C=C(CN)$_2$](PPh$_3$)Cp (35). A solution of [Cp(PPh$_3$)$_2$Ru]$_2$(μ-C$_4$) (200mg, 0.14mmol) in thf (20ml) was treated with tcne (20mg, 0.15mmol). The initially orange solution rapidly turned deep green, then deep red within a few minutes. The solution was allowed to stir for 15 minutes before the solvent was removed in vacuo. The residue was triturated with hexane to give Ru[η^3-C(CN)$_2$C{C≡C[Ru(PPh$_3$)$_2$Cp]}C=C(CN)$_2$](PPh$_3$)Cp (**35**) (150mg, 69%) as a brick red powder. Found C 68.45; H 4.10; N 4.23%. $C_{74}H_{55}N_4P_3Ru_2$ requires: C 68.62; H 4.25; N 4.32%. IR (nujol): ν(CN) 2210m; ν(C≡C) 1993s; ν(C=C) 1585w cm^{-1}; δ_H 7.50 - 7.20 (60H, m, Ph); 4.55, 4.43 (2 x 5H, 2 x s, 2 x Cp);

δ_C 224.7 [d, J_{CP} = 60 Hz, C(3)], 138.69 - 127.56 (m, Ph), 119.86, 119.76 (2 x s, 2 x CN), 112.26 [br, C(6)], 106.34 [br, C(5)], 91.43, 87.09 (2 x s, 2 x Cp), 81.58 [d, J_{CP} = 6 Hz, C(1)], 60.21 [s, C(4)], 14.09 [br, C(2)]; ES MS: *m/z* 1318 [M + Na]$^+$.

[Ru{C[=C(CN)$_2$]C{C≡C[Ru(PPh$_3$)$_2$Cp]}C(CN)$_2$}(PPh$_3$)Cp]$_2$ (36). Attempts to purify **35** by preparative TLC (light petroleum / acetone 55 / 45) resulted in the development of two bands. The top red band contained Ru{η^3-C(CN)$_2$CC[=C(CN)$_2$]C≡C[Ru(PPh$_3$)$_2$Cp]}(PPh$_3$)Cp (identified by ^{1}H NMR and IR spectroscopies). The second band was yellow, and yielded the CN bridged dimer [Ru{C[=C(CN)$_2$]C{C≡C[Ru(PPh$_3$)$_2$Cp]}C(CN)$_2$}(PPh$_3$)Cp]$_2$ (**36**) after crystallisation (CH_2Cl_2 / MeOH). Found C 68.59; H 4.18; N 4.37%. $C_{148}H_{110}N_8P_6Ru_4$ requires: C 68.62; H 4.25; N 4.32%. IR (nujol): ν(CN) 2202m; ν(C≡C) 1976s; ν(C=C) 1586, 1571w cm^{-1}; δ_H 7.61 - 6.87 (45H, m, Ph); 4.59, 4.26 (2 x 5H, 2 x s, 2 x Cp); δ_C 139.9 - 127.4 (m, Ph), 118.06, 115.23, 113.27 (3 x s, CN), 87.10, 81.59 (2 x s, 2 x Cp). FAB MS (*m/z*) 1296 [M / 2]$^+$; 1034 [M/2 - PPh$_3$]$^+$; 772 [M/2 - 2PPh$_3$]$^+$; 690 [Ru(PPh$_3$)$_2$Cp]$^+$.

W[C≡CC{=C(CN)$_2$}C{=C(CN)$_2$}H](CO)$_3$Cp (37). A solution of W(C≡CC≡CH)(CO)$_3$Cp (200 mg, 0.52 mmol) in CH_2Cl_2 (15 ml) was treated with tetracyanoethylene (67 mg, 0.52 mmol) and stirred for 5 min. The initially yellow solution turned an intense purple colour during this time. The solvent was removed and the residue extracted with the minimum volume of fresh CH_2Cl_2. The CH_2Cl_2 extracts were filtered dropwise into rapidly stirred hexane. The resulting purple precipitate was collected and crystallised (CH_2Cl_2/hexane) to give W{C≡CC[=C(CN)$_2$]C[=C(CN)$_2$]H}(CO)$_3$Cp (**37**) as dark purple blocks (225 mg, 84%). Crystals suitable for the X-ray study were obtained from 1,2-dichloroethane / hexane. Found: C 42.21; H 1.32%. $C_{18}H_6O_3N_4W$ requires: C 42.35; H 1.18%. IR (CH_2Cl_2) ν(CN) 2221w, ν(C≡C) 2078m, ν(CO) 2030s, 1970br cm^{-1}; δ_H 7.62 (1H, s, C[=C(CN)$_2$]H), 5.80 (5H, s, Cp); δ_C 221.05 [s, C(3); 209.15 (s, CO), 148.70 [s, C(2)], 94.41 [s, C(4)], 92.19 (s, Cp), 91.90 [s, C(1)]; FAB MS (*m/z*) 510 [M]$^+$.

Oxidative Coupling of M(C≡CC≡CH)(CO)$_3$Cp .

Preparation of the Hay catalyst CuCl.tmeda. Cuprous chloride (100 mg, 1.01 mmol) was suspended in dry acetone (5 ml), treated with tmeda (150 μl, 117 mg, 1.01 mmol) and stirred for 15 min. The finely divided suspension of unreacted CuCl was allowed to settle prior to use in the coupling reactions.

{Cp(CO)$_3$W}(C≡C)$_4${W(CO)$_3$Cp} (38). The Hay catalyst was added in small portions to a solution of W(C≡CC≡CH)(CO)$_3$Cp (500 mg, 1.3 mmol) in acetone (40 ml) whilst a stream of O$_2$ was bubbled through the reaction mixture. Addition of the CuCl.tmeda cataylst was ceased when the reaction was judged complete (TLC). The solvent was removed and the residue purified by column chromatography on Al_2O_3. A light petroleum / acetone gradiant (6 / 4 to 4 / 6) was used to elute a yellow-orange band, which yielded {Cp(CO)$_3$W}(C≡C)$_4${W(CO)$_3$Cp} (**38**) (420 mg, 85%) as an orange, microcrystalline solid. The analytical sample was crystallised from CH_2Cl_2 / hexane. The analytical sample contained 0.2 molecule CH_2Cl_2 which was observed in the ^{1}H NMR. Found: C 37.22; H 1.57%. $C_{24}H_{10}O_6W_2 \cdot 0{\cdot}2CH_2Cl_2$ requires: C 37.31; H 1.35%. IR (CH_2Cl_2) ν(C≡C) 2190w, ν(CO) 2043s, 1959vs cm^{-1}. δ_H 5.67 (s, Cp); δ_C 227.32 (s, CO), 210.26 (s, CO), 112.39 (br, C_α), 91.66 (s, Cp), 91.60 (s, C_β), 63.70 (s, C_γ), 60.91 (s, C_δ); ES MS (*m/z*) (with $AgNO_3$) 1631 [2M + Ag]$^+$, 1575 [2M + Ag - 2CO]$^+$, 911 - 854 [M + Ag + NCMe - n(CO)]$^+$ (n = 0 - 2), 813 [M + Ag - 2CO]$^+$.

{Cp(CO)$_3$Mo}(C≡C)$_4${Mo(CO)$_3$Cp} (39). Small aliquots of the Hay catalyst were added to Mo(C≡CC≡CH)(CO)$_3$Cp (200 mg, 0.68 mmol) in acetone (25 ml) while O$_2$ was bubbled through the solution. When the reaction was complete (TLC) the solvent was removed, and the residue purified by column chrmatography on Al_2O_3. Eluation with diethyl ether gave a dark orange fraction, which was diluted with *n*-hexane and

concentrated to give $\{Cp(CO)_3Mo\}(C\equiv C)_4\{Mo(CO)_3Cp\}$ (**39**) as a highly light-sensitive, burnt orange powder (80 - 120 mg, 40-60%). IR (CH_2Cl_2) $\nu(C\equiv C)$ 2140w, $\nu(CO)$ 2049s, 1973vs cm^{-1}; δ_H 5.78 (s, 5H, Cp); δ_C 237.22, 221.41 (2xs, CO), 112.24 (s, C_α), 93.12 (s, Cp), 92.22 (s, C_β), 63.47 (s, C_γ), 59.95 (s, C_δ); ES MS (added $AgNO_3$) (*m/z*) 734 $[M + Ag + NCMe]^+$.

Phosphine Exchange Reactions.

$\{Cp(PPh_3)(PMe_3)Ru\}C\equiv CC\equiv C\{Ru(PMe_3)(PPh_3)Cp\}$ (40). Complex **17** (150 mg, 0.10 mmol) was suspended in toluene (5 ml), treated with PMe_3 (110 µl, 1.2 mmol), sealed under vacuum, and heated in a 120 °C oil bath for 4 days. The solvent was removed from the clear orange solution in vacuo, and the oily residue triturated with hexane to give $\{Cp(PPh_3)(PMe_3)Ru\}C_4\{Ru(PMe_3)(PPh_3)Cp\}$ (**40**) (45 mg, 43%) as an air sensitive yellow powder. Found: C 63.43; H 5.38%. $C_{56}H_{58}P_4Ru_2$ requires: C 63.64, H 5.49%. IR (nujol) $\nu(C\equiv C)$ 1974 cm^{-1}; δ_H 7.70 - 7.15 (15H, m, Ph), 4.43 (5H, s, Cp), 1.17 (9H, br, PMe_3); δ_C 134 - 127.32 (m, Ph), 82.71 (s, Cp), 22.50 (br, PMe_3); ES MS (*m/z*) (low cone voltage) 1058 $[M]^+$, 796 $[M - PPh_3]^+$, 505 $[Ru(PMe_3)(PPh_3)Cp]^+$, 429 $[Ru(PPh_3)Cp]^+$.

$W(C\equiv CPh)(CO)_2(PPh_3)Cp$ (41): A solution of $W(C\equiv CPh)(CO)_3Cp$ (100 mg, 0.23 mmol) and PPh_3 (70 mg, 0.27 mmol) in CH_2Cl_2 (20 ml) was purged with nitrogen and treated with freshly sublimed tmno in several portions until the reaction was adjudged complete (IR spectroscopy; the $\nu(CO)$ 2038cm^{-1} band of the starting material was monitored). Preparative TLC (light petroleum / acetone 7 / 3) gave bright yellow needles of $W(C\equiv CPh)(CO)_2(PPh_3)Cp$ (**41**) (67 mg, 44%) from the only major band. Found: C 59.51; H 3.20%. $C_{33}H_{25}O_2PW$ requires: C 59.29; H 3.74%. IR (CH_2Cl_2) $\nu(C\equiv C)$ 2089w, $\nu(CO)$ 1949vs, 1863s cm^{-1}; δ_H 7.53 - 6.53 (20H, m, Ph), 5.46 (5H, s, Cp); δ_C 244.54 (br, WCO), 228.79 (d, J_{CP} = 5 Hz, WCO), 133.82 - 124.75 (m, Ph), 91.22

(s, Cp); ES MS (low cone voltage) (*m/z*) 668 $[M]^+$, (low cone voltage with NaOMe) 691 $[M + Na]^+$, (high cone voltage) 668 - 612 $[M - nCO]^+$ (n = 0 - 2).

*cis-W(C≡CC≡CPh)(CO)$_2$(PPh$_3$)Cp (**42**).* A solution of W(C≡CC≡CPh)(CO)$_3$Cp (240 mg, 0.52 mmol) and PPh$_3$ (145 mg, 0.55 mmol) in CH_2Cl_2 (50 ml) was purged with nitrogen and treated with tmno in portions until the reaction was complete (IR spectroscopy). The solution was filtered through a pad of silica gel, then further purified by preparative TLC to give yellow W(C≡CC≡CPh)(CO)$_2$(PPh$_3$)Cp (**42**) (67 mg, 20%) after crystallisation (CH_2Cl_2 / MeOH slow evaporation). Found: C 61.01; H 3.89%. $C_{35}H_{25}O_2PW$ requires: C 60.71; H 3.61%. IR (CH_2Cl_2) ν(C≡C) 2172m, 2039w, 1953vs, 1875s cm^{-1}. δ_H 7.52 - 7.20 (m, 20H, PPh$_3$ and Ph), 5.44 (s, 5H, Cp); δ_C 243.15 (d, J_{CP} = 22 Hz,WCO), 222.63 (d, J_{CP} = 20 Hz, WCO), 135.05 - 124.00 (m, Ph), 113.27 (d, J_{CW} = 4 Hz, C_α), 100.14 (s, C_β), 91.23 (s, Cp), 72.75, 72.2 (2 x s, C_γ / C_δ); δ_P 21.00 (t, J_{PW} = 121 Hz, PPh$_3$); ES-MS: (*m/z*) (low cone voltage with NaOMe) 715 $[M + Na]^+$.

*trans,trans-{Cp(PMe$_3$)(CO)$_2$W}C≡CC≡C{W(CO)$_2$(PMe$_3$)Cp} (**43**).* To a solution of {Cp(CO)$_3$W}C≡CC≡C{W(CO)$_3$Cp} (150 mg, 0.21 mmol) in degassed toluene (10 ml), PMe$_3$ (0.25 ml, 2.4 mmol) was added, and heated (110 - 120 °C) in vacuo for 10 days in the dark. After this time most of the solid had dissolved to give a yellow-brown solution, which was filtered and purified by preparative TLC (light petroleum / acetone 1:1). The major yellow band yielded orange *trans,trans* -{Cp(PMe$_3$)(CO)$_2$W}C≡CC≡C{W(CO)$_2$(PMe$_3$)Cp} (**43**) (30 mg, 18%) after crystallisation (CH_2Cl_2 / hexane). IR (THF) ν(CO) 1938vs, 1845vs cm^{-1}; δ_H 5.39 (s, 5H, Cp), 1.69 (dd, J_{HP} = 10 Hz, J_{HW} = 2 Hz, 18H, PMe$_3$). δ_C 247.32 (d, J_{CP} = 25 Hz, CO), 113.78 (br, C_α), 110.35 (s, C_β), 90.41 (s, Cp), 19.40 (d, J_{CP} = 37 Hz, PMe$_3$); ES MS (*m/z*) (with NaOEt) 1643 $[2M + Na]^+$, 833 $[M + Na]^+$.

Reactions with $Co_2(CO)_8$.

*$Co_2\{\mu\text{-}HC_2C{\equiv}C[W(CO)_3Cp]\}(CO)_6$ (**44**).* A solution of $W(C{\equiv}CC{\equiv}CH)(CO)_3Cp$ (150 mg, 0.39 mmol) in benzene (15 ml) was treated with $Co_2(CO)_8$ (135 mg, 0.40 mmol) in several portions over 15 min. The solvent was removed from the red-brown solution and the residue purified by preparative TLC (light petroleum / acetone 8 / 2). Crystallisation of the only significant band (CH_2Cl_2) gave deep red $Co_2\{\mu\text{-}HC_2C{\equiv}C[W(CO)_3Cp]\}(CO)_6$ (**44**) (100 mg, 38%). Found: C 32.49; H 1.00%. $C_{18}H_6O_9Co_2W$ requires: C 32.36; H 0.90%. IR(cyclohexane) ν(C≡C) 2091m, ν(CO) 2054vs, 2039s, 2024vs, 1965vs, 1954s cm^{-1}; δ_H 6.04 (1H, s, C_2H), 5.67 (5H, s, Cp). δ_C 227.70 (s, WCO), 210.15 (t, J_{CW} = 64 Hz, WCO), 199.66 (br, CoCO), 123.13 (s, C_α), 94.34 (s, C_β), 91.70 (s, Cp), 73.84 (s, C_γ), 71.56 (s, C_δ); FAB MS (*m/z*) 668 $[M]^+$, 640 - 528 $[M - nCO]^+$ (n = 1 - 5).

$Co_2[\mu\text{-}\{Cp(CO)_2Fe\}C_2C{\equiv}C\{W(CO)_3Cp\}](CO)_6$*(**45**).* A suspension of $\{Cp(CO)_3W\}C{\equiv}CC{\equiv}C\{Fe(CO)_2Cp\}$ (100 mg, 0.18 mmol) in benzene (15 ml) was treated with $Co_2(CO)_8$ (62 mg, 0.18 mmol). Preparative TLC (light petroleum / acetone 7/3) and crystallisation (CH_2Cl_2/*n*-hexane) gave red-brown needles of $Co_2[\mu\text{-}\{Cp(CO)_2Fe\}C_2C{\equiv}C\{W(CO)_3Cp\}](CO)_6$ (**45**) (102 mg, 67%). Found: C 34.45; H 1.29%. $C_{25}H_{10}O_{11}Co_2FeW.0.5\ CH_2Cl_2$ requires: C 34.45; H 1.24%. IR (cyclohexane) ν(CO) 2076s, 2039vs, 2009s, 2004sh, 1986m, 1960s, 1950s cm^{-1}; δ_H 5.67 (5H, s, WCp), 5.32 (s, 1H, CH_2Cl_2), 5.17 (5H, s, FeCp); δ_C 228.97 (s, WCO), 213.41 (s, WCO), 210.41 (s, FeCO); 201.66 (br, CoCO), 125.79 (br, C_α); 106.09 (s, C_β), 97.86 (s, C_γ), 91.85 (s, WCp), 86.68 (s, FeCp), 85.68 (s, C_δ); FAB-MS (*m/z*) 844 $[M]^+$, 816-592 $[M - nCO]^+$ (n = 1 - 9).

*$Co_2\{\mu\text{-}HC_2C{\equiv}C[Mo(CO)_3Cp]\}(CO)_6$(**46**).* A solution of $Mo(C{\equiv}CC{\equiv}CH)(CO)_3Cp$ (150 mg, 0.51 mmol) in benzene (15 ml) was treated with $Co_2(CO)_8$ (175 mg, 0.51 mmol) over 30 min. Preparative TLC (light petroleum / acetone 75 / 25) gave dark red

crystalline (cyclohexane) $Co_2\{\mu\text{-}HC_2C\equiv C[Mo(CO)_3Cp]\}(CO)_6$ (**46**) (113 mg, 40%). Found: C 37.56; H 1.15%. $C_{18}H_6O_9Co_2Mo$ requires: C 37.25; H 1.03%. IR (cyclohexane) ν(C≡C) 2091m, ν(CO) 2054vs, 2044s, 2029vs, 2024vs, 1977vs, 1967s cm^{-1}; δ_H 6.06 (s, 1H, C_2H), 5.57 (s, 5H, Cp); δ_C 237.63 (s, MoCO); 221.22 (s, MoCO), 199.64 (br, CoCO), 123.43 (s, C_α), 109.52 (s, C_β), 93.11 (s, Cp), 74.07 (s, C_γ), 71.35 (s, C_δ); FAB-MS (*m/z*) 526 - 330 $[M - nCO]^+$ (n = 2 - 9).

*$\{Cp(CO)_8Co_2W(\mu_3\text{-}C)\}C\equiv C\{(\mu_3\text{-}C)WCo_2(CO)_8Cp\}$ (**47a**).*

Dicobaltoctacarbonyl (96 mg, 0.28 mmol) was added in portions to a rapidly stirred suspension of $\{Cp(CO)_3W\}C\equiv CC\equiv C\{W(CO)_3Cp\}$ (100 mg, 0.14 mmol) in benzene (15 ml) in one portion. The suspension slowly dissolved over this time to give a deep red-brown solution. The solution was filtered and the filtrate purified by preparative TLC (light petroleum/acetone 8/2). The only significant band (red R_f 0.3) was crytallised (CH_2Cl_2/hexane) to give deep red blocks of $\{Cp(CO)_8Co_2W(\mu_3\text{-}C)\}C\equiv C\{(\mu_3\text{-}C)WCo_2(CO)_8Cp\}$ (**47a**) (66 mg, 38%). Found: C 28.99; H 0.80%. $C_{30}H_{10}O_{16}Co_4W_2$ requires: C 29.29; H 0.81%. IR (cyclohexane) ν(CO) 2077m, 2064m, 2040vs, 2030s, 2014m, 2003m, 1994m, 1944m, 1984sh, 1961s, 1951s, 1891w cm^{-1}. δ_H 5.56 (s, Cp). δ_C 202.96 (br, CO), 126.48 (s, μ_3-C), 91.32 (s, Cp); ES MS (after addition of NaOMe) (*m/z*) 1259 $[M+OMe]^-$.

*$\{Cp(CO)_8Co_2Mo(\mu_3\text{-}C)\}C\equiv C\{(\mu_3\text{-}C)MoCo_2(CO)_8Cp\}$ (**47b**).* The reaction between $Co_2(CO)_8$ (123 mg, 0.36 mmol) and $\{Cp(CO)_3Mo)C\equiv CC\equiv C\{Mo(CO)_3Cp\}$ (100mg, 0.18mmol) was carried in in a manner essentailly identical to that described for **47a** to yield $\{Cp(CO)_8Co_2Mo(\mu_3\text{-}C)\}C\equiv C\{(\mu_3\text{-}C)MoCo_2(CO)_8Cp\}$ (**47b**) (76 mg, 40%) after preparative TLC (light petroleum / acetone 7 / 3, R_f 0.65) and crystallisation (CH_2Cl_2 / hexane). Found: C 33.42; H 0.90%. $C_{30}H_{10}O_{16}Co_4Mo_2$ requires: C 34.15; H 0.95%. IR (cyclohexane) ν(CO) 2085m, 2074m, 2064m, 2044vs, 2038s, 2014m, 2005s, 1993m, 1975s, 1964s, 1954sh, 1897w cm^{-1}; δ_H 5.49 (s, Cp); δ_C 269.85 (s, CO),

207.90 (br, CO), 125.94 (s, μ_3-C), 93.45 (s, Cp); ES MS (*m/z*) (with NaOMe) 1084 $(M+OMe)^-$.

{Cp(CO)$_8$Co$_2$W(μ_3-C)}C≡C{(μ_3-C)MoCo$_2$(CO)$_8$Cp} (47c). The reaction between $Co_2(CO)_8$ (165 mg, 0.48 mmol) and {Cp(CO)$_3$W}C≡CC≡C{Mo(CO)$_3$Cp} (150 mg, 0.24 mmol) in benzene (15 ml) gave deep red {Cp(CO)$_8$Co$_2$W(μ_3-C)}C≡C{(μ_3-C)MoCo$_2$(CO)$_8$Cp} (**47c**) (97 mg, 18%) after preparative TLC (light petroleum / acetone 7 / 3, R_f 0.4) (CH_2Cl_2 / hexane). Found: C 31.40; H 0.89%. $C_{30}H_{10}O_{16}Co_4MoW$ requires: C 31.52; H 0.88%. IR (cyclohexane) ν(CO) 2085m, 2074s, 2066m, 2047vs, 2037m, 2025s, 2004s, 1941br; 1894w,br cm^{-1}. δ_H 5.57 (s, 5H, WCp), 5.49 (s, 5H, MoCp); δ_C 207.92, 202.85 (2 x br, CO), 127.65 (s, Co_2MoC), 124.76 (s, Co_2WC), 93.56 (s, MoCp), 91.21 (s, WCp); ES MS (*m/z*) (with NaOMe) 1173 $[M+OMe]^-$.

{Cp(CO)$_3$W}C≡CC$_2$[Co$_2$(CO)$_4$(μ-dppm)]{W(CO)$_3$Cp} (49). A solution of {Cp(CO)$_3$W}C≡CC≡C{W(CO)$_3$Cp} (100 mg, 0.14 mmol) and Co$_2$(μ-dppm)(CO)$_6$ (190 mg, 0.28 mmol) in benzene (15 ml) was warmed in an 80 °C oil bath for 4h. The solvent was removed and the residue purified by preparative TLC (light petroleum / acetone 7 / 3). The only significant band (purple, R_f 0.45) gave red crystals ($CHCl_3$ / methanol) of {Cp(CO)$_3$W}C≡CC$_2$[Co$_2$(CO)$_4$(μ-dppm)]{W(CO)$_3$Cp} (**49**) (134 mg, 72%). Found C 43.14, H 2.81%. $C_{49}H_{32}O_{10}P_2Co_2W_2.0.5CHCl_3$ requires: C 42.82, H 2.34%. IR (cyclohexane) ν(CO) 2039m, 2027m, 2000m, 1986s, 1956vs, 1939vs, 1923sh cm^{-1}; δ_H 7.51 - 7.08 (m, 20H, Ph), 5.87, 5.52 (2 x s, 2 x 5H, 2 x Cp), 3.86, 3.43 (2 x dt, J_{HH} = 12 Hz, J_{PH} = 11 Hz, CH_2P_2). δ_C 212.58 (t, J_{WC} = 3 Hz, WCO), 210.69 (s, WCO), 204.41 (br, CoCO), 139.29-127.67 (m, Ph), 109.50 (br, C_α), 95.62, 91.81 (2 x s, 2 x Cp), 76.28 (s, C_β), 33.72 (t, J_{CP} = 20 Hz, CH_2P_2).

ES-MS (*m/z*) (with NaOMe) 1351 $[M + Na]^+$, 1328 $[M]^+$, {at higher cone voltage} 1328 - 1132 $[M + H - nCO]^+$ (n = 0 - 7).

$Ru_3(\mu\text{-}H)[\mu_3\text{-}\eta^1,\eta^2\text{-}C_2C{\equiv}C\{W(CO)_3Cp\}](dppm)(CO)_7$ ***(50)***. A solution of $W(C{\equiv}CC{\equiv}CH)(CO)_3Cp$ (60 mg, 0.15 mmol) and $Ru_3(CO)_{10}(dppm)$ (100 mg, 0.10 mmol) in thf (15 ml) was heated at reflux point for 3h in the dark. Preparative TLC (light petroleum / acetone 75 / 40) and crystallisation (CH_2Cl_2/MeOH) of the bright yellow band (R_f 0.6) yielded $Ru_3(\mu\text{-}H)[\mu_3\text{-}\eta^1,\eta^2\text{-}C_2C{\equiv}C\{W(CO)_3Cp\}](dppm)(CO)_7$ (**50**) (120 mg, 92%). Found C 41.62, H 2.26%. $C_{44}H_{28}O_{10}P_2Ru_3W$ requires: C 41.72, H 2.21%. IR (CH_2Cl_2) ν(CO) 2062m, 2054m, 2037s, 2004vs, 1981s, 1948vs cm^{-1}; δ_H 7.63-7.10 (m, 60H, Ph), 5.65 (s, 10H, Cp[1]), 5.50 (s, 5H, Cp[2]), 4.39, 3.53 (2 x dt, J_{HH} = 13 Hz, J_{HP} = 11 Hz, 2 x 2H, CH_2P_2[1]), 4.39, 3.17 (2 x dt, J_{HH} = 12 Hz, J_{HP} = 12 Hz, 2 x 1H, CH_2P_2[2]), -19.21 (m, 2H, μ-H[1]), -19.74 (t, J_{HP} = 15 Hz, 1H, μ-H[2]); δ_C 229.07 (s, CO), 211.06 (s, CO), 152.17 (s, C_δ), 132.54 - 127.88 (m, Ph), 123.88 (s, C_γ), 91.81 (s, Cp), 74.31 (s, C_β), 72.18 (s, C_α), 49.51 (t, J_{CP} = 25 Hz, CH_2P_2); ES MS (*m/z*) (with NaOMe) 1289 [M + Na]$^+$, 1261 [M + Na - CO]$^+$, (-'ve ion with NaOMe) 1297 [M + OMe]$^-$, 1265 [M - H]$^-$.

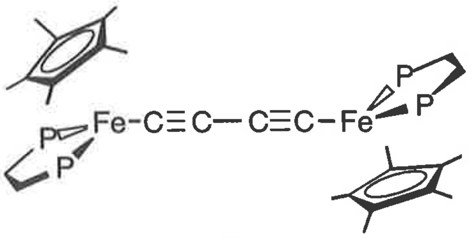
- CHAPTER 4 -

The Redox Chemistry of $\{Cp(PPh_3)_2Ru\}C{\equiv}CC{\equiv}C\{Ru(PPh_3)_2Cp\}$ and $\{Cp(PPh_3)(PMe_3)Ru\}C{\equiv}CC{\equiv}C\{Ru(PMe_3)(PPh_3)Cp\}$

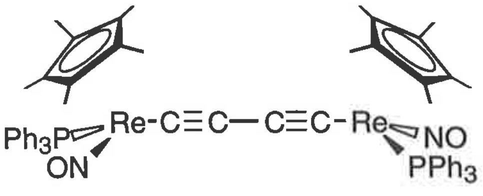
INTRODUCTION.

Diyndiyl complexes, in which a diacetylide ligand bridges two metal fragments, $[L_mM]C{\equiv}CC{\equiv}C[ML_m]$ have attracted the interest of several workers as models for, and precursors to, one-dimensional molecular wires [199]. Upon oxidation, these compounds also offer intriguing possibilities for the observation of unusual allotropes of carbon through the interaction of the metal d-orbitals with π-orbitals of appropriate symmetry from the C_4 chain.

The diyndiyl complexes $\{Cp^*(dppe)Fe\}C{\equiv}CC{\equiv}C\{Fe(dppe)Cp^*\}$ (**51**) and $\{Cp^*(PPh_3)(NO)Re\}C{\equiv}CC{\equiv}C\{Re(NO)(PPh_3)Cp^*\}$ (**52**) and some related oxidised compounds have been prepared recently [36, 43-45]. The chiral metal centres in **52** give rise to two pairs of diastereomers, which were identified by NMR spectroscopy, and separated by fractional crystallisation. The absolute configuration was determined by an X-ray diffraction study [45]. The electrochemical data collected for (*SS,RR*)-**2** and (*SR,RS*)-**2** are identical as the geometrical arrangement of ligands about the metal centre has no effect on the formal electrode potential of the complex.



(**51**)



SS,RR-(**52**)

In the present context, it is appropriate to consider a compound in which two identical redox active centres, each with a one-electron oxidised product, are linked by a bridging ligand L. The redox centres are distinguished by the labels M and M'. Two extreme scenarios are then possible:

(a) The bridging ligand L does not allow any electronic interaction between M and M' (L is an insulator). Using the nomenclature introduced by Robin and Day, the compound may be described as a Class I material [200]. The E^o values for the oxidation of M and M' will be essentially identical, differing only by a small statistical factor [$\Delta E^o = 2(RT/F) \ln 2$] [201]. The voltametric wave will have the shape of a one-electron process, but its magnitude will correspond to that of a two-electron process.

(b) There are very strong interactions between M and M' (L is a conductor). These complexes are described as Class III Robin and Day materials. The two E^o values will be significantly different, and in the CV two well separated waves, each corresponding to a one-electron process, will be observed. In general, the extent of the interaction between the metal centres will be reflected in the magnitude of ΔE^o ($\Delta E^o = |E^o_2 - E^o_1|$) [202]. However, it should be noted that the relationship between ΔE^o and electron delocalisation is not always simple, especially for weakly interacting redox centres, due to the effects of structural reorganisation, solvation and ion-pairing.

The one-electron oxidised products are formally mixed-valence complexes, the stability of which will be indicated by the magnitude of the comproportionation constant, K_c ($\ln K_c = \Delta E(F/RT)$ for one electron oxidation reactions [203]), as these species can only exist if the equilibrium indicated in Equation 20 lies well to the right.

$$[\{M(n)\}(\mu\text{-}L)\{M'(n)\}]^{m+} + [\{M(n+1)\}(\mu\text{-}L)\{M'(n+1)\}]^{(m+2)+} \rightleftharpoons [\{M(n)\}(\mu\text{-}L)\{M'(n+1)\}]^{(m+1)+}$$

n = formal oxidation number

Equation 20

The study of intramolecular electron-transfer reactions and mixed valence materials has been an area of considerable interest for many years. The reader is referred to one of the excellent review articles which deal exclusively with electron-transfer processes and mixed valence complexes for a more detailed theoretical treatment of the area [202, 204].

Both **51** and **52** undergo two reversible one-electron oxidations as evidenced by cyclic voltammetry [43, 44]. The large difference in the oxidation potentials [ΔE_{pa} (V): **51**, +0.72; **52**, +0.53V] indicate that there are strong interactions between the metal centres through the C_4 bridge.

The oxidised species **51.PF$_6$** and **51.[PF$_6$]$_2$** have been obtained through chemical oxidation of **51** with one or two equivalents of [FcH]PF$_6$ [43]. Both diastereomers of **52** have been oxidised with AgPF$_6$ in the appropriate stoichiometry to give **52.PF$_6$** and **52.[PF$_6$]$_2$**. It has been established that the unpaired electron in both of the mono-oxidised complexes **51.PF$_6$** and **52.PF$_6$** is delocalised over both metal centres [43, 44], and these compounds may therefore be described as Class III Robin and Day mixed-valence complexes [200]. Reduction of either diastereomer of **52.[PF$_6$]** with sodium naphthalenide gave **52**. These chemical oxidation and reduction reactions of **52** have been shown to proceed with retention of chirality at the metal centre [44].

The carbon bridges in the oxidised forms of **51** and **52** are significantly different. The spectral data obtained from **51.[PF$_6$]** and **51.[PF$_6$]$_2$** are consistent with the retention of diacetylide nature in the bridge [43]. However, it has been established that there is a significant reduction in the bond order of the carbon bridge from **52**, through **52.PF$_6$**, to **52.[PF$_6$]$_2$**. Crystallographic evidence indicates that the carbon ligand in **52.[PF$_6$]$_2$** is best described with a cumulenic structure (Figure 4, structure **K**) [44].

The ready accessibility of Ru(IV), compared with Fe(IV) in **51** or Re(IV) in **52**, suggested that related ruthenium complexes, such as $\{Cp(PPh_3)_2Ru\}C\equiv CC\equiv C\{Ru(PPh_3)_2Cp\}$ (**16**) and the mixed phosphine complex $\{Cp(PPh_3)(PMe_3)Ru\}C\equiv CC\equiv C\{Ru(PMe_3)(PPh_3)Cp\}$ (**40**) would repay study. The synthesis and characterisation of these complexes is described in Chapter 3.

RESULTS.

*Cyclic Voltammetry and Redox Chemistry of **16** and **40**.*

The initial scans in the cyclic voltammograms (CV) of **16** and **40** from -0.5 to +1.7 V in CH_2Cl_2 each contain four one-electron oxidation waves consistent with the oxidation of neutral diacetylide complexes in four steps, yielding mono-, di-, tri- and tetra-cations (Figure 18).

As would be expected for complex **40** bearing the more electron-donating PMe_3 ligands, the formal oxidation potentials of this complex are less positive than in **16**. All the redox process are well separated, with the differences in the formal potentials, ΔE^o, lying in the range 0.49 to 0.65V. These values reflect the large degree of electronic interaction that occurs between the metal centres through the C_4 bridge.

The waves in the cyclic voltammograms associated with the redox process $\mathbf{X}^{0/1+}$, $\mathbf{X}^{1+/2+}$ and $\mathbf{X}^{2+/3+}$ (**X** = **16**, **40**) are reversible, indicating the kinetic stability of the neutral complexes as well as of the mono-, di- and tri-cations under the conditions of the CV experiments. The tetra-cations $\mathbf{16}^{4+}$ and $\mathbf{40}^{4+}$ are more reactive species,

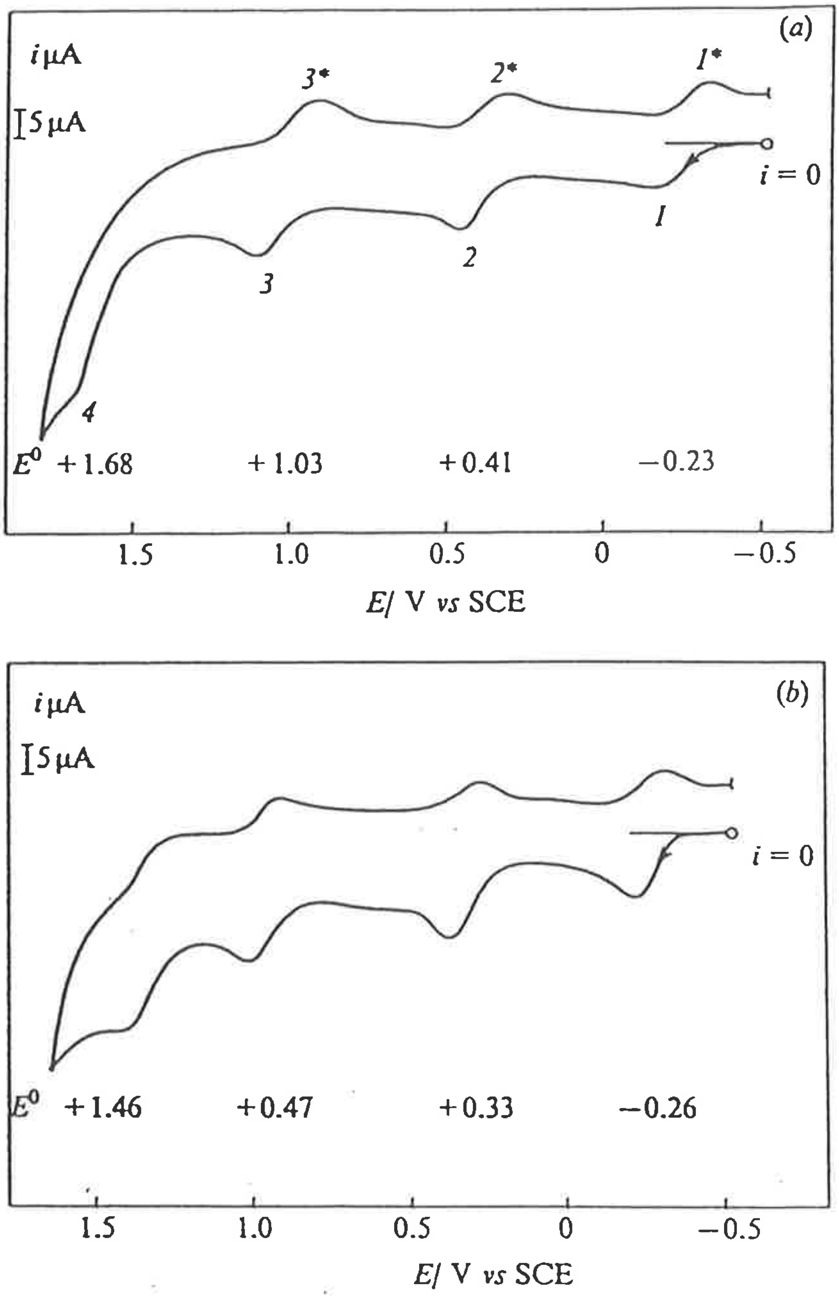


Figure 18 : (a) CV of complex **16**; (b) CV of complex **40**. $E^{o} = (E_{p.a.} + E_{p.c.}) / 2$.

undergoing fast chemical reactions after electrolysis at the electrode surface resulting in irreversible electrochemical behaviour for these oxidations. The large K_c values calculated from this data for **16**$^+$ (1.5 x 10^{11}), **16**$^{3+}$ (1.5 x 10^{11}), **40**$^+$ (2.1 x 10^{10}) and **40**$^{3+}$ (2.7 x 10^8) are comparable with those of the only other mixed valence complexes linked by a C_4 bridge that have been studied, namely **51**$^+$ (1.6 x 10^{12}) and **52**$^+$ (3 x 10^8) [43], and indicate the high thermodynamic stabilities of these unusual cationic species. The value of $E_p^{3/4}$ was used to calculate ΔE^o for the irreversible fourth oxidations. This assumes that any subsequent chemical reactions of the tetra-cations do not have any significant influence on the electrode potentials.

In accord with the electrochemical results, chemical oxidation of **16** with $AgPF_6$ gave deep green $[\{Cp(PPh_3)_2Ru\}C_4\{Ru(PPh_3)_2Cp\}][PF_6]$ (**16.PF$_6$**). Complex **16.PF$_6$** is paramagnetic, and only broad resonances were found in the ^1H NMR spectrum. The CV of **16.PF$_6$** is completely analogous to that of the neutral precursor **16**, and in the ES MS the parent ion at was observed at *m/z* 1430, with an isotope pattern in agreement with the proposed formulation of this complex.

Oxidation of **16.PF$_6$** with a further equivalent of $AgPF_6$, or treatment of **16** with 2.5 equivalents of the same oxidising agent afforded the dark-blue dication $[\{Cp(PPh_3)_2Ru\}C_4\{Ru(PPh_3)_2Cp\}][PF_6]_2$ (**16.[PF$_6$]$_2$**). In contrast to the mono-oxidised complex, **16.[PF$_6$]$_2$** is diamagnetic as a result of spin pairing through the carbon bridge and gave well-resolved NMR spectra . The Cp ligand gave rise to a singlet resonance in the ^1H NMR spectrum at somewhat lower field (δ 5.03) than the corresponding resonance in **16**. The chemical shift of the Cp ligand in other cationic complexes of $Ru(PR_3)_2Cp$ typically falls near δ 5. The ES MS of **16.[PF$_6$]$_2$** at low cone voltages gave an intense ion at *m/z* 715, with isotope peaks separated by 0.5 amu, consistent with a dicationic species.

After consideration of Equation 20 [M = $Ru(PPh_3)_2Cp$, n = 2], and the value of K_c calculated for this reaction from the electrochemical data, it was not surprising that mono-oxidised **16.PF$_6$** was also obtained as the sole product from the combination of **16** and **16.[PF$_6$]$_2$** in CH_2Cl_2. A similar result has been observed by Gladysz and co-workers in the related rhenium system [44].

Unfortunately, despite their thermodynamic and chemical stability, efforts to prepare the tri-cations **16**$^{3+}$ or **40**$^{3+}$ by chemical oxidation of the corresponding dications have so far been unsuccessful, primarily due to a lack of a suitable oxidising agent. Therefore, in order to gain insight into the nature of the carbon bridge in these species a spectroelectrochemical study, in which the species to be studied were generated by electrolysis in a modified spectrometer cell, was undertaken.

Spectroelectrochemical Studies

Infra-Red Reflection Absorption Spectroscopy (IRRAS).

IR spectra were collected in a modified infrared reflection absorption spectroscopic (IRRAS) cell. A highly polished disc of platinum serves as both the working electrode and reflector. The electrode surface is brought close to a CaF_2 window to form a thin film of solution in which the electrolysis takes place. The IR beam is passed through the window, the solution, reflected off the working electrode, and then passes back through the window into the collection optics. A detailed description of the apparatus has been published [205], and the appropriate details are summarised in the Experimental section of this Chapter.

Near-Infrared (NIR) and UV-Vis Spectroscopy:

The samples for NIR and UV-Vis spectroscopy were electrogenerated in an optically transparent thin-layer electrode (OTTLE) cell. The cell is simply a traditional 0.5 mm path length optical cuvette, modified to accommodate the counter and reference electrodes. The working electrode consists of a piece of platinum gauze, placed inside the cuvette. Again, the apparatus has been described in detail [206], and particular details relevant to this study are given in the Experimental section.

The IR spectrum of $\mathbf{16^+}$, electrogenerated from **16**, was characterised by an intense ν(CC) absorption at 1861cm^{-1}, which is at lower energy than the corresponding ν(CC) band observed for **16** [ν(CC) 1970 cm^{-1}]. The NIR region of $\mathbf{16^+}$ contained an intervalence charge transfer (IVCT) band at 11400 cm^{-1} (ε = 4000 M^{-1}.cm^{-1}), characteristic of the mixed-valence nature of this compound [204]. The only other feature observed in the electronic spectrum of $\mathbf{16^+}$ was an intense, broad band near 38000 cm^{-1} (ε = 14100 M^{-1}.cm^{-1}), which may be assigned to π-π^* transitions in the phenyl rings of the PPh_3 ligands. Solutions of $\mathbf{16^+}$ were reduced electrochemically to give **16** in both IRRAS and OTTLE experiments. There was no appreciable loss of material during the reduction, and spectra identical to those of the starting material were collected after completion of the reduction.

Controlled potential electrolysis of a solution of $\mathbf{16^+}$ gave $\mathbf{16^{2+}}$, for which an intense ν(CC) band was observed at 1760 cm^{-1}. There was no significant absorption in the NIR region, but a new feature was observed at 16300 cm^{-1} (ε = 14100 M^{-1}.cm^{-1}). Again, reduction of the electrolytically generated $\mathbf{16^{2+}}$ cation gave $\mathbf{16^+}$, which in turn could be reduced back to **16**. The reversibility of the system was further demonstrated by the observation of an isosbestic point near 14850 cm^{-1} during both the electrochemical oxidation of $\mathbf{16^+}$ to $\mathbf{16^{2+}}$ and the reduction of $\mathbf{16^{2+}}$ to $\mathbf{16^+}$.

A solution containing the trication $\mathbf{16^{3+}}$ was obtained by further electrolytic oxidation of $\mathbf{16^{2+}}$. In the IR region, a band was observed at 1650 cm^{-1}. A weak IVCT band was found at 16300 cm^{-1} (ε = 570 M^{-1}.cm^{-1}) for this mixed-valence compound, while the UV-Vis region was dominated by a strong band near 17300 cm^{-1}. The observation of isosbestic points and the recovery of clean spectra for the species in lower oxidation states after electrochemical reduction confirmed the reversibility of the redox process.

IRRAS experiments with $\mathbf{16^{4+}}$ gave a weak ν(CC) bands at 1937 and 2056 cm^{-1}. However complications introduced by rapid chemical reactions of this species and the long timescale required to perform the OTTLE experiment (8 min. per scan) hindered the recording of the NIR / UV-Vis spectrum of this species. The spectral data collected for **40**, and its related oxidised forms, were similar to those of the related species derived from **16** (Table 3).

DISCUSSION

The decrease of the ν(CC) bond stretching frequency on oxidation of **16** and **40** through the mono-, di- and tri-cations is consistent with a gradual decrease in bond order along the carbon chain. The IR evidence suggests that the carbon chain in $\mathbf{16^{+}}$ [ν(CC) 1861 cm^{-1}] and $\mathbf{40^{+}}$ [ν(CC) 1860 cm^{-1}] closely resembles that in **52.[PF$_6$]** [ν(CC) 1870 cm^{-1}] [44].

The presence of an IVCT band in the NIR region of the spectrum of in the mono-oxidised cations $\mathbf{16^{+}}$ and $\mathbf{40^{+}}$ is indicative of the formal mixed-valence nature of these complexes. The position of this band was found to be virtually independent of the solvent. This observation, when taken in conjunction with the presence of a single ν(CC) band at a position almost the exact average of that observed in neutral and dicationic complexes (see below) is conclusive evidence of the equivalence of the metal centres, and indicates that the lone electron in these species is fully delocalised over the six-atom Ru-C_4-Ru chain on the IR timescale (*ca.* 10^{-12} s). The carbon bridges in these mono-oxidised complexes are therefore similar to those found in the related rhenium and iron complexes $\{Cp^*(PPh_3)(NO)Re\}C_4\{Re(NO)(PPh_3)Cp^*\}$ and $\{Cp^*(dppe)Fe\}C_4\{Fe(dppe)(Cp^*\}$. The bridge may be described in terms of a series of

Table 3 : Significant IR, NIR, UV-Vis absorption bands for complexes **16**$^{n+}$ and **40**$^{n+}$. Oxidised complexes prepared by electroylisis at E V.

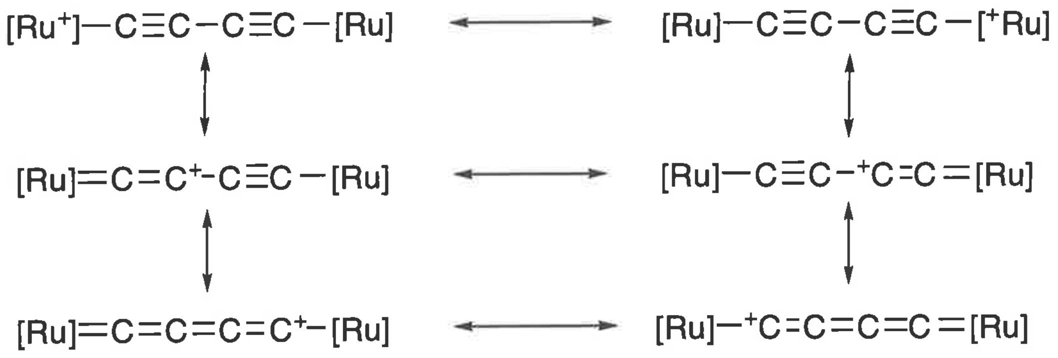
[**16**]$^{n+}$ {UV/Vis : 0.5M TBABF$_4$ (CH$_2$Cl$_2$), T = 223K, [**16**] = 7.0 x 10^{-4} M. IR : ν(CC), 0.1M [NBu$_4$]PF$_6$ (CH$_2$Cl$_2$), T = 298K}

n	UV/Vis cm^{-1} (ε M^{-1}cm^{-1})	E	IR cm^{-1}	E
0	32,200 (3300)	-0.20	1970	-0.22
1	11400 (4000), 37800 (14100)	+0.20	1861	+0.22
2	16300 (14100), 18500sh (3600), 32900 (12400)	+0.66	1760	+0.72
3	12600 (570), 17300 (10860), 27500 (21600)	+1.32	1650	+1.45
4	not observed		1937, 2041	+2.20

[**40**]$^{n+}$ {UV/Vis : 0.5M TBABF$_4$ (CH$_2$Cl$_2$), T = 223K, [**40**] = 8.0 x 10^{-4} M. IR : ν(CC), 0.1M [NBu$_4$]TBAPF$_6$ (CH$_2$Cl$_2$), T = 298K}

n	UV/Vis cm^{-1} (ε M^{-1}cm^{-1})	E	IR cm^{-1}	E
0	28000 (7700)	+0.0	1974	-0.20
1	10950 (11,100), 29200 (41300)	+0.20	1860	+0.20
2	16790 (38500), 36000 (44100)	+0.60	1771	+0.70
3	12000 (1500), 18450 (31200), 29500 (49700)	+1.26	1934	+1.30
4	not observed		1934, 2056	+1.70

resonances forms, which are illustrated in Figure 19. An alternate MO discription is discussed below.



16^+ $[Ru] = Ru(PPh_3)_2Cp$
40^+ $[Ru] = Ru(PMe_3)(PPh_3)Cp$

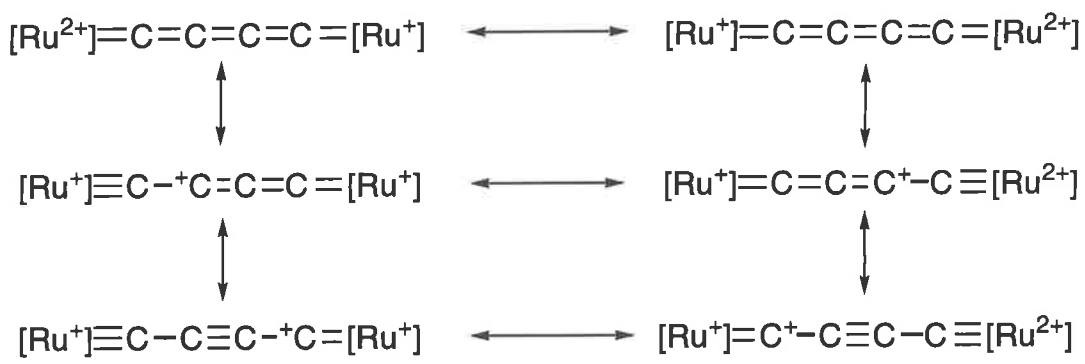
Figure 19.

In **16^{2+}** and **40^{2+}**, the C_4 chain has considerable cumulenic character (Figure 4, structure **K**), which is indicated by the low frequency of the ν(CC) band. Curiously, this is more in keeping with the situation found in the rhenium complex **52.[PF$_6$]$_2$** than in the iron complex **51.[PF$_6$]$_2$**.

$$\left[[Ru]{=}C{=}C{=}C{=}C{=}[Ru]\right]^{2+}$$

16^{2+} $[Ru] = Ru(PPh_3)_2Cp$
40^{2+} $[Ru] = Ru(PMe_3)(PPh_3)Cp$

The trications give rise to characteristic, if rather weak, IVCT bands associated with the mixed-valence nature of these species. The ν(CC) bands at 1650 cm^{-1} (**16^{3+}**) and 1660 cm^{-1} (**40^{3+}**) are consistent with a decrease in the CC bond order in the C_4 bridge compared with the cumulated chains in the di-cationic species. The tri-cations may then be represented by the resonance structures shown in Figure 20.



$\mathbf{16}^{3+}$ [Ru] = $Ru(PPh_3)_2Cp$
$\mathbf{40}^{3+}$ [Ru] = $Ru(PMe_3)(PPh_3)Cp$

Figure 20.

The ν(CC) absorptions of the highly reactive tetracations $\mathbf{16}^{4+}$ and $\mathbf{40}^{4+}$ at 2041 and 2056 cm^{-1} respectively are in a position that might be expected for a conjugated alkyne suggest that these species may be described by a structure similar to **L** (Figure 4). The short lifetime of the tetra-cations and the long timescale of the OTTLE experiments precluded measurement of the NIR / UV-Vis spectra of these species (ca. 8 min per scan).

$$\left[[Ru]{\equiv}C{-}C{\equiv}C{-}C{\equiv}[Ru] \right]^{4+}$$

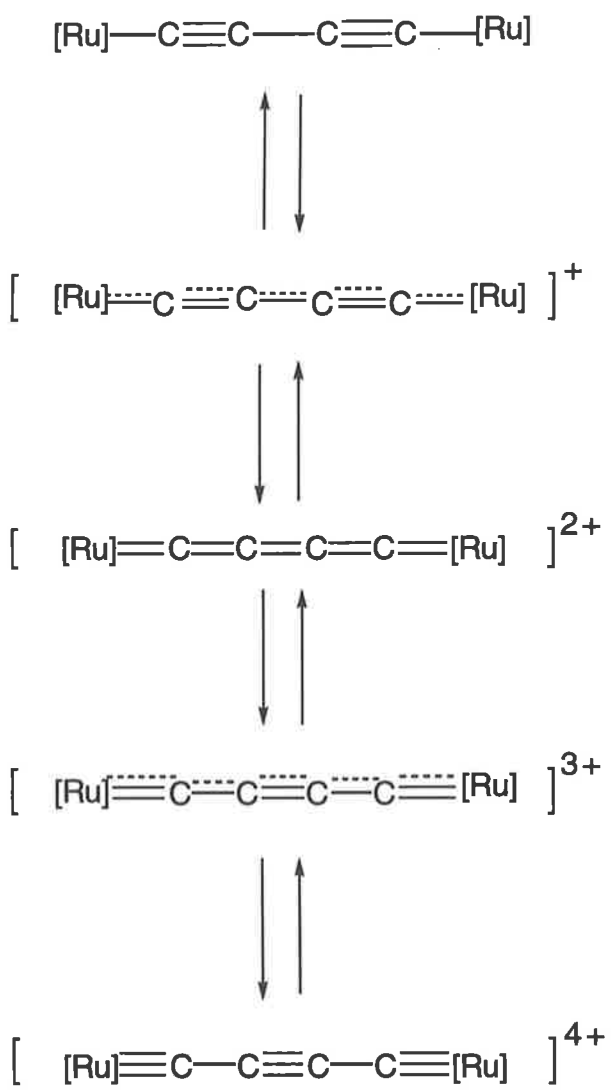
$\mathbf{16}^{4+}$ [Ru] = $Ru(PPh_3)_2Cp$
$\mathbf{40}^{4+}$ [Ru] = $Ru(PMe_3)(PPh_3)Cp$

It is not possible to be confident in the assignment of the bands in the electronic spectra of $\mathbf{16}^{n+}$ and $\mathbf{40}^{n+}$ (n = 0 - 3). It seems likely that these absorptions arise from metal-C_4 ligand charge transfer (MLCT) transitions, but a more definitive assignment awaits a detailed theoretical study [207], and the results of further experiments with several model compounds [208].

Lichtenberger *et al* . have examined the bonding interactions between the metal and diynyl ligand in the iron complex $Fe(C{\equiv}CC{\equiv}CH)(CO)_2Cp$ [209]. A strong σ-bond is formed by the overlap of the empty metal $d_{z}2$ and a filled diynyl ligand σ_{sp} orbital with appropriate symmetry, while the filled metal d_{xz} and d_{yz} orbitals combine with occupied butadiynyl π orbitals. The HOMOs are therefore Fe-C_4 π-anti-bonding in nature.

Preliminary calculations show that the two HOMOs in **16** are nearly degenerate and have similar M-C_4 π-anti-bonding (π*) character and are somewhat separated from the other occupied orbitals [210]. These initial theoretical studies suggest that the variation in the nature of the Ru-C bond as **16** (or **40**) is oxidised may be compared with ethane, ethene and acetylene. The neutral complex is comparable with ethane, and both HOMOs are filled. The dication is comparable with ethene, with one of the π* orbitals filled and the other vacant. Finally, the tetra-cation may be compared with the bonding situation in acetylene with both the Ru-C π* MOs unoccupied. An increase in Ru-C_α bond-order upon oxidation is therefore expected as electrons are removed from HOMOs which are anti-bonding with respect to the M-C_4 chain.

The stepwise variations in bond order along the Ru-C_4-Ru chain which occurs as **16** and **40** are oxidised are represented by the structures in Figure 21. These show conversion of the neutral diyndiyl complexes **16** and **40** through the dicarbenic complexes **16**$^{2+}$ and **40**$^{2+}$ to the dicarbynic complexes **16**$^{4+}$ and **40**$^{4+}$.



[Ru] = Ru(PPh_3)$_2$Cp (**16**) or Ru(PMe_3)(PPh_3)Cp (**40**).

Figure 21.

CONCLUSION.

The binuclear ruthenium diyndiyk complexes **16** and **40** behave as electron rich systems capable of losing up to four electrons from the Ru-C_4-Ru system, giving rise to a novel series of five oxidation states. These include (a) the formal mixed-valence Ru(II) / Ru(III) and Ru(III) / Ru(IV) cations, which on the basis of electrochemical and spectroscopic evidence are not only thermodynamically stable species but also contain a highly delocalised unpaired electron, and (b) the highly electron-deficient [Ru(IV)-C_4-Ru(IV)]$^{4+}$ cations. Two of the Ru(PPh_3)$_2$Cp series have been prepared by chemical means and isolated. Spectroelectrochemical techniques have allowed the nature of the C_4 bridge in the oxidised complexes to be probed.

- Experimental -

Cyclic Voltammetry.

The voltammograms were collected at room temperature from solutions of **16** and **40** in CH_2Cl_2 containing 0.1M $[NBu_4]BF_4$ as the supporting electrolyte, at 200 mV s^{-1}, using a glassy carbon working electrode, calomel reference electrode and platinum wire counter electrode.

Infra-Red Reflection Absorption Spectroscopy (IRRAS).

IR spectra were collected in a two-compartment, three-electrode electrochemical cell, modified to permit spectral monitoring. A platinum wire reference electrode is separated from the main body of the cell by a narrow capillary and glass frit, while the platinum disc working and platinum gauze counter electrodes are fitted into the body of the cell. The working electrode assembly is connected to a micrometer which allows the electrode surface to be brought close to a CaF_2 window to form a thin film of solution. The species to be studied is electrogenerated in this small volume of solution. The working and counter electrodes are effectively separated by the relatively slow diffusion of the solute in and out of this thin film. The working electrode is hard soldered to a brass rod, in which channels have been cut to allow passage of cold nitrogen; this provides a means of cooling the thin film. The IR beam is passed through the window, reflected off the highly polished working electrode, and passes back through the window into the collection optics.

Spectra were collected from samples cooled to ca. -50 °C.

Near-Infrared (NIR) and UV-Vis Spectroscopy:

The samples for NIR and UV-Vis spectroscopy were electrogenerated in an optically transparent thin-layer electrode (OTTLE) cell, mounted in a cryostatic cell block and cooled by a stream of cold, dry nitrogen. The cell consists of a traditional 0.5 mm path length optical cuvette, fashioned from one piece of fused silica, which expands to a cylindrical section to accommodate the reference (Ag/AgCl) and counter (Pt wire) electrodes, both of which were isolated from the bulk solution by glass frits. The working electrode consists of a piece of platinum gauze, placed inside the cuvette.

The spectra were collected from samples at -30 °C.

[{Cp(PPh$_3$)$_2$Ru}C≡CC≡C{Ru(PPh$_3$)$_2$Cp}][PF$_6$] ***(16.PF$_6$)***. A rapidly stirred solution of **16** (500 mg, 0.35 mmol) in CH_2Cl_2 (50 ml) was treated dropwise with a solution of $AgPF_6$ (89 mg, 0.35 mmol) in 1,2-dimethoxyethane (10 ml). The deep green solution was filtered through a pad of Celite to remove the precipitated Ag metal and the solvent removed. The residue was taken up in a small volume of CH_2Cl_2, and filtered into rapidly stirred Et_2O. The precipitate was collected, washed with Et_2O (3 x 10 ml), and dried to give [{Cp(PPh$_3$)$_2$Ru}C$_4${Ru(PPh$_3$)$_2$Cp}][PF$_6$] (**16.PF$_6$**) (400 mg, 73%) as a forest green powder. Found: C, 65.45; H, 4.36%. $C_{86}H_{70}P_5F_6Ru_2$ requires: C, 65.52; H 4.44%. IR (Nujol) ν(CC) 1861s cm^{-1}; δ_H 7.31, 7.11 (br, PPh$_3$), 5.0 (br, Cp); ES MS (*m/z*) (low cone voltage) 1430 [M]$^+$, 715 [M]$^{2+}$, 692 [Ru(PPh$_3$)$_2$(C$_5$H$_5$)]$^+$.

[{Cp(PPh$_3$)$_2$Ru}C≡CC≡C{Ru(PPh$_3$)$_2$Cp}][PF$_6$]$_2$ **(16[PF$_6$]$_2$)**. Complex **16** (500 mg, 0.35 mmol) in CH_2Cl_2 (50 ml) was treated dropwise with $AgPF_6$ (221 mg, 0.88 mmol) in 1,2-dimethoxyethane. During the addition the solution changed colour from orange through deep green to dark blue. The solvent was removed, and the residue extracted with CH_2Cl_2. The extracts were filtered into stirred hexane and the resulting dark blue precipitate crystallised (CH_2Cl_2/pentane) to give [{Cp(PPh$_3$)$_2$Ru}=C=C=C=C= {Ru(PPh$_3$)$_2$Cp}][PF$_6$]$_2$ (**16[PF$_6$]$_2$**) as a dark blue microcrystalline solid. Found: C, 60.57; H, 4.37%. $C_{88}H_{70}P_6F_{12}Ru_2$ requires: C 60.07, H 4.07%. IR (Nujol) ν(CC) 1766s cm^{-1}; δ_H 7.70 - 7.07 (m, 30H, PPh$_3$), 5.03 (s, 5H, Cp); δ_C 133.94 - 128.80 (m, Ph), 90.82 (s, Cp); ES MS (*m/z*) (low cone voltage) 715 [M]$^{2+}$.

- CHAPTER 5 -

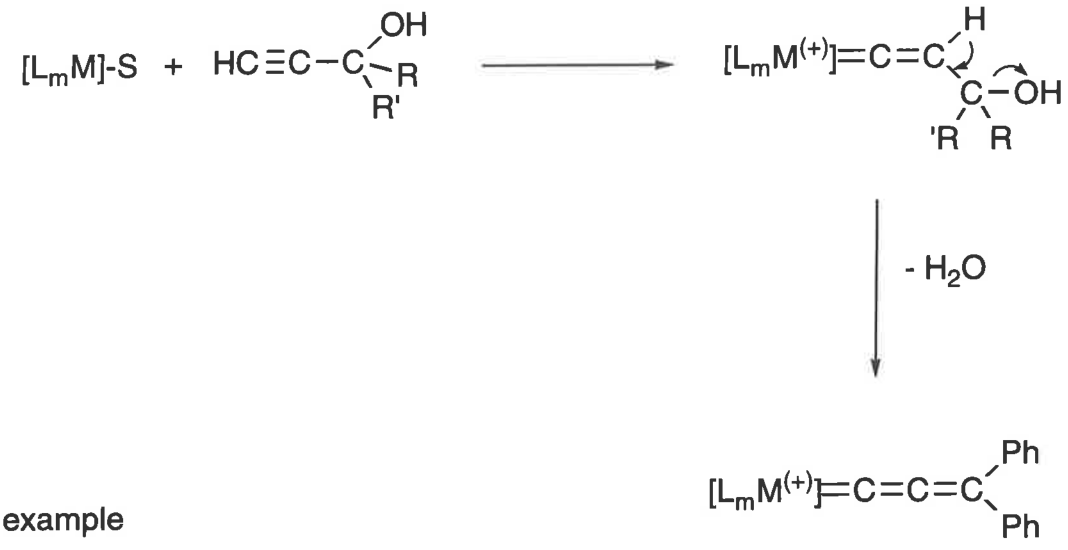
Some Chemistry of the Allenylidene and Butatrienylidene Ligands.

INTRODUCTION

Metal-vinylidene and allenylidene complexes constitute the first members of a family of unsaturated carbene complexes containing cumulated M=C and C=C double bonds. Whilst the chemistry of vinylidene complexes has been extensively investigated [96, 135], it is only recently that the higher analogues have received similar attention as a result of the potential material and synthetic applications of long unsaturated carbon chains mentioned previously. Several compounds with cumulated carbon chains linking two metal centres have also been synthesised in recent years [25].

Several methods have been used to prepare metal complexes with allenylidene ($C=C=CR_2$) ligands, the most useful of these being the 1,3-dehydration of substituted propargyl alcohols (Figure 22) [211]. A modification of this method has allowed the preparation of the metal-pentatetraenylidene complex, $[Ru=C=C=C=C=CR_2(Cl)(dppe)_2][PF_6]$ [212]. However, this method is obviously not appropriate for the preparation of metallacumulenes with an even number of carbon atoms in the unsaturated chain, of which few examples are known (see below).

At the commencement of the studies that form the subject of this thesis, the reactivity of complexes containing the longer unsaturated carbene ligands remained largely unexplored, although theoretical calculations suggested that the carbon centres would alternate in electrophilic (C_α, C_γ, etc) and nucleophilic (C_β, C_δ, etc) character [213]. The electron-deficient nature of the C_α and C_γ carbon centres in the unsaturated carbene ligand may also be derived from consideration of the simple resonance structures shown in Figure 23.



for example

$[L_mM]\text{-}S = \mathrm{RuCl(PMe_3)_2Cp,\ RuCl(PPh_3)_2(\eta\text{-}C_9H_7),}$
$\mathrm{RuCl_2(P^iPrCH_2CH_2OMe)_2,}$
$\mathrm{RuCl_2(PMe_3)(\eta\text{-}C_6Me_6)}$

R, R' = H, Ph, Me, $(C_5H_4)FeCp$

Figure 22.

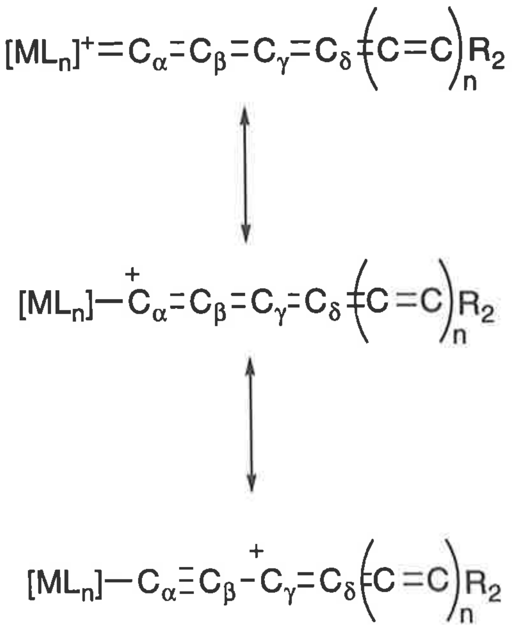


Figure 23.

These properties have been amply demonstrated for the vinylidene ligand. For example, the C_α atoms of various vinylidene cations are sufficiently electrophilic to be attacked by reagents such as methanol, to give methoxycarbenes [214], and cyanide, which yields η^1-cyanovinyl complexes [215]. Several vinylidene complexes are protonated at C_β to give carbyne compounds, illustrating the nucleophilic character of C_β in these compounds [96].

To test these predictions for the allenylidene ligand, some reactions of the complex $[Ru(C{=}C{=}CPh_2)(PPh_3)_2Cp][PF_6]$ (**53**) were studied. Given the steric protection of C_α afforded by the Cp and PPh_3 ligands, it was expected that nucleophilic attack would be directed toward C_γ. This was borne out by experiment, and reactions between **53** and a variety of C, O, and N based nucleophiles have resulted in exclusive attack at C_γ, yielding a number of new ruthenium complexes bearing unusual, functionalised acetylide ligands.

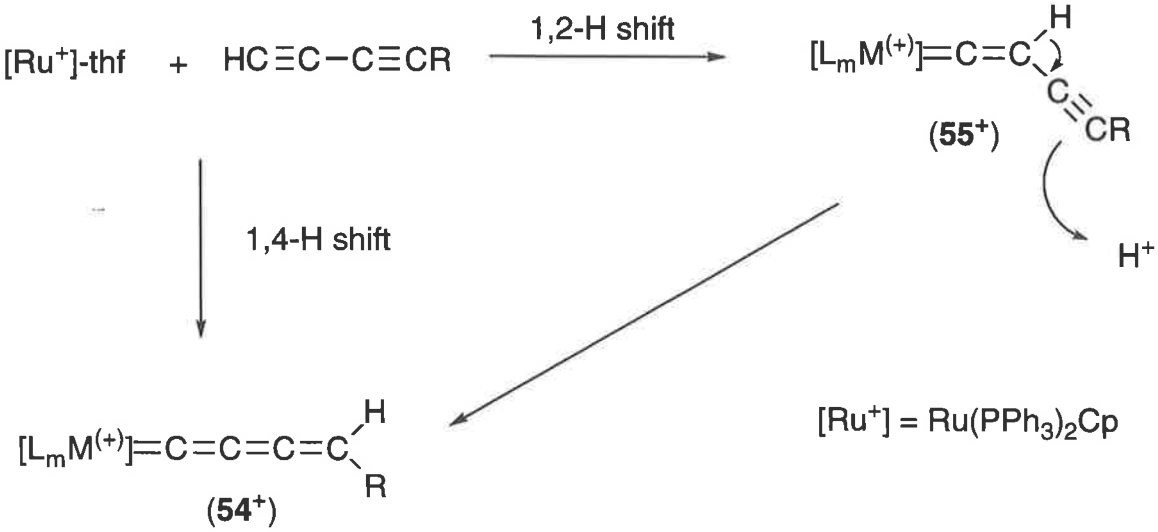
There are very few examples of complexes with butatrienylidene ($C{=}C{=}C{=}CR_2$) ligands. A structural study of the complex $Ru\{C{\equiv}CC(OCOCF_3)CMe_2\}(PPh_3)_2Cp$ suggested that this complex may be regarded as a tight ion pair between the butatrienylidene cation $[Ru(C{=}C{=}C{=}CMe_2)(PPh_3)_2Cp]^+$ and the triflate anion [216]. Protonation of $Ru(C{\equiv}CC{\equiv}CH)(PPh_3)_2Cp$ in moist thf gave $Ru\{C{\equiv}CC(O)Me\}(PPh_3)_2Cp$, probably by addition of water to the intermediate trienylidene cation $[Ru(C{=}C{=}C{=}CH_2)(PPh_3)_2Cp]^+$ (**54**$^+$) [41]. The trienylidene ligand has also been stabilised by coordination to an Ru_5 cluster [217].

Following the well-established precedent of isomerisation of terminal alkynes (including ethyne) to vinylidenes on transition metal centres via a 1,2-H shift [96, 135], we have studied the related reaction with buta-1,3-diyne. In this case, a 1,2-shift would afford the ethynylvinylidene cation $[Ru(C{=}CHC{\equiv}CH)(PPh_3)_2Cp]^+$ (**55**$^+$), whereas a 1,4-H shift would result in the formation of the butatrienylidene complex

$[Ru(C=C=C=CH_2)(PPh_3)_2Cp]^+$ (**54^+**) (Scheme 11). Interestingly *ab initio* calculations have suggested that free $:C=C=C=CH_2$ has almost the same stability as $:C=CH(C\equiv CH)$ [218].

The carbon atoms in the trienylidene ligand, $C=C=C=CR_2$, are expected to display similar alternating nucleophilic and electrophilic character to that found for vinylidene and allenylidene ligands. The isomeric cations **54^+** and **55^+** may therefore be distinguished by the products formed from their reactions with nucleophiles. The butatrienylidene complex **54^+** may be expected to give alkenyl-acetylides as a result of nucleophilic attack at the exposed C_γ [216], while similar reactions with the ethynyl vinylidene compound **55^+** would yield vinyl complexes upon reaction with nucleophilic reagents at C_α.

The cationic complex **$54.PF_6$** has now been shown to be conveniently prepared directly from the reaction of buta-1,3-diyne with $[Ru(thf)(PPh_3)_2Cp][PF_6]$ [219]. It has not yet been established if the trienylidene ligand is formed via an initial 1,2-H shift to give an intermediate ethynylvinylidene complex **55^+**, which then further rearranges to **54^+**, or if a direct 1,4-H shift is involved (Scheme 11).



Scheme 11.

RESULTS AND DISCUSSION.

Synthesis and reactions of [Ru(C=C=CPh$_2$)(PPh$_3$)$_2$Cp][PF$_6$] (53).

The reaction of RuCl(PPh$_3$)$_2$Cp with the alkynyl alcohol HC≡CCPh$_2$OH and NH$_4$PF$_6$ in methanol gave a deep maroon coloured solution, from which [Ru(C=C=CPh$_2$)(PPh$_3$)$_2$Cp][PF$_6$] (**53**) was isolated as a claret coloured powder in good yield (80%). The spectral data of **53** were in good agreement with that of other related allenylidene complexes, such as [Ru(C=C=CPh$_2$)(PMe$_3$)$_2$Cp]PF$_6$ [211], and included a strong band due to the asymmetric ν(C=C=C) stretch in the IR spectrum at 1934 cm^{-1}. The usual ν(PF) band was observed at 840 cm^{-1}. All three carbon centres of the allenylidene ligand were observed in the ^{13}C NMR spectrum, with a characteristically low field resonance, which showed coupling to two equivalent ^{31}P nuclei, assigned to C$_\alpha$ (δ 293.79).

Treatment of **53** with the anionic nucleophiles Me$^-$, MeO$^-$ or NC$^-$, as their respective Li, Na or K salts, gave the neutral acetylide complexes Ru(C≡CCPh$_2$R)(PPh$_3$)$_2$Cp [R = Me (**56**), OMe (**57**), CN (**58**)]. Similarly, treatment of **1** with cyclopentadiene in the presence of KO^{t}Bu gave Ru[C≡CCPh$_2$(C$_5$H$_5$)](PPh$_3$)$_2$Cp (**59**) (Equation 21).

$$[\mathrm{Ru}^+]{=}\mathrm{C}{=}\mathrm{C}{=}\mathrm{CPh_2} \quad + \quad \mathrm{Nu}^- \longrightarrow [\mathrm{Ru}]{-}\mathrm{C}{\equiv}\mathrm{C}{-}\mathrm{C(Nu)Ph_2}$$

[Ru] = Ru(PPh$_3$)$_2$Cp

Nu$^-$ = Me$^-$ (**56**), MeO$^-$ (**57**),
NC$^-$ (**58**), C$_5$H$_5^-$ (**59**).

Equation 21.

Complexes **56** - **59** were characterised by ν(C≡C) bands in the range 2065 - 2095 cm^{-1}. Coupling to ^{31}P (J_{CP} ca. 20 Hz) allowed C_α to be distinguished from C_β in the ^{13}C NMR spectra. The mass spectra of these complexes, obtained using either FAB or ES techniques, were consistent with the proposed structures. The spectra contained molecular ions and a fragment ion derived from loss of the acetylide ligand as well as fragment ions typically associated with the $Ru(PPh_3)_2Cp$ group.

A single crystal X-ray structure study was undertaken for each of the complexes **57** (Figure 24), **58** (Figure 25) and **59** (Figure 26). The structural features of the $Ru(PPh_3)_2Cp$ fragment are unremarkable. The phenyl rings of the $C{\equiv}CCPh_2R$ and PPh_3 ligands are disposed in such a way as to minimise any steric interactions. In general the bond lengths and angles of the acetylide ligands, which are listed in Table 4, fall within the range associated with other examples of these complexes. The most significant feature of these structures is the deviation from linearity of the Ru-C(1)-C(2) angle in **59** [171.1(7)°]. This is most likely a result of the increased steric interaction between the Ph and Cp substituents on C_γ and the bulky PPh_3 ligands.

A labile cationic complex (**60**) was obtained as a lemon yellow solid when **53** was dissolved in neat $NHMe_2$. Subjecting this solid to dynamic vacuum resulted in a slow change in colour to deep red, and **53** was recovered quantitatively. Similarly, solutions of **60** were deep red, and only **53** could be detected spectroscopically. On the basis of the IR spectrum [ν(C≡C) 2065 cm^{-1}; ν(PF) 843 cm^{-1}], and by comparison with the formation of **56** - **59**, complex **60** is formulated as $[Ru\{C{\equiv}CCPh_2(NHMe_2)\}(PPh_3)_2Cp][PF_6]$ (Equation 22).

Complex **57** reacted rapidly with traces of acid to give **53**. It is highly likely that addition of H^+ occurs at C_β of **57** and the resulting methoxyvinylidene complex then rapidly eliminates methanol to give **53** (Equation 23). The similarity to the reaction between $RuCl(PPh_3)_2Cp$ and $HC{\equiv}CCPh_2OH$ is obvious.

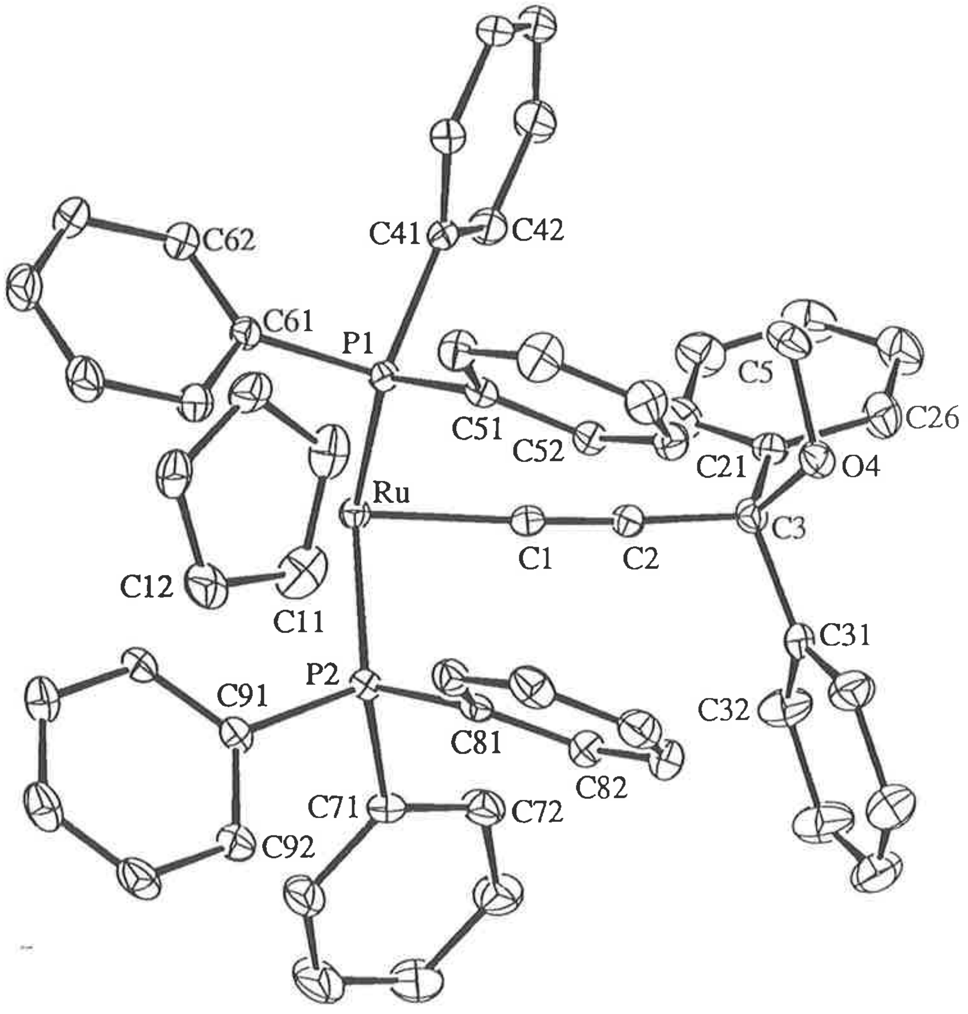


Figure 24 : A plot of a molecule of **57** showing the atom numbering scheme (by E.R.T. Tiekink).

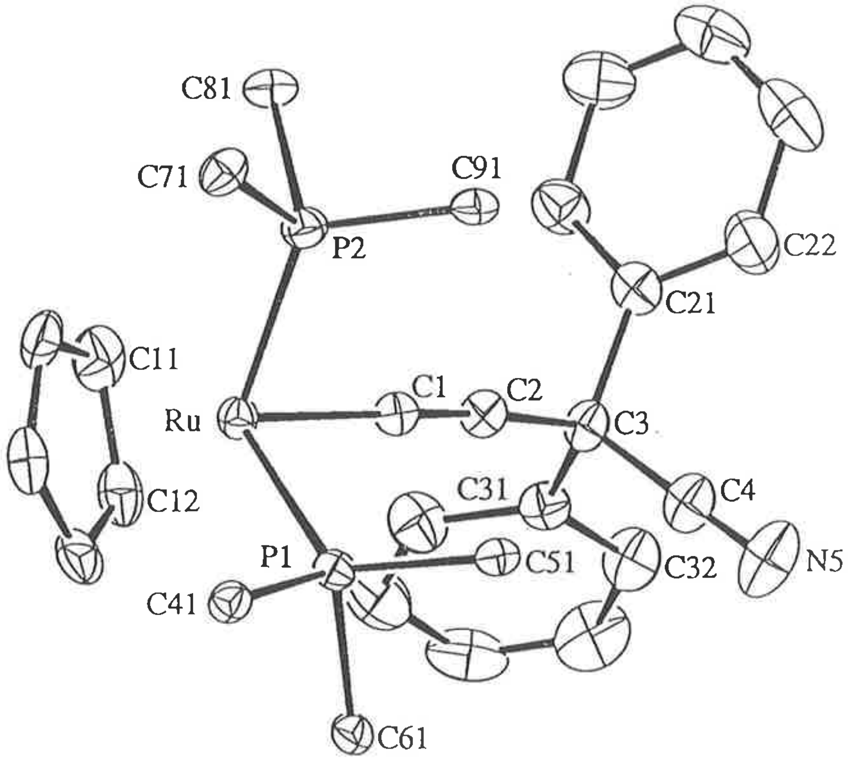


Figure 25 : A plot of a molecule of **58** showing the atom numbering scheme (by E.R.T. Tiekink).

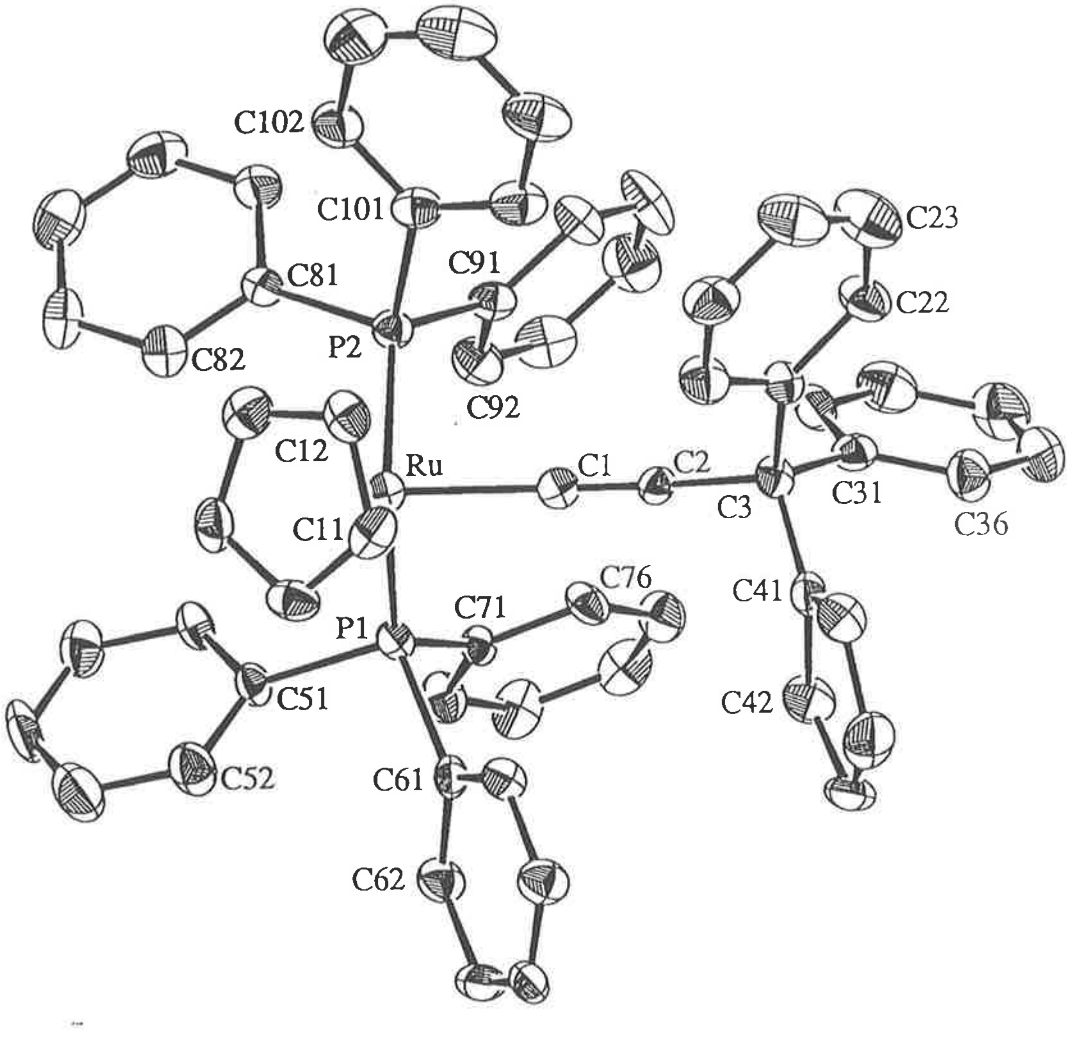
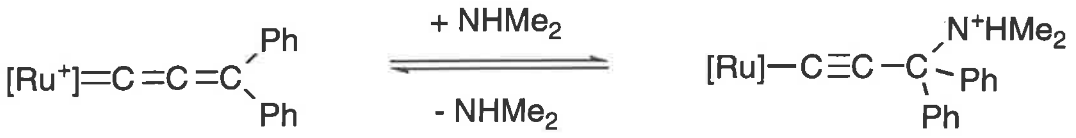


Figure 26 : A plot of a molecule of **59** showing the atom numbering scheme (by E.R.T. Tiekink).

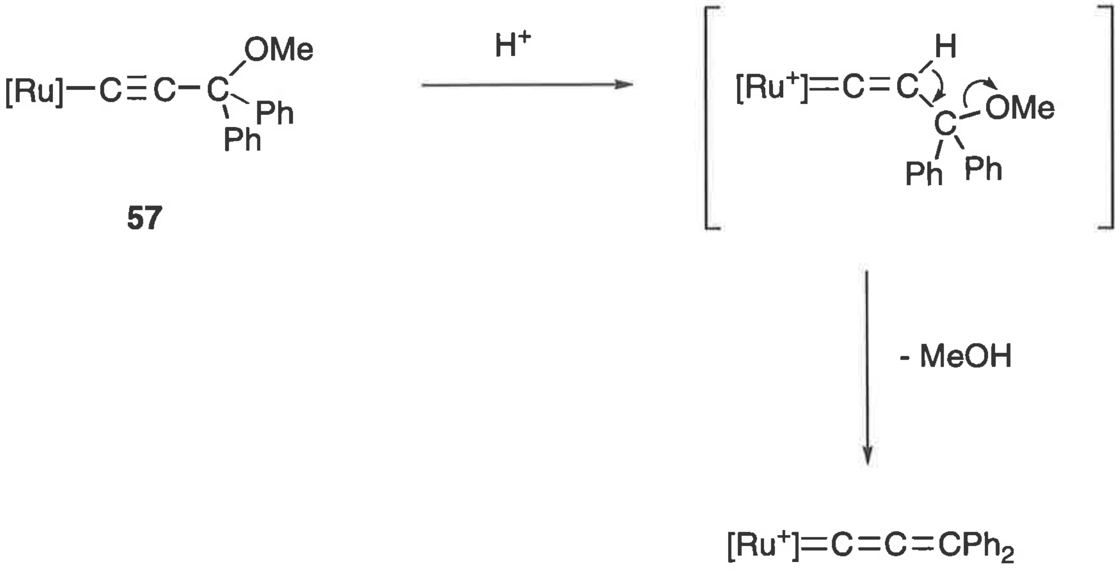
Table 4 : Important bond lengths (°) and angles (Å) for complexes **57**, **58** and **59**.

	57	**58**	**59**
Ru-P(1)	2.294(1)	2.308(1)	2.289(2)
Ru-P(2)	2.276(1)	2.277(1)	2.298(2)
Ru-C(1)	2.013(3)	2.002(4)	2.034(8)
C(1)-C(2)	1.204(4)	1.201(5)	1.202(9)
C(2)-C(3)	1.479(4)	1.482(5)	1.483(9)
C(3)-C(21)	1.542(4)	1.546(5)	1.544(9)
C(3)-C(31)	1.535(5)	1.556(5)	1.55(1)
C(3)-O(4)	1.448(4)		
O(4)-C(5)	1.416(4)		
C(3)-C(4)		1.491(6)	
C(4)-N(5)		1.134(5)	
C(3)-C(41)			1.54(1)
C(41)-C(42)			1.48(1)
C(42)-C(43)			1.50(1)
C(44)-C(45)			1.46(1)
C(45)-C(41)			1.332(9)
P(1)-Ru-P(2)	101.96(5)	100.61(5)	104.09(7)
P(1)-Ru-C(1)	89.09(9)	90.5(1)	90.2(2)
P(2)-Ru-C(1)	88.7(1)	88.8(1)	89.2(2)
Ru-C(1)-C(2)	174.8(3)	173.7(3)	171.1(7)
C(1)-C(2)-C(3)	177.3(3)	175.0(4)	174.0(8)
C(2)-C(3)-C(21)	111.1(3)	109.8(3)	108.7(6)
C(2)-C(3)-C(31)	109.1(3)	111.4(3)	111.5(6)
C(2)-C(3)-O(4)	111.3(3)		
C(2)-C(3)-C(4)		106.8(3)	
C(2)-C(3)-C(41)			108.3(6)



53 **60**

Equation 22.



57 **53**

Equation 23.

At about this time, a series of closely related and complimentary results were reported for the indenyl complex $[Ru(C=C=CPh_2)(PPh_3)_2(\eta^5\text{-}C_9H_7)]^+$ by Gimeno and co-workers [220, 221]. In light of these developments, and the rather unremarkable properties displayed by the allenylidene complex **53**, a decision was made leave these studies.

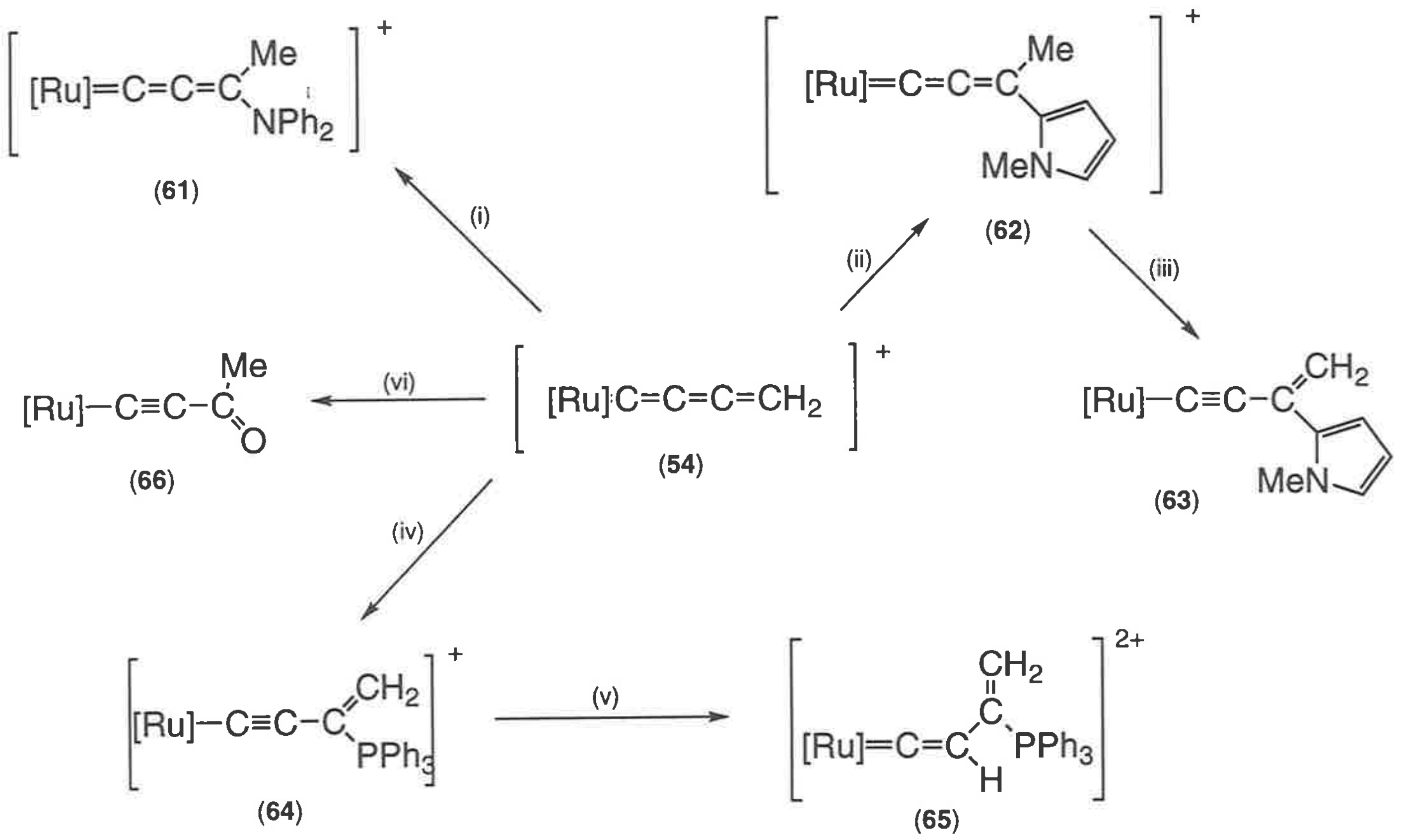
Reactions of an Intermediate Butatrienylidene Complex.

The reaction of [Ru(thf)(PPh_3)$_2$Cp][PF_6], prepared from RuCl(PPh_3)$_2$Cp and $AgPF_6$, with buta-1,3-diyne in the presence of diphenylamine gave the heteroallenylidene [Ru{C=C=CMe(NPh_2)}(PPh_3)$_2$Cp][PF_6] (**61**) (Scheme 12) [222].

Confirmation of the identity of **61** was achieved by a single crystal X-ray study, the details of which have been published [223]. Whilst several allenylidene compounds have been structurally characterised, few of these contain a cumulenic ligand terminated by elements other than carbon [224]. These previous studies suggested that there is a significant contribution to the electron distribution in the allenylidene ligand from two mesomeric forms [211]:

$$[M{=}C{=}C{=}CR_2]^+ \quad \text{<--->} \quad [M{-}C{\equiv}C{-}CR_2]^+$$

In the [Ru{C=C=CMe(NPh_2)}(PPh_3)$_2$Cp]$^+$ cations the Ru-C(1) [1.94 Å] and C(2)-C(3) [1.36 Å] distances appear to be longer, and C(2)-C(3) [1.22 Å] shorter, than those observed for [Ru(C=C=CPh_2)(PMe_3)$_2$Cp]$^+$ [Ru-C(1) 1.884(5), C(1)-C(2) 1.255(8), C(2)-C(3) 1.329(9) Å] [211]. Whilst some of this effect may be due to the difference in electron donor ability of PMe_3 versus PPh_3, it is also highly likely that the lone pair on the N atom further stabilises the [Ru(C≡C-CMe=NPh_2)]$^+$ form, resulting in an even greater contribution of this tautomer to the observed structure. The short C-N bond [1.33, 1.34(2) Å] is also consistent with this interpretation of the electronic distribution along the unsaturated metallacumulene chain [cf. C-N bonds of 1.47 Å in NH_2Me, 1.29 Å in CMe_2=N(OH)]. As predicted by Hoffmann and co-workers [225], and confirmed in other examples of these complexes [226, 227], the allenylidene ligand is positioned in such a way that the N-C(3)-C(4) plane coincides with the plane of symmetry in the molecule.



Scheme 12 : [Ru] = $Ru(PPh_3)_2Cp$. *Reagents*: (i) $NHPh_2$; (ii) *N*-methylpyrrole; (iii) BuLi; (iv) PPh_3; (v) H^+; (vi) H_2O.

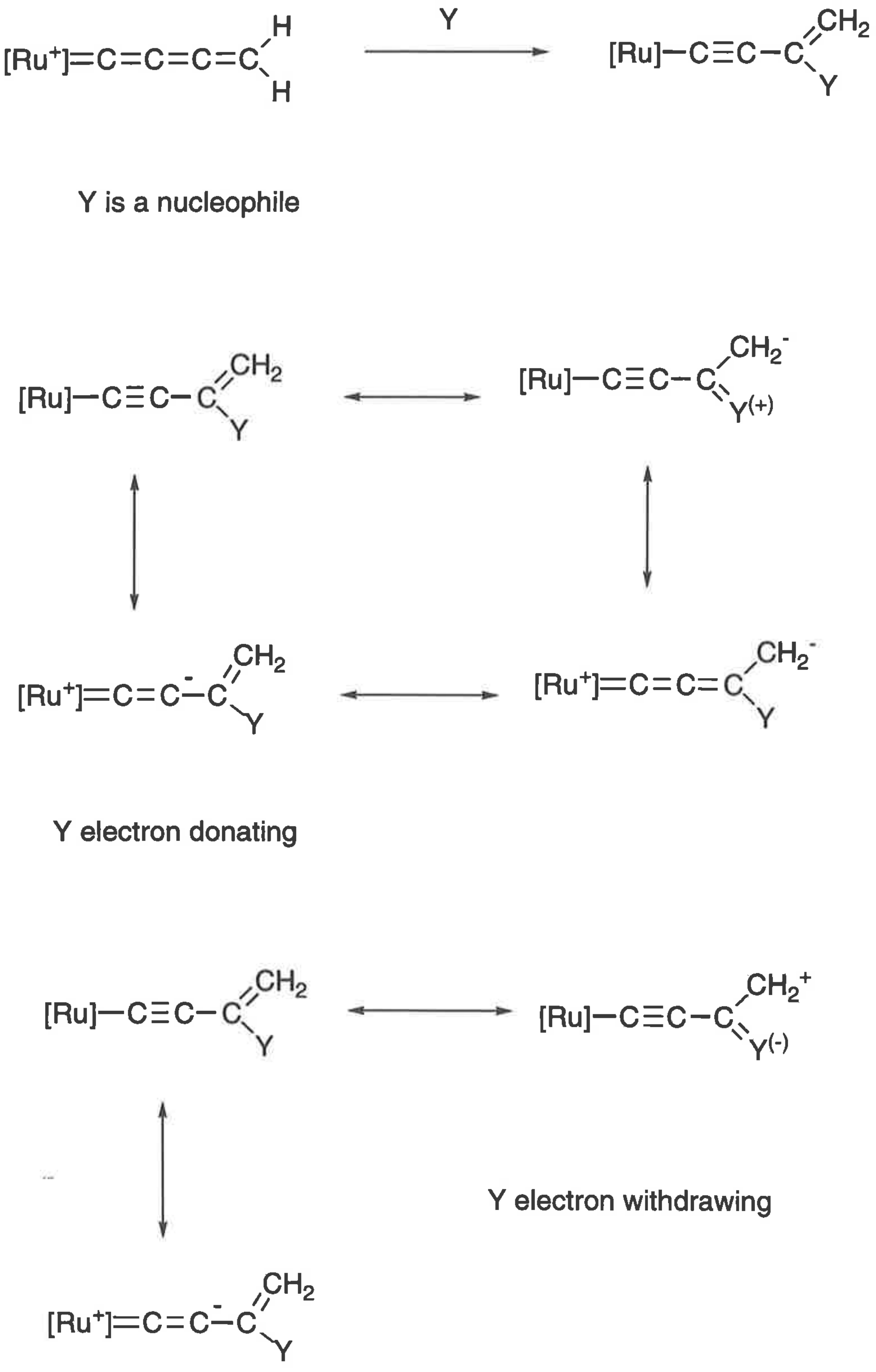
An analogous reaction using *N*-methylpyrrole as the trapping agent yielded the allenylidene [Ru{C=C=CMe(C_4H_3NMe)}(PPh_3)$_2$Cp][PF_6] (**62**). The methyl group is sufficiently acidic to be deprotonated by butyllithium, giving the unusual functionalised acetylide Ru{C≡CC(C_4H_3NMe-2)=CH_2}(PPh_3)$_2$Cp (**63**). The deprotonation is reversible, with water being a strong enough acid to regenerate the allenylidene **62**.

A complementary result was obtained when the aprotic nucleophile triphenylphosphine was employed. In this case the cationic alkenyl-acetylide [Ru{C≡CC(P^+Ph_3)=CH_2}(PPh_3)$_2$Cp][PF_6] (**64**) was isolated, there being no evidence for the formation of an allenylidene complex. Attempts to form the related allenylidene complex [Ru{C=C=CMe(P^+Ph_3)}(PPh_3)$_2$Cp][PF_6]$_2$ by reaction of **64** with strong acids such as HPF_6 result instead in the formation of the isomeric vinylvinylidene [Ru{C=CHC(PPh_3)=CH_2}(PPh_3)$_2$Cp][PF_6]$_2$ (**65**).

If the reaction between [Ru(thf)(PPh_3)$_2$Cp][PF_6] and buta-1,3-diyne is carried out in wet methanol or ethanol, Ru{C≡CC(O)Me}(PPh_3)$_2$Cp (**66**) [41] can be isolated; formation of **66** can be rationalised by loss of a proton from an intermediate formed by addition of water to C(3) in **54**.

The following rationale for the structures of compounds **62**, **63**, **65** and **66** is proposed. Interaction of buta-1,3-diyne with [Ru(thf)(PPh_3)$_2$Cp]$^+$ results in the displacement of the weakly coordinated thf ligand and concomitant 1,4 H-shift, to give the trienylidene cation **54**. Attack of nucleophiles at C(3) in metal trienylidenes is supported by the recent isolation of the metal trienylidene-trifluoroacetate complex noted above [216]. Compound **54**, whilst too reactive to be isolated, reacts with an available nucleophile, initially at C(3), to give an alkenylacetylide complex. In the cases of **62**, **63** and **66**, a further proton migration is required to form the isolated products, as summarised in Scheme 12.

The nature of the substituent attached to C(3) of a vinylacetylide complex appears to be critical in determining whether electrophilic attack occurs at C(2), to give an alkenyl-vinylidene, or at C(4), to give an allenylidene. Thus **64** and $Ru\{C{\equiv}CC{=}CH(CH_2)_4\}(PPh_3)_2Cp$ are protonated at C(2) to give the corresponding vinylidenes, whereas $Ru(C{\equiv}CCMe{=}CH_2)(PPh_3)_2Cp$ and **64** react with H^+ at C(4) to give $[Ru\{C{=}C{=}CMe(R)\}(PPh_3)_2Cp]PF_6$ (R = Me [41] or C_4H_3NMe-2). Other electron-rich vinylethynyl complexes $[Ru(C_2R)(PMe_3)_2Cp$; R = 1-cyclohexenyl, 1-cyclopentenyl, $CPr^i{=}CMe_2]$ also give vinylidenes [228]. Thus, the influence of the C(3) substituent appears to be more significant than the nature of the metal-ligand fragment in determining the course of the reaction. Electron-donating substituents activate the methylene carbon of the vinylethynyl ligand, affording allenylidenes upon reaction with H^+. Olefinic or electron-withdrawing substituents at C_γ do not activate the methylene carbon in this way, and the reaction proceeds as for most other acetylide complexes, and reaction with H^+ gives vinylidene complexes. Some simple resonance structures may be drawn which are consistent with these observations (Scheme 13).



Y is a nucleophile

Y electron donating

Y electron withdrawing

Scheme 13.

Reaction of $[Ru(=C=C=C=CH_2)(PPh_3)_2Cp]^+$ ($\mathbf{54^+}$) with aryl imines

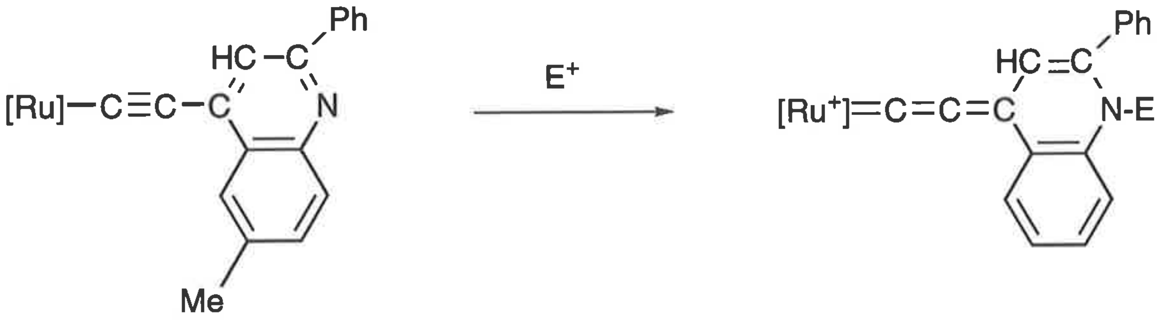
The possibility of involving both C_γ and C_δ in successive electro- and nucleophilic attack on a suitable dipolar substrate was investigated through the reactions of the cation $[Ru(C=C=C=CH_2)(PPh_3)_2Cp]^+$ with substituted *N*-aryl imines. The reactions afford 1:1 adducts containing either substituted 4-ethynylquinoline (**67**) or azabuta-1,3-dien-2-yl (**68**) ligands, depending on the electronic nature of the imine [229].

A solution of **54.PF$_6$**, prepared *in situ* from $[Ru(thf)(PPh_3)_2Cp]PF_6$ and diacetylene, was treated with two fold excess of N-*p*-tolylbenzimine at -78 °C. Upon warming to -50 °C, a colour change from orange to deep red was observed. The solution was allowed to warm to room temperature, and after work-up, bright yellow crystals of the ethynyl quinoline complex $Ru\{C{\equiv}C(2\text{-}Ph,\ 6\text{-}Me)C_9H_4N\}(PPh_3)_2Cp$ (**67**) were isolated. Complex **67** was characterised by a sharp ν(C≡C) stretch at 2051 cm^{-1}. The structure of the modified ligand was established by a single crystal X-ray diffraction study. A molecule of **67** is shown in Figure 27, and important bond lengths and angles are summarised in the caption.

The structure shows a conventional $Ru(PPh_3)_2Cp$ fragment attached by an Ru-C σ bond to a 2-phenyl-4-ethynyl-6-methyl quinoline ligand. The quinoline and PPh_3 ligands are oriented to minimise steric interactions. The parameters of the quinoline ligand are unremarkable.

Similar complexes were also obtained from reactions of **54.PF$_6$** with a variety of other *N*-arylimines while tricyclic heterocycles were obtained from naphthylimines [229]. A likely course for these reactions is described in Scheme 14. It is proposed that attack of the electron rich *ortho* carbon of the N-aryl group on the electron deficient C_γ of $\mathbf{54^+}$ is followed by attack of C_δ on the imine carbon. The formation of the aromatic quinoline fragment drives the formal elimination of H_2, which reduces a second molecule of the imine to the corresponding benzylamine (detected by gas chromatography).

These ethynylquinoline complexes are rather basic, and readily form deep claret coloured cationic complexes in the presence of traces of acid, and other electrophiles, characterised by intense $\nu(C{=}C{=}C)$ bands near 1990 cm^{-1}. The X-ray structure of the parent complex $[Ru\{C{\equiv}C(2\text{-}Ph)C_9H_4NH\}(PPh_3)_2Cp][BF_4]$ has been determined and indicates the heterocyclic N centre as the site of electrophilic attack [229]. There is no evidence of electrophilic attack at the acetylenic C_β carbon. *N*-Methylation of some of the quinoline complexes has been achieved using methyl triflate [229] (Equation 24).



67

E^+ is an electrophile

$[Ru] = Ru(PPh_3)_2Cp$

Equation 24

The presence of electron-withdrawing substitutents in the *meta* position on the *N*-aryl group reduces the nucleophilic character of the *ortho* carbon and results in the reaction proceeding down a different path. Thus, reaction between **54.PF$_6$** and $PhCH{=}N(C_6H_4NO_2\text{-}3)$ gave $Ru\{C{\equiv}CC(CH{=}CHPh){=}N(C_6H_4NO_2\text{-}3)\}(PPh_3)_2Cp$ (**68**) bearing a substituted azabuta-1,3-diene ligand, which has been fully characterised by a single-crystal X-ray study. Similar complexes were obtained from **54.PF$_6$** and A likely mechanism for the formation of these azabuta-1,3-diene complexes is given in Scheme 15.

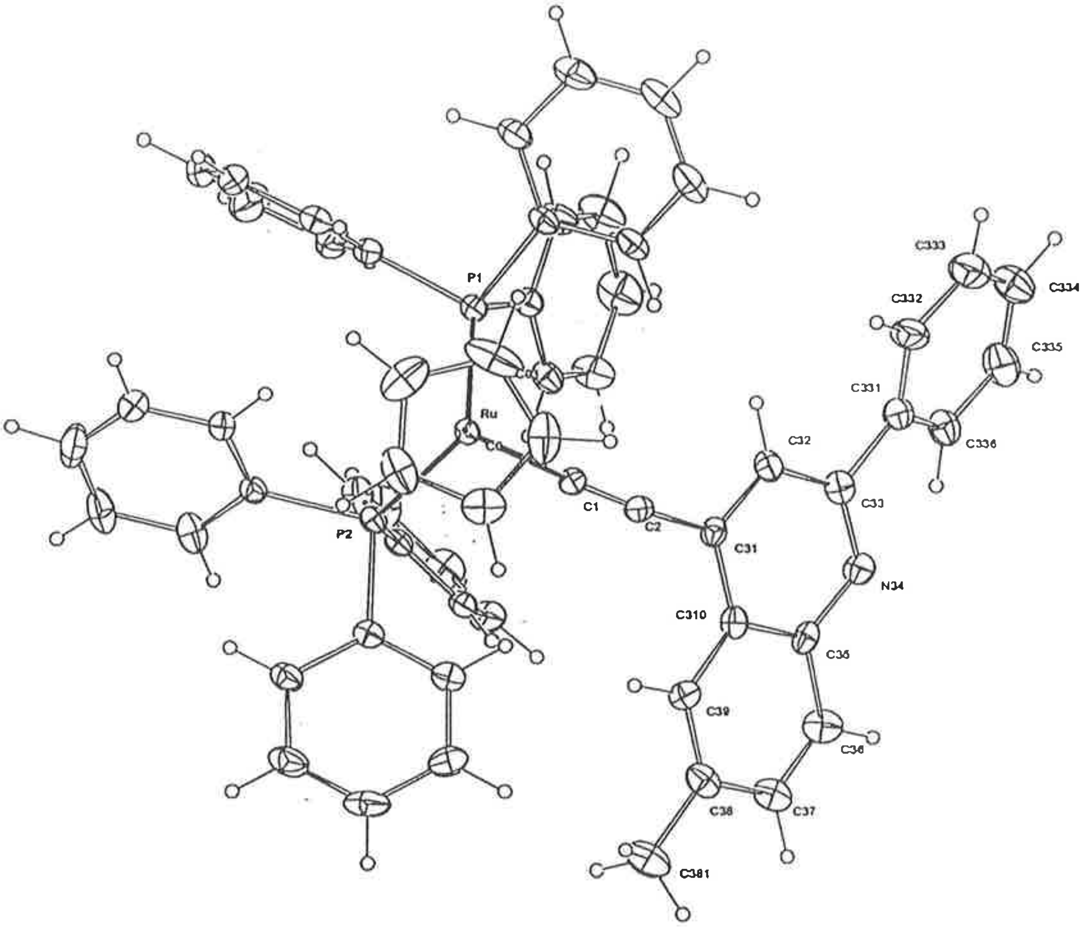
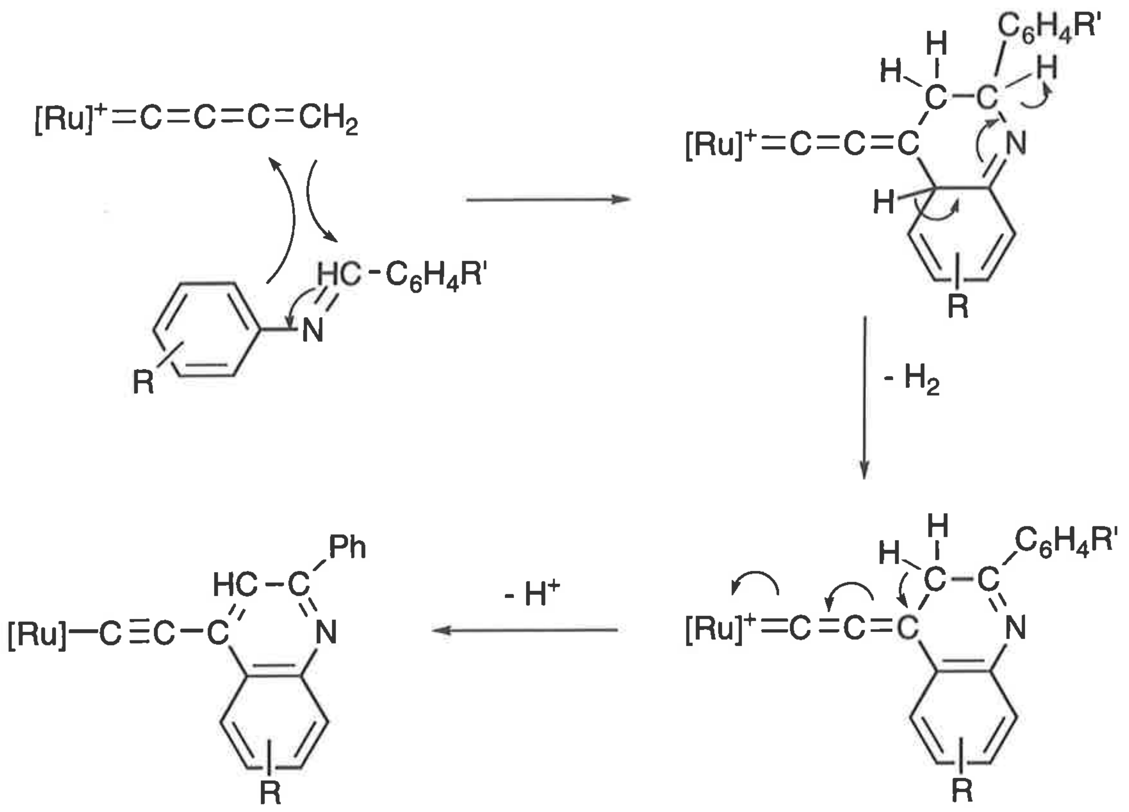
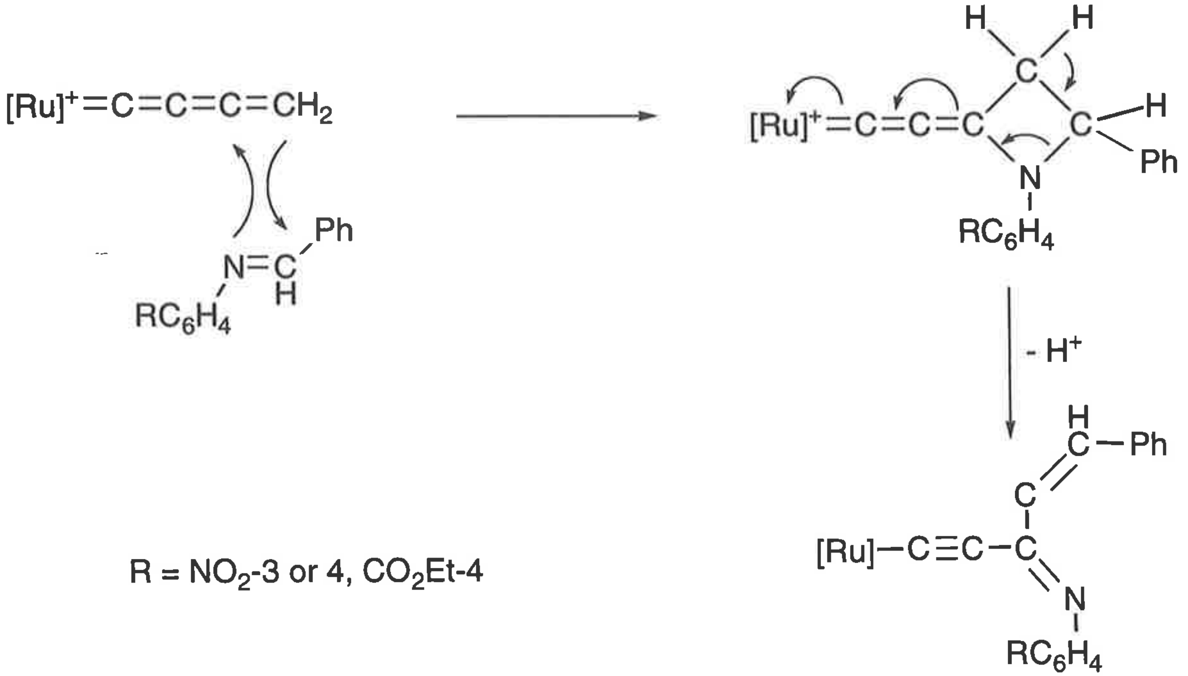


Figure 27 : A plot of a molecule of **67** showing the atom numbering scheme. Important bond lengths (Å) and angles (°): Ru-P(1) 2.22(1); Ru-P(2) 2.300(2); Ru-C(0) 1.88(-); Ru-C(1) 1.997(7); C(1)-C(2) 1.19(1); C(2)-C(31) 1.42(1); C(31)-C(32) 1.39(1); C(32)-C(33) 1.40(1); C(33)-C(331) 1.50(1); C(33)-N(34) 1.30(1); N(34)-C(35) 1.38(1); C(35)-C(36) 1.41(1); C(35)-C(310) 1.42(1); C(36)-C(37) 1.36(1); C(37)-C(38) 1.38(1); C(38)-C(381) 1.52(1); C(38)-C(39) 1.37(1); C(39)-C(310) 1.39(1); P(1)-Ru-P(2) 99.47(8); P(1)-Ru-C(1) 88.8(2); P(2)-Ru-C(1) 89.8(2); P(1)-Ru-C(0) 125.76(7); Ru-C(1)-C(2) 175.6(7); C(1)-C(2)-C(31) 170.2(8); C(31)-C(32)-C(33) 121.6(7); C(32)-C(33)-N(34) 122.7(7); C(32)-C(33)-C(331) 120.2(7); N(34)-C(35)-C(310) 122.9(7); C(35)-C(310)-C(31) 117.9(7); C(35)-C(36)-C(37) 121.1(8); C(36)-C(37)-C(38) 121.4(8); C(37)-C(38)-C(39) 118.6(8); C(38)-C(39)-C(310) 122.4(8); C(37)-C(38)-C(381) 119.3(8). C(0) is the centroid of the Cp ring.



R = H, 4-Me (**67**), 4-OMe; R' = H, 3- or 4-NO_2; [Ru] = $Ru(PPh_3)_2Cp$

Scheme 14.



R = NO_2-3 or 4, CO_2Et-4

Scheme 15.

CONCLUSION.

The allenylidene ligand in the complex $[Ru(C{=}C{=}CPh_2)(PPh_3)_2Cp]PF_6$ (**53**) is susceptible to attack at the exposed C_γ by a range of oxygen, nitrogen and carbon based nucleophiles. Reaction of buta-1,3-diyne with the labile ruthenium complex $[Ru(thf)(PPh_3)_2Cp]PF_6$ gives the complex $[Ru(C{=}C{=}C{=}CH_2)(PPh_3)_2Cp]PF_6$ (**54.PF$_6$**), containing the parent butatrienylidene ligand, *via* a formal 1,4-H shift. Reaction of **54.PF$_6$** with simple nucleophiles gives alkenyl vinylidene complexes, which may rearrange to give allenylidene complexes, while reaction of **54.PF$_6$** with substituted *N*-aryl imines gives complexes containing either ethynyl-quinoline or azabuta-1,3-dien-2-yl ligands.

- Experimental -

Standard conditions, as detailed in Chapter 2, were employed throughout.

Reagents. The compounds HC≡CCPh$_2$OH [230] and (4-Me)C$_6$H$_4$N=CHC$_6$H$_5$ [231] were prepared by the literature methods.

Dimethylamine (Aldrich), KCN (BDH), K$_2$CO$_3$ (BDH), KO^{t}Bu (Fluka) and were purchased and used as recieved.

Cyclopentadiene (Fluka) was distilled prior to use.

The synthesis and manipulation of buta-1,3-diyne has been described in Chapter 3.

[Ru(C=C=CPh$_2$)(PPh$_3$)$_2$Cp]PF$_6$ (53): RuCl(PPh$_3$)$_2$Cp (1 g, 1.38 mmol), HC≡CCPh$_2$OH (300 mg, 1.4 mmol) and NH$_4$PF$_6$ (225 mg, 1.38 mmol) were stirred in MeOH (100 ml) overnight. The resulting deep red solution was filtered to remove any unreacted metal complex, and the solvent removed from the filtrate. The deep red residue was extracted with a minimum volume of CH$_2$Cl$_2$ and filtered dropwise into an excess of rapidly stirred diethylether. The precipitated product was collected on a glass frit and washed with a small volume of cold ether. The filtrate was eveporated to dryness, and reworked as before to give a second crop of [Ru(C=C=CPh$_2$)(PPh$_3$)$_2$Cp]PF$_6$ (1.14 g, 80%). Found C 65.34, H 4.30%. C$_{56}$H$_{45}$P$_3$F$_6$Ru requires: C 65.50, H 4.39%. IR (CH$_2$Cl$_2$) ν(C=C=C) 1934, ν(PF) 840 cm^{-1}; δ_H 7.75 - 7.05 (40H, m, Ph), 5.12 (5H, s, Cp); δ_C 293.79 (t, J_{CP} = 19 Hz, C$_\alpha$), 209.44 (s, C$_\beta$), 159.60 (s, C$_\gamma$), 143.50-128.32 (m, Ph), 93.55 (s, Cp); δ_P 43.82 (s, PPh$_3$); FAB MS (*m/z*) 881 [M]$^+$; 619 [M - PPh$_3$]$^+$, 553 [M - PPh$_3$ - Cp]$^+$, 429 [M - PPh$_3$ - C$_3$Ph$_2$]$^+$.

***Ru[C≡CC(Me)Ph$_2$](PPh$_3$)$_2$Cp (56)*:** A solution of [Ru(C=C=CPh$_2$)(PPh$_3$)$_2$Cp]PF$_6$ (150 mg, 0.15 mmol) in thf (15 ml) was treated with 1 drop MeLi.LiBr (1.5M solution in Et$_2$O) and allowed to stir for 15 minutes. During this time the solution changed colour from red to green brown. The solvent was removed, the residue extracted with CH$_2$Cl$_2$ and the extracts filtered through a pad of Celite. The yellow solution was diluted with MeOH and concentrated to give a pale yellow powder, which was crystallised (CH$_2$Cl$_2$ / MeOH) to give Ru[C≡CC(Me)Ph$_2$](PPh$_3$)$_2$Cp (70 mg, 54 %). Found C 76.39%, H 5.36%. $C_{57}H_{49}P_2Ru$ requires: C 76.33%, H 5.47%. IR (nujol) ν(C≡C) 2090m cm^{-1}; δ_H 7.63 - 6.98 (40H, m, Ph), 4.29 (5H, s, Cp), 1.89 (3H, s, Me); δ_C 139.41 - 125.05 (m, Ph), 95.50 (t, J_{CP} = 23.4Hz, C_α), 93.51 (s, C_β), 85.02 (s, Cp), 47.16 (s, C_γ), 31.73 (s, Me); FAB-MS *m/z* 896 [M]$^+$, 881 [M - Me]$^+$, 691 [M - C$_2$C(Me)Ph$_2$]$^+$, 633 [M - PPh$_3$]$^+$, 619 [M - Me - PPh$_3$]$^+$, 429 [Ru(PPh$_3$)Cp]$^+$.

***Ru[C≡CC(OMe)Ph$_2$](PPh$_3$)$_2$Cp (57)*:** Addition of NaOMe (1 mol dm^{-3} in methanol) to [Ru(C=C=CPh$_2$)(PPh$_3$)$_2$Cp]PF$_6$ (150 mg, 0.15 mmol) in MeOH (10 ml) resulted in a rapid colour change frm deep red to yellow, and on stirring, a pale yellow precipitate formed. After five minutes, the solution was filtered and the pale yellow powder obtained recrystallised (CH$_2$Cl$_2$/MeOH) to yield yellow crystals of Ru[C≡CC(OMe)Ph$_2$] (PPh$_3$)$_2$Cp (120 mg, 88%). Found C 74.98, H 5.22%. $C_{57}H_{48}OP_2Ru$ requires: C 75.08%, H 5.27%. IR (nujol) ν(C≡C) 2070 cm^{-1}; δ_H 7.62 - 7.01 (40H, m, Ph), 4.35 (5H, s, Cp), 3.34 (3H, s, OMe); δ_C 147.27 - 126.87 (m, Ph), 110.51 (s, C_β), 107.52 (t, J_{CP} = 24 Hz, C_α), 85.25 (s, Cp), 82.36 (s, C_γ), 51.51 (s, OMe); ES MS (low cone voltage) (*m/z*) 912 [M]$^+$, 881 [M - OMe]$^+$, 732 [M - C$_2$C(OMe)Ph$_2$ + NCMe]$^+$.

***Ru[C≡C-C(CN)Ph$_2$](PPh$_3$)$_2$Cp (58)*:** A solution of [Ru(C=C=CPh$_2$)(PPh$_3$)$_2$Cp]PF$_6$ (150 mg, 0.15 mmol) in dry thf (15 ml), was treated with KCN (10 mg, 0.15 mmol) and heated at reflux for 12h. The solution changed colour from deep red to yellow. The solvent was removed on a vacuum line, and the yellow residue extracted with CH$_2$Cl$_2$ (2 x 5 ml). The extracts were filtered through celite and diluted with MeOH (5 ml). The yellow CH_2Cl_2 / MeOH solution was concentrated (ca. 5 ml) on the vacuum line, and the preciptated yellow solid collected on a glass frit, washed with several small portions of MeOH, dried and recrystallised (CH_2Cl_2 / MeOH) to give Ru[C≡CC(CN)Ph_2](PPh_3)$_2$Cp (108 mg, 81%). Found: C 71.79; H 4.73%. $C_{57}H_{45}NP_2Ru$ requires: C 75.50; H 4.97%. IR (nujol) ν(C≡C) 2083s cm^{-1}; δ_H 7.64 - 7.04 (40H, m, Ph); 4.34, (5H, s, Cp); δ_C 142.82 - 127.09 (m, Ph); 121.63 (s, CN); 110.66 (t, J_{CP} = 23.93 Hz, C_α); 103.25 (s, C_β); 85.25 (s, Cp); 50.83 (s, C_γ); FAB MS (*m/z*) 907 $[M]^+$, 691 [M - $C_2C(CN)Ph_2$]$^+$, 644 [M - PPh_3]$^+$, 455 [Ru(CN)(PPh_3)Cp]$^+$, 429 [Ru(PPh_3)Cp]$^+$.

Ru[C≡CC(C_5H_5)Ph_2](PPh_3)$_2$Cp (59): To a solution of [Ru(C=C=CPh_2)(PPh_3)$_2$Cp]PF_6 (200 mg, 0.19 mmol) in thf (15 ml), freshly distilled CpH [250 mg, 3.8 mmol] was added, followed by KO^tBu (50 mg, 0.45 mmol). The solution immediatel turned green-yellow. The solven was removed and the residue purified by column chromatography on Al_2O_3. Elution with light petroleum / acetone 8/2 gave a bright yellow band, which yielded Ru[C≡CC(C_5H_5)Ph_2] (130 mg, 70 %) after crystallisation (CH_2Cl_2 / MeOH). Found: C, 77.17; H, 5.75%. $C_{61}H_{50}P_2Ru$ requires: C, 77.46; H, 5.29%. IR (nujol) ν(C≡C) 2095m, ν(C=C) 1652br cm^{-1}. δ_H 7.48 - 6.98 (40H, m, Ph), 6.41, 6.27 (both 2H, both dd, $^3J_{HH}$ = 5 Hz, $^4J_{HH}$ = 1 Hz, CH=CH); 5.87 (1H, s, CH); 4.35 (5H, s, Cp); δ_C 157.41, 154.31, 148.93, 148.14, 136.6 (all s, C_5H_5), 148.93 - 125.2 (m, Ph), 115.47 (s, C_β), 96.13 (t, J_{CP} = 24.04Hz, C_α), 85.11 (s, Cp), 43.01 (s, C_γ); ES MS (*m/z*) 946 $[M + H]^+$, (with NaOMe) 968 $[M + Na]^+$.

[Ru{C≡C-CPh_2($NHMe_2$)}(PPh_3)$_2$Cp]PF_6 (60): Neat $HNMe_2$ (ca. 2 ml) was condensed into a schlenk flask containing [Ru(C=C=CPh_2)(PPh_3)$_2$Cp]PF_6 (100 mg, 0.097 mmol). The solid rapidly turned yellow and dissolved to give a bright yellow solution. The vessel was filled with dry nitrogen and the excess amine allowed to evaporate through a bubbler. The lemon yellow solid that resulted was tentatively identified as [Ru{C≡C-CPh_2($NHMe_2$)}(PPh_3)$_2$Cp]PF_6 (98 mg, 94%). Attempts to dry

the powder in vacuo resulted in a gradual colour change of the solid from yellow to deep red, and [Ru(C=C=CPh$_2$)(PPh$_3$)$_2$Cp]PF$_6$ was isolated quantitatively. Similarly, when the solid was dissolved in a range of solvents (acetone, CDCl$_3$, CH$_2$Cl$_2$, thf, MeOH), a red solution was obtained, from which only [Ru(C=C=CPh$_2$)(PPh$_3$)$_2$Cp]PF$_6$ could be isolated in high yield. Found C 62.30, H 5.44, N 3.60%. $C_{58}H_{52}NP_3F_6Ru$ requires: C 64.98, H 4.86, N 1.31%. IR (nujol) ν(C≡C) 2065m, ν(PF) 843br cm^{-1}.

Ru{C≡CC$_9$H$_4$(6-Me-2-Ph)}(PPh$_3$)$_2$Cp ***(67)***: RuCl(PPh$_3$)$_2$Cp (150 mg, 0.207 mmol) was dissolved in thf (20 ml) and treated with AgPF$_6$ (54 mg, 0.206 mmol) and allowed to stir for 5 minutes. The resulting orange solution was cooled to -78°C, then filtered into a second flask containing HC≡CC≡CH (4.0mmol) and N-tolylbenzimine (50 mg, 0.256 mmol) in thf (5 ml), also at -78 °C. The cold bath was removed and the mixture allowed to reach room temperature. During this time the solution changed colour from orange to a deep red. The solution was treated with KOBu (25 mg, 0.225 mmol) and the solvent removed. The residue was purified by column chromatography on Al$_2$O$_3$. Elution with Et$_2$O gave a deep yellow band which afforded the product (50 mg, 26 %) after crystallisation (Et$_2$O / pentane). Found: C 75.50; H 5.00; N 1.48%. $C_{59}H_{47}NP_2Ru$ requires: C 75.97; H 5.04; N 1.50%. IR (nujol): ν(C≡C) 2051, ν(C=C) 1568, 1537 cm^{-1}; δ_H 8.24 - 7.05 (35H, m, aromatic), 4.43 (5H, s, Cp), 2.36 (3H, s, CH$_3$); FAB MS (*m/z*) 933 [M]$^+$, 671 [M - PPh$_3$]$^+$, 428 [Ru(PPh$_3$)Cp]$^+$.

- Appendix 1 -

Molecular structure of $RuBr(PPh_3)_2Cp$

The compound $RuBr(PPh_3)_2Cp$ (**69**) was obtained as the byproduct of a reaction involving LiMe containing LiBr (see Chapter 3). The molecular structure of **69**, as a CH_2Cl_2 solvate is shown in Figure A1 and selected structural parameters of are given in Table A1, together with those reported earlier for the analogous chloro compound [232], and the related osmium compounds $OsX(PPh_3)_2Cp$ (X = Cl [233], Br [234]). The CH_2Cl_2 solvates of all four complexes are isomorphous. In all complexes, the metal environments may be regarded as distorted octahedral, one face being occupied by the cyclopentadienyl group and the opposite one by the halide and two phosphorus atoms. The ligand dispositions are similar, suggesting that these are determined more in response to a tightly packed intramolecular array than to lattice forces. There are no unusually close contacts within the lattice.

The two phenyl groups nearest to the Cp ring have relatively parallel dispositions vis-à-vis the plane of the latter; the remaining phenyl ring in each ligand lies essentially normal to, and projects away from, that plane. The third ring of ligand 2, in projection normal to the Cp ring plane, lies over C(226), while that of ligand 1 lies over C(111); each has a different inclination to the Ru-Br vector.

Some molecular parameters are remarkably invariant: X-M-C(0) [C(0) is the centroid of the Cp ring] range over 1.3°, P-M-C(0) over 1.7° , P-M-P over 0.8°. In the solvated complexes X-M-P(2) are very tightly ranged within 0.2°, the value for the unsolvated complex being more than 2° greater, while X-M-P(1) are more variable, spanning 1.7° overall. Among the distances, <M-C(Cp)> span only 0.01_5 Å except for the $Os/Br/CH_2Cl_2$ solvate, small at 2.17_7Å. Not surprisingly, this complex also provides the outlier in M-C(0) values (1.81_8Å), a difference probably too large to be consequent solely upon lack of correction for (probably insignificant) libration effects. Variations of similar magnitude are found also among M-P distances, with close correlations only to the metal atoms. In most cases, M-C(1,5) are shorter than the values for M-C(2-4), possibly a consequence of *trans* effects, but more probably because of variations in intramolecular environmental strain.

Replacement of Ru by Os results in increased M-Cl and M-C(0) but decreased M-Br and M-P, consistent with reduced Lewis basicity for Br versus Cl, while it might be argued that the diminution in <Os-C(Cp)> on passing from X = Cl to X = Br reflects increased back-bonding to the ring from the more electron-rich metal atom in the Br complex.

One of the first comparative studies of second and third row transition metal organometallic complexes was that of $MMe_2(PMePh_2)_2$ (M = Pd and Pt) [235], in which metal-ligand distances were greater for Pt than for Pd with σ-bonding (hard) ligands, and the opposite for π-bonding (soft) ligands. As can be seen from Table A1, the present case does not illustrate any regular trends of this type. For example, whereas Δ(M-Cl) is +0.012 Å for the chloro complexes, it is -0.025 for the bromo derivatives. Similarly, Δ[M-C(cp)] are -0.014 and +0.024 Å for the Cl and Br complexes, respectively. Only for Δ(M-P) (-0.006 and -0.032 Å) are the Os distances consistently shorter. It is suggested that the reasons for this anomalous behaviour is to be found in the steric hindrance between the ligands found in these pseudo-octahedral complexes, such hindrance being conspicuously absent in the square-planar Pd and Pt complexes mentioned above.

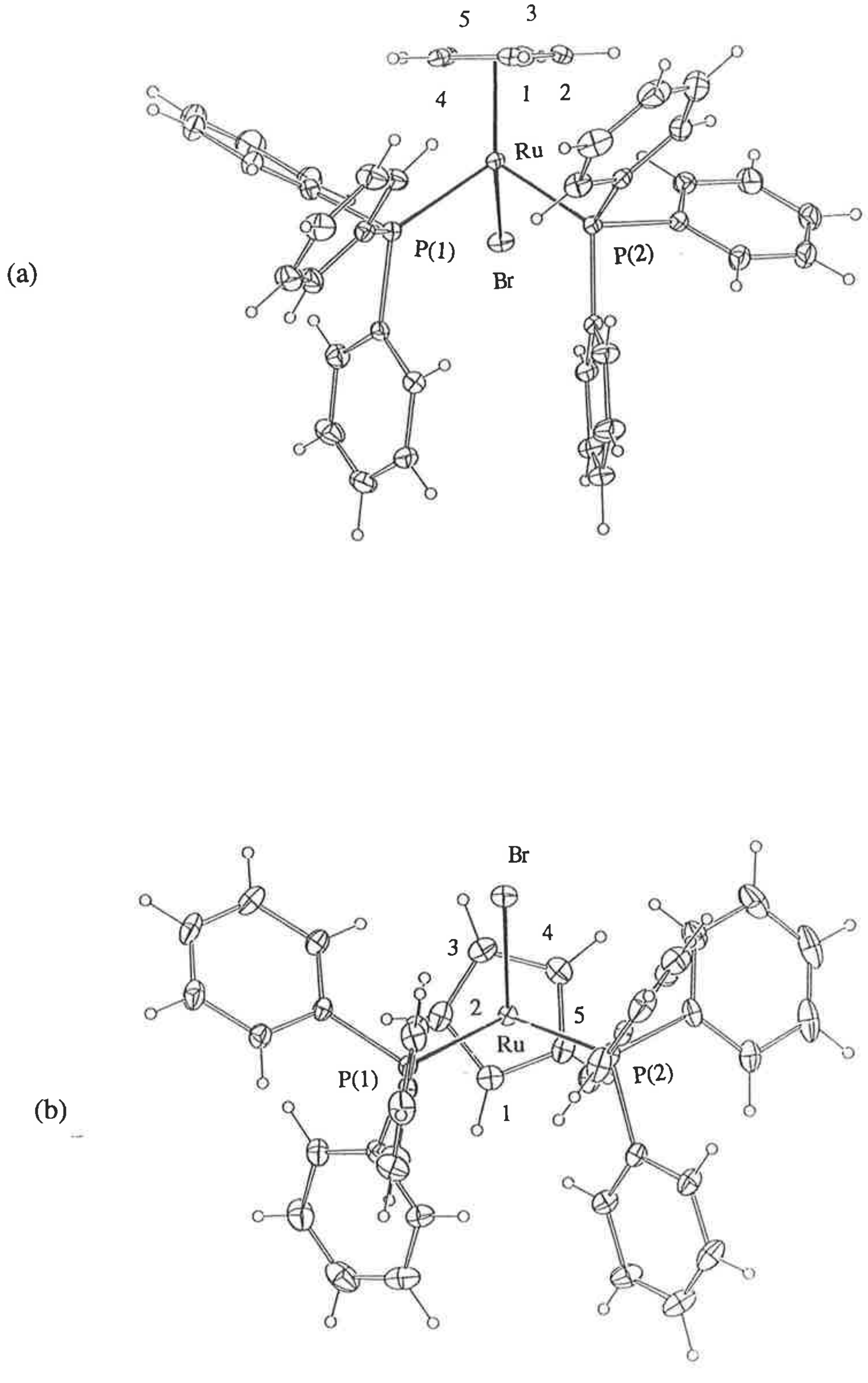


Figure A1 : A plot of a molecule of **69** (a) normal to; (b) through the Cp ring (by B.W. Skelton and A.H. White).

Table A1. Structural parameters for $MX(PPh_3)_2Cp.CH_2Cl_2$

M	Ru	Os	Ru	Os
X	Cl	Cl	Br	Br
Ref.	[232]	[233]	This work	[234]
Bond lengths (Å)				
M-X	2.448(1)	2.460(2)	2.5683(8)	2.5438(9)
M-P(1)	2.323(1)	2.320(2)	2.323(2)	2.290(2)
M-P(2)	2.329(1)	2.319(2)	2.329(2)	2.297(2)
M-C(1)	2.179(3)	2.183(6)	2.172(4)	2.150(6)
M-C(2)	2.211(3)	2.230(6)	2.214(5)	2.197(6)
M-C(3)	2.218(3)	2.235(6)	2.220(5)	2.189(7)
M-C(4)	2.218(3)	2.230(6)	2.212(5)	2.192(6)
M-C(5)	2.189(3)	2.192(5)	2.186(4)	2.155(6)
M-C(cp) (av.)	2.20	2.214	2.201	2.177
M-C(0)	1.843	1.856	1.848	1.818
Bond angles (°)				
X-M-P(1)	90.11(3)	89.77(5)	90.77(4)	90.48(5)
X-M-P(2)	88.37(3)	88.44(6)	88.36(4)	88.45(5)
P(1)-M-P(2)	103.55(3)	103.23(6)	103.18(5)	103.13(7)
X-M-C(0)	123.8	123.4	123.0	122.9
P(1)-M-C(0)	120.9	121.3	121.0	122.7
P(2)-M-C(0)	122.0	122.3	122.4	120.9

- Appendix 2 -

Publications and Presentations by the Author arising from this Work

Publications

1. Cyclopentadienyl-Ruthenium and -Osmium Chemistry XL. X-Ray Crystal Structures of $MBr(PPh_3)_2(\eta\text{-}C_5H_5).CH_2Cl_2$ (M = Ru, Os), *Aust. J. Chem.*, 1995, **48**, 1887 (with M.I. Bruce, B.W. Skelton, E.R.T. Tiekink, A. Werth and A.H. White).

2. Some transition-metal complexes of silylated 1,3 diynes, *J. Chem. Soc., Dalton Trans.*, 1996, 1551 (with M.I. Bruce, A. Werth, B.W. Skelton and A.H. White).

3. Alkenylvinylidene and allenylidene complexes: evidence for the formation of a metal trienylidene intermediate, *Chem. Commun.*, 1996, 1009 (with M.I. Bruce, P. Hinterding, B.W. Skelton and A.H. White).

4. Five oxidation states in metal-bonded C_4 chains, *Mendeleev Commun.*, 1996, 200 (with M.I. Bruce, L.I. Denisovich, S.M. Peregudova and N.A. Ustynyuk).

5. Syntheses of metal diynyl complexes: novel routes to all-carbon ligands, *Chem. Commun.*, 1996, 2405 (with M.I. Bruce and M. Ke).

Conference Contributions

The Royal Australian Chemical Institute Inorganic Division National Conference (IC '94)
4 - 7 July 1994 Perth, WA, Australia.
*Some chemistry of unsaturated C_n ligands (with C.J. Adams, M.I. Bruce, M. Schulz, B.W. Skelton, A.H. White and N.N. Zaitseva).
*Some chemistry of the all-carbon ligand C_4 (with M.I. Bruce).

1995 International Chemical Congress of Pacific Basin Societies (Pacifichem '95) 17 - 22 December 1995 Honolulu, Hawaii, USA.

*Synthesis and reactions of ruthenium and tungsten complexes containing unsaturated C_4 chains (with M.I. Bruce, B.W. Skelton, A.H. White, L.I. Denisovich and N.A. Ustynyuk).

The Royal Australian Chemical Institute Inorganic Division National Conference (IC '96) 30 June - 4 July 1996 Townsville, Qld, Australia.

*The redox chemistry of two ruthenium diacetylides - Towards molecular wires? (with M.I. Bruce, L. Denisovich, S.M. Peregudova and N. Ustynyuk).

XVIIth International Conference on Organometallic Chemistry 7 - 12 July 1996 Brisbane, Qld, Australia

*Some chemistry of an Ru_3 cluster containing $W(C\equiv CC\equiv CH)(CO)_3Cp$ as a ligand (with M.I. Bruce, B.W. Skelton, A.H. White and N.N. Zaitseva).

*Transition metal diacetylides and other carbon toys (with M.I. Bruce, M. Ke, B.W. Skelton and A.H. White).

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