SOME CHEMISTRY OF METAL ALKYNYLS: FORMATION OF MOLECULAR SQUARES

by

Benjamin Craig Hall
B.Sc. (Hons)

A thesis presented for the degree of Doctor of Philosophy

The Department of Chemistry
The University of Adelaide
October, 2000.

CONTENTS

	Page
Chapter 1.	
Introduction.	1
Chapter 2.	
Chemistry of Neutral Vinylidenes.	
Introduction.	30
Results and Discussion.	33
Experimental.	66
References.	78
Chapter 3.	
Some Complexes from 1,4-bis-diethynylbenzene.	
Introduction.	81
Results and Discussion.	83
Experimental.	98
References.	105
Chapter 4.	
Molecular Squares and Tweezers.	
Introduction.	109
Results and Discussion.	111
Experimental.	139
References.	154
Chapter 5.	
Preparation of Novel Alkynyl-Gold(I) Compounds.	
Introduction.	158
Results and Discussion.	160
Experimental.	170
References.	174
Appendix.	177

ABSTRACT

This thesis continues the study into the reactivity of metal alkynyl fragments, in particular the formation of compounds containing two or more alkynes, resulting in the preparation of complexes with interesting properties and reactivities.

Chapter two describes the preparation of neutral vinylidenes and investigates some of their unusual reactivity. Addition of sodium methoxide in the presence of 2-e ligands results in the formation of chiral alkynyl compounds with the formal elimination of HCl. When this reaction takes place in the presence of terminal acetylenes, di-, tri- and tetramerisation occurs.

Chapter three investigates some of the chemistry of the dialkyne, 1,4-bis-trimethylsilylethynylbenzene. The inclusion of an extra acetylene fragment effects the reactivity of these compounds, with the metal bonded acetylene acting as a typical metal acetylide while the other acts as a free terminal acetylene. Copper(I) coupling using Cadiot-Chodkiewicz conditions allows for the formation of heterobimetallic compounds which are relatively rare.

Chapter four examines the effect of having two alkynyl chains in close proximity, with a study of the reactivity of *cis*-$Pt(C{\equiv}CC{\equiv}CH)_2(L_2)$. These molecules have been termed "molecular tweezers" due to their ability to form complexes with simple molecules. They also make attractive precursor materials for the formation of molecular squares, with an internal angle of approximately 90°. A technique is described for a high yield synthesis of neutral molecular squares, which have been structurally characterised.

Chapter five describes the formation of gold(I) compounds containing the butadiyndiyl fragment. Copper coupling with $AuCl(PPh_3)$ and $Au_2Cl_2(\mu\text{-dppm})$ results in the formation of alkynyl complexes. The presence of short Au...Au contacts confine the $Au_2(\mu\text{-dppm})$ fragment to U-shaped geometry. Using the techniques developed in chapter four, a high yield synthesis of molecular rectangles are described.

STATEMENT

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

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

Benjamin C. Hall

ACKNOWLEDGEMENTS

Thank you is perhaps one of the easiest words to say, but sometimes it fails to fully capture the immense gratitude I have for the people who have influenced and helped me not just for the duration of this PhD, but in life.

To my supervisor, Professor Michael Bruce, I can not express the how grateful I am for everything that you have done for me. You showed belief in me when others perhaps did not and gave me an opportunity when others perhaps wouldn't. I've really enjoyed my time working with you, and I hope I've justified the faith that you have shown in me.

It's been a real privilege working in this lab, to be surrounded by people of the likes of Dr. Natasha Zaitseva and Dr. Paul Low, both of whom have taught me the practical side of our chemistry. I thank them for their patience and friendship over the years. I also would like to acknowledge the post-docs and visitors who have worked in the lab over the years, namely Dr. Brian Kelly and Dr. Karine Coustas. Hopefully I have been of similar help to more recent members of the lab: Josh, Mark, Nat, Ben, Andrew and Kathy. I thank you and wish you all the best in the future.

Much of this work would not be possible if it were not for the expertise of many other people. I'd like to thank Professor Allan White and Brian Skelton for their tireless efforts regarding the acquisition of crystal structures. Professor Brian Nicholson for initially running and later advising on ES mass spectroscopy. Phil Clements for help with NMR spectroscopy, and lastly the technical staff for fixing things when they went wrong.

Lastly, I would like to acknowledge the unwavering support of my family, they are always there for me, supporting and encouraging me to be the best I can be.

THANK YOU

ABBREVIATIONS

In general

Å	angstroms
acac	acetylacetonate
Ar	Aryl
av.	average
bipy	bipyridine
b.p.	boiling point
Bu	butyl
^{n}Bu	normal butyl
^{t}Bu	tertiary butyl
ca.	Circa
calc.	Calculated
Cp	cyclopentadienyl
Cp*	pentamethylcyclopentadienyl
d	days
dbu	1,8-diazabicyclo[5.4.0]undec-7-ene
dmso	dimethylsulfoxide
dppe	1,2-bis(diphenylphosphino)ethane
dppee	1,2-bis(diphenylphosphino)ethylene
dppf	1,1'-bis(diphenylphosphino)ferrocene
dppm	bis(diphenylphosphino)methane
dppp	1,3-bis(diphenylphosphino)propane
e.g.	for example
en	ethylenediamine
Et	ethyl
eV	electron volt
g	grams
h	hours
Hz	hertz
K	kelvins
L	ligand or litres
[L_mM]	general metal-ligand fragment

M	metal or molarity
Me	methyl
mg	milligram
MHz	megahertz
min.	minutes
ml	millilitres
mmol	millimole
OAc	acetate
OTf	triflate
Ph	phenyl
^{i}Pr	isopropyl
ppn	bis(triphenylphosphine)iminium
r.t.	room temperature
R_f	retardation factor (TLC)
tbaf	tetrabutylammonium fluoride
tcne	tetracyanoethylene
thf	tetrahydrofuran
TLC	thin layer chromatography
V	Volts
X	anion

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 Spectroscopy (MS)

ES	Electrospray
FAB	Fast atom bombardment
M	molecular ion
m/z	mass per unit charge

For Nuclear Magnetic Resonance Spectroscopy (NMR)

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

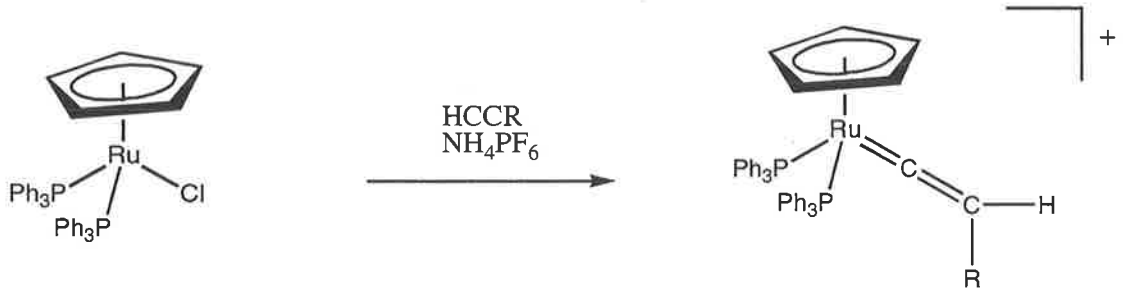
Chapter 1

Introduction

Acetylenic coupling and the preparation of compounds containing one or more alkynyl groups are currently receiving renewed interest from researchers. The formation of compounds containing sterically undemanding mono-, di- and oligo-alkynyl moieties are finding increasing applications in the search for advanced materials having interesting electronic and optical properties.[1-3]

Transition metals have long been used in the stabilisation of conjugated organic molecules, not only due to the steric protection afforded by the bulky metal fragment, but also due to the participation of the metal in the π-delocalisation and the potential for interaction of the metal d-orbitals with the conjugated π-orbitals of the organic moiety.[4-8] The metal-to-ligand and ligand-to-metal charge transfers also produce a reordering of the π-electron distribution of the coordinated ligands at the metal centre.[9,10] The coordination of the alkynyl anion to a metal centre transfers nucleophilicity from C_α, the carbon atom closest to the metal atom, to C_β, the second carbon atom in the chain. Electrophilic attack on the alkynyl C_β atom is charge controlled, while nucleophilic attack on C_α is frontier orbital controlled.[11]

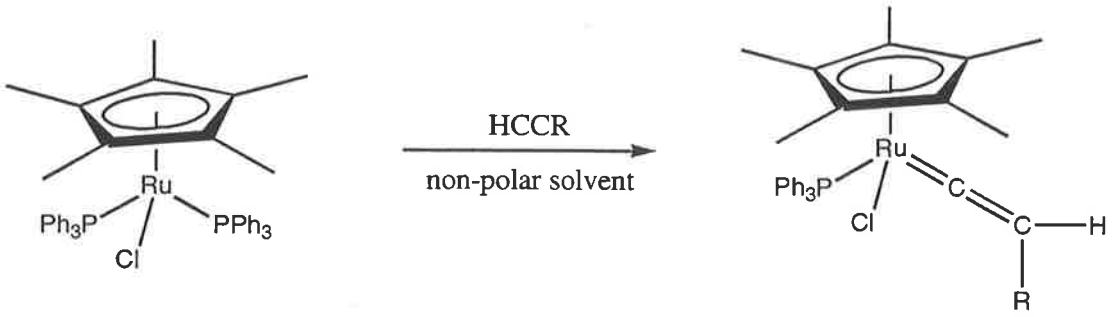
A characteristic reaction of metal alkynyls is the addition of electrophiles at C_β, producing cationic vinylidene complexes. Such electrophiles include H^+,[12,13] Me^+,[14,15], $C_7H_7^+$,[16] ArN_2^+,[17] and X^+ (X = Cl, Br and I).[18] Additionally, vinylidene complexes can also be formed directly by the addition of 1-alkynes to transition metal complexes, MXL_mCp [M = Ru, Fe; X = Cl, Br, I; L_m = phosphines]. This rearrangement can occur via several different mechanisms including η^2-η^1 slippage of an intermediate η^2 complex, or by a concerted 1, 2-hydrogen shift. Thus, the reaction of $RuCl(PR_3)_2Cp$ with 1–alkynes in polar solvents results in the formation of cationic vinylidene complexes of the type $[Ru(C{=}CHR)(PR_3)_2Cp]^+$ (Scheme 1).



Scheme 1 : Formation of cationic vinylidenes.

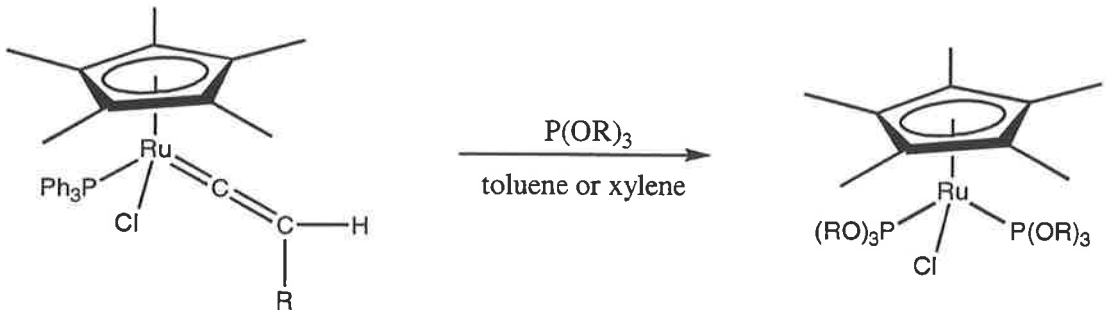
The dative bond formed between the ligand and the metal involves a metal-carbon σ-bond and a π-bond from the metal d orbitals to the π* orbitals of C_α. Some comparisons can be made between the carbonyl ligand and the unsaturated vinylidene moiety.[19] The vinylidene ligand has one of the highest π-acceptor capacities known with only SO_2 and CS exceeding phenylvinylidene in electron withdrawing power.[20] The extreme electron deficiency of C_α is reflected in low field NMR shifts, ca. ~350 ppm, due to strong deshielding.[11] Since the first metal vinylidene complex was fully characterised in 1966,[21] a variety of such complexes have been reported, with several reviews appearing.[11,22,23]

Until recently, most vinylidene complexes from the Group 8 metals have been cationic, due to the ready displacement of the halide ion in polar solvents. The introduction of bulky ligands to the $[MXL_2Cp]$ fragment, such as replacement of cyclopentadiynyl, Cp, with pentamethylcyclopentadienyl, Cp*, has a marked effect on the reactivity of these compounds. The combination of the increased steric bulk and increased electron donating ability facilitates the loss of a single L group. In non-polar solvents, reactions with terminal alkynes result in the retention of the chloride ion and loss of a single phosphine ligand, ensuring the formation of neutral vinylidene complexes (Scheme 2). Interestingly, if the same reaction is done in polar solvents, then the corresponding cationic vinylidene is formed.



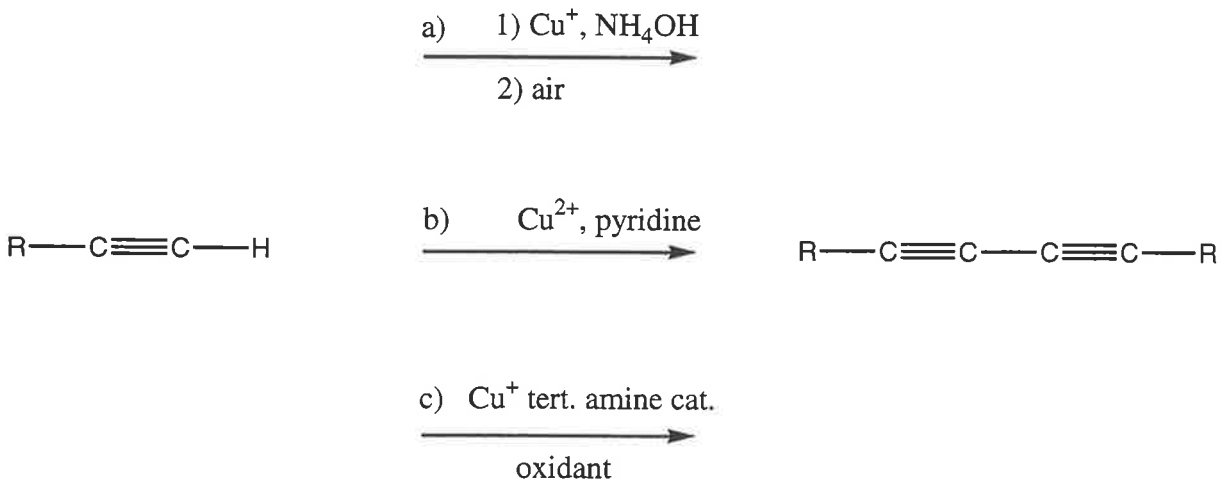
Scheme 2 : Formation of neutral vinylidenes.

The reactivity of these neutral vinylidene complexes is noticeably different from that of cationic vinylidenes. For example, addition of phosphite to neutral vinylidene complexes in refluxing toluene or xylene results in the displacement of the vinylidene moiety as well as the initial phosphine (Scheme 3).[24]



Scheme 3 : Addition of phosphite to neutral vinylidene complexes.

Complexes containing multiple alkynyl groups have shown promising results as one-dimensional wires. The ability of the π-electrons of the alkynyl units to delocalise over the entire metal-carbon chain allows for electronic communication between metal centres. Carbon-rich ligands containing multiple alkynyl units can be prepared using many different synthetic approaches. Symmetrical coupling of free acetylenes under mild conditions was discovered over a century ago by Glaser[25,26] (Scheme 4a) and this procedure has been significantly improved since by Eglinton[27,28] and Hay[29] (Scheme 4b and 4c).

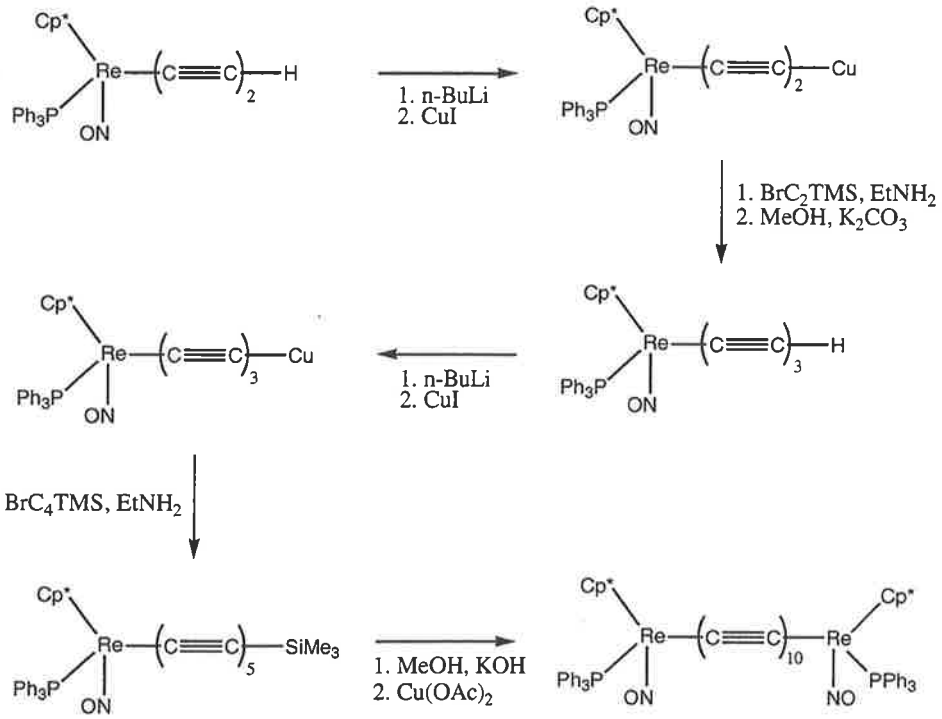


Scheme 4 : Symmetrical coupling of acetylenes using (a) Glaser, (b) Eglinton and (c) Hay conditions.

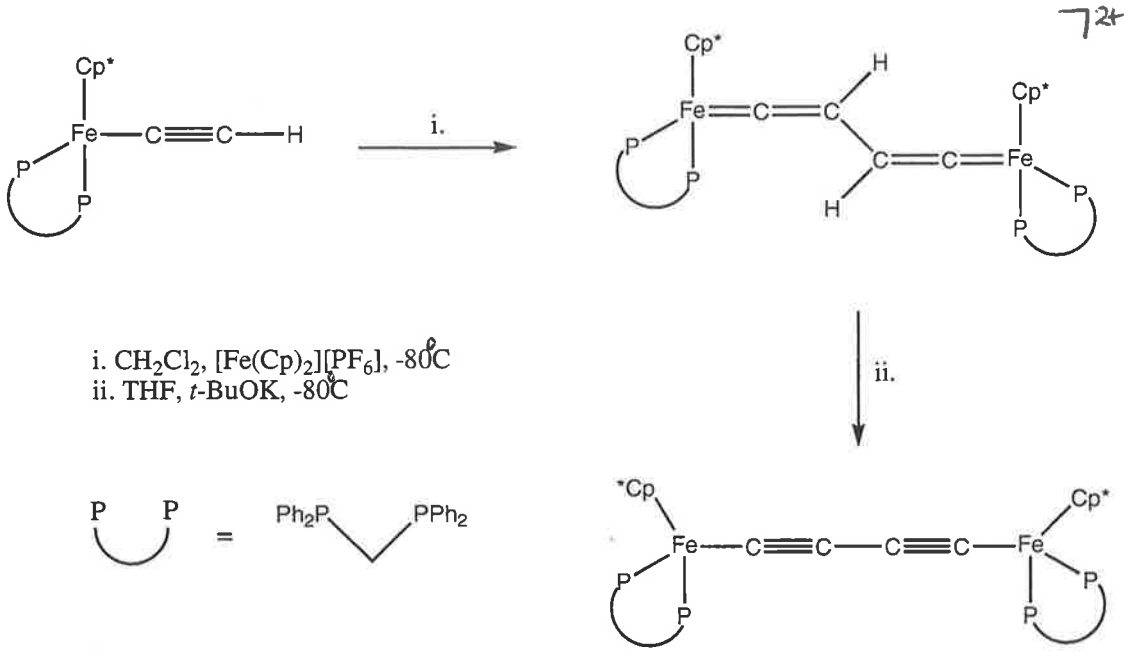
These synthetic methods are also applicable to the formation of metal dialkynyl complexes. Hay coupling conditions have been extensively used in the preparation of homometallic complexes, in which each end is capped with two identical ML_m fragments.[30,31]

Complexes containing the butadiynyl ligand (μ-C_4) are typically prepared from a protected butadiynyl precursor, such as $Me_3SiC{\equiv}CC{\equiv}CSiMe_3$, or from a terminal diacetylene, such as 1,3-butadiyne. Such complexes are usually obtained by metal-halogen or metal-metal exchange from dilithiated, dihalogenated or otherwise activated acetylenes or by utilising the coupling methodologies mentioned previously.

Bimetallic complexes of butadiyne can be obtained through either the coupling of two organometallic terminal alkynes under Hay conditions or through the direct reaction of an activated butadiyne with two equivalents of a metal complex. Terminal alkyne coupling was used to good effect by Gladysz and coworkers, who have succeeded in isolating complexes of up to 20 carbons capped by $Re(NO)(PPh_3)Cp^*$ (Scheme 5).[32] Lapinte has also prepared binuclear iron complexes via deprotonation of an intermediate di-vinylidene complex (Scheme 6).[33]

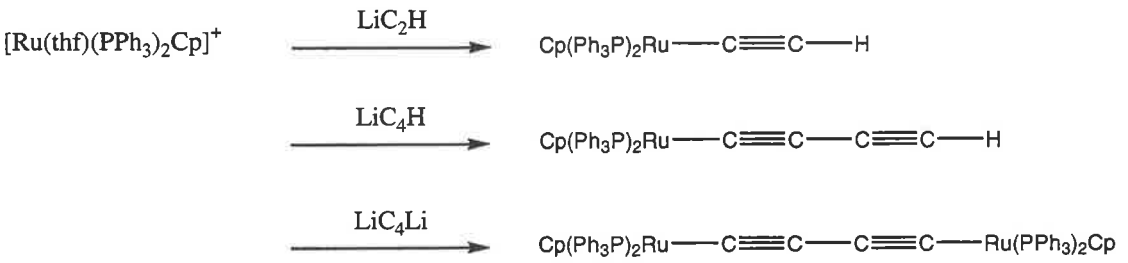


Scheme 5 : Stepwise lengthening of the carbon chain in Gladysz rhenium system.



Scheme 6 : Deprotonation of an intermediate bis-vinylidene complex.

Mononuclear and binuclear complexes of ruthenium have been prepared by Bruce,[34,35] with the displacement of the chloride ion from $RuCl(PR_3)_2Cp$ by $AgPF_6$ resulting in the coordination of thf to form the weakly coordinated cation $[Ru(thf)(PR_3)_2Cp]^+$, which readily reacts with alkynyl anions and dianions (Scheme 7).



Scheme 7 : Preparation of mononuclear and binuclear ruthenium complexes.

The butadiynyl-ruthenium complex described above is a good example of one of the potential uses for this type of compound. Electrochemical oxidation showed this Ru-C_4-Ru system is capable of losing four electrons, giving rise to a novel series of five oxidation states, including the mixed-valence Ru(II) / Ru(III) and Ru(III) / Ru(IV) cations (Figure 1).[35] Successive oxidation potentials for the first three reversible processes where found at –0.23, +0.41 and +1.03 V, while the fourth irreversible oxidation was found at +1.68 V. Spectroelectrochemical techniques have since been used to investigate the change in bond order as each electron is removed. A detailed theoretical study was used to probe the structure of the conjugated all-carbon ligand at each stage of the oxidation. It was found that both the metal centres and the carbon atoms of the C_4 bridge were affected with removal of the electrons housed in the MO's delocalised over the Ru-C_4-Ru chain. Through these studies we can consider the rods as electronic wires which mediate the directional motion of electronic excitation energy from one active centre to the other.

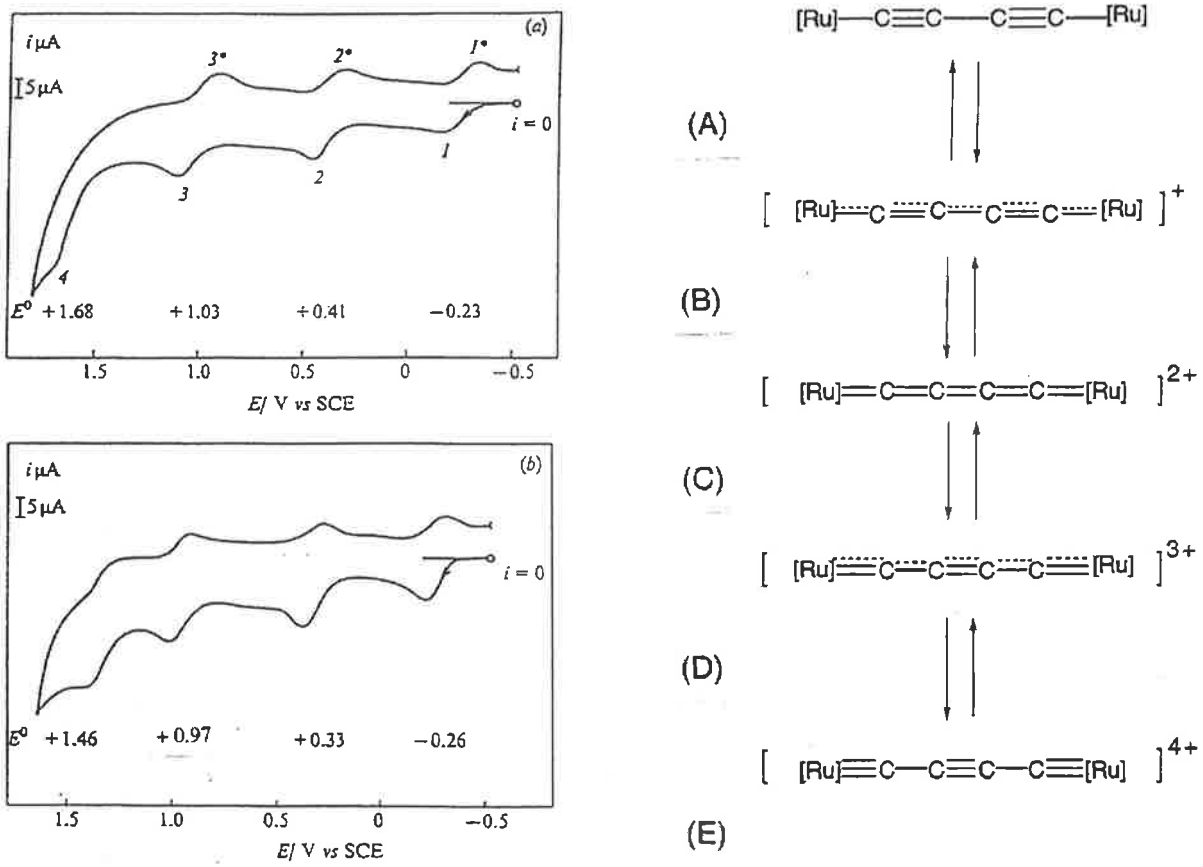
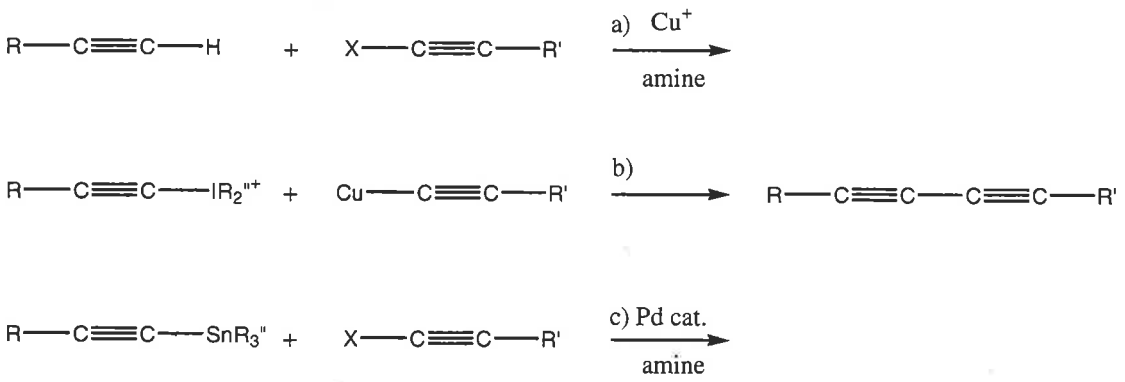


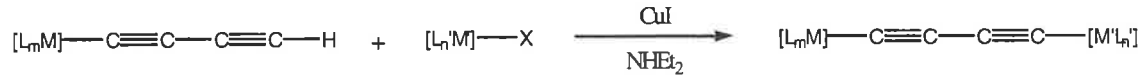
Figure 1 : Cyclic voltammogram of $\{Ru(PR_3)Cp\}_2(\mu\text{-}C{\equiv}CC{\equiv}C)$ R = Ph and Me, and the resulting valence structures.

Unsymmetrical coupling of terminal acetylenes was developed by Cadiot and Chodkiewicz[36] and can be accomplished under a variety of conditions (Scheme 8a).[37-43] In most reactions copper alkynyls seem to be key intermediates. Coupling alkynyliodonium salts with copper(I) acetylides gives diynes in good yields[44] (Scheme 8b) and Stille coupling (Scheme 8c) of stannylated alkynes provides a copper-free coupling method.[45]



Scheme 8 : Unsymmetrical coupling methods. (a) Cadiot and Chodkiewicz coupling, (b) alkynyliodonium salts and (c) stannylated alkynes.

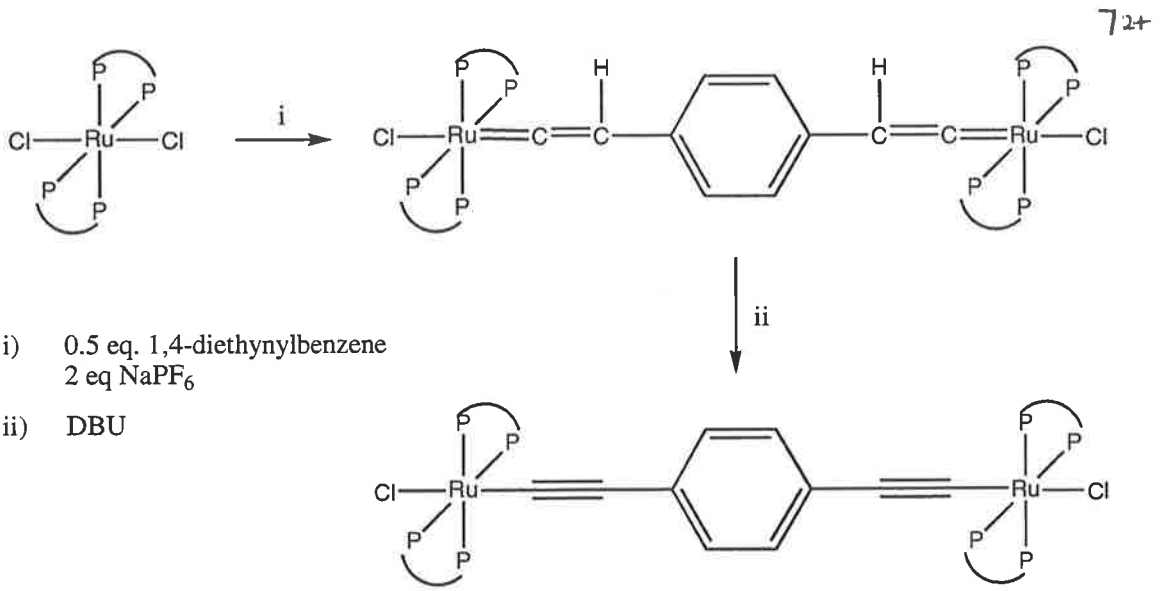
The formation of heterometallic complexes, which contain different ML_m fragments at each end, are inherently more difficult to synthesise. Presently there are very few examples of heterobimetallic complexes, the following $[ML_m]$-C_n-$[M'L'_n]$ having been reported: ML_m = Fe(CO)(L)Cp [L = CO, PPh_3], $M'L'_n$ = $M'(CO)_3Cp$ (M' = Mo, W);[46] ML_m = Re(NO)(PPh_3)Cp*, $M'L'_n$ = *trans*-$PdCl(PEt_3)_2$, *trans*-$Rh(CO)(PPh_3)_2$;[47] ML_m = $Pt(PR_3)_2$, $M'L'_n$ = $PdCl(PR_3)_2$.[48] Formation of these compounds is typically achieved in a stepwise fashion, with two sequential couplings utilising the synthetic methods developed by Cadiot and Chodkiewicz. The initial coupling results in the formation of a metal diynyl complex, of the general structure $[ML_m](C{\equiv}CC{\equiv}CH)$ [ML_m = $Fe(CO)_2Cp$, $Mo(CO)_3Cp$, $W(CO)_3Cp$, Pt(dppe)]. Addition of the second $[M'L_n']$ fragment is achieved by addition of a catalytic amount of CuI in an amine base, the reaction proceeds quickly and in high yield to form the mixed-metal complex (Scheme 9).



Scheme 9 : Preparation of mixed-metal diynyl complexes.

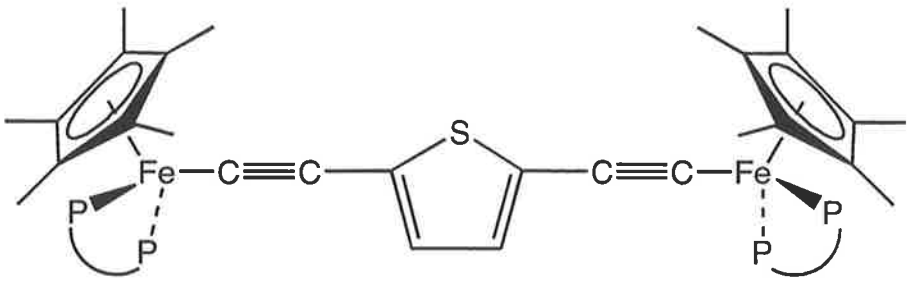
The effectiveness of this method was surveyed by Bruce and coworkers who were able to demonstrate that the terminal alkynyl group in $W(C{\equiv}CC{\equiv}CH)(CO)_3Cp$ could be readily coupled with a wide variety of metal halide complexes under the same copper(I)-catalysed reactions, managing to prepare a series of heterometallic complexes in which the Group 6 metal atom was tethered to other metals from Group 6 to Group 12 via the C_4 bridge.[30]

The inclusion of aromatic organic units into the carbon chain has been widely studied, and in particular, using the dialkyne 1,4-diethynylbenzene. Lavastre[49] and Faulkner[50] prepared $\{RuCl(L_2)_2\}_2(\mu\text{-}C{\equiv}CC_6H_4C{\equiv}C)$ [L_2 = dppm, dppe] (Scheme 10) via deprotonation of an intermediate vinylidene complex. Both complexes exhibited considerable delocalisation along the carbon chains, with the Ru(II) / Ru(III) cations being accessible. Field similarly prepared the analogous iron derivative.[51]



Scheme 10 : $\{RuCl(L_2)_2\}_2(\mu\text{-}C{\equiv}CC_6H_4C{\equiv}C)$ [L_2 = dppm, dppe].

Likewise, other organic fragments can be introduced into the carbon chain. Lapinte and coworkers have recently prepared the iron complex, Cp*(dppe)Fe-C≡C-2,5-C_4H_2S-C≡C-Fe(dppe)Cp* (**A**) which has shown electrochemical behaviour comparable to the related μ-C_4 compound.[52] The introduction of these organic units constitute an attractive means of chain extension of molecular wires, and in comparison with μ-C_8 compounds, the synthesis is greatly facilitated and the electron conduction between the two metal centres are apparently unaffected.



Cp*(dppe)Fe-C≡C-2,5-C_4H_2S-C≡C-Fe(dppe)Cp* (**A**)

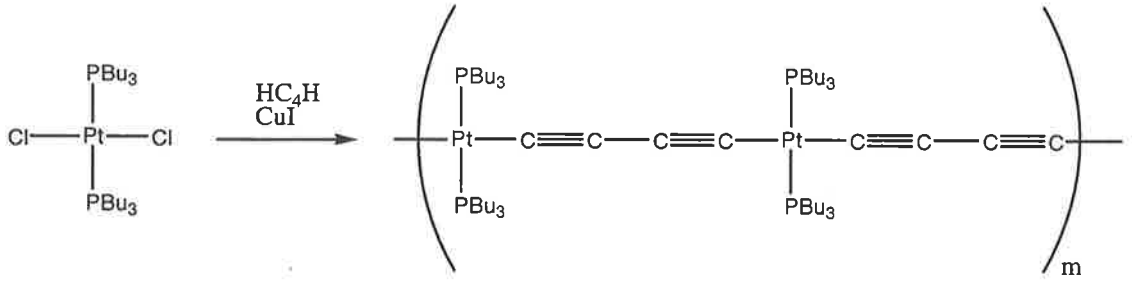
As with the other diyndiyl complexes heterometallic compounds containing organic fragments in the carbon chain are relatively rare with only Ru / Pd, Fe / Pd or Fe / Ni complexes being recently described.[53]

The formation of metal-containing polymers is of particular interest as they might exhibit properties either difficult or impossible to achieve with conventional organic polymers.[54,55] For example, polymeric materials in which metal centres are bridged by dialkynyls such as –C≡CC≡C- or –C≡C-R-C≡C- [R = aromatic rings, disilanes, or disiloxanes)[56] are attracting great attention and are known to display electrical conducting, non-linear optical or liquid crystalline properties.

Polymeric copper and mercury alkynyls were reported as early as 1960 and were proposed to have a linear geometry.[57] Mercury alkynyls have since been found to be useful alkynyl-exchange reagents, however they have not been extensively studied.

The first family of linear ethynylgold(I) complexes were prepared by Vicente, who showed that reaction of [ppn][Au(acac)$_2$] with acetylene gave [ppn][Au(C≡CH)$_2$]. Similarly, [ppn][Au(acac)$_2$] reacts with different alkynes to give [ppn][Au(C≡CR)$_2$] [R = Bu^t, SiMe$_3$, CH$_2$X (X = Cl, Br, OH), C$_6$H$_4$NO$_2$-4, C$_6$H$_4$C≡CH-4, C$_6$H$_4$C$_6$H$_4$NO$_2$-4,4', C$_6$H$_4$CH=CHC$_6$H$_4$NO$_2$-4,4'-E].[58,59] Puddephatt and coworkers have since developed the chemistry of linear gold polymers, which often display short intermolecular Au…Au contacts.[60]

In the 1970s, Hagihara and coworkers reported the first soluble polyynes containing Pt and Pd metal atoms in the main chain.[61,62] The 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≡CC≡CH)$_2$(PBu$_3$)$_2$ in 82% yield. An adjustment to the stoichiometry leads to di- or trimetallic species, or higher oligomers (Scheme 11). Subsequent work from this group has resulted in a general synthetic route to Group 10 metal containing polyynes, which can be prepared from dehydrohalogenation, oxidative coupling and alkynyl ligand exchange.[62,63]

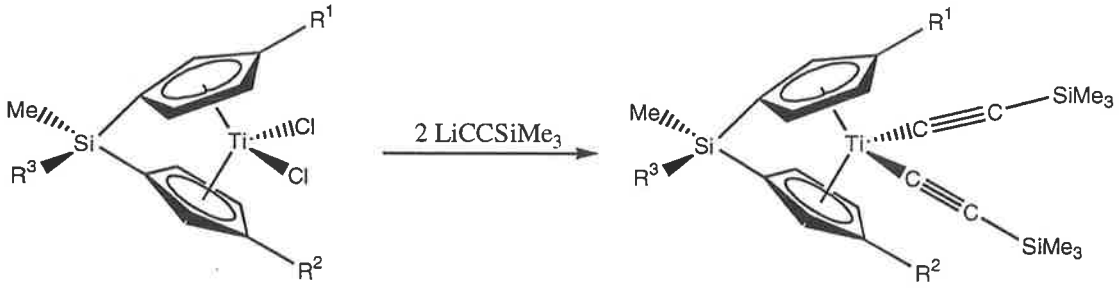


Scheme 11 : Preparation of a *trans*-$Pt(C{\equiv}CC{\equiv}CH)_2(PBu_3)_2$ polymer.

The first method involves a polycondensation reaction between metal halides and di-terminal alkynes via a copper(I) halide dehydrohalogenation process.[48,61,62,64-66] These reactions are typically performed in amine solvents such as diethylamine or piperidine. The second method involves oxidative homocoupling of the *bis*-alkynyl complexes in the presence of a catalytic amount of copper(I) halides and O_2 as the oxidising agent, more commonly referred to as the Hay coupling reaction.[29,67] Neither of these methods could be applied to metals of Group 8 and 9 due to instability of the starting complexes, however methods developed by Marder,[68,69] Lewis[70-73] and Lappert[74] have since resolved these difficulties.

Metal complexes bearing polyalkynyl fragments in which the polyalkyne chains are at angles other than 180° to each other are also attractive targets. In addition to the applications discussed previously for the linear C_n type molecules, the close proximity of the electron-rich triple bonds may serve to stabilise various mononuclear fragments or small molecules. These types of complexes have been given the term "molecular tweezers" and have properties reminiscent of traditional host-guest chemistry.

Van Koten, Lang and coworkers have prepared many complexes containing the Group 4 metals: titanium[75-78], zirconium[79] and hafnium[80], typically prepared from $Li(C{\equiv}C)_nR$ (n = 1, 2; R = $SiMe_3$, ^{t}Bu, Ph, Fc) and the corresponding dihalide metal complex. The reaction of $[(\eta^5\text{-}C_5H_3R)(\eta^5\text{-}C_5H_3R')SiMeR'']TiCl_2$ with two equivalents of $LiC{\equiv}CSiMe_3$ yielded the bis(alkynyl) *ansa*-titanocenes as the only isolated complex (Scheme 12).



Scheme 12 : Preparation of *bis*-alkynyl *ansa*-titanocenes.

Stabilisation of small metallic fragments have been explored by Lang employing $[Ti](C{\equiv}CSiMe_3)_2$ {[Ti] = $(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$} for the stabilisation of low-valent M(CO), $M(PR_3)$ (M = Ni,[81-83] Co,[83,84] Pt[85]) and $M(C_6F_5)_2$ (M = Pd, Pt[86]) as well as monomeric MX (M = Cu,[87] Ag,[88] Au[89]; X = singly bonded inorganic or organic ligand) and MCl_2 (M = Fe, Co, Ni[87,90]) entities, resulting in the formation of the η^2-coordinated monomeric ML_n building block (Figure 2). The feature about this coordination mode is the decrease of the bite angle θ (C_α-Ti-C_α') of the bis(alkynyl) titanocene fragment due to the tweezer effect of the $[Ti](C{\equiv}CSiMe_3)_2$ moiety,[79] often resulting in a *trans*-deformation of the $TiC{\equiv}CSiMe_3$ arm (Figure 2). Coordination of metal fragments can be followed by NMR and IR spectroscopy. The ^{13}C NMR showed a δ 20 ppm downfield shift for the C_α carbon, while the ν(C≡C) stretch shifted to lower wavenumbers, thus indicating a weakening of the C≡C triple bonds of the alkynyl ligands, due to the complexation.

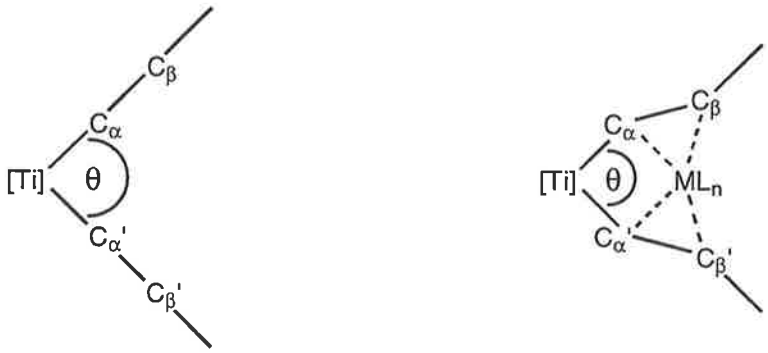


Figure 2 : Formation of the η^2-coordinated monomeric ML_n.

Square-planar platinum and palladium complexes are also potential bidentate systems (MX_2L_2) for tweezer formation. The use of these fragments allows for the formation of 90° subunits when *cis* precursors are used as the initial material. A number of methodologies are available for the synthesis of alkynylplatinum(II) complexes. Most involve the transfer of an alkynyl group from another metal to a platinum halide complex, others require the addition of the alkyne in the presence of a base. The reaction of *cis*-$PtCl_2L_2$ (L_2 = dppe, dmpe) with $Me_3SnC{\equiv}CR$ or $Me_3Sn(C{\equiv}CR)_2$ (R = H, Me, $SiMe_3$, Ph) in refluxing thf gives the corresponding *cis*-$Pt(C{\equiv}CR)_2L_2$ complex.[91]

Preparation of supramolecular species.

Rapid growth in the field of molecular design has resulted in a new synthetic strategy for the preparation of compounds with organised structures. This class of compounds is attracting increasing attention due to phenomena such as self-assembly, inclusion complexes, molecular recognition and non-covalent interactions. Contemporary supramolecular chemistry has its roots in the classic covalent macrocycles such as crown ethers, cyclophanes, cyclodextrins, calixarenes, cryptands, spherands and so on, predominantly featuring weak interactions such as hydrogen bonding, hydrophilic-hydrophobic interactions, π-π-stacking, electrostatic and van der Waals forces.

A completely different approach to the formation supramolecular species is by spontaneous self-assembly of precursor building blocks under appropriate conditions. This methodology has been successfully employed in the preparation of metal helicates,[92,93] oligomeric chains,[94] step ladders,[94] grids,[94] rings and cages[94] and more recently, dendrimers.[95,96]

The assemblies of these structures depend on the shape and individual properties of each component. Molecular architecture that employs transition metals and dative bonding to achieve structurally well defined, highly ordered compounds relies on the fact that fewer metal-ligand bonds are needed owing to their greater strength. Another advantage lies in the existence of a large variety of transition metals with

different coordination numbers, thus enabling the building of compounds with tremendous variations in shape and size.

The simultaneous assembly of preconstructed building blocks offers some important advantages over stepwise bond formation, the resulting syntheses being highly convergent and thus requiring fewer steps than the corresponding covalent syntheses. Also, since non-covalent interactions are usually established very rapidly, final product formation is fast and facile. The presence of these kinetically labile non-covalent interactions between the constituents results in the formation of relatively defect-free assemblies with self-maintained integrity since the usual equilibria between the constituents and the final products contribute to the self-rearrangement of components and correction of defects.

The design of artificial self-assembling systems is still in its early stages and requires the consideration of many factors, such as the type and strength of the bonds between various components, the symmetry of both the constituents and the entire self-assembled structure, the precise positioning of the coordination sites of the components, temperature, solvent polarity and possibly many others. The first step in solving these problems is the development of relatively simple, self-assembling structures of the desired shape and symmetry.

Principles and Design Strategies.

The structural and functional features of self-assembled supramolecular entities result from the configuration of their precursor components. Since transition metals have coordination sites with specific geometries that depend upon their electronic structure they can serve as acceptor subunits. These can be linked together via donor building blocks that form the rigid frame of the assembled entity. Both subunits must be multidentate or at least bidentate to form the desired cyclic structure.

The construction of cyclic geometries that contain a transition metal requires consideration of the angles required in the binding sites of both the donors and the acceptors. There are two main types based on the these angles, linear subunits, that possess reactive subunits with a 180° orientation relative to each other, and angular

subunits with smaller angles.[97] When these are combined the structure of the resulting species will be dependent on the symmetry and number of binding sites on each subunit. The assembly of a molecular triangle requires the coupling of three subunits with an internal angle of 60°. A molecular square can be prepared either by combining four linear and four angular building blocks, or by coupling two different angular subunits. Molecular pentagons by combining five linear components with five angular subunits that possess and internal angle of 109.5° and molecular hexagons from six linear and six angular subunits of 120° (Figure 3).

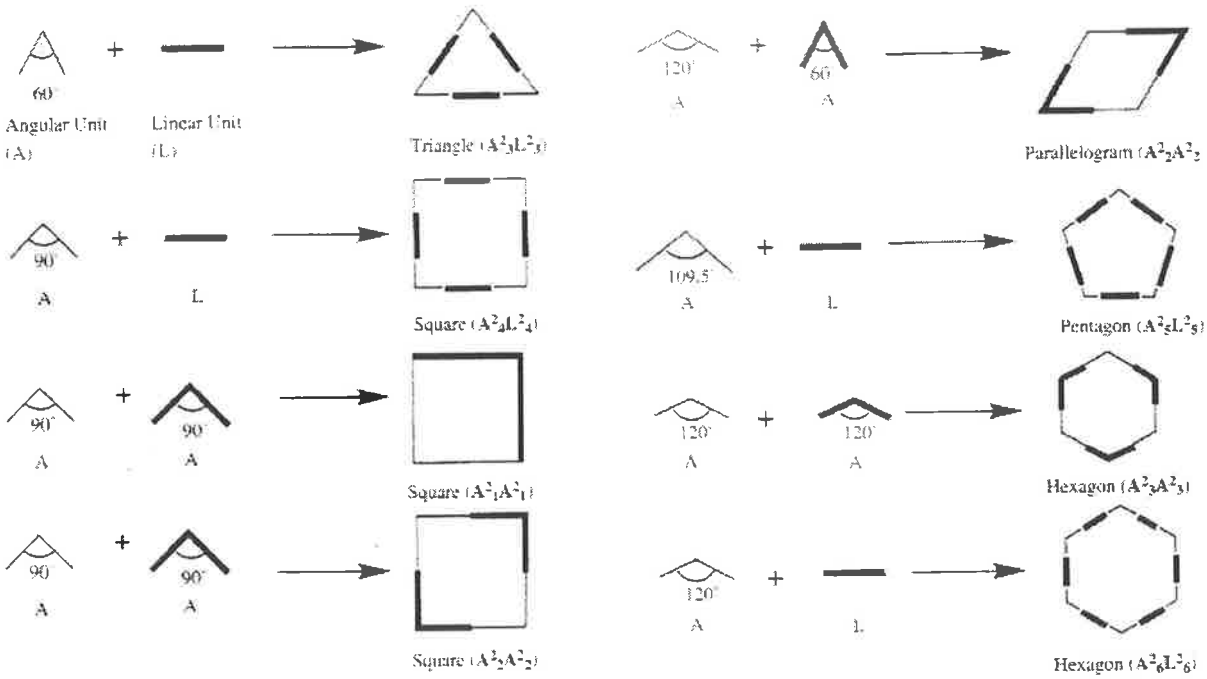
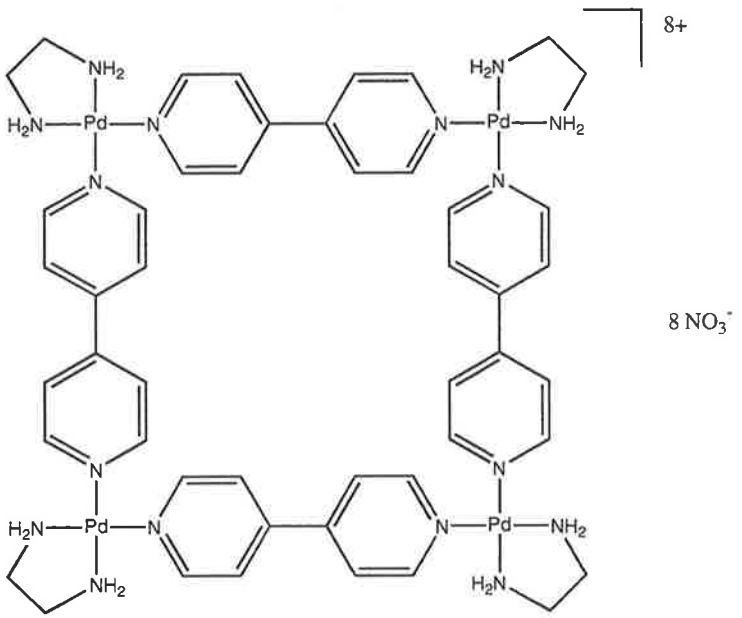


Figure 3 : Possible combinations of the building blocks necessary for the construction of polygons. Reproduced from P. J. Stang, *Chem. Eur. J.*, **1998**, *4*, No 1.

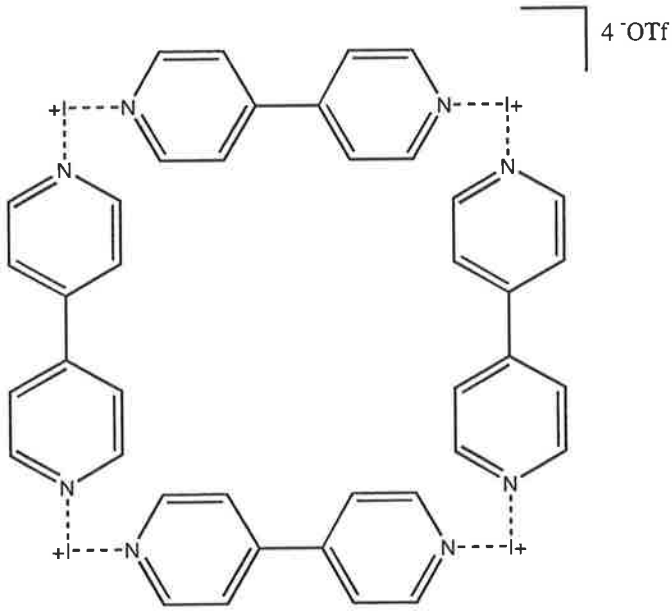
Construction of Molecular Squares.

The assembly of molecular squares can be achieved via a number of methods as outlined in Figure 3. Transition metals are ideally suited for the formation of the angular units, as there are many examples of suitable precursor complexes. Such examples include square planar complexes of Pd and Pt[98-100] or octahedral complexes.[101] Bivalent four-coordinate complexes of Pd and Pt can be forced into the *cis*-geometry by reaction with bisphosphines such as dppe, dppp or dppf. If the remaining coordination sites are occupied by labile ligands such as triflate, then upon interaction with linear units, a square assembly can be formed. Square complexes were first prepared by Fujita and coworkers who used [*cis*-(en)M(NO_3)$_2$] (M = Pd and Pt) and 4,4'-bipy (**B**) to form water soluble species. Furthermore, these compounds served as suitable hosts for various aromatic guests such as naphthalene, 1,4-dimethoxybenzene and others. [98-100]

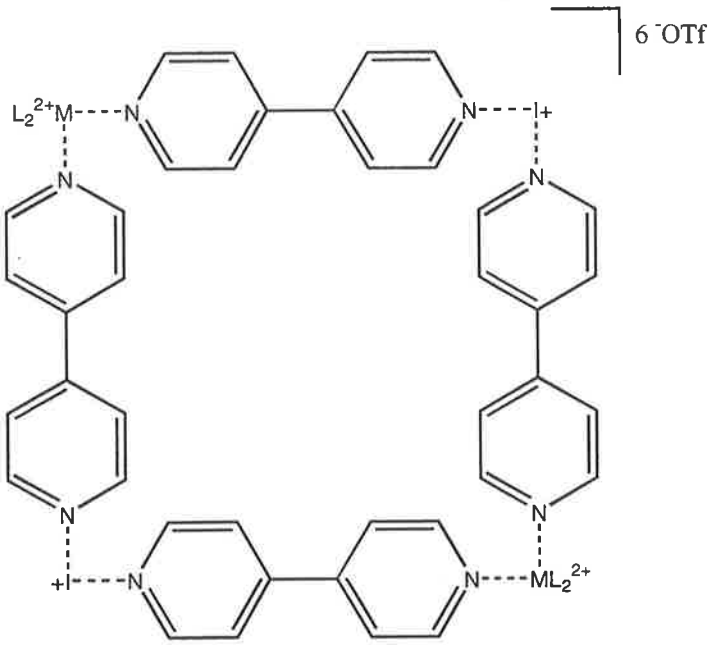


[(*cis*-en)Pd(NO_3)$_2$] and 4, 4'-bipy (**B**).

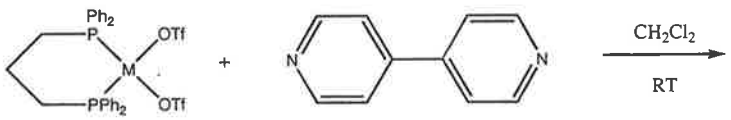
Stang and coworkers have been prolific in the area of square preparation, initially reporting the formation of a square tetraiodonium-aryl species (**C**).[102] In this compound the hypervalent iodine plays the role of the 90° corner subunits. The reaction of equimolar amounts of bis-(heteroaryl)iodonium triflates with bis-triflate complexes of palladium or platinum bisphosphines resulted in the formation of hybrid molecular squares (**D**).[103,104] Reaction of the triflate complexes with 4, 4'-bipy in CH_2Cl_2 at room temperature resulted in the formation of molecular squares in a matter of minutes in excellent yields (Scheme 13). The reactions each gave essentially one product and attempts to isolate possible intermediates, or to observe them by NMR spectroscopy have been unsuccessful. If pyrazine is used in place of 4,4'-bipy then only the monomer is formed, presumably due to the steric bulk of the phenyl groups on the dppp ligand. Using this methodology a vast array of squares have been prepared simply by varying the linear edge.[105,106]

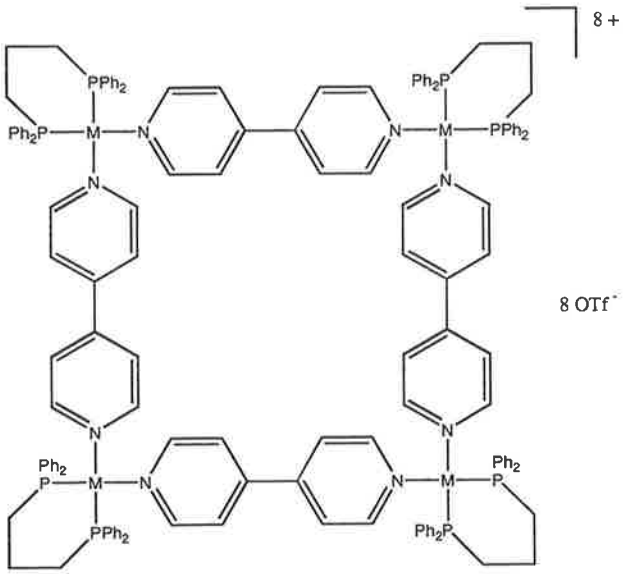


Square tetraaryl tetraiodonium species (**C**).



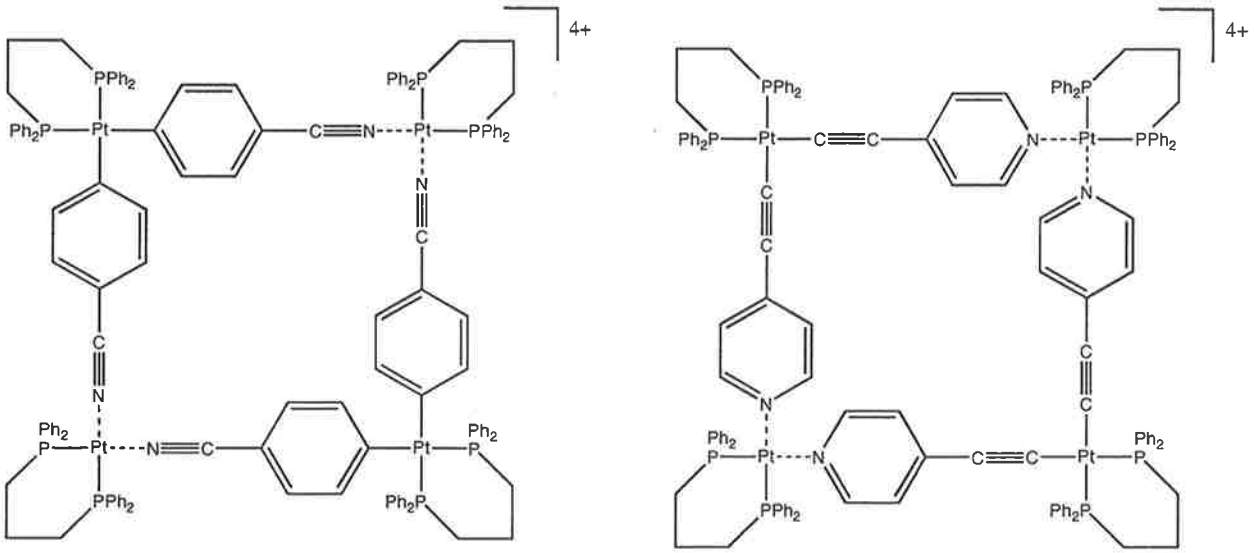
Formation of hybrid molecular squares (**D**).





Scheme 13 : Formation of Stang squares.

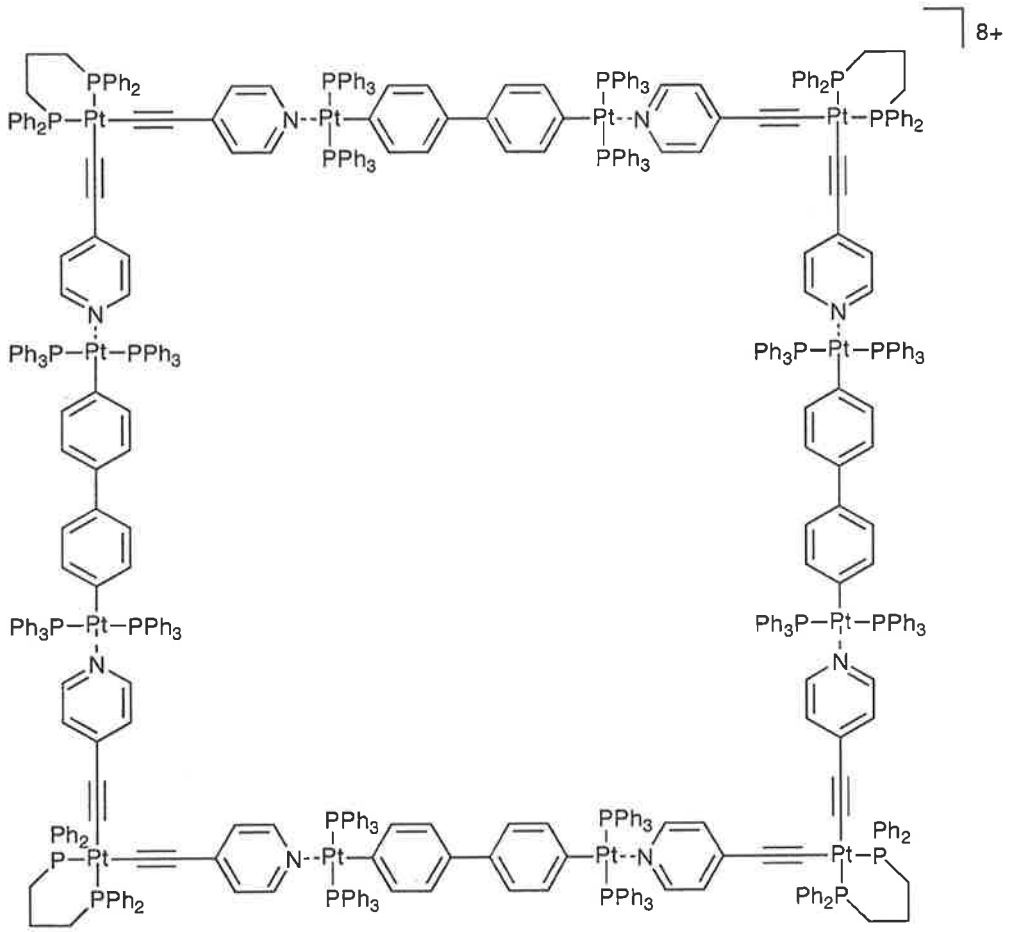
Squares prepared utilising this method are usually highly charged, typically +8. In order for molecular squares of lower charge to be prepared, covalent bonds between the corner subunit and the linear chain need to be formed. The easiest approach to this is to preconstruct neutral monomeric units with bidentate functionality. The preparation of these compounds is easily accomplished and is related to those used for the study of molecular tweezers. The synthesis of neutral monomeric subunits was first utilised by Stang, who used two structural motifs for the subunits, based on 4-iodobenzonitrile or 4-ethynylpyridine.[107] Lithiation, followed by immediate addition of $PtCl_2$(dppp) resulted in the formation of the monomer units in 83% and 68% yields respectively. Addition of these compounds to $Pt(OTf)_2$(dppp) resulted in the formation of molecular squares in which two of the corners are of neutral charge, however the overall charge of the molecule is still +4 (**E**).



Squares with neutral charged corners (**E**).

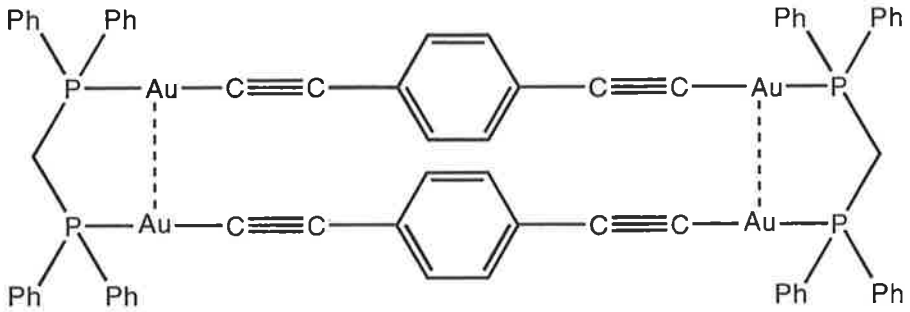
The preparation of larger squares is also readily achieved and demonstrates the versatility and ease with which these compounds are formed. The size of the cavity can easily be lengthened by extending the size of the linker units or with the inclusion of *trans*-metal species (**F**).[108] Squares of this size belong to the category of "ultrafine" particles, with edge dimensions of about 3.4 nm and 4.8 nm across the diagonal.

Although not commented on further here, larger geometries have been prepared utilising the same basic building techniques. These include two-dimensional hexagons[109] and three-dimensional octahedrons.[110,111]



Squares with nm-size cavities (**F**).

Formation of other shapes are also possible, with a series of gold compounds with rectangular geometry having been described (**G**).[112] These compounds make use of close Au...Au interactions and this affinity of gold atoms having prompted many studies and being termed "aurophilicity". These short contacts have been calculated to have a bond energy of the order of 5 – 10 kcal mol^{-1} and are comparable to that of a hydrogen bond.[113] Intramolecular Au...Au contacts lend significant stabilisation of multinuclear gold complexes and can confine compounds to a specific geometry.[114,115] The formation of intramolecular Au...Au contacts in the related complexes $(AuX)_2(\mu\text{-dppm})$ (dppm = $Ph_2PCH_2PPh_2$, X = Cl, $C{\equiv}CBu^t$), orient the X groups in the same direction.[114,115] Puddephatt and coworkers were able to use this principle in the formation of 26- and 34-membered rectangular gold rings.[112]



Rectangular gold compounds (**G**).

Work Described in this Thesis

While the preparation of cationic vinylidene complexes has been known for many years, the preparation of their corresponding neutral vinylidene analogues is rare. The retention of the chloride ion, and the ease in which the vinylidene proton is deprotonated by base may give rise to interesting compounds. The preparations of several neutral vinylidene complexes are described and their reactivities are explored. Addition of base in the presence of 2-e donor ligands result in the formation of chiral metal alkynyls. When the same reaction is done in the presence of 1-alkynes then di-, tri- or tetramerisation occurs. The preparation of compounds containing the substituted dialkyne, 1,4-bis-trimethylsilylethynylbenzene is then described, in which the reactivity of each alkynyl fragment is explored. Coupling methodologies mentioned above were used to prepare heterometallic complexes spaning transition metal elements from Group 6 to Group 12. These coupling methodologies were then used to prepare *cis*-bis-diyndiyl complexes of platinum. The reaction of buta-1,3-diyne, HC≡CC≡CH, with *cis*-$PtCl_2(L_2)$ yielded diyndiyl complexes, $Pt(C{\equiv}CC{\equiv}CH)_2(L_2)$. The reactivity of the diynyl ligand, C≡CC≡CH, in these complexes has been examined. The close proximity of the alkynyl chains allows for stabilisation of reactive metal fragments in a similar fashion to the "molecular tweezers" described by Lang and van Koten. The complexes *cis*-$Pt(C{\equiv}CC{\equiv}CH)_2(L_2)$ proved to be attractive precursors for the formation of neutral molecular squares. A method for their formation is detailed. The preparation of other geometries is also explored with the formation of a rectangular gold compound. The preparation of linear gold(I) compounds also enabled the formation of larger molecular square molecules.

REFERENCES.

(1) Beck, W.; Niemer, B.; Wieser, M. *Angew. Chem., Int. Engl. Ed.* **1993**, *32*, 923.

(2) Hunter, A. D. *Organometallics* **1989**, *8*, 1118.

(3) Chukwu, R.; Hunter, A. D.; Santarsiero, B. D. *Organometallics* **1992**, *11*, 589.

(4) Pollagi, T. P.; Stoner, T. C.; Dallinger, R. F.; Gilbert, T. M.; Hopkins, M. D. *J. Am. Chem. Soc.* **1991**, *113*, 703.

(5) Calabrese, J. C.; Cheng, L.-T.; Green, J. C.; Marder, S. R.; Tam, W. *J. Am. Chem. Soc.* **1991**, *113*, 7227.

(6) Meyers, L. K.; Langhoff, C.; Thompson, M. *J. Am. Chem. Soc.* **1992**, *114*, 7560.

(7) Lichtenberger, D. L.; Renshaw, S. K.; Bullock, R. M. *J. Am. Chem. Soc.* **1993**, *115*, 3276.

(8) Lichtenberger, D. L.; Renshaw, S. K.; Wong, A.; Tagge, C. D. *Organometallics* **1993**, *12*, 3522.

(9) Frasier, C. C.; Guha, S.; Chen, W. P.; Cockerman, M. P.; Porter, P. L.; Chauchard, E. A.; Lee, C. H. *Polymer* **1987**, *28*, 553.

(10) Stoner, T. C.; Dallinger, R. F.; Hopkins, M. D. *J. Am. Chem. Soc.* **1990**, *112*, 5651.

(11) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197.

(12) Davison, A.; Selegue, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 7763.

(13) Bruce, M. I.; Wallis, R. C. *J. Organomet. Chem.* **1978**, *161*, C1.

(14) Davison, A.; Selegue, J. P. *J. Am. Chem. Soc.* **1980**, *102*, 2455.

(15) Berke, H. *Z. Naturforsch., Teil B* **1980**, *35*, 86.

(16) Bruce, M. I.; Humphrey, M. G.; Koutsantonis, G. A.; Liddell, M. J. *J. Organomet. Chem.* **1987**, *320*, 217.

(17) Bruce, M. I.; Humphrey, M. G.; Liddell, M. J. *J. Organomet. Chem.* **1987**, *321*, 91.

(18) Bruce, M. I.; Koutsantonis, G. A.; Liddell, M. J.; Nicholson, B. K. *J. Organomet. Chem.* **1987**, *320*, 217.

(19) King, R. B. *Ann. N.Y. Acad. Sci.* **1974**, *239*, 171.

(20) Antonova, A. B.; Kolobova, N. E.; Petrovsky, P. V.; Lokshin, B. V.; Obezyuk, N. S. *J. Organomet. Chem.* **1977**, *137*, 55.

(21) Mills, O. S.; Redhouse, A. D. *J. Chem. Soc., Chem. Commun.* **1968**, 444.

(22) Stang, P. J. *Chem. Rev.* **1978**, *78*, 383.

(23) Bruce, M. I.; Swincer, A. G. *Adv. Organometal. Chem.* **1983**, *22*, 59.

(24) Bruce, M. I.; Hall, B. C.; Tiekink, E. R. T. *Aust. J. Chem.* **1997**, *50*, 1097.

(25) Glaser, C. *Ber. Dtsch. Chem. Ges.* **1869**, *2*, 422.

(26) Glaser, C. *Ann, Chem.* **1870**, *154*, 137.

(27) Behr, O. M.; Eglinton, G.; Galbraith, A. R.; Raphael, R. A. *J. Chem. Soc.* **1960**, 3614.

(28) Eglinton, G.; Galbraith, A. R. *Chem. Ind.* **1956**, 737.

(29) Hay, A. S. *J. Org. Chem.* **1962**, *27*, 3320 and references therin.

(30) Bruce, M. I.; Ke, M.; Low, P. J. *Chem. Commun.* **1996**, 2405.

(31) Bruce, M. I.; Ke, M.; Low, P. J.; Skelton, B. W.; White, A. H. *Organometallics* **1998**, *17*, 3539.

(32) Bartik, T.; Bartik, B.; Brady, M.; Dembinski, R.; Gladysz, J. *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 414.

(33) Lapinte, C.; Narvor, N. L.; Toupet, L. *J. Am. Chem. Soc.* **1995**, *117*, 7129.

(34) Low, P. J. Ph.D Thesis, University of Adelaide, **1996**.

(35) Bruce, M. I.; Low, P. J.; Costuas, K.; Halet, J.-F.; Best, S. P.; Heath, G. A. *J. Am. Chem. Soc.* **2000**, *122*, 1949.

(36) Cadiot, P.; Chodkiewicz, W. *Chemistry of Acetylenes*; Marcel Dekker: New York, **1969**.

(37) Brandsma, L.; Verkruijsse, H. D. *Synthesis of Acetylenes, Allenes and Cumulenes*; Elsevier: Amsterdam, **1981**.

(38) Bohlmann, F.; Herbst, P.; Gleinig, H. *Chem. Ber.* **1961**, *94*, 948.

(39) Berscheid, R.; Vogtle, F. *Synthesis* **1992**, 58.

(40) Chodkiewicz, W. *Ann. Chim. (Paris)* **1957**, *2*, 819.

(41) Eglinton, G.; McRae, W. *Adv. Org. Chem.* **1963**, *4*, 225.

(42) Black, H. K.; Horn, D. H. S.; Weedon, B. G. L. *J. Chem. Soc* **1954**, 1704.

(43) Miller, J. A.; Zweifel, G. *Synthesis* **1983**, 128.

(44) Kitamura, T.; Lee, C. H.; Taniguchi, H.; Masumoto, M.; Sano, Y. *J. Org. Chem.* **1994**, *59*, 8053.

(45) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508.

(46) Wong, A.; Kang, P. C. W.; Tagge, C. D.; Leon, D. R. *Organometallics* **1990**, *9*, 1992.

(47) Weng, W.; Bartik, T.; Brady, M.; Bartik, B.; Ramsden, J. A.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1995**, *117*, 11922.

(48) Sonogashira, K.; Kataoka, S.; Hagihara, N. *J. Organomet. Chem.* **1978**, *160*, 319.

(49) Lavastre, O.; Plass, J.; Bachmann, P. *Organometallics* **1997**, *16*, 184.

(50) Faulkner, C. W.; Ingham, S. L.; Khan, M. S.; Lewis, J.; Long, N. J. *J. Organomet. Chem.* **1994**, *482*, 139.

(51) Field, L. D.; George, A. V.; Laschi, F.; Malouf, E. Y.; Zanello, P. *J. Organomet. Chem.* **1992**, *425*, 347.

(52) Stang, S. L.; Paul, F.; Lapinte, C. *Organometallics* **2000**, *19*, 1035.

(53) Lavastre, O.; Even, M.; Dixneuf, P. H.; Pacreau, A.; Vairon, J. P. *Organometallics* **1996**, *15*, 1530.

(54) Zeldin, M.; Wynne, K. J.; Allock, H. R. *Inorganic and Organometallic Polymers: Macromolecules Containing Silicon, Phosphorus and Other Inorganic Elements*; American Chemical Society: Washington, DC, **1988**.

(55) Laine, R. M. *Inorganic and Organometallic Polymers with Special Properties*; Kluwer: Boston, **1992**.

(56) Porter, P. L.; Guha, S.; Kang, K.; Frazier, C. C. *Polymer* **1991**, *32*, 1756 and references therin.

(57) Hay, A. S. *J. Org. Chem.* **1960**, *25*, 1275.

(58) Vicente, J.; Chicote, M. T.; Abrisqueta, M. D.; Jones, P. G. *Organometallics* **1997**, *16*, 5628.

(59) Vicente, J.; Chicote, M. T.; Abrisqueta, M. D. *J. Chem. Soc., Dalton Trans.* **1995**, 497.

(60) Puddephatt, R. J. *Chem. Commun.* **1998**, 1055.

(61) Fujikura, Y.; Sonogashira, K.; Hagihara, N. *Chem. Lett.* **1975**, 1067.

(62) Sonogashira, K.; Takahashi, S.; Hagihara, N. *Macromolecules* **1977**, *10*, 879.

(63) Hagihara, N.; Sonogashira, K.; Takahashi, S. *Adv. Polym. Sci.* **1981**, *41*, 149.

(64) Takahashi, S.; Kariya, M.; Yatake, T.; Sonogashira, K.; Hagihara, N. *Macromolecules* **1978**, *11*, 1063.

(65) Takahashi, S.; Ohyama, Y.; Murata, E.; Sonogashira, K.; Hagihara, N. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 349.

(66) Takahashi, S.; Morimoto, H.; Murata, E.; Kataoka, S.; Sonogashira, K.; Hagihara, N. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 565.

(67) Takahashi, S.; Murata, E.; Sonogashira, K.; Hagihara, N. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 661.

(68) Fyfe, H. B.; Mlekuz, M.; Zaragarian, D.; Marder, T. B. In *Organic Materials for Nonlinear Optics II*; Hahn, R. A., Bloor, D., Eds.; The Royal Society of Chemistry: Cambridge, **1991**; Vol. Spec. Pub. No. 91.

(69) Fyfe, H. B.; Mlekuz, M.; Zaragarian, D.; Taylor, N. J.; Marder, T. B. *J. Chem. Soc., Chem. Commun.* **1991**, 188.

(70) Davies, S. J.; Johnson, B. F. G.; Lewis, J.; Raithby, P. *J. Organomet. Chem.* **1991**, *414*, C51.

(71) Johnson, B. F. G.; Kakkar, A. K.; Khan, M. S.; Lewis, J.; Raithby, P. *J. Organomet. Chem.* **1991**, *409*, C12.

(72) Khan, M. S.; Kakkar, A. K.; Ingham, S. L.; Raithby, P. R.; Lewis, J.; Spenser, B.; Whittman, F.; Friend, R. H. *J. Organomet. Chem.* **1994**, *472*, 247.

(73) Faulkner, C. W.; Ingham, S. L.; Khan, M. S.; Lewis, J.; Long, N. J.; Raithby, P. R. *J. Organomet. Chem.* **1994**, *482*, 139.

(74) Cardin, C. J.; Cardin, D. J.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1977**, 767.

(75) Janssen, M. D.; Herres, M.; Zsolnai, L.; Grove, D. M.; Spek, A. L.; Lang, H.; Van Koten, G. *Organometallics* **1995**, *14*, 1098.

(76) Lang, H.; Weber, C. *Organometallics* **1995**, *14*, 4415.

(77) Lang, H.; Blau, S.; Pritzkow, H.; Zsolnai, L. *Organometallics* **1995**, *14*, 1850.

(78) Lang, H.; Frosch, W.; Wu, I. Y.; Blau, S.; Nuber, B. *Inorg. Chem.* **1996**, *35*, 6266.

(79) Lang, H.; Blau, S.; Nuber, B.; Zsolnai, L. *Organometallics* **1995**, *14*, 3216.

(80) Back, S.; Rheinwald, G.; Zsolnai, L.; Huttner, G.; Lang, H. *J. Organomet. Chem.* **1998**, *563*, 73.

(81) Yasufuku, K.; Yamazaki, H. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 2664.

(82) Lang, H.; Imhof, W. *Chem. Ber.* **1992**, *125*, 1307.

(83) Lang, H.; Herres, M.; Zsolnai, L. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 429.

(84) Lang, H.; Zsolnai, L. *J. Organomet. Chem.* **1991**, *406*, C5.

(85) Ciriano, M.; Howard, J. A. K.; Spencer, J. L.; Stone, F. G. A.; Wadepohl, H. *J. Chem. Soc., Dalton Trans.* **1979**, 1749.

(86) Fornies, J.; Lalinde, E.; Martinez, F.; Moreno, M. T.; Welch, A. J. *J. Organomet. Chem* **1993**, *455*, 271.

(87) Lang, H.; Herres, M.; Zsolnai, L.; Imhof, W. *J. Organomet. Chem.* **1991**, *409*, C7.

(88) Lang, H.; Herres, M.; Zsolnai, L. *Organometallics* **1993**, *12*, 5008.

(89) Lang, H.; Köhler, K.; Zsolnai, L. *Chem. Commun.* **1996**, 2044.

(90) Herres, M.; Lang, H. *J. Organomet. Chem.* **1994**, *480*, 235.

(91) Sebald, A.; Wrackmeyer, B. *Z. Naturforsch., Teil B* **1983**, *38*, 1156.

(92) Williams, A. *Chem. Eur. J.* **1997**, *3*, 15.

(93) Constable, E. C. *Polynuclear Transition Metal Helicates*; Pergamon: Oxford, **1996**.

(94) Baxter, P. N. W. *Metal Ion Directed Assembly of Complex Molecular Architectures and Nanostructures*; Permagon: Oxford, **1996**.

(95) Liu, G. X.; Puddephatt, R. J. *Organometallics* **1996**, *15*, 5257.

(96) Achar, S.; Vittal, J. J.; Puddephatt, R. J. *Organometallics* **1996**, *15*, 43.

(97) Stang, P. J.; Olenyuk, B. *Acc. Chem. Res.* **1997**, *30*, 502.

(98) Fujita, M.; Yazaki, J.; Ogura, K. *J. Am. Chem. Soc.* **1990**, *112*, 5645.

(99) Fujita, M.; Nagao, S.; Iida, M.; Ogata, K.; Ogura, K. *J. Am. Chem. Soc.* **1993**, *115*, 1574.

(100) Fujita, M.; Yazaki, J.; Kuramachi, T.; Ogura, K. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 1837.

(101) Slone, R. V.; Hupp, J. T.; Stern, C. L.; Albrecht-Schmitt, T. E. *Inorg. Chem.* **1996**, *35*, 4097.

(102) Stang, P. J.; Olenyuk, B.; Chen, K. *Synthesis* **1995**, 937.

(103) Stang, P. J.; Chen, K. *J. Am. Chem. Soc.* **1995**, *117*, 1667.

(104) Stang, P. J.; Chen, K.; Arif, A. M. *J. Am. Chem. Soc.* **1995**, *117*, 8793.

(105) Stang, P. J.; Cao, D. H.; Saito, S.; Arif, A. *J. Am. Chem. Soc.* **1995**, *117*, 6273.

(106) Stang, P. J.; Cao, D. H. *Organometallics* **1994**, *116*, 4981.

(107) Whiteford, J. A.; Lu, C. V.; Stang, P. J. *J. Am. Chem. Soc.* **1997**, *119*, 2524.

(108) Manna, J.; Whiteford, J. A.; Stang, P. J.; Muddiman, D. C.; Smith, R. D. *J. Am. Chem. Soc.* **1996**, *118*, 8731.

(109) Stang, P. J.; Persky, N. E.; Manna, J. *J. Am. Chem. Soc.* **1997**, *119*, 4777.

(110) Fujita, M.; Ogura, D.; Miyazawa, M.; Oka, H.; Yamaguchi, K.; Ogura, K. *Nature* **1995**, *378*, 469.

(111) Stang, P. J.; Olenyuk, B.; Muddiman, D. C.; Smith, R. D. *Organometallics* **1997**, *16*, 3094.

(112) Irwin, M. J.; Rendina, L. M.; Vittal, J. J.; Puddephatt, R. J. *Chem. Commun.* **1996**, 1281.

(113) Schmidbaur, H. *Chem. Revs.* **1995**, 391.

(114) Schmidbaur, H.; Wohlenben, A.; Wagner, F.; Orama, O.; Hutt, G. *Chem. Ber.* **1977**, *110*, 1748.

(115) Payne, N. C.; Ramachandran, R.; Puddephatt, R. J. *Can. J. Chem.* **1995**, *73*, 6.

Chapter 2

Chemistry of Neutral Vinylidenes

INTRODUCTION.

The complexes $[M(C{=}CHR^1)L_2Cp]^+$ and the related acetylides $M(C{\equiv}CR)L_2Cp$ [M = Fe, Ru, Os; L = CO, PR_3, $P(OR)_3$] have played a seminal role in the development of the chemistry of the vinylidene ligand.[1,2] Many workers have explored their reactivity and they are beginning to feature in organic chemistry.[3-5] Many early studies of these complexes were made using d^6 and d^8 metal centres, of which the $M(PR_3)_2Cp$[2,6] and $MCl(PPr^i_3)_2$[7,8] (M = Fe, Ru, Os; PR_3 = tertiary phosphine or phosphite) fragments predominate. Such complexes can easily be obtained from 1-alkynes and their formation is facilitated by the presence of electron-rich metal centres. The kinetic stability of these complexes is enhanced by the presence of bulky ligands, such as PPh_3, which offer steric protection to C(1) of the vinylidene ligand. For the Group 8 complexes, coordination of the 1-alkyne is followed by the isomerisation to the vinylidene, probably by a concerted 1,2-hydrogen shift and the formation of the M-C bond.[9]

Recently solid experimental evidence has been obtained for an alternative route involving oxidative addition of the 1-alkyne to the metal centre, followed by the migration of the metal-bonded hydrogen to C(2).[10] Vinylidene complexes of other transition metals have also been studied, particularly neutral complexes of Rh and Ir by Werner's group[11] and cationic derivatives of the $RuX(dppm)_2$[12] and $RuCl(PR_3)(\eta\text{-arene})$[13] systems which have been studied extensively by Dixneuf and coworkers.

The introduction of the bulky 1,2,3,4,5–pentamethylcyclopentadienyl, Cp*, group has seemingly little effect on the synthesis of vinylidene complexes in the ruthenium system, the complexes $[Ru(C{=}CHR)(PMe_2Ph)_2Cp^*]^+$ (R = H, Ph, CH_2OH, CH_2OMe and CHMeOMe) being described.[14] More recently, it was found that the intermediate

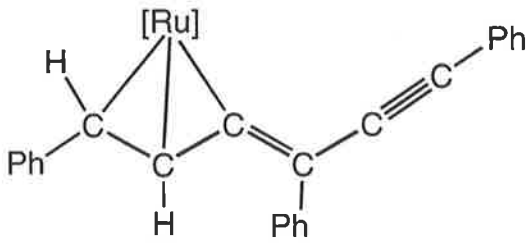
hydridoalkynyl complexes RuH(C_2R)(dppee)Cp* [R = Ph, CO_2Me, $SiMe_3$; dppee = bis-1,2(diphenylphosphino)ethylene] could be obtained from RuCl(dppee)Cp* and 1-alkynes in MeOH in the presence of Na[BPh_4].[15] These complexes rearrange irreversibly to the corresponding vinylidene complexes. However, until recently, most vinylidene complexes were cationic, of the type [Ru(C=CHR)(PR'$_3$)$_2$Cp]$^+$, which were obtained from the precursor chloro complex [RuCl(PR'$_3$)$_2$Cp] by dissociation of the halide, especially in polar solvents, such as MeOH.[16] Conversely, in the case of the larger PPh_3 ligand, the reaction takes a different course. The well-established loss of a bulky PPh_3 ligand from RuCl(PPh_3)$_2$Cp[17] can be applied to the formation of neutral vinylidene complexes. Thus, the reaction of RuCl(PPh_3)$_2$Cp* and 1-alkynes in MeOH gives a mixture of cationic [Ru(C=CCHR)(PPh_3)$_2$Cp*]$^+$ and neutral RuCl(C=CHR)(PPh_3)Cp*, due to the displacement of Cl^- or PPh_3 respectively from the precursor, owing to the presence of the bulky Cp* and PPh_3 ligands. When this reaction is run in non-polar solvent (benzene) the tendency for the Cl^- to ionise is reduced and thus the neutral vinylidene is obtained in higher yield.

Displacement of one of the PR_3 ligands and formation of a neutral vinylidene complex had not been observed prior to the commencement of this work, although publications since have described related complexes, such as RuCl(C=CHPh){PPr$^i_2$$CH_2$C(O)OMe-*O,P*}Cp*[18], RuCl(C=$CHCO_2$Me){PPh_3}Cp*[19] and RuCl(C=CHPh)(PPh_3){HB($pz)_3$} in which the dimerisation of 1-alkynes to substituted butenynes was catalysed.[20] Other neutral vinylidene ruthenium(II) complexes prepared during the course of this work include $RuCl_2$(C=CHPh){PPr$^i_2$$CH_2$C(O)OMe-*O,P*}(*P*-PPr$^i_2$$CH_2CO_2$Me),[21] $RuCl_2$(C=CHPh)($PPh_2C_2H_4NMe_2$-*N,P*)($PPh_2C_2H_4NMe_2$-*P*),[22] RuX_2(C=CHPh)(EPr$^i_2$$C_2H_4$OMe-*O,P*)(PPr$^i_2$$CH_2$OMe-*P*) [E = P or As; X_2 = Cl_2, Br_2, BrCl or $(CN)_2$][8,23] and $RuCl_2$(C=CHR)(pnp) [R = Ph or C_6H_4Me-*p*; pnp = PrN($C_2H_4PPh_2)_2$].[24,25]

This chapter describes reactions of the neutral vinylidene complexes in the presence of base (NaOMe or $NHMe_2$) and another ligand, L ($\neq$ PPh_3), which have afforded chiral complexes Ru(C≡CR)(L)(PPh_3)Cp* by formal 1,3-elimination of HCl.[2] These complexes were formed with a variety of ligands, including CO, C_2H_4, O_2 and S_2.

Addition of cationic electrophiles to the alkynyl compounds gives the corresponding cationic vinylidene complexes.

The finding that $RuH_3(PR_3)Cp^*$ (R = Ph, Cy, Me) are effective catalysts for the dimerisation of 1-alkynes to 1,3- and *cis*- and *trans*-1,4-enynes has been interpreted in terms of coupling of alkynyl and vinylidene ligands at the ruthenium centre with the stereochemistry being determined by the orientation of the vinylidene.[26] It was noted also that 1,2,3-trienes were obtained from HC≡CR (exclusively for R = CH_2Ph, 16% for R = Bu^t) and that trimers or higher oligomers were obtained with smaller alkynes. Later, it was found that the complex $Ru(C{\equiv}CPh)(PPh_3)_2Cp^*$ catalysed the dimerisation of HC≡CR (R = Ph, CO_2Me) via the novel allylic complex, $Ru\{\eta^3$-$PhCHCHC{=}CPh(C{\equiv}CPh)\}(PPh_3)Cp^*$ **21**.[27,28] The complex may be solvated or possess an agostic Ru...H interaction as found spectroscopically for the product obtained from $RuCl(C{=}CHBu^t)(PPh_3)Cp^*$ and C_2Me_2.[29]



21

Independently, we have found that complex **21** is formed in the reaction between $RuCl(C{=}CHPh)(PPh_3)Cp^*$ **3** and an excess of HC≡CPh in the presence of NaOMe. Further examination of this reaction and the use of alkynyl anions as reagents have resulted in the formation of complexes containing organic ligands derived from two, three or four molecules of alkyne. The organic ligands are linear oligomers and these reactions represent a novel method of coupling alkynes at a ruthenium centre.

RESULTS AND DISCUSSION.

The reaction between $RuCl(PPh_3)_2Cp^*$ **1**[30,31] and phenylacetylene was carried out in refluxing ethanol in a manner similar to that described for $RuCl(PPh_3)_2Cp$ and related complexes [32]. After cooling, addition of metallic sodium to the brown solution resulted in formation of a yellow precipitate, which was characterised as the anticipated phenylethynyl complex $Ru(C{\equiv}CPh)(PPh_3)_2Cp^*$ (**2**, Scheme 1) by elemental analysis, IR and NMR spectroscopy. The IR spectrum contained $\nu(C{\equiv}C)$ at 2066 cm^{-1} and the ^1H NMR spectrum contained resonances for the Cp* methyl groups at δ 1.19 and a multiplet for the aromatic protons between δ 7.0 - 7.5. The ^{13}C NMR spectrum contained resonances for the Cp* carbons at δ 9.49 (Me) and 93.46 (ring C) and C(1) of the C≡CPh group at δ 122.56. The FAB mass spectrum contained M^+ at *m/z* 862, which fragmented by loss of Ph, C_2Ph and PPh_3 groups.

A similar reaction between **1** and HC≡CPh in refluxing benzene produced a red solution, from which a red crystalline complex **3** was separated by preparative TLC in 67% yield. A small amount of **2** was also obtained. Complex **3** was identified as $RuCl(C{=}CHPh)(PPh_3)Cp^*$ by means of an X-ray structure determination (Figure 1). In the IR spectrum, $\nu(C{=}C)$ bands at 1590 and 1606 cm^{-1} were present. Characteristic NMR data included ^1H resonances at δ 1.48 (Cp*) and 4.51 (=CH) and ^{13}C NMR signals at δ 9.53 and 112.99 (Me and ring C of Cp*), C(2) at δ 102.34 and the characteristic low field doublet at δ 339.95 for the Ru-C= carbon. The FAB mass spectrum did not contain a molecular ion, but showed $[M - Cl]^+$ and $[M - C{=}CHPh]^+$ at *m/z* 601 and 534, respectively. The bond parameters of the $RuCl(PPh_3)Cp^*$ moiety is similar to those reported in other related complexes. The Ru-Cl and Ru-P distances fall within the normal ranges, although they are somewhat shorter than those found in $RuCl(PPh_3)_2Cp$,[33-35] probably because of relief of steric strain that occurs in the latter complex. The Ru-C(Cp*) distances range between 2.20 - 2.35(2) Å, again similar to those found in Ru-Cp complexes. Of note are the Ru-C(vinylidene) distances, which at 1.80(1) and 1.84(1) Å respectively, are shorter than those found in the cationic analogues. This may reflect the increase in back-bonding between Ru and the vinylidene compared with that in the cation.

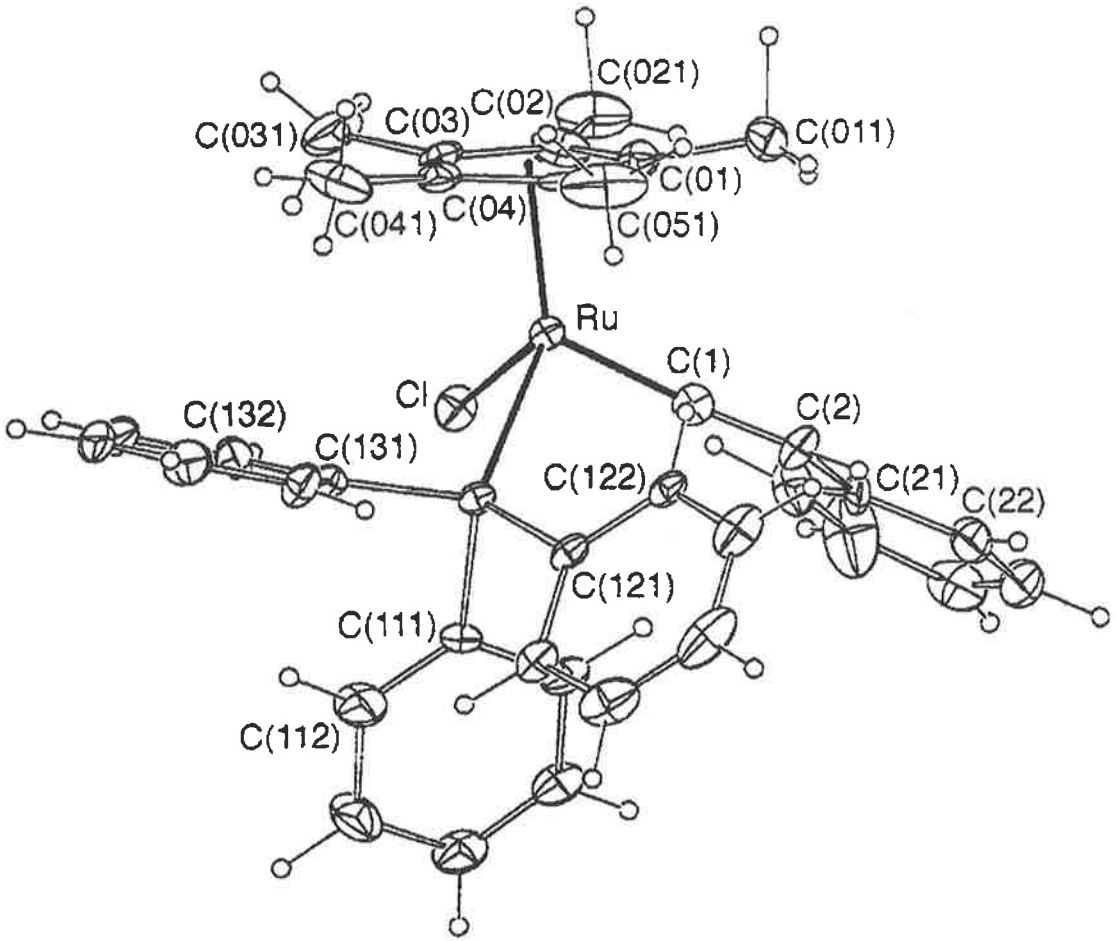


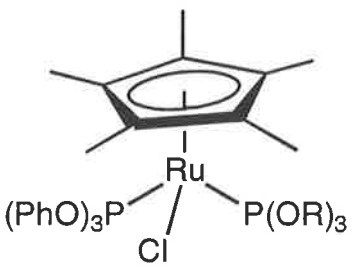
Figure 1 : Molecular projection of RuCl(C=CHPh)(PPh_3)Cp* **3** normal to the Ru-Cp*(centroid) vector.

Complex **3** is a novel and readily available example of a neutral vinylidene complex containing a d^6 metal centre. It has important potential as an intermediate in further reactions. The Cl ligand can be replaced by anionic nucleophiles, while the Cp* and tertiary phosphine ligands render the metal centre extremely electron-rich. As will be shown below the chemistry of **3** is significantly different from that of related cationic $[Ru(C{=}CHR)(PR'_3)_2Cp]^+$ complexes which has been extensively developed.[1]

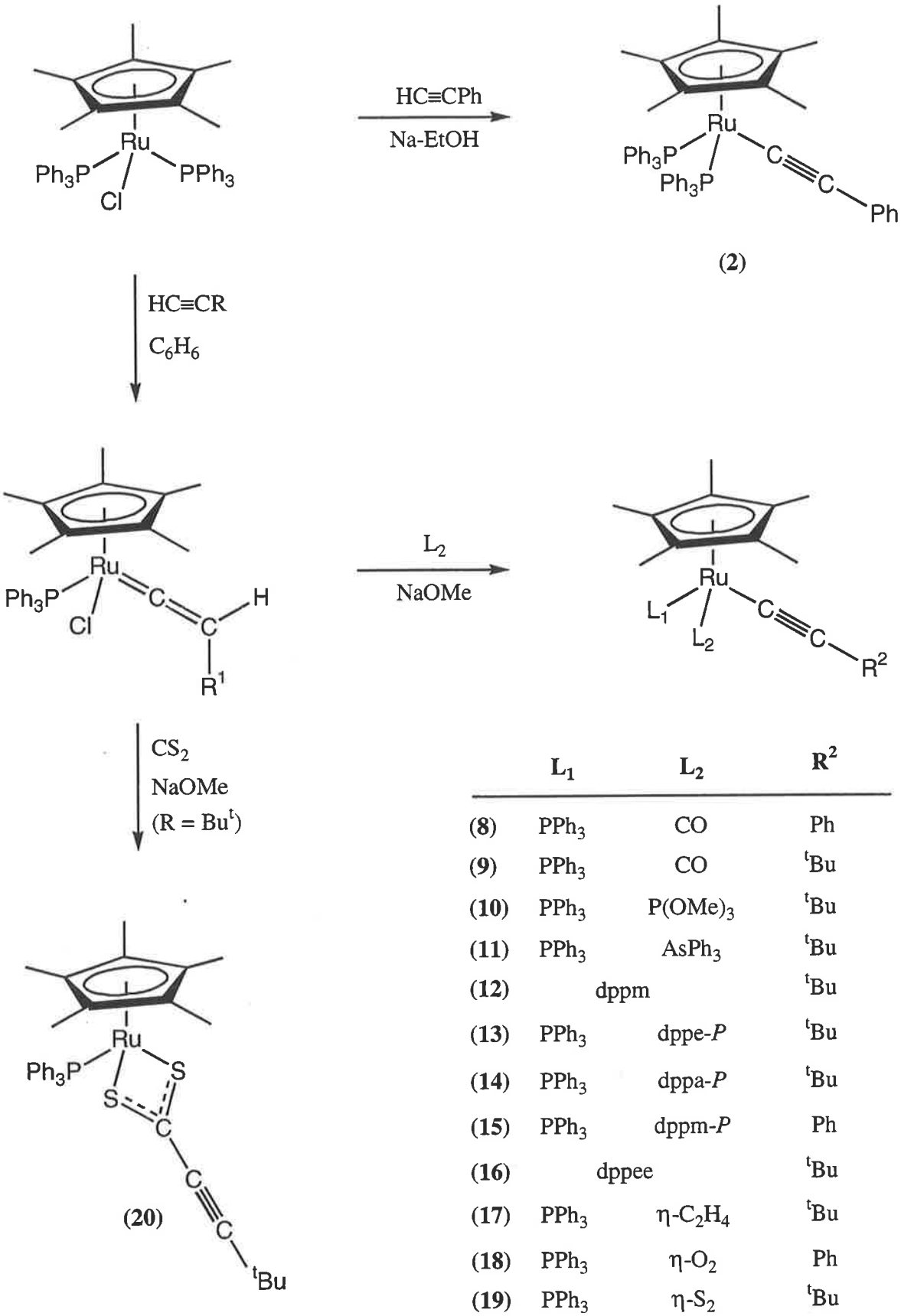
Similar reactions with $HC{\equiv}CBu^t$ and $HC{\equiv}CSiMe_3$ gave the corresponding red or orange neutral vinylidene complexes RuCl(C=CHR)(PPh_3)Cp* [R = Bu^t **4**, $SiMe_3$ **5**], the former being characterised by the low field ^{13}C NMR resonance at δ 336.38. Other spectroscopic data were consistent with these structures and are detailed in the

experimental section. A yellow product was obtained from propyne, but characterised only spectroscopically as $RuCl(C{=}CHMe)(PPh_3)Cp^*$ **6**. If the reaction between **1** and $HC{\equiv}CBu^t$ was carried out in more polar solvents, such as ethanol, and the resulting cationic vinylidene was deprotonated with sodium, the anticipated yellow acetylide $Ru(C{\equiv}CBu^t)(PPh_3)_2Cp^*$ **7** was obtained instead. The IR spectra of this complex contained a $\nu(C{\equiv}C)$ band at 2080 cm^{-1}.

The reactivities of these complexes have been probed briefly. The reaction of **3** with phosphite ligands in refluxing xylene resulted in the unusual displacement of the vinylidene and formation of $RuCl\{P(OR)_3\}_2Cp^*$ (R = Me or Ph).[36] This reaction contrasts those of the cationic Cp analogues, which are generally resistant to ligand exchange. We sought milder conditions to preserve the vinylidene or derived ligands and have found that treatment of complexes **3** or **4** with 2-e donor ligands (L) in the presence of base (NaOMe) readily afforded the corresponding acetylides $Ru(C{\equiv}CR)(L)(PPh_3)Cp^*$ [R = Ph, L = PPh_3, CO, O_2; R = Bu^t, L = PPh_3, CO, C_2H_4, dppe-*P*, dppa-*P*, S_2, $P(OMe)_3$, $AsPh_3$] (Scheme 1). Thus, a solution containing **4** and an excess of PPh_3 in methanol was treated with NaOMe, whereupon it changed colour from red to yellow and rapidly afforded a yellow precipitate of **7**, identified by comparison with the product described above.



R = Me or Ph



	L_1	L_2	R^2
(8)	PPh_3	CO	Ph
(9)	PPh_3	CO	^{t}Bu
(10)	PPh_3	$P(OMe)_3$	^{t}Bu
(11)	PPh_3	$AsPh_3$	^{t}Bu
(12)	dppm		^{t}Bu
(13)	PPh_3	dppe-*P*	^{t}Bu
(14)	PPh_3	dppa-*P*	^{t}Bu
(15)	PPh_3	dppm-*P*	Ph
(16)	dppee		^{t}Bu
(17)	PPh_3	η-C_2H_4	^{t}Bu
(18)	PPh_3	η-O_2	Ph
(19)	PPh_3	η-S_2	^{t}Bu

Scheme 1 : R^1 = Ph **3**, Bu^t **4**, $SiMe_3$ **5**, Me **6**.

The neutral vinylidene complexes were converted to the carbonyl complexes $Ru(C{\equiv}CR)(CO)(PPh_3)Cp^*$ [R = Ph **8**, Bu^t **9**] when NaOMe was added to solutions of **3** or **4** whilst passing CO through them. Complex **9** was also obtained by adding $AgPF_6$ to a solution of **4** in acetonitrile, which had been saturated with CO. A white precipitate (AgCl) formed. We could not isolate any intermediate such as $[Ru(C{=}CHR)(CO)(PPh_3)Cp^*]^+$, but after filtration, deprotonation with NaOMe afforded yellow **9**. The new complexes are characterised by ν(CO) bands at 1915 and 1928 cm^{-1}, and ν(C≡C) absorptions at 2095 and 2100 cm^{-1}, respectively. Other typical spectral properties include the Cp* and Bu^t (if present) resonances in the ^1H and ^{13}C NMR spectra and parent ions which fragment by loss of CO, PPh_3 and C_2R groups. The ^{13}C NMR spectra also contain doublets for the CO groups at δ 206.4 and 207.2, respectively.

The two complexes described above are chiral, although we have not tried to separate the individual enantiomers. However, extension of this reaction to ligands with Group 15 donor atoms allowed the synthesis of several related complexes $Ru(C{\equiv}CR)(L)(PPh_3)Cp^*$, of which we have characterised examples with R = Bu^t, L = $P(OMe)_3$ **10**, $AsPh_3$ **11**, dppm **12**, dppe-*P* **13**, dppa-*P* **14**, and R = Ph, L = dppm-*P* **15**. Of some interest is the finding that under the mild reaction conditions, potentially chelating ligands (dppm, dppe) formed complexes in which they are monodentate, in principle allowing the construction of bimetallic species. Not surprisingly, the linear diphosphine $C_2(PPh_2)_2$ (dppa) also acts as a monodentate ligand in **14**. In contrast, the ligand *cis*-$PPh_2CH{=}CHPPh_2$ (dppee) formed $Ru(C{\equiv}CBu^t)(\eta^2\text{-dppee})Cp^*$ **16** with expulsion of PPh_3. All of these complexes were identified by microanalysis and from the appropriate spectral properties, of which the most useful were their mass spectra, which contained parent ions which fragmented by loss of C≡CR, Ph and PPh_3 groups. In addition, the molecular structures of complexes **9** (Figure 2), **12** (Figure 3), **13** (Figure 4) and **16** (Figure 5) have been determined by X-ray crystallography with pertinent bond angle and lengths shown in Table 1.

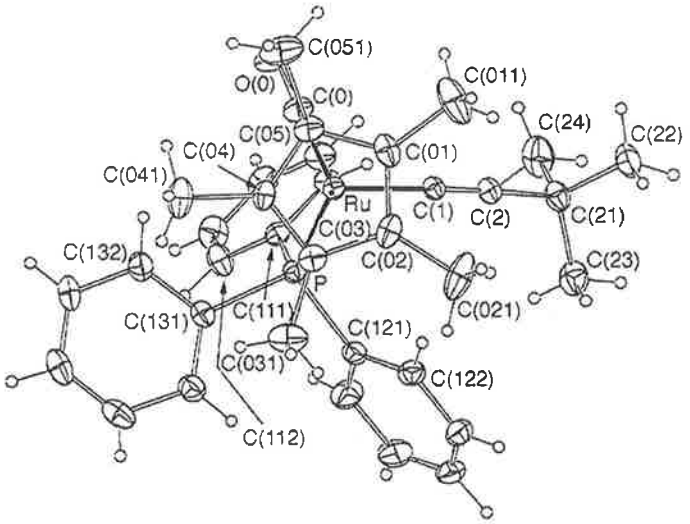


Figure 2 : Projection of a molecule of Ru(C≡CBu^t)(CO)(PPh_3)Cp* **9** down the Ru-Cp* (centroid) vector.

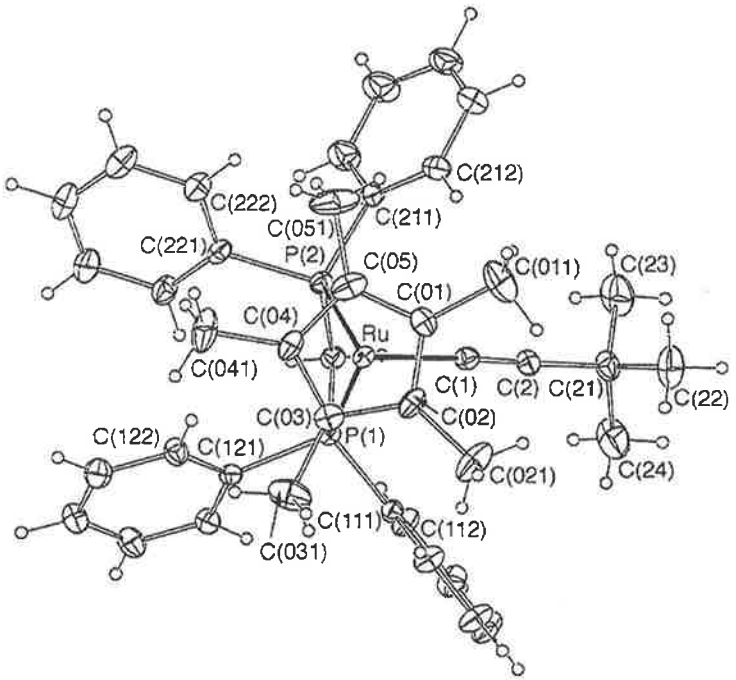


Figure 3 : Projection of a molecule of Ru(C≡CBu^t)(dppm)Cp* **12** down the Ru-Cp*(centroid) vector.

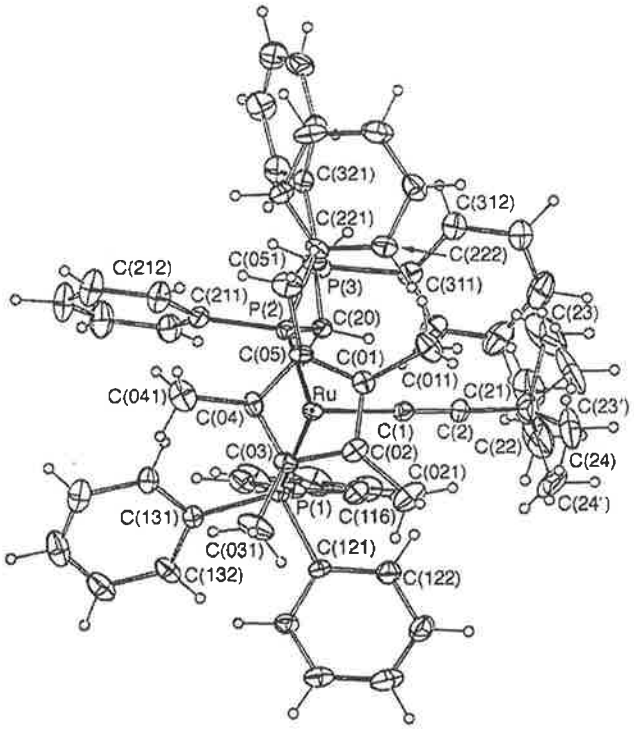


Figure 4 : Molecular projection of Ru(C≡CBu^t)(dppe)Cp* **13** down the Ru-Cp*(centroid) vector.

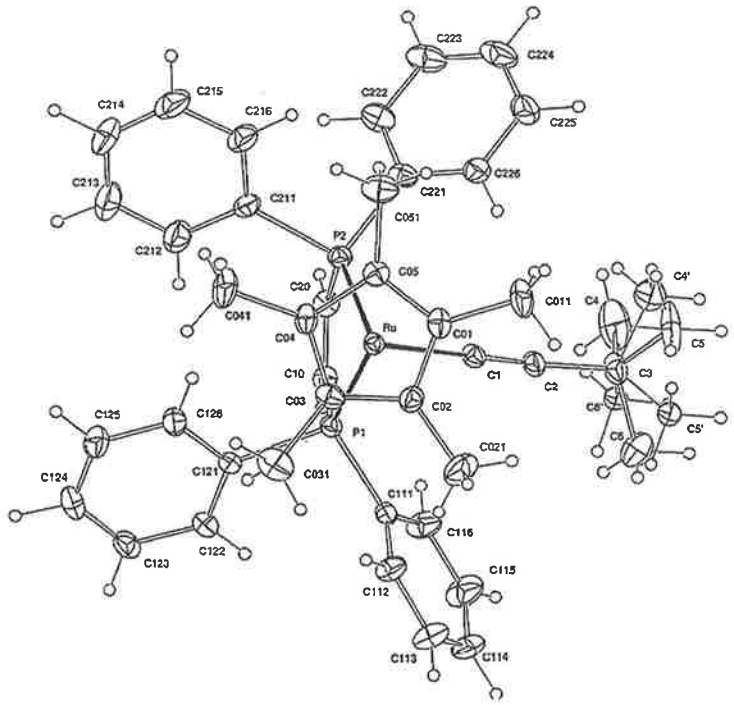


Figure 5 : Molecular projection of Ru(C≡CBu^t)(dppee)Cp* **16** down the Ru-Cp*(centroid) vector.

The ready incorporation of 2-e donor ligands under mild conditions at the Ru centre encouraged us to examine reactions with other ligands capable of π-bonding. Examples of neutral complexes of this type are rare in $Ru(PR_3)_2Cp$ chemistry, although a wide range of cationic adducts $[Ru(\eta^2\text{-}L)(PMe_3)_2Cp]^+$ (L = alkene, alkyne, allene, butadiene) is known.[37-41] The reaction of **4** with ethene in the presence of NaOMe readily afforded $Ru(C{\equiv}CBu^t)(\eta^2\text{-}C_2H_4)(PPh_3)Cp^*$ **17**, obtained as yellow crystals which were characterised by a single-crystal X-ray structure determination (Figure 6). The IR spectrum contains ν(C≡C) at 2088 and ν(C=C) at 1570 cm^{-1}, while the ^1H NMR spectrum contains a doublet for the ethylenic protons at δ 1.66. The ^{13}C resonances for the coordinated C_2H_4 ligand appear as doublets at δ 39.39 and 51.56; other signals are similar to those found for other complexes described above.

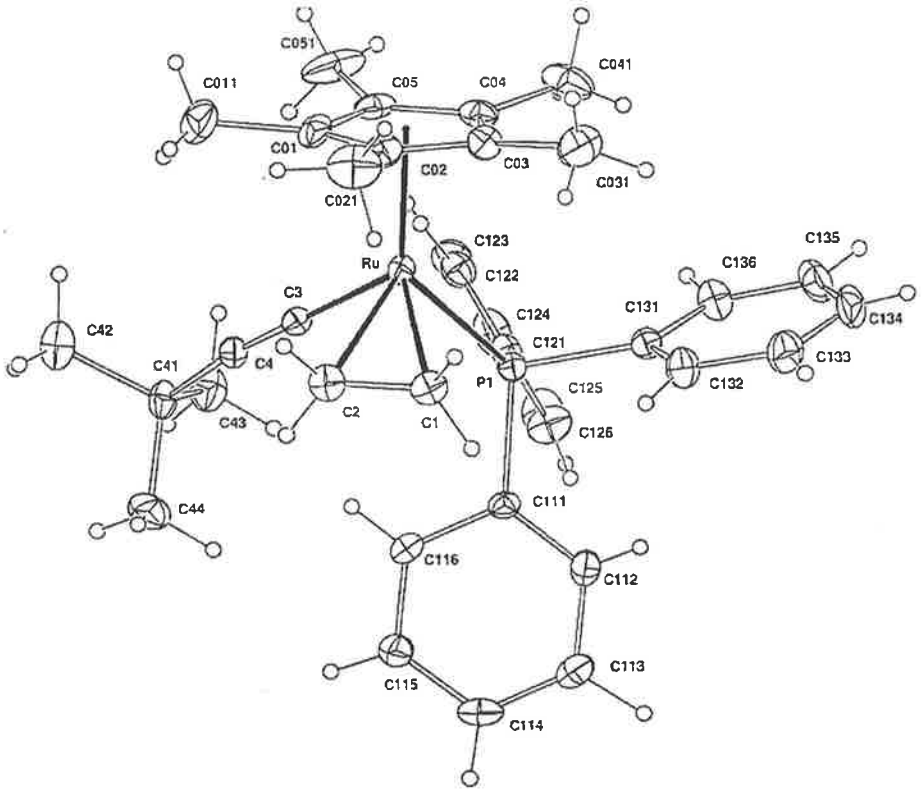


Figure 6 : Molecular projection of $Ru(C{\equiv}CBu^t)(\eta^2\text{-}C_2H_4)(PPh_3)Cp^*$ **17** normal to the Ru-Cp*(centroid) vector.

The η^2-O_2 complex, first obtained serendipitously during recrystallisation of a sample of **2**, can be made directly by passing oxygen through a solution of **3** while adding NaOMe. The complex Ru(C≡CPh)(η^2-O_2)(PPh_3)Cp* **18** forms red-orange crystals (Figure 7). The ν(C≡C) and ν(O=O) absorptions are found at 2094 and 914 cm^{-1}, respectively, while the NMR spectrum contains the expected resonances from the $Cp^*$and Ph groups. There is no parent ion in the mass spectrum: however, the ion [M - O]$^+$ (*m/z* 616) fragments further by loss of O, Ph, C≡CPh and PPh_3 groups.

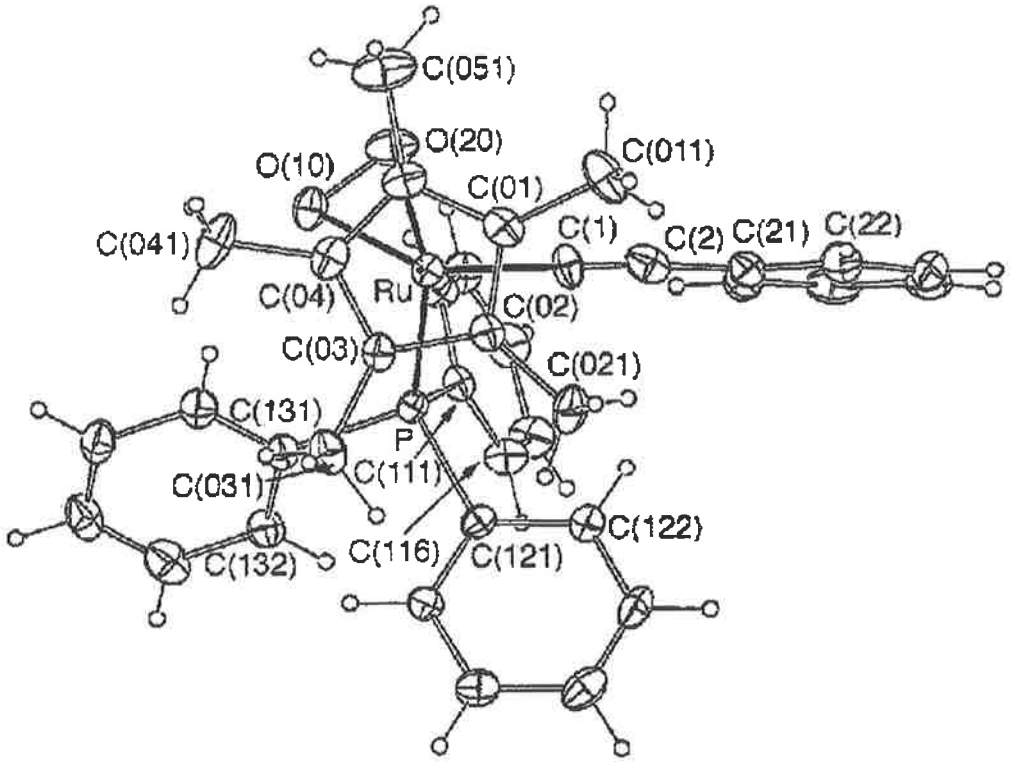


Figure 7 : Molecular projection of Ru(C≡CPh)(η^2-O_2)(PPh_3)Cp* **18** down the Ru-Cp*(centroid) vector.

The sulfur analogue, $Ru(C{\equiv}CBu^t)(\eta^2\text{-}S_2)(PPh_3)Cp^*$ **19** (Figure 8) was formed when S_8 was added to a solution of **4** in MeOH, followed by an excess of NaOMe. A grey-green complex was obtained after separation by TLC. It has $\nu(C{\equiv}C)$ and $\nu(S{=}S)$ bands at 2114 and 1248 cm^{-1}, respectively. Resonances for the Bu^t, Cp* and Ph groups were present in the NMR spectra and the parent ion decomposed by loss of S, $C{\equiv}CBu^t$ and PPh_3 groups.

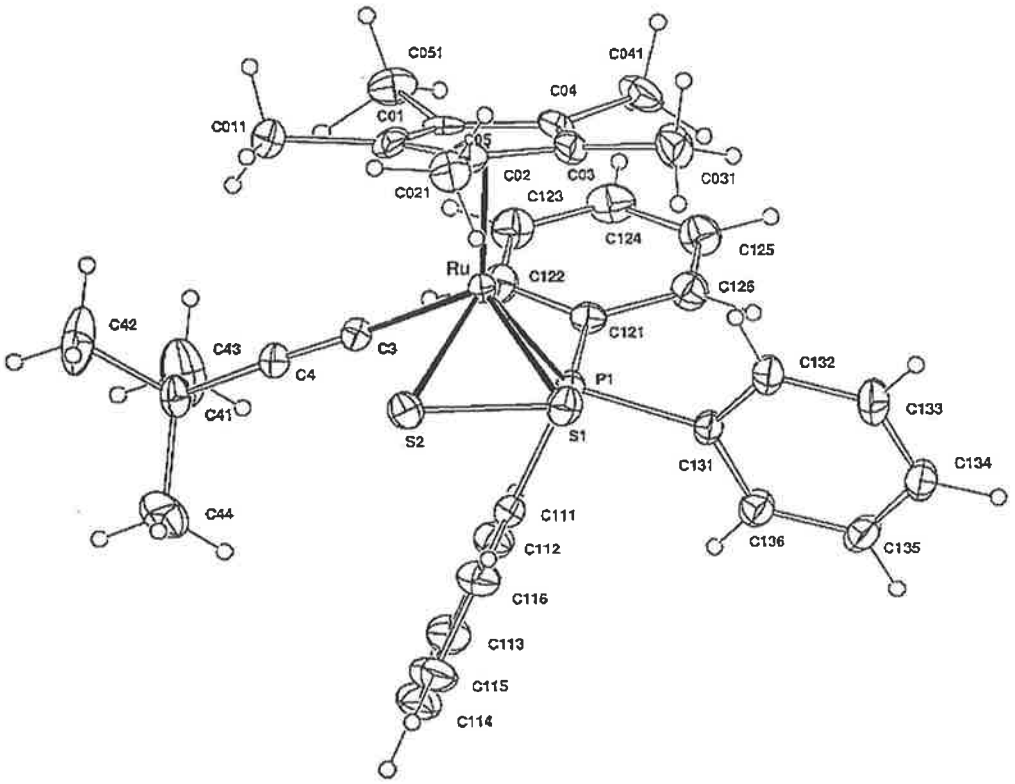


Figure 8 : Molecular projection of $Ru(C{\equiv}CBu^t)(\eta^2\text{-}S_2)(PPh_3)Cp^*$ **19** normal to the Ru-Cp*(centroid) vector.

The ability of small molecules to coordinate to the metal centre is illustrated in a different way in the reaction between **4** and CS_2. An olive-green complex was obtained and identified as $Ru(S_2CC{\equiv}CBu^t)(PPh_3)Cp^*$ **20** by an X-ray study (Figure 9). Characteristic spectroscopic features include ν(C≡C) and ν(CS) bands at 2195 and 1288 cm^{-1} in the IR spectrum and resonances for the Bu^t, Cp* and Ph groups in the NMR spectra. The two acetylenic carbons appeared at δ 97.2 and 123 ppm.

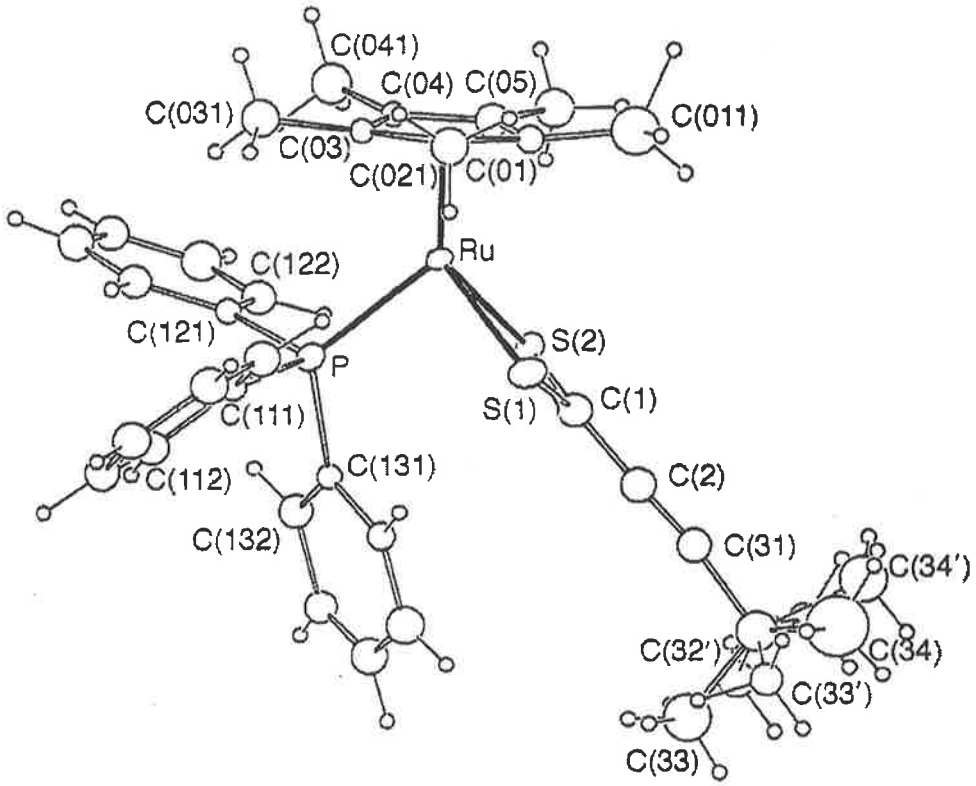


Figure 9 : Molecular projection of $Ru(S_2CC{\equiv}CBu^t)(PPh_3)Cp^*$ **20** normal to the Ru-Cp*(centroid) vector.

The complexes described above, like **3**, adopt the familiar 'piano-stool' structure, with C≡CR, L and PPh_3 ligands forming the 'legs' in all except **12**, **16** and **20**, which contain chelating dppm, dppee or $S_2CC_2Bu^t$ ligands, respectively. The geometry about the ruthenium is pseudo-octahedral, angles between the Ru-L (L = single-atom donor, non-Cp* ligand) vectors being close to 90° [range 83.3(2) **17** to 95.74(8)° **13**]. Larger excursions are found with **18** and **19**, containing O_2 and S_2 ligands, where small P-Ru-C≡ angles of 80.3(1) and 80.1(1)°, respectively, are found. In **12**, the small bite of the chelating dppm ligands results in a P-Ru-P angle of 70.99(5)°.

The Ru-PPh_3 distances range between 2.267(2) and 2.334(1) Å, the extremes being found for complexes **12** and **19**. For the unidentate phosphine, the Ru-P distance is similar, at 2.288(2) Å. With the dppm and dppee complexes **12** and **16**, the Ru-P distances are between 2.244(2) and 2.271(2) Å. The Ru-C(Cp*) distances range between 2.20(3) and 2.311(4) Å, the Ru-ring centroids showing similar variability. The Ru-C(1) distances [1.987(6)-2.058(9) Å] may be compared to the value of 2.016(3) Å found in $Ru(C{\equiv}CPh)(PPh_3)_2Cp$.[42,43]

The η^2-O_2 ligand in **18** is asymmetrically bound, with Ru-O distances of 2.169 and 2.186(7) Å. These values are considerably longer than those found in the related cations $[Ru(\eta^2\text{-}O_2)(L_2)Cp^*][BPh_4]$ [2.023, 2.040(3) (L_2 = dppe);[44] 2.029, 2.035(8) Å (L_2 = dppf)[45] possibly because of the increased steric hindrance afforded by the PPh_3 and Cp* ligands in **18**. The O-O separation is 1.363(4) Å, somewhat shorter than the values of 1.398(5) and 1.381(11) Å found in the cationic complexes. For **19**, the Ru-S distances are experimentally identical at 2.384(2) Å and the S-S separation is 2.010(2) Å. We are not aware of any comparable η^2-S_2 complex of ruthenium; the Ru-S distance in $Ru(SH)(CO)(PPh_3)Cp$ is 2.381(3) Å,[46] while in $[Ir(\eta^2\text{-}S_2)(dppe)_2]^+$, the S-S separation is 2.066(6) Å.[47]

The structure of the ethene complex **17** shows the C=C double bond [1.39(1) Å] is parallel to the Cp* ring plane, with a slightly asymmetric attachment to the metal [Ru-C(1,2) 2.186, 2.170(9) Å]. These values are comparable with Ru-C distances of 2.168(10), 2.194(9) Å found in $[RuH(\eta^2\text{-}C_2H_4)(PPh_3)(\eta\text{-}C_6Me_6)][PF_6]$,[48] although the C-C separation of 1.410(3) Å in the latter is somewhat longer as a result of reduced back-bonding from the cationic metal centre.

The dithiocarboxylate ligand in **20** is attached symmetrically by the two S atoms [Ru-S(1,2) 2.35, 2.37(1) Å] and has internal S-C bonds of 1.67, 1.70(4) Å. The alkynyl substituent shows normal geometries, the complex having an overall similarity to $Ru(S_2CC{\equiv}CPh)(PPh_3)Cp$ in which Ru-S distances of 2.336(3), 2.353(4) Å and thiolate C-S separations of 1.68, 1.71(1) Å were found.[49]

Reactions with Alkynes.

Instead of the expected complex Ru(C≡CPh)(η-HC_2Ph)(PPh_3)Cp*, or possibly the analogous phenylvinylidene derivative, the reaction between RuCl(=C=CHPh)(PPh_3)Cp* **3** and phenylethyne, carried out in the presence of NaOMe, afforded a yellow solid. We have determined the structures of two crystalline forms, one of which was the 1.5-benzene solvate described independently by others,[27] whose composition corresponded to the incorporation of two additional HC≡CPh molecules into **3**, namely Ru{η^3-CHPhCHC=CPh(C≡CPh)} (PPh_3)Cp* **21**. The second form is solvent-free and both structures are experimentally identical (Figure 10). The same complex could be isolated, in lower yield, from a reaction between **3** and LiC≡CPh. The reactions to be described below are summarised in Scheme 2

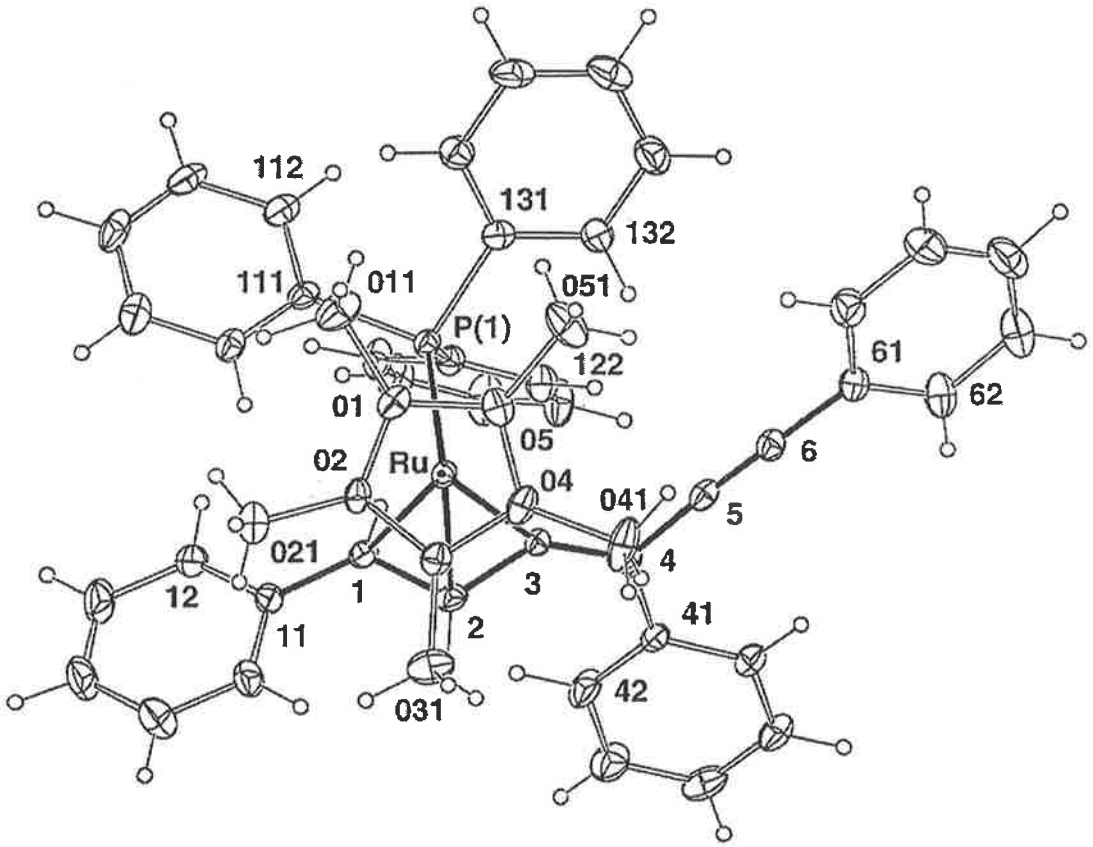
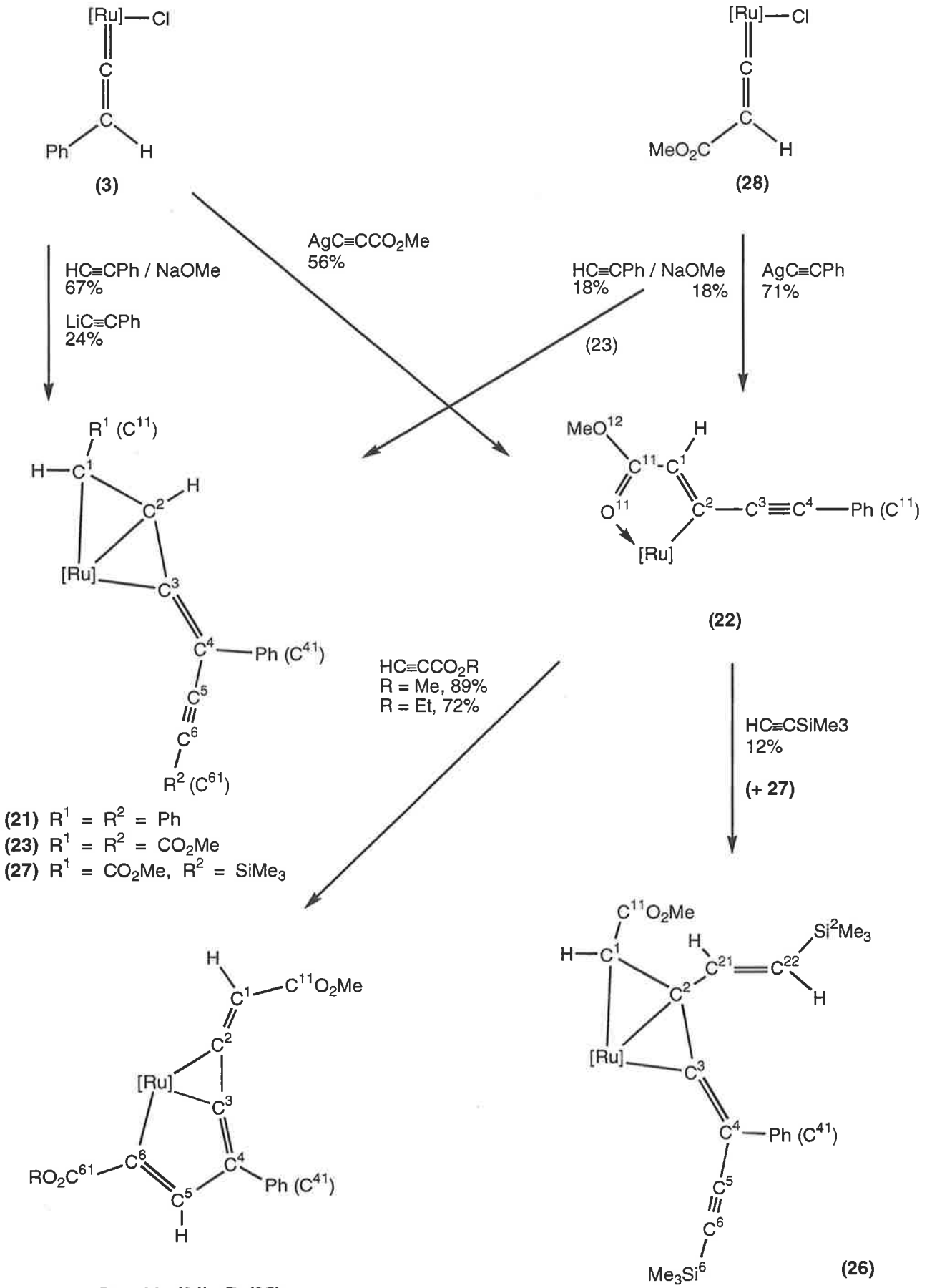


Figure 10 : Ru{η^3-CHPhCHC=CPh(C≡CPh)}(PPh_3)Cp* **21** down the Ru-Cp* (centroid) vector.

Scheme 2 : Reactions with acetylenes.



In order to find out more about these unusual systems, we examined the reaction between **3** and $AgC{\equiv}CCO_2Me$. A red-brown complex was isolated in 56% yield and identified as $Ru\{\eta^1,O\text{-}C(C{\equiv}CPh){=}CHC(O)OMe\}(PPh_3)Cp^*$ **22** by an X-ray structural determination (Figure 11). This material was also formed from the reaction between $RuCl\{{=}C{=}CH(CO_2Me)\}(PPh_3)Cp^*$ **28**[50] and $AgC{\equiv}CPh$. Treatment of **28** with NaOMe in the presence of an equimolar amount of $HC{\equiv}CPh$ gave a mixture of **21** and **22**. The spectroscopic properties of **22** were consistent with its solid-state structure, with bands in the IR spectrum at 2163, 1724 and 1558 cm^{-1} being assigned to $\nu(C{\equiv}C)$, $\nu(CO)$ and $\nu(C{=}C)$ absorptions, respectively. In the ^1H NMR spectrum, doublet resonances at δ 1.40 and 6.25, having relative intensities 15/1, were assigned to the Cp* and =CH protons, respectively. The CO_2Me protons gave rise to a singlet resonance at δ 3.33 and the Ph multiplet was between δ 7.17 and 7.50. The ^{13}C NMR spectrum contained signals for Cp* (δ 10.82 and 86.99) and CO_2Me groups (δ 52.80 and 181.26), as well as for the two $C{\equiv}C$ (δ 99.05 and 100.57) and =CH carbons (δ 122.97). The ion $[M - H]^+$ was present in the ES Mass Spectrum.

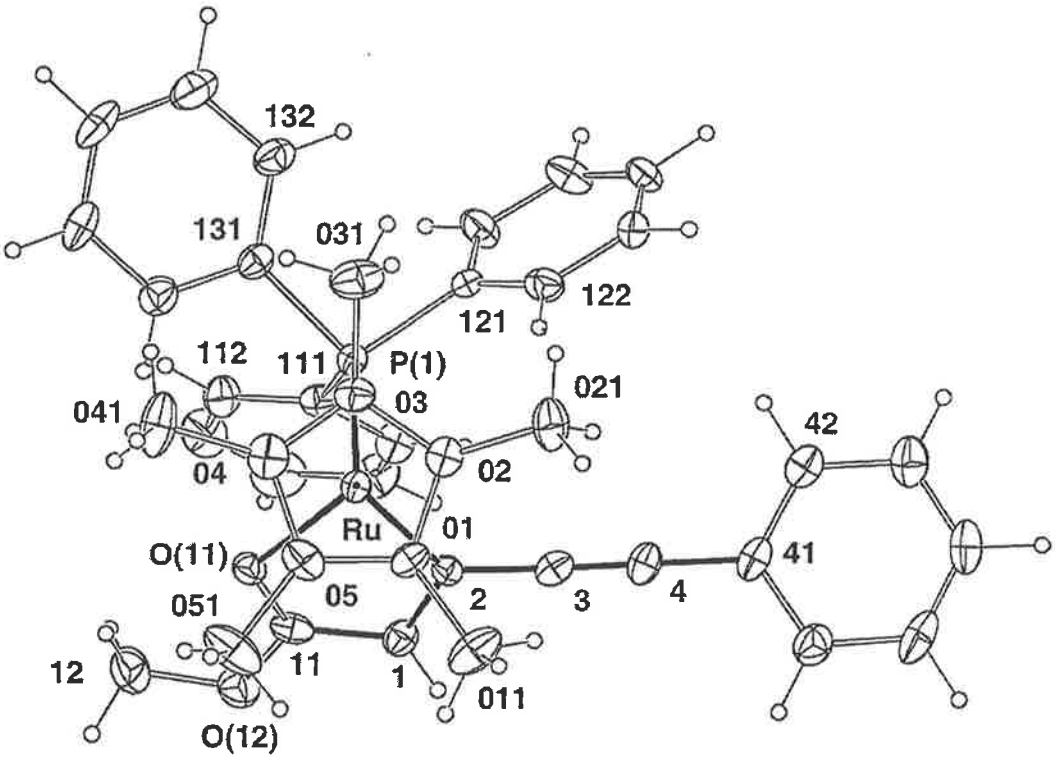


Figure 11 : Plot of a molecule of $Ru\{\eta^1,O\text{-}C(C{\equiv}CPh){=}CHC(O)OMe\}(PPh_3)Cp^*$ **22** down the Ru-Cp* (centroid) vector.

In this complex, two alkyne molecules have combined to form a five-membered chelate RuC_3O ring, C(3) forming a σ bond to the metal [Ru-C(2) 2.032(8) Å], while the ester carbonyl oxygen forms a donor bond [Ru-O(11) 2.156(5) Å]. Atoms C(3)-C(4) are separated by a triple bond, while C(1)-C(2) is a double bond. Both the Ru-P [2.281(3) Å] and average Ru-C(Cp*) separations [2.19_2 Å] are shorter than those found in the other five complexes, probably as a result of there being less steric interaction with the ring substituents.

A different complex incorporating two additional alkyne molecules was formed from **3** and $HC{\equiv}CCO_2Me$ in the presence of NaOMe. This was identified as $Ru\{\eta^3\text{-}CH(CO_2Me)CHC{=}CPh(C{\equiv}CCO_2Me)\}(PPh_3)Cp^*$ **23** by means of a single-crystal X-ray structural study (Figure 12), and was accompanied by a small amount of **22**. The IR spectrum of **23** contained bands assigned to ν(C≡C) at 2186, ν(CO) at 1706 and ν(C=C) at 1616 and 1594 cm^{-1}, while two singlets in the ^1H NMR spectrum at δ 3.70 and 3.94 indicated the presence of two non-equivalent CO_2Me groups. Other resonances included a doublet at δ 1.47 (Cp*) and two double doublets at δ 2.27 and 3.59 for the two CH protons. In the ^{13}C NMR spectrum, the Cp* (δ 9.16 and 93.67), CO_2Me (δ 50.52, 52.32 and 217.0; the two ester CO resonances are accidentally equivalent) and C≡C carbons (δ 79.43 and 94.05) were accompanied by resonances at δ 112.11, 139.33, 155.55 and 174.73, assigned to the carbons of the C_4 chain. From solutions containing NaOMe, the highest ion in the ES mass spectrum was $[M + Na]^+$ at *m/z* 791.

Complex **22** reacts with $HC{\equiv}CCO_2R$ (R = Me, Et) to give the 1,3,4,5-tetraenyl complexes $Ru\{\eta^1,\eta^2\text{-}C(CO_2R){=}CHCPh{=}C{=}C{=}CH(CO_2Me)\}(PPh_3)Cp^*$ [R = Me **24**, Et **25**], each obtained as a single product. Both complexes were characterised by single-crystal X-ray structure determinations (Figure 13) and their spectroscopic properties were consistent with these structures. The Cp* proton doublets are at δ 1.56 (R = Me) and 1.52 (Et), while the common CO_2Me groups are found at δ 3.33 and 3.37, respectively. This assignment is assisted by replacement of the CO_2Me signal at δ 3.29 in the ^1H NMR spectrum of **24** by the CH_2 multiplet at δ 3.61 for **25**.

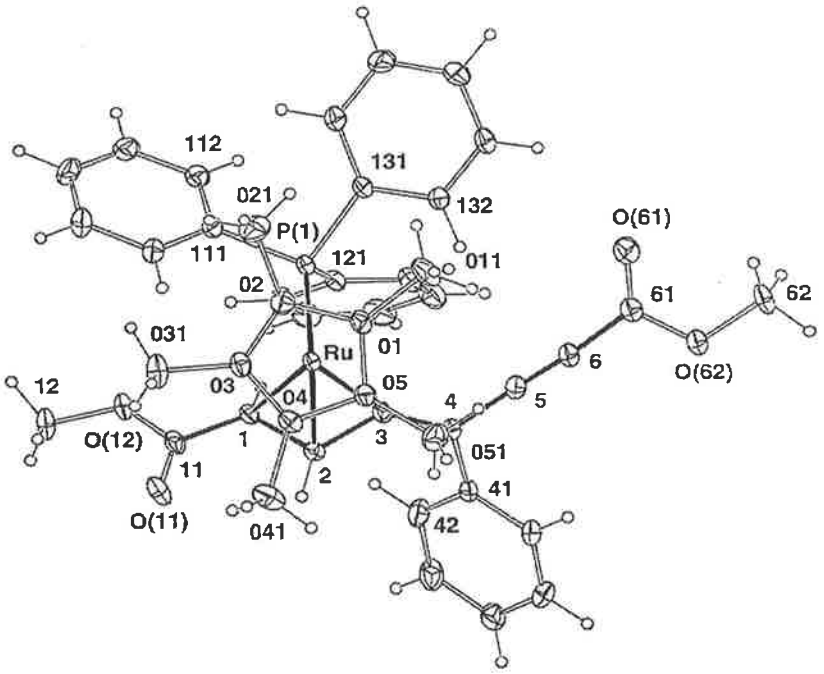


Figure 12 : Plot of a molecule of Ru{η^3-CH(CO_2Me)CHC=CPh(C≡CCO_2Me)}(PPh_3)Cp* **23** down the Ru-Cp* (centroid) vector.

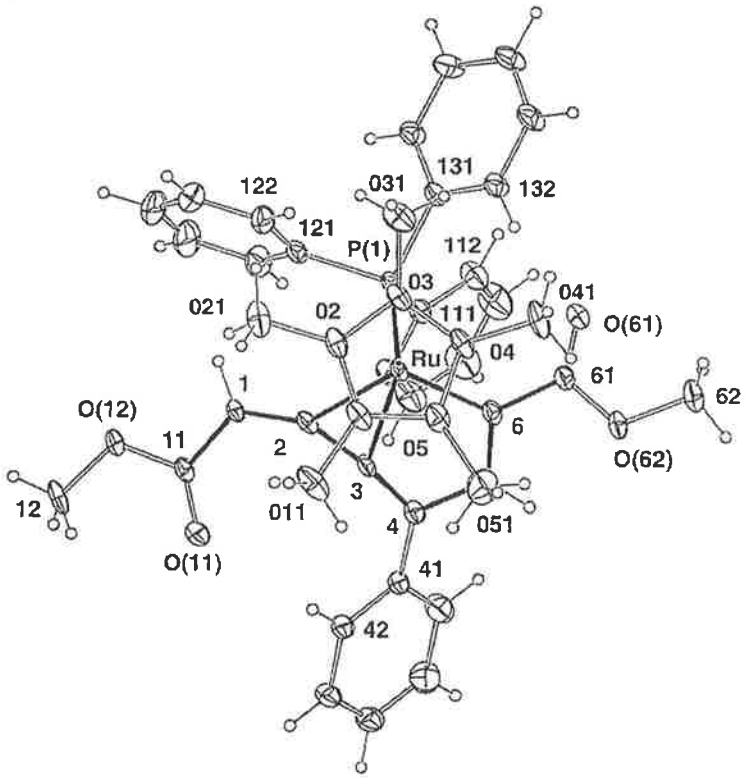


Figure 13 : Plot of a molecule of Ru{η^1,η^2-C(CO_2Me)=CHCPh=C=C=CH(CO_2Me)}(PPh_3)Cp* **24** down the Ru-Cp* (centroid) vector.

The structures of Ru{η^3-CH(CO_2Me)CHC=CPh(C≡CCO_2Me)}(PPh_3)Cp* **23** and Ru{η^3-CH(CO_2Me)C(CH=$CHSiMe_3$)C=CPhC≡$CSiMe_3$}(PPh_3)Cp* **24** are closely related to that of **21**, differing only in the substituents which, however, exert some influence on the geometrical parameters. Thus, an asymmetric allylic interaction of the ruthenium with atoms C(1,2,3) [Ru-C(1) 2.243(5), 2.214(3) Ru-C(2) 2.117(5), 2.154(2) Ru-C(3) 2.025(4), 2.044(3) Å] results from the presence of a double bond between C(3)-C(4) [1.349(6), 1.352(5) Å], i.e. the ligands are η^3-butadienyls. These data can be compared with those for **21**, in which the Ru-C and the C-C distances are consistent with the same arrangement of multiple bonds.

The molecular structures of **24** and **25** are closely related and only **24** is depicted; the structural determination of **25** enables us to comment on the site of addition of the third alkyne molecule. The organic ligands in each of these complexes is a linear oligomer derived from three alkyne molecules and is attached to the ruthenium by a π bond to C(2)-C(3) [2.104(4), 2.066(5); 2.086(5), 2.072(6) Å; values for molecule 1 of each complex given] and a σ bond to C(6) [2.082(5); 2.089(6) Å]. Atoms C(1-4) form a cumulene, of which only the central C=C double bond is coordinated to ruthenium, while there is also a double bond between atoms C(6,7). The ligand is thus a 3-vinylbuta-1,2,3-triene, which is an isomer of the diene found in **23**. The substituents on atoms C(3,5,7) have normal geometries. There are close parallels between these structures and that of the complex Ru{η^1,η^2-C(CF_3)=CHC(CF_3)=CC=CH(CF_3)}(PPh_3)Cp, obtained from HC≡CCF_3 and RuH(PPh_3)$_2$Cp[51], where, for example, the Ru-C distances are 2.11(1) Å (σ-bonded) and 2.05, 2.09(1) Å (π-bonded).

Finally, a complex containing an organic ligand derived from four alkyne molecules is obtained when **3** is treated with HC≡$CSiMe_3$. The only tractable product was yellow crystalline Ru{η^3-CH(CO_2Me)C(CH=$CHSiMe_3$)C=CPhC≡$CSiMe_3$}(PPh_3)Cp* **26**, characterised by an X-ray structural study (Figure 14). This complex has spectroscopic properties consistent with its solid-state structure, with a single ν(C≡C) band at 2115 and a ν(CO) absorption at 1699 cm^{-1}. In the ^{1}H NMR spectrum, appropriate signals can be assigned to $SiMe_3$ (δ -0.23, 0.46), Cp* (1.47), CO_2Me (3.59) and CH protons (5.46, 6.66 and one beneath the Ph multiplet). The ES mass

spectrum contains M^+ at *m/z* 880. The ES mass spectrum of a second product, which could only be obtained as an unstable yellow oil, contained M^+ at *m/z* 782 and singlet resonances at δ -0.74, 1.66 and 3.53 which we assign to $SiMe_3$, Cp* and CO_2Me protons, respectively. These data are consistent with the formulation Ru{η^3-$CH(CO_2Me)CHC{=}CPh(C{\equiv}CSiMe_3$}$(PPh_3)$Cp* **27** and its formation can be accounted for by reactions analogous to those leading to complex **24**. In both **23** and **26**, atom C(1) carries H and CO_2Me substituents, while C(3) carries the phenyl and alkynyl groups. In **26**, the central C(2) of the allyl also carries the *trans*-CH=CH($SiMe_3$) group [C(21)-C(22) 1.329(6) Å].

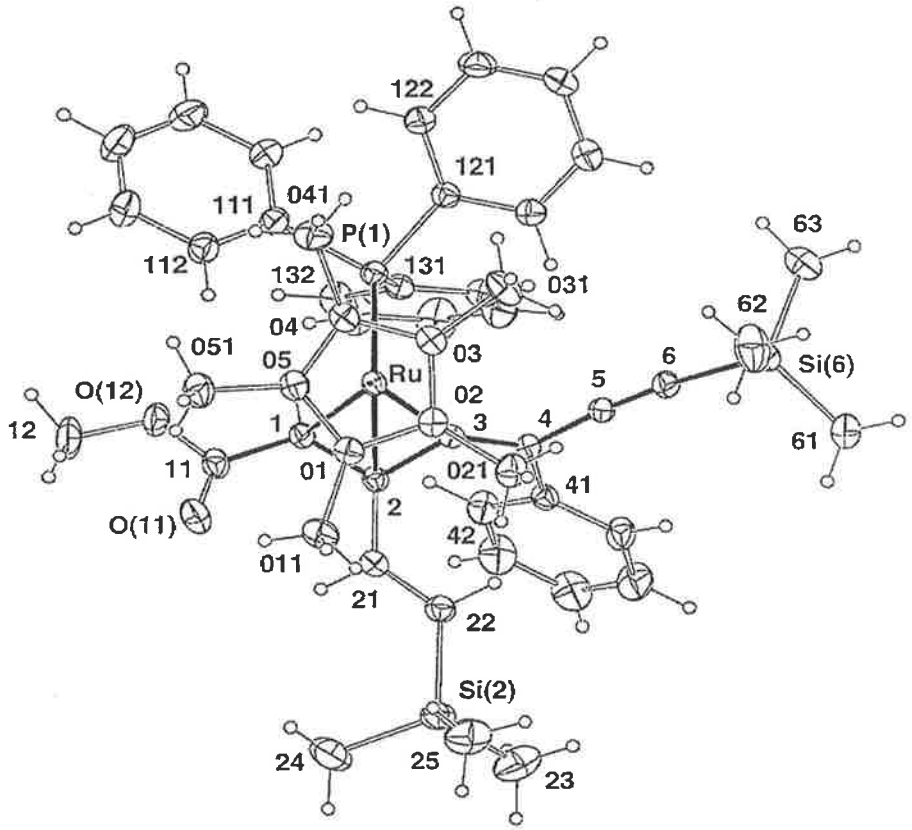


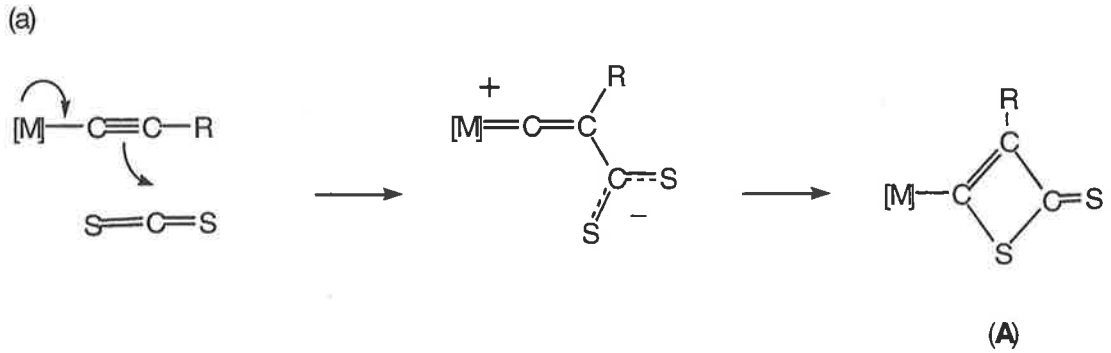
Figure 14 : Plot of a molecule of Ru{η^3-$CH(CO_2Me)C(CH{=}CHSiMe_3)$ $C{=}CPhC{\equiv}CSiMe_3$}(PPh_3)Cp* **26** down the Ru-Cp* (centroid) vector.

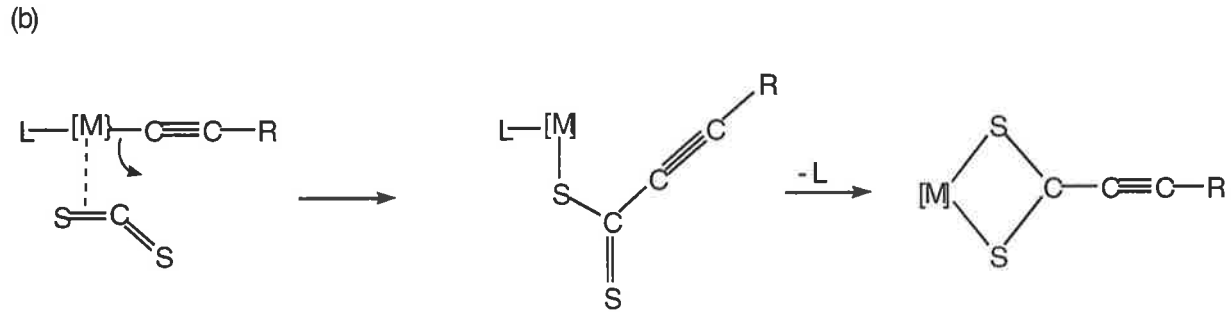
The present study describes the formation of neutral vinylidene derivatives of ruthenium, formed by displacement of a bulky PPh_3 ligand from the $RuCl(PPh_3)_2Cp^*$ precursor by 1-alkynes, with concomitant isomerisation to the vinylidene by 1,2-H shifts. This chemistry contrasts with the normal displacement of chloride that occurs when $RuCl(PPh_3)_2Cp$ reacts with 1-alkynes to give cationic $[Ru(C{=}CHR)(PPh_3)_2Cp]^+$. The latter reaction is also observed with **1** in polar solvents and similar studies have been reported with precursors having less bulky tertiary phosphine ligands.[14] As mentioned above, structurally related complexes have been prepared using the hemi-labile chelating ligand $PPh_2CH_2CH_2OMe$, when the donor oxygen atom is displaced by the vinylidene.[18]

Very recently, complex **3** has been described by others,[27] who noted the apparent generation of the 16-e intermediate $Ru(C{\equiv}CPh)(PPh_3)Cp^*$ when it was treated with NEt_3. Our chemistry is similar, a formal base-induced 1,3-elimination of HCl resulting by deprotonation of the vinylidene to the corresponding acetylide. We have no evidence for the formation of the supposed 16-e intermediate and prefer to consider that these reactions generate a weakly solvated intermediate (either by MeOH or thf). In the presence of other, stronger 2-e donor ligands, the solvent is displaced to give $Ru(C{\equiv}CR)(L)(PPh_3)Cp^*$ (R = Bu^t, Ph). In this way we have prepared several complexes where L is carbonyl, tertiary phosphine, arsine or phosphite, olefin, dioxygen or disulfur. X-ray crystallographic studies of these complexes confirms the assigned structures based on the 'piano stool' arrangement of the three ligands below a capping Cp* ligand. In cyclopentadienyl-ruthenium chemistry, the η^2-O_2, η^2-S_2, and η^2-C_2H_4 ligands are unusual, although during the course of this work, some other examples have been reported, if not structurally characterised.[52]

Formal addition of CS_2 to the acetylide forming the alkynyldithiocarboxylate ligand has been observed on several previous occasions. Thus, both $Fe(C{\equiv}CMe)(dppe)Cp$[53] and $Ru(C{\equiv}CC_6H_9)(PMe_3)_2Cp$[54] afford the 2*H*-thiete-2-thione complexes [(**A**); Scheme 3(a)] by addition of CS_2 to C_β and subsequent ring closure. A different product is obtained from $Ru(C{\equiv}CPh)(PPh_3)_2Cp$, when the alkynyldithiolato complex

$Ru(S_2CC{\equiv}CPh)(PPh_3)Cp$, analogous to **20**, is formed.[49] This reaction may proceed by initial coordination of CS_2 in the η^2 mode, followed by migration of the alkynyl group to the central C atom [Scheme 3(b)]. An alternative mechanism, involving cycloaddition, ring opening and rearrangement has been advanced for the formation of similar complexes from CS_2 and complexes $Fe(C{\equiv}CR)(L)(L')Cp$ (L = CO, L' = PPh_3, R = Ph, Bu^t; LL' = dppe, R = Ph),[55] requiring cleavage of the C-R bond, for which little precedent exists.





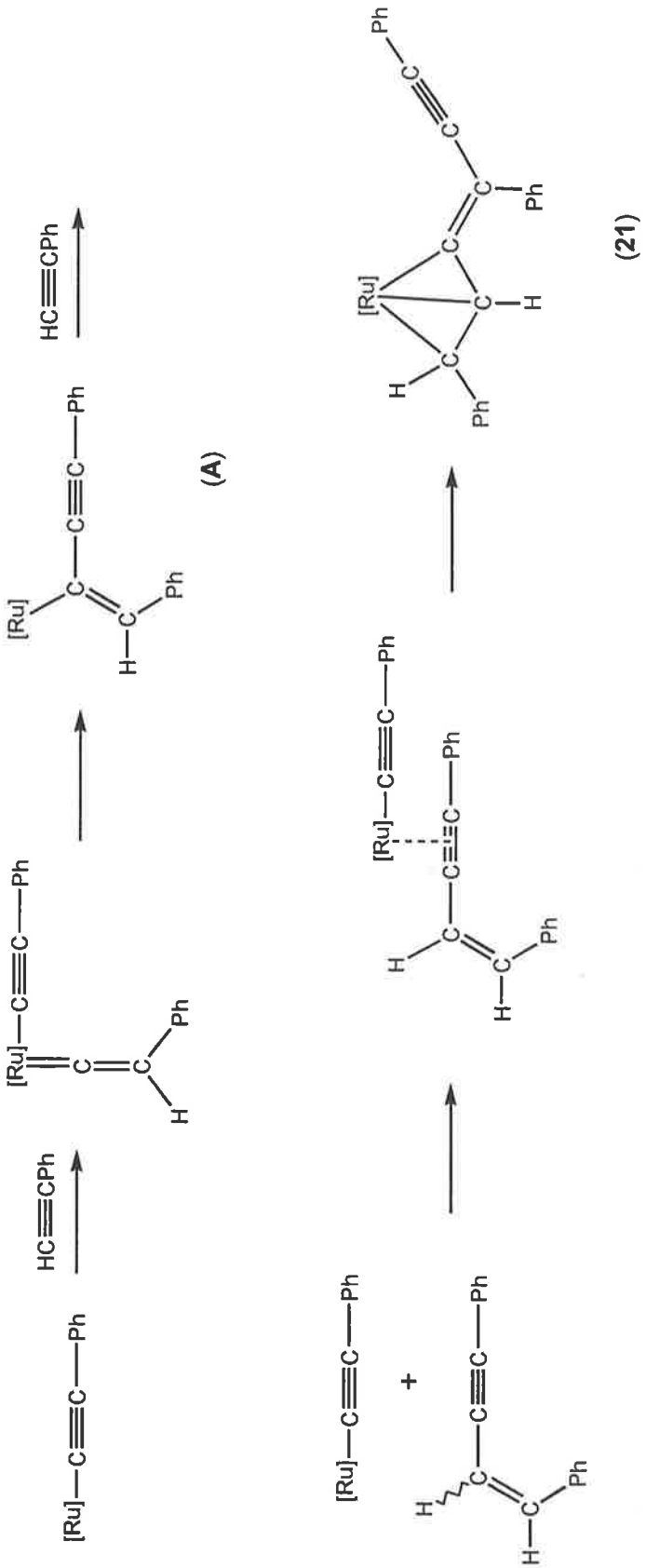
Scheme 3 : Mechanism for the formation of the alkynyldithiolato complex $Ru(S_2CC{\equiv}CPh)(PPh_3)Cp^*$ **20**.

Determination of molecular structures **21-26** allows some comment on the likely mechanisms of their formation. In the earlier report on **21**, it was suggested that trimerisation of the alkyne (HC≡CPh) occurred by initial coordination of phenylethyne to the alkynylruthenium centre as the phenylvinylidene, followed by dimerisation to intermediate (**A**). Displacement of the dimer by HC≡CPh with regeneration of the alkynylruthenium centre is followed by coordination of the dimer and intramolecular C-C bond formation occurs (formally insertion of the third alkyne

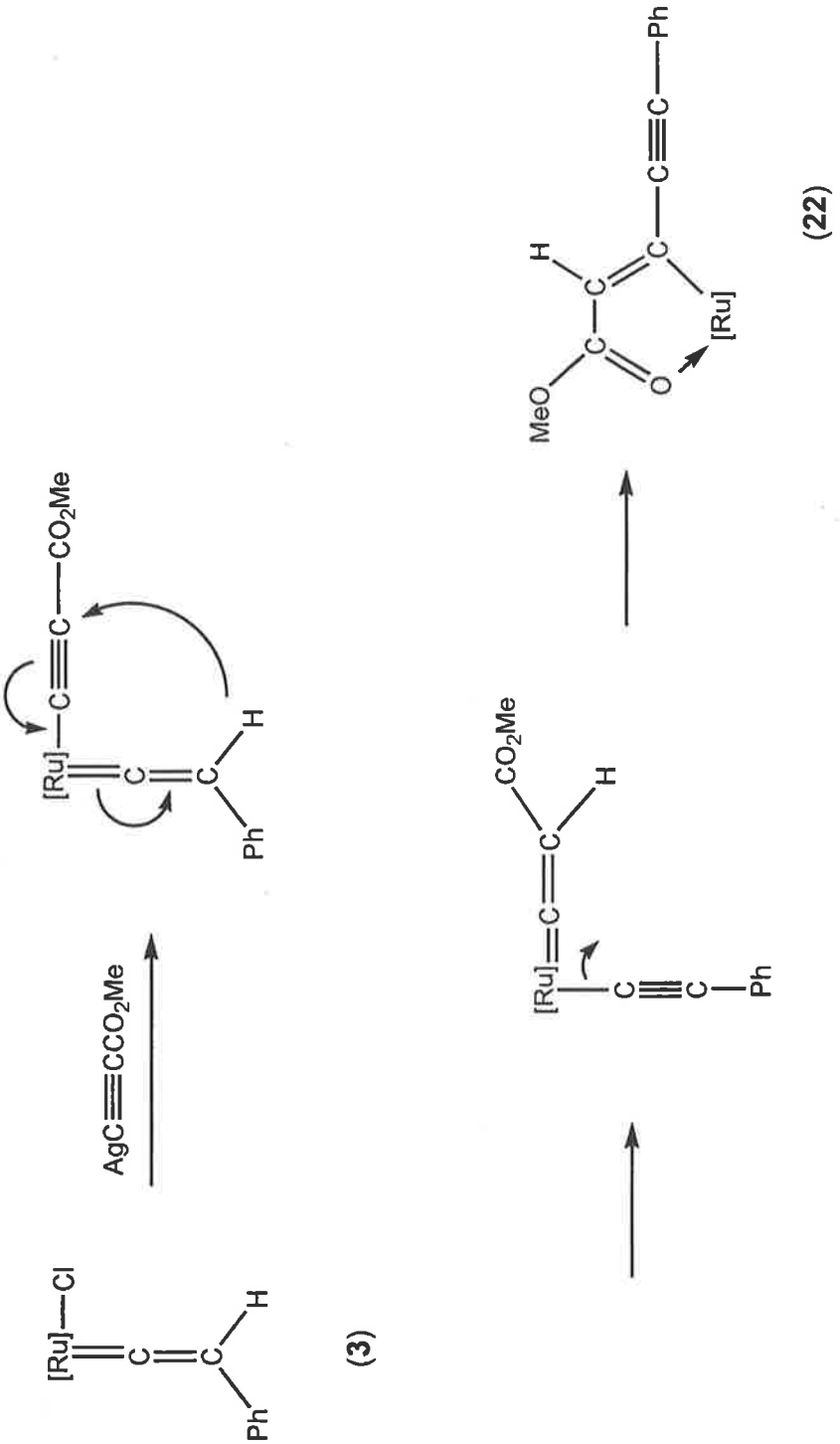
into a Ru-C bond of the dimer; Scheme 4). Subsequent rearrangement involves coordination of the terminal olefinic bond to give **21**. This reaction course is encouraged by the steric bulk of the Cp* and PPh_3 ligands, which offer some stability to the postulated 16-e intermediates.

The first reaction we describe affords a product **22** which contains a ligand formed by formal combination of the phenylethynyl group with the ester vinylidene in precursor complex **28**. The same complex is formed in the reverse reaction, namely between **3** and $AgC{\equiv}CCO_2Me$. These results can be explained if replacement of the chloride in **3** is followed by a proton shift from the phenylvinylidene to the methoxycarbonylethynyl group, followed by insertion of the resulting vinylidene $:C{=}CH(CO_2Me)$ ligand into the Ru-C(sp) bond. Further reaction is prevented by chelation of the ester carbonyl group into the vacant coordination site on the metal centre (Scheme 5). The formation of **21** in the reaction of **28** with phenylethyne in the presence of base suggests that the intermediate containing the $:C{=}CH(CO_2Me)$ ligand is labile towards replacement by phenylvinylidene, an observation consistent with previously observed reactivities of complexes containing these two ligands.

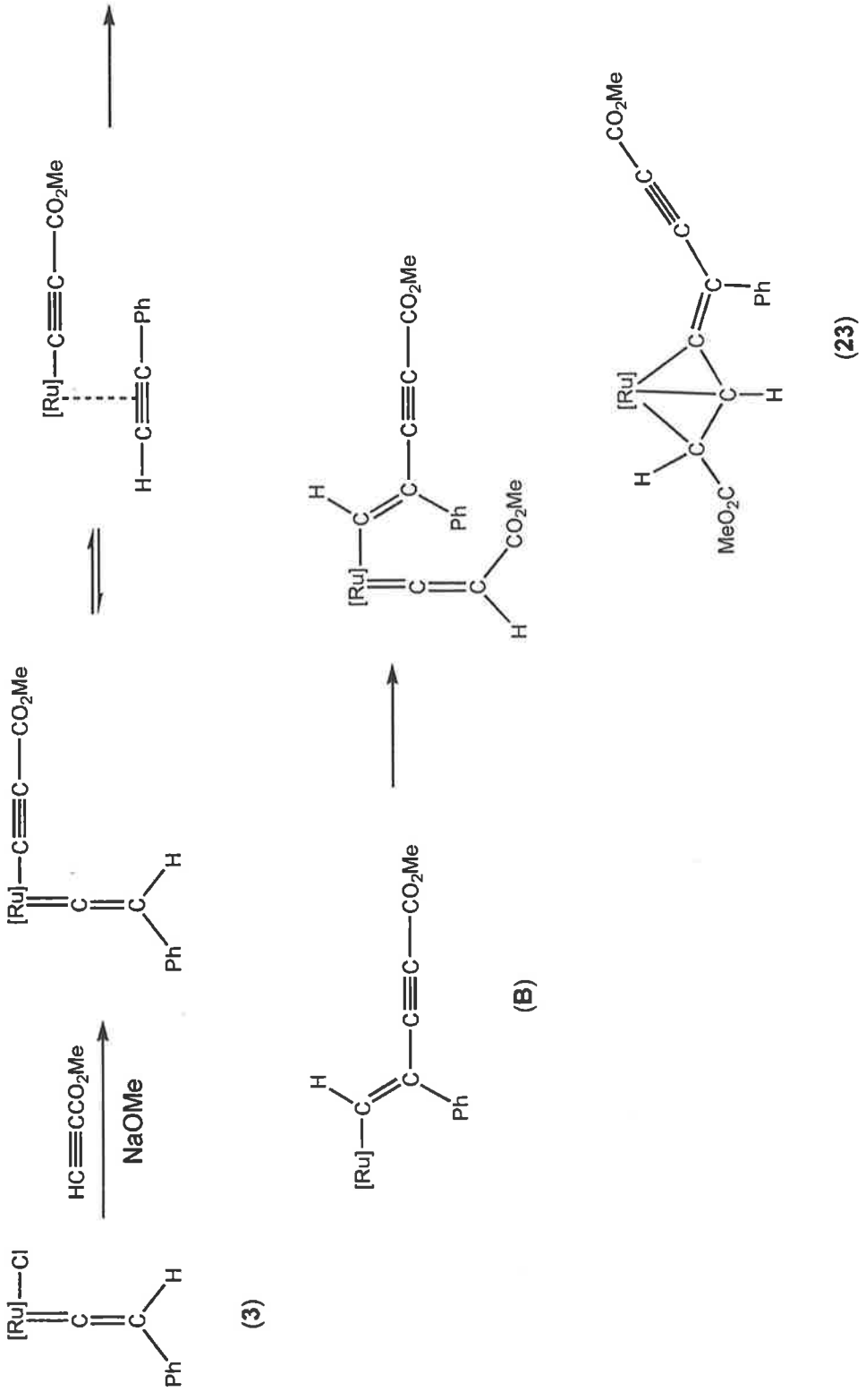
In the reaction between **3** and methyl propiolate in the presence of base, we find specific formation of **23**, which has a structure analogous to that of **21**, but with the terminal Ph groups replaced by CO_2Me, suggesting that in this case, dimerisation of the alkyne does not occur before complexation to the metal. We suggest that the first step in this reaction is replacement of chloride by the methyl propiolato group. Isomerisation of the phenylvinylidene to η^2-phenylethyne and insertion into the Ru-C(sp) bond gives coordinatively unsaturated intermediate (**B**). Addition of a second molecule of methyl propiolate as its vinylidene isomer is followed by insertion into the Ru-C(sp^2) bond and coordination of the terminal C=C double bond, as suggested for **21** (Scheme 6). Indeed, the formation of **21** from **3** and $HC{\equiv}CPh$ can also be described by an analogous sequence of reactions, which has the advantage of not requiring the formation of the alkyne dimer.



Scheme 4 : Proposed mechanism for the formation of **21**.

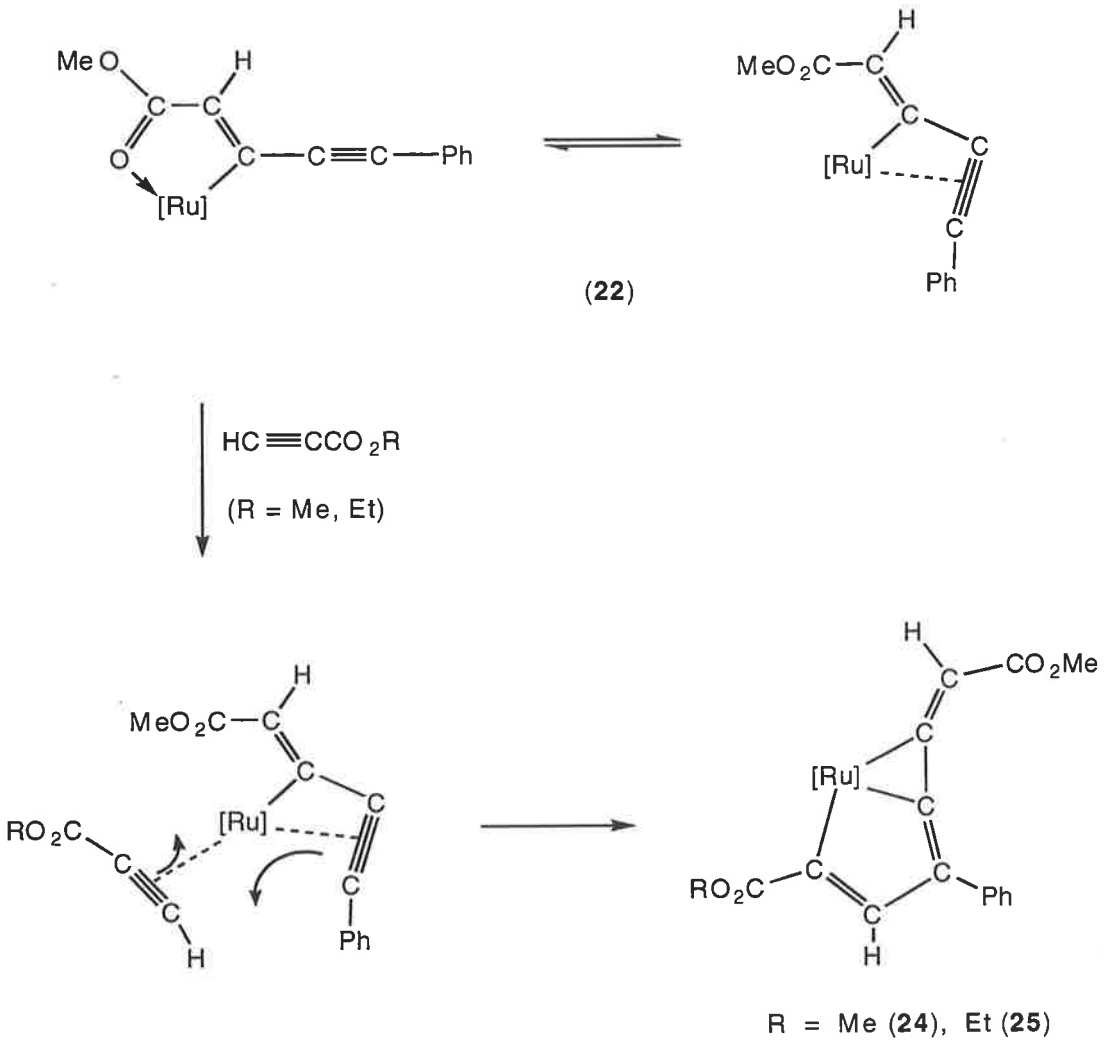


Scheme 5 : Proposed mechanism for the formation of **22**.



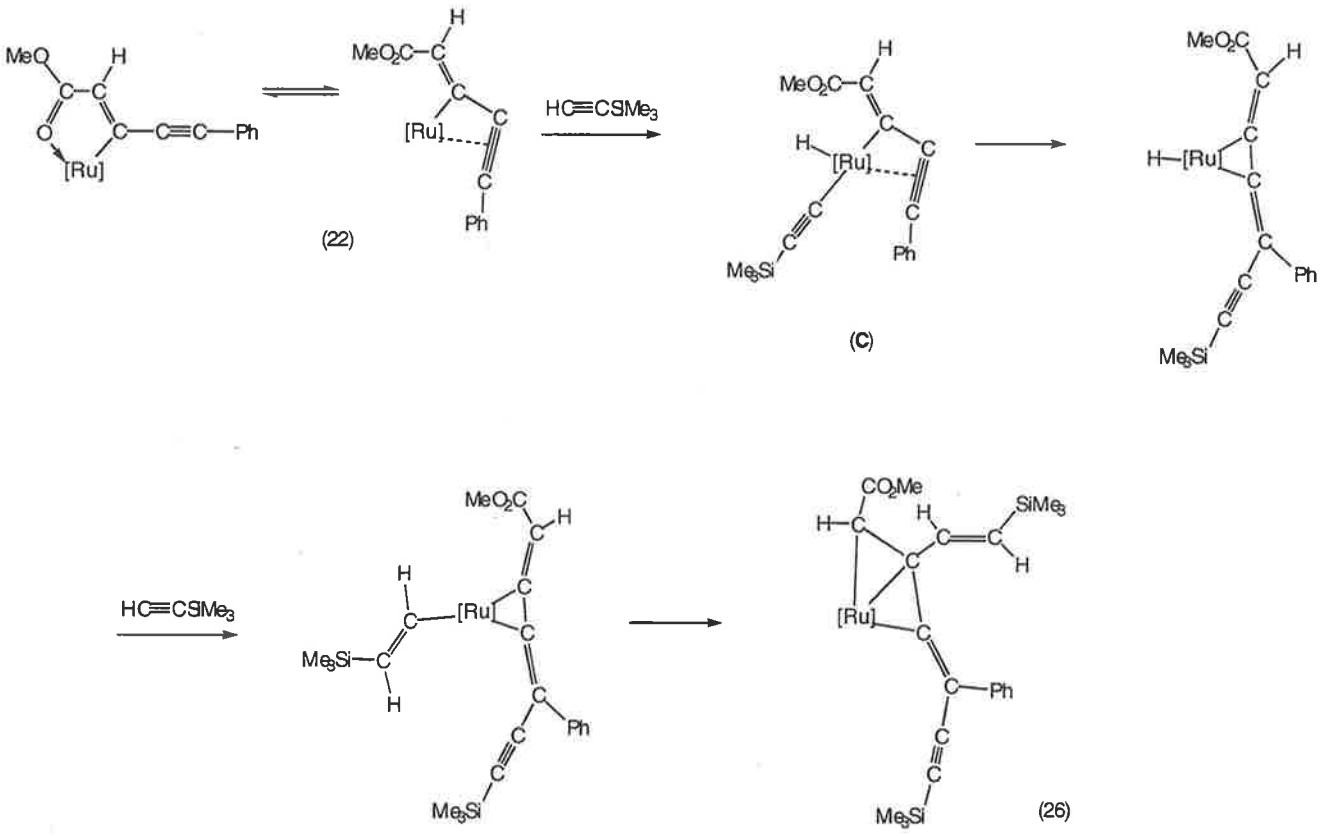
Scheme 6 : Proposed mechanism for the formation of **23**.

In an attempt to determine whether complex **22** is an intermediate en route to **23**, we reacted it with alkyl propiolates (methyl and ethyl). From these reactions we obtained complexes **24** and **25**, which were shown to contain cumulene ligands formed by addition of the alkyl ester to the "dimeric" ligand in **22**. The site of addition, defined as that closest to the metal centre by the presence of methyl or ethyl ester groups, respectively, can be accounted for if **22** isomerises to the η^2-alkyne isomer by displacement of the ester carbonyl group. This may require the presence of the alkyl propiolate, which can coordinate to the metal centre and couple to the Ph end of the coordinated C≡C triple bond (Scheme 7). We note that the organic ligand in these complexes is isomeric to that in **23**, which may be explained by a proton shift analogous to that found in conventional alkyne-allene rearrangements.



Scheme 7 : Proposed mechanism for the formation of **24** and **25**.

The reaction between **22** and $HC{\equiv}CSiMe_3$ gave an unprecedented type of complex containing a ligand derived from four alkyne molecules. In this case, we suggest that isomerisation of **22** and addition of the free alkyne affords an η^2-alkyne intermediate similar to that shown in Scheme 7, which then undergoes an internal oxidative addition to the metal centre the give hydrido-alkynyl intermediate (**C**). This is followed by coupling of the alkynyl and η^2-alkyne moieties, insertion of a second molecule of $HC{\equiv}CSiMe_3$ into the Ru-H bond of (**C**), followed by coupling of the resulting vinyl with the terminal vinyl moiety to afford **26** (Scheme 8).



Scheme 8 : Proposed mechanism for the formation of **26**.

CONCLUSIONS.

The synthesis of neutral ruthenium-vinylidene complexes by displacement of a bulky PPh_3 ligand from precursor $RuCl(PPh_3)_2Cp^*$ contrasts with the chemistry of the related Cp analogue, which loses chloride and forms the cationic vinylidene complexes. The neutral complexes readily eliminate HCl on treatment with base: in the presence of 2-e donor ligands, complexes of the type $Ru(C_2R)(L)(PPh_3)Cp^*$ are formed which, if $L \neq PPh_3$, are chiral at the metal centre. In addition to the usual tertiary phosphine, phosphite or arsine ligands, L may be an unsaturated hydrocarbon (olefin, alkyne), H_2 or Group 16 donor ligands. These reactions proceed under very mild conditions and offer a novel extension of the already extensive cyclopentadienyl-ruthenium-vinylidene and -acetylide chemistry.

This work has also demonstrated an innovative series of stepwise reactions of 1-alkynes with the neutral ruthenium vinylidene complexes $RuCl(=C=CHR)(PPh_3)Cp^*$ which result in a series of complexes containing ligands derived from between two and four alkyne molecules. Direct trimerisation or cyclotrimerisation of alkynes does not occur, instead individual steps involving single coupling of two alkyne-derived ligands take place. These reactions appear to proceed by stepwise insertions of the alkyne into Ru-C σ-bonds or by coupling of two alkynes at the ruthenium centre. In some cases, isomerisation of the alkyne to the corresponding vinylidene may precede these reactions. We have sought to demonstrate formation of possible intermediates by alternative syntheses, taking advantage of the presence of the chloride ligand in **2** and its ability to be replaced by alkynyl groups by means of reactions with alkali metal or silver derivatives of the alkynes, the latter being chosen to facilitate removal of chloride as insoluble AgCl.

Table 1 : Selected bond parameters (bond lengths in Å, angles in °) for complexes **2**, **9**, **12**, **13**, **16–26**.

Complex	**2**	**9**	**12**
R	Ph	Bu^t	Bu^t
L^1	PPh_3	PPh_3	dppm
L^2	PPh_3	CO	
Ru-C≡	2.006(4)	2.032(3)	2.029(5)
Ru-P(1)	2.311(1)	2.309(1)	2.267(2)
Ru-L^2	2.313(1)	1.828(4)	2.271(5)
Ru-C(Cp*)	2.247 – 2.290(4)	2.223 – 2.311(4)	2.211 – 2.257(6)
(av)	2.27	2.26	2.24
C≡C	1.216(6)	1.197(4)	1.186(7)
≡C-R	1.423(5)	1.495(5)	1.495(7)
Other			
P(1)-Ru-C≡	86.2(1)	84.52(8)	80.6(1)
P(1)-Ru-L^2	99.56(4)	90.4(1)	70.99(5)
≡C-Ru-L^2	89.5(1)	91.3(2)	85.5(1)
Ru-C≡C	173.9(3)	177.6(3)	176.0(4)
C≡C-R	178.5(5)	174.7(4)	178.4(5)

Complex	**13**	**16**	**17**
R	Bu^t	Bu^t	Bu^t
L^1	PPh_3	dppee	PPh_3
L^2	dppe-P		C_2H_4
Ru-C≡	2.058(9)	2.025(8)	2.034(6)
Ru-P(1)	2.272(2)	2.244(2)	2.300(3)
Ru-L^2	2.288(2)	2.247(2)	2.186(8), 2.170(9)
Ru-C(Cp*)	2.243 – 2.287(9)	2.215 – 2.280(8)	2.215 – 2.292(7)
(av)	2.27	2.24	2.25
C≡C	1.21(1)	1.17(1)	1.189(8)
≡C-R	1.47(2)	1.51(1)	1.490(8)
Other			C=C, 1.39(1)
P(1)-Ru-C≡	89.4(2)	82.3(2)	83.3(2)
P(1)-Ru-L^2	95.74(8)	82.72(8)	84.0(2), 103.6(2)
≡C-Ru-L^2	85.5(1)	87.0(2)	109.4(3), 80.7(3)
Ru-C≡C	171.0(7)	177.3(7)	179.0(5)
C≡C-R	178.1(9)	173.8(8)	174.1(7)

Complex	**18**	**19**	**20**
R	Ph	Bu^t	Bu^t
L^1	PPh_3	PPh_3	PPh_3
L^2	O_2	S_2	$S2C{\equiv}CBu^t$
Ru-C≡	2.022(4)	2.024(5)	-
Ru-P(1)	2.327(1)	2.334(1)	2.303(9)
Ru-L^2	2.032(3), 2.048(3)	2.383(2), 2.049(3)	2.37(1), 2.350(9)
Ru-C(Cp*)	2.204 – 2.297(4)	2.206 – 2.301(7)	2.20 – 2.23(3)
(av)	2.25	2.26	2.21
C≡C	1.158(5)	1.200(8)	1.17(4)
≡C-R	1.467(5)	1.480(8)	1.52(5)
Other	O=O, 1.363(4)	S=S, 2.010(2)	S-C, 1.70, 1.67(4)
P(1)-Ru-C≡	80.3(1)	80.1(1)	-
P(1)-Ru-L^2	85.63(9), 103.97(9)	84.72(6), 107.00(7)	93.7(4), 90.6(3)
≡C-Ru-L^2	118.3(1), 87.6(1)	121.1(2), 81.3(2)	-
Ru-C≡C	172.5(4)	175.4(4)	-
C≡C-R	172.6(4)	177.5(8)	172(4)

For **20** : S(1)-Ru-S(2) 71.4(3), S(1)-C(1)-S(2) 110(2), S-C(1)-C(2) 128, 122(3)°.

Complex	**21**	**22**	**23**
Ru-P	2.311, 2.323(2)	2.281(3)	2.329(2)
Ru-C(Cp*)	2.220-2.256, 2.231-2.273(6)	2.178-2.224(9)	2.203-2.274(5)
(av)	2.23_6, 2.24_3	2.19_2	2.23_4
Ru-C(1)	2.305, 2.294(6)	-	2.243(5)
Ru-C(2)	2.124, 2.135(6)	2.032(8)	2.117(5)
Ru-C(3)	2.029, 2.037(6)	-	2.025(4)
C(1)-C(2)	1.434, 1.426(9)	1.35(1)	1.426(7)
C(1)-C(11)	1.448, 1.461(8)	1.44(1)	1.470(8)
C(2)-C(3)	1.408, 1.421(8)	1.41(1)	1.429(7)
C(3)-C(4)	1.339, 1.340(9)	1.19(1)	1.349(6)
C(4)-C(5)	1.431, 1.439(9)	-	1.456(8)
C(4)-C(41)	1.503, 1.494(9)	1.44(1)	1.473(7)
C(5)-C(6)	1.193(9), 1.19(1)	-	1.180(9)
C(6)-C(61)	1.448(9), 1.44(1)	-	1.441(9)
C(11)-O(11)	-	1.23(1)	1.203(8)
C(11)-O(12)	-	1.36(1)	1.353(7)
P-Ru-C,O(1)	83.7, 84.9(2)	87.7(2)	-
P-Ru-C(2)	106.7, 106.4(2)	90.3(2)	-
P-Ru-C(3)	93.8, 93.5(2)	-	92.0(2)
C(11)-C(1)-C(2)	124.6, 124.8(5)	112.9(7)	119.7(5)
C(1)-C(2)-C(3)	119.6, 121.2(5)	118.8(7)	115.6(5)
C(2)-C(3)-C(4)	134.1, 134.2(6)	177.7(8)	131.2(5)
C(3)-C(4)-C(5)	120.6, 120.9(6)	-	120.0(4)
C(3)-C(4)-C(41)	124.0, 123.3(6)	178.9(9)	-
C(4)-C(5)-C(6)	176.6, 174.6(7)	-	-
C(5)-C(6)-C(61)	176.3, 177.7(7)	-	-
C(1)-C(11)-O(11)	-	121.1(8)	-
C(1)-C(11)-O(12)	-	117.0(8)	-

Complex	**24**	**25**	**26**
Ru-P	2.335, 2.338(1)	2.330, 2.337(2)	2.3322(9)
Ru-C(Cp*)	2.217-2.360, 2.231-2.372(6)	2.223-2.351, 2.208-2.368(7)	2.213-2.274(5)
(av)	2.28_2, 2.29_0	2.28_1, 2.28_0	2.23_4
Ru-C(1)	-	-	2.214(3)
Ru-C(2)	2.104, 2.087(4)	2.086, 2.087(5)	2.154(2)
Ru-C(3)	2.066, 2.083(5)	2.072, 2.077(5)	2.044(3)
Ru-C(6)	2.082, 2.085(5)	2.089, 2.096(5)	-
C(1)-C(2)	1.337, 1.332(6)	1.344, 1.363(6)	1.425(5)
C(1)-C(11)	1.452, 1.465(6)	1.429, 1.439(7)	1.486(5)
C(2)-C(3)	1.342, 1.343(7)	1.339, 1.333(7)	1.419(4)
C(3)-C(4)	1.348, 1.337(7)	1.353, 1.343(8)	1.352(5)
C(4)-C(5)	1.453, 1.456(7)	1.443(8), 1.455(7)	1.445(4)
C(4)-C(41)	1.472, 1.487(7)	1.461(9), 1.466(8)	1.485(3)
C(5)-C(6)	1.348, 1.366(8)	1.338(9), 1.367(8)	1.202(5)
C(6)-C(61)	1.487, 1.486(7)	1.483(8), 1.460(7)	-
C(6)-O(61)	1.193, 1.183(7)	1.187, 1.189(7)	-
C(6)-O(62)	1.337, 1.347(7)	1.338, 1.299(7)	-
C(11)-O(11)	1.197, 1.200(7)	1.203, 1.207(7)	1.196(4)
C(11)-O(12)	1.355, 1.356(7)	1.351, 1.348(6)	1.349(5)
P-Ru-C,O(1)	-	-	83.89(8)
P-Ru-C(2)	88.8, 89.2(2)	89.2, 90.0(1)	104.42(9)
P-Ru-C(3)	103.5, 103.7(1)	103.1, 104.8(2)	88.56(9)
P-Ru-C(6)	89.5, 89.6(1)	88.3, 89.6(2)	-
C(11)-C(1)-C(2)	122.5, 122.3(4)	123.2, 121.6(5)	-
C(1)-C(2)-C(3)	151.9, 150.9(5)	149.7, 151.6(5)	115.6(3)
C(2)-C(3)-C(4)	158.5, 160.6(5)	161.2, 161.3(5)	134.3(2)
C(3)-C(4)-C(5)	109.8, 111.5(4)	109.9, 110.8(5)	121.8(2)
C(4)-C(5)-C(6)	115.7, 114.8(4)	116.7, 115.2(5)	175.2(3)
C(5)-C(6)-C(61)	115.7, 113.9(5)	117.1, 115.3(5)	-
C(1)-C(11)-O(11)	127.5, 127.6(4)	127.4, 128.0(5)	-
C(1)-C(11)-O(12)	110.3, 110.0(4)	111.2, 110.0(5)	-

EXPERIMENTAL

General Experimental Conditions.

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

Instrumentation.

Infrared spectra were obtained on a Perkin-Elmer 1720X FT IR spectrometer. Solution spectra were obtained by means of a 0.5mm path length solution cell with NaCl windows. Nujol mull spectra were obtained from samples mounted between NaCl discs. NMR spectra were recorded on Bruker ACP 300 (^{1}H at 300.13 MHz, ^{13}C at 75.47 MHz, ^{31}P at 121.50 MHz) or Varian Gemini 200 (^{1}H at 199.80 MHz, ^{13}C at 50.29 MHz) spectrometers. Samples were dissolved in $CDCl_3$ (Sigma) and spectra were recorded using 5mm sample tubes. Electrospray mass spectra (ES MS) were obtained from samples dissolved in MeOH unless otherwise indicated. Solutions were injected into a VG Platform II spectrometer via a 10µl injection loop, or by direct infusion into a Finnegan LCQ instrument. Nitrogen was used as the drying and nebulising gas. Samples were examined at cone voltages in the range 20 - 80V to find the best conditions. Chemical aids to ionisation are indicated where used.

EXPERIMENTAL.

Starting materials. $RuCl_3.xH_2O$ (Johnson Matthey) was used as received. Chemical reagents were laboratory grade and used as received. 1,2,3,4,5-pentamethylcyclopentadiene was prepared according to the literature procedure[56]. $RuCl(PPh_3)_2Cp^*$ **1**[57,58] was obtained as described below, and $RuCl\{=C=CH(CO_2Me)\}(PPh_3)Cp^*$ **28**[29] was prepared by literature methods; $HC{\equiv}CCO_2R$ (R = Me, Et) were obtained by esterification of propiolic acid (Aldrich).

$RuCl(PPh_3)_2Cp^*$ **1**.

$RuCl_3{\cdot}xH_2O$ (500 mg, 2.41 mmol) and Cp*H (655 mg, 4.82 mmol) were dissolved in of EtOH (30 ml) and heated under reflux for 90 min, after which a solution of PPh_3 (2.525 g, 9.64 mmol) and NaOEt (46 mg of Na in 2ml of EtOH) in EtOH (40 ml) was added dropwise. The solution was then refluxed for 18 h. The orange-yellow precipitate which separated was collected and washed with EtOH (2 x 5 ml) and hexane (2 x 5 ml) to give $RuCl(PPh_3)_2Cp^*$ **1** (1.28 g, 70%).

$Ru(C_2Ph)(PPh_3)_2Cp^*$ **2**.

To a suspension of **1** (500 mg, 0.628 mmol) in EtOH (60 ml), phenylacetylene (100 mg, excess) was added and the mixture was refluxed for 2 h, turning brown in colour. At room temperature Na (60 mg, 2.6 mmol) was added, giving a yellow precipitate. The product was collected and washed with cold EtOH and pentane to give yellow $Ru(C_2Ph)(PPh_3)_2Cp^*$ **2** (205 mg, 38%). Recrystallisation (benzene / pentane) gave yellow crystals suitable for X-ray studies. Anal. Found: C, 75.73; H, 6.21 $C_{54}H_{50}P_2Ru$ calcd.: C, 75.25; H, 5.81; M, 862. IR (nujol): ν(C≡C) 2066m cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.19 (s, 15H, C_5Me_5), 7.02 - 7.57 (m, 35H, Ph). ^{13}C NMR ($CDCl_3$): δ 9.49 (s, $C_5\mathit{Me}_5$), 93.46 (s, C_5Me_5), 113.04 (s, ≡*C*Ph), 122.56 (s, RuC), 126.71 - 137.67 (m, Ph). FAB MS: 862, M^+; 785, $[M - Ph]^+$; 761, $[M - C_2Ph]^+$; 684, $[M - C_2Ph - Ph]^+$; 600, $[M - PPh_3]^+$; 499, $[Ru(PPh_3)(C_5Me_5)]^+$; 421, $[Ru(PPh_2)(C_5Me_5)]^+$.

*RuCl(C=CHPh)(PPh_3)Cp** **3**.

Complex **1** (100 mg, 0.126 mmol) and phenylacetylene (15 mg, 0.126 mmol) were dissolved in benzene (30 ml). The reaction mixture was refluxed for 30 minutes, during which time the solution became red in colour. After removal of solvent, the residue was dissolved in CH_2Cl_2 and separated by preparative TLC to give three bands. The upper yellow band (R_f 0.8) contained $Ru(C_2Ph)(PPh_3)_2Cp^*$ **2** (5 mg, 5%). The second band (R_f 0.65) was recrystallised (CH_2Cl_2 / MeOH) to give red crystals of $RuCl(C=CHPh)(PPh_3)Cp^*$ **3** (55 mg, 67%). Anal. Found: C, 66.80; H, 5.62 $C_{36}H_{36}ClPRu$ calcd.: C, 67.96; H, 5.66; M, 636. IR (nujol): ν(C=C) 1606m, 1590m cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.48 (s, 15H, C_5Me_5), 4.51 (s, 1H, =CH), 6.8 - 7.5 (m, 20H, Ph). ^{13}C NMR ($CDCl_3$): δ 9.53 (s, $C_5\mathit{Me}_5$), 102.34 (s, =CH), 112.99 (s, C_5Me_5), 123.88 - 134.07 (m, Ph), 339.95 [d, *J*(CP) = 24.75 Hz, Ru*C*]. FAB MS: 636, M^+; 600, $[M - Cl]^+$; 534, $[M - C=CHPh]^+$; 499, $[Ru(PPh_3)(C_5Me_5)]^+$; 363, $[Ru(PPh_3)]^+$; 237, $[Ru(C_5Me_5)]^+$. The third pink band (R_f 0.4) contained an uncharacterised solid (5 mg).

*RuCl(C=CHBu^t)(PPh_3)Cp** **4**.

A mixture of **1** (100 mg, 0.126 mmol) and 3,3-dimethyl-1-butyne (100 mg, 1.25 mmol) in benzene (30 ml) was heated under reflux for 30 min, the solution becoming deep red. Removal of solvent and separation of a CH_2Cl_2 extract of the residue by preparative TLC (acetone / hexane, 3:7) gave two bands. The upper band (R_f 0.70) was recrystallized (CH_2Cl_2 / MeOH) to give red crystals of $RuCl(C=CHBu^t)(PPh_3)Cp^*$ **4** (60 mg, 78%). Anal. Found: C, 65.37; H, 6.48 $C_{34}H_{40}ClPRu.MeOH$ calcd.: C, 64.85; H, 6.84; M, 616. IR (nujol): ν(C=C) 1626m cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.93 (s, 9H, CMe_3), 1.41 (s, 15H, C_5Me_5), 3.38 (s, 1H, =CH), 7.25 - 7.68 (m, 15H, Ph). ^{13}C NMR ($CDCl_3$): δ 9.40 (s, $C_5\mathit{Me}_5$), 29.66 (s, $C\mathit{Me}_3$), 32.05 (s, $\mathit{C}Me_3$), 100.93 (s, C_5Me_5), 120.49 (s, =CH), 127.16 - 134.44 (m, Ph), 336.38 [d, *J*(CP) = 24.38 Hz, RuC]. FAB MS: 615, M^+; 580, $[M - Cl]^+$; 534, $[M - C=CHCMe_3]^+$; 499, $[Ru(PPh_3)(C_5Me_5)]^+$; 421, $[Ru(PPh_2)(C_5Me_5)]^+$. The second band (R_f 0.5) was not characterised.

*RuCl(C=CHSiMe$_3$)(PPh$_3$)Cp** **5**.

A mixture of **1** (100 mg, 0.125 mmol) and HC_2SiMe_3 (0.02 g, 0.3 mmol) was heated in refluxing benzene (20 ml) for 30 min. Solvent was removed and the residue was dissolved in CH_2Cl_2 and separated by preparative TLC (acetone / hexane, 1:4). An orange band (R_f 0.44) gave orange crystals (from hexane) of RuCl(C=CHSiMe$_3$)(PPh$_3$)Cp* **5** (41 mg, 52%). Anal. Found: C, 62.36; H, 6.33 $C_{33}H_{40}ClPRuSi$ calcd.: C, 62.76; H, 6.34; M, 632. IR (nujol): ν(C=C) 1609m cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.06 (s, 9H, $SiMe_3$), 1.41 [d, *J*(HP) = 1.34 Hz, 15H, C_5Me_5], 2.91 (s, 1H, =CH), 7.26 - 7.54 (m, 15H, Ph). ^{13}C NMR ($CDCl_3$): δ 0.63 (s, $SiMe_3$), 8.65 (s, C_5Me_5), 92.33 (s, =CH), 99.41 (s, C_5Me_5), 126.88 - 133.78 (m, Ph), 321.67 (s, RuC). FAB mass spectrum: 587, [M – 3Me]$^+$; 559, [M – $SiMe_3$]$^+$; 534, [M – C=CHSiMe$_3$]$^+$; 525, [Ru(C_2H)(PPh_3)(C_5Me_5)]$^+$; 499, [Ru(PPh_3)(C_5Me_5)]$^+$.

*RuCl(C=CHMe)(PPh3)Cp** **6**.

Prop-1-yne was passed into a solution of **1** (100 mg, 0.126 mmol) in benzene (30 ml); after 30 min, the solution was golden-yellow in colour. Solvent was removed and the residue dissolved in CH_2Cl_2 and separated (preparative TLC; acetone / hexane, 3:7). The top yellow band (R_f 0.44) contained RuCl(C=CHMe)(PPh_3)Cp* **6** (30 mg, 42%) which was recrystallised (CH_2Cl_2 / MeOH) to give yellow needle-like crystals. IR (nujol): ν(C=C) 1586m, 1571m cm^{-1}. FAB mass spectrum: 561, [M – CH_2]$^+$; 534, [M - C=CHMe]$^+$; 499, [Ru(PPh_3)(C_5Me_5)]$^+$; 457, [RuCl(PPh_2)(C_5Me_5)]$^+$; 421, [Ru(PPh_2)(C_5Me_5)]$^+$. The other band was not characterised.

*Ru(C$_2$Bu^t)(PPh$_3$)$_2$Cp** **7**.

(a) A mixture of 3,3-dimethyl-1-butyne (100 mg, excess) and **1** (500 mg, 0.62 mmol) in EtOH (60 ml) was refluxed for 2 hours, turning brown in colour. Addition of Na (60 mg, 0.26 mmol) at room temperature gave a yellow precipitate. The product was filtered and washed with cold EtOH and pentane to give Ru(C_2Bu^t)(PPh_3)$_2$Cp* **7** (156 mg, 29%). Recrystallisation (benzene / pentane) gave yellow crystals. Anal. Found: C, 73.95; H, 6.18 $C_{52}H_{54}P_2Ru$ calcd.: C, 74.20; H, 6.42; M, 842. IR (nujol): ν(C≡C) 2080m cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.14 (s, 15H, C_5Me_5), 1.37 (s, 9H, CMe_3), 7.02 - 7.57 (m, 30H, Ph). ^{13}C NMR ($CDCl_3$): δ 9.38 (s, $C_5\mathit{Me}_5$), 30.04 (c, $C\mathit{Me}_3$), 33.01 (s, $\mathit{C}Me_3$), 92.62 (s, C_5Me_5), 99.34 (s, ≡$\mathit{C}Bu^t$), 117.94 (s,

RuC), 126.35 - 137.85 (m, Ph). FAB mass spectrum: 842, M^+; 761, $[M - C_2Bu^t]^+$; 580, $[M - PPh_3]^+$; 499, $[Ru(PPh_3)(C_5Me_5)]^+$; 421, $[Ru(PPh_2)(C_5Me_5)]^+$; 314, $[Ru(C_2Bu^t)(C_5Me_5)]^+$; 233, $[Ru(C_5Me_5)]^+$.

(b) NaOMe [from Na (92 mg) in MeOH (2 ml)] was added to a warm solution containing **4** (100 mg, 0.162 mmol) and of PPh3 (84.9 mg, 0.324 mmol) in MeOH (20 ml) when the red solution immediately turned yellow. Cooling in an ice bath gave a yellow precipitate, which was filtered to give **7** (100 mg, 73%).

$Ru(C_2Ph)(CO)(PPh_3)Cp^*$ **8**.

A stream of CO was passed through a solution of **3** (100mg, 0.157 mmol) in MeOH (20 ml) for 10 min, after which excess NaOMe [from Na (0.092 g) in MeOH (2 ml)] was added, resulting in a change in colour from red to yellow. Solvent was removed and the residue was chromatographed. The upper yellow band (R_f 0.7) contained yellow $Ru(C_2Ph)(CO)(PPh_3)Cp^*$ **8** (45 mg, 46 %). Anal. Found: C, 69.80; H, 5.69 $C_{37}H_{35}OPRu$ calcd.: C, 70.80; H, 5.62; M, 628. IR (nujol): ν(C≡C) 2095m; ν(CO) 1915s cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.50 (s, 15H, C_5Me_5); 7.26 - 7.57 (m, 15H, Ph). ^{13}C NMR ($CDCl_3$): δ 9.37 (s, $C_5\mathit{Me}_5$), 96.32 (s, C_5Me_5), 103.81 (s, ≡CPh), 123.95 (s, RuC), 127.47 - 134.11 (m, Ph), 206.44 [t, J(CP) = 22.7 Hz, CO].

$Ru(C_2Bu^t)(CO)(PPh_3)Cp^*$ **9**.

a) Using $AgPF_6$, CO and NaOMe. A stream of CO was passed into a solution of **4** (100 mg, 0.162 mmol) in CH_3CN (30 ml) for 10 min. $AgPF_6$ (41 mg (0.126 mmol) was then added. Over 3.5 h the solution changed from red through apricot to yellow in colour and contained a white precipitate (AgCl). After filtration, deprotonation with NaOMe [from Na (40 mg) in MeOH (4 ml)] gave a dark orange solution. Solvent was removed and the residue was separated by preparative TLC (acetone / hexane, 3:7). The upper band (R_f 0.8) was recrystallised (CH_2Cl_2 / MeOH) to give fine yellow crystals of $Ru(C_2Bu^t)(CO)(PPh_3)Cp^*$ **9** (54 mg, 54%). Anal. Found: C, 69.04; H, 6.36 $C_{35}H_{39}OPRu$ calcd.: C, 69.08; H, 6.41; M, 608. IR (nujol): ν(C≡C) 2100m; ν(CO) 1928s, 1911s cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.99 (s, 9H, CMe_3), 1.60 [d, J(HP) = 1.43 Hz, 15H, C_5Me_5], 7.25 - 7.64 (m, 15H, PPh_3). ^{13}C NMR ($CDCl_3$): δ 9.70 (s, $C_5\mathit{Me}_5$), 29.31 (s, $C\mathit{Me}_3$), 32.70 (s, $\mathit{C}Me_3$), 90.50 (s, ≡CBu^t), 118.45 (s, RuC), 127.49 -

135.32 (m, Ph), 207.23 [d, *J*(CP) = 20.9 Hz, CO]. FAB mass spectrum: 608, M^+; 580, $[M - CO]^+$; 527, $[M - C_2But]^+$; 499, $[Ru(PPh_3)(C_5Me_5)]^+$; 421, $[Ru(PPh_2)(C_5Me_5)]^+$; 342, $[Ru(PPh)(C_5Me_5)]^+$. The lower band (R_f = 0.55) was orange in colour and is uncharacterised.

b) Deprotonation with NaOMe in the presence of CO. A solution of **4** (100 mg, 0.16 mmol) in MeOH (20 ml) was treated with CO as above. After 10 min, NaOMe [excess, from Na (0.92 g) in MeOH (2 ml)] was added. On warming to ~50°C the solution became yellow. Work-up as above gave a yellow band (R_f 0.8) containing $Ru(C_2Bu^t)(CO)(PPh_3)Cp^*$ **9** (40 mg, 41%).

$Ru(C_2Bu^t)\{P(OMe)_3\}(PPh_3)Cp^*$ **10**.

An excess of NaOMe was added to a mixture of **4** (100 mg, 0.162 mmol) and of trimethyl phoshite (19.8 mg, 0.162 mmol) in MeOH (20 ml). Work-up of the resulting yellow solution by preparative TLC (acetone / hexane 3:7) gave a major yellow band (R_f 0.85) which afforded $Ru(C_2Bu^t)\{P(OMe)_3\}PPh_3)Cp^*$ **10** (70 mg, 61%) as a yellow solid. Anal. Found: C, 57.72; H, 6.37 $C_{37}H_{48}O_3P_2Ru$ calcd.: C, 57.86; H, 6.39; M, 703. IR (nujol): ν(C≡C) 2086m; ν(PO) 1030s cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.17 (s, 9H, CMe_3), 1.47 (s, 15H, C_5Me_5), 3.34 [d, *J*(HP) = 10.7 Hz, 9H, OMe], 7.24 - 7.80 (m, 15H, Ph). ^{13}C NMR ($CDCl_3$): δ 9.58 [d, *J*(CP) = 8.9 Hz, $C_5\mathit{Me_5}$], 29.50 (s, $C\mathit{Me_3}$), 32.97 [d, *J*(CP) = 7.6 Hz, $\mathit{C}Me_3$], 51.96 [d, *J*(CP) = 5.9 Hz, OMe], 93.42 (s, C_5Me_5), 116.80 (s, RuC), 116.86 [d, *J*(CP) = 1.81 Hz, ≡CBu^t], 126.32 - 139.22 (m, Ph). FAB mass spectrum: 703, M^+; 624, $[M - C_2Bu^t]^+$; 580, $[M - P(OMe)_3]^+$; 499, $[Ru(PPh_3)(C_5Me_5)]^+$; 441, $[M - PPh_3]^+$.

$Ru(C_2Bu^t)(AsPh_3)(PPh_3)Cp^*$ **11**.

Orange crystals (from CH_2Cl_2 / MeOH) of $Ru(C_2Bu^t)(AsPh_3)(PPh_3)Cp^*$ **11** (55 mg, 40%) were obtained from **4** (100 mg, 0.162 mmol) and $AsPh_3$ (50 mg, 0.162 mmol) in MeOH (10 ml) after treatment with an excess of NaOMe and work-up as above. Anal. Found: C, 65.57; H, 6.07 $C_{42}H_{54}AsPRu.CH_2Cl_2$ calcd.: C, 66.36; H, 6.08; M, 885. IR (nujol): ν(C≡C) 2078m cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.19 (s, 15H, C_5Me_5), 1.37 (s, 9H, CMe_3), 7.03 - 7.57 (m, 30H, Ph). ^{13}C NMR ($CDCl_3$): δ 9.40 (s, $C_5\mathit{Me_5}$), 29.77 (s, $C\mathit{Me_3}$), 32.13 (s, $\mathit{C}Me_3$), 92.48 (s, $\mathit{C_5}Me_5$), 100.90 (s, ≡CBu^t), 120.50 (s,

RuC), 126.29 - 134.68 (m, Ph). FAB mass spectrum: 884, M^+; 803, $[M - C_2Bu^t]^+$; 725, $[M - Ph - C_2Bu^t]^+$; 668, $[Ru(AsPh_3)(PPh_3)]^+$; 580, $[M - AsPh_3]^+$; 499, $[Ru(PPh_3)(C_5Me_5)]^+$; 421, $[Ru(PPh_2)(C_5Me_5)]^+$.

*Ru(C_2Bu^t)(dppm)Cp** **12**.

An excess of NaOMe was added to a mixture of **4** (100 mg, 0.162 mmol) and dppm (24.5 mg, 0.324 mmol) in warm MeOH (20 ml). The red solution immediately turned yellow, the precipitate which separated on cooling was recrystallised (CH_2Cl_2 / MeOH) to give Ru(C_2Bu^t)(dppm)Cp* **12** (150 mg, 95%). Anal. Found: C, 68.06; H, 6.25 $C_{41}H_{46}P_2Ru.CH_2Cl_2$ calcd.: C, 68.70; H, 6.05; M, 702. IR (nujol): ν(C≡C) 2078m cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.15 (s, 15H, C_5Me_5), 1.48 (s, 9H, CMe_3), 2.81 (s, 2H, CH_2), 7.03 - 7.70 (m, 20H, Ph). ^{13}C NMR ($CDCl_3$): δ 9.41 (s, $C_5\mathit{Me_5}$), 28.04 [t, *J*(CP) = 22.9 Hz, CH_2], 33.54 (s, $C\mathit{Me_3}$), 92.49 (s, C_5Me_5), 112.40 (s, ≡CBu^t), 113.20 (s, RuC), 125.99 - 135.26 (m, Ph). FAB mass spectrum: 702, M^+; 621, $[Ru(dppm)(C_5Me_5)]^+$; 317, $[M - dppm]^+$.

*Ru(C_2Bu^t)(PPh_3)(dppe-P)Cp** **13**.

This complex was prepared in a similar manner to **12** above, from **4** (100 mg, 0.162 mmol) and dppe (124 mg, 0.324 mmol) in MeOH (20 ml) with an excess of NaOMe. The yellow precipitate was recrystallised (CH_2Cl_2 / MeOH) to give Ru(C_2Bu^t)(PPh_3)(dppe-*P*)Cp* **13** (142 mg, 89%). Anal. Found: C, 72.96; H, 6.46 $C_{60}H_{63}P_3Ru$ calcd.: C, 73.67; H, 6.49; M, 978. IR (nujol): ν(C≡C) 2075m cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.17 (s, 15H, C_5Me_5), 1.23 (s, 9H, CMe_3), 2.09 [t, *J*(HP) = 3.8 Hz, 4H, CH_2], 6.90 - 7.52 (m, 35H, Ph). ^{13}C NMR ($CDCl_3$): δ 9.50 (s, $C_5\mathit{Me_5}$), 23.87 (s, CH_2), 29.90 (s, $C\mathit{Me_3}$), 33.22 (s, $\mathit{C}Me_3$), 92.38 (s, C_5Me_5), 92.52 (s, ≡CBu^t), 115.95 (s, RuC), 126.50 - 138.13 (m, Ph). FAB mass spectrum: 978, M^+; 897, $[M - C_2Bu^t]^+$; 716, $[M - PPh_3]^+$; 635, $[M - C_2Bu^t - PPh_3]^+$; 580, $[M - dppe]^+$; 499, $[Ru(PPh_3)(C_5Me_5)]^+$.

*Ru(C_2Bu^t)(PPh_3)(dppa-P)Cp** **14**.

Similarly, **4** (100 mg, 0.162 mmol) and dppa (64 mg, 0.162 mmol) in warm MeOH (20 ml), after treatment with an excess of NaOMe, afforded Ru(C_2Bu_t)(PPh_3)(dppa-*P*)Cp* **14** (120 mg, 76%). Anal. Found: C, 70.02; H, 5.85 $C_{60}H_{59}P_3Ru.CH_2Cl_2$ calcd.: C, 69.18; H, 5.80; M, 974. IR (nujol): ν(C≡C) 2079m cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.09 (s, 15H, C_5Me_5), 1.29 (s, 9H, CMe_3), 6.50 - 7.73 (m, 35H, Ph). ^{13}C NMR ($CDCl_3$): δ 9.29 (s, $C_5\mathit{Me}_5$), 30.20 (s, $C\mathit{Me}_3$), 33.22 (s, $\mathit{C}Me_3$), 93.07 (s, C_5Me_5), 94.56 (s, ≡CBu^t), 118.02 (s, RuC), 126.59 - 138.19 (m, Ph). FAB mass spectrum: 974, M^+; 893, $[M - C_2Bu^t]^+$; 712, $[M - PPh_3]^+$; 629, $[M - C_2Bu^t - PPh_3]^+$; 580, [M - dppa]$^+$; 499, $[Ru(PPh_3)(C_5Me_5)]^+$.

*Ru(C_2Ph)(PPh_3)(dppm-P)Cp** **15**.

Similarly, a mixture of **3** (100 mg, 0.157 mmol) and dppm (60.4 mg, 0.157 mmol) in warm MeOH (20 ml) was treated with an excess of NaOMe to give, after work-up and recrystallisation, yellow Ru(C_2Ph)(PPh_3)(dppm-*P*)Cp* **15** (116 mg, 75%). Anal. Found: C, 74.40; H, 5.92 $C_{61}H_{57}P_3Ru$ calcd.: C, 74.45; H, 5.84; M, 984. IR (nujol): ν(C≡C) 2060m cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.20 (s, 15H, C_5Me_5), 2.80 [t, J(HP) = 1.36 Hz, 2H, CH_2], 6.66 - 7.78 (m, 40H, Ph). ^{13}C NMR ($CDCl_3$): δ 10.50 (s, $C_5\mathit{Me}_5$), 30.05 (s, CH_2), 89.40 (s, C_5Me_5), 100.00 s, ≡CPh), 124.80 (s, RuC), 125.80 - 136.84 (m, Ph). FAB mass spectrum: 984, M^+; 723, $[M - PPh_3]^+$; 600, [M - dppm]$^+$; 499, $[Ru(PPh_3)(C_5Me_5)]^+$.

*Ru(C_2Bu^t)(dppee)Cp** **16**.

The reaction between **4** (100 mg, 0.162 mmol) and dppee (64.2 mg, 0.162 mmol) in MeOH (20 ml) was carried out in similar fashion. An excess of NaOMe was added to the warm solution, whereupon a yellow precipitate separated. After work-up, Ru(C_2Bu^t)(dppee)Cp* **16** (110 mg, 94%) was obtained. Anal. Found: C, 70.81; H, 6.00 $C_{42}H_{46}P_2Ru$ calcd.: C, 70.65; H, 6.49; M, 714. IR (nujol): ν(CO) 2076m; ν(C=C) 1585m cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.23 (s, 15H, C_5Me_5), 1.41 (s, 9H, CMe_3), 6.45 [t, J(HP) = 6.7 Hz, 2H, =CH], 6.94 - 7.63 (m, 20H, Ph). ^{13}C NMR ($CDCl_3$): δ 10.00 (s, $C_5\mathit{Me}_5$), 30.08 (s, $C\mathit{Me}_3$), 33.41 (s, $\mathit{C}Me_3$), 92.67 (s, C_5Me_5), 115.49 (s, ≡CBu^t), 118.07 (s, RuC), 126.33 - 146.90 (m, Ph), 146.78 (s, =CH). FAB mass spectrum: 714 M^+; 633, $[M - C_2Bu^t]^+$; 579, $[M - C_5Me_5]^+$; 317, [M - dppee]$^+$.

*Ru(C_2Bu^t)(η-C_2H_4)(PPh_3)Cp** **17**.

Ethene was passed into a solution of **4** (100 mg, 0.162 mmol) in MeOH (20 ml) for 20 min. To the red solution excess NaOMe (as above) was added and the mixture was warmed on a water bath. Solvent was removed from the yellow solution until a precipitate formed. After cooling and filtration, recrystallisation (CH_2Cl_2 / MeOH) gave yellow crystals of Ru(C_2Bu^t)(η-C_2H_4)(PPh_3)Cp* **17** (50 mg, 50%). Anal. Found: C, 62.58; H, 6.21 $C_{36}H_{43}PRu.1.25CH_2Cl_2$ calcd.: C, 62.66; H, 6.42; M, 608. IR (nujol): ν(C≡C) 2088m; ν(C=C) 1570s cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.97 (s, 9H, CMe_3), 1.50 (s, 15H, C_5Me_5), 1.66 [d, J(HP) = 4.20 Hz, 2H, $=CH_2$], 7.20 - 7.70 (m, 15H, Ph). ^{13}C NMR ($CDCl_3$): δ 9.60 (s, $C_5\mathit{Me}_5$), 30.42 (s, $C\mathit{Me}_3$), 30.78 (s, $\mathit{C}Me_3$), 39.39 (s, CH_2), 51.56 (s, CH_2), 90.93 (s, C_5Me_5), 105.19 (s, ≡CBu^t), 124.21 (s, RuC), 127.10 - 136.02 (m, Ph). FAB mass spectrum: 608, M^+; 580, [M – C_2Bu^t]$^+$; 499, [Ru(PPh_3)(C_5Me_5)]$^+$; 421, [Ru(PPh_2)(C_5Me_5]$^+$.

*Ru(C_2Ph)(η-O_2)(PPh_3)Cp** **18**.

Oxygen was passed through a solution of **3** (100 mg, 0.157 mmol) in MeOH (20 ml) for 10 min. Addition of an excess of NaOMe resulted in a change to red-orange. The orange precipitate which separated on cooling was filtered and recrystallised (C_6H_6 / pentane) to give red crystals of Ru(C_2Ph)(η-O_2)(PPh_3)Cp* **18** (76 mg, 77%). Anal. Found: C, 64.79; H, 5.44 $C_{36}H_{35}O_2PRu$ calcd.: C, 65.02; H, 5.38; M, 632. IR (nujol): ν(C≡C) 2094m; ν(OO) 914m cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.53 [d, *J*(HP) = 1.2 Hz, 15H, C_5Me_5], 6.74 - 7.45 (m, 20H, Ph). ^{13}C NMR ($CDCl_3$): δ 9.03 (s, $C_5\mathit{Me}_5$), 103.90 (s, C_5Me_5), 105.32 (s, ≡CPh), 123.44 (s, RuC), 125.02 - 134.29 (m, Ph). FAB mass spectrum: 616, [M - O]$^+$; 600, [M - 2O]$^+$; 525, [M - 2O - Ph]$^+$; 513, [M - 2O – C_2Ph]$^+$; 499, [Ru(PPh_3)(C_5Me_5)]$^+$; 421, [Ru(PPh_2)(C_5Me_5)]$^+$.

*Ru(C_2Bu^t)(η-S_2)(PPh_3)Cp** **19**.

A mixture of **4** (100 mg, 0.162 mmol) and S_8 (10.4 mg, 0.324 mmol) in warm MeOH (20 ml) was treated with an excess of NaOMe, when the solution changed to grey-green. Work-up by preparative TLC gave a grey-green band (R_f 0.8) containing Ru(C_2Bu^t)(η-S_2)(PPh_3)Cp* **19** (64.1 mg, 62%), which formed khaki-green crystals from CH_2Cl_2 / MeOH. Anal. Found: C, 63.19; H, 6.05 $C_{34}H_{39}PRuS_2$ calcd.: C, 63.35; H, 6.06; M, 644. IR (nujol): ν(C≡C) 2114m; ν(SS) 1248m cm^{-1}. ^1H NMR ($CDCl_3$): δ

0.91 (s, 9H, CMe_3), 1.49 [d, *J*(HP) = 1.25 Hz, 15H, C_5Me_5], 7.17 - 7.63 (m, 15H, Ph). ^{13}C NMR ($CDCl_3$): δ 8.95 (s, $C_5\mathit{Me}_5$), 29.44 (s, $C\mathit{Me}_3$), 32.15 (s, $\mathit{C}Me_3$), 101.68 (s, C_5Me_5), 101.72 (s, RuC), 124.67 (s, ≡CBu^t), 126.79 - 135.38 (m, Ph). FAB mass spectrum: 643, M^+; 562, $[M - C_2Bu^t]^+$; 533, $[M - C_2Bu^t - S]^+$; 499, $[Ru(PPh_3)(C_5Me_5)]^+$; 381, $[M - PPh_3]^+$.

$Ru(S_2CC_2Bu^t)(PPh_3)Cp^*$ **20**.

Similarly, **4** (100 mg, 0.162 mmol) and carbon disulfide (24.4 mg, 0.324 mmol) dissolved in MeOH (20 ml), with an excess of NaOMe, gave an olive-green precipitate of $Ru(S_2CC_2Bu^t)(PPh_3)Cp^*$ **20** (51 mg, 48%) on cooling, which was recrystallised from CH_2Cl_2 / MeOH as the 0.5MeOH solvate. Anal. Found: C, 62.76; H, 5.77 $C_{35}H_{39}PRuS_2$ calcd.: C, 63.46; H, 5.85; M, 656. IR (nujol): ν(C≡C) 2195m; ν(CS) 1288m cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.17 (s, 9H, CMe_3), 1.50 [d, *J*(HP) = 1.42 Hz, 15H, C_5Me_5], 7.27 - 7.50 (m, 15H, Ph). ^{13}C NMR ($CDCl_3$): δ 10.54 (s, $C_5\mathit{Me}_5$), 28.89 (s, $C\mathit{Me}_3$), 30.54 [d, *J*(CP) = 8.85 Hz, $\mathit{C}Me_3$], 88.03 (s, C_5Me_5), 97.20 (s, ≡CBu^t), 123.0 (s, ≡$\mathit{C}CS_2$), 127.25 - 135.62 (m, Ph), 191.80 (s, CS_2). FAB mass spectrum: 656, M^+; 499, $[Ru(PPh_3)(C_5Me_5)]^+$; 394, $[M - PPh_3]^+$.

$Ru\{\eta^3\text{-}CHPhCHC{=}CPh(C{\equiv}CPh)\}(PPh_3)Cp^*$ **21**.

(a) With HC≡CPh / NaOMe. A mixture of **3** (100 mg, 0.157 mmol) and HC≡CPh (32 mg, 0.314 mmol) in MeOH (20 ml) was treated with an excess of NaOMe [from Na (0.92 g) in MeOH (2 ml)], after which the colour of the solution slowly changed from red to yellow. Cooling (0°C) gave a yellow precipitate of $Ru\{\eta^3\text{-}CHPhCHC{=}CPh(C{\equiv}CPh)\}(PPh_3)Cp^*$ **21** (84 mg, 67%). Anal. Found: C, 77.30; H, 5.89. $C_{52}H_{47}PRu$ calcd.: C, 77.68; H, 5.85; M, 804. IR (nujol): ν(C≡C) 2181 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.36 [d, *J*(HP) = 1.4 Hz, 15H, Cp*], 3.02 [dd, *J*(HH) = 9 Hz, *J*(HP) = 14 Hz, 1H, =CH], 3.38 [dd, *J*(HH) = 9 Hz, *J*(HP) = 3.7 Hz, 1H, =CH], 6.98 - 7.69 (m, 30H, Ph). ^{13}C NMR ($CDCl_3$): δ 9.76 (s, $C_5\mathit{Me}_5$), 86.21 (s, ≡CPh), 92.12 (s, C_5Me_5), 95.42 (s, $C\mathit{C}$Ph), 124.0 - 131.0 (m, Ph), 96.3, 114,00, 192.50 (C_3 chain). FAB MS: 804, M^+; 727, $[M - Ph]^+$; 679, $[M - C_4Ph]^+$; 601, $[Ru(CCPh)(PPh_3)Cp^*]^+$; 542, $[M - PPh_3]^+$; 499, $[Ru(PPh_3)Cp^*]^+$. Selected lit. values.[28] ^1H NMR: δ 1.36 (s, Cp*), 3.00 [dd, *J*(HH) = 8 Hz, *J*(HP) = 14 Hz, =CH], 3.68 [dd, *J*(HH) = 8.8 Hz, *J*(HP)

= 3.7 Hz, CH], 7.0 - 7.8 (m, Ph). ^{13}C NMR: δ 10.8 (C_5Me_5), 93.4 (C_5Me_5), 96.4, 114.8, 125.3, 192.6 (carbon chain).

(b) With LiC≡CPh. LiC≡CPh (24 mg, 0.24 mmol) in thf (2 ml) was added to **3** (100 mg, 0.162 mmol) in the same solvent (10 ml) cooled to –55 °C. After warming to r.t. and stirring for 1 h, evaporation and chromatography of the residue (alumina column) afforded **21** (30 mg, 24%).

*Ru{η^1,O-C(C≡CPh)=CHC(O)OMe}(PPh$_3$)Cp** **22**.

A solution of **3** (300 mg, 0.48 mmol) in thf (30 ml) was treated with AgC≡CCO$_2$Me (92 mg, 0.48 mmol) and the mixture was stirred at r.t. for 2 h. The filtered solution (alumina) was evaporated and an acetone extract was separated by preparative TLC to give recovered **3** (12 mg, 4%) and Ru{η^1,*O*-C(C≡CPh)=CHC(O)OMe}(PPh$_3$)Cp* **22** (180 mg, 56%). X-ray quality crystals were obtained from pentane. Anal. Found: C, 70.18; H, 5.85. $C_{40}H_{39}O_2PRu$ calcd.: C, 70.28; H, 5.71%; M, 684. IR (cyclohexane): ν(C≡C) 2163w; ν(CO) 1724m; ν(C=C) 1558m cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.40 [d, *J*(HP) = 1.2 Hz, 15H, Cp*], 3.33 (s, 3H, CO$_2$Me), 6.25 [d, *J*(HP) = 3.2 Hz, 1H, CH], 7.17 - 7.50 (m, 20H, Ph). ^{13}C NMR ($CDCl_3$): δ 10.82 (s, C_5Me_5), 52.80 (s, OMe), 86.99 (s, C_5Me_5), 99.05, 100.57 (2x s, ≡C), 122.97 (s, CH), 127.16 - 137.17 (m, Ph), 181.26 (s, CO$_2$Me). ES mass spectrum (MeOH, *m/z*): 683, [M – H]$^+$; 499, [Ru(PPh$_3$)Cp]$^+$; 422, [Ru(PPh$_2$)Cp*]$^+$.

*Ru{η^3-CH(CO$_2$Me)CHC=CPh(C≡CCO$_2$Me)}(PPh$_3$)Cp** **23**.

An excess of NaOMe was added to a solution of **3** (100 mg, 0.16 mmol) and HC≡CCO$_2$Me (40 mg, 0.48 mmol) in MeOH (30 ml). After removal of solvent, the residue was separated by preparative TLC (acetone / hexane, 1:4) into several bands. The major product was in a bright yellow band (R_f 0.50) which gave Ru{η^3-CH(CO$_2$Me)CHC=CPh(C≡CCO$_2$Me)}(PPh$_3$)Cp* **23** (69.6 mg, 58%) as yellow crystals (CH_2Cl_2 / EtOH). Anal. Found: C, 68.60; H, 5.52. $C_{44}H_{43}O_4PRu$ calcd.: C, 68.84; H, 5.61%; M, 767. IR (cyclohexane): ν(C≡C) 2186m; ν(CO$_2$Me) 1706s; ν(C=C) 1616w, 1594w cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.47 [d, *J*(HP) = 1.4 Hz, 15H, Cp*], 2.27 [dd, *J*(HH) = 7.8 Hz, *J*(HP) = 14.7 Hz, 1H, CH], 3.59 [dd, *J*(HH) = 7.8 Hz, *J*(HP) = 3.8 Hz, 1H, CH], 3.70, 3.94 (2 x s, 2 x 3H, CO$_2$Me), 7.04 - 7.35 (m, 20H,

Ph). ^{13}C NMR ($CDCl_3$): δ 9.16 [d, *J*(CP) = 8.5 Hz, C_5Me_5], 50.52, 52.32 (2x s, CO_2Me), 79.43, 94.05 (2x s, C≡C), 93.67 (s, C_5Me_5), 124.58 - 139.33 (m, Ph), 112.11, 139.33, 155.55, 174.73 (C_4 chain), 217.0 (s, CO_2Me). ES mass spectrum (MeOH + NaOMe, *m/z*): 791, $[M + Na]^+$; 767, $[M - H]^+$; 736, $[M - H - OMe]^+$. A brown band (R_f 0.58) contained **22** (5.7 mg, 5.3%).

*Reactions of RuCl{=C=CH(CO₂Me)}(PPh₃)Cp** **28**.

(a) With silver phenylacetylide. Silver phenylacetylide (188 mg, 0.9 mmol) was added to a solution of **28** (365 mg, 0.6 mmol) in thf (40 ml). After stirring for 4 h at r.t. in the dark, the red solution was filtered through alumina, evaporated in vacuo and an acetone extract of the residue was purified by preparative TLC (acetone / hexane, 1:4). The major brown band (R_f 0.58) was extracted with acetone and gave Ru{η¹,*O*-C(C≡CPh)=CHC(O)OMe}(PPh_3)Cp* **22** as a red-brown solid (288 mg, 71%), identified by comparison with the compound prepared as above.

(b) With ethynylbenzene and sodium methoxide. A solution of **28** (62 mg, 0.1 mmol) and HC≡CPh (30 mg, 0.3 mmol) in MeOH (7 ml) was treated with a slight excess of NaOMe and stirred for 30 min at r.t., after which time starting complex **28** was no longer present (TLC). After removal of solvent, the residue was separated (TLC, acetone / hexane, 1:4) into four fractions, all containing small amounts of material. Products from the bands with R_f 0.58 and 0.46 were identified as **22** (5 mg, 18%) and **21** (15 mg, 18%), respectively.

*Recations of Ru{η¹,O-C(C≡CPh)=CHC(O)OMe}(PPh₃)Cp** **22**.

(a) With methyl propiolate. A mixture **22** (38 mg, 0.06 mmol) and HC≡CCO_2Me (10 mg, 0.12 mmol) was heated in refluxing hexane (20 ml) for 3 h. Separation of the major product by preparative TLC afforded Ru{η¹,η²-C(CO_2Me)=CHCPh=C=C=CH(CO_2Me)}(PPh_3)Cp* **24** (38.2 mg, 89%), contained in the red band (R_f 0.57). Dark red crystals were obtained from CH_2Cl_2 / MeOH. Anal. Found: C, 68.66; H, 5.77. $C_{44}H_{43}O_4PRu$ calcd.: C, 68.84; H, 5.61%; M, 768. IR (cyclohexane): ν(C≡C) 1953w; ν(CO) 1781m, 1723m, 1690s cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.56 [d, *J*(HP) = 1.2 Hz, 15H, Cp*], 3.29, 3.33 (2x s, 2x 3H, CO_2Me), 4.49 [d, *J*(HP) = 1.5 Hz, 1H, CH], 6.92 - 7.51 (m, 20H, Ph), 7.80 [d, *J*(HP) = 3.8 Hz, 1H, CH]. ES mass spectrum

(MeOH + NaOMe, *m/z*): 791, $[M + Na]^+$; 775, $[M + Na - O]^+$; 691, $[M - Ph]^+$; 506, $[M - PPh_3]^+$; 499, $[Ru(PPh_2)Cp^*]^+$.

(b) With ethyl propiolate. A similar reaction to (a), **22** (50 mg, 0.07 mmol) and $HC{\equiv}CCO_2Et$ (14 mg, 0.4 mmol), gave $Ru\{\eta^1,\eta^2\text{-}C(CO_2Et){=}CHCPh{=}C{=}C{=}CH(CO_2Me)\}(PPh_3)Cp^*$ **25** (41 mg, 72%) as red crystals (from CH_2Cl_2 / MeOH). Anal. Found: C, 68.83; H, 5.88. $C_{45}H_{45}O_4PRu$ calcd.: C, 69.14; H, 5.76%; M, 782. IR (cyclohexane): ν(CO) 1787m, 1699s cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.01 (m, 3H, Me), 1.52 [d, *J*(HP) = 1.6 Hz, 15H, Cp*], 3.37 (s, 3H, CO_2Me), 3.61 (m, 2H, OCH_2), 4.36 [d, *J*(HP) = 3 Hz, 1H, CH], 6.92 - 7.52 (m, 20H, Ph), 7.69 [d, *J*(HP) = 3.4 Hz, 1H, CH]. ES mass spectrum (MeOH + NaOMe, *m/z*): 805, $[M + Na]^+$; 781, $[M - H]^+$.

(c) With ethynyltrimethylsilane. A mixture of **22** (135 mg, 0.2 mmol) and ethynyltrimethylsilane (120 mg, 0.6 mmol) was heated in refluxing hexane (30 ml) for 2 h, after which the colour of the solution had changed from red to dark yellow. Two products were separated by preparative TLC (acetone / hexane, 1:4). The first bright yellow band (R_f 0.76) contained $Ru\{\eta^3\text{-}CH(CO_2Me)C(CH{=}CHSiMe_3)C{=}CPhC{\equiv}CSiMe_3\}(PPh_3)Cp^*$ **26** (21 mg, 12%), obtained as yellow crystals from hexane. Anal. Found: C, 67.89; H, 7.09. $C_{50}H_{59}O_2PRuSi_2$ calcd.: C, 68.26; H, 6.71%; M, 880. IR (cyclohexane): ν(C≡C) 2115m; ν(CO) 1699s cm^{-1}. ^1H NMR ($CDCl_3$): δ -0.23, 0.46 (2x s, 2x 9H, $SiMe_3$), 1.47 [d, *J*(HP) = 1.2 Hz, 15H, Cp*], 3.59 (s, 3H, CO_2Me), 5.46 [d, *J*(HH) = 18.9 Hz, 1H, CH], 6.66 [d, *J*(HH) = 18.9 Hz, 1H, CH], 6.59 - 7.26 (m, 21H, Ph + CH). ES mass spectrum (MeOH, *m/z*): 880, M^+; 618, $[M - PPh_3]^+$; 603, $[M - PPh_3 - Me]^+$; 547, $[M - PPh_3 - SiMe_3]^+$. The second product was contained in a yellow band (R_f 0.64) and was obtained as a yellow oil, which was unstable towards chromatography and in solution. This was tentatively identified as $Ru\{\eta^3\text{-}CH(CO_2Me)CHC{=}CPh(C{\equiv}CSiMe_3)\}(PPh_3)Cp^*$ **27**. IR (cyclohexane): ν(C≡C) 2144w; ν(CO) 1707m cm^{-1}. ^1H NMR ($CDCl_3$): δ -0.74 (s, 9H, $SiMe_3$), 1.66 (s, 15H, Cp*), 3.53 (s, 3H, CO_2Me), 6.71 - 7.83 (m, 20H, Ph). ES mass spectrum (MeOH + NaOMe, *m/z*): 805, $[M + Na]^+$; 782, M^+; 520, $[M - PPh_3]^+$; 505, $[M - PPh_3 - Me]^+$; 449, $[M - PPh_3 - SiMe_3]^+$.

REFERENCES.

(1) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197.

(2) Bruce, M. I.; Swincer, A. G. *Adv. Organomet. Chem.* **1983**, *22*, 59.

(3) Trost, B. M.; Kulawiec, R. J.; Hammes, A. *Tetrahedron Lett.* **1993**, *34*, 587.

(4) Trost, B. M.; Kulawiec, R. J. *J. Am. Chem. Soc.* **1992**, *114*, 5579.

(5) Trost, B. M.; Dyker, G.; Kulawiec, R. J. *J. Am. Chem. Soc.* **1990**, *112*, 7809.

(6) Davies, S. G.; McNally, J. P.; Smallridge, A. J. *Adv. Organomet. Chem.* **1990**, *30*, 1.

(7) Werner, H. *Nachr. Chem. Tech. Lab.* **1992**, *40*, 435.

(8) Werner, H. *J. Organomet. Chem.* **1994**, *475*, 45.

(9) Silvestre, J.; Hoffmann, R. *Helv. Chim. Acta* **1985**, *68*, 1461.

(10) De los Rios, I.; Tenorio, M. J.; Puerta, M. C.; Valerga, P. *J. Am. Chem. Soc.* **1997**, *119*, 6529.

(11) Wolf, J.; Lass, R. W.; Manger, M.; Werner, H. *Organometallics* **1995**, *14*, 7809.

(12) Touchard, D.; Haquette, P.; Pirio, N.; Toupet, L.; Dixneuf, P. H. *Organometallics* **1993**, *12*, 3132.

(13) Bozec, R. L.; Ouzzine, K.; Dixneuf, P. H. *Organometallics* **1991**, *10*, 2768.

(14) Lagadec, R. L.; Roman, E.; Toupet, L.; Muller, U.; Dixneuf, P. H. *Organometallics* **1994**, *13*, 5030.

(15) De los Rios, I.; Tenoriom, M. J.; Puerta, M. C.; Valerga, P. *J. Chem. Soc., Chem Commun.* **1995**, 1757.

(16) Haines, R. J.; du Preez, A. L. *J. Organomet. Chem.* **1975**, *84*, 357.

(17) Bruce, M. I. *Comprehensive Organometallic Chemistry*; Pergamon: Oxford, **1982**, *4*, 783.

(18) Braun, T.; Steinert, P.; Werner, H. *J. Organomet. Chem.* **1995**, *488*, 169.

(19) Braun, T.; Meuer, P.; Werner, H. *Organometallics* **1996**, *15*, 4075.

(20) Slugovc, C.; Mereiter, K.; Zobetz, E.; Schmid, R.; Kirchner, K. *Organometallics* **1996**, *15*, 5275.

(21) Werner, H.; Stark, A.; Steinert, P.; Grunwald, C.; Wolf, J. *Chem. Ber.* **1995**, *128*, 49.

(22) Shen, J.-Y.; Slugovc, C.; Wiede, P.; Mereiter, K.; R.Schmid; Kirchner, K. *Inorg. Chim. Acta* **1998**, *268*, 69.

(23) Martin, M.; Gevert, O.; Werner, H. *J. Chem. Soc., Dalton Trans.* **1994**, 2275.

(24) Bianchini, C.; Glendenning, L.; Peruzzini, M.; Romerosa, A.; Zanobini, F. *J. Chem. Soc., Chem. Commun.* **1994**, 2219.

(25) Bianchini, C.; Innocenti, P.; Peruzzini, M.; Romerosa, A.; Zanobini, F. *Organometallics* **1996**, *15*, 272.

(26) Yi, C. S.; Liu, N. *Organometallics* **1996**, *15*, 3968.

(27) Yi, C. S.; Liu, N.; Rheingold, A. L.; Liable-Sands, L. M.; Guzei, I. A. *Organometallics* **1997**, *16*, 3729.

(28) Yi, C. S.; Liu, N.; Rheingold, A. L.; Liable-Sands, L. M. *Organometallics* **1997**, *16*, 3910.

(29) Yi, C. S.; Liu, N. *Organometallics* **1998**, *17*, 3158.

(30) Treichel, P. M.; Komar, A.; Vicenti, P. J. *Synth. React. Inorg. Metal-Org. Chem.* **1984**, *14*, 383.

(31) Lehmkuhl, H.; Bellenbaum, M.; Grundke, J.; Maurmann, H.; Krüger, C. *Chem. Ber.* **1988**, *121*, 1719.

(32) Bruce, M. I.; Hameister, C.; Swincer, A. G.; Wallis, R. C. *Inorg. Synth.* **1982**, *21*, 78.

(33) Bruce, M. I.; Hall, B. C.; Zaitseva, N. N.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1996**, *522*, 307.

(34) Bruce, M. I.; Wong, F. S.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1981**, 1398.

(35) Tiekink, E. R. T. *Z. Kristallogr.* **1992**, 158.

(36) Bruce, M. I.; Hinterding, P.; Tiekink, E. R. T. *Z. Kristallogr.* **1993**, *205*, 287.

(37) Bruce, M. I.; Hall, B. C.; Tiekink, E. R. T.; Zaitseva, N. N. *Aust. J. Chem.* **1997**, *50*, 1097.

(38) Treichel, P. M.; Komar, D. A. *Inorg. Chim. Acta.* **1980**, *42*, 277.

(39) Bruce, M. I.; Hambley, T. W.; Rodgers, J. R.; Snow, M. R.; Wong, F. S. *Aust. J. Chem.* **1982**, *35*, 1323.

(40) Itoh, K.; Nagashima, H.; Ohshima, T.; Oshima, N.; Nishiyama, H. *J. Organomet. Chem.* **1984**, *272*, 179.

(41) Katajima, N.; Kono, A.; Ueda, W.; Moro-oka, Y.; Ikawa, T. *J. Chem. Soc., Chem. Commun.* **1986**, 674.

(42) Labroue, D.; Pince, R.; Queau, R. *J. Organomet. Chem.* **1991**, *402*, 363.

(43) Wisner, J. M.; Batczak, T. J.; Ibers, J. A. *Inorg. Chim. Acta.* **1985**, *100*, 115.

(44) Bruce, M. I.; Humphrey, M. G.; Snow, M. R.; Tiekink, E. R. T. *J. Organomet. Chem.* **1986**, *314*, 213.

(45) Kirchner, K.; Mauthner, K.; Mereitner, K.; Schmidt, R. *J. Chem. Soc., Chem. Commun.* **1993**, 892.

(46) Sato, M.; Asai, M. *J. Organomet. Chem.* **1996**, *508*, 121.

(47) Shaver, A.; Plouffe, P.-Y. *Inorg. Chem.* **1994**, *33*, 4327.

(48) Bonds, W. D.; Ibers, J. A. *J. Am. Chem. Soc.* **1972**, *94*, 3413.

(49) Werner, H.; Kletzin, H.; Hohn, A.; Paul, W.; Knaup, W.; Ziegler, M. L.; Serhadli, O. *J. Organomet. Chem.* **1986**, *306*, 227.

(50) Bruce, M. I.; Liddell, M. J.; Snow, M. R.; Tiekink, E. R. T. *J. Organomet. Chem* **1988**, *352*, 199.

(51) Bruce, M. I.; Hall, B. C.; Skelton, B. W.; Tiekink, E. R. T.; White, A. H.; Zaitseva, N. N. *Aust. J. Chem* **2000**, *53*, 99.

(52) Bruce, M. I.; Gardner, R. C. F.; Howard, J. A. K.; Stone, F. G. A.; Welling, M.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1977**, 621.

(53) De los Rios, I.; Tenorio, M. J.; Padilla, J.; Puerta, M. C.; Valerga, P. *Organometallics* **1996**, *15*, 4565.

(54) Selegue, P. *J. Am. Chem. Soc.* **1982**, *104*, 119.

(55) Selegue, J. P.; Young, B. A.; Logan, S. L. *Organometallics* **1991**, *10*, 1972.

(56) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; Lastra, E. *J. Organomet. Chem.* **1996**, *510*, 207.

(57) Fendrick, C. M.; Schertz, L. D.; Mintz, E. A.; Marks, T. J. *Inorg. Synth.* **1992**, *29*, 193.

(58) Conroy-Lewis, F. M.; Simpson, S. J. *J. Organomet. Chem.* **1987**, *322*, 221.

(59) Luo, L.; Nolan, S. P.; Fagan, P. J. *Organometallics* **1993**, *12*, 4305.

Chapter 3

Some Complexes from 1,4-bis-diethynylbenzene

INTRODUCTION.

The electronic properties and structures of metal centres linked by unsaturated carbon chains are a topic of current interest.[1-4] The metal acetylide linkage has proven to be especially popular in these respects, and consequently the chemistry of transition metal alkynyl, diynyl and higher polyynyl complexes has undergone something of a renaissance, with a view to the preparation of molecular wires and other nanoscale devices. Recent developments include the preparation of an extensive series of complexes which have shown reasonable non-linear optical properties[5-9] and the synthesis of interesting luminescent complexes containing metal-capped carbon chains, such as $[Cu_3(\mu\text{-dppm})\{\mu^3\text{-}\eta^1\text{-}C{\equiv}CC_6H_4C{\equiv}C[Re(CO)_3(bipy)]\text{-}4\}_2]^+$ and related complexes.[10,11] Some of our efforts in this area have been directed towards overcoming the synthetic challenges associated with the preparation of organometallic compounds in which metal centres are linked by conjugated bridging ligands of well-defined geometry. In particular, there is a need for synthetic methods which yield metal acetylide complexes, but do not require the isolation and manipulation of the parent terminal alkynes. We have recently described the use of buta-1,3-diyne as a reagent for the preparation of diynyl $[ML_m]C{\equiv}CC{\equiv}CH$ and both homo- and heterometallic diynediyl $[ML_m]C{\equiv}CC{\equiv}C[M'L'_n]$ complexes using a copper(I) catalyst.[4,12] While this has proven to be a versatile method for the preparation of $M(CO)_nCp$ derivatives, the reaction sequence failed when applied to more electron–rich metal centres such as $RuCl(PPh_3)_2Cp$ or $RuCl_2(dppm)_2$. This limitation, coupled with the obvious need for extreme caution when manipulating buta-1,3-diyne, prompted us to examine the use of acetylenic synthons bearing masked C≡CH functionalities.

In addition, the consequence of introducing two or more alkynyl groups on the chemistry of these systems is also of interest. In this connection, the prototypical dialkyne is 1,4-bis-diethynylbenzene, 1,4-$(HC{\equiv}C)_2C_6H_4$. Over the past two decades, homobinuclear derivatives of most of the transition metals have been described, those of most interest containing metals of Groups 8-11.[13-22] Among these, some have been shown to possess appreciable non-linear optical properties,[23] while unusual luminescent complexes containing copper or silver clusters linked by the $C{\equiv}CC_6H_4C{\equiv}C$ group have been described.[24] Heterometallic systems of this type are relatively rare,[25,26] largely because of the difficulty in preparing suitable precursor complexes $[ML_m]$-$C{\equiv}C$-C_6H_4-$C{\equiv}CH$. Our own interests in the chemistry of the $Ru(PR_3)_2Cp$ and related systems has recently led us to make several derivatives of the dialkyne, 1,4-$HC{\equiv}CC_6H_4C{\equiv}CH$.

RESULTS AND DISCUSSION.

The reaction of $RuCl(PPh_3)_2Cp$ with the trimethylsilyl-protected alkynes $Me_3SiC{\equiv}CR$ (R = Ph, $C_6H_4C{\equiv}CSiMe_3$) and KF in methanol afforded the alkynyl, diynyl or diynediyl products in good to excellent yields as yellow or orange microcrystalline precipitates.

In the case of $Ru(C{\equiv}CPh)(PPh_3)_2Cp$ **1**, a mixture of $RuCl(PPh_3)_2Cp$, $PhC{\equiv}CSiMe_3$ and KF was heated in refluxing MeOH for a few minutes. When **1** precipitated it could be isolated by filtration in 84% yield. The product was readily identified by comparison of its spectral data with those obtained from an authentic sample.[27,28]

The bright yellow $Ru(C{\equiv}CC_6H_4C{\equiv}CSiMe_3\text{-}4)(PPh_3)_2Cp$ **2** was similarly prepared from $1,4\text{-}(Me_3SiC{\equiv}C)_2C_6H_4$; it precipitated from the reaction solution before the cleavage of the second $\equiv CSiMe_3$ bond could occur. Two $\nu(C{\equiv}C)$ bands were observed in the IR spectrum at 2155 and 2078 cm^{-1}, the higher energy absorption probably arising from the $C{\equiv}CSiMe_3$ group. In the ^1H and ^{13}C NMR spectra singlet Cp resonances were found at δ 4.30 and 85.21 respectively, while the retention of the $SiMe_3$ group was evidenced by singlet resonances at δ_H 0.22 and δ_C 0.13. The acetylenic carbons were found at δ_C 123.46 [C_α, J(CP) = 25 Hz], 116.71, 115.10 and 106.48 while the ES mass spectrum contained the M^+ ion at *m/z* 888. Recrystallisation from CH_2Cl_2 / hexane resulted in crystals suitable for X-ray analysis (Figure 1). It is appropriate to compare the structure with that of $Ru(C{\equiv}CPh)(PPh_3)_2Cp$ **1**,[27,28] from which there is little significant difference. Thus the Ru-C(1) and C(1)-C(2) distances are respectively 2.021(6), 1.173(9), and 2.017(5), 1.214(7)Å, with angles at C(1) and C(2) of 177.5(7), 171.8(8) and 177.4(4), 170.6(5)°. In the $C{\equiv}CSiMe_3$ fragment of **2** the C≡C and Si-C bond lengths are 1.21(1) and 1.817(8)Å, with angles at C(2041) and C(2042) of 177(1) and 174.2(9)°, respectively. These parameters are within previously measured ranges, the most notable difference being the barely significant shortening of the C(1)-C(2) bond compared with that in the phenylethynyl complex.

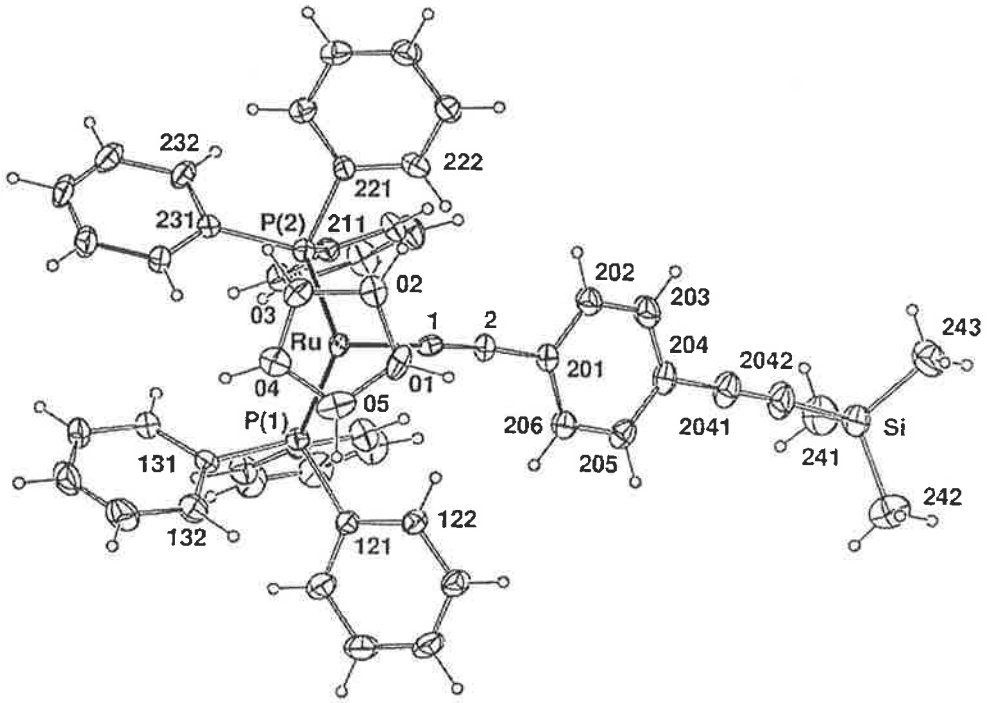
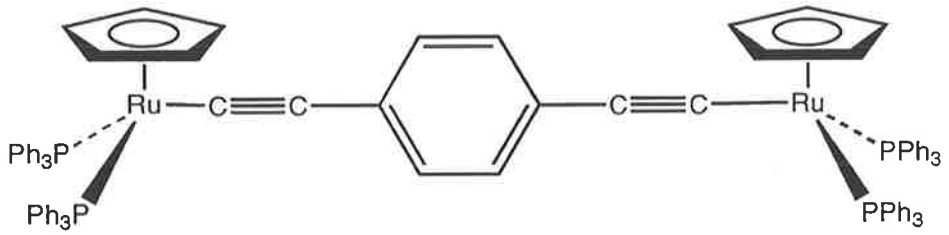


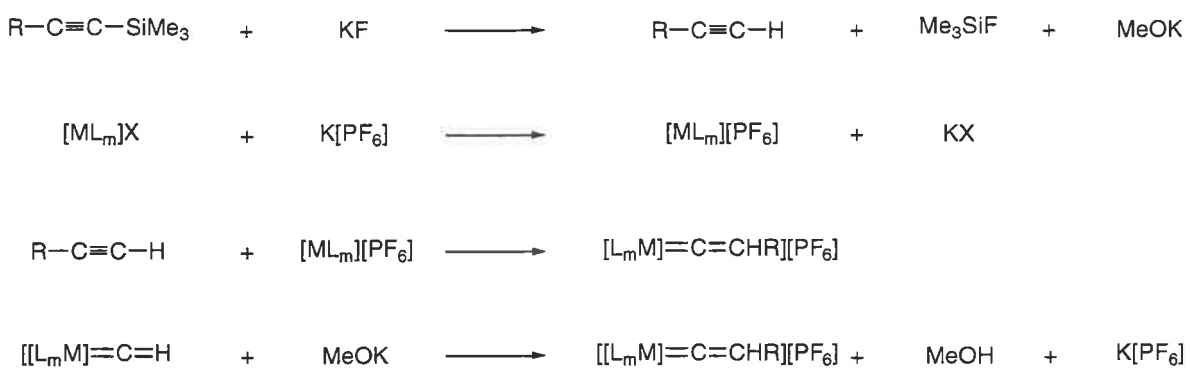
Figure 1 : A plot of a molecule of **2** showing the atom numbering scheme.

The remaining acetylenic $SiMe_3$ group in complex **2** was also amenable to metallation. Thus, subsequent treatment of **2** with $RuCl(PPh_3)_2Cp$ also in the presence of KF, carried out in a solvent mixture of thf - MeOH in which the solubility of **2** was improved, afforded the orange binuclear complex 1,4-$\{CpRu(PPh_3)_2(C{\equiv}C)\}_2C_6H_4$ **3** in 43% yield. A single ν(C≡C) band was found in the IR spectrum at 2089 cm^{-1}, while the chemically equivalent Cp ligands gave rise to only one singlet resonance in the ^1H (δ_H 4.34) and ^{13}C (δ_C 85.15) NMR spectra. The acetylenic carbons were found at δ_C 115.10 and 106.40 ppm. Owing to the relatively poor solubility of **3** in common solvents, the signal-to-noise ratio in the ^{13}C NMR spectrum was low, and the expected coupling to phosphorus could not be resolved. The ES mass spectrum contained M^+ at *m/z* 1506 and a fragment ion at *m/z* 720 representing the loss of three PPh_3 ligands.



3

More recently, Lapinte and coworkers[29] have described the formation of the iron (II) acetylide complexes 1,3-{Cp*(dppe)FeC≡C}$_2$C$_6$H$_4$ and 1, 3, 5–{Cp*(dppe)FeC≡C}$_3$-C$_6$H$_3$ from methanolic solutions of FeCl(dppe)Cp* and C$_6$(C≡CSiMe$_3$)$_2$H$_4$ or C$_6$(C≡CSiMe$_3$)$_3$H$_3$ in the presence of KF and KPF_6 salts, while Me$_3$SiC≡CC≡CSiMe$_3$, RuCl(PPh$_3$)$_2$Cp and KF were used in the synthesis of {Ru(PPh$_3$)$_2$Cp}$_2$(μ-C≡CC≡C).[30] The Dixneuf group has obtained the diynyl complex RuCl{C≡CC≡CCPh$_2$(OSiMe$_3$)}(PMe$_3$)(η^6-C$_6$Me$_6$) from the reaction of RuCl$_2$(PMe$_3$)(η^6-C$_6$Me$_6$) with Me$_3$SiC≡CC≡CCPh$_2$(OSiMe$_3$) in the presence of both NHPr$^i_2$ and $NaPF_6$.[31] The Lapinte group has proposed the mechanism shown in Scheme 1 to explain the formation of their complexes.[29] Initial protodesilylation of the trimethylsilyl-substituted acetylene by a fluoride ion generates the terminal acetylene *in situ*, together with an equivalent amount of strong base KOMe. The KPF_6 salt acts as a halide abstractor and helps promote co-ordination of the terminal alkyne to the metal centre leading to the formation of an intermediate vinylidene complex. Finally, the vinylidene cation is deprotonated by KOMe yielding the acetylide complex as the final product.



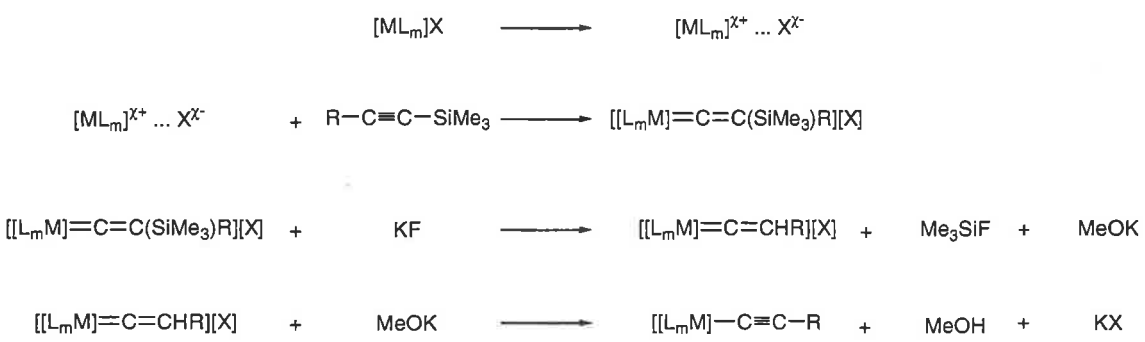
Scheme 1 : The mechanism proposed by Lapinte.[29]

A similar mechanism may be invoked to explain the formation of $Ru(C{\equiv}CPh)(PPh_3)_2Cp$ **1** from $SiMe_3C{\equiv}CPh$ and $\{Ru(PPh_3)_2Cp\}_2(\mu\text{-}C{\equiv}CC_6H_4C{\equiv}C)$ from $Ru(C{\equiv}CC_6H_4C{\equiv}CSiMe_3\text{-}4)(PPh_3)Cp$, as described above. However the formation of other complexes such as $Ru\{(C{\equiv}C)_nPh\}(PPh_3)_2Cp$ from $Me_3Si(C{\equiv}C)_nPh$ (n = 2 or 3), $Ru(C{\equiv}CC_6H_4C{\equiv}CSiMe_3\text{-}4)(PPh_3)_2Cp$ from $Me_3SiC{\equiv}CC_6H_4C{\equiv}CSiMe_3\text{-}4$ and $[Ru(PPh_3)_2Cp]_2\{\mu\text{-}(C{\equiv}C)_n\}$ from $SiMe_3(C{\equiv}C)_nSiMe_3$ (n = 2 or 3) is more difficult to rationalise in this manner.

In the case of $Me_3SiC{\equiv}CC_6H_4C{\equiv}CSiMe_3\text{-}4$ it may reasonably be expected that both $SiMe_3$ groups would display similar reactivity towards fluoride-induced desilylation and consequently that the removal of both $SiMe_3$ groups would occur essentially concurrently. In order to account for the formation of $Ru(C{\equiv}CC_6H_4C{\equiv}CSiMe_3\text{-}4)(PPh_3)_2Cp$ via the Lapinte mechanism the initial monodesilylation of $Me_3SiC{\equiv}CC_6H_4C{\equiv}CSiMe_3\text{-}4$ to give $HC{\equiv}CC_6H_4C{\equiv}CSiMe_3\text{-}4$ must be followed by the metallation sequence with a combined reaction rate several orders of magnitude faster than that of the cleavage of the second $\equiv CSiMe_3$ bond.

An alternative interpretation of these results is embodied in the reaction mechanism shown in Scheme 2. In methanol the Ru-Cl bond is significantly ionised, which offers a point of entry for the silyl-substituted alkyne into the metal co-ordination sphere, followed by, or possibly concomitant with, a 1,2-silyl shift to give a silylvinylidene. 1,2-Silyl shifts have been reported previously.[32-34] Nucleophilic attack by the

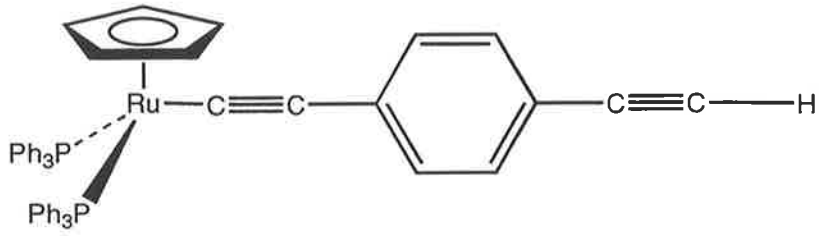
fluoride ion on the silicon centre then generates the alkynyl complex which, in our system, precipitates from the reaction mixture. In the case of the bis(silyl)alkynes precipitation of the product acetylides may occur either before [in the case of $Ru(C{\equiv}CC_6H_4C{\equiv}CSiMe_3\text{-}4)(PPh_3)_2Cp$] or after the reaction of the second silyl group [as with $\{Ru(PPh_3)_2Cp\}_2\{\mu\text{-}(C{\equiv}C)_n\}$]. Dixneuf and coworkers[31] have proposed a similar mechanism to explain the activation of 1-silyl-1,3-diynes by ruthenium (II) complexes.



Scheme 2 : Alternative mechanism for desilylation involving a silylvinylidene intermediate.

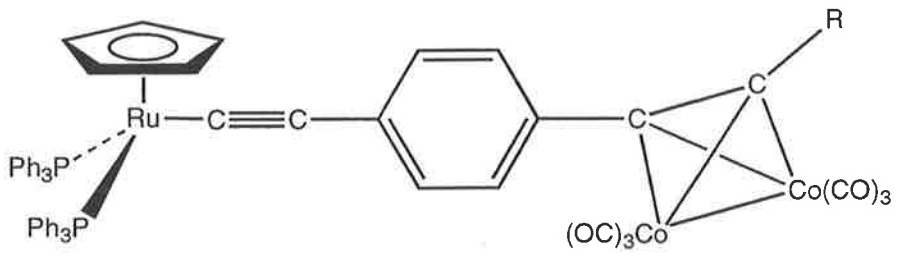
The ease with which these complexes are obtained is noteworthy. While the vast majority of these complexes are symmetrically metallated homobimetallic complexes, Dixneuf's group has been successful in the preparation of complexes of general form $\{ML_m\}C{\equiv}CC_6H_4C{\equiv}CSiR_3\text{-}4$ [ML_m = 1,1'-diiodoferrocene, Ru(dppe)$_2$; R = Pr^i_3],[25,35] which is closely related to the analogous $Ru(C{\equiv}CC_6H_4C{\equiv}CSiMe_3\text{-}4)(PPh_3)_2Cp$ complexes described here. Dixneuf's compounds were prepared from $HC{\equiv}CC_6H_4C{\equiv}CSiPr^i_3\text{-}4$, which is obtained in four steps from $IC_6H_4NH_2\text{-}4$ in 50% overall yield.[36] The isolation of the asymmetric derivative $Ru(C{\equiv}CC_6H_4C{\equiv}CSiMe_3\text{-}4)(PPh_3)_2Cp$ directly from the symmetrical reagent $Me_3SiC{\equiv}CC_6H_4C{\equiv}CSiMe_3\text{-}4$ which is readily available on a gram scale,[37] results from the low solubility of the monosubstituted complex in the reaction solvent, and has provided us with a useful point of entry to the chemistry of the monometallated 1,4-bis-diethynylbenzene complexes.[38]

The $SiMe_3$ group in **2** can be replaced by H in the reaction with $[NBu_4]F$,[39] from which yellow $Ru(C{\equiv}CC_6H_4C{\equiv}CH\text{-}4)(PPh_3)_2Cp$ **4** was obtained in 89% yield. Characteristic spectroscopic features include ν(≡CH) and ν(C≡C) bands at 3289 and 2071 cm^{-1}, respectively, singlet Cp resonances at δ_H 4.35 and δ_C 85.34, and the acetylenic carbons at δ 54.50, 94.93, 115.08 and 115.78 ppm. The ES mass spectrum of a solution with added NaOMe contained $[M + Na]^+$ at *m/z* 839. Complex **2** can be regenerated from **4** by treatment with $LiBu^n$ and $SiClMe_3$, in 89% yield, indicating that the remaining ≡CH group can be metallated readily and is thus a potential source of many related complexes.



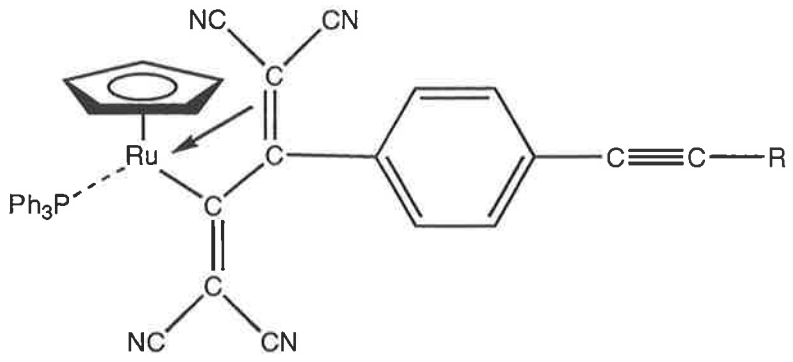
4

Reactions between **2** or **4** and $Co_2(CO)_8$ afforded the expected adducts $Co_2\{\mu\text{-}\eta^2\text{-}4\text{-}RC{\equiv}CC_6H_4C{\equiv}C[Ru(PPh_3)_2Cp]\}(CO)_6$ [R = $SiMe_3$ **5**, H **6**] as dark green crystalline solids. The IR spectra contained ν(CO) bands between 2065 and 2018 cm^{-1}, for **5** only, a ν(C≡C) absorption at 2084 cm^{-1}. In **5**, the $SiMe_3$ group gave signals at δ_H 0.07 and δ_C 0.92 ppm corresponding to the methyl hydrogens and carbons respectively, while in **6**, the ≡CH proton resonance was at δ 1.26 ppm. Singlet Cp resonances were found at δ_H 4.33 and 4.30 and at δ_C 85.41 and 85.44 ppm, respectively. The acetylenic carbon resonances are found between δ 84.26 and 115.68 ppm. For **6**, the CO groups resonated as a singlet at δ 212.74 ppm. The ES mass spectra contained M^+ at *m/z* 1101 (for **5**) and $[M + Na]^+$ at *m/z* 1197 (for **6**). While these data do not unequivocally indicate the site of addition, we suggest that it is the least hindered C≡CR group which is attached to the $Co_2(CO)_6$ fragment, due to the steric bulk imposed by the $Co_2(CO)_6$ fragment.



R = $SiMe_3$ **5**, H **6**

A characteristic reaction of transition metal alkynyl complexes is cycloaddition of tetracyanoethene to the C≡C triple bond to give a cyclobutenyl complex, which may undergo subsequent ring-opening to give a buta-1,3-dien-3-yl derivative, which in turn may displace a 2-e ligand from the metal centre to give an η^3-enyl complex.[40,41] The reactions of **2** and **4** with tetracyanoethene both proceed readily at ambient temperature to give deep green solutions which turn orange-yellow when heated. Both isolated products were obtained as yellow crystals and were identified as the η^3-enyl complexes Ru{η^3-$C(CN)_2C(C_6H_4C{\equiv}CR\text{-}4)C{=}C(CN)_2$}($PPh_3$)Cp [R = $SiMe_3$ **7**, H **8**]. The loss of one PPh_3 ligand suggested by the elemental analyses was confirmed by the ES mass spectra, which showed $[M + Na]^+$ ions at *m/z* 776 and 704, respectively. The spectra also contained aggregate ions formed by clustering of two or three molecules of the complex about the Na^+ ion at *m/z* 1531 $[2M + Na]^+$ for **7** and *m/z* 2069 $[3M + Na]^+$ and *m/z* 1387 $[2M + Na]^+$ for **8**. In their IR spectra, ν(CN) bands were found between 2223 and 2162 cm^{-1} and ν(C≡C) bands around 2140 cm^{-1}. The NMR spectra also confirmed that there was only one PPh_3 ligand present. In addition, characteristic singlet Cp resonances were found in the ^1H and ^{13}C NMR spectra; for **7**, the $SiMe_3$ group gave signals at δ_H 0.26 and δ_C -0.24 ppm, while the ≡CH proton signal was at δ 3.23 ppm. In **8**, the acetylenic carbons were found between δ 110.96 and 115.61 and the CN carbons between δ 118.38 and 118.70 ppm. Final confirmation of the molecular structure was achieved by a single-crystal X-ray structure determination carried out on **7**, which showed that, in contrast to the reaction with $Co_2(CO)_8$, the cyano-olefin adds to the ruthenium-bonded C≡C triple bond.



R = $SiMe_3$ **7**, H **8**

A plot of a molecule of **8** is shown in Figure 2, significant bond distances and angles, together with corresponding values for the closely related complex Ru{η^3-$C(CF_3)_2CPhC{=}C(CN)_2$}(PPh_3)Cp **9** are shown in Table 1.[42] The metal is coordinated by the η-C_5H_5 group [Ru-C(cp) 2.195(7)-2.237(9), av. 2.22 Å] (av. 2.24 Å in **9**), the PPh_3 ligand [Ru-P(1) 2.383(1) Å; cf. 2.411(2) Å in **9**] and the cyanocarbon ligand [Ru-C(1), 2.212(6), Ru-C(2) 2.118(5), Ru-C(3) 1.980(7) Å; corresponding values for **9**: 2.202(7), 2.138(7), 1.977(7) Å]. The mode of attachment of this ligand is essentially identical to that found in **9** and is similar to several other examples.[42-47] The pattern of C-C separations along the chain is also similar, with values of 1.471(8), 1.422(8) and 1.341(9) Å for C(1)-C(2), C(2)-C(3) and C(3)-C(4), respectively. These values are consistent with an Ru-η^2-C(1)=C(2) interaction and a degree of multiple bonding in the Ru-C(3) bond. The substituent at C(2) has normal C-C separations, with C(2)-C(21) 1.497(6), C(24)-C(241) 1.438(7) and C(241)-C(242) 1.159(8) Å, the latter being an unperturbed C≡C triple bond.

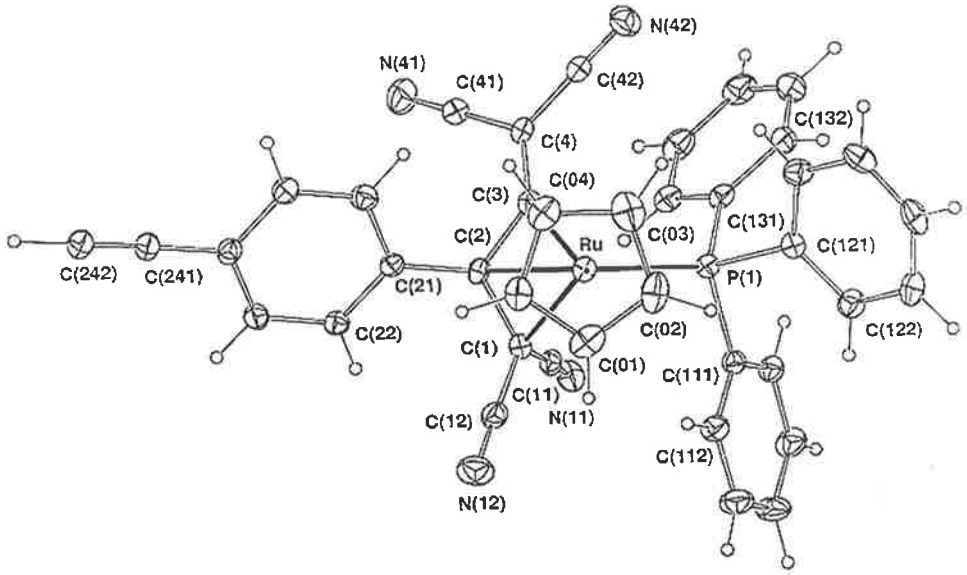
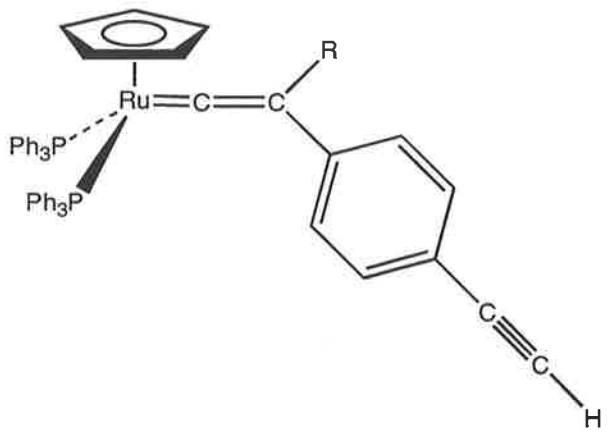


Figure 2 : A plot of a molecule of **8** showing the atom numbering scheme.

The reactivity of **4** was further investigated with other electrophiles. Addition of HPF_6 to the orange solution of **4** in methanol resulted in a rapid colour change to cherry red. The reddish-pink solid which was isolated from the reaction mixture was identified as the expected vinylidene complex $[Ru\{=C=CH(C_6H_4C{\equiv}CH\text{-}4)\}(PPh_3)_2Cp][PF_6]$ **10**. The characteristic low-field triplet resonance for the Ru-C atom was found at δ 273.09, while in the ^1H NMR spectrum, resonances at δ 3.15 and 3.71 ppm are assigned to the vinylidene and ethynyl protons, respectively. In the ES mass spectrum, $[M - PF_6]^+$ is found at *m/z* 817.

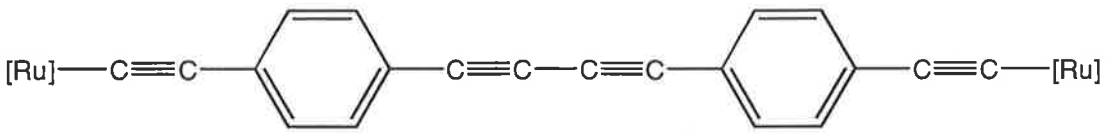


R = H **10**, Me **11**

Similarly, addition of methyl triflate to **4** afforded pink [Ru{=C=CMe(C_6H_4C≡CH-4)}(PPh_3)$_2$Cp][OTf] **11**. The ES mass spectrum contained [M - OTf]$^+$ at *m/z* 831, while the ≡CH and =CMe protons resonated at δ 3.04 and 1.91 ppm, respectively. In the ^{13}C NMR spectrum, the Me and Cp singlets were at δ 11.84 and 83.10 ppm, respectively; the Ru-C signal was not observed.

As described above, metallation of the ethynyl group in **4** can be achieved with LiBu. Conventional coupling of the alkyne with iodobenzene, using a combined palladium(0) / copper(I) catalyst (Sonogashira coupling)[48] afforded Ru(C≡CC_6H_4C≡CPh-4)(PPh_3)$_2$Cp **12** in 98% yield. This complex was identified by elemental analysis, from its ES mass spectrum (M$^+$ at *m/z* 888) and from the NMR spectra, which contained the appropriate resonances. The IR spectrum contained ν(C≡C) bands at 2148 and 2065 cm^{-1}.

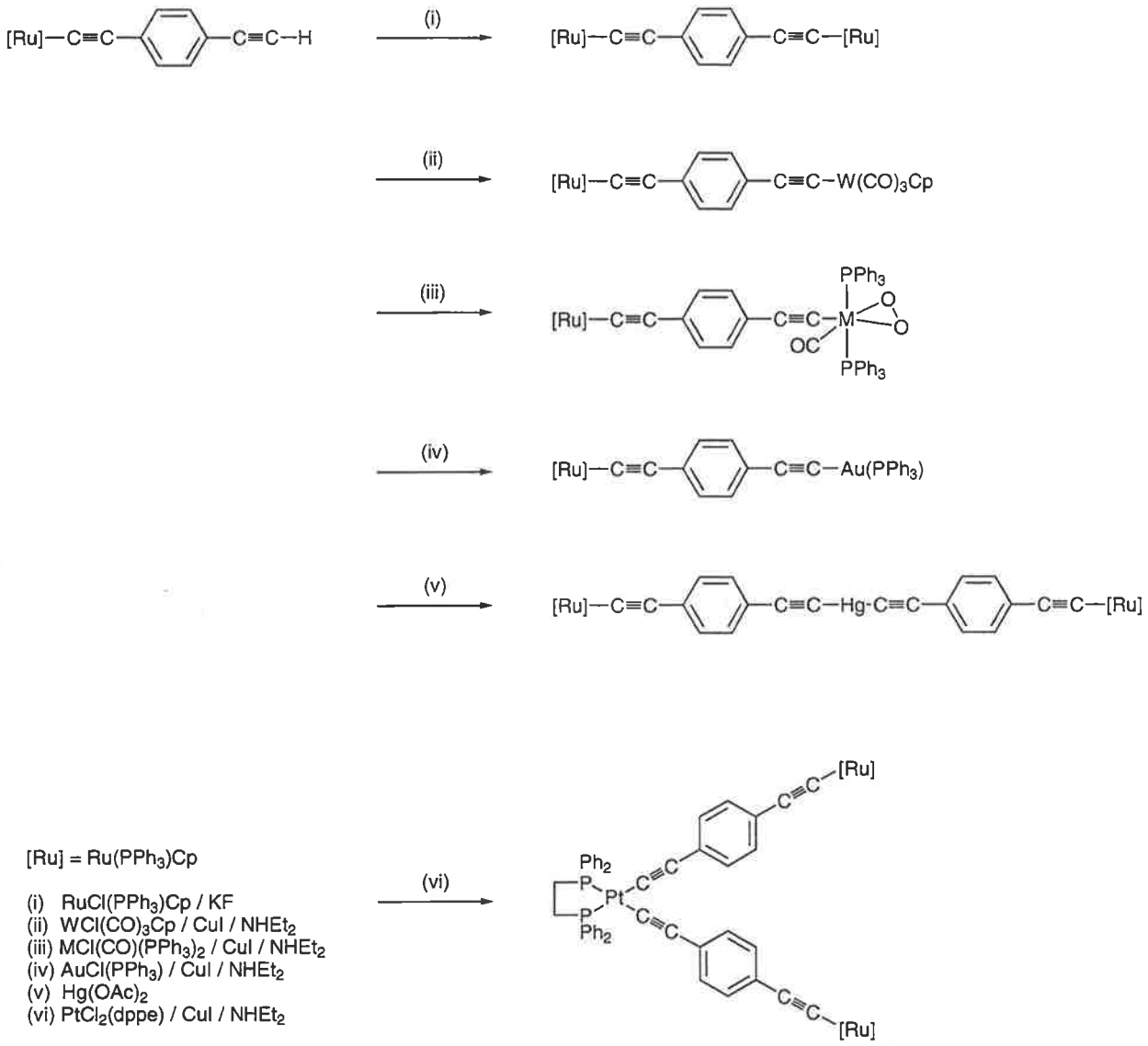
Oxidative coupling of **4**, using dioxygen and a Cu(I) / tmed catalyst,[49] produced a yellow powder tentatively identified as {Cp(Ph_3P)$_2$Ru}(μ-C≡CC_6H_4C≡CC≡CC_6H_4C≡C){Ru(PPh_3)$_2$Cp} **13** from its ES mass spectrum, which contained M$^+$ at *m/z* 1630. The IR spectrum contained a ν(C≡C) band at 2067 cm^{-1}; the compound was not soluble enough for meaningful NMR spectra to be obtained.



13

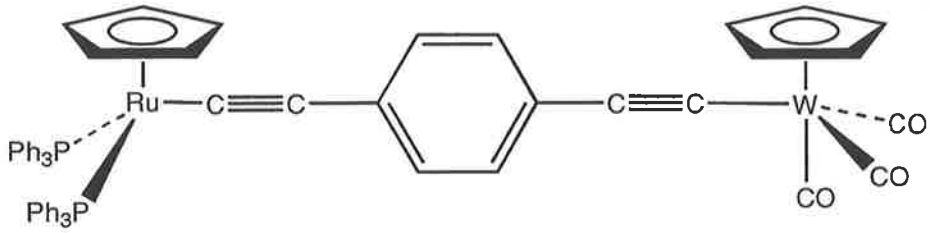
The electronic properties of oligomeric metal-yne polymers based upon a {M-C≡CC_6H_4C≡C-} repeating unit have recently been examined theoretically.[50] The synthesis of **3** demonstrates that symmetrical species containing two ruthenium(II) centres can be obtained from **4**. We have extended these studies to complexes containing ruthenium linked to tungsten(II), rhodium(I), iridium(I), platinum(II),

gold(I) and mercury(II) moieties (Scheme 3). These materials were made via copper(I)-catalysed coupling reactions between **4** and $WCl(CO)_3Cp$, $MCl(CO)(PPh_3)_2$ (M = Rh, Ir), $PtCl_2(dppe)$ and $AuCl(PPh_3)$; the mercury derivative was obtained directly from **4** and $Hg(OAc)_2$.



Scheme 3.

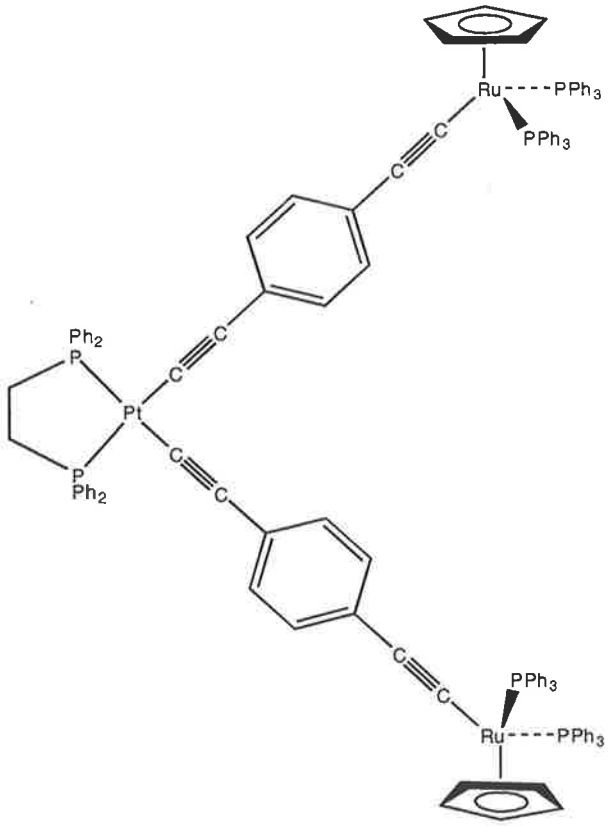
The W-Ru complex, $\{Cp(CO)_3W\}(\mu\text{-}C{\equiv}CC_6H_4C{\equiv}C)\{Ru(PPh_3)_2Cp\}$ **14** was isolated as a yellow powder in 90% yield. The IR spectrum contained a $\nu(C{\equiv}C)$ band at 2070 cm^{-1} and two terminal $\nu(CO)$ bands at 2034 and 1951 cm^{-1} as expected for the $W(CO)_3Cp$ group. The two Cp singlets were found at δ_H 4.31 and 5.63 and at δ_C 85.16 and 91.63 ppm, assigned to the Ru-Cp and W-Cp groups, respectively. The ES mass spectrum of a solution containing NaOMe contained M^+ and $[M + Na]^+$ ions at *m/z* 1148 and 1170, respectively.



14

The Group 8 / 9 complexes were identified as the dioxygen adducts $\{Cp(Ph_3P)_2Ru\}(\mu\text{-}C{\equiv}CC_6H_4C{\equiv}C)\{M(\eta\text{-}O_2)(CO)(PPh_3)_2\}$ [M = Rh **15**, Ir **16**], as shown by the $\nu(O_2)$ bands around 830 cm^{-1}. Single $\nu(CO)$ absorptions at ca 2065 cm^{-1} confirmed the presence of the oxidised M(III) centre. Other spectroscopic properties were consistent with the proposed structures, including M^+ at *m/z* 1505 (for **15**) and $[M + MeCN]^+$ at *m/z* 1632 (for **16**). The ready formation of dioxygen adducts of similar complexes, such as $\{Cp(OC)_3M\}(\mu\text{-}C{\equiv}CC{\equiv}C)\{M'(\eta\text{-}O_2)(CO)(PPh_3)_2\}$ (M = Mo, W; M' = Rh, Ir) has been observed previously[51] and is probably a result of the increased electron density on the M(I) centre in the alkynyl complexes.

The reaction between **4** and $PtCl_2(dppe)$ afforded the dialkynyl compound $Pt\{C{\equiv}CC_6H_4C{\equiv}C[Ru(PPh_3)_2Cp]\text{-}4\}_2(dppe)$ **17** in 90% yield as a yellow powder. The compound was characterised by microanalysis, from its ES mass spectrum obtained in the presence of Ag^+ ($[M + Ag]^+$ at *m/z* 2331) and from the expected resonances in the ^1H and ^{13}C NMR spectra. This complex is another example of the now large class of "tweezer complexes",[52] exemplified by the *cis*-bisalkynyl derivatives of titanium[53-55] and platinum[56,57] and the compounds described in chapter 4.



17

Ready replacement of the ethynyl hydrogen in **4** by the isolobal $Au(PPh_3)$ group gave yellow $\{Cp(Ph_3P)_2Ru\}(\mu\text{-}C{\equiv}CC_6H_4C{\equiv}C)\{Au(PPh_3)\}$ **18**. As expected, the spectroscopic properties of **18** do not differ much from those of **4**, with the exception of the contributions from the $Au(PPh_3)$ group; the $\nu(C{\equiv}C)$ absorption is at 2068 cm^{-1}. The ES mass spectrum contains M^+ at *m/z* 1275.

Direct reaction between **4** and $Hg(OAc)_2$ in thf solution occurred on heating to give a yellow precipitate. Its insolubility precluded our obtaining NMR spectra, but a $\nu(C{\equiv}C)$ band at 2068 and M^+ at *m/z* 1830 in the ES mass spectrum support the proposed formulation of the product as the mercury-bridged complex $Hg\{C{\equiv}CC_6H_4C{\equiv}C[Ru(PPh_3)_2Cp]\text{-}4\}_2$ **19**.

The homo- and heterometallic complexes **13-16** and **18** are novel examples of compounds in which an extensive unsaturated carbon-rich chain bridges two metal centres. In the case of **17** and **19**, two such chains are attached to a single metal centre

(Pt, Hg) capped by the ruthenium fragment. The electronic and optical properties of such extended systems are currently of great interest and are being investigated. However, we note that in the related iron complex {Cp*(dppe)Fe}(μ-C≡CC_6H_4C≡C){Fe(dppe)Cp*},[58] the degree of electronic interaction between the iron centres, as shown by electrochemical studies, appears to be considerably less than that found in analogous systems containing all-carbon links such as C_4. In the present case, preliminary CV data indicate that **3** undergoes two reversible 1-e oxidations.

Table 1 : Selected bond parameters for **8** and **9**.

	8	**9**
Bond lengths		
Ru-P	2.383(1)	2.411(2)
Ru-C(1)	2.212(6)	2.202(7)
Ru-C(2)	2.118(5)	2.138(7)
Ru-C(3)	1.980(7)	1.977(7)
Ru-C(cp)	2.195-2.237(9)	2.218-2.273(8)
(av.)	2.22	2.24
C(1)-C(2)	1.471(8)	1.46(1)
C(2)-C(3)	1.422(8)	1.42(1)
C(2)-C(21)	1.497(6)	1.499(9)
C(3)-C(4)	1.341(9)	1.37(1)
C(24)-C(241)	1.438(7)	-
C(241)-C(242)	1.159(8)	-
C-CN	1.422-1.444(8)	1.43(1) (x2)
(av.)	1.437	
C-N	1.133(8)-1.15(1)	1.12, 1.13(1)
(av.)	1.143	
Bond angles		
P(1)-Ru-C(1)	96.1(5)	101.0(2)
P(1)-Ru-C(2)	115.5(1)	122.0(2)
P(1)-Ru-C(3)	92.3(1)	98.7(2)
C(1)-Ru-C(3)	70.5(2)	70.3(3)
Ru-C(1)-C(2)	66.7(3)	68.0(4)
Ru-C(2)-C(21)	128.0(4)	130.9(4)
Ru-C(3)-C(2)	75.0(4)	76.0(4)
Ru-C(3)-C(4)	146.9(4)	149.9(6)

EXPERIMENTAL

Reagents. $Ru(C{\equiv}CPh)(PPh_3)_2Cp$ **1**,[27] $Ru\{\eta^3\text{-}C(CF_3)_2CPhC{=}C(CN)_2\}(PPh_3)Cp$ **9**,[42] $WCl(CO)_3Cp$,[59] $RhCl(CO)(PPh_3)_2$,[60] $IrCl(CO)(PPh_3)_2$,[60] $PtCl_2(dppe)$[61] and $AuCl(PPh_3)$[62] were prepared as described previously. Copper(I) iodide (Ajax), $IrCl_3.3H_2O$ (Johnson Matthey), triphenylphosphine, tetracyanoethene (Fluka), HPF_6 (Aldrich), methyl triflate (Aldrich), Hg(OAc) (Fluka) and iodomethane (Ajax) were used as received.

$Ru(C{\equiv}CC_6H_4C{\equiv}CSiMe_3)(PPh_3)_2Cp$ **2**.

A mixture of $Me_3SiC{\equiv}CC_6H_4C{\equiv}CSiMe_3$ (45 mg, 1.66 mmol), $RuCl(PPh_3)_2Cp$ (1210 mg, 1.66 mmol) and KF (98 mg, 1.66 mmol) was stirred in refluxing MeOH (80 ml) overnight. After this time the orange suspension had become bright yellow. The solvent was filtered off to give a yellow powder (1280 mg, 87%). The crude product was then chromatographed on an alumina column eluting with acetone / hexane, 3:7. Concentration of the yellow fraction, filtration and washing with hexane gave $Ru(C{\equiv}CC_6H_4C{\equiv}CSiMe_3)(PPh_3)_2Cp$ **3** as a yellow powder (960 mg, 64%). Anal. Found: C, 72.43; H, 5.39. $C_{54}H_{48}P_2RuSi$ calcd.: C, 72.20; H, 5.59%; M, 888. IR (nujol): ν(C≡C) 2155, 2078 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.22 (s, 9H, $SiMe_3$), 4.30 (s, 5H, Cp), 7.0 - 7.50 (m, 30H, ArH). ^{13}C NMR ($CDCl_3$): δ 0.13 (s, $SiMe_3$), 85.21 (s, Cp), 116.71, 115.10, 106.48 (3s, C≡C), 123.46 [t, *J*(CP) = 25Hz, RuC≡*C*], 127.54 - 138.96 (m, Ph). ES mass spectrum (MeOH, *m/z*): 888, M^+.

1,4-{$Cp(PPh_3)_2Ru(C{\equiv}C)$}$C_6H_4$ **3**.

$RuCl(PPh_3)_2Cp$ (262 mg, 0.370 mmol) was dissolved in a solvent mixture of thf / MeOH (20 ml / 20 ml), KF (21 mg, 0.370 mmol) and **4** (50 mg, 0.185 mmol) was added. The solution was then heated under reflux for 16 hours and an orange precipitate formed, which was collected and washed with hexane. 1,4-$\{Cp(PPh_3)_2Ru(C{\equiv}C)\}C_6H_4$ **3** (120 mg, 43 %). Anal. Found: C, 72.56; H, 5.49. $C_{92}H_{74}P_4Ru_2$.MeOH calcd.: C, 72.64; H, 5.11%; M, 1506. IR (nujol): ν(C≡C) 2089 cm^{-1}. ^1H NMR ($CDCl_3$): 4.34 (s, 5H, Cp) 6.97 - 7.50 (m, 64H, Ph). ^{13}C NMR ($CDCl_3$): 85.18 (s, Cp), 106.40 (s, C), 115.10 (s, C), 127.15 - 138.98 (m, Ph). ES mass spectrum (MeOH, *m/z*): 1507, M^+; 720, $[M - 3PPh_3]^+$; 690, $[CpRu(PPh_3)_2]^+$.

$Ru(C{\equiv}CC_6H_4C{\equiv}CH)(PPh_3)_2Cp$ **4**.

The silylated complex **2** (0.5 g, 0.56 mmol) was stirred in degassed thf (40 ml) and methanol (10 ml) with $[NBu_4]F$ (0.6 mg, 0.6 mmol) overnight. The solvent was removed under reduced pressure and the residue passed down an alumina column (acetone / hexane, 3:7). The first yellow fraction was evaporated and the resulting yellow solid was collected to give $Ru(C{\equiv}CC_6H_4C{\equiv}CH)(PPh_3)_2Cp$ **3** (407 mg, 89%). Anal. Found: C, 73.87; H, 5.13. $C_{51}H_{40}RuP_2.MeOH$ calcd.: C, 73.57; H, 5.23%; M, 816. IR (nujol): ν(≡CH) 3289sm; ν(C≡C) 2071s; ν(C=C) 1594m cm^{-1}. ^1H NMR ($CDCl_3$): 3.10 (s, 1H, C_2H), 4.35 (s, 5H, Cp), 7.0 - 7.50 (m, 30H, ArH). ^{13}C NMR ($CDCl_3$): 29.24 (s, C_δ), 94.93 (s, C_β), 85.34 (s, Cp), 115.08 (s, C_γ), 115.78 (s, C_α), 127.21 - 139.71 (m, PPh_3 and ArH). ES mass spectrum (MeOH, with NaOMe, *m/z*): 839.2, $[M + Na]^+$.

Reactions with $Co_2(CO)_8$.

(a) With **2**.

$Co_2(CO)_8$ (39 mg, 0.113 mmol) in benzene (10 ml) was added to complex **2** (100 mg, 0.113 mmol) in benzene (10 ml). The resulting solution turned dark green in colour after stirring 30 min at room temperature. The solvent was removed and the resulting residue was recrystallised from CH_2Cl_2 / hexane. Green crystals of $Co_2\{\mu\text{-}\eta^2\text{-}SiMe_3C_2C_6H_4C{\equiv}C[Ru(PPh_3)_2Cp]\}(CO)_6$ **5** (89 mg, 71%) were obtained. Anal. found: C, 61.11; H, 3.93. $C_{60}H_{48}RuCo_2P_2O_6Si$ calcd.: C, 61.33; H, 4.12%; M, 1174. IR (CH_2Cl_2): ν(C≡C) 2084m; ν(CO) 2048s, 2018m cm^{-1}. ^1H NMR ($CDCl_3$): 1.26 (s, 1H, CH), 4.30 (s, 5H, Cp), 7.16 - 7.47 (m, 34H, ArH). ^{13}C NMR ($CDCl_3$): 84.26 (s, C≡C), 85.44 (s, Cp), 103.33 (s, C≡C), 113.17 (s, C≡C), 127.22 - 139.37 (m, Ar and PPh_3), 212.74 (s, CO). ES mass spectrum (MeOH, *m/z*): 1197, $[M + Na]^+$; 1174, M^+.

(b) With **4**.

Similarly, $Co_2(CO)_8$ (43 mg, 0.123 mmol) and complex **4** (100 mg, 0.123 mmol) in benzene (20 ml), stirring for 20 min gave a deep green solid, which was purified by preparative TLC (acetone / hexane, 3:7). The green band (R_f 0.80) was recrystallised from CH_2Cl_2 / hexane to give olive-green crystals of $Co_2\{\mu\text{-}\eta^2\text{-}HC_2C_6H_4C{\equiv}C[Ru(PPh_3)_2Cp]\}(CO)_6$ **6** (77.4 mg, 57%). Anal. found: C, 63.71; H, 3.93. $C_{57}H_{40}O_6P_2RuCo_2.C_6H_6$ calcd.: C, 64.13; H, 3.93; M, 1102. IR (CH_2Cl_2):

ν(C≡C) 2084m; ν(CO) 2065m, 2048s, 2018s cm^{-1}. ^1H NMR ($CDCl_3$): 0.07 (s, 9H, TMS), 4.33 (s, 5H, Cp), 7.06 - 7.48 (m, 34H, ArH). ^{13}C NMR ($CDCl_3$): 0.92 (s, TMS), 85.41 (s, Cp), 115.68 (s, C≡C), 127.22 - 139.35 (m, Ar and PPh_3). ES mass spectrum (MeOH with NaOMe, *m/z*): 1102, M^+.

Reactions with tetracyanoethene.

(a) With **2**.

Tetracyanoethene (15 mg, 0.113 mmol) was added to a solution of **2** (100 mg, 0.113 mmol) in thf (20 ml) and the mixture was then heated under reflux for 3 h. Initially the yellow solution turns green, but after the reflux the solution was orange-yellow. Solvent was removed and the residue purified by preparative TLC (acetone / hexane, 3:7). An orange-yellow band (R_f 0.65) was crystallised (CH_2Cl_2 / hexane) to give yellow crystals of Ru{η^3-C[=C(CN)$_2$]C(C_6H_4C≡CSiMe_3)=C(CN)$_2$}(PPh_3)Cp **7** (90 mg, 97%). Anal. found: C, 66.24; H, 4.58. $C_{42}H_{33}N_4PRuSi$ calcd.: C, 66.83, H, 4.41%; M, 754. IR (nujol): ν(CN) 2223s, 2211s, 2162m, 2147m; ν(C=C) 1605m, 1435m cm^{-1}. ^1H NMR ($CDCl_3$): 0.26 (s, 9H, $SiMe_3$), 4.75 (s, 5H, Cp), 7.26 - 7.57 (m, 19H, ArH). ^{13}C NMR ($CDCl_3$): -0.24 (s, $SiMe_3$), 6.99 (s, C_β), 65.70 (s, C_δ), 85.27 (s, C_α), 92.34 (s, Cp), 97.73 (s, C≡C), 103.95 (s, C≡C), 115.61 (s, CN), 118.43 (s, CN), 118.57 (s, CN), 118.69 (s, CN), 124.37 - 134.62 (m, Ar and PPh_3), 220.35 (s, C_3). ES mass spectrum (MeOH with NaOMe, *m/z*): 1531, $[2M + Na]^+$; 777, $[M + Na]^+$.

(b) With **4**.

Similarly, complex **4** (100 mg, 0.123 mmol) and tcne (16 mg, 0.123 mmol) in thf (20 ml) were heated under reflux for 3 h. A bright yellow band (R_f 0.4) which gave yellow crystals of Ru{η^3-C[=C(CN)$_2$]C(C_6H_4C≡CH)=C(CN)$_2$}(PPh_3)Cp **8** (57 mg, 68%) from CH_2Cl_2 / MeOH. Crystals suitable for X-ray analysis were grown from CH_2Cl_2 / hexane. Anal. Found: C, 66.95; H, 3.70. $C_{39}H_{25}N_4PRu.MeOH$ calcd.: C, 67.21; H, 4.09%; M, 682. IR (CH_2Cl_2): ν(CN) 2360s, 2344s, 2331m; ν(C≡C) 2110m cm^{-1}. ^1H NMR ($CDCl_3$): 3.23 (s, 1H, C_2H), 4.77 (s, 5H, Cp), 7.45 - 7.56 (m, 19H, ArH). ^{13}C NMR ($CDCl_3$): 6.97 (s, C_β), 65.47 (s, C_δ), 82.62 (s, C_α), 92.36 (s, Cp), 110.96 (s, C≡C), 115.61 (s, C≡C), 118.38 (s, CN), 118.52 (s, CN), 118.70 (s, CN), 124.25 - 134.62 (m, Ar and PPh_3). ES mass spectrum (MeOH with NaOMe, *m/z*): 2069, $[3M + Na]^+$; 1387, $[2M + Na]^+$; 705, $[M + Na]^+$.

Reactions of $Ru(C{\equiv}CC_6H_4C{\equiv}CH)(PPh_3)_2Cp$ **4**.

(a) With HPF_6.

A few drops of HPF_6 were added to a solution of **4** (100 mg, 0.123 mmol) in MeOH (20 ml) and the mixture was stirred at r.t. for 10 min, after which the solution was cherry red. Solvent was removed and the residue was dissolved in CH_2Cl_2; the solution was added dropwise to cold rapidly stirred Et_2O to give a reddish-pink precipitate of $[Ru\{=C=CH(C_6H_4C{\equiv}CH)\}(PPh_3)_2Cp][PF_6]$ **10** (101 mg, 85%). Anal. Found: C, 62.70; H, 4.67. $C_{51}H_{41}F_6P_3Ru.MeOH$ calcd.: C, 62.76; H, 4.56%; M, 961. IR (nujol): ν(C=C) 1675m, 1630m, 1591s cm^{-1}. ^1H NMR ($CDCl_3$): 3.71 (s, 1H, ≡CH), 5.40 (s, 5H, Cp), 7.04 - 7.78 (m, 34H, ArH). ^{13}C NMR ($CDCl_3$): 92.20 (s, C_δ), 95.46 (s, Cp), 111.84 (s, C_γ), 119.53 (s, C_β), 126.68 - 133.99 (m, Ph and PPh_3), 197.39 (s, C_α). ES mass spectrum (MeOH, *m/z*): 817, $[M - PF_6]^+$; 429, $[CpRu(PPh_3)]^+$.

(b) With methyl triflate.

Addition of CF_3SO_3Me (20 mg, 0.123 mmol) to a solution of **4** (100 mg, 0.123 mmol) in CH_2Cl_2 (10 ml) at r.t.; after 20 min, the solution was red. The solvent was removed and the residue was dissolved in CH_2Cl_2 and added to rapidly stirred cold Et_2O, to give a pink precipitate, which was collected and air-dried. This solid was identified as $[Ru\{=C=CMe(C_6H_4C{\equiv}CH)\}(PPh_3)_2Cp][OTf]$ **11** (76 mg, 63%). Anal. Found: C, 63.37; H, 3.60. $C_{52}H_{43}F_3O_3P_2RuS.0.5CH_2Cl_2$ calcd.: C, 62.81; H, 4.30%; M, 980. IR (nujol): ν(C=C) 1661m, 1546m; $\nu(CF_3SO_3)$ 1273s cm^{-1}. ^1H NMR ($CDCl_3$): 3.04 (s, 1H, C_2H), 5.17 (s, 5H, Cp), 5.34 (s, 3H, Me), 6.88 - 7.41 (m, 34H, ArH). ^{13}C NMR ($CDCl_3$): 11.84 (s, Me), 83.10 (s, Cp), 94.47 (s, C), 95.46 (s, C), 121.37 - 134.39 (m, Ph). ES mass spectrum (MeOH, *m/z*): 831, $[M - CF_3SO_3]^+$; 569, $[M - CF_3SO_3 - PPh_3]^+$.

(c) With $WCl(CO)_3Cp$.

A mixture of **4** (100 mg, 0.123 mmol) and $WCl(CO)_3Cp$ (45 mg, 0.123 mmol) was stirred vigorously with CuI (ca 3 mg) in degassed diethylamine (20 ml) in the dark for 1 h. The yellow precipitate was collected, washed with hexane and dried under vacuum to give $\{Cp(OC)_3W\}(\mu\text{-}C{\equiv}CC_6H_4C{\equiv}C)\{Ru(PPh_3)_2Cp\}$ **14** (127 mg, 90%). Anal. found: C, 62.01; H, 4.41. $C_{59}H_{44}O_3P_2RuW$ calcd.: C, 61.66; H, 3.86%; M, 1148. IR (nujol): ν(C≡C) 2070m; ν(CO) 2034m, 1951m cm^{-1}. ^1H NMR ($CDCl_3$):

4.31 (s, 5H, Cp), 5.63 (s, 5H, Cp), 7.06 - 7.46 (m, 34H, ArH). ^{13}C NMR ($CDCl_3$): 85.16 (s, Cp), 91.63 (s, Cp), 115.14 (s, C≡C), 121.48 (s, C≡C), 127.16 - 139.38 (m, Ar and PPh_3), 211.48 (s, CO). ES mass spectrum (MeOH, with NaOMe, *m/z*): 1171, [M + Na]$^+$; 1148, M$^+$.

(d) With $RhCl(CO)(PPh_3)_2$.

Similarly, $RhCl(CO)(PPh_3)_2$ (85 mg, 0.123 mmol) was added to **4** (100 mg, 0.123 mmol) in a mixture of $NHEt_2$ / thf (20 ml, 3:1) with a catalytic amount of CuI (ca 5mg). After stirring 2 h in the dark, the resulting solution was then chromatographed on alumina (acetone / hexane, 3:7). An intense yellow band afforded $\{Cp(Ph_3P)_2Ru\}(\mu\text{-}C{\equiv}CC_6H_4C{\equiv}C)\{Rh(\eta\text{-}O_2)(CO)(PPh_3)_2\}$ **15** as a yellow powder (42 mg, 23%). Anal. Found: C, 66.62; H, 4.81. $C_{88}H_{69}O_3P_4RhRu.CH_2Cl_2$ calcd.: C, 67.33; H, 4.51%; M, 1505. IR (nujol): ν(C≡C) 2065m; ν(CO) 1961sm; ν(C=C) 1588sm cm^{-1}. ^{1}H NMR ($CDCl_3$): 4.35 (s, 5H, Cp), 7.11 - 7.72 (m, 64H, ArH). ^{13}C NMR ($CDCl_3$): 85.43 (s, Cp), 93.50 (s, C≡C), 103.37 (s, C≡C), 127.40 - 138.90 (m, Ar and PPh_3), 212.80 (s, CO). ES mass spectrum (MeOH, *m/z*): 1505, M$^+$; 1243, [M - PPh_3]$^+$.

(e) With $IrCl(CO)(PPh_3)_2$.

A similar reaction using $IrCl(CO)(PPh_3)_2$ (100 mg, 0.123 mmol) gave a yellow powder of $\{Cp(Ph_3P)_2Ru\}(\mu\text{-}C{\equiv}CC_6H_4C{\equiv}C)\{Ir(\eta\text{-}O_2)(CO)(PPh_3)_2\}$ **16** (112 mg, 57%). Anal. Found: C, 66.41; H, 4.36. $C_{88}H_{69}IrO_3P_4Ru$ calcd.: C, 66.32; H, 4.37; M, 1515. IR (nujol): ν(C≡C) 2069m; ν(CO) 1953sm cm^{-1}. ^{1}H NMR ($CDCl_3$): 4.30 (s, 5H, Cp), 7.04 - 8.30 (m, 64H, ArH). ^{13}C NMR ($CDCl_3$): 85.38 (s, Cp), 97.98 (s, C≡C), 115.68 (s, C≡C), 127.38 - 139.54 (m, Ar and PPh_3). ES mass spectrum (MeOH, *m/z*): 1515, M$^+$.

(f) With $PtCl_2(dppe)$.

$PtCl_2$(dppe) (61 mg, 0.092 mmol) was added to a diethylamine / dmf (6 ml / 4 ml) solution containing **4** (150 mg, 0.184 mmol) and a catalytic amount of CuI (ca 4 mg). A yellow precipitate formed in the solution after 10 min. and after a further hour, the solvent was partly removed. Addition of MeOH (10 ml) caused further precipitation. Filtration gave a yellow powder of $Pt\{C{\equiv}CC_6H_4C{\equiv}C[Ru(PPh_3)_2Cp]\}_2$(dppe) **17** (67

mg, 33%). Anal. Found: C, 69.16; H, 4.74. $C_{128}H_{102}P_6PtRu_2$ calcd.: C, 69.08; H, 4.63%; M, 2223. IR (nujol): ν(C≡C) 2074s cm^{-1}. ^1H NMR ($CDCl_3$): 2.43 (m, 4H, CH_2), 4.31 (d, 10H, Cp), 6.93 - 7.49 (m, 88H, ArH). ^{13}C NMR ($CDCl_3$): 36.26 (s, CH_2), 85.16 (s, Cp), 93.42 (s, C≡C), 103.29 (s, C≡C), 113.16 (s, C≡C), 115.26 (s, C≡C), 127.131 - 139.44 (m, Ph and PPh_3). ES mass spectrum (MeOH + AgOAc, *m/z*): 2330, $[2M + 2Ag]^{2+}$.

(g) With AuCl(PPh₃).

Similarly, a mixture of $AuCl(PPh_3)$ (61 mg, 0.123 mmol) with a catalytic amount of copper iodide (ca 5 mg) in diethylamine (15 ml) was treated with **4** (100 mg, 0.123mmol). There was immediate formation of a bright yellow precipitate, which was collected and dried to give $\{Cp(Ph_3P)_2Ru\}(\mu\text{-}C{\equiv}CC_6H_4C{\equiv}C)\{Au(PPh_3)\}$ **18** (76 mg, 49%). Anal. Found: C, 65.20; H, 4.40. $C_{69}H_{54}Au\,P_3Ru$ calcd.: C, 65.04; H, 4.27; M, 1274. IR (nujol): ν(C≡C) 2068m; ν(C=C) 1588m cm^{-1}. ^1H NMR ($CDCl_3$): 4.60 (s, 5H, Cp), 7.20 – 7.57 (m, 49H, ArH). ^{13}C NMR ($CDCl_3$): 85.42 (s, Cp), 127.59 – 133.95 (m, Ar and PPh_3). ES mass spectrum (MeOH, *m/z*): 1274.8, M^+.

(h) With Hg(OAc)₂.

A mixture of **4** (100 mg, 0.123 mmol) and $Hg(OAc)_2$ (19 mg, 0.061 mmol) in thf (20ml) was heated under reflux for 3 h. The yellow precipitate which formed was collected, washed with hexane and air dried to give $Hg\{C{\equiv}CC_6H_4C{\equiv}C[Ru(PPh_3)_2Cp]\}_2$ **19** (50 mg, 45%). Anal. Found: C, 70.98; H, 5.09. $C_{102}H_{78}HgP_4Ru_2$ calcd.: C, 70.51; H, 4.53%; M, 1830. IR (nujol): ν(C≡C) 2068s cm^{-1}. ES mass spectrum (MeOH, *m/z*): 1830, M^+; 429, $[Ru(PPh_3)_2Cp]^+$.

Preparation of Ru(C≡CC₆H₄C≡CPh)(PPh₃)₂Cp **12**.

Iodobenzene (100 mg, 0.5 mmol) was added to a mixture of **4** (198 mg, 0.243 mmol), CuI (ca 4 mg) and $Pd(PPh_3)_4$ (14 mg, 0.012 mmol) in $NHEt_2$ (30 ml). After 2 hours stirring at r.t. in the dark, the solution was filtered into hexane (50 ml) to give a bright yellow precipitate of $Ru(C{\equiv}CC_6H_4C{\equiv}CPh)(PPh_3)_2Cp$ **12** (212 mg, 98%). Anal. Found: C, 72.43; H, 5.21. $C_{57}H_{44}P_2Ru.0.5PhI$ calcd: C, 72.50; H, 4.71%; M, 892. IR (nujol): ν(C≡C) 2148sm, 2065m cm^{-1}. ^1H NMR ($CDCl_3$): 4.46 (s, 5H, Cp), 7.10 - 7.72 (m, 39H, ArH). ^{13}C NMR ($CDCl_3$): 85.64 (s, Cp), 106.18 (s, C≡C), 127.78 -

134.46 (m, Ph and PPh_3). ES mass spectrum (MeOH, *m/z*): 892, M^+; 630, $[M - PPh_3]^+$.

Oxidative coupling of **4**.

Addition of tmed (150 µl, 1.01 mmol) to a suspension of CuCl (100 mg, 1.01 mmol) in acetone (5 ml) gave a blue-green solution after 15 min. In a separate flask, dioxygen was passed into a solution of **4** (200 mg, 0.24 mmol) in acetone (40 ml) via a glass frit. The copper catalyst was added dropwise until **4** was no longer present (TLC). Evaporation and extraction of the residue with CH_2Cl_2 left a yellow insoluble material, tentatively identified as 1,4-$\{Ru(PPh_3)_2Cp(C{\equiv}C)\}_2C_6H_4$ **13** (61 mg, 31%). Anal. Found: C, 68.24; H, 4.93. $C_{102}H_{78}P_4Ru_2.2.5CH_2Cl_2$ calcd.: C, 68.13; H, 4.54%; M, 1630. IR (nujol): ν(C≡C) 2067s cm^{-1}. ES mass spectrum (MeOH, *m/z*): 1630, M^+.

Conversion of **4** *to* **2**.

LiBu (61 µl of a 2M solution in hexane, 0.122 mmol) was added to a cold (-78°C) solution of **4** (100 mg, 0.122 mmol) in thf (20 ml) and the mixture was stirred for 15 min. Addition of $SiClMe_3$ (15 µl, 0.122 mmol), warming to r.t. and separation of the product by chromatography on alumina gave **2** (105 mg, 89%).

REFERENCES.

(1) Bartik, T.; Weng, W.; Ramsden, J. A.; Szafert, S.; Falloon, S. B.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc* **1998**, *120*, 11071.

(2) Guillemont, M.; Toupet, L.; Lapinte, C. *Organometallics* **1998**, 1928.

(3) Woodworth, B. E.; Templeton, J. L. *J. Am. Chem. Soc.* **1996**, *118*, 7418.

(4) Bruce, M. I.; Ke, M.; Low, P. J. *Chem. Commun.* **1996**, 2405.

(5) Bunz, U. H. F. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 969.

(6) Lang, H. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 547.

(7) Beck, W.; Neimer, B.; Weiser, H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 923.

(8) Iwamura, H.; Matsuda, K. *Modern Acetylenic Chemistry*; VCH: Weinheim, **1995**.

(9) Paul, F.; Lapinte, C. *Coord. Chem. Rev.* **1998**, *178-180*, 431.

(10) Yam, V. W.-W. *J. Photochem. Photobiol.* **1997**, *106*, 75.

(11) Yam, V. W.-W.; Lau, V. C.-Y.; Cheung, K.-K. *Organometallics* **1996**, *15*, 1740.

(12) Bruce, M. I.; Ke, M.; Low, P. J.; Skelton, B. W.; White, A. H. *Organometallics* **1998**, *17*, 3539.

(13) Werner, H.; Rappert, T.; Wolf, J. *Isr. J. Chem.* **1990**, *30*, 377.

(14) Fyfe, H. P.; Mlekuz, M.; Zargarian, D.; Taylor, N. J.; Marder, T. B. *J. Chem. Soc., Chem. Commun.* **1991**, 188.

(15) Stang, P. J.; Tykwinski, R. *J. Am. Chem. Soc.* **1992**, *114*, 4411.

(16) Hagihara, N.; Sonogashira, K.; Takahashi, S. *Adv. Polym. Sci.* **1980**, *41*, 149.

(17) Frazier, C. C.; Guha, S.; Chen, W. P.; Cockerman, M. P.; Porter, P. L.; Chauchard, E. A.; Lee, C. H. *Polymer* **1987**, *28*, 553.

(18) Davies, S. J.; Johnson, B. F. G.; Khan, M. S.; Lewis, J. *J. Chem. Soc., Chem Commun.* **1991**, 187.

(19) Khan, M. S.; Davies, S. J.; Kakkar, A. K.; Schwartz, D.; Lin, B.; Johnson, B. F. G.; Lewis, J. *J. Organomet. Chem.* **1992**, *424*, 87.

(20) Osakada, K.; Tadashi, T.; Tanaka, M.; Yamamoto, T. *J. Organomet. Chem.* **1994**, *473*, 359.

(21) Jia, G.; Puddephatt, R. J.; Scott, T. D.; Vittal, J. J. *Organometallics* **1993**, *12*, 3656.

(22) Yam, V. W.-W.; Choi, S. W.-K. *J. Chem. Soc., Dalton Trans.* **1996**, 4227.

(23) Whittall, I. R.; McDonaugh, A. M.; Humphrey, M. G.; Samoc, M. *Adv. Organomet. Chem.* **1998**, *42*, 291.

(24) Yam, V. W.-W.; Fung, W. K.-M.; Wong, K. M.-C.; Lau, V. M.-C.; Cheung, K.-K. *Chem. Commun.* **1998**, 777.

(25) Lavastre, O.; Even, M.; Dixneuf, P. H.; Pacreau, A.; Vairon, J.-P. *Organometallics* **1996**, *15*, 1530.

(26) Lavastre, O.; Plass, J.; Bachmann, P.; Guesmi, S.; Moinet, C.; Dixneuf, P. H. *Organometallics* **1997**, *16*, 184.

(27) Bruce, M. I.; Humphrey, M. G.; Snow, M. R.; Tiekink, E. R. T. *J. Organomet. Chem.* **1986**, *314*, 213.

(28) Whitall, I. R.; Humphrey, M. G.; Persoons, A.; Houbrechts, S. *Organometallics* **1996**, *15*, 1935.

(29) Weyland, T.; Lapinte, C.; Frapper, G.; Calhorda, M. J.; Halet, J.-F.; Toupet, L. *Organometallics* **1997**, *16*, 2024.

(30) Bruce, M. I.; Denisovich, L. I.; Low, P. J.; Peregudova, S. M.; Ustynyuk, N. A. *Mendeleev Commun.* **1996**, 200.

(31) Peron, D.; Romero, A.; Dixneuf, P. H. *Gazz. Chim. Ital.* **1994**, *124*, 497.

(32) Gauss, C.; Veghini, D.; Berke, H. *Chem. Ber.* **1997**, *130*, 183.

(33) Rappert, T.; Nurnberg, O.; Werner, H. *Organometallics* **1993**, *12*, 1359.

(34) Werner, H.; Lass, R. W.; Gervert, O.; Wolf, J. *Organometallics* **1997**, *16*, 4077.

(35) Lavestre, O.; Even, M.; Toccon, C.; Dixneuf, P. H.; Pacreau, A.; Vairon, J.-P. *Macromol. Symp.* **1997**, *122*, 71.

(36) Lavastre, O.; Oliver, L.; Dixneuf, P. H.; Sibandhit, S. *Tetrahedron* **1996**, *52*, 5495.

(37) Maroni, M.; Moigne, J. L.; Luzzati, S. *Macromolecules* **1994**, *227*, 562.

(38) Bruce, M. I.; Hall, B. C.; Low, P. J.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1999**, *592*, 74.

(39) Wong, A.; Kang, P. C. W.; Tagge, C. D.; Leon, D. R. *Organometallics* **1990**, *9*, 1992.

(40) Bruce, M. I.; Hambley, T. W.; Snow, M. R.; Swincer, A. G. *Organometallics* **1985**, *4*, 494.

(41) Bruce, M. I.; Hambley, T. W.; Snow, M. R.; Swincer, A. G. *Organometallics* **1985**, *4*, 501.

(42) Bruce, M. I.; Hambley, T. W.; Liddell, M. J.; Snow, M. R.; Swincer, A. G.; Tiekink, E. R. T. *Organometallics* **1990**, *9*, 96.

(43) Bruce, M. I.; Hambley, T. W.; Snow, M. R.; Swincer, A. G. *Organometallics* **1985**, *4*, 494, 501.

(44) Bruce, M. I.; Humphrey, P. A.; Snow, M. R.; Tiekink, E. R. T. *J. Organomet. Chem.* **1986**, *303*, 417.

(45) Bruce, M. I.; Duffy, D. N.; Liddell, M. J.; Snow, M. R.; Tiekink, E. R. T. *J. Organomet. Chem.* **1987**, *335*, 365.

(46) Bruce, M. I.; Liddell, M. J.; Snow, M. R.; Tiekink, E. R. T. *Organometallics* **1988**, *7*, 343.

(47) Bruce, M. I.; Hambley, T. W.; Liddell, M. J.; Swincer, A. G.; Tiekink, E. R. T. *Organometallics* **1990**, *9*, 2886.

(48) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, 4467.

(49) Hay, A. S. *J. Org. Chem.* **1962**, *27*, 3320.

(50) Frapper, G.; Kertesz, M. *Inorg. Chem.* **1993**, *32*, 732.

(51) Bruce, M. I.; Hall, B. C.; Low, P. J.; Smith, M. E.; Nicholson, B. K.; Skelton, B. W.; White, A. H. *Inorg. Chim. Acta.* **2000**, *300-302*, 633.

(52) Lang, H.; Köhler, K.; Blau, S. *Coord. Chem. Rev.* **1995**, *143*, 113.

(53) Lang, H.; Frosch, W.; Wu, I. Y.; Blau, S.; Nuber, B. *Inorg. Chem.* **1996**, *35*, 6266.

(54) Varga, V.; Hiller, J.; Polasek, M.; Thewalt, U.; Mach, K. *J. Organomet. Chem.* **1996**, *514*, 219.

(55) Janssen, M. D.; Köhler, K.; Herres, M.; Dedieu, A.; Smeets, W. J. J.; Spek, A. L.; Grove, D. M.; Lang, H.; Van Koten, G. *J. Am. Chem. Soc.* **1996**, *118*, 4817.

(56) Ara, I.; Berebguer, J. R.; Fornies, J.; Lalinde, E.; Moreno, M. T. *J. Organomet. Chem.* **1996**, *510*, 63.

(57) Ara, I.; Berenguer, J. R.; Fornies, J.; Lalinde, E. *Inorg. Chim. Acta.* **1997**, *264*, 199.

(58) Narvor, N. L.; Lapinte, C. *Organometallics* **1995**, *14*, 634.

(59) Hoffman, N. W. *Inorg. Chim. Acta.* **1984**, *88*, 59.

(60) Collman, J. P.; Jr, C. P. S.; Kubota, M. *Inorg. Synth.* **1990**, *28*, 270.

(61) Yasufuku, K.; Noda, H.; Yamazaki, H. *Inorg. Synth.* **1989**, *26*, 369.

(62) Bruce, M. I.; Nicholson, B. K.; Shawkataly, O. bin. *Inorg. Synth.* **1989**, *26*, 325.

Chapter 4

Molecular Squares and Tweezers

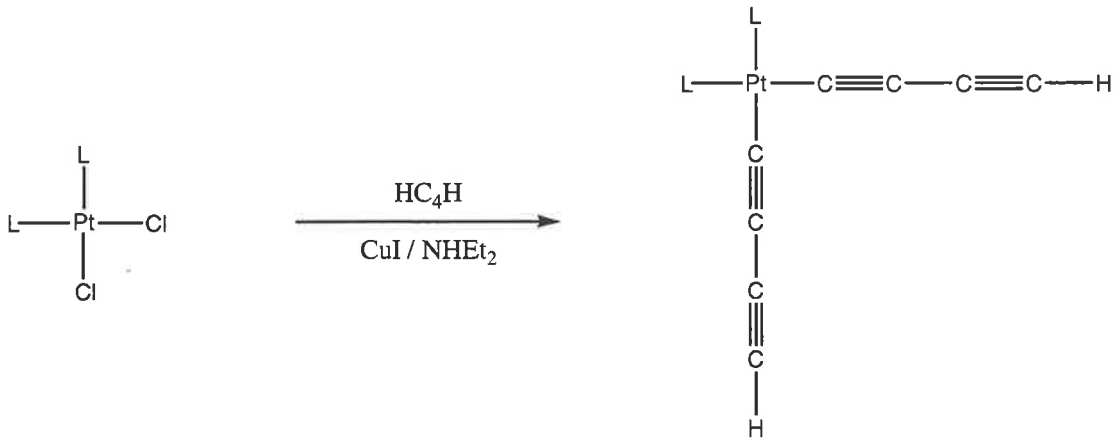
INTRODUCTION.

The design and synthesis of molecules having specific 2D or 3D architectures is of much current interest, such structures include molecular rods, squares, hexagons and boxes.[1,2] Assemblies of molecular squares containing transition metals by supramolecular techniques, using square planar PtL_2 systems as corners, were among the first areas of success. As edges, a variety of *exo*-bidentate ligands have been employed including *N*-donor ligands such as 4,4'-bipyridyl or 2,7-diazapyrene, and more recently 4-phenyl- or 4-ethynylpyridines and 4,4'-biphenyldiyl. Stang and coworkers have reported high yield syntheses of complexes such as $[\{Pt[\mu\text{-}4,4'\text{-}bpy)\}L_2\}_4]^{8+}$ (L = PEt_3, L_2 = dppp),[3] $[\{Pt(\mu\text{-}C_6H_4CN\text{-}4)L_2\}_4]^{4+}$[4] or $[\{Pt(\mu\text{-}C{\equiv}CC_5H_4N\text{-}4)L_2\}_4]^{4+}$.[5] The challenge of making similar molecules having atomic chains as edges, for example, those consisting of only four carbon atoms, the buta-1,3-diyn-1,4-diyl ligand, has aesthetic appeal as well as a practical advantage, since the resulting complexes are neutral and enclose larger cavities than exist in molecules in which the edges consist of aromatic or similar bulky groups.

In the last few years the synthesis and properties of several metal complexes containing the buta-1,3-diyn-1,4-yl ligand have been reported.[6-13] These complexes have been obtained either directly from buta-1,3-diyne, or from silylated or stannylated derivatives of the diyne. In turn, we have used $W(C{\equiv}CC{\equiv}CH)(CO)_3Cp$ to demonstrate the possibility of linking two metal centres, which may be either the same or different, via the unsaturated C_4 chain.[14] In related studies, it has been shown that electronic communication between the two metal centres may occur in selected instances, particularly when electron-rich centres are joined together and detailed studies have been carried out on $\{Re(NO)(PPh_3)Cp^*\}_2(\mu\text{-}C{\equiv}CC{\equiv}C)$,[7] $\{Fe(dppe)Cp^*\}_2(\mu\text{-}C{\equiv}CC{\equiv}C)$[15] and $\{Ru(PPh_3)_2Cp\}_2(\mu\text{-}C{\equiv}CC{\equiv}C)$.[16] All of the

systems described so far have been one-dimensional. In order for 2D or 3D molecules to be built, the reactive metal sub-units need to bear at least *bi-* or *multi-*dentate functionality. One of the most extensively used metal bidentate systems is that of square planar platinum(II) (PtX_2L_2) which allows for the formation of 90° and 180° sub-units depending whether *cis-* or *trans-* compounds are used as the initial materials.

Reactions of alkynes with *cis-* platinum compounds result in the formation of *cis-*bisalkynyl complexes (Scheme 1), which have received increasing attention from researchers as "molecular tweezers", due to their ability to include small reactive compounds in the bite of the alkyne arms.[17] These compounds are important precursors for the formation of larger complexes, including molecular squares.



Scheme 1 : Formation of *cis*-bisalkynyl complexes

This chapter describes the preparation and structural characterisation of several molecular tweezers and their self-assembly with appropriate *cis*-$PtX_2(L)_2$ (X = OTf; L = PEt_3, dppe and dppp) complexes to give molecular squares. During the completion of this work, a related neutral square, $\{Pt(C{\equiv}CC{\equiv}C)(dcpe)\}_4$ (dcpe = dicyclohexylphosphinoethane) was published by Youngs.[18]

RESULTS AND DISCUSSION.

Preparation of cis-bis-platinum alkynyl compounds.

The Group 10 complexes $MCl_2(PR_3)_2$ have long been known to undergo ready coupling reactions with terminal alkynes and polyynes in presence of Cu(I) catalysts, with many examples arising from the work of the Hagihara group on polyynyl systems containing metals in the polymer backbone.[8-11,19-22] In more recent times, there has been a resurgence in interest in these compounds, and as a result a new approach to the construction of M-C≡C bonds involving the reactions of $MCl_2(PR_3)_2$ with alkynyltins being reported.[12,13,23,24]

The chloroplatinum complexes, *cis*-$PtCl_2(L)_2$ (L = PEt_3, L_2 = dppe, dppp) react with buta-1,3-diyne in a dmf / diethylamine solution in the presence of CuI to afford *cis*-$Pt(C{\equiv}CC{\equiv}CH)_2(L)_2$ (L = PEt_3 **1**, L_2 = dppe **3**, dppp **5**) in high yields. These white or pale yellow complexes could be recrystallised from hexane / benzene or hexane / CH_2Cl_2 mixtures and their identities have been confirmed crystallographically. The spectroscopic properties were in accord with their solid-state structures. In the IR spectra of **1**, bands at 3249 and 2147 cm^{-1} were assigned to ν(≡CH) and ν(C≡C) absorptions respectively, while similar bands were found at 3288 and 2147 cm^{-1} for **3** and at 3296 and 2151 cm^{-1} for **5**. In the ^1H NMR spectra, the acetylenic protons are found at δ ca 1.8 ppm and show triplet coupling to the two equivalent ^{31}P nuclei. Other signals are consistent with the phosphine substituents present, with **1** showing signals arising from the ethyl groups at δ 1.08 (CH_3) and δ 1.97 (CH_2). Both **3** and **5** showed peaks corresponding to the phenyl rings, δ ca 7.30 – 7.90, and a multiplet corresponding to the methylene protons of the phosphine backbone at δ 2.42 or δ 2.70 ppm for **3** and **5** respectively. In the ^{13}C NMR spectra, relatively weak signals were recorded for the carbon chains, with C_α typically found at δ ca 94, C_β at δ ca 80, C_γ at δ ca 62 and C_δ at δ ca 72; all signals were singlets with no discernible coupling to Pt or P. The ^{31}P NMR spectra contained the usual apparent triplets at δ 5.44 [J(PPt) = 2262 Hz] for **1**, at δ 43.26 [J(PPt) = 2288 Hz] for **3** and at δ -6.69 [J(PPt) = 2204 Hz] for **5**. These are all consistent with the *cis*- orientation of the two tertiary phosphine

nuclei.[25] The ES mass spectra of **1**, **3** and **5** are similar, with addition of alkali metal ions resulting in the formation of ion clusters, $[M + M']^+$ and $[2M + M']^+$ ($M' = Na^+$ or Ag^+) as the only observable ions. These observations prompted a more detailed study into the formation of $[M + M']^+$ ions, which will be discussed later in this chapter.

A similar reaction between $PtCl_2$(cod) and the diyne afforded an unstable brown material which was not fully characterised. However, addition of one equivalent of dppe to the initial reaction mixture afforded a quantitative yield of **3**, consistent with the intermediate formation of $Pt(C{\equiv}CC{\equiv}CH)_2$(cod) **13** and subsequent replacement of the cod by the dppe ligand. This method could prove useful in the preparation of further examples not otherwise readily obtained.

*Molecular structures of cis-$Pt(C{\equiv}CC{\equiv}CH)_2(L)_2$ ($L = PEt_3$ **1**, L_2 = dppe **3**, dppp **5**).*
Plots of a single molecule of each of the three complexes are shown in Figures. 1 - 3 and important structural parameters are collected in Table 1. Bond parameters are similar for all three complexes. As can be seen, the platinum atom has approximate square planar coordination, the bulk of the PEt_3 ligands in **1** causing the P-Pt-P angles to expand to 105.22(4)°, whereas the angle subtended at Pt in the chelate complexes are strongly dependent on the bite-angles of the bisphosphines. Thus, we find values for P(1)-Pt-P(2) of 86.2(1) and 97.02(8)° for **3** and **5** respectively. There are similar variations in the C-Pt-C angles [86.5(2), 93.2(5) and 88.9(3)° for **1**, **3** and **5** respectively] while the P-Pt-P angles vary between 84.1(1) and 90.5(3)°.

The Pt-P distances are 2.319(1) **1**, 2.269(3) **3** and 2.304, 2.305(2) Å **5**, which may be compared with values of 2.20(8) for $PtCl_2$(dppe)[26] and 2.233(1), 2.2317(8) Å for $PtCl_2$(dppp)[27]. The Pt-C distances are 1.976(4) **1**, 2.02(1) **3** and 1.997, 2.002(9) Å **5** [cf. Pt-C 2.10, 2.04 Å in *cis*-$Pt(C{\equiv}CPh)_2(PPh_3)_2$[28]]. Along the C_4 chain from the metal, alternate short and long C-C separations of 1.218, 1.390 and 1.174(6) Å (for **1**), 1.17, 1.36 and 1.16(2) Å (for **3**) and 1.21, 1.36, 1.17(1) Å (for **5**) confirm retention of the two conjugated C≡C triple bonds with little delocalisation in each chain. The

H atoms were not refined. In **1**, angles at the carbon atoms of the chain range between 179.2(4) and 179.7(7)°, i.e. the C_4 chains are linear within experimental error. In contrast, the C_4 chains are distinctly non-linear in **3** and **5** with the corresponding angles ranging from 171.7(9) to 176(1)° (for **3**) and 171.0(8) to 178(1)° (for **5**) and the largest departures from linearity being found at C_1 and C_2. These deviations are ascribed to steric influences of the phenyl groups of the chelate ligands. The facile bending of C_n chains has been recently noted in a series of rhenium complexes containing longer C_n chains (n = 6 or 8) and is evident, although not further commented upon, in the structures of similar complexes of Gladysz where n = 20.[29] Perhaps surprisingly, it is also borne out in the molecular mechanics study reported below. Of interest is the size of the anisotropic displacements for C(4), which are nearly twice those for the other three carbon atoms of the chain. It is evident that deformation of the C_4 chain is a low energy process.

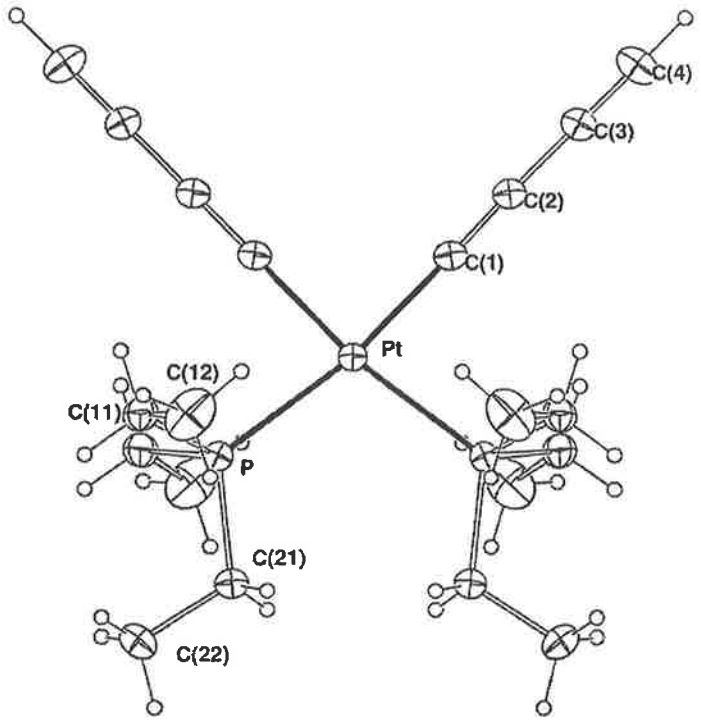


Figure 1 : Molecular projection of $Pt(C{\equiv}CC{\equiv}CH)_2(PEt_3)_2$ **1**.

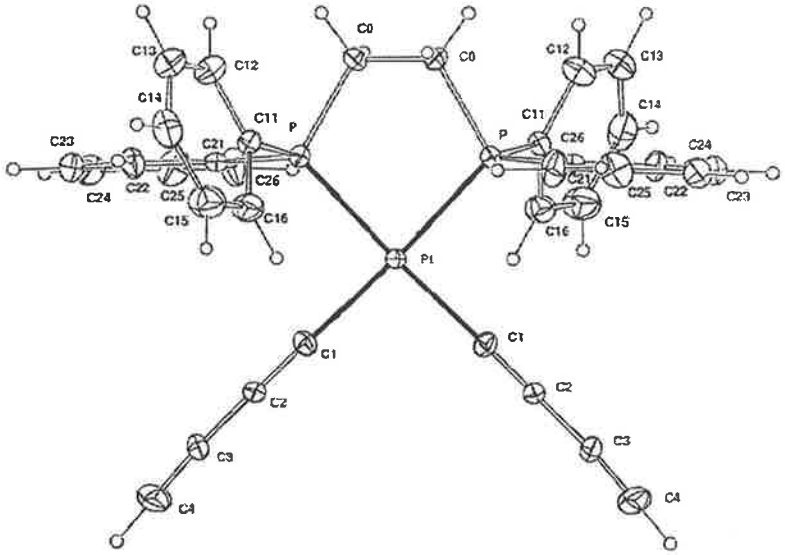


Figure 2 : Molecular projection of $Pt(C{\equiv}CC{\equiv}CH)_2(dppe)$ **3.**

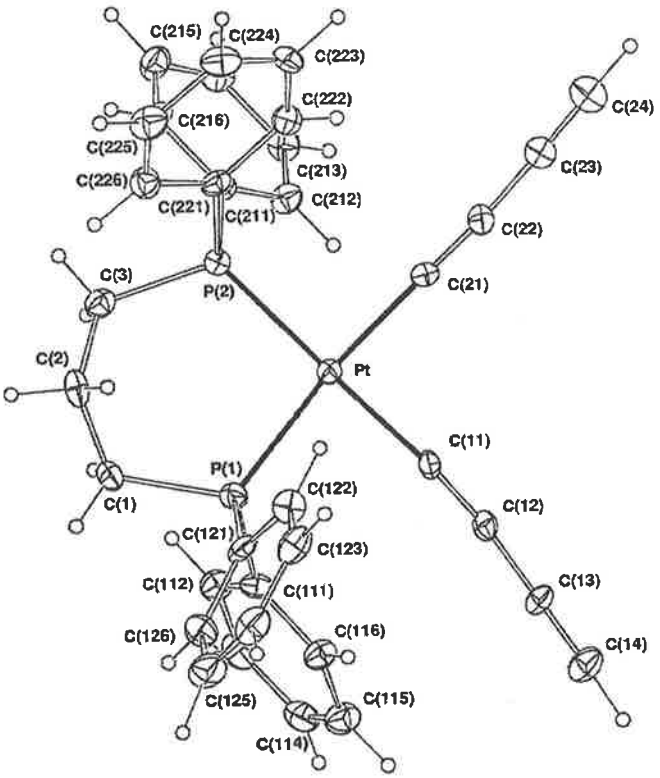


Figure 3 : Molecular projection of $Pt(C{\equiv}CC{\equiv}CH)_2(dppp)$ **5.**

The reaction of $W(C{\equiv}CC{\equiv}CH)(CO)_3Cp$ with $PtCl_2(dppe)$ under Cu(I)-catalysed conditions described above gave $Pt\{C{\equiv}CC{\equiv}C[W(CO)_3Cp]\}_2(dppe)$ **4** (74%) following chromatography and crystallisation. The pale-yellow complex **4** was characterised by a two band ν(CO) pattern and resonances in the ^1H and ^{13}C NMR spectra characteristic of the Cp ligands (δ_H 5.56; δ_C 91.68) which are chemically equivalent in solution. The low solubility of **4** hampered the observation of the diyndiyl carbons as well as the methylene carbons of the dppe ligand. The ES mass spectrum, obtained with solutions in MeCN containing formic acid, gave an $[M + H]^+$ ion at *m/z* 1356, while an ion at *m/z* 1342 was formulated as $[M + 2H + MeCN - CO]^+$. The use of MeCN solutions containing $AgNO_3$ resulted in formation of doubly-charged aggregate ions with masses and isotopic distributions consistent with the formulations $[(M + H + MeCN + AgNO_3)_2]^{2+}$ (*m/z* 1566) and $[(M + Ag)_2]^{2+}$ (*m/z* 1464). The complexes *cis*-$Pt\{C{\equiv}CC{\equiv}C[W(CO)_3Cp]\}_2(PEt_3)_2$ **2** and $Pt\{C{\equiv}CC{\equiv}C[W(CO)_3Cp]\}_2(dppp)$ **6** were obtained from similar reactions with *cis*-$PtCl_2(PEt_3)_2$ and $PtCl_2(dppp)$ in 77 and 78% yields, respectively. As described in the Experimental section, **2** and **6** have spectroscopic properties in accord with their formulations, with aggregate ions being found in ES mass spectra measured with solutions containing either NaOMe or $AgNO_3$. The more soluble PEt_3 derivative afforded X-ray quality crystals, which allowed confirmation of its molecular structure.

Molecular structure of cis-$Pt\{C{\equiv}CC{\equiv}C[W(CO)_3Cp]\}_2(PEt_3)_2$ **2**.

The molecular projection of a molecule of **2** is shown in Figure 4 and important bond parameters are collected in Table 1. It can be seen that the platinum retains approximate square planar geometry with the two $C_4[W(CO)_3Cp]$ groups and two PEt_3 ligands each being mutually *cis*. The angles at Pt are C(1)-Pt-C(1') 86.4(4), C(1)-Pt-P(1) 82.6, 91.1(3) and P(l)-Pt-P(1') 100.3(1)° [sum, 360.4°] with associated asymmetries in the pairs of C-Pt-P (*cis* and *trans*) angles. The relative bulk of the pair of PEt_3 ligands, which pack in a "geared" manner, results in an opening of the angle between them. The Pt-C [2.007(9), 1.99(1) Å] and Pt-P distances [2.315, 2.303(3) Å] are within the ranges observed for many other complexes containing Pt-C(sp) and Pt-P bonds.

Of interest are the C_4 chains linking the three metal centres. The C-C separations along each chain are alternately short-long-short, indicating retention of the diyndiyl formulation. From Pt to W, $C_{(n)}$ - $C_{(n+1)}$ (n = 1, 2 or 3) are 1.22, 1.19(1); 1.38, 1.40(1); 1.21, 1.18(2) Å, suggesting a small delocalisation of electron density from the C≡C triple bonds into the C-C single bond at the centre of the chain. Angles at the respective carbon atoms are 172.5, 170(1); 178, 177(1); 178, 176(1)° with the bending at the carbons adjacent to the platinum no doubt arising from steric interactions caused by the PEt_3 ligands. Each molecule of **2** is accompanied stoichiometrically by a counterpart solvent $CHCl_3$ molecule, which does not appear to exhibit any unusually short contacts.

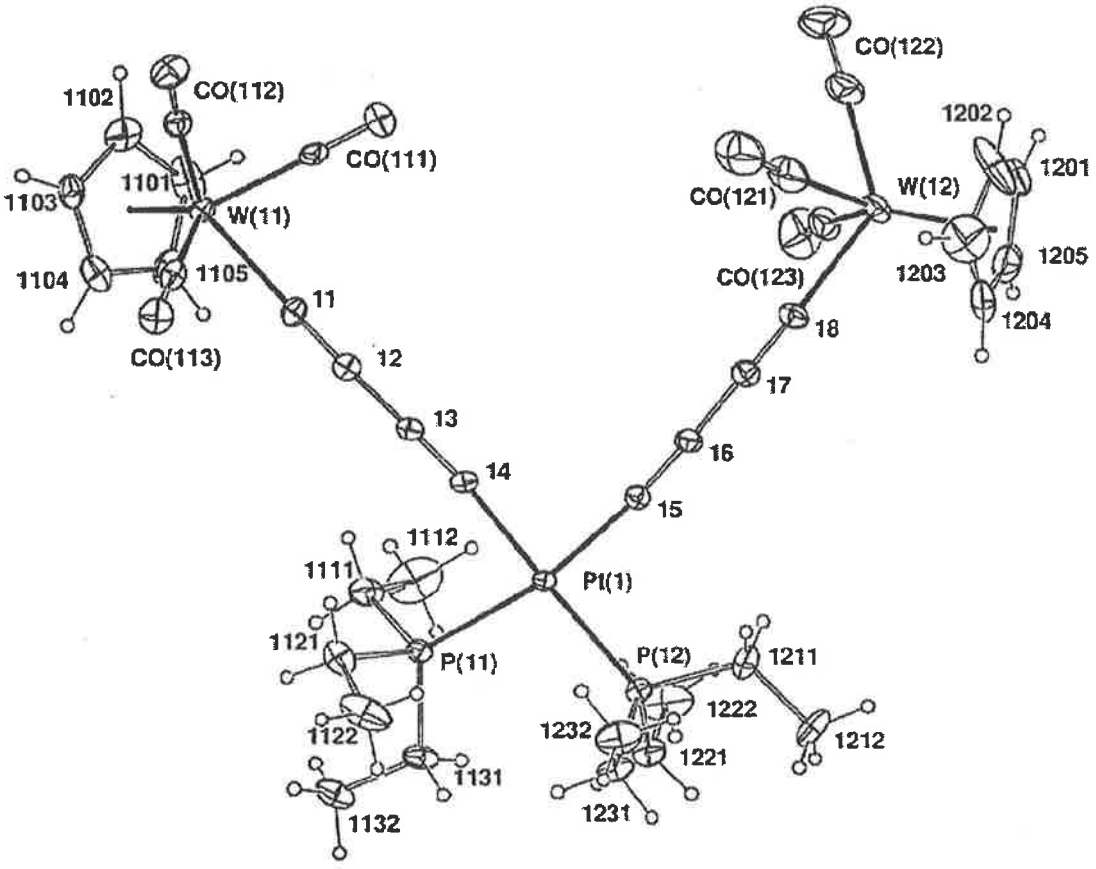


Figure 4 : Molecular projection of *cis*-Pt{C≡CC≡C[W(CO)$_3$Cp]}$_2$(PEt$_3$)$_2$ **2**.

Interestingly, these deformations are accurately modelled by simple molecular mechanics calculations performed with the *Spartan* program, the results of which can be found in Table 2. These calculations were obtained from the energy-minimised structure obtained by the sybyl minimiser and do not take into account any intermolecular effects. Due to *Spartan's* inability to model third row transition metal elements, semi-empirical and *ab initio* methods were unable to be calculated. Professor Jean-François Halet performed a more detailed computation analysis at the University of Renne. A number of assumptions were made to correctly model the calculations, namely that the platinum nuclei are so big, that to reproduce it well additional corrections were necessary. These corrections are called relativistic corrections, which assumes that the weight of the electrons is dependent on their velocity. For $Pt(C{\equiv}CC{\equiv}CH)_2(dppp)$ **5**, the calculation obtained a Pt-C distance of 2.005, 2.008 Å, Pt-P distance of 2.361, 2.368 Å, with a C-Pt-C angle of 89.97° and P-Pt-P angle of 92.18°. The bending of the carbon chain was also observed with a distortion of approximately 3° along the chain. The energy gap between the HOMO and LUMO orbitals was calculated to be 3.066 eV, which indicated that the compound should be stable to reduction. The four HOMO's are a linear combination between the carbon chain π orbitals and the corresponding d metal orbitals, suggesting that oxidation effects the $Pt(C_4)_2$ skeleton which would lead to a shortening of Pt-C distance, a lengthening of C_α - C_β, a shortening of C_β - C_γ, and a lengthening of C_γ - C_δ.

Reactions with $Co_2(CO)_8$ and $Co_2(CO)_6(\mu$-dppm).

The cobalt complexes $Co_2(CO)_8$ and $Co_2(CO)_6(\mu$-dppm) have long been used to probe the reactivity of metal acetylides. Reactions between $Co_2(CO)_8$ and $Pt(C{\equiv}CC{\equiv}CR)_2(dppe)$ [R = H **3**, $W(CO)_3Cp$ **4**] resulted in the formation of many products in low yield. However when $Co_2(CO)_6(\mu$-dppm) was used, the reaction gave essentially one product in high yield, with addition occurring at the less sterically hindered C≡C triple bond.

Reaction of **3** with two equivalents of $Co_2(CO)_6(\mu\text{-dppm})$ resulted in the formation of red $Pt\{C{\equiv}CC_2H[Co_2(\mu\text{-dppm})(CO)_4]\}_2(dppe)$ **7** in a yield of 50%. Coordination of $Co_2(CO)_6(\mu\text{-dppm})$ fragments to both alkyl arms was established by IR, NMR, ES mass spectroscopy and ultimately single crystal X-ray analysis. The IR spectrum in CH_2Cl_2 showed three medium intensity peaks, 2016 cm^{-1} corresponding to ν(C≡C); 1990 and 1960 cm^{-1} for ν(CO). The ^{31}P NMR gave two signals, a platinum triplet at δ 34.96 [*J*(PPt) = 2258 Hz] and a single peak at δ 20.66 corresponding to the two equivalent dppm ligands of the $Co_2(CO)_4(\mu\text{-dppm})$ fragments. The negative ion ES mass spectrum in CH_2Cl_2 / MeOH with added NaOMe showed a parent ion at *m/z* 1919 with successive loss of up to eight CO groups. The positive ion mode showed a single peak at *m/z* 1942 corresponding to the $[M + Na]^+$ ion. A molecule of **7** is shown in Figure 5. The important bond length and angles are summarised in Table 1. The structure shows two $Co_2(CO)_6(\mu\text{-dppm})$ clusters attached to the least sterically hindered C≡C bonds.

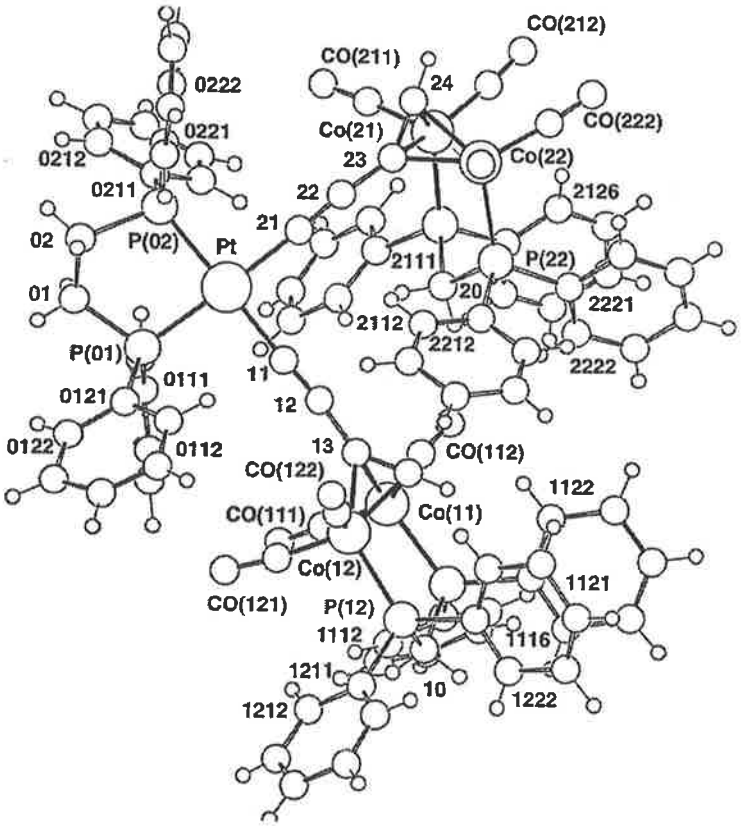
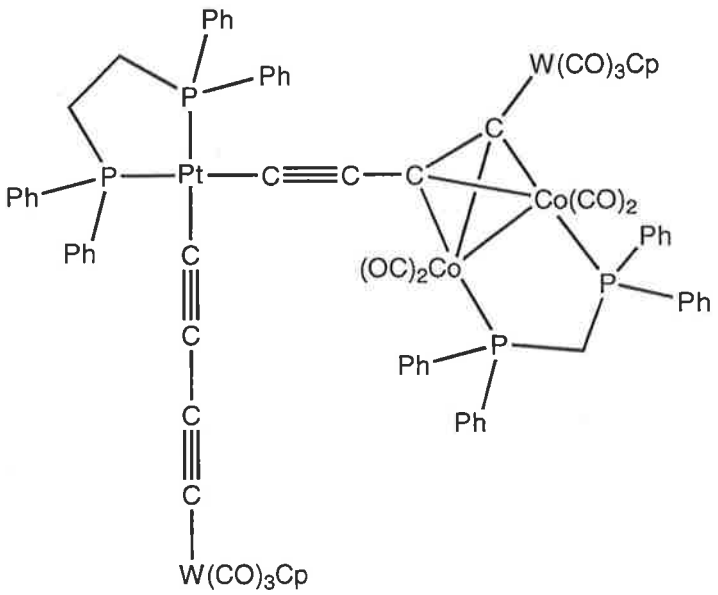


Figure 5 : Molecular projection of $Pt\{C{\equiv}CC_2H[Co_2(\mu\text{-dppm})(CO)_4]\}_2(dppe)$ **7**.

However, when two equivalents of $Co_2(CO)_6(\mu$-dppm) are reacted with **4**, only a single $Co_2(CO)_6(\mu$-dppm) fragment is added to one carbon chain, presumably because of the increased steric bulk afforded by the $W(CO)_3Cp$ moiety. The ^1H and ^{13}C NMR show two Cp resonances (δ_H 5.22 and 5.31; δ_C 91.65 and 94.05) from the non-equivalent $W(CO)_3Cp$ fragments. The ν(CO) spectrum of **8** approximates to a superposition of the usual $W(CO)_3Cp$ and $Co_2(CO)_4(\mu$-dppm) spectra. The ES mass spectrum contained a molecular ion at *m/z* 1967, with peaks appearing at *m/z* 1939, 1911, 1883 and 1855 corresponding to successive loss of up to four carbonyl ligands.

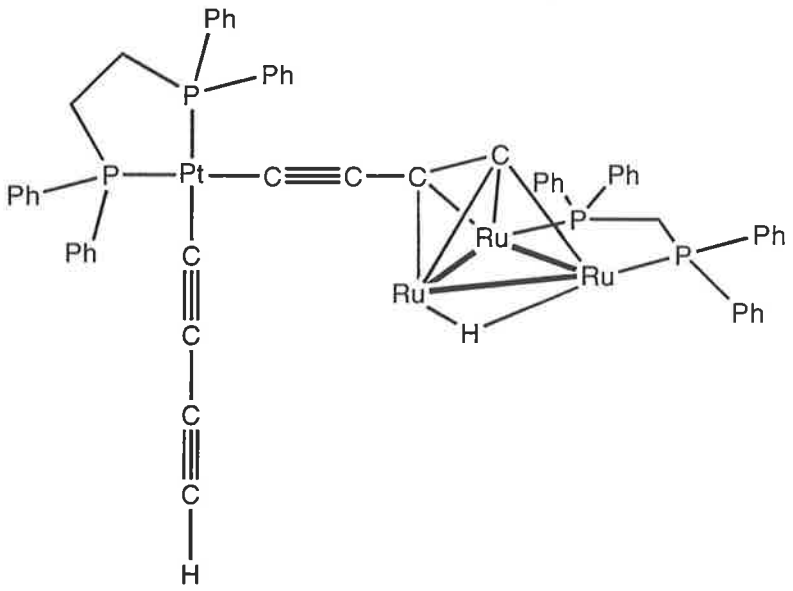


8

Reaction with $Ru_3(\mu$-dppm)$(CO)_{10}$.

In a manner completely analogous to the reactions of simple organic 1-alkynes,[30] facile oxidative additions of **3** with the metal cluster $Ru_3(CO)_{10}(\mu$-dppm) gave complexes containing μ_3-η^1,η^2 bonded alkynyl ligands in high yield. The reaction of two equivalents of $Ru_3(\mu$-dppm)$(CO)_{10}$ with **3** afforded yellow $Ru_3(\mu$-H)$\{\mu_3$-η^1,η^2-$C_2C{\equiv}C[Pt(dppe)(C{\equiv}CC{\equiv}CH)]\}(\mu$-dppm)$(CO)_7$ **9**. Microanalysis, NMR and ES mass spectroscopy determined that only one Ru_3 cluster had added, presumably due to steric considerations. The negative ion ES mass spectrum with added NaOMe

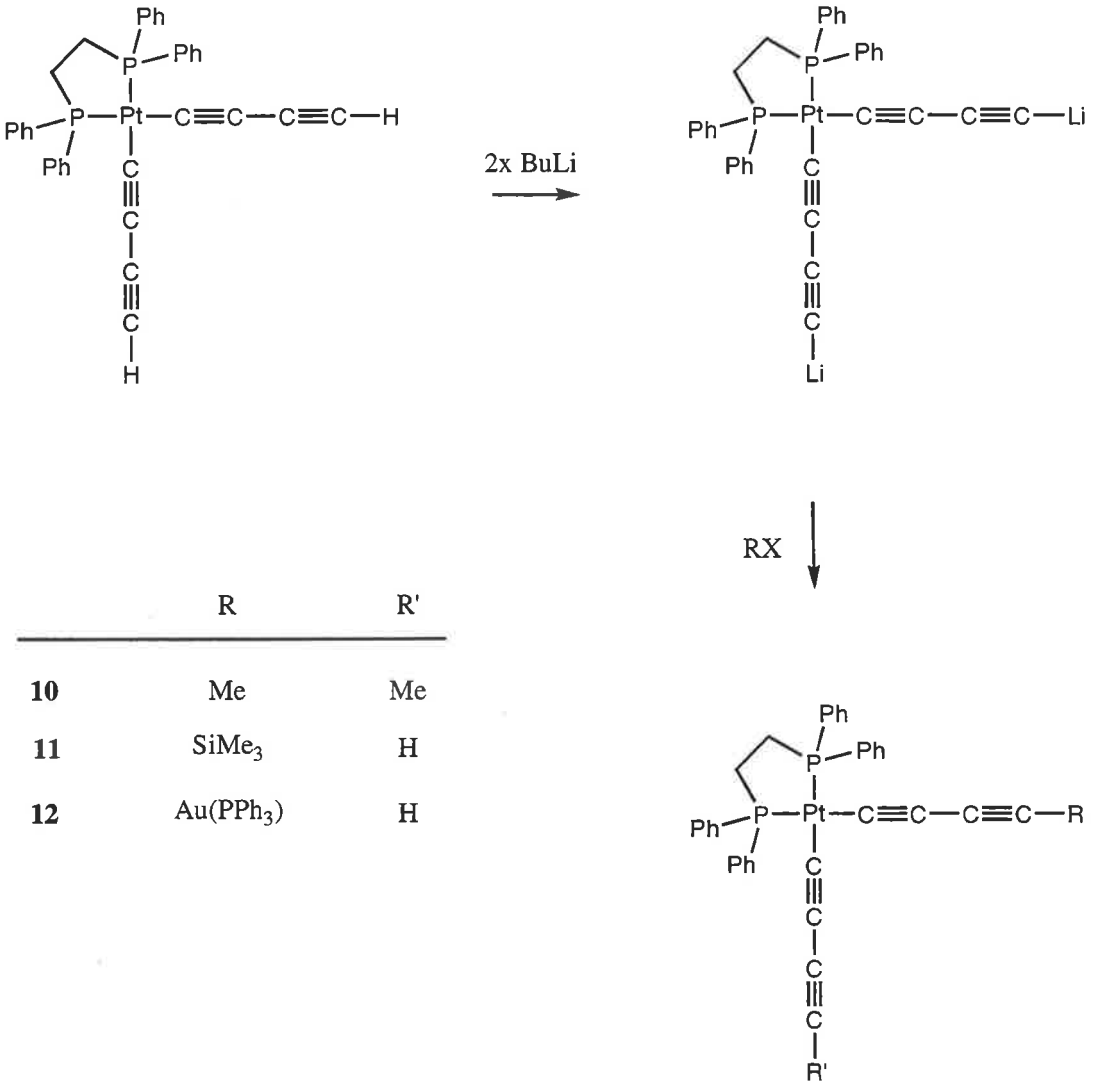
showed a $[M + OMe]^-$ ion at *m/z* 1608, M^- at *m/z* 1577 and further fragmentation due to successive loss of carbonyl ligands. A doublet resonance in the hydride region of the ^1H NMR spectrum was seen at δ –19.39, *J*(PtH) = 34 Hz, and is similar to that of $Ru_3(\mu\text{-}H)\{\mu_3\text{-}\eta^1,\eta^2\text{-}C2C{\equiv}C[W(CO)_3Cp]\}(\mu\text{-}dppm)(CO)_7$.[31]



9

Lithiation reactions.

Reactions with lithio reagents and metal alkynyls have been known to give reactive lithiated intermediates (Scheme 2). These lithiated intermediates have proved to be useful in the preparation of both main-group and transition metal complexes and provide a route into the functionalisation of the terminal carbon atom. Thus when **3** was treated with two equivalents of BuLi at –78°C an orange solution was formed, which was assumed to contain the dilithio compound, $Pt(C{\equiv}CC{\equiv}CLi)_2(dppe)$. Addition of two equivalents of methyl iodide resulted in the formation of the dimethyl derivative **10** in a yield of 93%. The compound was characterised by NMR and ES mass spectroscopy. The ^1H and ^{13}C NMR showed δ_H 1.28 and δ_C 50.76 ppm for the two equivalent methyl groups. The ES mass spectrum in CH_2Cl_2 / MeOH contained two peaks, the parent ion at *m/z* 719 and an $[M + Li]^+$ peak at *m/z* 726.



	R	R'
10	Me	Me
11	$SiMe_3$	H
12	$Au(PPh_3)$	H

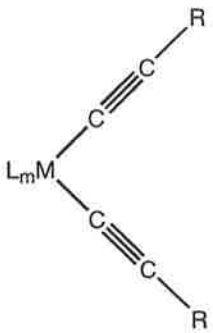
Scheme 2 : Lithation of $Pt(C{\equiv}CC{\equiv}CH)_2(dppe)$.

Under the same conditions as described above, treatment of **3** with BuLi followed by $SiClMe_3$ resulted in the unexpected formation of the monosilylated complex, $Pt(C{\equiv}CC{\equiv}CH)(C{\equiv}CC{\equiv}CSiMe_3)(dppe)$ **11** (68%). The IR spectrum contained two $\nu(C{\equiv}C)$ stretches at 2149 and 2089 cm^{-1}. The ^1H and ^{13}C NMR spectra both contained high field signals at δ_H 0.07 ppm and δ_C 1.30 ppm for $SiMe_3$. In the ES mass spectrum the base peak at *m/z* 715 corresponding to $[M - C_4H]^+$ was seen, followed by successive losses of two Me groups at *m/z* 685 and *m/z* 670.

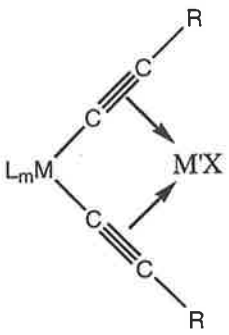
Similarly, $AuCl(PPh_3)$ also reacts with the dilithio intermediate to give the mono-substituted product, $Pt\{C{\equiv}CC{\equiv}C[Au(PPh_3)]\}(C{\equiv}CC{\equiv}CH)(dppe)$ **12**, in a yield of 60% which was identified from IR, ^1H NMR and ES mass spectroscopy. The IR spectrum in nujol contained two $\nu(C{\equiv}C)$ stretches at 2140 and 2084 cm^{-1}. The ^1H NMR in dmso showed a singlet at δ 1.22 ppm corresponding to the acetylenic hydrogen, while the integration of the aromatic region indicated the addition of only one $Au(PPh_3)$ fragment. The ES mass spectrum in MeOH contained a single peak corresponding to the molecular ion at *m/z* 1150. Complex **12** could also be prepared by treating **3** with $AuCl(PPh_3)$ under standard Cadiot-Chodkiewicz conditions. Molecular modelling of $Pt(C{\equiv}CC{\equiv}C[Au(PPh_3)])_2(dppe)$ showed no steric interactions between the two alkynyl chains due to the bulky PPh_3 groups. This indicated no steric influence for the formation of mono-adducts over the bis-adducts. Thus the formation of mono-substituted products in **11** and **12** could only be explained by the presence of base causing the mono-desilylation or loss of $AuPPh_3$ during their preparation.

Tweezer reactions.

In general, bis(σ-alkynyl) organometallic compounds **A** can be used for the synthesis of binuclear complexes **B** containing σ, π-alkynyl ligands as the bridging groups between two metal atoms.



A



B

Compounds of this type have been termed "organometallic π tweezers".[17,32,33] In molecules of type **B**, the $L_nM\{(C{\equiv}C)_nR\}_2$ fragments act as a host molecule with M^IX (M^I = Cu, Ag) fragments as guests. The aim is to simultaneously use the steric stabilisation of organic group R and the chelating effect to prepare stable molecules of type **B**.

The simplest method to prepare these molecules is via the direct addition of $[M^IX]_n$ to compounds of type **A**. Thus when Cu(SCN) or Ag(SCN) are added to **3**, compounds **14** and **15** are formed respectively in excellent yields, with the silver derivative being sensitive to light, decomposing readily under standard laboratory conditions. Evidence for their formation was established by IR, NMR, ES mass spectroscopy and microanalysis. The IR spectra of **14** and **15** showed stretches at 2155 cm^{-1} due to the presence of the thiocyanate group and ν(C≡C) which is lower than that of the parent material [2098 **14** and 2093 cm^{-1} **15**]. This is in agreement with backbonding of the alkyne to the $[M^IX]$ fragment. While ^1H NMR spectrum showed very little change from the parent material, the ^{13}C NMR spectrum showed a downfield shift of C_α and C_β due to complexation. The ES mass spectra of **14** and **15** were similar with M^+ at *m/z* 755 for **14** and *m/z* 798 for **15**. Also present were peaks corresponding to $[2M + Cu]^+$ at *m/z* 1447 for **14** and $[2M + Ag]^+$ at *m/z* 1491 for **15**. Presently no X-ray structural information is available for **14** and **15** but it is assumed that these compounds would adopt the structure of related compounds[17,32,34-37] in which the $[M^IX]$ fragments are essentially trigonal planar comprising η^2-coordination of both alkynyl groups and η^1-bonding of the SCN ligand.

Complexes **16** and **17** were similarly prepared by addition of $[M(NCMe)_4][BF_4]$ (M = Cu, Ag) to **3**, to give complexes of type **B** in high yields. The IR spectra of **16** and **17** are similar with stretches arising from the alkynyl chains ν(C≡CH) and ν(C≡C) at 3255 and 2141 cm^{-1} for **16**; 3281 and 2139 cm^{-1} for **17**, with both spectra having a broad ν(BF) stretch at 1060 cm^{-1}. The ^1H NMR spectrum showed very little change from **3** with the exception of signals arising from MeCN. The ^{13}C NMR spectrum again showed a downfield shift of C_α and C_β due to complexation of a

[M(MeCN)][BF_4] fragment. The ES mass spectra of **16** and **17** showed similar trends with [M^3 + Ag(MeCN)]$^+$ at *m/z* 839 for **16** and [M^3 + Cu(MeCN)]$^+$ at *m/z* 796 for **17**. Also present were peaks corresponding to [$2M^3$ + Ag]$^+$ at *m/z* 1491 for **16** and [$2M^3$ + Cu]$^+$ at *m/z* 1447 for **17**. Further ES mass spectrometry experiments were used to determine whether **16** or **17** were the more stable species. Thus when **17** was treated with one equivalent of [$Ag(NCMe)_4$][BF_4] a peak corresponding to the formation of **16** at *m/z* 799 [M^3 + Ag]$^+$ was observed, conversely when **16** was treated with one equivalent of [$Cu(NCMe)_4$][BF_4] there was no change in the mass spectrum. From this we can conclude that [Ag(NCMe)][BF_4] is more strongly held than [Cu(NCMe)][BF_4]. This result prompted us to look further into the interactions with other metal ions using electrospray mass spectrometry.

Electrospray mass spectroscopy (In collaboration with B. K. Nicholson).

It is now generally accepted that the technique of ES mass spectrometry is a reliable way of determining what ionic species are present in a solution, since the gentle ionisation process transfers ions intact to the gas phase for analysis in the mass spectrometer. As a consequence, several ES mass spectrometry studies have investigated semi-quantitatively the interaction of ions with complexing ligands. The area has been reviewed[38] and more recent examples include the relative binding of Group 1 ions by cholic acid derivatives,[39] the complexation of metal ions by crown ethers and related ligands,[40-43] or by cryptands and valinomycin.[44] The use of metal ions, particularly Ag^+, to form ions from neutral species for analysis by ES mass spectrometry is now well established for substrates with π-electron density and for metal carbonyls.[45-49]

We have examined possible association reactions of **2**, **3** and **5** [M = M^2, M^3 and M^5] with alkali-metal cations (M') in aqueous methanol. The ES mass spectra of all complexes were similar, containing [M + M']$^+$ ions. If the relative intensities relate to the stabilities of the adduct ions, there is no obvious relationship between them, but the sequence of intensities suggests that the controlling factor in their formation is the ease of desolvation of the alkali metal cation.

The availability of complexes containing polyalkyne units arranged in different ways provided interesting substrates for investigating possible interactions with metal ions, making use of the ES mass spectrometry technique to screen varying combinations rapidly and on a small scale. The general area of "cation-π-interactions" is currently of interest because of applications in many systems.[50] Competition experiments between Cu^+ and Ag^+ adducts indicated that the latter were more stable, Ag^+ displacing Cu^+ but not vice versa. However, this interpretation may be clouded by solvation of the Group 11 ions by MeCN.

When a solution of **5** (≡ M^5) in MeOH was treated with Ag^+ ions, an ES mass spectrum of the resulting solution showed clean peaks at *m/z* 813 and 1519, corresponding to $[M^5 + Ag]^+$ and $[2M^5 + Ag]^+$, respectively. Similar results were obtained in EtOH, while in MeCN ions $[M^5 + Ag + MeCN]^+$ dominated at lower cone voltages, with increasing amounts of $[M^5 + Ag]^+$ as the cone voltage was raised.

When the same complex in MeOH was treated with Li^+ ions, there was a strong ion corresponding to $[M^5 + Li + MeOH]^+$ (*m/z* 744) and a weaker signal from $[2M^5 + Li]^+$ (*m/z* 1418) at a cone voltage of 20V. At 40V a peak at $[M^5 + Li]^+$ (*m/z* 712) is dominant while at 80V the ion at *m/z* 744 has vanished. The relative intensity of the *m/z* 1418 signal remains roughly constant as the cone voltage changes.

With the larger cations Na^+, K^+, Rb^+, Cs^+ and Tl^+ (M') the spectra are simpler, giving mainly ions of the type $[M^5 + M']^+$, with no solvated equivalents even at low cone voltages, together with weaker $[2M^5 + M']^+$ species.

To gauge the selectivity towards different ions, a solution of **5** was treated with an equimolar mixture of the mono-charged cations as their chlorides in MeOH solution. The resulting mass spectrum recorded with a cone voltage of 30V is shown in Figure 6, and shows selectivity in the order $Cs^+ > Tl^+ > Rb^+ > K^+ > Na^+ > Li^+$. At first sight, this seems counter-intuitive since it might have been expected that the more polarising cations would form stronger adducts with the alkyne groups on the metal complex. Taken in isolation, the stability of cation-π interactions is normally found to

lie in the order $Li^+ > Na^+ > K^+$, etc,[50] the reverse of the trend found and illustrated in Figure 6. However the observed order in the present study is understandable in terms of competition between the alkyne groups and the solvent molecules for sites about the M^+ ions. Li^+ will be strongly solvated by MeOH so the alkyne group would compete poorly giving weak adducts, whereas for the larger cations such as Cs^+, MeOH molecules would be more readily displaced. Alternatively, it can be rationalised in terms of hard-soft acid-base theory; the alkyne group is a soft base while MeOH is hard, so the adduct with **5** would be most favoured for the softest acid, i.e. the larger cation. Not unexpectedly, none of these Group 1 cations competes effectively with Ag^+ for adduct formation. Note that the observed selectivity is not a size-based one related to a "tweezer" effect, since similar results were found for polyalkyne complexes where no tweezer effect is possible.

In MeCN solutions containing the same mixture of cations, **5** gave a similar spectrum to that in Figure 6 except that the relative intensities of the Tl^+ and Rb^+ adducts were reversed and that of the Li^+ adduct was barely detectable, i.e. $Cs^+ > Rb^+ > Tl^+ > K^+ > Na^+ >> Li^+ \sim 0$, the differences presumably reflecting the strength of solvation of the cations in MeOH and MeCN respectively.

Adducts of **5** with more complex mono-charged cations can be obtained. Thus when a mixture of **5** and PhHg(OAc) in MeOH was introduced to the mass spectrometer, a signal at *m/z* 984 was readily assigned to the $[M^5 + HgPh]^+$ ion. The use of $HgMe^+$ to derivatise neutral nitrogen bases has been previously reported,[51] but we are not aware of other examples involving an HgR^+-π type complexation.

With more highly charged ions, no simple adducts were formed with **5**. Thus for solutions containing with Ba^{2+}, Cd^{2+}, Sn^{2+}, Pb^{2+} or Hg^{2+} (as their nitrates) no species of the type $[M^5 + cation]^+$ or $[M^5 + cation + NO_3]^+$ could be identified. Presumably these more highly charged cations are too strongly solvated to become attached to the alkyne groups of **5**. Only with added Cu^{2+} were identifiable species recorded, but these were $[M^5 + Cu]^+$ and $[2M^5 + Cu]^+$ arising from *in situ* reduction of the Cu(II) to

Cu(I). When **5** was treated with a mixture of Cu^{2+} and 1,10-phenanthroline a very strong, clean signal corresponding to $[M^5 + Cu(phen)]^+$ was found at *m/z* 949.

To determine whether **5**, with four C≡C triple bonds, is acting in a tweezer fashion, analogous experiments were carried out with the complex $C_8\{W(CO)_3Cp\}_2$.[52] This has the same number of alkyne groups, but they are arranged so that they cannot exert a tweezer effect. The results were similar. With Li^+ ions in MeOH, $C_8\{W(CO)_3Cp\}_2$ (M^W) gave signals assigned to $[M^W + Li]^+$, $[M^W + Li + MeOH]^+$ and $[M^W + Li + 2MeOH]^+$ at a cone voltage of 30V, while Na^+ gave the corresponding $[M^W + Na]^+$ together with a weak $[M^W + Na + MeOH]^+$. The other cations Ag^+, K^+, Rb^+, Cs^+ and Tl^+ gave $[M^W + cation]^+$ only, with no solvated equivalents even at low cone voltages. However when $[Cu(MeCN)_4][BF_4]$ was added to a MeOH solution of $C_8\{W(CO)_3Cp\}_2$ the major ion was $[M + Cu + MeCN]^+$. These observations are entirely consistent with competition of the cations between solvent and alkyne groups discussed earlier.

When a solution of $C_8\{W(CO)_3Cp\}_2$ was treated with the equimolar mixture of cations, the relative intensities of the signals were $Cs^+ > Tl^+ > Rb^+ > K^+ > Na^+ > Li^+ \sim 0$, i.e. very similar to the distribution shown in Figure 6 for **5**, except that for $C_8\{W(CO)_3Cp\}_2$, negligible amounts of the Li^+ adduct were formed in competition with the other cations. This also suggests that the selectivity arises through competition with solvation, rather than by a size-dependent tweezer effect.

One difference between the two complexes was the observation that $C_8\{W(CO)_3Cp\}_2$ in MeOH without added cations gave rise to peaks assignable to M^+ and $[M - nCO]^+$ ions (n = 1, 2, 3, 4, depending on cone voltage) arising from oxidation to the radical cation in the mass spectrometer. While this is not unknown for electron-rich species, it is a relatively rare type of ionisation under normal electrospray conditions,[45,53-55] and no similar signals were found for **5**.

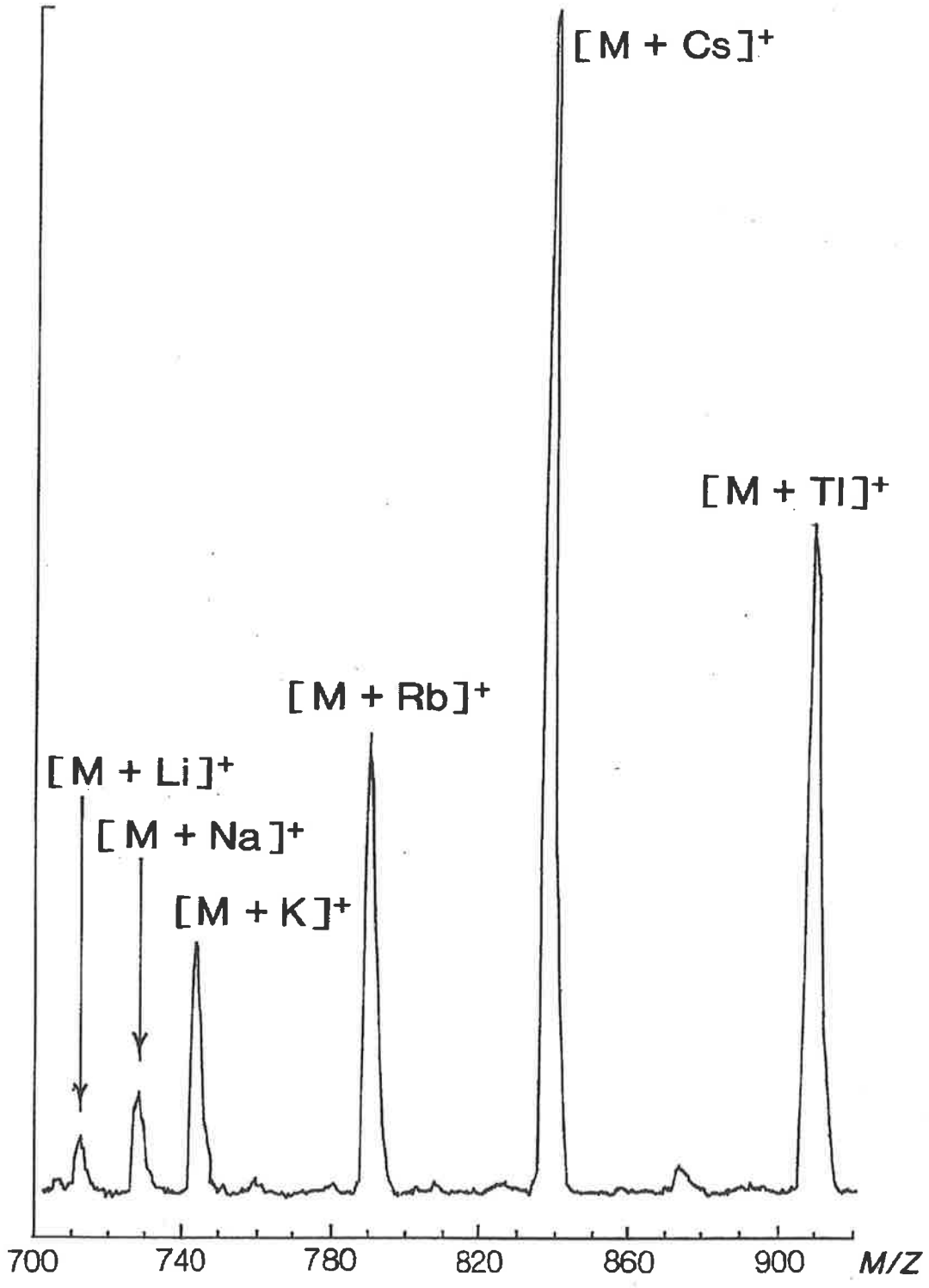


Figure 6 : ES mass spectrum of $Pt(C{\equiv}CC{\equiv}CH)_2(dppp)$ **5** with a mixture of alkali metal cations.

In a separate competition experiment, MeOH solutions containing equal amounts of $C_8\{W(CO)_3Cp\}_2$ and **3** with different cations were examined to assess their relative ease of adduct formation. With Cs^+, the $[M^3 + Cs]^+$ signal was about three times as intense as that from $[M^W + Cs]^+$, while for the other cations (Tl^+, Rb^+, K^+, Na^+ and Li^+) the adducts formed by $C_8\{W(CO)_3Cp\}_2$ were barely detectable in relation to the very strong $[M^3 + M']^+$ ions. This shows that the platinum complex with two orthogonal C_4H groups attaches to the cations more strongly than the tungsten example with a linear C_8 unit. This may be due to a small tweezer effect, but other explanations such as a more delocalised π-cloud for the C_8 compared to the two C_4H groups can also be proposed.

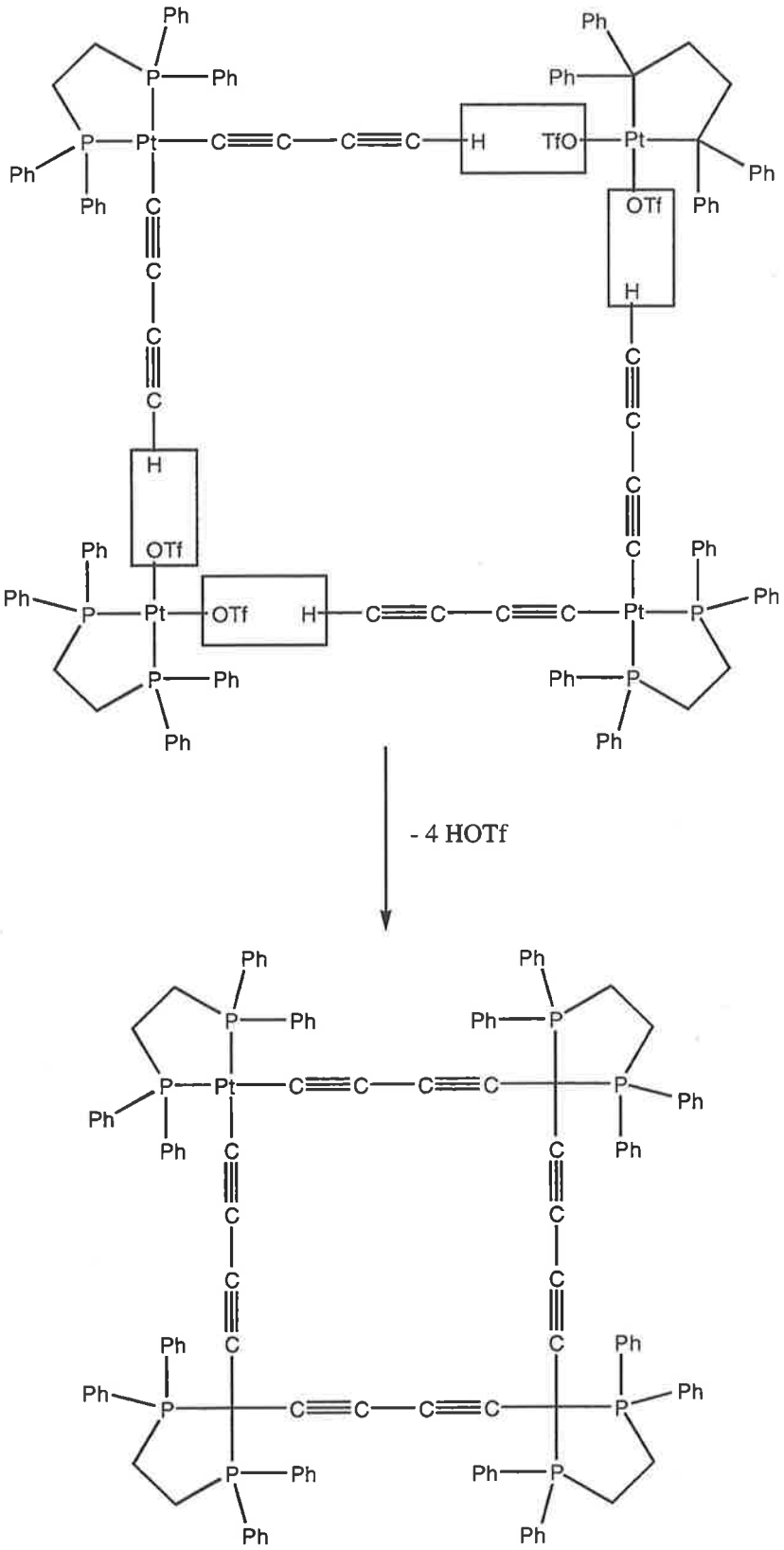
Complex **6** was also examined in MeOH and EtOH, although solubility was very limited. This also provided $[M^6 + M']^+$ signals for M' = Li^+, Na^+, K^+ and Cs^+. More interestingly, with Ag^+ ions the dominant signal at *m/z* 1478 could be assigned to a $[2M^6 + 2Ag]^{2+}$ species, since the interpeak spacing in the isotope pattern was 0.5 mass units. It is not obvious why dimerisation occurred in this sample whilst it was not found for the other complexes examined.

The general pattern that is found for these complexes is that the strongest adducts form for the Group 11 cations Ag^+ and Cu^+, as would be expected for complexes involving π–interactions. With the Group 1 cations, where non-covalent (electrostatic) forces are proposed, the most abundant adducts are with the least strongly solvated cation Cs^+, where the weakly coordinating alkyne groups can most readily displace solvent molecules. This also explains the lack of ions involving association with multiply charged ions where solvation by MeOH would be even stronger. This is in direct contrast to the ES mass spectral work referred to above where complexation of the ions by crown ethers and other *O*- or *N*-donor ligands is involved. Stronger adducts were formed with the more polarising cations and 2^+ cations gave identifiable adducts. The similarity of results for tweezer type substrates and linear ones suggests that there is no size-related tweezer effect with the Group 1 cations.

It is also clear that in choosing cations for derivatising neutral substrates for ES mass spectral studies, the nature of the substrate directs the choice. Where the functional groups are hard, with N or O donor atoms for example, then smaller cations such as Li^+ are preferred and for soft functional groups, especially those with π-electrons, softer cations such as Ag^+ or Cs^+ respond better.

Construction of molecular squares.

The availability of the *cis*-bis(buta-1,3-diyn-1-yl) complexes **1, 3** and **5** to form the two edges and corner of a square suggested their incorporation into square molecules. By coupling two molecules with appropriate platinum complexes, the two other corners may be provided. Addition of **1**, **3**, or **5** to $PtCl_2(L_2)$ under copper catalysed coupling conditions resulted in the formation of polymers, probably due to the rate of reaction. In order to slow the rate of reaction down, the copper catalyst method was abandoned and $PtCl_2(L_2)$ was reacted with AgOTf to give $Pt(OTf)_2(L_2)$ as triflate is a better leaving group. Addition of **1**, **3** or **5** with $Pt(OTf)_2(L_2)$ resulted in the formation of ions corresponding to square compounds, observable by ES mass spectra, however these complexes tended to decompose rapidly due to the formation of triflic acid, a byproduct of the coupling reaction. Addition of a base and the use of high dilution techniques resulted in the quantitative self-assembly of square compounds, $\{Pt(\mu\text{-}C{\equiv}CC{\equiv}C)(L)_2\}_4$ (Scheme 3), with little decomposition or polymer formation. Isolation of the products was achieved by evaporation, to a smaller volume, and addition of hexane. Cream coloured solids were precipitated and identified as $\{Pt(\mu\text{-}C{\equiv}CC{\equiv}C)(PEt_3)_2\}_4$ **18**, $\{Pt(\mu\text{-}C{\equiv}CC{\equiv}C)(dppe)\}_4$ **19** and $\{Pt(\mu\text{-}C{\equiv}CC{\equiv}C)(dppp)\}_4$ **20** when NaOAc was used, or $\{Pt(\mu\text{-}C{\equiv}CC{\equiv}C)(PEt_3)_2\}_4.[NH_2Et_2]$ [OTf] **21**, $\{Pt(\mu\text{-}C{\equiv}CC{\equiv}C)(dppe)\}_4.[NH_2Et_2][OTf]$ **22** and $\{Pt(\mu\text{-}C{\equiv}CC{\equiv}C)$ $(dppp)\}_4.[NH_2Et_2][OTf]$ **23** when $NHEt_2$ was used as the base. This method also allowed for the formation of mixed ligand squares, by using $Pt(C{\equiv}CC{\equiv}CH)(L_2)$ and $Pt(OTf)_2(L'_2)$ combinations where $L \neq L'$. In this way, the compounds $\{Pt(\mu\text{-}C{\equiv}CC{\equiv}C)$ $(PEt_3)_2\}_2\{Pt(\mu\text{-}C{\equiv}CC{\equiv}C)(dppe)\}_2.[NH_2Et_2][OTf]$ **24**, $\{Pt(\mu\text{-}C{\equiv}CC{\equiv}C)(PEt_3)_2\}_2$ $\{Pt(\mu\text{-}C{\equiv}CC{\equiv}C)(dppp)\}_2.[NH_2Et_2][OTf]$ **25** and $\{Pt(\mu\text{-}C{\equiv}CC{\equiv}C)(dppe)\}_2\{Pt(\mu\text{-}C{\equiv}CC{\equiv}C)(dppp)\}_2.[NH_2Et_2][OTf]$ **26** were prepared.



Scheme 3 : Formation of molecular squares.

The IR spectrum of **18** revealed a single weak ν(C≡C) at 2144 cm^{-1}, while the ^{1}H and ^{13}C NMR spectra revealed only peaks arising from the PEt_3 group. The atoms of the carbon chain were not detected probably because of their long relaxation times. The ^{31}P NMR spectrum contained a triplet at δ -0.40 with *J*(PPt) = 2260 Hz consistent with the presence *cis*-PEt_3 ligands. The ES mass spectrum of **18** in the presence of NaOMe revealed a single ion cluster at *m/z* 1940 corresponding to $[M + Na]^+$. The IR spectrum of **19** contained a single medium intensity ν(C≡C) band at 2148 cm^{-1}, while the ^{1}H NMR spectrum contained resonances for the CH_2 and Me protons at δ 2.32 and 1.34, respectively. The two carbons of the C_4 bridge were found at δ 92.23 and 110.39 in the ^{13}C NMR spectrum [in dmso; *J*(CP) or *J*(CPt) was not resolved]. The ^{31}P NMR spectrum contains a triplet at δ 39.63 with *J*(PPt) = 2257 Hz. Similarly, the IR spectrum of **20** contained a single ν(C≡C) band at 2148 cm^{-1}. The ^{1}H and ^{13}C NMR spectra contained signals arising from the dppp ligand with no C≡C peaks being detected, again possibly due to large relaxation times. The ^{31}P NMR spectrum contained a triplet at δ -7.69 *J*(PPt) = 2188 Hz for the dppp ligand. The ES mass spectra of solutions, containing NaOMe contained a single peak at *m/z* 2643 which corresponds to the $[M + Na]^+$ adduct ion.

Molecular structure of {Pt(μ-C≡CC≡C)(dppe)}$_4$ **19.**

Square complexes crystallise with some reluctance. However, from a sample of **19** prepared using NaOAc as base, we obtained single crystals from aqueous dmso which proved to be suitable for X-ray diffraction studies. Plots of a molecule of **19** are shown in Figures 7 and 8, significant structural parameters being collected in Table 1. Comparison with the structure of the precursor complex **3** shows that the Pt-C [1.95-2.03(1) Å], C≡C [1.18-1.22(2) Å], C-C [1.39-1.44(2) Å] and Pt-P distances [2.256-2.285(3) Å] are closely similar; the angles at Pt subtended by the two C_4 edges are between 87.2 and 90.6(5)° in **19**, compared with 93.2(5)° in **3**. Along the edges, angles at the three carbons range between 173 and 179(2)°. The separations of the Pt atoms are 7.726-7.798(1) Å (along the edges) and 10.703, 11.265(1) Å (along the diagonals). For the Pt_4 plane, χ^2 is 18696, δPt(1-4) being 0.084, -0.084, 0.083 and -

0.083(1) Å, and δP(n1,n2) -0.162, 0.805; 0.173, 0.178; 0.360, -0.302 and 0.109, -0.190(4) Å.

We note that the phenyl groups of the dppe ligands lie over the C_4 edges, but are bent away and do not interfere sterically with each other, the angles C(1)-Pt-C(1') and P-Pt-P' in **3** being 93.2(5)° and 86.2(1)° respectively. This contrasts the situation for {Pt(μ-C≡CC≡C)(dppp)}$_4$, in which molecular modelling suggests that significant strain occurs as a result of the proximity of the phenyl rings on adjacent dppp ligands, which are oriented towards each other due to the $(CH_2)_3$ backbone. Further evidence for the steric influence comes from the X-ray structure of **5**, which has angles of 88.9(3)° and 97.02(8)° for C(1)-Pt-C(1') and P-Pt-P' respectively.

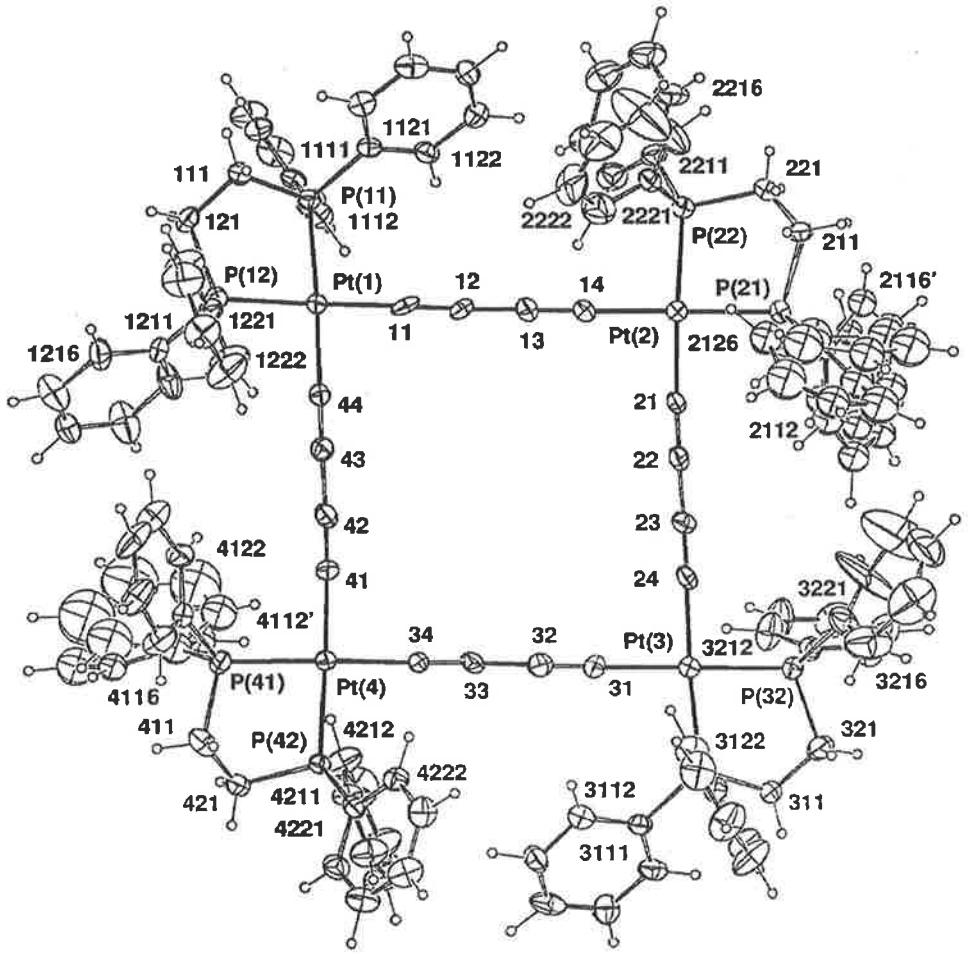


Figure 7 : Molecular projection of {Pt(μ-C≡CC≡C)(dppe)}$_4$ **19**. Perpendicular to the $Pt_4(C_4)_4$ plane.

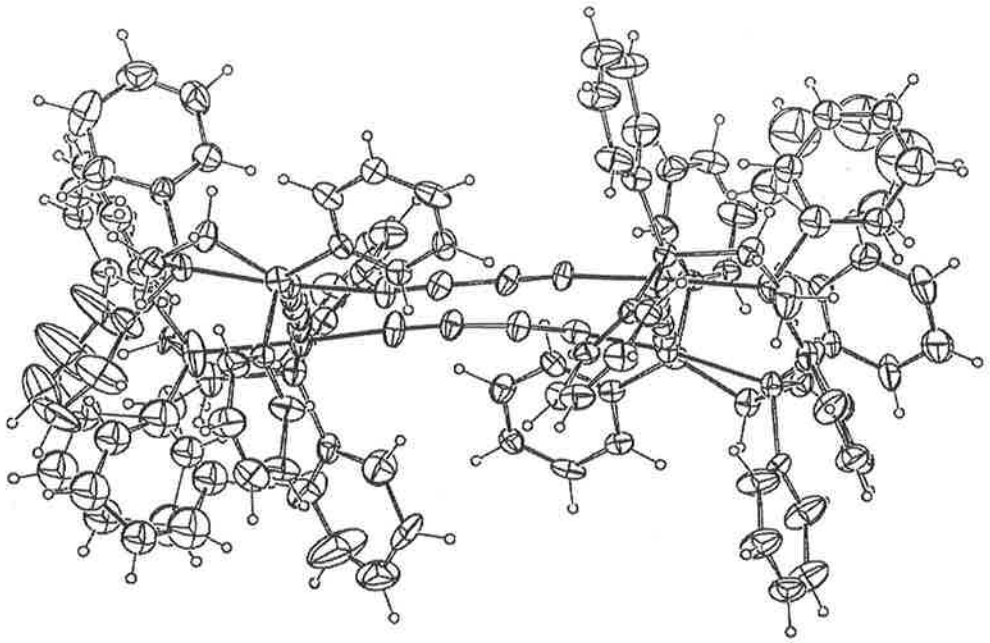


Figure 8 : Molecular projection of $\{Pt(\mu\text{-}C{\equiv}CC{\equiv}C)(dppe)\}_4$ **19**. Side view.

The unit cell contained one H_2O and ca 4.5 Me_2SO molecules; there seems to be no obvious cause of the packing of these molecules relative to the squares which adopt a zig-zag layer conformation along *c*. A subsequent study was carried out on a crystal which proved to contain ten molecules of dmso in the unit cell. No significant differences in the geometrical parameters of the two square molecules were found.

Professor Jean-François Halet and coworkers performed computational modelling of **19**, but due to the size of the molecule relativistic corrections were unable to be used, however the optimisations obtained were still quite accurate. Modelling of the compound revealed that the chains were bent on average 1-2 degrees. The HOMO – LUMO gap was calculated to be 1.882 eV, which indicates that reduction would be difficult. The ionisation potential was calculated to be 4.792 eV, which is comparable to reported molecular wires, such as $\{CpRu(PPh_3)_2\}_2(\mu\text{-}C{\equiv}CC{\equiv}C)$.[56] The HOMO orbitals are a combination of the d-orbitals of platinum and the π-orbitals of the carbon chains, with a similar geometry change to that described for **5**, however this change is quite small as it is delocalised over the whole square skeleton.

The products isolated from reactions of *cis*-$Pt(OTf)_2(L)_2$ using $NHEt_2$ as a base were each found to be associated with one equivalent of $[NH_2Et_2][OTf]$. The formulas $\{Pt(\mu\text{-}C{\equiv}CC{\equiv}C)(L)_2\}_4.[NH_2Et_2][OTf]$ (L = PEt_3 **21**; L_2 = dppe **22**, dppp **23**) were assigned on the basis of their elemental analyses, NMR and ES mass spectra. The IR spectra of **21-23** vary little from those of the analogous compounds **18-20**. However in the NMR spectra, peaks corresponding to the presence of $[NH_2Et_2][OTf]$ were seen, δ_H 0.8 - 1.44 and δ_C 10.93 – 11.18 for $NH_2(CH_2\mathit{CH_3})_2$ and δ_H 2.64 - 3.07 and δ_C 41.41 – 41.94 for $NH_2(\mathit{CH_2}CH_3)_2$. The ES mass spectrum of **22** in dmso contained a single ion at *m/z* 2640 corresponding to $[M - OTf]^+$. MS/MS experiments on this peak showed the formation of the two daughter ions $[M - NH_2Et_2OTf]^+$ (*m/z* 2566) and $[M - NH_2Et_2OTf - dppe]^+$ (*m/z* 2242). The spectrum of **23** in CH_2Cl_2 / MeOH showed a similar spectrum with a single peak at *m/z* 2696 assigned to $[M - OTf]^+$. A brief survey of the inclusion of substituted ammonium triflates were undertaken with the amine used in the preparation of the **21** adduct being varied. The resulting product was analysed by ES mass spectroscopy. In each case, a substituted ammonium triflate adduct was formed. When $NHEt_2$ was used, the base peak corresponded to $[M - OTf]^+$ (*m/z* 1990), followed by successive losses of up to three PEt_3 ligands which could be followed by MS/MS experiments. Similar results were seen with $NHCy_2$ and $NHPr^i_2$ with $[M - OTf]^+$ peaks at *m/z* 2097 and *m/z* 2017 respectively. Even the bulky base, dbu, formed $[M - OTf]^+$ as the major peak at *m/z* 2068. Interestingly, in all cases peaks were present that could only be explained by loss of a $Pt(PEt_3)_2$ group.

With the exception of the peaks due to the inclusion of $[NH_2Et_2][OTf]$, the NMR spectra of squares **21-23** vary little from those of the "pure" squares, with only minor differences in chemical shifts and coupling constants.

The synthetic method is also applicable to the formation of mixed ligand squares, simply by varying $Pt(C{\equiv}CC{\equiv}CH)_2(L_2)$ and $Pt(OTf)_2(L'_2)$ such that $L \neq L'$. When **3** was mixed with $Pt(OTf)_2(PEt_3)_2$ under the conditions described above, $\{Pt(\mu\text{-}C{\equiv}CC{\equiv}C)\ (PEt_3)_2\}_2\{Pt(\mu\text{-}C{\equiv}CC{\equiv}C)(dppe)\}_2.[NH_2Et_2][OTf]$ **24** was formed in good yield. This compound was readily identified by NMR and ES mass spectroscopy.

The ^{1}H NMR showed signals arising from the presence of the two different phosphine ligands, δ 0.12 (Me) and δ 1.01 (CH_2) for the PEt_3 and δ 2.36 and δ 6.33 – 7.07 for dppe. The ^{31}P NMR spectra contained two triplet signals at δ 5.08 J(PPt) = 2338 Hz and 40.76 J(PPt) = 2323 Hz for the PEt_3 and dppe ligands, respectively and the ES mass spectra contained a single peak at *m/z* 2314 corresponding to $[M - OTf]^+$. Similar reaction of **5** with $Pt(OTf)_2(PEt_3)_2$ gave $\{Pt(\mu\text{-}C{\equiv}CC{\equiv}C)(PEt_3)_2\}_2\{Pt(\mu\text{-}C{\equiv}CC{\equiv}C)(dppp)\}_2.[NH_2Et_2][OTf]$ **25**. The ^{31}P NMR spectra contained two signals with triplet coupling arising from the platinum at δ –7.69 [J(PPt) = 2284 Hz] and 6.15 [J(PPt) = 2209 Hz] for the dppp and PEt_3 ligands, respectively. The ES mass spectra contained a single peak for $[M - OTf]^+$ at *m/z* 2344, with no ions corresponding to homo-ligand complexes being present. Lastly, **3** reacts with $Pt(OTf)_2(dppp)$ to give $\{Pt(\mu\text{-}C{\equiv}CC{\equiv}C)(dppe)\}_2\{Pt(\mu\text{-}C{\equiv}CC{\equiv}C)(dppp)\}_2.[NH_2Et_2][OTf]$ **26**. The ^{31}P NMR spectra showed two triplet resonances from dppp and dppe at δ –3.45 [J(PPt) = 3408 Hz] and 43.36 [J(PPt) = 2288 Hz] respectively. The ES mass spectra contained a single peak corresponding to $[M - OTf]^+$ at *m/z* 2665. We have not been able to obtain single crystals of the substituted ammonium triflate adducts, **21-26**, suitable for X-ray studies, so we cannot say how the cation and anion are accommodated by the square molecule. However, the cation is strongly attached to the neutral complex and can be removed by washing with sodium acetate solution, but not by extensive extraction with a variety of polar solvents.

Molecular complexes.

It is also to be expected that these square complexes, in which access to the internal corners is relatively unrestricted, would show significant activity towards association with cations. In this, their behaviour would be similar to the many "tweezer" complexes that have been described, which contain *cis* oriented alkynyl groups. This was proven to be the case with the addition of solutions containing Cu(I) or Ag(I) to **19** resulting in the appearance of ions corresponding to $[M + Cu]^+$ (*m/z* 2629) or $[M + Ag + MeCN]^{2+}$ (*m/z* 1356), respectively. Light brown or cream solids were obtained by addition of $\{Cu(OTf)\}_2C_6H_6$ or AgOTf, respectively, to solutions of **19**, followed by reactions with $Pt(OTf)_2(dppe)$. The same products were also obtained by adding the Group 11 reagents to **19** directly. These compounds gave analytical data

consistent with the formation of 1:1 adducts of **19** and M(OTf) (M = Cu or Ag); in their IR spectra two ν(C≡C) absorptions were present (at 2127 and 2088 cm^{-1} for **27**; 2147 and 2088 cm^{-1} for **28**), while their ^{31}P NMR spectra each contained two resonances in ratio 3:1, with significantly different chemical shifts and *J*(PPt) values, δ 43.24 [*J*(PPt) = 2246 Hz] and 46.40 [*J*(PPt) = 3598 Hz] for **27** and at δ 42.31 [*J*(PPt) = 2336 Hz] and 44.24 [*J*(PPt) = 3652 Hz] for **28**. Their ES mass spectra contained ions corresponding to the formation of 1:1 adducts with peaks at *m/z* 2629 $[M - OTf]^+$ for **27** and 1356 $[M - OTf + CH_3CN]^{2+}$ for **28**. These data suggest incorporation of a single Cu^+ or Ag^+ cation into the square, although we have not yet been able to get structural confirmation of this feature.

Further examples of these complexes were obtained from reactions between **5** and four equivalents of $[M(NCMe)_4][BF_4]$ (M = Cu, Ag) in acetonitrile, both yielding cream coloured solids on workup. The Cu(I) adduct **29** contains two $Cu(NCMe)(BF_4)$ fragments, identified from ^1H, ^{13}C and ^{31}P NMR spectra which showed two triplet signals at δ 40.03 [*J*(PPt) = 2275 Hz] and δ 43.35 [*J*(PPt) = 3604 Hz] in a 1:1 ratio. The difference in both the shift and coupling constant suggested the incorporation of $[Cu(NCMe)_4][BF_4]$ into two of the corners of the square. ES mass spectra of the compound showed a doubly charged peak at *m/z* 1388, corresponding to $[M - 2BF_4]^{2+}$. In contrast **30** contains four $[Ag(NCMe)][BF_4]$ units, as determined by NMR and ES mass spectroscopy. The ^{31}P NMR spectrum showed a triplet peak at δ 42.40 [*J*(PPt) = 2421 Hz] corresponding to the dppe ligand. The ES mass spectrum in CH_3CN showed peaks at *m/z* 3156 corresponding to $[M + 4Ag + 4MeCN]^+$, *m/z* 3115 $[M + 4Ag + 3MeCN]^+$ and a doubly charged peak corresponding to 1535 $[M + 4Ag + 2MeCN]^{2+}$.

Table 1 : Selected bond parameters for **1**, **3**, **5**, **7** and **19**.

Bond lengths (Å)	**1**	**3**	**5**	**7**	**19**
Pt-C(1)	1.976 (4)	2.02 (1)	1.997 (9)	2.02 (3)	2.027 (8)
C(1)-C(2)	1.218 (6)	1.17 (2)	1.21 (1)	1.22 (4)	1.17 (1)
C(2)-C(3)	1.390 (6)	1.36 (2)	1.36 (1)	1.38 (4)	1.40 (1)
C(3)-C(4)	1.174 (7)	1.16 (2)	1.17 (1)	1.32 (4)	1.22 (1)
Pt-P	2.319 (1)	2.269 (3)	2.304 (2)	2.262 (8)	2.287 (3)
Bond Angles (deg.)					
C(1)-Pt-C(1')	86.5 (2)	93.2 (5)	88.9 (3)	90 (1)	86.5 (2)
C(1)-Pt-P	84.1 (1)	90.5 (3)	84.7 (3)	91.4 (8)	84.1 (1)
P-Pt-P'	105.22 (4)	86.2 (1)	97.02 (8)	86.0 (3)	105.22 (4)
Pt-C(1)-C(2)	179.2 (4)	171.7 (9)	175.2 (8)	173 (2)	179.2 (4)
C(1)-C(2)-C(3)	179.8 (5)	176 (1)	173.6 (9)	173 (3)	179.8 (5)
C(2)-C(3)-C(4)	179.7 (5)	175 (1)	178 (1)	144 (3)	179.7 (5)
C(1)-Pt-P	170.7 (1)	173.7 (3)	170.9 (3)	176 (8)	170.7 (1)

Table 2 : *Spartan* molecular calculations on **1**, **3** and **5**.

	1	**3**	**5**
Energy of minimisation (kcal/mol)	-14.413	-1.197	-3.766
Pt-C_1	2.1983	2.1984	2.1983
C_1-C_2	1.2033	1.2034	1.2033
C_2-C_3	1.3790	1.3792	1.3790
C_3-C_4	1.2038	1.2038	1.2037
Pt-P_1	2.5056	2.4942	2.4987
Pt-P_2	2.5066	2.4942	2.4987
C_1-Pt-C_1'	90.1558	89.5761	90.4284
Pt-C_1-C_2	179.5363	179.7133	179.0459
C_1-C_2-C_3	179.7741	179.8502	179.5061
C_2-C_3-C_4	179.9552	179.9666	179.8638
P_1-Pt-P_2	92.2639	85.9078	88.6576

EXPERIMENTAL.

Reagents. Buta-1,3-diyne,[57] *cis*-$PtCl_2(PEt_3)_2$,[58] *cis*-$Pt(OTf)_2(PEt_3)_2$,[3] *cis*-$PtCl_2$(dppe),[59] *cis*-$Pt(OTf)_2$(dppe),[3] *cis*-$PtCl_2$(dppp),[60] *cis*-$Pt(OTf)_2$(dppp),[3] $W(C{\equiv}CC{\equiv}CH)(CO)Cp$,[14] $Co_2(\mu\text{-dppm})(CO)_6$,[61] $Ru_3(\mu\text{-dppm})(CO)_{10}$,[62] $AuCl(PPh_3)$,[63] $[Ag(NCMe)_4][BF_4]$[64] and $[Cu(NCMe)_4][BF_4]$[64] were prepared by the cited literature methods.

cis-Pt(C≡CC≡CH)$_2$(PEt$_3$)$_2$ **1.**

CuI (10 mg, 0.05 mmol) and buta-1,3-diyne (5.1 mmol as a 2.8M solution in thf) were added sequentially to a solution of *cis*-$PtCl_2(PEt_3)_2$ (250 mg, 0.51 mmol) in dmf (12 ml) / $NHEt_2$ (3 ml), and stirred for 30 min. Solvents were removed in vacuo and the residue was stirred with water (30 ml). The crude material obtained was washed with several portions of water, methanol and Et_2O and then extracted with CH_2Cl_2. The extracts were concentrated down to 5 ml and filtered through celite into rapidly stirred hexane. The resulting white precipitate was collected, washed with cold hexane and air dried to give *cis*-$Pt(C{\equiv}CC{\equiv}CH)_2(PEt_3)$ **1** (231 mg, 80%). Crystals suitable for X-ray study were grown from CH_2Cl_2 / hexane by slow diffusion. Anal. Found: C, 43.54; H, 5.73. $C_{20}H_{32}P_2Pt.0.5CH_2Cl_2$ calcd.: C, 43.05; H, 5.81%; M, 529. IR (nujol): ν(C≡CH) 3249s; ν(C≡C) 2147s cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.08 [dt, *J*(HP) = 8 Hz, 18H, Me], 1.81 [t, *J*(HP) = 4.6 Hz, 2H, C≡CH], 1.97 [dq, *J*(HP) = 8 Hz, 12H, CH_2]. ^{13}C NMR: δ 8.23 [t, *J*(CP) = 16 Hz, Me], 16.90 (m, CH_2), 60.89 (s, C_δ), 72.04 (s, C_γ), 80.97 (s, C_β), 94.69 (s, C_α). ^{31}P NMR (dmso): δ 5.44 [s, *J*(PPt) = 2262 Hz, PEt_3]. ES mass spectrum (MeOH + Na^+, *m/z*): 1081, $[2M + Na]^+$; 552, $[M + Na]^+$.

cis-Pt(C≡CC≡CW(CO)$_3$Cp)$_2$(PEt$_3$)$_2$ **2.**

A similar reaction using CuI (ca. 8 mg), *cis*-$PtCl_2(PEt_3)_2$ (100 mg, 0.20 mmol) and $W(C{\equiv}CC{\equiv}CH)(CO)_3Cp$ (152 mg, 0.40 mmol) in thf / $NHEt_2$ (1/1, 10ml) gave $Pt(C{\equiv}CC{\equiv}C[W(CO)_3Cp])_2(PEt_3)_2$ **2** (183 mg, 77%). Recrystallisation ($CHCl_3$ / hexane) gave crystals of the mono $CHCl_3$ solvate suitable for X-ray analysis. Anal.

Found: C, 34.49; H, 3.29. $C_{36}H_{40}P_2O_6W_2Pt.CHCl_3$ calcd.: C, 34.38; H, 3.16; M, 1193. IR (CH_2Cl_2): ν(CO) 2038s, 1951vs cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.04 [dt, *J*(HP) = 8 Hz, 18H, PCH_2Me]. 1.93 [dq, *J*(HP) = 8 Hz. 12H, PCH_2Me], 5.59 (s, 10H, Cp). ^{13}C NMR ($CDCl_3$): δ 8.37 (s. PCH_2Me), 16.89 (m, PCH_2Me), 58.90 (s, C_γ), 91.77 (s, Cp), 93.69 (s, C_β), 116.15 (s. C_α), 211.22 (s, CO), 230.57 (s, CO). ^{31}P NMR (dmso): δ 5.90 [s, *J*(PPt) = 2250 Hz, PEt_3]. ES mass spectrum (MeOH + NaOMe, *m/z*): 1216, $[M + Na]^+$; 1189, $[M + Na - CO]^+$; 1160, $[M + Na - 2CO]^+$; 1132, $[M + Na - 3CO]^+$.

Pt(C≡CC≡CH)$_2$(dppe) **3**.

Similarly, $PtCl_2$(dppe) (1.0 g, 1.5 mmol) in dmf (45 ml) / $NHEt_2$ (15 ml), CuI (30 mg, 0.15 mmol) and buta-1,3-diyne (15 mmol as a 2.8M solution in thf) were stirred for 15 min. A white precipitate was obtained of $Pt(C{\equiv}CC{\equiv}CH)_2$(dppe) **3** (1.0 g, 96%). Crystals suitable for X-ray study were grown from CH_2Cl_2 / hexane by slow diffusion. Anal. Found: C, 59.25; H, 3.76. $C_{34}H_{26}P_2Pt$ calcd.: C, 59.09; H, 3.76 %; M, 691. IR (nujol): ν(C≡CH) 3288w; ν(C≡C) 2147s cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.82 [t, *J*(HP) = 4Hz, 1H, C≡CH], 2.42 (m, 2H, $P(CH_2)_2P$), 7.44 - 7.89 (m, 10H, PPh_2). ^{13}C NMR ($CDCl_3$): δ 27.80 (unresolved dd, CH_2P), 61.74 (s, C_γ), 71.75 (s, C_δ), 77.21 (s. C_β), 93.70 (s, C_α), 128.41 - 133.53 (m, Ph). ^{31}P NMR (dmso): δ 43.26 [s, *J*(PPt) = 2288 Hz]. FAB mass spectrum (*m/z*): 692, $[M + H]^+$; 642, $[M + H - C_4H]^+$; 593, $[M - 2C_4H]^+$. ES mass spectrum (MeCN + Ag^+, *m/z*): 1490, $[2M + Ag]^+$; 939, $[M + Ag + MeCN]^+$; 799, $[M + Ag]^+$.

Pt(C≡CC≡CW(CO)$_3$Cp)$_2$(dppe) **4**.

A solution of $PtCl_2$(dppe) (150 mg. 0.23 mmol) in dmf / $NHEt_2$ (10 ml, 4:3) was treated sequentially with CuI (ca. 5 mg) and $W(C{\equiv}CC{\equiv}CH)(CO)_3Cp$ (175 mg, 0.46 mmol) and the resulting dark yellow solution was stirred at r.t. in the dark for 15 min. Evaporation of solvent and chromatography (Al_2O_3 column) gave a yellow fraction with light petroleum / acetone mixtures. The CH_2Cl_2 extracts of the solid obtained from this fraction were filtered into an excess of MeOH. The resulting precipitate was collected and washed several times with Et_2O and crystallised (benzene / hexane) to give $Pt\{C{\equiv}CC{\equiv}C[W(CO)_3Cp]\}_2$(dppe) **4** (230 mg, 73%) as a pale yellow powder.

Anal. Found: C, 44.44; H, 2.60. $C_{50}H_{34}O_6P_2PtW_2$ calcd.: C, 44.25; H, 2.51; M, 1355. IR (CH_2Cl_2): ν(CO) 2038s, 1952vs cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.31 (m, 4H, CH_2), 5.56 (s, 5H, Cp), 7.38 - 8.03 (m, 20H, Ph). ^{13}C NMR ($CDCl_3$): 91.68 (s, Cp), 128.56 - 133.67 (m, Ph). ES mass spectrum (with formic acid / MeCN, positive ion, *m/z*): 1357, $[M + H]^+$; 1329, $[M + H - CO]^+$; (in MeCN, with $AgNO_3$, positive ion, *m /z*): 1566, $[(M + H + MeCN + AgNO_3)_2]^{2+}$; 1464, $[(M + Ag)_2]^{2+}$.

Pt(C≡CC≡CH)$_2$(dppp) **5**.

A mixture of $PtCl_2$(dppp) (1.0 g, 1.47 mmol) in dmf (45 ml) / $NHEt_2$ (15 ml), CuI (30 mg, 0.15 mmol) and buta-1,3-diyne (15 mmol as a 2.8M solution in thf) and stirred for 30 min. Reduction of the solvent, followed by addition of water gave a white Pt(C≡CC≡CH)$_2$(dppp) **5** (831 mg, 80%). Crystals suitable for the X-ray study were grown from CH_2Cl_2 / hexane by slow diffusion. Anal. Found: C, 59.51; H, 4.08. $C_{34}H_{28}P_2Pt$ calcd.: C, 59.57; H, 4.00 %; M, 705. IR (nujol): ν(C≡CH) 3296vs; ν(C≡C) 2151s cm^{-1}. ^1H NMR (dmso): δ 1.71 [t, *J*(HP) = 23Hz, 2H, C≡CH], 2.70 (m, 6H, $P(CH_2)_3P$), 7.31 - 7.72 (m, 20H, PPh_2). ^{13}C NMR (dmso): δ 64.40 (s, C_δ), 72.02 (s, C_γ), 128.23 - 133.41 (m, Ph). ^{31}P NMR (dmso): δ -6.69 [s, *J*(PPt) = 2204 Hz, dppp]. ES mass spectrum (MeOH + Ag^+, *m/z*): 1519, $[2M + Ag]^+$; 813, $[M + Ag]^+$.

Pt{C≡CC≡C[W(CO)$_3$Cp]}$_2$(dppp) **6**.

To a solution of $PtCl_2$(dppp) (500 mg, 0.74 mmol) in thf (25 ml) and $NHEt_2$ (25 ml), CuI (15 mg) and W(C≡CC≡CH)$(CO)_3$Cp (563 mg, 1.47 mmol) was added and the resulting mixture stirred in the dark for 6 h. The bright yellow product was then filtered and washed with H_2O, MeOH, EtOH, and Et_2O and air-dried. Recystallisation from CH_2Cl_2 / hexane gave Pt{C≡CC≡C[$W(CO)_3$Cp]}$_2$ (dppp).0.5CH_2Cl_2 **6** (785 mg, 78%). Anal. Found: C, 43.30: H, 2.83. $C_{51}H_{36}O_6PtW_2.0.5CH_2Cl_2$ calcd.: C, 42.94; H, 2.63%; M, 1370. IR (CH_2Cl_2): ν(CO) 2039s, 1952vs cm^{-1}. ^1H NMR (dmso): δ 2.65 (m, 6H, CH_2), 5.82 (s, 10H, Cp), 7.42 - 7.70 (m, 20H, Ph). ^{13}C NMR (dmso): δ 92.84 (s, Cp), 128.26 - 133.80 (m, Ph), 214.24 (s, CO), 222.22 (s, CO). ^{31}P NMR (dmso): δ -7.15 [s, *J*(PPt) = 2194 Hz,

dppp]. ES mass spectrum (MeOH + Na^+, *m/z*): 1393, $[M + Na]^+$; 1337, $[M + Na - 2CO]^+$; 1060, $[M + Na - W(CO)_3Cp]^+$; (in MeCN + $AgNO_3$): 1477, $[M + Ag]^+$.

Pt(C≡CC$_2$H[Co$_2$(μ-dppm)(CO)$_4$])$_2$(dppe) 7.

To a solution of **3** (100 mg, 0.145 mmol) in thf (20 ml), $Co_2(\mu\text{-dppm})(CO)_6$ (193 mg, 0.289 mmol) was added and heated under reflux for 30 minutes. TLC showed the formation of a burgundy coloured compound. The solvent was removed and the residue was dissolved in CH_2Cl_2 and chromatographed on silica plates (acetone / hexane, 4:6), a burgundy band at R_f = 0.65 was collected and recrystallised from CH_2Cl_2 / pentane. The compound was identified as $Pt(C{\equiv}CC_2H[Co_2(\mu\text{-dppm})(CO)_4])_2(dppe)$ **7** (140 mg, 50%). Anal. Found: C, 57.30; H, 3.63. $C_{92}H_{70}O_8P_6PtCo_2$ calcd.: C, 57.54; H, 3.67 %; M, 1919. IR (CH_2Cl_2): ν(CO) 2016, 1990, 1960 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.86 (s, 2H, C_2H), 2.45 (m, 4H, dppe CH_2), 3.53 (m, 4H, 2 x dppm CH_2), 6.98 - 7.99 (m, 60H, Ph). ^{13}C NMR ($CDCl_3$): δ 29.05 (m, CH_2), 29.57 (m, CH_2), 127.65 - 138.46 (m, Ph). ^{31}P NMR ($CDCl_3$): δ 20.66 (s, dppm), 34.96 [s, *J*(PtP) = 2259 Hz, dppe]. ES mass spectrum (CH_2Cl_2, *m/z*): 1919, M^-; 1891 – 1695, $[M - nCO]^-$ (*n* = 1 – 8).

Pt(C≡CC≡C[W(CO)$_3$Cp])(C≡CC$_2$W(CO)$_3$Cp[Co$_2$(μ-dppm)(CO)$_4$])(dppe) 8.

Similarly, **4** (100 mg, 0.074 mmol) was dissolved in 20 ml of thf. $Co_2(\mu\text{-dppm})(CO)_6$ (99 mg, 0.148 mmol) was added and the resulting solution heated at reflux point for 1 hour. TLC showed the formation of a yellow-brown coloured compound. The solvent was removed and the residue was dissolved in CH_2Cl_2 and chromatographed on silica plates (acetone / hexane, 5:7). A yellow-brown band at R_f = 0.65 was collected and recrystallised from CH_2Cl_2 / pentane. The compound was identified as $Pt(C{\equiv}CC{\equiv}C[W(CO)_3Cp])(C{\equiv}CC_2W(CO)_3Cp[Co_2(\mu\text{-dppm})(CO)_4])(dppe)$ **8** (60 mg, 41%). IR (CH_2Cl_2): ν(CO) 2036m, 2026s, 1989sh, 1974s, 1945br cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.30 (m, 4H, dppe CH_2), 3.30 (m, 2H, dppm CH_2), 5.22 (s, 5H, Cp), 5.36 (s, 5H, Cp), 6.98 - 7.99 (m, 40H, Ph). ^{13}C NMR ($CDCl_3$): δ 28.22 (m, CH_2), 30.85 (m, CH_2), 91.50 (s, Cp), 94.05 (s, Cp), 127.26 - 139.93 (m, Ph), 211.08 (s, CO),

213.46 (s, CO). ^{31}P NMR ($CDCl_3$): δ 37.91 (s, dppm), 39.27 [s, *J*(PtP) = 2257 Hz, dppe]. ES mass spectrum (MeOH + NaOMe, *m/z*): 1967, M^+; 1939 - 1855 [M – *n*CO]$^-$ (*n* = 1 – 4).

$Ru_3(\mu\text{-}H)\{\mu_3\text{-}\eta^1,\eta^2\text{-}C_2C{\equiv}CPt(dppe)(C{\equiv}CC{\equiv}CH)\}(\mu\text{-}dppm)(CO)_7$ **9.**

To a solution of **3** (69.1 mg, 0.1 mmol) in thf (30 ml), $Ru_3(CO)_{10}$(dppm) (100 mg, 0.1 mmol) was added and heated at reflux point for 10 h. The solvent was removed and the residue extracted with CH_2Cl_2 and plated on silica (acetone / hexane, 4:6.). A yellow band developed at R_f 0.5, which was collected and recrystallised from CH_2Cl_2 / hexane. The compound was identified as $Ru_3(\mu\text{-}H)\{\mu_3\text{-}\eta^1,\eta^2\text{-}C_2C{\equiv}CPt(dppe)(C{\equiv}CC{\equiv}CH)\}(\mu\text{-}dppm)(CO)_7$ **9** (88.3 mg, 56%). Anal. Found: C, 50.02; H, 3.07. $C_{69}H_{48}O_{10}P_4PtRu_3$ calcd.: C, 49.95; H, 2.92 %; M, 1577. IR (CH_2Cl_2): ν(CO) 2060m, 2054s, 1999m, 1943br cm^{-1}. ^{1}H NMR ($CDCl_3$): δ -19.39 [d, *J*(PtH) = 34 Hz, 1H, RuH], 2.36 (m, 4H, dppe), 3.45 (m, 2H, dppm), 4.36 (m, 2H, dppm), 6.65 - 8.05 (m, 40H, Ph). ^{13}C NMR ($CDCl_3$): δ 28.89 (s, CH_2), 29.70 (s, CH_2), 128.48 - 133.88 (m, Ph). ES mass spectrum (CH_2Cl_2): 1608, [M + OMe]$^-$; 1577, M$^-$; 1549 - 1465 [M – *n*CO]$^-$ (*n* = 1 – 4).

$Pt(C{\equiv}CC{\equiv}CMe)_2(dppe)$ **10.**

A solution of **3** (100 mg, 0.145 mmol) in thf (15 ml) was cooled to -30°C in a MeOH / N_2 bath. ^{t}BuLi (260 μl, 0.432 mmol) was then added via syringe and the solution stirred for 10 minutes. The yellow solution darkened to an orange colour. MeI (82 mg, 0.579 mmol) was added and the resulting solution warmed to room temperature. MeOH was added and the solution formed a cream coloured precipitate, which was collected and washed with EtOH, MeOH, Et_2O and hexane and then air-dried. The product was identified as $Pt(C{\equiv}CC{\equiv}CMe)_2$(dppe) **10** (97 mg, 93%). IR (nujol): ν(C≡C) 2148s, 2082m cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.28 (br s, 6H, CH_3), 2.39 (m, 4H, CH_2), 7.40 - 7.83 (m, 20H, Ph). ^{13}C NMR ($CDCl_3$): δ 28.25 (m, dppe-CH_2), 50.76 (s, Me), 61.71 (s, C_δ), 71.81 (s, C_γ), 93.09 (s, C_β), 96.96 (s, C_α), 128.48 – 133.95 (m, dppe-Ph). ES mass spectrum (CH_2Cl_2 / MeOH, *m/z*): 729.9, [M + Li]$^+$; 716, M$^+$.

Pt(C≡CC≡CH)(C≡CC≡CSiMe$_3$)(dppe) **11.**

Similarly, **3** (100 mg, 0.145 mmol) was dissolved in 15 ml of thf and cooled to -30°C in a MeOH / N_2 bath. ^{t}BuLi (260µl, 0.432 mmol) was then added. $SiClMe_3$ (630 µg, 0.579 mmol) was then added and the resulting solution was warmed to room temperature. MeOH was added and the solution formed a cream coloured precipitate, which was collected and washed with EtOH, MeOH, Et_2O and hexane. Crude solid was then extracted with CH_2Cl_2 and added dropwise to cold hexane forming a cream coloured precipitate which was identified as Pt(C≡CC≡CH)(C≡CC≡CSiMe$_3$)(dppe) **11** (75mg, 68%). IR (nujol): ν(C≡C) 2149s, 2089m cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.07 (s, 9H, $SiMe_3$), 1.75 (s, 1H, C_2H), 2.34 (m, 4H, CH_2), 7.41 - 7.79 (m, 20H, Ph). ^{13}C NMR ($CDCl_3$): δ 1.30 (s, $SiMe_3$), 28.83 (m, dppe-CH_2), 79.07 (m, C≡C), 126.8 – 133.63 (m, dppe-Ph). ES mass spectrum (CH_3CN, *m/z*): 715, $[M - C_4H]^+$; 685, $[M - C_4H - 2Me]^+$; 670, $[M - C_4H - 3Me]^+$; 642, $[M - C_4H - TMS]^+$.

Pt(C≡CC≡CH)(C≡CC≡C[Au(PPh$_3$)](dppe) **12.**

a) As above, **3** (100 mg, 0.145 mmol) was dissolved in 15 ml of thf and cooled to -30°C in a MeOH / N_2 bath. ^{t}BuLi (260 µl, 0.432 mmol) was then added. $AuCl(PPh_3)$ (142 mg, 0.290 mmol) was then added and the resulting solution allowed to warm to room temperature. MeOH was added and the solution formed a cream coloured precipitate, which was collected and washed with EtOH, MeOH, Et_2O and hexane and then air-dried. The compound was identified as Pt(C≡CC≡CH)(C≡CC≡C[Au(PPh$_3$)](dppe) **12** (198 mg, 60%). IR (nujol): ν(C≡C) 2140m, 2084m cm^{-1}. ^{1}H NMR (dmso): δ 1.22 (s, 1H, C_4H), 2.32 (m, 4H, CH_2), 7.28 - 7.83 (m, 35H, Ph). ^{13}C NMR (dmso): δ 27.11 (m, CH_2), 128.85 - 133.85 (m, Ph). ES mass spectrum (CH_2Cl_2 / MeOH, *m/z*): 1150, M^+.

b) Alternatively, **3** (100 mg, 0.145 mmol) was dissolved in a solution of $NHEt_2$ / thf (5 ml / 10 ml). Addition of a catalytic amount of CuI (~3 mg, 0.0145 mmol) followed by $AuCl(PPh_3)$ (143 mg, 0.289 mmol) with stirring at room temperature for 1 h resulted in the formation of a cream coloured precipitate. Identified as Pt(C≡CC≡CH)(C≡CC≡C[Au(PPh$_3$)](dppe) (115mg, 69%).

Pt(C≡CC≡CH)$_2$(cod) **13.**

To a solution of $PtCl_2$(cod) (200 mg, 0.54 mmol) in dmf / $NHEt_2$ (5 ml / 3 ml), CuI (9 mg, 0.054 mmol) was added followed by 2.5 ml of buta-1,3-diyne (5.36 mmol, 2.2M solution in thf). The solution was stirred at room temperature for 15 min and the solvent was then removed. Water (10 ml) was then added and Pt(C≡CC≡CH)$_2$(cod) **13** separated as a brown sticky solid, which rapidly decomposes upon attempted isolation (121 mg, 56%). IR (nujol): ν(C≡CH) 3270; ν(C≡C) 2131 cm^{-1}. The complex is also unstable in solution. However addition of dppe (213 mg, 0.536 mmol) in EtOH (15 ml) and stirring at r.t. for 15 min gave Pt(C≡CC≡CH)$_2$(dppe) (368 mg, 99%) after precipitation from cold hexane.

Complexes with Pt(C≡CC≡CH)$_2$(dppe) – "Tweezer complexes"

Pt(C≡CC≡CH)$_2$(dppe).Cu(SCN) **14.**

A solution of **3** (100 mg, 0.145 mmol) and Cu(SCN) (36 mg, 0.29 mmol) in MeCN (20 ml) was stirred at room temperature for 1 h, the yellow solution changing to a cream-orange colour. The solution was filtered and reduced to dryness under vacuo. Extraction of the residue with CH_2Cl_2 followed by dropwise addition to cold hexane, gave an orange precipitate of Pt(C≡CC≡CH)$_2$(dppe).Cu(SCN) **14** (112 mg, 95%). IR (CH_2Cl_2): ν(C≡C) 2098m; ν(CN) 2155s cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.77 (unresolved m, 1H, C≡CH), 2.35 (m, 4H, dppe-CH_2), 7.16 - 7.83 (m, 20H, dppe-Ph). ^{13}C NMR ($CDCl_3$): δ 28.09 (m, dppe-CH_2), 61.72 (s, C≡C), 71.80 (s, C≡C), 93.11 (s, C≡C), 100.00 (s, C≡C), 128.47 - 133.47 (m, dppe-Ph). ^{31}P NMR ($CDCl_3$): δ 37.13 [s, *J*(PPt) = 2297 Hz, dppe]. ES mass spectrum (CH_2Cl_2/MeOH, *m/z*): 691, [M - Cu(NCS)]$^+$; 755, [M + Cu]$^+$; 1446, [2M + Cu]$^+$.

Pt(C≡CC≡CH)$_2$(dppe).Ag(SCN) **15.**

Similarly, **3** (100 mg, 0.145 mmol) and Ag(SCN) (48 mg, 0.29 mmol) were dissolved in MeCN (20 ml) and stirred at r.t. for 1 h, the yellow solution changing to a cream-yellow colour. The filtered solution was evaporated and a CH_2Cl_2 extract of the residue added dropwise to cold hexane to give a cream precipitate of

$Pt(C{\equiv}CC{\equiv}CH)_2(dppe).Ag(SCN)$ **15** (124 mg, 99%). IR (CH_2Cl_2): ν(C≡C) 2093m; ν(CN) 2154s cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.77 [t, 1H, *J*(PH) = 4.2 Hz, C≡CH], 2.32 (m, 4H, dppe-CH_2), 7.41 - 7.83 (m, 20H, dppe-Ph). ^{13}C NMR ($CDCl_3$): δ 27.72 (s, dppe-CH_2), 61.75 (s, C_δ), 71.77 (s, C_γ), 93.60 (s, C_β), 107.92 (s, C_α), 128.45 - 133.53 (m, dppe-Ph). ^{31}P NMR ($CDCl_3$): δ 41.16 [s, *J*(PPt) = 2302.93 Hz, dppe]. ES mass spectrum (dmso, *m/z*): 1490, $[2Pt(C{\equiv}CC{\equiv}CH)_2(dppe) + Ag]^+$; 798, $[Pt(C{\equiv}CC{\equiv}CH)_2(dppe) + Ag]^+$. MS^2 on *m/z* 1490 gave daughter ions at *m/z* 1465 [- $C_4H]^+$, *m/z* 1381 [- $Ag]^+$ and *m/z* 799 [- $Pt(C{\equiv}CC{\equiv}CH)_2(dppe)]^+$.

$[Pt(C{\equiv}CC{\equiv}CH)_2(dppe).Ag(NCMe)][BF_4]$ **16.**

Similarly, **3** (150 mg, 0.217 mmol) and $[Ag(NCMe)_4][BF_4]$ (51 mg, 0.217 mmol) were dissolved in MeCN (20 ml) and stirred at r.t. for 1 h. After evaporation, a CH_2Cl_2 extract (5 ml) was added dropwise to cold rapidly stirred Et_2O (100 ml) to give a cream precipitate of $[Pt(C{\equiv}CC{\equiv}CH)_2(dppe).Ag(NCMe)][BF_4]$ **16** (124 mg, 62%). Anal. Found: C, 46.88; H, 3.28. $C_{36}H_{29}BF_4NP_2AgPt$ calcd.: C, 46.58; H, 3.15%; M, 928. IR (nujol): ν(C≡CH) 3255m; ν(C≡C) 2141m; ν(BF) 1061s cm^{-1}. ^1H NMR (CD_3CN): δ 1.95 (s, 2H, C≡CH), 2.00 (s, 3H, MeCN), 2.41 (m, 4H, dppe-CH_2), 7.36 - 7.65 (m, 20H, dppe-Ph). ^{13}C NMR (CD_3CN): δ 1.18 (s, MeCN), 28.33 (m, dppe-CH_2), 65.96 (s, C_δ), 69.60 (s, C_γ), 79.29 (s, C_β), 102.54 (s, C_α), 129.92 - 134.27 (m, dppe-Ph). ^{31}P NMR (CD_3CN): δ 46.23 [s, *J*(PPt) = 2434 Hz]. ES mass spectrum (MeCN, *m/z*): 1491, $[2M + Ag]^+$; 1441, $[2M + Ag - C_4H]^+$; 839, $[M + Ag + MeCN]^+$; 799, $[M + Ag]^+$.

$[Pt(C{\equiv}CC{\equiv}CH)_2(dppe).Cu(NCMe)][BF_4]$ **17.**

Similarly, **3** (150 mg, 0.217 mmol) and $[Cu(NCMe)_4][BF_4]$ (41 mg, 0.217 mmol) was dissolved in MeCN (20 ml) and isolated as described above, resulting in the formation of cream $[Pt(C{\equiv}CC{\equiv}CH)_2(dppe).Cu(NCMe)][BF_4]$ **17** (154 mg, 80%). Anal. Found: C, 48.88; H, 3.38. $C_{36}H_{29}BF_4NP_2CuPt$ calcd.: C, 48.97; H, 3.31%; M, 883. IR (nujol): ν(C≡CH) 3281m; ν(C≡C) 2139m; ν(BF) 1060s cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.75 (s, 2H, C≡CH), 2.00 (s, 3H, MeCN), 2.53 (m, 4H, dppe-CH_2), 7.46 -

7.72 (m, 20H, dppe-Ph). ^{13}C NMR ($CDCl_3$): δ 1.82 (s, *Me*CN), 29.67 (s, dppe-CH_2), 65.33 (s, C_δ), 67.56 (C_γ), 77.42 (C_β), 99.21 (s, C_α), 116.29 (s, CH_3CN), 129.29 - 133.02 (m, dppe-Ph). ^{31}P NMR (CD_3CN): δ 42.18 [s, *J*(PPt) = 2409 Hz, dppe]. ES mass spectrum (MeCN, *m/z*): 1447, $[2M + Cu]^+$; 1396, $[2M + Ag - C_4H]^+$; 796, $[M + Cu + NCMe]^+$; 755, $[M + Cu]^+$.

Syntheses of molecular squares.

{Pt(μ-C≡CC≡C)(PEt$_3$)$_2$)}$_4$ **18.**

A solution of NaOAc (76 mg, 538 mmol) in MeOH (10ml) was added to **1** (72.5 mg, 0.137 mmol) in CH_2Cl_2 (50 ml). To this solution $Pt(OTf)_2(PEt_3)_2$ (100 mg, 0.137 mmol) in CH_2Cl_2 (10 ml) was added via syringe pump over a period of 2 h during which time the initial pale yellow solution darkened in colour. Removal of solvent, extraction with CH_2Cl_2 (5 ml) and filtration into rapidly stirred cold hexane gave a cream precipitate of $\{Pt(\mu\text{-}C{\equiv}CC{\equiv}C)(PEt_3)_2\}_4$ **18** (183 mg, 70%). Anal. Found: C, 40.43; H, 5.97. $C_{64}H_{120}P_8Pt_4$ calcd.: C, 40.07; H, 6.31 %; M, 1917. IR (nujol): ν(C≡C) 2144 cm^{-1}. ^{1}H NMR (dmso): δ 1.02 (m, 72H, PCH_2CH_3), 1.92 (m, 48H, PCH_2CH_3). ^{13}C NMR (dmso): δ 8.07 (s, PCH_2CH_3), 16.48 [dq, *J*(CP) = 17.13 Hz, PCH_2CH_3]. ^{31}P NMR (dmso): δ -0.40 [s, *J*(PPt) = 2260 Hz, PEt_3]. ES mass spectrum (CH_2Cl_2 / MeOH + NaOMe, *m/z*): 1940, $[M + Na]^+$.

{Pt(μ-C≡CC≡C)(dppe)}$_4$ **19.**

Similarly, **3** (77.5 mg, 0.112 mmol) in CH_2Cl_2 (50 ml) and NaOAc (61 mg, 0.448 mmol) in MeOH (5 ml) followed by addition of $Pt(OTf)_2$(dppe) (100 mg, 0.112 mmol) in CH_2Cl_2 (10 ml) via syringe pump for 2 h. A cream precipitate of $\{Pt(\mu\text{-}C{\equiv}CC{\equiv}C)(dppe)\}_4$ **19** (207 mg, 72%) was obtained. Anal. Found: C, 55.86; H, 3.77. $C_{120}H_{96}P_8Pt_4$ calcd.: C, 56.17; H, 3.77%; M, 2566. IR (nujol): ν(C≡C) 2148m cm^{-1}. ^{1}H NMR (dmso): δ 2.35 (m, 4H, CH_2), 7.08 - 7.73 (m, 20H, Ph). ^{13}C NMR (dmso): δ 24.10 (m, CH_2 dppe), 128.69 – 133.25 (m, Ph dppe). ^{31}P NMR (dmso): δ 43.32 [s, *J*(PPt) = 3605 Hz, dppe]. ES mass spectrum (CH_2Cl_2/MeOH + NaOMe, *m/z*): 1333, $[M + 4Na]^{2+}$.

{Pt(μ-C≡CC≡C)(dppp)}$_4$ **20.**

Similarly, **5** (78 mg, 0.11 mmol) was dissolved in CH_2Cl_2 (50 ml) and a NaOAc solution [60 mg, 0.44 mmol of NaOAc in MeOH (10ml)]. $Pt(OTf)_2$(dppp) (100 mg, 0.11 mmol) in CH_2Cl_2 (10 ml) was added via syringe pump over 2 h. Removal of solvent followed by addition of hexane resulted in the formation of cream {Pt(μ-C≡CC≡C)(dppp)}$_4$ **20** (210 mg, 73%). Anal. Found: C, 56.29; H, 3.89. $C_{124}H_{104}P_8Pt_4$ calcd.: C, 56.78; H, 4.00%; M, 2622. IR (nujol): ν(C≡C) 2148 cm^{-1}. ^{1}H NMR (dmso): δ 2.60 (m, 6H, dppp CH_2), 7.05 – 7.74 (m, 20H, dppp Ph). ^{13}C NMR (dmso): δ 24.78 (m, dppp CH_2), 127.56 – 133.74 (m, dppp Ph). ^{31}P NMR (dmso): δ -7.69 [s, *J*(PPt) = 2188 Hz, dppp]. ES mass spectrum (CH_2Cl_2/MeOH + NaOMe, *m/z*): 2643, $[M + Na]^+$.

[Pt(μ-C≡CC≡C)(PEt$_3$)$_2$]$_4$.[NH$_2$Et$_2$][OTf] **21.**

Compound **1** (50 mg, 0.09 mmol) was dissolved in CH_2Cl_2 (50 ml) and $NHEt_2$ (1 ml). $Pt(OTf)_2(PEt_3)_2$ (68 mg, 0.09 mmol) was dissolved in CH_2Cl_2 (10 ml) and slowly added via syringe pump over 2 h. The initial pale yellow solution darkened to an orange-light brown colour. Partial evaporation and filtration into stirred hexane gave a cream precipitate of {Pt(μ-C≡CC≡C)$(PEt_3)_2$}$_4$.$[NH_2Et_2][OTf]$ **21** (121 mg, 63%). Anal. found: C, 38.27; H, 6.47. $C_{69}H_{132}NO_3P_8SF_3Pt_4$ calcd.: C, 38.71; H, 6.21%; M, 2138. IR (nujol): ν(C≡C) 2136m; ν(OTf) 1254m, 1222m, 1030m cm^{-1}. ^{1}H NMR (dmso): δ 0.64 [dt, *J*(HP) = 7.5 Hz, 72H, $PCH_2\mathit{CH_3}$], 0.83 [dd, *J*(HH) = 6.3 Hz, 48H, $NH_2(CH_2\mathit{CH_3})_2$], 1.56 [t, *J*(HH) = 6.9 Hz, 6H, $P\mathit{CH_2}CH_3$], 2.64 (unresolved m, 4H, $NH_2(\mathit{CH_2}CH_3)_2$). ^{13}C NMR (dmso): δ 8.21 (s, $PCH_2\mathit{CH_3}$), 11.04 (s, $NH_2(CH_2\mathit{CH_3})_2$), 16.65 [dq, *J*(CP) = 17.13 Hz, $P\mathit{CH_2}CH_3$], 41.60 (s, $NH_2(\mathit{CH_2}CH_3)_2$), 93.09 (m, C_β) 94.98 (m, C_α). ^{31}P NMR (dmso): δ -0.43 [s, *J*(PPt) = 2260 Hz, PEt_3]. ES mass spectrum (MeOH, *m/z*): 1990, $[M - OTf]^+$; 1635, $[M – OTf - 3PEt_3]^+$; 1558, $[M – OTf - Pt(PEt_3)_2]^+$. MS^2 on *m/z* 1990 gave one daughter ion at *m/z* 1560 $[- Pt(PEt_3)_2]^+$. MS^3 on *m/z* 1560 gave two daughter ions at *m/z* 1485 $[- NH_2Et_2]^+$ and *m/z* 1368 $[- PEt_3 - NH_2Et_2]^+$. MS^4 on *m/z* 1485 gave one daughter ion at *m/z* 1368 $[- PEt_3]^+$. MS^5 on *m/z* 1368 gave one daughter ion at *m/z* 1251 $[- PEt_3]^+$.

Similar preparations were carried out using $NHCy_2$, $NHPr^i_2$ and dbu as bases. The following products were characterised by ES mass spectroscopy:

(a) $NHCy_2$ (M = $\{Pt(\mu\text{-}C{\equiv}CC{\equiv}C)(PEt_3)_2\}_4.[NH_2Cy_2][OTf]$ = *m/z* 2246).
ES mass spectrum (CH_2Cl_2, *m/z*): 2097, $[M - OTf]^+$; 1666, $[M - OTf - Pt(PEt_3)_2]^+$. MS^2 on *m/z* 2097 gave one daughter ion at *m/z* 1666 $[- Pt(PEt_3)_2]^+$.

(b) $NHPr^i_2$ (M = $\{Pt(\mu\text{-}C{\equiv}CC{\equiv}C)(PEt_3)_2\}_4.[NH_2 Pr^i_2][OTf]$ = *m/z* 2166).
ES mass spectrum (CH_2Cl_2, *m/z*): 2017, $[M - OTf]^+$; 1587, $[M - OTf - Pt(PEt_3)_2]^+$. MS^2 on *m/z* 2017 gave two daughter ions at *m/z* 1585 $[- Pt(PEt_3)_2]^+$ and *m/z* 1485 $[- NH_2Pr^i_2 - Pt(PEt_3)_2]^+$.

(c) dbu (M = $\{Pt(\mu\text{-}C{\equiv}CC{\equiv}C)(PEt_3)_2\}_4.[dbuH][OTf]$ = *m/z* 2068).
ES mass spectrum (CH_2Cl_2, *m/z*): 2068, $[M]^+$; 1639, $[M - Pt(PEt_3)_2]^+$.

$\{Pt(\mu\text{-}C{\equiv}CC{\equiv}C)(dppe)\}_4.[NH_2Et_2][OTf]$ **22.**
Compound **3** (77.5 mg, 0.112 mmol) was dissolved in CH_2Cl_2 (50 ml) and $NHEt_2$ (1 ml). $Pt(OTf)_2(dppe)$ (100 mg, 0.112 mmol) in CH_2Cl_2 (10 ml) was then added via syringe pump for 2 h. A cream precipitate of $\{Pt(\mu\text{-}C{\equiv}CC{\equiv}C)(dppe)\}_4.[NH_2Et_2][OTf]$ **22** (181 mg, 58%) was obtained. Anal. found: C, 53.82; H, 3.75; N, 0.49. $C_{125}H_{108}NO_3P_8SF_3Pt_4$ calcd.: C, 53.82; H, 3.90; N, 0.50 %; M, 2788. IR (nujol): ν(C≡C) 2148m; ν(OTf) 1274m, 1223m, 1032m cm^{-1}. ^1H NMR (dmso): δ 1.34 [t, *J*(HH) = 9.6 Hz, 6H, $NH_2(CH_2\mathit{CH_3})_2$], 2.32 (m, 4H, CH_2), 3.05 [q, *J*(HH) = 6.6 Hz, 4H, $NH_2(\mathit{CH_2}CH_3)_2$], 7.11 - 7.83 (m, 20H, Ph). ^{13}C NMR (dmso): δ 10.93 [s, $NH_2(CH_2\mathit{CH_3})_2$], 27.48 (m, CH_2 dppe), 41.41 [s, $NH_2(\mathit{CH_2}CH_3)_2$], 92.23 (m, C_α), 110.39 (m, C_β), 127.03 - 133.26 (m, Ph). ^{31}P NMR (dmso): δ 39.63 [s, *J*(PPt) = 2257 Hz, dppe]. ES mass spectrum (MeCN, *m/z*): 2673, $[M + CH_3CN - OTf]^+$; 2640, $[M - OTf]^+$; 2604, $[M + CH_3CN - NH_2Et_2 - OTf]^+$; 2566, $[M - NH_2Et_2 - OTf]^+$. ES mass spectrum (dmso, *m/z*): 2640, $[M - OTf]^+$. MS^2 on *m/z* 2640 gave two daughter ions at *m/z* 2566 $[- NH_2Et_2]^+$ and *m/z* 2242 $[-$ dppe$]^+$.

{Pt(μ-C≡CC≡C)(dppp)}$_4$.[NH$_2$Et$_2$][OTf] **23.**

Similarly, **5** (78 mg, 0.110 mmol) and Pt(OTf)$_2$(dppp) (100 mg, 0.110 mmol) gave cream {Pt(μ-C≡CC≡C)(dppp)}$_4$.[NH$_2$Et$_2$][OTf] **23** (195 mg, 68%). Anal. Found: C, 54.92; H, 4.30; N, 0.50. $C_{129}H_{116}NO_3P_8SF_3Pt_4$ calcd.: C, 54.45; H, 4.11; N, 0.49 %; M, 2845. IR (nujol): ν(C≡C) 2148m; ν(OTf) 1274m, 1223m, 1032m cm^{-1}. ^{1}H NMR (dmso): δ 1.44 [t, *J*(HH) = 6.9 Hz, 6H, NH$_2$(CH$_2$*CH$_3$*)$_2$], 2.44 (m, 6H, CH$_2$), 3.07 [q, *J*(HH) = 7.2 Hz, 4H, NH$_2$(*CH$_2$*CH$_3$)$_2$], 6.89 - 7.52 (m, 20H, Ph). ^{13}C NMR (dmso): δ 11.18 [s, NH$_2$(CH$_2$*CH$_3$*)$_2$], 18.72 (m, CH$_2$), 24.51 (m, CH$_2$), 41.94 [s, NH$_2$(*CH$_2$*CH$_3$)$_2$], 109.23 (s, C≡C), 127.70 – 137.66 (m, dppp Ph). ^{31}P NMR (dmso): δ -8.02 [s, *J*(PPt) = 2189 Hz, dppp]. ES mass spectrum (CH$_2$Cl$_2$/MeOH, *m/z*): 2696, [M - OTf]$^+$.

{Pt(μ-C≡CC≡C)(PEt$_3$)$_2$}$_2${Pt(μ-C≡CC≡C) (dppe)}$_2$.[NH$_2$Et$_2$][OTf] **24.**

Similarly, **3** (100 mg, 0.145 mmol) and Pt(OTf)$_2$(PEt$_3$)$_2$ (105 mg, 0.145 mmol) gave a cream precipitate of {Pt(μ-C≡CC≡C)(PEt$_3$)$_2$}$_2${Pt(μ-C≡CC≡C)(dppe)}$_2$.[NH$_2$Et$_2$] [OTf] **24** (203 mg, 56%). Anal. Found: C, 47.43; H, 4.46; N, 0.60. $C_{97}H_{120}NO_3P_8SF_3Pt_4$ calcd.: C, 47.26; H, 4.90; N, 0.57%; M, 2464. IR (nujol): ν(C≡C) 2131m; ν(OTf) 1272m, 1223m, 1032m cm^{-1}. ^{1}H NMR (dmso): δ 0.12 [m, 36H, P(CH$_2$*CH$_3$*)$_3$], 1.01 [m, 24H, P(*CH$_2$*CH$_3$)$_3$], 1.70 [m, 6H, NH$_2$(CH$_2$*CH$_3$*)$_2$], 2.36 (m, 8H, dppe CH$_2$), 6.33 - 7.07 (m, 40H, dppe Ph). ^{13}C NMR (dmso): δ 2.67 [s, P(CH$_2$*CH$_3$*)$_3$], 7.38 [s, P(*CH$_2$*CH$_3$)$_3$], 12.01 [s, NH$_2$(CH$_2$*CH$_3$*)$_2$], 29.86 (m, dppe CH$_2$), 43.32 [s, NH$_2$(*CH$_2$*CH$_3$)$_2$], 124.46 - 132.27 (m, dppe Ph). ^{31}P NMR (dmso): δ 5.08 [s, *J*(PPt) = 2338 Hz, PEt$_3$], 40.756 [s, *J*(PPt) = 2323 Hz, dppe]. ES mass spectrum (MeCN, *m/z*): 2314, [M - OTf]$^+$.

{Pt(μ-C≡CC≡C)(PEt$_3$)$_2$}$_2${Pt(μ-C≡CC≡C)(dppp)}$_2$.[NH$_2$Et$_2$][OTf] **25.**

Similarly, **5** (96.6 mg, 0.137 mmol) and Pt(OTf)$_2$(PEt$_3$)$_2$ (100 mg, 0.137 mmol) gave a cream precipitate of {Pt(μ-C≡CC≡C)(PEt$_3$)$_2$}$_2${Pt(μ-C≡CC≡C)(dppp)}$_2$.[NH$_2$Et$_2$] [OTf] **25** (193 mg, 57%). Anal. found: C, 47.98; H, 4.81; N, 0.56. $C_{99}H_{124}NO_3P_8SF_3Pt_4$ calcd.: C, 47.69; H, 5.01; N, 0.56%; M, 2493. IR (nujol): ν(C≡C) 2149m; ν(OTf) 1290m, 1224m, 1029m cm^{-1}. ^{1}H NMR (dmso): δ 1.08 [m,

36H, $P(CH_2CH_3)_3$], 1.22 [m, 6H, $NH_2(CH_2CH_3)_2$], 1.72 [m, 6H, $NH_2(CH_2CH_3)_2$], 1.96 [m, 24H, $P(CH_2CH_3)_3$], 2.99 (m, 12H, dppp CH_2), 7.12 - 7.71 (m, 40H, dppp Ph). ^{13}C NMR (dmso): δ 8.13 [s, $P(CH_2CH_3)_3$], 11.17 [s, $NH_2(CH_2CH_3)_2$], 16.14 [s, $P(CH_2CH_3)_3$], 24.00 (m, dppp CH_2), 41.62 [s, $NH_2(CH_2CH_3)_2$], 92.38 (m, C≡C), 118.53 (m, C≡C), 127.85 - 133.51 (m, dppp Ph). ^{31}P NMR (dmso): δ -7.69 [s, *J*(PPt) = 2284 Hz, dppp], 6.15 [s, *J*(PPt) = 2209 Hz, PEt_3]. ES mass spectrum (MeCN, *m/z*): 2344, $[M - OTf]^+$.

{Pt(μ-C≡CC≡C)(dppe)}$_2${Pt(μ-C≡CC≡C)(dppp)}$_2$.[NH_2Et_2][OTf] **26.**

Similarly, **3** (76 mg, 0.11 mmol) and $Pt(OTf)_2$(dppp) (100 mg, 0.11 mmol) gave cream {Pt(μ-C≡CC≡C)(dppe)}$_2${Pt(μ-C≡CC≡C)(dppp)}$_2$.[NH_2Et_2][OTf] **26** (169 mg, 60%). Anal. found: C, 53.94; H, 4.05; N, 0.69. $C_{127}H_{112}NO_3P_8SF_3Pt_4$ calcd.: C, 54.14; H, 4.00; N, 0.50%; M, 2814. IR (nujol): ν(C≡C) 2149m, 2086m; ν(OTf) 1286m, 1244m, 1029m cm^{-1}. ^1H NMR (dmso): δ 1.17 [t, 6H, *J*(HH) = 9 Hz, $NH_2(CH_2CH_3)_2$], 2.53 (m, CH_2), 2.91 [m, 4H, $NH_2(CH_2CH_3)_2$], 6.92 - 7.83 (m, 20H, Ph). ^{13}C NMR (dmso): δ 11.30 [s, $NH_2(CH_2CH_3)_2$], 28.56 (m, CH_2 dppp). 29.45 (m, CH_2 dppe), 41.64 [s, $NH_2(CH_2CH_3)_2$], 100.28 (s, C≡C), 128.38 – 134.06 (m, Ph). ^{31}P NMR (dmso): δ 43.36 [s, *J*(PPt) = 2288 Hz, dppe], -3.45 [s, *J*(PPt) = 3408 Hz, dppp]. ES mass spectrum (CH_2Cl_2/MeOH, *m/z*): 2665, $[M - OTf]^+$.

Formation of complexes with Group 11 cations.

{Pt(μ-C≡CC≡C)(dppe)}$_4$.CuOTf.[NH_2Et_2][OTf] **27.**

Compound **3** (77.5 mg, 0.112 mmol) and Cu(OTf) (24 mg, 0.112 mmol) were dissolved in CH_2Cl_2 (50 ml) and $NHEt_2$ (1 ml). To this solution, $Pt(OTf)_2$(dppe) (100 mg, 0.112 mmol) in CH_2Cl_2 (10 ml) was added via syringe pump over a period of 2 h. The initial pale yellow solution darkened to an orange-brown colour. The solvent was reduced to ca. 5ml and filtered into rapidly stirred cold hexane, forming a light brown precipitate of {Pt(μ-C≡CC≡C)(dppe)}$_4$.CuOTf.[NH_2Et_2][OTf] **27** (202 mg, 65%). Anal. found: C, 50.21; H, 3.80; N, 0.60. $C_{126}H_{108}NO_6P_8S_2F_6Pt_4Cu$ calcd.: C, 50.41; H, 3.63; N, 0.46%, M, 2778. IR (nujol): ν(C≡C) 2127m, 2088m; ν(OTf) 1280m,

1261m, 1224m, 1030m cm^{-1}. ^{1}H NMR (dmso): δ 3.05 (q, 4H, CH_2), 7.11 - 7.83 (m, 20H, Ph). ^{13}C NMR (dmso): δ 27.40 (m, CH_2 dppe), 127.06 - 133.32 (m, Ph). ^{31}P NMR (dmso): δ 43.243 [s, *J*(PPt) = 2246 Hz, dppe], 46.40 [s, *J*(PPt) = 3598 Hz, dppe]. ES mass spectrum (MeCN, *m/z*): 2629, $[M - OTf]^+$; 1335, $[M - OTf + MeCN]^{2+}$.

{Pt(μ-C≡CC≡C)(dppe)}$_4$.AgOTf.[NH_2Et_2][OTf] **28.**

Similarly, addition of $Pt(OTf)_2$(dppe) (100 mg, 0.112 mmol in CH_2Cl_2 (10 ml) to **3** (77.5 mg, 0.112 mmol) and AgOTf (29 mg, 0.112 mmol) in CH_2Cl_2 (50 ml) and $NHEt_2$ (1 ml) gave cream {Pt(μ-C≡CC≡C)(dppe)}$_4$.AgOTf.[NH_2Et_2][OTf] **28** (300 mg, 95%). Anal. found: C, 49.56; H, 3.09; N, 0.60. $C_{126}H_{108}NO_6P_8S_2F_6Pt_4Ag$ calcd.: C, 49.68; H, 3.57; N, 0.46%; M, 3046. IR (nujol): ν(C≡C) 2147m, 2088m; ν(OTf) 1271m, 1248m, 1226m, 1031m cm^{-1}. ^{1}H NMR (dmso): δ 3.07 (m, 4H, CH_2), 6.85 - 7.49 (m, 20H, Ph). ^{13}C NMR (dmso): δ 10.96 [s, $NH_2(CH_2\mathit{CH_3})_2$], 28.56 (m, CH_2), 41.34 [s, $NH_2(\mathit{CH_2}CH_3)_2$], 128.42 - 133.32 (m, PPh_2). ^{31}P NMR (dmso): δ 42.21 [s, *J*(PPt) = 2336 Hz, dppe], 44.24 [s, *J*(PPt) = 3652 Hz, dppe]. ES mass spectrum (MeCN, *m/z*): 1356, $[M - OTf + MeCN]^{2+}$; 1335, $[M - OTf]^{2+}$; 678, $[M - OTf + MeCN]^{4+}$.

{Pt(μ-C≡CC≡C)(dppe)}$_4$.[Cu(NCMe)BF_4]$_2$ **29.**

A solution of $[Cu(NCMe)_4][BF_4]$ (24 mg, 0.12 mmol) and **19** (75 mg, 0.03 mmol) in CH_2Cl_2 (20 ml) was stirred at room temperature for 1 h. The solvent was then removed and redissolved in CH_2Cl_2 and the filtered solution was added dropwise to cold rapidly stirred Et_2O (100 ml). A cream precipitate was formed, identified as {Pt(μ-C≡CC≡C)(dppe)}$_4$.[Cu(NCMe)BF_4]$_2$ **29** (32 mg, 37%). Found: C, 51.97; H, 3.71, N, 0.71. $C_{124}H_{102}N_2P_8B_2F_8Pt_4Cu_2$ calcd.: C, 50.50; H, 3.48; N, 0.94%; M, 2949. IR (nujol): ν(C≡C) 2087m; ν(BF) 839s cm^{-1}. ^{1}H NMR (dmso): δ 2.5 (s, 3H, *Me*CN), 2.99 (m, 4H, CH_2), 7.19 – 7.89 (m, 20H, Ph). ^{13}C NMR (dmso): δ 28.64 (m, CH_2), 121.89 (s, Me*C*N), 127.85 – 134.11 (m, dppe Ph). ^{31}P NMR (dmso): δ 40.03 [s, *J*(PPt) = 2275 Hz, dppe], 43.35 [s, *J*(PPt) = 3604 Hz, dppe]. ES mass spectrum (MeCN, *m/z*): 1388, $[M - 2BF_4]^{2+}$.

[Pt(μ-C≡CC≡C)(dppe)]$_4$.[Ag(NCMe)BF$_4$]$_4$ **30.**

Similarly, [Ag(NCMe)$_4$][BF$_4$] (57 mg, 0.16mmol) and **19** (100 mg, 0.04 mmol) in CH_2Cl_2 (20 ml) gave cream [Pt(μ-C≡CC≡C)(dppe)]$_4$.[Ag(NCMe)BF$_4$]$_4$ **30** (95 mg, 67%). The compound darkens upon standing, eventually turning black, and consistent elemental analyses have not been obtained. IR (nujol): ν(C≡C) 2097m; ν(BF) 823s cm^{-1}. ^{1}H NMR (dmso): δ 2.09 (s, 3H, *Me*CN), 2.54 (m, 4H, CH_2), 7.20 – 8.37 (m, 20H, Ph). ^{13}C NMR (dmso): δ 28.36 (m, CH_2), 127.72 - 134.84 (m, PPh_2). ^{31}P NMR (dmso): δ 42.40 [s, *J*(PPt) = 2421 Hz, dppe]. ES mass spectrum (MeCN, *m/z*): 3156, [M + 4Ag + 4MeCN]$^+$; 3115, [M + 4Ag + 3MeCN]$^+$; 1535, [M + 4Ag + 2MeCN]$^{2+}$.

REFERENCES.

(1) Stang, P. J.; Olenyuk, B. *Acc. Chem. Res.* **1997**, *30*, 502.

(2) Fujita, M. *Comprehensive Supramolecular Chemistry*; Elsevier: Oxford, **1996**.

(3) Stang, P. J.; Cao, D. H.; Saito, S.; Arif, A. M. *J. Am. Chem. Soc.* **1995**, *117*, 6273.

(4) Stang, P. J.; Whiteford, J. A. *Organometallics* **1994**, *13*, 2524.

(5) Whiteford, J. A.; Lu, C. V.; Stang, P. J. *J. Am. Chem. Soc.* **1997**, *119*, 2524.

(6) Wong, A.; Kang, P. C. W.; Tagge, C. D.; Leon, D. R. *Organometallics* **1990**, *9*, 1992.

(7) Weng, W.; Bartik, T.; Brady, M.; Bartik, B.; Ramsden, J. A.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1995**, *117*, 11922.

(8) Sonogashira, K.; Kataoka, S.; Takahashi, S.; Hagihara, N. *J. Organomet. Chem.* **1978**, *160*, 319.

(9) Takahashi, S.; Morimoto, H.; Murata, E.; Kataoka, S.; Sonogashira, K.; Hagihara, N. *Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 565.

(10) Sonogashira, K.; Ohga, K.; Takahashi, S.; Hagihara, N. *J. Organomet. Chem.* **1980**, *188*, 237.

(11) Takahashi, S.; Ohyama, Y.; Murata, E.; Sonogashira, K.; Hagihara, N. *Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 339.

(12) Johnson, B. F. G.; Kakkar, A. K.; Khan, M. S.; Lewis, J.; Dray, A. E.; Friend, R. H.; Whttmann, F. *J. Mater. Chem.* **1991**, *1*, 485.

(13) Lewis, J.; Fyfe, M. S.; Wittmann, F.; Friend, R. H.; Dray, A. E. *J. Organomet. Chem.* **1992**, *425*, 165.

(14) Bruce, M. I.; Hall, B. C.; Low, P. J.; Smith, M. E.; Nicholson, B. K.; Skelton, B. W.; White, A. H. *Inorg. Chim. Acta.* **2000**, *300-302*, 633.

(15) Coat, F.; Guillevic, M.-A.; Toupet, L.; Paul, F.; Lapinte, C. *Organometallics* **1997**, *16*, 5988.

(16) Bruce, M. I.; Denisovich, L. I.; Low, P. J.; Peregudova, S. M.; Ustynyuk, N. A. *Mendeleev. Commun.* **1996**, 200.

(17) Lang, H.; Köhler, K.; Blau, S. *Coord. Chem. Rev.* **1995**, *143*, 113.

(18) AlQaisi, S. M.; Galat, K. J.; Chai, M.; Ray III, D. G.; Rinaldi, P. L.; Tessier, C. A.; Youngs, W. J. *J. Am. Chem. Soc.* **1998**, *120*, 12149.

(19) Takahashi, S.; Murata, E.; Sonogashira, K.; Hagihara, N. *Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 661.

(20) Sonogashira, K.; Yatake, T.; Tohda, T.; Takahashi, S.; Hagihara, N. *J. Chem. Soc., Chem. Commun.* **1977**, 291.

(21) Sonogashira, K.; Takahashi, S.; Hagihara, N. *Macromolecules* **1977**, *10*, 879.

(22) Fujikura, Y.; Sonogashira, K.; Hagihara, N. *Chem. Lett.* **1975**, 1067.

(23) Khan, M. S.; Davies, S. J.; Kakkar, A. K.; Schwartz, D.; Lin, B.; Johnson, B. F. G.; Lewis, J. *J. Organomet. Chem.* **1992**, *424*, 87.

(24) Davies, S. J.; Johnson, B. F. G.; Khan, M. S.; Lewis, J. J. *Chem. Soc., Chem. Commun.* **1991**, 187.

(25) Burrows, A. D.; Michael, D.; Mingos, P.; Lawrence, S. E.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **1997**, *8*, 1295.

(26) Farrer, D. H.; Ferguson, G. *J. Cryst. Spectr. Res.* **1982**, *12*, 465.

(27) Robertson, G. B.; Wickramasinghe, W. A. *Acta. Cryst., Section C* **1987**, *43*, 1694.

(28) Bonamico, M.; Dessy, G.; Fares, V.; Russo, M. V.; Scaramuzza, L. *Cryst. Struct. Comm.* **1977**, *6*, 39.

(29) Bartik, T.; Bartik, B.; Brady, M.; Dembinski, R.; Gladysz, J. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 414.

(30) Bruce, M. I.; Skelton, B. W.; White, A. H.; Zaitseva, N. N. *J. Chem. Soc., Dalton Trans.* **1996**, 3151.

(31) Bruce, M. I.; Low, P. J. , unpublished data.

(32) Lang, H.; Herres, M. *Trends in Organometallic Chemistry*; Council of Scientific Research: India, **1995**.

(33) Chen, C. W.; Whitcock, H. W. *J. Am. Chem. Soc.* **1978**, *100*, 4921.

(34) Köhler, K. , University of Heidelberg, **1994**.

(35) Lang, H.; Köhler, K.; Zsolnai, L. *Chem. Ber.* , in press.

(36) Lang, H.; Herres, M.; Zsolnai, L. *Organometallics* **1993**, *12*, 5008.

(37) Lang, H.; Herres, M.; Zsolnai, L.; Imhof, W. *J. Organomet. Chem.* **1991**, *409*, C7.

(38) Vicenti, M. *J. Mass Spectrometry* **1995**, *30*, 925.

(39) Brady, P. A.; Sanders, J. K. M. *New J. Chem.* **1998**, 411.

(40) Colton, R.; Mitchell, S.; Traeger, J. C. *Inorg. Chim. Acta* **1995**, *231*, 87.

(41) Wang, K.; Han, X.; Gross, R. W.; Gokel, G. W. *J. Am. Chem. Soc.* **1995**, *117*, 7680.

(42) Young, D. S.; Hung, H. Y.; Liu, L. K. *J. Mass Spectrom.* **1997**, *32*, 432.

(43) Young, D. S.; Hung, H. Y.; Liu, L. K. *Rapid Commun. Mass Spectrom.* **1997**, *11*, 769.

(44) Ralph, S. F.; Iannitti, P.; Kanitz, R.; Sheil, M. M. *Eur. Mass Spectrom.* **1996**, *2*, 173.

(45) Henderson, W.; Nicholson, B. K.; McCaffrey, L. J. *Polyhedron* **1998**, *17*, 4291 and refs therein.

(46) Canty, A. J.; Colton, R. *Inorg. Chim. Acta* **1994**, *220*, 99.

(47) Henderson, W.; McIndoe, J. S.; Nicholson, B. K.; Dyson, P. J. *J. Chem. Soc., Dalton Trans.* **1998**, 519.

(48) Inokuchi, F.; Miyahara, Y.; Inazu, T.; Shinkai, S. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1364.

(49) Bayer, E.; Gfrorer, P.; Rentel, C. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 992.

(50) Ma, J. C.; Dougherty, D. A. *Chem. Rev.* **1997**, *97*, 1303.

(51) Canty, A. J.; Colton, R. *Inorg. Chim. Acta* **1994**, *215*, 179.

(52) Bruce, M. I.; Ke, M.; Low, P. J.; Skelton, B. W.; White, A. H. *Organometallics* **1998**, *17*, 3539.

(53) Berkel, G. J. V.; McLuckey, S. A.; Glish, G. L. *Anal. Chem.* **1992**, *64*, 1586.

(54) Berkel, G. J. V.; Zhou, F. *Anal. Chem.* **1995**, *67*, 2916.

(55) Liu, T. Y.; Shiu, L. L.; Luh, T. Y.; Her, G. R. *Rapid Commun. Mass Spectrom.* **1995**, *9*, 93.

(56) Bruce, M. I.; Low, P. J.; Costuas, K.; Halet, J.-F.; Best, S. P.; Heath, G. A. *J. Am. Chem. Soc.* **2000**, *122*, 1949.

(57) Brandsma, L. *Preparative Acetylenic Chemistry*; Elsevier: Amsterdam, **1971**.

(58) Appleton, T. G.; Bennett, M. A.; Tomkins, I. B. *J. Chem. Soc., Dalton Trans.* **1976**, 439.

(59) Yasufuku, K.; Noda, H.; Yamazaki, H. *Inorg. Synth.* **1989**, *26*, 369.

(60) Slack, D. A.; Baird, M. C. *Inorg. Chim. Acta.* **1977**, *24*, 277.

(61) Chia, L. S.; Cullen, W. R. *Inorg. Chem.* **1975**, *14*, 482.

(62) Bruce, M. I.; Nicholson, B. K.; Williams, M. L. *Inorg. Synth.* **1989**, *26*, 271.

(63) Bruce, M. I.; Nicholson, B. K.; Shawkataly, O. bin *Inorg. Synth.* **1989**, *26*, 325.

(64) Kubas, G. J. *Inorg. Synth.* **1990**, *28*, 68.

Chapter 5

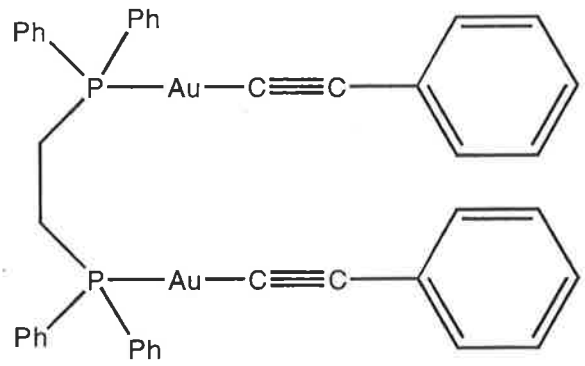
Preparation of Novel Alkynyl-Gold(I) Compounds

INTRODUCTION.

Alkynyls of copper(I), silver(I) and gold(I) have been shown to have remarkable photophysical and photochemical properties.[1] The highly flexible bonding modes of the alkynyls and the various coordination geometries of the metal centres have resulted in complexes with very different molecular structures. The chemistry of these metal alkynyls has attracted enormous attention, in particular, the emerging interest in their potential application to the field of materials science. The linear geometry of the alkynyl unit are attractive precursors for oligermeric and polymeric materials which may possess properties such as non-linear optics, electrical conductivity, liquid crystallinity and luminescence.

The coordination geometry of gold(I) complexes are either two-coordinate (linear) or three-coordinate (trigonal planar), and the structures of gold(I) alkynyls are typically different from that of silver(I) and copper(I) alkynyls. In addition, many compounds containing gold show short Au...Au contacts due to relativistic effects which give rise to a variety of structural motifs.[2,3] Recently, oligomeric and polymeric gold(I) alkynyl complexes have received increasing attention from researchers as they show luminescent properties.[4-22]

The first reported gold(I) alkynyl to show luminescence was described in 1993, in which the emissive behaviour of $Au_2(\mu\text{-dppe})(C{\equiv}CPh)_2$ (**A**) was recorded.[12]



(A)

This compound did not contain any intramolecular Au...Au interactions, but two $Au_2(\mu\text{-dppe})(C{\equiv}CPh)_2$ units interact with each other having a intermolecular separation of 3.153(2) Å. The use of dppm allowed for the formation of intramolecular Au...Au contacts in the related complexes, $(AuX)_2(\mu\text{-dppm})$ [dppm = $Ph_2PCH_2PPh_2$, X = Cl, $C{\equiv}CBu^t$], forcing the X groups to align in the same direction.[23,24] Puddephatt and coworkers were able to use this feature in the formation of 26- and 34-membered macrocyclic gold rings.[25]

Continuing our research into the formation of complexes with interesting molecular geometries we looked into the possibility of using gold systems as possible precursor materials. Gold compounds often display a property known as aurophilicity, which could be used to predetermine coordination positions, thus enabling complexes with specific geometries to be formed.

We sought to prepare macrocyclic gold complexes utilising the butadiynyl ligand as the sides of a molecular rectangle, as well as using linear gold(I) complexes to extend the length of molecular wires and to produce larger square molecules.

RESULTS AND DISCUSSION.

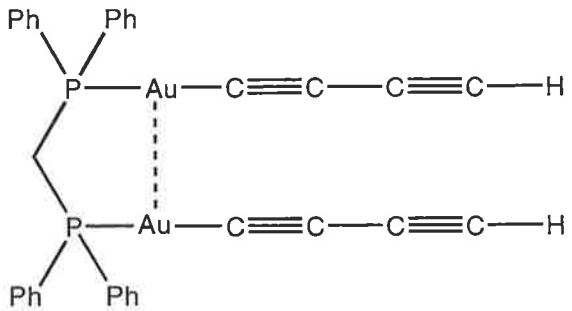
The most common synthetic route to alkynylgold complexes is from the reactions of oligomeric or polymeric compounds, $(AuC{\equiv}CR)_n$, with other ligands such as phosphines. The alkynyl ligand bridges by bonding to one gold atom though a σ-bond and to a second gold atom via the π-electrons of the triple bond.[26] Alkynylgold compounds are known to be potentially explosive, such as Au_2C_2, thus the preparation of goldethynyl compounds containing C_4 ligands was approached with caution. Reactive gold fragments are considerably stabilised by complexation with phosphine ligands, so that existing acetylenic coupling methods could be employed to form complexes of the type (L)Au(C≡CC≡CH) (L = phosphines) with exchange of alkynyl fragments to appropriate gold halides.

Copper-catalysed coupling of $AuCl(PPh_3)$ and buta-1,3-diyne under Cadiot-Chodkiewicz conditions, resulted in the formation of $Au(C{\equiv}CC{\equiv}CH)(PPh_3)$ **1** in a yield of 75%. The compound was identified from IR, ^1H, ^{13}C NMR, ES mass spectroscopy, elemental analysis and ultimately X-ray crystallography. The IR spectrum in nujol contained two characteristic peaks, ν(≡CH) at 3283 and ν(C≡C) at 2148 and 2081 cm^{-1}. The ^1H NMR spectrum contained a peak corresponding to acetylenic hydrogen at δ 1.76 ppm, while the ^{13}C NMR spectrum contained peaks at δ 60.39, 69.43, 128.79 and 129.55 ppm for C_δ, C_γ, C_β and C_α, respectively assigned based on comparison with other buta-1,3-diynyl compounds described previously. The ES mass spectra in MeOH showed a molecular ion at *m/z* 508, with an ion at *m/z* 459 corresponding to $[Au(PPh_3)]^+$.

1

Using a modification of the procedure to make $AuCl(PPh_3)$, two equivalents of $AuCl(SMe_2)$ were added to dppm resulting in the formation of $Au_2Cl_2(\mu\text{-dppm})$ as a white precipitate in 97% yield. The chelating ligand dppm was chosen because it allows for the formation of intramolecular Au...Au bonding. This forces the two chlorine atoms to align parallel to each other forming a U-shaped compound in which the Au...Au separation is approximately 3.5 Å.[23]

Utilising similar conditions described for the preparation of **1**, addition of $Au_2Cl_2(\mu\text{-dppm})$ to buta-1,3-diyne resulted in the formation of $Au_2(\mu\text{-dppm})(C{\equiv}CC{\equiv}CH)_2$ **2** as a cream precipitate in a yield of 74%. The IR spectrum in nujol showed a band at 3131 cm^{-1} corresponding to $\nu(\equiv CH)$ and two bands at 2140 and 2080 cm^{-1} for $\nu(C{\equiv}C)$. The ^1H NMR spectrum contained peaks arising from the dppm ligand with a 2H multiplet of the phosphine backbone at δ 3.57 ppm and phenyl hydrogens at δ 7.06 – 7.76 ppm and a singlet at δ 2.52 ppm corresponding to the terminal alkynyl hydrogen of the butadiynyl chains. The ^{13}C NMR spectrum contained peaks corresponding to dppm with a methylene peak at δ 25.57 ppm and signals for the carbon chain appearing at δ 65.36, 71.37, 84.07 and 89.72 ppm, for C_δ, C_γ, C_β and C_α, respectively. The ES mass spectrum in a mixture of dmso and MeOH gave two ions, the molecular ion, M^+, at *m/z* 874 and an ion at *m/z* 826 corresponding to $[Au_2(\mu\text{-dppm})(C_4H)]^+$.



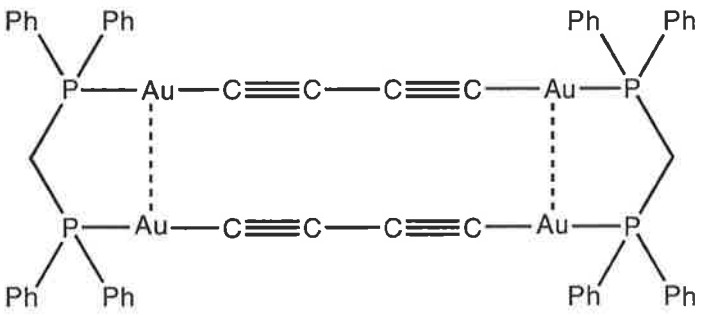
2

At this time we have been unable to obtain suitable crystals for X-ray analysis, however the complex can be compared with a related compound, $Au_2(\mu\text{-dppm})(C{\equiv}CBu^t)_2$.[24] The later molecule is U-shaped, with an intramolecular Au...Au contact of 3.331 (1) Å. The Au(I) centre is approximately linearly coordinated by the phosphorus atom and the acetylide group, while the arms are slightly distorted from the ideal values of 180° due to steric repulsion between the $C{\equiv}CBu^t$ groups.

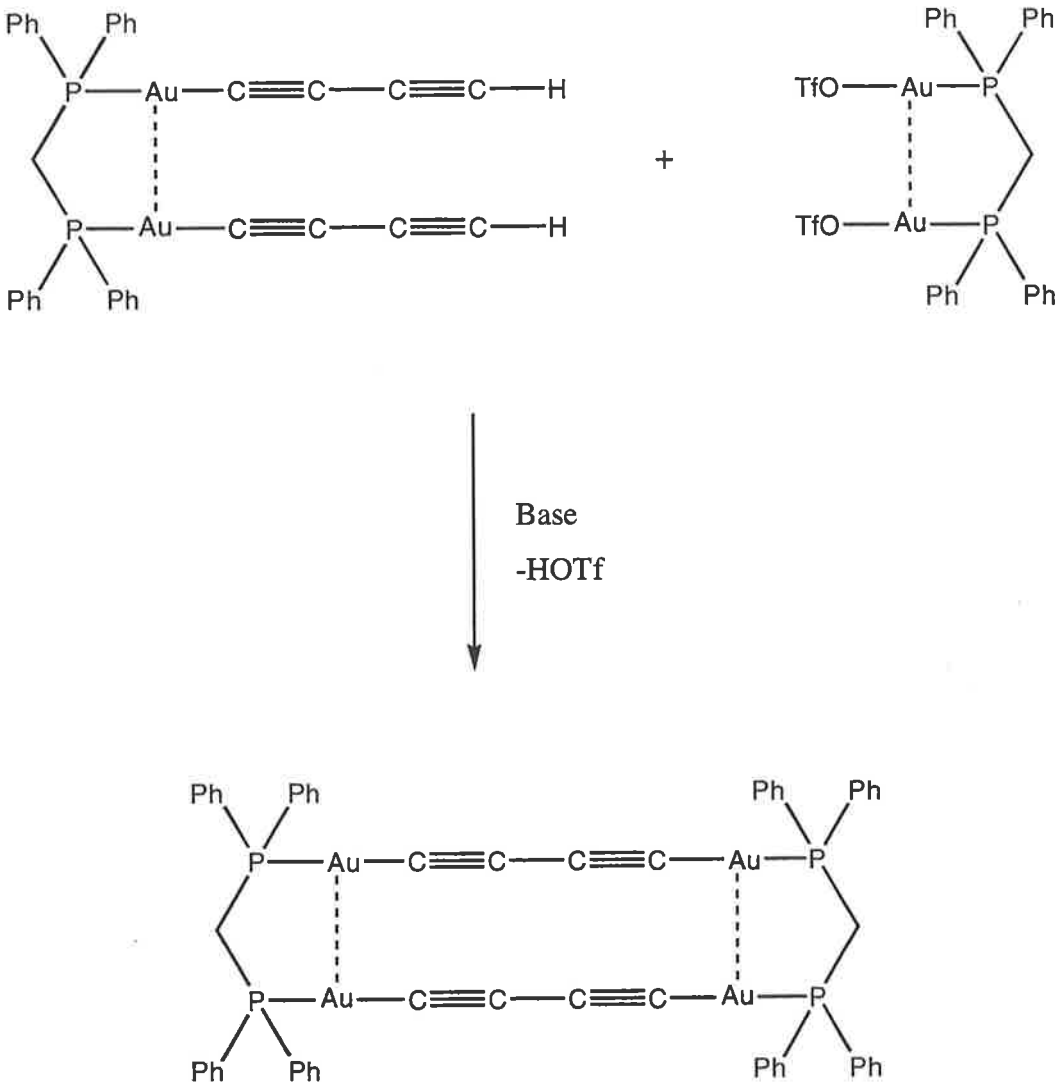
Similarly, yellow $Au_2(\mu\text{-dppm})\{C{\equiv}CC{\equiv}C[W(CO)_3Cp]\}_2$ **3** was obtained by addition of two equivalents of $W(C{\equiv}CC{\equiv}CH)(CO)_3Cp$ to **1**, and isolated in a yield of 77%. The IR spectrum in nujol gave a band at 2039 cm^{-1} for $\nu(C{\equiv}C)$ and the $\nu(CO)$ bands of the $W(CO)_3Cp$ group were found at 2039 and 1954 cm^{-1}. The ^1H NMR spectrum contained signals corresponding to the phosphine and the $W(CO)_3Cp$ moieties, with a singlet Cp resonance at δ 5.60 ppm integrating to 10H. The carbons of the butadiynyl chain were not detected in the ^{13}C NMR spectrum, probably due to long relaxation times. The Cp and dppm methylene carbons were seen at δ 91.91 and δ 44.05 ppm respectively. The ES mass spectrum with added NaOMe, gave an ion at *m/z* 1567 corresponding to $[M + Na]^+$, with additional ions detected at *m/z* 1163 and 778 due to the successive loss of the $C{\equiv}CC{\equiv}CW(CO)_3Cp$ fragments. The increased steric bulk of the $W(CO)_3Cp$ moieties may lead to the breaking of the intramolecular Au...Au contact, leading to the opening of the Au-phosphine backbone; presently we have been unable to grow crystals suitable for X-ray analysis to confirm the exact conformation of **3**.

Formation of molecular rectangles based on the $Au_2(\mu\text{-dppm})$ subunit has been reported previously by Puddephatt and coworkers,[25] who used isocyanide and aryl diacetylide ligands as the carbon linkers. Similarly, we sought to prepare rectangular complexes that contained the butadiyndiyl ligand as the carbon linker. In order to facilitate the ease of rectangle formation, $Au_2Cl_2(\mu\text{-dppm})$ was treated with two equivalents of AgOTf to yield $Au_2(OTf)_2(\mu\text{-dppm})$ in quantitative yield. The $Au_2(OTf)_2(\mu\text{-dppm})$ was then dissolved in CH_2Cl_2 and slowly added via syringe pump to a solution of **2**, under the high dilution conditions described in the previous chapter (Scheme 1). Removal of the solvent and addition of hexane resulted in the

precipitation of cream $\{Au_2(\mu\text{-dppm})\}_2(\mu\text{-C}{\equiv}\text{CC}{\equiv}\text{C})_2$ **4** in a yield of 87%. The IR spectrum in nujol showed a single $\nu(C{\equiv}C)$ band at 2141 cm^{-1}. The ^1H NMR spectrum showed signals at δ 2.42 and 7.28 – 8.05 ppm and in the ^{13}C NMR spectrum at δ 24.26 and 128.74 – 133.36 ppm for the methylene and phenyl groups of the dppm ligand respectively. An unresolved multiplet was seen at δ 89.32 ppm assigned to the alkynyl carbons of the buta-1,3-diynyl chain. The ^{31}P NMR spectrum contained a single peak at δ 34.50 ppm arising from the equivalent dppm phosphorus nuclei. The ES mass spectrum with added NaOMe in benzene contained three ions at *m/z* 1725, 1675 and 1653 corresponding to $[M + NH_2Et_2]^+$, $[M + Na]^+$ and M^+ respectively. The $[M + NH_2Et_2]^+$ peak forming form the interaction with $[NH_2Et_2][OTf]$ formed in the initial reaction. The high selectivity for ring formation relies on the U-shaped conformations of **2** and $Au_2(OTf)_2(\mu\text{-dppm})$ being maintained in solution, a process favoured by the short intramolecular Au…Au contacts.



4



Scheme 1 : Formation of $\{Au_2(\mu\text{-dppm})\}_2(\mu\text{-C}\equiv\text{CC}\equiv\text{C})_2$ **4**

On one occasion, crystallisation of a solution of **2** resulted in the formation of a single crystal suitable for X-ray analysis (Figure 2). The X-ray structure revealed the formation of an unexpected *trianglo*-copper complex, $Cu_3(\mu_3\text{-}I)(\mu\text{-}dppm)_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CC{\equiv}CAuC{\equiv}CC{\equiv}CH)$ **7**. The *trianglo*-copper core is presumably formed by re-arrangement of **2** with CuI, which was used to catalyse the initial coupling. As a result of the transfer of dppm to CuI, an $Au(C{\equiv}CC{\equiv}CH)_2^-$ fragment may be formed *in situ*, which then further reacts with the copper cluster to form the resulting product. Compounds containing the *trianglo*-copper cluster have been described previously by Gimeno[27,28] and Yam[29-40] and are reported to show considerable luminescent properties.

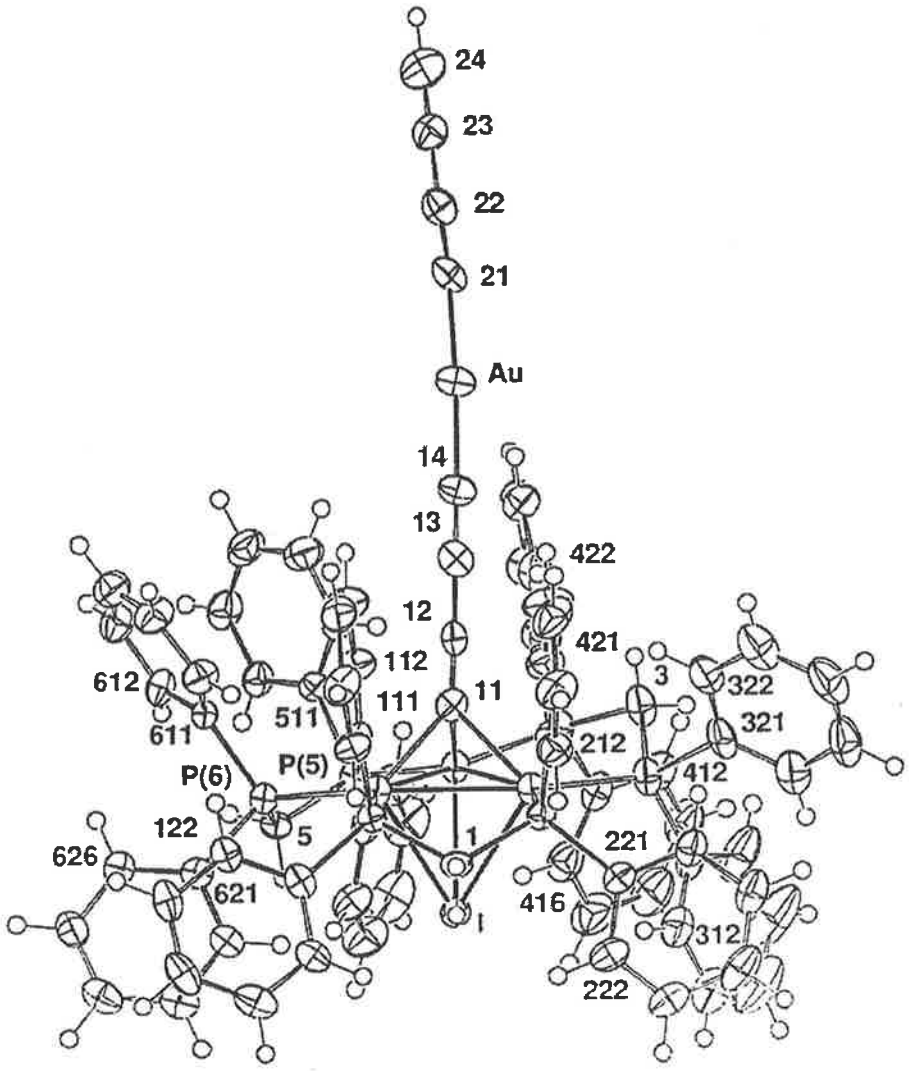


Figure 2 : $Cu_3(\mu_3\text{-}I)(\mu\text{-}dppm)_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CC{\equiv}CAuC{\equiv}CC{\equiv}CH)$ **7**.

The Cu_3 core is an equilateral triangle with internal angles for Cu_1-Cu_2-Cu_3 of 61.67(2)°, Cu_1-Cu_3-Cu_2 59.86(2)° and Cu_2-Cu_1-Cu_3 58.47(2)° [sum 180°]. The C_4AuC_4H chain is slightly bent from the ideal 180° with the largest departure being 176.1(5)° for C_{11}-C_{12}-C_{13} with an angle at C_{14}-Au-C_{21} of 178.3(2)°. The three Cu-I distances average 2.83 Å, with Cu_1-I being 2.9055(8), Cu_2-I at 2.7804(7) and Cu_3-I at 2.8002(7) Å. The C-C separations alternate between C≡C and C-C character with C_{11}-C_{12} 1.196(8), C_{12}-C_{13} 1.380(8), C_{13}-C_{14} 1.238(9), C_{14}-Au 1.864(6), Au-C_{21} 1.972(6) C_{21}-C_{22} 1.224(8), C_{22}-C_{23} 1.345(8) and C_{23}-C_{24} 1.210(9) Å. The C_{11}-C_{12} distance is considerable shorter than those of the other alkynyl carbons, this is due to the μ_3-η^1 bonding mode.

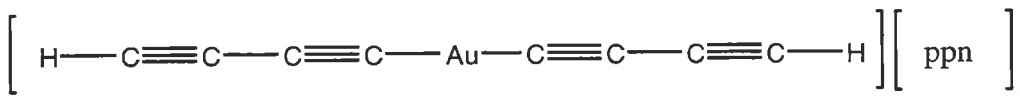
In order to prepare this compound logically, each section of the compound was prepared sequentially. The Cu_3 core was prepared by a 1:1 addition of dppm to CuI, resulting in the formation of $[Cu_3(\mu\text{-dppm})_3I_2]I$ in near quantitative yield.

In order to prepare the linear alkynylgold component of **7**, the synthetic method described by Vicente was used.[41,42] Acetylacetonato (acac) is a classic ligand in coordination chemistry.[43,44] It is well known that the acac ligand usually occupies one or two coordination sites, and is a useful synthetic intermediate because they react with protic acids through the following reaction:

$$\mathbf{[M](acac) + BH \Rightarrow [M]B + Hacac}$$

In addition, the byproduct acetylacetone is very easily separated from the other reaction products. Thus, [ppn][$Au(acac)_2$] was prepared as described previously.[45,46] Ethynylgold(I) complexes were prepared by Vicente showed that the reaction of [ppn][$Au(acac)_2$] with acetylene gave [ppn][$Au(C{\equiv}CH)_2$]. Similarly, [ppn][$Au(acac)_2$] reacts with other alkynes to give [ppn][$Au(C{\equiv}CR)_2$] [R = Bu^t, $SiMe_3$, CH_2X (X = Cl, Br, OH), $C_6H_4NO_2$-4, $C_6H_4C{\equiv}CH$-4, $C_6H_4C_6H_4NO_2$-4,4', $C_6H_4CH{=}CHC_6H_4NO_2$-4,4'-E].[41,42]

Thus, addition of 1,3-butadiyne with [ppn][Au(acac)$_2$] under basic conditions resulted in the formation of a white precipitate which was identified as [ppn][Au(C≡CC≡CH)$_2$] **5** in 96% yield. The IR spectrum in nujol showed two bands at 3302 and 2141 cm^{-1} corresponding to ν(≡CH) and ν(C≡C) respectively. The ^{1}H NMR spectrum contained a singlet at δ 2.50 ppm integrating to 2H for the acetylenic hydrogens and a 30H multiplet between δ 7.39 – 7.66 ppm for the ppn phenyl hydrogens. The ^{13}C NMR spectrum contained signals for the butadiynyl carbon atoms at δ 83.56 (C_α), 71.84 (C_β) and 56.73 ppm (C_δ) with C_γ not detected. The assignments were made by comparison with previously described compounds. The negative ion ES mass spectrum in a mixture of CH_2Cl_2 and MeOH showed a single intense ion at *m/z* 295 corresponding to [Au(C$_4$H)$_2$]$^-$.



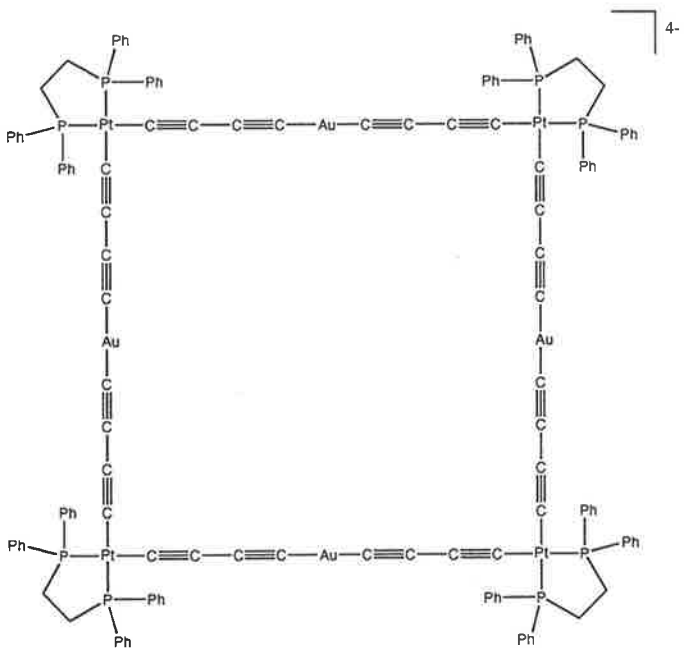
5

The related W(C≡CC≡CH)(CO)$_3$Cp complex was prepared using the same conditions as **5**, forming a yellow salt identified as [ppn][Au(C≡CC≡CW(CO)$_3$Cp)$_2$] **6** in a yield of 85%. The IR spectrum in nujol showed bands ν(CO) at 1959 and 1924 cm^{-1} characteristic of the W(CO)$_3$Cp moiety and a single ν(C≡C) band at 2029 cm^{-1}. The ^{1}H and ^{13}C NMR spectra contain resonances from the cyclopentadienyl group of W(CO)$_3$Cp as a 10H singlet appearing at δ_H 5.20 and δ_C 91.60 ppm, while the ppn cation gave a 30H multiplet between δ_H 7.40 – 7.67 and δ_C 126.22 – 133.91 ppm. The triple bonds of the carbon chain were poorly resolved with only one carbon being detected at δ 63.57 ppm due to long relaxation times. The negative ion ES mass spectrum in MeOH showed a base peak at *m/z* 959 corresponding to [Au{C$_4$[W(CO)$_3$Cp]}$_2$]$^-$ with two other ions at *m/z* 931 and 903 assigned to loss of carbonyls.

Similarly, addition of **1** to [ppn][Au(acac)$_2$] resulted in the formation of a white solid identified as [ppn][Au{C≡CC≡C[Au(PPh$_3$)]}$_2$] **8** in a yield of 73%. The IR spectrum in nujol showed peaks corresponding to ν(C≡C) at 2140 and 2080 cm^{-1}. Whereas the ^{1}H NMR spectrum in $CDCl_3$ contained a single multiplet between δ 7.46 – 7.73 ppm for the aromatic hydrogens of the ppn and PPh_3 phenyl groups. The ^{13}C NMR spectrum contained two peaks of low intensity at δ 88.34 and 118.78 ppm, which were assigned to the butadiynyl chain, with a large multiplet between δ 126.18 – 134.38 due to the phenyl carbons of the ppn and PPh_3 groups. The negative ion ES mass spectrum in a mixture of CH_2Cl_2 and MeOH produced a single ion at *m/z* 1211 corresponding [Au{C≡CC≡C[Au(PPh$_3$)]}$_2$]$^-$.

Having obtained each component needed for the preparation of **7**, equivalent amounts of [Cu$_3$(μ-I$_2$)(dppm)$_3$]I and **5** were combined in thf and stirred for 4h. Upon workup a white precipitate was obtained and identified as [{Cu$_3$(μ-I)(μ-dppm)$_3$}$_2$(μ-C≡CC≡CAuC≡CC≡C)]I **9** in a yield of 50%, the yield increasing to 100% if a ratio of 2:1 is used. Under these reaction conditions, the addition of the second Cu$_3$(μ-I)(μ-dppm)$_3$ fragment appears to be a favourable process. The compound was identified from microanalysis, IR, NMR and mass spectrometry. The IR spectra contained two ν(C≡C) bands at 2137 and 2084 cm^{-1}. The ^{1}H NMR spectrum only contained peaks arising from the dppm ligands, with an unresolved multiplet between δ 3.12 – 3.81 ppm for the methylene hydrogens of the phosphine backbone, while the phenyl hydrogens appear between δ 6.82 – 7.62 ppm. The ^{13}C NMR spectrum also only contained peaks corresponding to the dppm ligand with a multiplet at δ 28.42 for CH_2 and δ 127.93 – 133.93 ppm for the phenyl hydrogens, the carbon atoms of the butadiynyl chains where not resolved due to long relaxation times. The ES mass spectra in CH_2Cl_2 contained a [M + H]$^+$ ion at *m/z* 3232, with successive loss of dppm ligands at *m/z* 2849, 2463 and 2079 respectively.

The compounds, **5**, **6** and **8** demonstrate the ability of gold(I) compounds to form linear complexes. The complex [ppn][$Au(acac)_2$] could thus be used as a possible linker to extend the length of molecular wires or in the preparation of larger molecular geometries, such as the molecular squares described in the previous chapter. Thus, addition of [ppn][$Au(acac)_2$] to $Pt(C{\equiv}CC{\equiv}CH)_2(dppe)$ via syringe pump over 1h resulted in the formation of a white solid identified as $[\{(dppe)Pt(\mu\text{-}C{\equiv}CC{\equiv}CAuC{\equiv}CC{\equiv}C)\}_4][ppn]_4$ **10** in a yield of 91%. Correct microanalytical analysis and spectroscopic data confirmed the formulation of the proposed complex. The IR spectra contained two ν(C≡C) bands at 2142 and 2073 cm^{-1}. The ^1H NMR spectrum only contains peaks arising from the dppe ligands, with an unresolved multiplet at δ 2.46 ppm for the methylene hydrogens of the phosphine backbone, while the phenyl hydrogens appear between δ 7.15 – 7.94 ppm. The ^{13}C NMR spectrum contained peaks corresponding to the dppe ligand with a multiplet at δ 26.99 ppm for CH_2 and δ 126.10 – 133.74 ppm for the phenyl hydrogens. Peaks corresponding to the carbon atoms of the butadiynyl chain were seen at δ 60.31, 76.08, 97.26 and 99.56 ppm for C_δ, C_γ, C_β and C_α respectively. The ES mass spectra in CH_2Cl_2 contained an ion with a splitting of 0.5 mass units at *m/z* 2310.5 corresponding to $[M - 2ppn]^{2-}$.



10

EXPERIMENTAL.

Starting Materials: $AuCl(PPh_3)$,[47] $AuCl_2(\mu\text{-dppm})$,[25] $Au_2(OTf)_2(\mu\text{-dppm})$,[25] $[ppn][Au(acac)_2]$,[46] $W(C{\equiv}CC{\equiv}CH)(CO)_3Cp$,[48] $[Cu_3(\mu\text{-}I)_2(\mu\text{-dppm})_3]I$[49,50] were prepared by the cited literature methods.

$Au(C{\equiv}CC{\equiv}CH)(PPh_3)$ **1.**

To a suspension of $AuCl(PPh_3)$ (1.17 g, 2.37 mmol) in $NHEt_2$ / thf (30 ml / 15 ml), CuI (46 mg, 0.24 mmol) followed rapidly by $HC{\equiv}CC{\equiv}CH$ (23 ml, 3.1 mmol of a 1.34 M solution) was added and stirred at room temperature for 15 min. The solution was filtered and then washed with hexane. The solvent was then removed and the residue extracted with CH_2Cl_2 and loaded onto a squat column. The product was eluted with CH_2Cl_2, addition of hexane and reduction of solvent resulted in the formation of a pale yellow solid identified as $Au(C{\equiv}CC{\equiv}CH)(PPh_3)$ **1** (908 mg, 75%). Anal. Found: C, 49.75; H, 3.26. $C_{22}H_{16}PAu.0.5CH_2Cl_2$ requires: C, 49.09; H, 3.12; M, 508. IR (nujol): $\nu(C{\equiv}CH)$ 3283; $\nu(C{\equiv}C)$ 2148 cm^{-1}. ^1H NMR ($CHCl_3$): δ 1.76 (s, 1H, C≡CH), 7.30 – 7.63 (m, 15H, Ph). ^{13}C NMR ($CDCl_3$): δ 60.39 (s, C_δ), 69.39 (s, C_γ), 128.79 (s, C_β), 129.55 (s, C_α), 120.58 – 133.80 (m, Ph). ES mass spectrum (CH_2Cl_2 / MeOH, *m/z*): 508, M^+; 459, $[M - C_4H]^+$.

$Au_2(C{\equiv}CC{\equiv}CH)_2(\mu\text{-dppm})$ **2.**

$Au_2Cl_2(\mu\text{-dppm})$ (300 mg, 0.34 mmol) was dissolved in $NHEt_2$ / thf (10 ml / 5 ml). CuI (5 mg) and $HC{\equiv}CC{\equiv}CH$ (1.5 ml, 3.4 mmol of 2.4 M solution) was then rapidly added and left to stir at room temp for 30 minutes, forming a white precipitate. The solution was filtered and washed with EtOH, MeOH and Et_2O and air dried, giving $Au_2(C{\equiv}CC{\equiv}CH)_2(\mu\text{-dppm})$ **2** (220 mg, 74%). Anal. Found: C, 45.57; H, 2.77. $C_{33}H_{24}P_2Au_2$ requires: C, 45.23; H, 2.76%; M, 874. IR (nujol): $\nu(C{\equiv}CH)$ 3131; $\nu(C{\equiv}C)$ 2140, 2080 cm^{-1}. ^1H NMR ($CHCl_3$): δ 2.52 (s, 2H, C≡CH), 3.57 (m, 2H, CH_2), 7.06 – 7.76 (m, 20H, Ph). ^{13}C NMR (dmso): δ 25.57 (s, CH_2), 65.36 (s, C_δ), 71.37 (s, C_γ), 84.07 (s, C_β), 89.72 (s, C_α), 129.03 – 133.60 (m, Ph). ES mass spectrum (dmso / MeOH added NaOMe, *m/z*): 874, M^+; 826, $[M - C_4H]^+$.

$Au_2\{C{\equiv}CC{\equiv}C[W(CO)_3Cp]\}_2(\mu\text{-}dppm)$ **3.**

$Au_2Cl_2(\mu\text{-dppm})$ (100 mg, 0.11 mmol) was dissolved in $NHEt_2$ (10 ml). CuI (5 mg) and $W(C{\equiv}CC{\equiv}CH)(CO)_3Cp$ (90 mg, 0.22 mmol) was then added and left to stir at room temp for 10 minutes, forming a bright yellow precipitate. The solution was filtered and washed with EtOH, MeOH and Et_2O and air dried, giving $Au_2\{C{\equiv}CC{\equiv}C[W(CO)_3Cp]\}_2(\mu\text{-dppm})$ **3** (130 mg, 77%). IR (nujol): $\nu(C{\equiv}C)$ 2144; $\nu(CO)$ 2039, 1954 cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.94 (s, 2H, CH_2), 5.60 (s, 10H, Cp), 7.29 – 7.64 (m, 20H, Ph). ^{13}C NMR (dmso): δ 44.05 (s, CH_2), 91.91 (s, Cp), 129.28 – 133.80 (m, Ph). ES mass spectrum (MeOH added NaOMe, *m/z*): 1563, $[M + Na]^+$; 1162, $[M - C_4W(CO)_3Cp]^+$; 779, $[M - 2C_4W(CO)_3Cp]^+$.

$Au_2(\mu\text{-}dppm)(\mu\text{-}C{\equiv}CC{\equiv}C)_2Au_2(\mu\text{-}dppm)$ **4.**

To a CH_2Cl_2 / $NHEt_2$ (20 ml / 1 ml) solution of **2** (170.4 mg, 0.195 mmol) $Au_2(OTf)_2(\mu\text{-dppm})$ (209 mg, 0.195 mmol) in CH_2Cl_2 (10 ml) was added over a period of 1 h via syringe pump, then left to stir for an additional 30 minutes. The solvent was then removed and extracted with CH_2Cl_2 and added to cold hexane, precipitating cream $Au_2(\mu\text{-dppm})(\mu\text{-}C{\equiv}CC{\equiv}C)_2Au_2(\mu\text{-dppm})$ **4** (280 mg, 87%). IR (nujol): $\nu(C{\equiv}C)$ 2141 cm^{-1}. ^1H NMR (dmso): δ 2.49 (m, 4H, CH_2), 7.28 – 8.05 (m, 40H, Ph). ^{13}C NMR (dmso): δ 24.26 (m, CH_2), 89.39 (m, C≡C), 128.74 – 133.36 (m, Ph). ^{31}P NMR (dmso): δ 34.50 (s, dppm). ES mass spectrum (benzene, *m/z*): 1725, $[M + NH_2Et_2]^+$; 1675, $[M + Na]^+$; 1653, $[M + H]^+$.

$[ppn][Au(C{\equiv}CC{\equiv}CH)_2]$ **5.**

$[ppn][Au(acac)_2]$ (100 mg, 0.11 mmol) was dissolved in $NHEt_2$ / CH_2Cl_2 (10 ml / 2 ml). To this solution $HC{\equiv}CC{\equiv}CH$ (0.5 ml, 1.1 mmol) was added and stirred at room temperature for 1 h. The solution turned yellow in colour. The solvent was removed and the residue extracted with CH_2Cl_2 and the filtered solution added dropwise to cold Et_2O forming a cream coloured precipitate identified as $[ppn][Au(C{\equiv}CC{\equiv}CH)_2]$ **5** (85 mg, 96%). Anal. Found: C, 63.16; H, 3.86, N, 1.77. $C_{44}H_{32}NP_2Au$ requires: C, 63.37; H, 3.87; N, 1.68%; M, 833. IR (nujol): $\nu(C{\equiv}CH)$ 3302; $\nu(C{\equiv}C)$ 2141 cm^{-1}. ^1H NMR ($CHCl_3$): δ 2.50 (s, 2H, C≡CH), 7.39 – 7.66 (m, 30H, Ph). ^{13}C NMR ($CDCl_3$):

δ 56.73 (s, C≡CH), 71.84 (s, C≡C), 83.56 (s, C≡C), 125.83 – 133.89 (m, Ph). ES mass spectrum (CH_2Cl_2 / MeOH, *m/z*): 295, [M – ppn]$^-$.

[ppn][Au{C≡CC≡C[W(CO)$_3$Cp]}$_2$] **6**.

Similarly, [ppn][Au(acac)$_2$] (100 mg, 0.12 mmol) was dissolved in $NHEt_2$ / CH_2Cl_2 (10 ml / 2 ml) and W(C≡CC≡CH)(CO)$_3$Cp (91.4 mg, 0.24 mmol) was added and stirred at room temperature for 1 h. The solution turned yellow in colour. The solvent was removed and the residue extracted with CH_2Cl_2 and the filtered solution added dropwise to cold Et_2O forming yellow [ppn][Au{C≡CC≡C[W(CO)$_3$Cp]}$_2$] **6** (157 mg, 85%). Anal. Found: C, 48.05; H, 2.74, N, 0.98. $C_{60}H_{40}NP_2O_6AuW_2$ requires: C, 48.12; H, 2.69; N, 0.94%; M, 1497. IR (nujol): ν(C≡C) 2029; ν(CO) 1959, 1924 cm^{-1}. ^{1}H NMR ($CHCl_3$): δ 5.20 (s, 10H, Cp), 7.40 – 7.67 (m, 30H, Ph). ^{13}C NMR (dmso): δ 63.57 (s, C≡C), 91.60 (s, Cp), 126.22 – 133.91 (m, Ph). ES mass spectrum (CH_2Cl_2 / MeOH added NaOMe, *m/z*): 959, [M – ppn]$^-$; 931, [M – ppn - CO]$^-$; 903, [M – ppn - 2CO]$^-$.

[ppn][Au{C≡CC≡C[Au(PPh$_3$)]}$_2$] **8**.

Similarly, [ppn][Au(acac)$_2$] (92 mg, 0.1 mmol) was dissolved in $NHEt_2$ / CH_2Cl_2 (1 ml / 10 ml) and **1** (100 mg, 0.2 mmol) was added and stirred at room temperature for 2 h. The solvent was removed and the residue extracted with CH_2Cl_2 and the filtered solution added dropwise to cold Et_2O forming a white precipitate identified as [ppn][Au{C≡CC≡C[Au(PPh$_3$)]}$_2$] **8** (125 mg, 73%). Anal. Found: C, 54.91; H, 3.61, N, 1.21. $C_{80}H_{60}NP_4Au_3$ requires: C, 54.89; H, 3.43; N, 0.80%; M, 1750. IR (nujol): ν(C≡C) 2140, 2080 cm^{-1}. ^{1}H NMR ($CHCl_3$): δ 7.46 – 7.73 (m, 60H, Ph). ^{13}C NMR ($CDCl_3$): δ 88.34, 118.78 (s, C≡C), 126.18 – 134.38 (m, Ph). ES mass spectrum (CH_2Cl_2 / MeOH added NaOMe, *m/z*): 1211 [M – ppn]$^-$.

[{Cu_3(μ-I)(μ-dppm)$_3$}$_2$(μ-C≡CC≡CAuC≡CC≡C)]I **9**.

[Cu_3(μ-I)$_2$(μ-dppm)$_3$]I (41.4 mg, 0.024 mmol) and [ppn][Au(C≡CC≡CH)$_2$] (20 mg, 0.024 mmol) was dissolved in 5 ml of thf and left to stir for 4 h. The solvent was then removed and the residue dissolved in CH_2Cl_2 and added to hexane giving a white precipitate which was found to be [{Cu_3(μ-I)(μ-dppm)$_3$}$_2$(μ-C≡CC≡CAuC≡CC≡C)]I **9** (41 mg, 50%). Anal. Found: C, 56.46; H, 4.08. $C_{158}H_{132}I_3P_{12}Cu_6Au$ requires: C, 56.49; H, 3.96%; M, 3361. IR (nujol): ν(C≡C) 2137, 2084 cm^{-1}. ^{1}H NMR ($CHCl_3$): δ 3.12 – 3.81 (unresolved multiplet, CH_2), 6.82 – 7.62 (m, Ph). ^{13}C NMR (dmso): δ 28.42 (m, CH_2), 127.93 – 133.93 (m, Ph). ES mass spectrum (CH_2Cl_2, *m/z*): 3232, [M + H]$^+$; 2847, [M – dppm]$^+$; 2463, [M – 2dppm]$^+$; 2079, [M – 3dppm]$^+$; 1346, [Cu_3(dppm)$_3$]$^+$.

[{(dppe)Pt(μ-C≡CC≡CAuC≡CC≡C)}$_4$][ppn]$_4$ **10**.

Pt(C≡CC≡CH)$_2$(dppe) (100 mg, 0.145 mmol) was dissolved in CH_2Cl_2 (20 ml). To this solution, [ppn][Au(acac)$_2$] (135 mg, 0.145 mmol) in CH_2Cl_2 (10 ml) was added via syringe pump over a period of 1h. The solvent was then removed and extracted with CH_2Cl_2 and added dropwise to cold hexane, giving a white compound identified as [{(dppe)Pt(μ-C≡CC≡CAuC≡CC≡C)}$_4$][ppn]$_4$ **10** (191 mg, 91%). Anal. Found: C, 58.38; H, 4.08, N, 0.99. $C_{280}H_{216}N_4P_{16}Au_4Pt_4$ requires: C, 58.98; H, 3.82; N, 0.98 %; M, 5697. IR (nujol): ν(C≡C) 2142, 2073 cm^{-1}. ^{1}H NMR (dmso): δ 2.46 (m, CH_2), 7.15 – 7.94 (m, Ph). ^{13}C NMR (dmso): δ 26.99 (m, dppe-CH_2), 60.31 (m, C≡C), 76.08 (m, C≡C), 97.26 (m, C≡C), 99.56 (s, C≡C), 126.10 – 133.74 (m, dppe-Ph / ppn). ^{31}P NMR (dmso): δ 21.39 (s, *J*(PPt) = 107 Hz, ppn), 43.03 (s, *J*(PPt) = 2289 Hz, dppe) . ES mass spectrum (CH_2Cl_2, *m/z*): 2310.5 [M – 2ppn]$^{2-}$.

REFERENCES:

(1) Yam, V. W.-W.; Lo, K. K.-W.; Wong, K. M.-C. *J. Organomet. Chem.* **1999**, *578*, 3.

(2) Puddephatt, R. J. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: Oxford, **1987**; Vol. 5.

(3) Grohmann, A.; Schmidbaur, H. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, **1995**; Vol. 3.

(4) King, C.; Wang, J. C.; Khan, M. N. I.; Frackler Jr., J. P. *Inorg. Chem.* **1989**, *28*, 2145.

(5) Yam, V. W.-W.; Poon, C. K.; Kwong, H. L.; Che, C. M. *J. Chem. Soc., Dalton Trans.* **1990**, 3215.

(6) Yam, V. W.-W.; Lai, T. F.; Che, C. M. *J. Chem. Soc., Dalton Trans.* **1990**, 3747.

(7) Yam, V. W.-W.; Lee, W. K. *J. Chem. Soc., Dalton Trans.* **1993**, 2097.

(8) McCleskey, T. M.; Gray, H. B. *Inorg. Chem.* **1992**, *31*, 1733.

(9) Weissbart, B.; Toronto, D. V.; Balch, A. L.; Tinti, D. S. *Inorg. Chem.* **1996**, *35*, 2490.

(10) Yam, V. W.-W.; Choi, S. W.-K. *J. Chem. Soc., Dalton Trans.* **1994**, 2057.

(11) Vickery, J. C.; Olmstead, M. M.; Fung, E. Y.; Balch, A. L. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1179.

(12) Li, D.; Hong, X.; Che, C. M.; Lo, W. C.; Peng, S. M. *J. Chem. Soc., Dalton Trans.* **1993**, 2929.

(13) Che, C. M.; Yip, H. K.; Lo, W. C.; Peng, S. M. *Polyhedron* **1994**, *13*, 887.

(14) Shieh, S. J.; Hong, X.; Peng, S. M.; Che, C. M. *J. Chem. Soc., Dalton Trans.* **1994**, 3067.

(15) Yam, V. W.-W.; Choi, S. W.-K. *J. Chem. Soc., Dalton Trans.* **1996**, 4227.

(16) Yam, V. W.-W.; Choi, S. W.-K.; Cheung, K. K. *Organometallics* **1996**, *15*, 1734.

(17) Yam, V. W.-W.; Choi, S. W.-K.; Cheung, K. K. *J. Chem. Soc., Dalton Trans.* **1996**, 3411.

(18) Hong, X.; Cheung, K. K.; Guo, C. X.; Che, C. M. *J. Chem. Soc., Dalton Trans* **1994**, 1867.

(19) Muller, T. E.; Choi, S. W. K.; Mingos, D. M. P.; Murphy, D.; Williams, D. J.; Yam, V. W. W. *J. Organomet. Chem.* **1994**, *484*, 209.

(20) Xiao, H.; Cheung, K. K.; Che, C. M. *J. Chem. Soc., Dalton Trans.* **1996**, 3699.

(21) Tzeng, B. C.; Lo, W. C.; Che, C. M.; Peng, S. M. *Chem. Commun.* **1996**, 181.

(22) Irwin, M. J.; Vittal, J. J.; Puddephatt, R. J. *Organometallics* **1997**, *16*, 3541.

(23) Schmidbaur, H.; Wohlleben, A.; Wagner, F.; Orama, O.; Hutt, G. *Chem. Ber.* **1977**, *110*, 1748.

(24) Payne, N. C.; Ramachandran, R.; Puddephatt, R. J. *Can. J. Chem.* **1995**, *73*, 6.

(25) Irwin, M. J.; Rendina, L. M.; Vittal, J. J.; Puddephatt, R. J. *Chem. Commun.* **1996**, 1281.

(26) Mingos, D. M. P.; Yau, J.; Menzer, S.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1894.

(27) Gamasa, M. P.; Gimeno, J.; Lastra, E.; Aguirre, A.; Garcia-Granda, S. *J. Organomet. Chem.* **1989**, *378*, C11.

(28) Diez, J.; Gamasa, M. P.; Gimeno, J.; Aguirre, A.; Garcia-Granda, S. *Organometallics* **1991**, *10*, 380.

(29) Yam, V. W.-W. *J. Photochem. Photobiol. A Chem.* **1997**, *106*, 75.

(30) Yam, V. W.-W.; Lo, K. K.-W.; Fung, W. K.-M.; Wang, C. R. *Coord. Chem. Rev.* **1998**, *171*, 17.

(31) Yam, V. W.-W.; Lee, W. K.; Lai, T. F. *Organometallics* **1993**, *12*, 2383.

(32) Yam, V. W.-W.; Lee, W. K.; Yeung, P. K.-Y.; Phillips, D. *J. Phys. Chem.* **1994**, *98*, 7545.

(33) Yam, V. W.-W.; Lee, W. K.; Cheung, K. K.; Crystall, D.; Phillips, D. *J. Chem. Soc., Dalton Trans.* **1996**, 3283.

(34) Yam, V. W.-W.; Lee, W. K.; Cheung, K. K. *J. Chem. Soc., Dalton Trans.* **1996**, 2335.

(35) Yam, V. W.-W.; Choi, S. W.-K.; Chan, C. L.; Cheung, K. K. *Chem. Commun.* **1996**, 2067.

(36) Yam, V. W.-W.; Fung, W. K.-M.; Cheung, K. K. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1100.

(37) Yam, V. W.-W.; Lee, W. K.; Cheung, K. K.; Lee, H. K.; Leung, W. P. *J. Chem. Soc., Dalton Trans.* **1996**, 2889.

(38) Yam, V. W.-W.; Fung, W. K.-M.; Wong, M. T. *Organometallics* **1997**, *16*, 1772.

(39) Yam, V. W.-W.; Fung, W. K.-M.; Cheung, K. K. *Chem. Commun.* **1997**, 963.

(40) Yam, V. W.-W.; Fung, W. K.-M.; Cheung, K. K. *Organometallics* **1998**, *17*, 3293.

(41) Vicente, J.; Chicote, M. T.; Abrisqueta, M. D.; Jones, P. G. *Organometallics* **1997**, *16*, 5628.

(42) Vicente, J.; Chicote, M. T.; Abrisqueta, M. D. *J. Chem. Soc., Dalton Trans.* **1995**, 497.

(43) Gibson, D. *Coord. Chem. Rev.* **1969**, *4*, 225.

(44) Mehrotra, R. C.; Bohra, R.; Gaur, D. P. *Metal β-Diketonates and Allied Derivatives*; Academic Press: London, **1978**.

(45) Vicente, J.; Chicote, M. T.; Saura-Llamas, I.; Lagunas, M. C. *J. Chem. Soc., Chem. Commun.* **1992**, 915.

(46) Vicente, J.; Chicote, M. T. *Inorg. Synth.* **1998**, *32*, 172.

(47) Bruce, M. I.; Nicholson, B. K.; Shawkataly, O. bin. *Inorg. Synth.* **1989**, *26*, 325.

(48) Bruce, M. I.; Hall, B. C.; Low, P. J.; Smith, M. E.; Nicholson, B. K.; Skelton, B. W.; White, A. H. *Inorg. Chim. Acta.* **2000**, *300-302*, 603.

(49) Marsich, N.; Camus, A.; Cebulec, E. *Inorg. Nucl. Chem.* **1972**, *34*, 933.

(50) Bresciani, N.; Marsich, G.; Nardin, G.; Randaccio, L. *Inorg. Chim. Acta.* **1974**, *10*, L5.

CORRECTIONS

Professor A. H. White and Dr B. W. Skelton of the University of Western Australia preformed all X-ray structure determinations described in this thesis.

Solvent in the crystal lattice is reported in the microanalytical data for compounds on page 67, line –7; page 70, line –4; page 71, line 9; page 72, line 4; page 73, line 7; page 74, line 10; page 98, line –4; page 99, line –1; page 100, line –7; page 101, line 8; page 101, line 19; page 102, line 11; page 103, line –3; page 104, line –3; page 139, line 17 and page 141, line –4. Evidence for the inclusion of these solvent molecules were seen in the associated NMR spectra but was erroneously excluded from the reported NMR peaks, these solvent molecules showed peaks at their expected spectral positions.

The coupling constant for complexes appearing on page 142, line 15; page 145, line –8; page146, line 5; page 146, line 10; page 147, line 3; page 147, line –11; page 147, line –2; page 148, line 10; page 148, line –6; page 149, line –5; page 150, line 10; page 150, line –9; page 151, line 5; page 151, line 17; page 152, line 3; page 152, line 15; page 152, line –2; page 153, line 8 and page 172, line –2 is that of the pseudo triplet arising from the coupling of platinum to phosphorus. The value of the coupling constant is the distance between the two outer peaks. The reported chemical shift is that of the middle peak of the triplet.

The appearance of the $[M + Li]^+$ peak in the ES MS spectra described on page 120, line –1 and page 143, line –1 is thought to have been a carryover from the lithiation step in the reaction.

In some instances, values in the NMR spectra were quoted to too many significant figures, these should be rounded accordingly with values for the NMR spectra to the nearest 0.01. Similarly, in the mass spectra values should be rounded to the nearest whole number.

The deformations mentioned on page 117 were not that significant when modelled using the *Spartan* molecular mechanics. The observed deformations in the X-ray structures were reproduced utilising the *ab initio* calculations, which takes into account relativistic effects.

Abstract, line 3	"alkynyl ligands", not "alkynes"
Abstract, line 10	"affects", not "effects"
Abreviations	"Ångstrom", not "angstrom"; "aryl", not "Aryl"; "ca", not "ca."; "Kelvins", not "kelvins"; include "cod" "cyclooctadiene"
Page 2, line -7	"cyclopenadienyl", not "cyclopenadiynyl"
Page 4, scheme 4	"NH_3(aq)", not "NH_4OH"
Page 7, line 6	"were", not "where"
Page 8, line –2	"proceeding", not "proceeds"
Page 8, line –12	delete "the formation of"
Page 14, line 7	"Me_2Sn", not "Me_3Sn"
Page 14, line –10	formation of supramolecular
Page 15, line –2	", namely", not "based on the these angles"

Page 16, line –2	"an", not "and"
Page 20, Figure caption	"neutral and charged"
Page 21, line 9	"octahedra", not "octahedrons"
Page 22, line 1	"is", not "are"
Page 24, ref 1	*"Int. Ed. Engl."*
Page 24, ref 15	delete "Teil"
Page 26, ref 56	"therein"
Page 26, ref 58, 59	More appropriate reference: *Organometallics* (2000), **19**, 2968
Page 28, ref 91	delete "Teil"
Page 29, ref 113	"*Rev.*", not "*Revs.*"
Page 30, line 7	", which is", not "and they are"
Page 31, line –7	"…OMe-*O, E*", not "…OMe-*O, P*"
Page 33, line -8	"are", not "is"
Page 35, line –9	"contrasts with those"
Page 44, para 3	"increased", not "reduced"
Page 52, line –10	"confirm", not "confirms"
Page 59, line 5	"to", not "the"
Page 68, line –1	"s", not "c"
Page 70, line 12	"phosphite"
Page 70, line 14	"…}(PPh_3)", not "…}PPh_3)"
Page 73, line 9	"4H", not "2H"
Page 76, line 4	737, $[M - OMe]^+$, not 736, $[M - H- OMe]^+$
Page 76, line –10	"Reactions", not "Recations"
Page 79, ref 43	"Bartczak"
Page 80, ref 54	"Selegue, J. P."
Page 81	"(μ-dppm)$_3$"
Page 81-108, header; Contents page; Chapter 3 title; Page 87, line -2	delete "bis-"
Page 86, line 3	"(PPh_3)$_2$"
Page 94, line 6	1171, $[M + Na]^+$, not 1170, $[M + Na]^+$
Page 98, line 18	"34H", not "30H"
Page 98, line –10 and –5	"…}$_2C_6H_4$"
Page 98, line –3	"10H", not "5H"
Page 99, line 6	replace "**3**" with "**4**"
Page 104, compound 13	$\{Ru(PPh_3)_2CpC_2C_6H_4C_2\}_2$
Page 106, ref 23	replace "McDonaugh" with "McDonagh" More appropriate reference: *Adv. Organomet. Chem.* (1999), **43**, 349
Page 106, ref 28	"Whittall"
Page 107, ref 60	Collman, J. P; Sears Jr., C. P; Kubota, M *Inorg. Synth.* (1990), **28**, 92
Page 110, line –1	replace "dicyclohexylphosphinoethane" with "1,2-bis(dicyclohexylphosphino)ethane"
Page 111, line 3	in the presence
Page 112, line –8	C-Pt-P, not P-Pt-P
Page 117, line –10	"affects", not "effects"
Page 118, line 3	replace "alkyl" with "alkynyl"
Page 119, line 6	spectra obtained in the negative ion mode

Page 120, line 3	replace "…PtH…" with "…PH…"
Page 120, line 4	subscript 2 in formula
Page 124, line 5	replace "were" with "was"
Page 124, line 5	replace "species" with "specie"
Page 124, line 12	replace "spectroscopy" with "spectrometry:
Page 135, line –1	
Page 132, line 5	"presence of *cis*…"
Page 139, line 3	"…$(CO)_3Cp$…"
Page 139, line 15	"…$(PEt_3)_2$"
Page 141, line 3	replace "5H" with "10H"
Page 144, line 6	"The crude"
Page 144, line 14	"])"
Page 144, line –9	
Page 144, line –1	
Page 147, line 8	"0.54 mmol", not "538 mmol"
Page 147, line –1	"$[M + 2Na + NaOMe]^{2+}$", not "$[M + 4Na]^{2+}$"
Page 150, line –8	"40.76", not "40.756"
Page 151, line 14	"80H", not "20H"
Page 152, line 3	"43.24", not "43.243"
Page 152, line –5	"16H", not "4H" and "80H", not "20H"
Page 154, ref 12	replace "Whttmann" with "Wittmann"
Page 155, ref 24	"*J. Chem*…."
Page 155, ref 25	replace "Michael, D; Mingos, P." with "Mingos, D. M. P."
Page 158, line 10	replace "oligermeric" with "oligomeric"
Page 158, line –9	replace "geometry" with "geometries"
Page 162, line 3	"latter"
Page 162, line 9	replace "2039" with "2144"
Page 163, line –4	"from". not "form"
Page 165, line 3	"*triangulo*"
Page 165, line 4	
Page 165, line –3	
Page 166, line 9	replace "considerable" with "considerably"
Page 168, line 3	delete "Whereas"
Page 168, line 10	"corresponding to"
Page 168, line 12	replace "…I_2)…" with "…$I)_2$…"
Page 168, line –3	replace "where" with "were"
Page 170, line 2	"$Au_2Cl_2(\mu\text{-dppm})_2$"
Page 171, line 3	replace "was" with "were"
Page 173, line 3	
Page 176, ref 41,42	More appropriate reference: *Organometallics* (2000), **19**, 2968.
Page 177, ref 4	"Oligomerisation", not "oligermerisation"

Appendix 1

Publications by the Author arising from this Work

1. Some neutral ruthenium vinylidene complexes and a novel 1,3-elimination reaction: preparation of chiral ruthenium acetylides, *J. Organomet. Chem.*, **1996**, 522, 307 (with M. I. Bruce, N. N. Zaitseva, B. W. Skelton and A. H. White).

2. Reactions of $RuCl(C{=}CHBu^t)(PPh_3)(\eta\text{-}C_5Me_5)$ with tertiary phosphites: molecular structure of $RuCl\{P(OPh)_3\}_2(\eta\text{-}C_5Me_5)$, *Aust. J. Chem.*, **1997**, 50, 1097 (with M. I. Bruce and E. R. T. Tiekink).

3. Preparation and reactions of some neutral pentamethylcyclopentadienyl-ruthenium vinylidene complexes, *J. Chem. Soc., Dalton Trans.*, **1998**, 1793 (with M. I. Bruce, N. N. Zaitseva, B. W. Skelton and A. H. White).

4. Oligermerisation of alkynes at a pentamethylcyclopentadienyl-ruthenium centre, *J. Chem. Soc., Dalton Trans.*, **2000**, 2279 (with M. I. Bruce, N. N. Zaitseva, B. W. Skelton and A. H. White).

5. Some pentamethylcyclopentadienyl-ruthenium derivatives of methyl propiolate, *Aust. J. Chem.*, **2000**, 53(2), 99 (with M. I. Bruce, N. N. Zaitseva, E. R. T. Tiekink, B. W. Skelton and A. H. White).

6. Some ruthenium complexes derived from 1,4-diethynylbenzene: molecular structure of $Ru\{\eta^3\text{-}C[{=}C(CN)_2]C(C_6H_4C{\equiv}CH\text{-}4){=}C(CN)_2\}(PPh_3)Cp$, *J. Organomet. Chem.*, **1999**, 592, 74 (with M. I. Bruce, P. J. Low, B. W. Skelton and A. H. White).

7. An efficient synthesis of polyynyl and polyynediyl complexes of ruthenium(II), *J. Chem. Soc., Dalton Trans.*, **1999**, 3719 (with M. I. Bruce, B. D. Kelly, P. J. Low, B. W. Skelton and A. H. White).

8. Heterometallic complexes containing C_4 chains. X-ray structures of $\{Cp(CO)_3W\}C{\equiv}CC{\equiv}C\{Ir(CO)(PPh_3)_2(O_2)\}$ and *cis*-$Pt\{C{\equiv}CC{\equiv}C[W(CO)_3Cp]\}_2(PEt_3)_2$, *Inorg. Chim. Acta.*, **2000**, 300-302, 633 (with M. I. Bruce, P. J. Low, M. E. Smith, B. W. Skelton and A. H. White).