Mixed Metal Acetylide Complexes

PRADEEP MATHUR, SAURAV CHATTERJEE AND VIDYA D. AVASARE
Chemistry Department
Indian Institute of Technology-Bombay
Powai, Bombay 400 076, India

Published in Advances in Organometallic Chemistry, Volume 55, 2007, Pages 201-277
http://dx.doi.org/10.1016/S0065-3055(07)55004-5
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. Introduction</td>
<td>3</td>
</tr>
<tr>
<td>II. Mixed Group 8 Metal Acetylide Complexes</td>
<td>4</td>
</tr>
<tr>
<td>III. Mixed Group 10 Metal Acetylide Complexes</td>
<td>13</td>
</tr>
<tr>
<td>IV. Mixed Group 11 Metal Acetylide Complexes</td>
<td>15</td>
</tr>
<tr>
<td>V. Mixed Group 6 - 9 Metal Acetylide Complexes</td>
<td>19</td>
</tr>
<tr>
<td>VI. Mixed Group 10 - 12 Metal Acetylide Complexes</td>
<td>71</td>
</tr>
<tr>
<td>VII. Other Mixed Metal Acetylide Complexes</td>
<td>79</td>
</tr>
<tr>
<td>VIII. Abbreviations</td>
<td>99</td>
</tr>
</tbody>
</table>

References
I

INTRODUCTION

Complexes containing C₂ hydrocarbyl ligands occupy a very important position in the development of di-, tri- and polynuclear organometallic chemistry. Recognition that monovalent anions of alk-1-ynes, [RC≡C]⁻ are isoelectronic to cyanide ion and CO prompted the first preparation of metal alkynyl complexes in 1953.¹,² Since then, a number of synthetic strategies have been developed and chemistry of metal acetylide complexes has grown tremendously.³⁻¹² Ability of the alkynyl part (-C≡CR) of the metal acetylides to bind to metal centres in a variety of bonding modes enables a large number of acetylide – bridged polynuclear complexes to be synthesised.¹³⁻²⁶ The presence of metal and electron - rich C≡C moiety in acetylide complexes facilitates cluster growth reactions, and frequently, coupling of acetylide moieties to form polycarbon chains on cluster frameworks is observed.²⁷⁻³⁰

In this review, focus is given on mixed – metal acetylide complexes which have been prepared from metal – acetylide precursor complexes. Particular emphasis is given on aspects of variation of acetylide bonding on mixed – metal polynuclear frameworks and on reactivity of the polycoordinated acetylide ligand. Since, we recently reviewed oxo - incorporated metal acetylide complexes,³¹ these are excluded from the present review. A large majority of the acetylide – bridged mixed metal complexes contains metals of the same group of the Periodic Table and, therefore, we have subdivided the review based on different groups. Although, several examples exist of mixed – metal acetylide complexes containing metals from groups 6, 7, 9 and 12, quite surprisingly, we
could not find any example of mixed – metal acetylide complexes containing metals only from one of these groups.

II
MIXED GROUP 8 METAL ACETYLIDE COMPLEXES

Most of the mixed metal acetylide complexes of this particular group are those associated with Cp, Cp* and carbonyl ligands. A number of synthetic studies have been carried out for polynuclear C2 complexes derived from ethynyl and diethynediyl iron complexes. Reaction of the ethynyliron complexes [\((\eta^5\text{-C}_5\text{R}_5)\text{Fe(CO)}_2\text{-C≡C-H}\) (R = H, 1; R = Me, 2)] with [Ru3(CO)12] in refluxing benzene affords triruthenium \(\mu\cdot\eta^1\cdot\eta^2\cdot\eta^2\)-acetylide cluster compounds [Ru3(CO)9(\(\mu\cdot\eta^1\cdot\eta^2\cdot\eta^2\)-C≡C-{(\(\eta^5\text{-C}_5\text{R}_5)\text{Fe(CO)}_2\})})] (R = H, 4; R = Me, 5) (Scheme 1).32 On the other hand, the reaction of the ethynediyldiiron complex, \[{(\eta^5\text{-C}_5\text{Me}_5)\text{Fe(CO)}_2\text{-C≡C-{(\eta^5\text{-C}_5\text{Me}_5)\text{Fe(CO)}_2\})}}\] (3) with [Ru3(CO)12], gives a complicated mixture of products, from which [Cp*2Fe2Ru2(\(\mu_4\)-C2)(CO)10] (6) and [Cp*2Fe2Ru6(\(\mu_6\)-C2)(CO)17] (7) have been isolated and characterized by X-ray crystallography as permetalated ethene and permetalated ethane complexes respectively (Scheme 2).32 The four metal atoms in 6 form an open-rectangular array embedded in which is a C2 ligand. Compound 7 is an octanuclear compound with two C2 units above and below a Ru4 plane arranged perpendicular to each other. Two of the edges of the central Ru4 plane are bridged by Ru(CO)3 groups and the other two by FeCp* moieties.
On reflux of a THF solution of a mixture of [Fe$_2$(CO)$_9$] and 6, iron-substituted derivative of 5, complex [Ru$_2$Fe($\mu$-H)(CO)$_9$(μ$_3$-C≡C-{($\eta^5$-C$_5$Me$_5$)Fe(CO)$_2$})] ($\mathbf{8}$) is formed. Treatment of 6 with CF$_3$SO$_3$H, HBF$_4$.OEt$_2$ or CF$_3$COOH forms an unstable cationic species $\mathbf{9}$, which has been characterised solely by spectroscopy, as it readily converts to [{($\eta^5$-C$_5$Me$_5$)Fe(CO)}$^+$ X$^-$ (Scheme 3).$^{32}$
Thermolysis of the mixed-metal tetranuclear cluster \([\mu_3-\text{C}≡\text{C}-\{\eta^5-\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\}]\text{Ru}_3(\mu-\text{H})(\text{CO})_9\) (4) affords two products: \([\text{CpFeRu}_6(\mu_5-\text{C}_2)(\mu_5-\text{C}_2\text{H})(\text{CO})_{16}]\) (10) and \([\text{Cp}_2\text{Fe}_2\text{Ru}_6(\mu_6-\text{C}_2\text{C}_2)(\text{CO})_{17}]\) (11) (Scheme 4). The anion \([\mu_3-\text{C}≡\text{C}-\{\eta^5-\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\}]\text{Ru}_3(\text{CO})_{9}^-\) (12) derived from 4 undergoes coupling of the \([(\text{C}_2\text{FeRu}_3)]\) core to give compound 11 and a heptanuclear cluster \([\text{Cp}_2\text{Fe}_2\text{Ru}_5(\mu_5-\text{C}_2\text{C}_2)(\text{CO})_{17}]\) (14), a coordinatively saturated compound with 112 cluster valence electrons bearing two six-electron donating \text{C}_2\) ligands.
Treatment of 6 with R-chloropropionic acid results in an addition reaction yielding a μ-hydrido μ-carboxylato derivative, [(μ₄-C=CH₂)(μ-H)(μ-κ¹,κ¹-CH₃CHClCOO)Fe₂Ru₂Cp²(CO)₈] (15). On irradiation of a THF solution of 6, in presence of diphosphines, [Ph₂P(CH₂)ₙPPh₂] (n= 1, 2), the substituted products [(μ₄-C=C=CH₂)Fe₂Ru₂Cp²(CO)₈{μ-Ph₂P(CH₂)ₙPPh₂}] (n = 1, 16a; n = 2, 16b) are formed. Treatment of 16 with HBF₄.OEt₂ results in protonation at the C=C unit to give the cationic μ₄-C₂H complex, [(μ₄-C=CH)Fe₂Ru₂Cp²(CO)₁₂(dpmm)]BF₄ (17) which on reduction with [NEt₄] BH₄ results in elimination of one of the iron fragments to afford a
trinuclear acetylide cluster, \([\mu_3\text{-C≡CH}]\text{FeRu}_2\text{Cp}^*(\text{CO})_5(\text{dppm})\) (18a). On the other hand, treatment of 17 with \(\text{H}_2\text{SiPh}_2\) leads to hydrogen addition to give the trinuclear \(\mu_3\text{-HC≡CH}\) complex \([\mu_3\text{-HC≡CH}][\mu\text{-H}]\text{FeRu}_2\text{Cp}^*(\text{CO})_5(\text{dppm})\) (18b). Thus, the \(\mu_3\text{-HC≡CH}\) ligand in 18b arises from formal hydrogenation of the \(\mu_4\text{-C=C}\) ligand in 16a and the ligand transformations are realized by the flexible coordination capability of the \(\text{C}_2\) ligand. Cluster expansion of 16a with \([\text{Co}_2(\text{CO})_8]\) gives

\([\mu_3\text{-C=Fe}(\text{CO})_2\text{Cp}^*]\text{FeRu}_2\text{CoCp}^*(\text{CO})_12(\text{dppm})\) (19) (Scheme 5).\(^{34a}\)
Thermal reaction of a THF solution of ethynediyl complex \([\{\text{Cp}_2\text{Ru(CO)}_2\}_2(\mu-\text{C≡C})\}] (20) with diiron nonacarbonyl gives \([\text{Cp}_2\text{Fe}_2\text{Ru}_2(\mu_4-\text{C≡C})(\mu-\text{CO})(\text{CO})_8]) (21)\) (Figure 1).34b
Highly conjugated polycarbon–metal systems, the zwitterionic \( \mu \)-but-2-yn-1-ylidene-4-yldyne complex \([\text{Ru}_3(\text{CO})_{10}(\mu_3-\text{C}–\text{C}≡\text{C}–\mu-\text{C})\text{Fe}_2\text{Cp}^*\text{C}(\text{CO})_3]\) (23) and the dimerized product with a cumulenic \( \mu \)-C\( _8 \) ligand, \([\{\text{Cp}^*\text{Fe}\}_4\text{Ru}_2(\text{CO})_{13}[\mu_6-\text{C}\_8–\text{C}(=\text{O})]\) (24a) have been isolated from the reactions of butadiynediylidmetal complex, \[{\{\eta^5-\text{C}_5\text{Me}_5}\text{Fe}(\text{CO})_2}\}_–\text{C}≡\text{C}–\text{C}≡\text{Fe}(\eta^5-\text{C}_5\text{Me}_5)(\text{CO})_2\}] (22a) with \([\text{Ru}_3(\text{CO})_{12}]\) (Scheme 6). An isostructural \( \text{C}_8 \) complex 24b is obtained on reaction of the Fe-Ru mixed metal complex \[{\{\eta^5-\text{C}_5\text{Me}_5}\text{Fe}(\text{CO})_2}\}_–\text{C}≡\text{C}–\text{C}≡\text{Ru}(\eta^5-\text{C}_5\text{Me}_5)(\text{CO})_2\}] (22b) with \([\text{Ru}_3(\text{CO})_{12}]\). A zwitterionic acetylide cluster-type product \[{\{\eta^5-\text{C}_5\text{Me}_5}\text{Fe}(\text{CO})_2}\}_–\text{C}≡\text{C}–\text{C}≡\text{Fe}(\eta^5-\text{C}_5\text{Me}_5)(\text{CO})_2\}] (22c) with \([\text{Fe}_2(\text{CO})_9]\) (Figure 2). \(^{35a}\) X-ray crystallography reveals a pentanuclear structure containing a dinuclear \( \mu-\eta^1,\eta^2 \)-acetylide cationic species and a trinuclear \( \mu_3 \)-acetylide anionic species.
Scheme 6.

Figure 2.

Thermolytic reaction of a THF solution of \([\{\text{CpRu}(\text{PPh}_3)_2\}_2\{\mu-C\equiv C\}_n]\) \((n = 3, \ 26a; \ n = 4, \ 26b)\) with \([\text{Fe}_2(\text{CO})_9]\) afford the corresponding heterometallic complexes \([\text{Fe}_3\{\mu_3-C\equiv C\{\text{Ru}(\text{PPh}_3)\text{Cp}\}_2(\text{CO})_9\}] (27a)\) and \([\text{Fe}_3\{\mu_3-C\equiv C\{\text{Ru}(\text{PPh}_3)_2\text{Cp}\}_2(\text{CO})_9\}] (27b)\) respectively (Scheme 7). \(^{35b}\)

Scheme 7.
The triosmium acetylide cluster, \([\text{Os}_3(\mu-H)(\mu_3-C\equiv C\text{Me})(\text{CO})_9]\) (28) reacts with \([\text{Ru}_3(\text{CO})_{12}]\) in refluxing hexane to give the tetranuclear \([\text{RuOs}_3(\mu_4-H\text{C}_2\text{Me})(\text{CO})_{12}]\) (29) (Scheme 8).36a

![Scheme 8](image)

Scheme 8.

Reaction of a dichloromethane solution of cis-\([\text{(dppm)}_2\text{RuCl}_2]\) with trans-\([\text{(dppm)}_2(\text{Cl})\text{Os}(\text{C}≡\text{C-p-C}_6\text{H}_4-\text{C}≡\text{CH})]\) and \(\text{NaPF}_6\) gives a vinylidene complex, which converts to trans-\([\text{(dppm)}_2(\text{Cl})\text{Os}(\text{C}≡\text{C-p-C}_6\text{H}_4-\text{C}≡\text{C-Ru(Cl)(dppm)}_2]\) (30) on addition of DBU in the reaction mixture (Scheme 9).36b

![Scheme 9](image)

Scheme 9.

On reflux of a benzene solution containing \([\text{Fe}_2\text{M(CO)}_9(\mu_3-\text{E})_2]\) (M = Ru; E = S, Se) (31a, b) and \([\text{Fe}(\eta^5-\text{C}_5\text{H}_4\text{E}′\text{CH}_2\text{C}≡\text{CH})_2]\) (E′ = S, 32a; Se, 32b) unusual ferrocenyl containing heterometal clusters \([\text{Fe}(\eta^5-\text{C}_5\text{H}_4\text{E}′\text{CH}_2\text{C}≡\text{CH})(\eta^5-\text{C}_5\text{H}_4\{\text{Fe}_2\text{M(CO)}_8(\mu-\text{E})(\mu_3-\text{E})(\text{E′CHCCH}_2)\}]_2]\) (M = Ru, E = Se and E′ = Se, 33a; M = Ru, E = S and E′ = Se, 33b) are formed (Scheme 10).37 The molecular structure of 33b consists of a butterfly FeRuS_2 unit attached to a \{FeSeC(H)=CCH_2\} five-membered ring which is bonded via Se atom to the C_5H_4 ring of a \{(\eta^5-\text{C}_5\text{H}_4)(\eta^5-\text{C}_5\text{H}_4\text{SeCH}_2\text{C}≡\text{CH})\text{Fe}\} unit.
III
MIXED GROUP 10 METAL ACETYLIDE COMPLEXES

Reaction of trans-bis(tri-n-butylphosphine)diethynylnickel (34) with l-alkynes in the presence of an amine complex of a copper(I) salt as a catalyst gives quantitatively alkynyl ligand exchange products. In this synthetic method, complex 34 reacts with appropriate α,ω-diethynyl compounds to afford high molecular weight linear polymers (35-38) in good yields.38 This procedure provides a convenient route to heterometallic nickel-platinum-poly-yne polymers (Scheme 11).
Formation of heterodinuclear Pt-Pd anionic complexes [([C₆F₅]₂Pt(CCR)₂Pd(η³-C₃H₅)]⁻ (R = Ph, tBu, SiMe₃) (42a-c) and neutral trinuclear complexes [([η³-C₃H₅)Pd}₂{Pt(CCR)₄}] (R = Ph, tBu, SiMe₃) (41a-c) have been reported from the reactions of anionic substrates 39, [Pt(C≡CR)₄]²⁻ or 40, cis-[Pt(C₆F₅)₂(C≡CR)₂]²⁻ with [{Pd (η³-C₃H₅)Cl}₂] complex (Scheme 12).³⁹

Scheme 12.

The reaction of mononuclear platinum acetylide complexes [cis-Pt(CCR)₂L₂] (R = Ph, tBu; L = PPh₃) towards cis-[Pd(C₆F₅)(thf)₂] (43) results in the formation of dimetallic Pt-Pd (R =Ph, 44; R = tBu, 45) complexes (Scheme 13).⁴⁰

Scheme 13.
MIXED GROUP 11 METAL ACETYLIDE COMPLEXES

New aspects of chemistry and bonding have emerged from reactions of the anionic linear metal acetylide complexes $[\text{M(C}_2\text{Ph)}_2]^{-}$ with metal phenylacetylide polymers $[\text{M(C}_2\text{Ph)}_n]_n$ (M = Cu, Ag, Au). The reactions involve depolymerization, ethynylation and condensation to form novel clusters. Thus, the homonuclear $[\text{Ag}_5(\text{C}_2\text{Ph)}_6]^-$ and heteronuclear $[\text{Au}_2\text{Cu(}\text{C}_2\text{Ph)}_4]^-$, $[\text{Au}_3\text{M}_2(\text{C}_2\text{Ph)}_6]^-$ (M = Cu, Ag), $[\text{Ag}_6\text{Cu}_7(\text{C}_2\text{Ph)}_14]^-$, and $[\text{AuAg}_6\text{Cu}_6(\text{C}_2\text{Ph)}_14]^-$ complexes have been obtained. Extension of ethynylation reactions to neutral complexes resulted in formation of $[\text{Au}_2\text{Ag}_2(\text{C}_2\text{Ph)}_4(\text{PPh}_3)_2]$, $[\text{Ag}_2\text{Cu}_2(\text{C}_2\text{Ph)}_4(\text{PPh}_3)_4]$, $[\text{AuAg(}\text{C}_2\text{Ph)}_2]_n$, $[\text{AuCu(}\text{C}_2\text{Ph)}_2]_n$, and $[\text{AgCu(}\text{C}_2\text{Ph)}_2]_n$.

Mixed gold-silver and gold-copper phenylacetylide polymers $[\{\text{AuM(}\text{C}_2\text{Ph)}_2\}_n]$ (M = Ag, 46; M = Cu, 47) have been made by the reaction of $[\text{Au(}\text{C}_2\text{Ph)L}]$ (L = AsPh$_3$, P(OPh)$_3$) with $[\{\text{Ag(}\text{C}_2\text{Ph)}\}_n]$ (48) and $[\{\text{Cu(}\text{C}_2\text{Ph)}\}_n]$ (49) respectively. The gold-silver polymer 46 has also been prepared by the reaction of $[\text{AuClPPh}_3]$ with $[\{\text{Ag(}\text{C}_2\text{Ph)}\}_n]$.41

Another heterometallic gold-silver cluster, $[\text{Au}_2\text{Ag}_2(\text{C}_2\text{Ph)}_4(\text{PPh}_3)_2]$ (50) has been prepared by the reaction of $[(\text{PPh}_3)\text{AuC}_2\text{Ph}]$ and $[\text{AgC}_2\text{Ph}]_n$ and also by the reaction of PPh$_3$ with the polymer $[\text{AuAg(}\text{C}_2\text{Ph)}_2]_n$ (46) (Scheme 14).42 The structure of 50 consists of a linear arrangement of two phenylacetylide groups about each gold atom, with each silver atom asymmetrically $\pi$-bonded to two triple bonds and one phosphine ligand (Figure 3).
Figure 3.

Scheme 14.

 Reaction of \([\text{Au}_2(\text{C}_2\text{Ph})_3]^−\) and \([\text{AgC}_2\text{Ph}]\) gives a gold-silver pentanuclear cluster \([\text{Au}_3\text{Ag}_2(\text{C}_2\text{Ph})_6]^−\) (51) (Scheme 15).43

\[
\begin{align*}
\text{[N(PPh}_3)_2][\text{Au}_2(\text{C}_2\text{Ph})_3] + [\text{AgC}_2\text{Ph}] & \rightarrow 1/2[\text{N(PPh}_3)_2][\text{Au}_3\text{Ag}_2(\text{C}_2\text{Ph})_6] + 1/2[\text{N(PPh}_3)_2][\text{Au}(\text{C}_2\text{Ph})_2] \\
\end{align*}
\]

Scheme 15.

The pentanuclear cluster \([\text{Au}_3\text{Ag}_2(\text{C}_2\text{Ph})_6]^−\) (51) has also been obtained from the reaction between \([\text{Ag}(\text{C}_2\text{Ph})_2]^−\) and the polymer complex \([\{\text{AuAg}(\text{C}_2\text{Ph})_2\}_n]\) (46) (Scheme 16).44
Homonuclear silver complex $[\text{Ag}_5(C_2\text{Ph})_6]^{-}$ (52) and heteronuclear silver-copper complex $[\text{Ag}_4\text{Cu}(C_2\text{Ph})_6]^{-}$ (53) have been obtained by the reactions of silver phenylacetylide with the linear complex anions $[\text{Ag}(C_2\text{Ph})_2]^{-}$ and $[\text{Cu}(C_2\text{Ph})_2]^{-}$, respectively (Figure 4).  

![Figure 4](image-url)

The reaction of $[\text{Cu}(C_2\text{Ph})_2]^{-}$ and $[\{\text{AuCu}(C_2\text{Ph})_2\}_n]^{-}$ (47) affords the cluster $[\text{Au}_2\text{Cu}(C_2\text{Ph})_4]^{-}$ (54) or $[\text{Au}_3\text{Cu}_2(C_2\text{Ph})_6]^{-}$ (55) depending on the molar ratio of the reactants. The pentanuclear cluster $[\text{N}^n\text{Bu}_4][\text{Au}_3\text{Cu}_2(C_2\text{Ph})_6]$ (55) is also obtained by the reaction of $[\text{N}^n\text{Bu}_4][\text{Au}(C_2\text{Ph})_2]$ with a mixture of $[\text{AuC}_2\text{Ph}]_n$ and $[\text{CuC}_2\text{Ph}]_n$. X-ray structural data for 55 reveals a trigonal bipyramidal arrangement of metal atoms with two copper atoms in the apical and three gold atoms in the equilateral positions. Each gold atom is $\sigma$-bonded to two acetylide groups in almost linear co-ordination while each
copper atom is asymmetrically π-bonded to three alkyne groups (Figure 5). In contrast, the reaction of [Cu(C2Ph)2]− and [{AuAg(C2Ph)2}n] (46) gives the expected complex [Au3Ag2(C2Ph)6]− (51) and the trinuclear [AuAg6Cu6(C2Ph)14]− (56) (Scheme 17).46

\[
\begin{align*}
[Cu(C2Ph)2]^- + 2[AuAg(C2Ph)2] & \rightarrow [Au2Ag2Cu(C2Ph)6]^-
\text{unstable} \\
[Au2Ag2Cu(C2Ph)6]^- & \rightarrow [AgCu(C2Ph)2] + [Au2Ag(C2Ph)4]^-
2[Au2Ag(C2Ph)4]^- & \rightarrow [Au3Ag2(C2Ph)6]^- + [Au(C2Ph)2]^-
[Au(C2Ph)2]^- + 6[AgCu(C2Ph)2] & \rightarrow [AuAg6Cu6(C2Ph)14]^-
\end{align*}
\]

Scheme 17.

A trinuclear cluster, [Au3AgCu(C2Ph)6]− (57) has been prepared by the reaction of [Au3Cu2(C2Ph)6]− (55) with a mixture of gold phenylacetylide and silver phenylacetylide. Complex 57 is also obtained by the addition of [Au3Ag2(C2Ph)6]− (51) to [{AuCu(C2Ph)2}n] (47) or by the reaction of [Au2Cu(C2Ph)4]− (54) with [{AuAg(C2Ph)2}n] (46). High nuclearity heterometallic cluster [AuAg6Cu6(C2Ph)14]− (56) has been synthesized by the reaction of a dichloromethane solution of polymeric [{Ag(C2Ph)}n], [{Cu(C2Ph)}n] and [Ag(C2Ph)2]. Other synthetic methods to prepare 56
include reaction of \([\text{Au}_3\text{Cu}_2(\text{C}_2\text{Ph})_6]^-\) (55) or \([\text{Au}_3\text{Ag}_2(\text{C}_2\text{Ph})_6]^-\) (51) with a mixture of [\{\text{Ag}(\text{C}_2\text{Ph})\}_n] \text{ and } [\{\text{Cu}(\text{C}_2\text{Ph})\}_n].^48\) Room temperature reaction of the linear complex \([\text{Ag}(\text{C}_2\text{Ph})_2]^-\) and a mixture of [\{\text{Cu}(\text{C}_2\text{Ph})\}_n] \text{ and } [\{\text{Ag}(\text{C}_2\text{Ph})\}_n] \text{ in dichloromethane affords the silver-copper heteronuclear cluster } [\text{Ag}_6\text{Cu}_7(\text{C}_2\text{Ph})_{14}]^- (57). \text{ When } [\text{Cu}(\text{C}_2\text{Ph})_2]^- \text{ or halide ions, } X^- \text{ (} X = \text{Cl, Br, I}) \text{ are treated with } [\{\text{Ag}(\text{C}_2\text{Ph})\}_n] \text{ and } [\{\text{Cu}(\text{C}_2\text{Ph})\}_n], \text{ cluster } 57 \text{ is obtained.}^47\text{ An X-ray diffraction study of cluster } 57 \text{ reveals a 13-atom bimetallic anionic cluster with two types of Cu atoms, one inside the body of the cluster and six on its surface. The surface atoms form a distorted trigonal bipyramidal geometry whereas the internal Cu atom linearly coordinates two C}_2\text{Ph groups in addition to six Cu-Ag bonding interactions and three tetranuclear } [\text{Ag}_2\text{Cu}_2(\text{C}_2\text{Ph})_4] \text{ subclusters (Figure 6).}^49\text{ Figure 6.} 

V

MIXED GROUP 6 - 9 METAL ACETYLIDE COMPLEXES

The metal acetylides \([\text{Cp(CO)}_2\text{MC}≡\text{CR}]\) (58a, \( M = \text{Fe, } \text{R = Ph}\) \text{ and } 58b-c, \( M = \text{Ru, } \text{R = Ph, } ^1\text{Bu, Me}\)) react with \([\text{Co}_2(\text{CO})_8]\) \text{ to form the acetylide-bridged trinuclear}
mixed metal complexes \([\text{Co}_2(\text{CO})_6\text{-}\mu-(\text{Cp(}\text{CO})_2\text{MC}≡\text{CR})]\) \((M = \text{Fe and } R = \text{Ph}, \text{59}; M = \text{Ru and } R = \text{Ph, } ^1\text{Bu, Me}, \text{60a-c})\) (Figure 7).\(^{50}\)

\[
\begin{align*}
\text{Cp(}\text{CO})_2\text{Fe} & \quad \text{Cp(}\text{CO})_2\text{Ru} \\
\text{Co(}\text{CO})_3 & \quad \text{Co(}\text{CO})_3 \\
\text{Ph} & \quad \text{R} \\
\text{59a} & \quad \text{60a; } R = \text{Ph} \\
\text{} & \quad \text{60b; } R = ^1\text{Bu} \\
\text{} & \quad \text{60c; } R = \text{Me}
\end{align*}
\]

Figure 7.

Compounds with a tetrahedral \(\text{C}_2\text{Co}_2\) core, \([\text{Co}_2(\text{CO})_6(\mu-\eta^2,\eta^2-MCCH)]\) \((M = \text{CpFe}(\text{CO})_2, \text{62a}; M = \text{Cp*Fe}(\text{CO})_2, \text{62b})\) have been obtained by the interaction of THF solution of ethynyliron complexes \([\{\text{CpFe}(\text{CO})_2\}-\text{C}≡\text{CH}]\) \((\text{61a})\) and \([\{\text{Cp*Fe}(\text{CO})_2\}-\text{C}≡\text{CH}]\) \((\text{61b})\) with \([\text{Co}_2(\text{CO})_8]\) respectively. The reaction of the ethynyldiiron complex \([\{\text{Cp*Fe}(\text{CO})_2\}-\text{C}≡\text{C}-\{\text{Cp*Fe}(\text{CO})_2\}]\) \((\text{63})\) with \([\text{Co}_2(\text{CO})_8]\) similarly affords the deep green adduct \([\text{Cp*Fe}[\text{Co(}\text{CO})_2]_2(\mu-\text{CO})_2(\mu-\mu^1,\eta^2,\eta^2-\text{CC-Fp*})]\) \((\text{64})\), which shows fluxional properties at ambient temperature (Scheme 18).\(^{51}\)

\[
\begin{align*}
\text{M} & \quad \text{C}≡\text{C} \quad \text{H} \quad \text{Co(}\text{CO})_8 \quad \text{THF} \\
61a; M = \text{CpFe}(\text{CO})_2 & \quad 62a; M = \text{CpFe}(\text{CO})_2 \\
61b; M = \text{Cp*Fe}(\text{CO})_2 & \quad 62b; M = \text{Cp*Fe}(\text{CO})_2
\end{align*}
\]

Scheme 18.

Photolytic reaction of \([[(\mu-\eta^2,\eta^2-M\text{-C}≡\text{C-H})\text{Co}_2(\text{CO})_6]]\) \((M = \text{CpFe}(\text{CO})_2, \text{62a}; M = \text{Cp*Fe}(\text{CO})_2, \text{62b})\) produces pentanuclear clusters \([[(\eta^5-\text{C}_{5}\text{R}_{5})_2\text{Fe}_2\text{Co}_3(\mu-\text{CCH})(\text{CO})_{10}]]\)
(R = H, 65a; R = Me, 65b), respectively, via an apparent addition reaction of a ($\eta^5$-C$_5$R$_5$)FeCo(CO)$_n$ fragment to 62. On the other hand, thermolysis of 62a gives the Fe-free hexacobalt cluster compound $[(\mu$-CH=CH)$\{($\mu_3$-C)Co$_3$(CO)$_9$)$\}_2$ (66), whereas when 62b is thermolyzed, the Fe-Co dimer without the C$_2$H ligand, [Cp*Fe(CO)(μ-CO)$_2$Co(CO)$_3$] (67) is obtained, in addition to the photolysis product 65b. Reduction of 62 with hydrosilanes gives 1,2 disilylethylene and the tetranuclear μ-vinylidene cluster $[(C_5R_5)FeCo_3(\mu_4$-C=CH$_2$)(CO)$_9$] (R = H, 68a; R = Me, 68b) by hydrosilylation and hydrometallation of the C$_2$H ligand, respectively (Scheme 19).$^{52}$

![Scheme 19. Interaction of the trinuclear ethynyl complexes [Co$_2$(CO)$_6$[$(\mu$-$\eta^5$-C$_5$R$_5$)Fe(CO)$_2$C≡CH] (R = H, 62a; R = Me, 62b) with [Fe$_2$(CO)$_9$] results in the formation of a tetranuclear vinylidene intermediate [Co$_2$Fe(CO)$_9$[$\mu_3$-C≡C(H)Fe($\eta^5$-C$_5$R$_5$)]Co$_2$(CO)$_{10}$] (69) which undergo thermal decarbonylation to produce the tetranuclear acetylide clusters $[(\mu_4$-C$_2$H)$[$($\eta^5$-C$_5$R$_5$)Fe]FeCo$_2$(CO)$_{10}$]$^a_b$ (Scheme 20).

Similarly, the addition reaction of [($\eta^5$-C$_5$R$_5$)Fe(CO)$_2$C≡CH] (61a,b) to the trimetallic
species RuCO₂(CO)₁₁ affords the ruthenium analogue of the vinylidene complex [Co₂Ru(CO)₉[μ₃-C=C(H)Fe(η⁵-C₅R₅)(CO)]₂ (71a,b), which decarbonylates to [(μ₄-C₂H)[(η⁵-C₅R₅)Fe]RuCo₂(CO)₁₀] (72a,b) (Scheme 21).⁵³

A formal replacement of (η⁵-C₅Me₄Et)Fe(CO) moiety of a triiron μ₃-η¹,η²,η²-acetylide cluster compound 73a by an isolobal Co(CO)₃ fragment occurs when cluster 73a reacts with [Co₂(CO)₈] (Scheme 22).⁵⁴a
The triiron acetylide cluster compound [PPN] [Fe₃(CO)₉C≡C(OAc)] (74a) [PPN = (Ph₃P)₂N⁺] reacts with [Fe(CO)₄]²⁻ at room temperature to produce the metalated acetylide cluster [PPN][Fe₃(CO)₉C≡CFe(CO)₄] (74b). Further metalation of 74b with excess [Co₂(CO)₈] produces a hexametallic cluster [PPN][Fe₃Co₃(C₂)(CO)₁₈] (76). The reaction proceeds by formation of two intermediate compounds, the dicarbide-containing cluster compound [PPN][Fe₄Co₂(C₂)(CO)₁₈] (75a) and the acetylide [PPN][Fe₂Co(CO)₉CCFe(CO)₄] (75b) (Scheme 23).
A number of iron-cobalt mixed metal cluster compounds have been obtained by sequential addition of [Co$_2$(CO)$_8$] and [Fe$_2$(CO)$_9$] to [Cp*Fe(CO)$_2$-C≡C≡C-H] (77) (Scheme 24). Their formation involves addition of a metal fragment to the C≡C bonds, reorganization of the cluster framework, transfer of metal fragments, valence isomerization of the C$_4$(H) linkage and 1,2-H shift of the C$_4$H ligand.
Sequential addition of [Co₂(CO)₈] and [Fe₂(CO)₉] to the butadiynediyl iron complex (78) results in formation of the mixed Fe/Co complexes 86 and 87 and the C₄-bridged Co₆ cluster 88 (Scheme 25).
Compound 77 also reacts with [Mo₂Cp₂(CO)₄] at room temperature or with [CpMoCo(CO)₇] at 50 °C to yield mixed metal acetylide complexes 89, [Cp*Fe(CO)₂C₄H{Cp₂Mo₂(CO)₄}] and 90, [Cp*Fe(CO)₂C₄H{CpMoCo(CO)₅}]. On further reaction with [Co₂(CO)₈], 89 gives 91 (Scheme 26).
Reaction of \([\text{Co}_2(\text{CO})_8]\) with the acetylide complexes, \([\text{M}(\text{C}≡\text{C}≡\text{CR})(\text{CO})_3\text{Cp}]\) (\(\text{M} = \text{Mo, W; R = H, Fe(CO)_2Cp}\)) \(\textbf{(92a-c)}\) afford simple adducts \(\textbf{(93a-c)}\) containing a \(\text{Co}_2(\text{CO})_6\) group attached to the least sterically-hindered \(\text{C}≡\text{C}\) triple bond (Scheme 27). In contrast, bis-cluster complexes \([\{\text{Cp(OC)}_8\text{Co}_2\text{M(μ}_3\text{C})\}C≡\text{C}\{\text{(μ}_3\text{C})\text{Co}_2\text{M′(CO)}_8\text{Cp}\}]\) (\(\text{M} = \text{M′ = Mo, W; M = Mo, M′ = W}\)) \(\textbf{(95a-c)}\) have been obtained when \([\text{M}(\text{C}≡\text{C}≡\text{CR})(\text{CO})_3\text{Cp}]\) (\(\text{M} = \text{Mo, W; R = M(CO)_3Cp (M = Mo, W), Fe(CO)_2Cp}\)) \(\textbf{(94a-c)}\) are used to react with \([\text{Co}_2(\text{CO})_8]\) (Scheme 28). Reaction between \([\text{Co}_2(\text{μ-dppm})(\text{CO})_6]\) and \([\{\text{W(CO)}_3\text{Cp}\}_2(\text{μ-C}_4)\}]\) affords \([\text{Co}_2(\text{μ-dppm})(\text{μ-}[\text{Cp(OC)}_3\text{W}]\text{C}_2\text{C}=\text{C}[\text{W(CO)}_3\text{Cp})(\text{CO})_4]\) \(\textbf{(97)}\). 56a

\[\begin{array}{c}
\text{Cp(OC)}_3\text{M}C≡C≡C≡CR & \xrightarrow{\text{Co}_2(\text{CO})_8} & \text{(CO)}_3\text{Co}C≡\text{C≡C≡R} \\
\text{92a; M = Mo; R = H} & & \text{93a; M = Mo; R = H} \\
\text{92b; M = W; R = H} & & \text{93b; M = W; R = H} \\
\text{92c; M = W; R = Fe(CO)_2Cp} & & \text{93c; M = W; R = Fe(CO)_2Cp}
\end{array}\]

Scheme 27.
Scheme 28.

Reaction of a THF solution of \([\{W(CO)_3Cp\}_2(\mu-C_8)\] and \([Co_2CO_8]\) gives mono and di-adducts, \([\{W(CO)_3Cp\}_2(\mu-C_8[Co_2(CO)_6]\}) (98a) and \([\{W(CO)_3Cp\}_2(\mu-C_8-[Co_2(CO)_6]\}) (98b) (Figure 8). Thermolytic reaction between \([\{W(CO)_3Cp\}_2(\mu-C_8)\] and \([Co_2(\mu-dppm)(CO)_6]\) under benzene reflux affords \([\{W(CO)_3Cp\}_2(\mu-C_8[Co_2(\mu-dppm)(CO)_4]\}) (99a) and two isomeric products, \([\{W(CO)_3Cp\}_2(\mu-C_8[Co_2(\mu-dppm)(CO)_4]\}) (99b) and \([\{W(CO)_3Cp\}_2(\mu-C_8[Co_2(\mu-dppm)(CO)_4]\}) (99c) (Figure 9).\textsuperscript{56b}
Deprotonation of the alkyne-bridged clusters \([\text{RuCo}_2(\text{CO})_9(\mu_3-\text{RC}≡\text{CH})]\) (100a-d) with triethylamine and further reaction with the organometallic halides \([\text{Cp(OCO)}_2\text{FeCl}]\) (101), \([\text{Cp(OCO)}_2\text{RuCl}]\) (102), \([\text{Cp(PPh}_3\text{)}\text{NiCl}]\) (103), and \([\text{Cp(OCO)}_3\text{MoCl}]\) (104) in presence of catalytic amounts of copper(I) iodide results in incorporation of the metal species as organometallic acetylides \(\text{MC}≡\text{CR}\) into the \(\text{RuCo}_2\text{M}\) metal frameworks (105-111) (Scheme 29). With acids, the resulting acetylide-bridged clusters are reconverted to the starting materials.\(^{57}\)
A pentanuclear heterometallic acetylide complex \([\text{Cp}_2\text{Mo}_2\text{Ru}_3(\text{CO})_{10}(\text{C}≡\text{CPh})_2]\) (113) has been prepared by the thermolysis reaction of a toluene solution of metal acetylide \([\text{CpMo}(\text{CO})_3(\text{C}≡\text{CPh})]\) with \([\text{Ru}_3(\text{CO})_{12}]\) (Figure 10). \(^\text{58}\)
Room temperature reaction of $[\text{W}(\equiv\text{C} \equiv \text{CH})(\text{CO})_3\text{Cp}]$ with the reactive $[\text{Ru}_3(\text{CO})_{10}(\text{NCMe})_2]$ forms initially $[\text{Ru}_3\{\mu_3\text{-HC}_2\text{C}=\text{C}[\text{W}(\text{CO})_3\text{Cp}]\}(\mu\text{-CO})(\text{CO})_9]$ (114), which readily transforms to $[\text{Ru}_3(\mu\text{-H})\{\mu_3\text{-C}_2\text{C}=\text{C}[\text{W}(\text{CO})_3\text{Cp}]\}(\text{CO})_9]$ (115) on benzene reflux and to 116 on reaction with excess of $[\text{W}(\equiv\text{C} \equiv \text{CH})(\text{CO})_3\text{Cp}]$ (Scheme 30).\textsuperscript{59} Similarly, reaction with $[\text{Ru}_3(\mu\text{-dppm})(\text{CO})_{10}]$ forms three interconverting isomers of $[\text{Ru}_3(\mu\text{-H})\{\mu_3\text{-C}_2\text{C}=\text{C}[\text{W}(\text{CO})_3\text{Cp}]\}(\mu\text{-dppm})(\text{CO})_{12}]$ (117-119) (Scheme 31).
Further reaction of [Ru$_3$(μ-H){μ$_3$-C$_2$C≡C[W(CO)$_3$Cp]}(CO)$_9$] (115) with [Ru$_3$(CO)$_{12}$] affords [{Ru$_3$(μ-H)(CO)$_9$}(μ$_3$-η$_2^2$,μ$_3$-η$_2^2$-C$_2$C$_2$){Ru$_2$W(CO)$_8$Cp}] (120a), while reaction with [Fe$_2$(CO)$_9$] gives an analogous product 120b, in which three of the ruthenium sites are partially occupied by a total of one or two iron atoms (Scheme 32). Treatment of [Ru$_3$(μ-H){μ$_3$-C$_2$C≡C[W(CO)$_3$Cp]}(CO)$_9$] (115) with [Co$_2$(CO)$_8$] forms a vinylidene cluster [{CoRu$_2$(CO)$_9$}(μ$_3$-η$_2^2$,μ$_3$-η$_2^2$-CCHC$_2$){CoRuW(CO)$_8$Cp}] (121) by a process involving the transfer of cluster-bound hydride to the C$_4$ ligand. 

Scheme 31.
Reaction of a dichloromethane solution of 1,6-bis(trimethylsilyl)hexa-1,3,5-triyne (122) with \([\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]\) yields \([\text{Os}_3(\text{CO})_9(\mu-\text{CO})(\mu_3-\eta^1,\eta^1,\eta^2-\text{Me}_3\text{SiC}_2\text{C}_2\text{C}_2\text{C}_2\text{SiMe}_3)]\) (123), which on reflux in heptane with \([\text{Ru}_3(\text{CO})_{12}]\) gives \([\text{Os}_3\text{Ru}(\text{CO})_{12}(\mu_4-\eta^1,\eta^2,\eta^1,\eta^2-\text{Me}_3\text{SiC}_2\text{C}_2\text{C}_2\text{SiMe}_3)]\) (124). However, thermal reaction between 122 and \([\text{Ru}_3(\text{CO})_{12}]\) forms a butterfly cluster \([\text{Ru}_4(\text{CO})_{12}(\mu_4-\eta^1,\eta^2,\eta^1,\eta^2-\text{Me}_3\text{SiC}_2\text{C}_2\text{C}_2\text{SiMe}_3)]\) (125a) and the ruthenole complex \([\text{Ru}_2(\text{CO})_6\{\mu-\eta^2,\eta^5-\text{C}\equiv\text{C}\equiv\text{SiMe}_3\}\{\text{C}≡\text{C}≡\text{SiMe}_3\}]\) (125b). In the room temperature reaction between cluster 125a and \([\text{Co}_2(\text{CO})_8]\), a slippage of the butterfly cluster core along the hexatriyne chain occurs and \([\{\text{Ru}_4(\text{CO})_{12}\}\{\text{Co}_2(\text{CO})_6\}(\mu_4-\eta^1,\eta^2,\eta^1,\eta^2;\mu-\eta^2,\eta^2-\text{Me}_3\text{SiC}_2\text{C}_2\text{C}_2\text{SiMe}_3)]\) (126) is obtained (Scheme 33).
Scheme 33.

Reaction of a benzene solution of [{Cp(PPh₃)₂Ru}₂(μ-C≡C)₃] with [Co₂(CO)₈] or [Co₂(μ-dppm)(CO)₆] gives [{Ru(PPh₃)₂Cp}₂{μ-C≡C₂{Co₂(CO)₆}(C≡C)}] (127a) and [{Ru(PPh₃)₂Cp}₂{μ-C≡C₂{Co₂(μ-dppm)(CO)₄}C≡CC≡C}] (127b), while [{Ru(PPh₃)₂Cp}₂{μ-C≡C₂{Co₂(μ-dppm)(CO)₄}C≡CC≡C}] (127c) has been obtained from a thermal reaction of [{Cp(PPh₃)₂Ru}₂(μ-C≡C)₄] with [Co₂(μ-dppm)(CO)₆] (Scheme 34).³⁵b
Scheme 34.

A heterometallic CoRu₅ cluster, \([\text{CoRu}_5(\mu_4-\text{PPh})(\mu_4-\text{C}_2\text{Ph})(\mu-\text{PPh}_2)(\text{CO})_{12}(\eta^5-\text{C}_5\text{H}_5)]\) (129) has been isolated from the reaction between \([\text{Ru}_5(\mu_5-\text{C}_2\text{PPh}_2)(\mu-\text{PPh}_2)(\text{CO})_{13}]\) (128) and \([\text{Co}(\text{CO})_2(\eta-\text{C}_5\text{H}_5)]\) (Figure 11). Its structure consists of a square pyramidal Ru₅Co unit, and a Ru(Ph)C₂-group attached to it through two ruthenium and one cobalt atoms.

The reaction between \([\text{Ru}_3(\mu_3-\eta^2-\text{PhC}_2\text{C}_2\text{Ph})(\mu-\text{CO})(\text{CO})_9]\) and \([\text{Co}_2(\text{CO})_8]\) affords a pentametallic cluster \([\text{Co}_2\text{Ru}_3(\mu_5-\eta^2,\eta^2-\text{PhC}_2\text{C}_2\text{Ph})(\text{CO})_{14}]\) (130) in quantitative yield. The X-ray determined molecular structure consists of a Co₂Ru₃ bow-tie cluster straddled by the PhC₂C₂Ph ligand, the two C≡C triple bonds are attached to the five metal atoms by \(2\sigma(2\text{Ru})\) and \(\pi(\text{Co})\) bonding modes (Figure 12).
A dihydride complex \([\text{Cp}^*\text{Rh}(\mu_2-1,2-S_2C_6H_4)(\mu_2-H)\text{Ru(H)(PPh}_3)_2]\) (131) reacts with excess of \(p\)-tolylacetylene at room temperature to afford a mixture of \(cis\) and \(trans\) isomers of alkynyl hydride complex, \([\text{Cp}^*\text{Rh}(\mu_2-1,2-S_2C_6H_4)(\mu_2-H)\text{Ru(C≡CTol-}
\text{p})(\text{PPh}_3)_2]\) (132a). On the other hand, reaction of 131 with trimethylsilylacetylene gives, exclusively the \(cis\) isomer of \([\text{Cp}^*\text{Rh}(\mu_2-1,2-S_2C_6H_4)(\mu_2-H)\text{Ru(C≡CSiMe}_3)(\text{PPh}_3)_2]\) (132b) (Scheme 35). The mechanism involves hydrogen transfer from 131 to the alkyne, followed by oxidative addition of a second equivalent of the alkyne to the dinuclear core of \([\text{Cp}^*\text{Rh}(\mu_2-1,2-S_2C_6H_4)\text{Ru(PPh}_3)_2]\) unit.

Figure 12.

Thermal reaction of \([\text{Fe}_3\text{(CO)}_9(\mu_3-E)_2]\), \((E=\text{Se, 133a; Te, 133b})\) with \(\left[(\eta^5-C_5H_5)\text{M(CO)}_3(\text{C≡CPh})\right]\) \((M=\text{Mo, W, 134a, b})\) in the presence of trimethylamine-N-oxide (TMNO), in acetonitrile solvent yield the mixed-metal clusters \(\left[(\eta^5-C_5H_5)\text{MFe}_2(\mu_3-E)_2(\text{CO})_7(\eta^1-\text{CCPh})\right]\) \((E=\text{Se and } M=\text{Mo, 135}; E=\text{Se and } M=\text{W, 136}; E=\text{Te and } M=\text{Mo, 137}; E=\text{Te and } M=\text{W, 138})\) bearing \(\eta^1\)-acetylide groups. Further
reaction of 135 or 137 with dicobaltoctacarbonyl at room temperature gives the mixed-metal cluster compound \([\eta^5-C_5H_5]MoFe_2Co_2(\mu_3-E)_2(CO)_9(\eta-CCPh)\) (139, 140) (Scheme 36).  

When a toluene solution containing \([Fe_3(CO)_9(\mu_3-E)_2]\) (E = S, Se or Te) and \([W(\eta^5-C_5Me_5)(CO)_3(CCPh)]\) is subjected to reflux, mixed metal clusters \([W_2Fe_3(\eta^5-C_5Me_5)_2(\mu_3-E)_2\{\mu_4-CC(Ph)C(Ph)C}\}]\) (E = S, 141; Se, 142) are formed. 64 The molecule is made up of a Fe₃W₂ metal core which is enveloped by terminal and bridging carbonyl ligands and a \(\mu_4\)-\{CC(Ph)C(Ph)C\} unit. The five metal atoms are arranged in the form of an open triangular bipyramidal polyhedron wherein the three Fe atoms occupy the basal plane while the two W centres are at the axial positions (Scheme 37).
When a toluene solution of the acetylide complex, \([\text{Mo}(\eta^5-\text{C}_5\text{H}_5)(\text{CO})_3(\text{C}≡\text{CPh})]\) is thermally reacted with \([\text{Fe}_3(\text{CO})_9(\mu_3-\text{E})_2]\) (\(\text{E} = \text{S}, \text{Se}\)), formation of mixed metal clusters, \([(\eta^5-\text{C}_5\text{H}_5)_2\text{Mo}_2\text{Fe}_3(\text{CO})_8(\mu_3-\text{E})_2\{\mu_5-\text{CC(Ph)CC(Ph)}\}\}] (\(\text{E} = \text{S}, 143; \text{Se}, 144\)), \([(\eta^5-\text{C}_5\text{H}_5)_2\text{Mo}_2\text{Fe}_4(\text{CO})_9(\mu_3-\text{E})_2(\mu_4-\text{CCPh})_2]\) (\(\text{E} = \text{S}, 145; \text{Se}, 146\)) and \([(\eta^5-\text{C}_5\text{H}_5)_2\text{Mo}_2\text{Fe}_3(\text{CO})_7(\mu_3-\text{E})_2\{\mu_5-\text{CC(Ph)C(Ph)C}\}\}] (\(\text{E} = \text{S}, 147; \text{Se}, 148\)) are observed featuring head to tail coupling of two acetylide groups, two uncoupled acetylide groups and a tail to tail coupling of two acetylide groups, respectively, on the chalcogen bridged Fe/Mo cluster framework (Scheme 38). The head-to-tail acetylide-coupled \(\mu_5\)-{CC(Ph)CC(Ph)} unit of 143/144 acts as an eight electron donor to the cluster core. The basic cluster geometry of 147/148 consists of a twisted bow-tie type \(\text{Fe}_3\text{MoE}\) unit, one of the faces is capped by a second Mo atom, and the second face is capped by one terminal carbon atom of an \{CC(Ph)C(Ph)C\} unit.
Under similar thermolytic conditions, formation of clusters \([(\eta^5-C_5H_5)W_2Fe_3(CO)\eta(\mu_3-E)_2(\mu_3-\eta^2-CCPh)(\mu_3-\eta^1-CCH_2Ph)]\) (E = S, 149; Se, 150) and \([(\eta^5-C_5H_5)WF_{e2}(CO)\eta(\mu-CCPh)]\) (151) has been observed in reactions of \([W(\eta^5-C_5H_5)(CO)_{\eta}(\mu-3-E)]\) (E = S, Se) (Scheme 39).65
When a benzene solution containing \([\text{Fe}_3(\text{CO})_9(\mu_3-\text{S})_2], [\eta^5-\text{C}_5\text{R}_5\text{Mo}(\text{CO})_3(\equiv\text{CPh})] (\text{R} = \text{H, Me}), \text{H}_2\text{O} \text{ and Et}_3\text{N} \text{ are photolysed with continuous bubbling of argon a rapid formation of cluster \([\eta^5-\text{C}_5\text{R}_5\text{MoFe}_2(\text{CO})_6(\mu_3-\text{S})(\mu-\text{SCCH}_2\text{Ph})]\) (\text{R} = \text{H}, 152; \text{R} = \text{Me}, 153) \text{ is observed (Scheme 40).}^{66} \text{ The H}_2\text{O molecule acts as a source of protons as confirmed by labeling experiment, and Et}_3\text{N works as a phase transfer catalyst}

\[\text{Et}_3\text{N}:\text{H}_2\text{O} \rightarrow \text{Et}_3\text{N} \text{ and } \text{H}_2\text{O}\]

\[\text{Scheme 40.}\]
Photolytic reaction of metal acetylide complexes with simple metal carboxyls has been used to form heterometallic acetylide bridged complexes. For instance, photolytic reaction of a benzene solution of [Fe(CO)₅] and [(η⁵-C₅R₅)Mo(CO)₃(C≡CPh)] (R = H, Me) under continuous bubbling of argon results in a rapid formation of [(η⁵-C₅R₅)Fe₂Mo(CO)₈(μ₃-η¹:η²:η²-CPh)] (R = H, 154; Me, 155) and [(η⁵-C₅H₅)Fe₃Mo(CO)₁₁(μ₄-η¹:η¹:η²:η¹-CPh)] (156) (Scheme 41). The structure of 154 consists of a MoFe triangle and a μ₃-η¹,η²,η² acetylide ligand. The molecular structure of 156 comprises of an open Fe₃Mo butterfly arrangement with an acetylide group bonded in μ₃-η¹ mode.

Scheme 41.

However, when a benzene solution containing a mixture of [(η⁵-C₅Me₅)Mo(CO)₃(C≡CPh)], [Fe(CO)₅] and [PhC≡CH] are photolysed, formation of alkyne-acetylide coupled mixed metal cluster [(η⁵-C₅Me₅)Fe₂Mo(CO)₇(μ₃-C(H)C(Ph)C(Ph)=C)] (157) is obtained in moderate yield (Scheme 42). The molecular structure of 157 consists of a Fe₂Mo triangle with a {C(H)=C(Ph)C(Ph)=C} ligand triply bridging the Fe₂Mo face.

Scheme 42.
When a mixed metal cluster \([\text{Fe}_2\text{Ru}(\text{CO})_9(\mu_3-\text{E})_2]\) (\(\text{E} = \text{S} \text{ or Se}\)) has been reacted with \([(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3(\text{C}=\text{CPh})]\) (\(\text{M} = \text{Mo or W}\)) in toluene reflux condition, heterometallic clusters \([(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2\text{RuM}_2(\text{CO})_6(\mu_3-\text{E})_2\{\mu_4-\text{CC(Ph)(Ph)C}\}] (\(\text{M} = \text{Mo and E = S, 158; M = Mo and E = Se, 159; M = W and E = S, 160; M = W and E = Se, 161}\) and \([(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2\text{Ru}_2\text{M}_2(\text{CO})_9(\mu_3-\text{E})_2\{\mu_3-\text{CCPh}\}_2]\) (\(\text{M} = \text{W and E = S, 162; M = W and E = Se, 163}\), have been isolated from the reaction mixtures (Scheme 43). The molecular structure of 158 consists of an open trigonal bipyramidal \(\text{Fe}_2\text{RuMo}_2\) metal core enveloped by terminal and bridging carbonyl ligands and a \(\mu_4-\{\text{CC(Ph)(Ph)C}\}\) unit. Structure of 162 can be described as a \(\text{FeRuW}_2\)S distorted square pyramid core, in which the WRu edge is bridged by a \(\text{Fe}(\text{CO})_3\)S and the RuFe edge by a \(\text{Ru}(\text{CO})_3\) unit. One acetylide group caps the \(\text{W}_2\text{Ru}\) face in a \(\eta^1, \eta^2, \eta^2\) fashion and another caps the open \(\text{FeRuW}\) face in a similar bonding mode.

When a toluene solution of a Fe/W mixed metal cluster, \([\text{Fe}_2\text{W}(\text{CO})_{10}(\mu_3-\text{S})_2]\) is heated at 80 °C with the tungsten acetylide complex \([(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3(\text{CCPh})]\), the \(\text{Fe}_2\text{W}_3\) mixed metal \([(\eta^5\text{-C}_5\text{H}_5)_2\text{W}_3\text{Fe}_2\text{S}_2(\text{CO})_{12}(\text{CCPh})_2]\) (164) was isolated (Scheme 44). Its structure consists of a \(\text{Fe}_2\text{WS}_2\) trigonal bipyramidal unit in which the W atom...
is attached to two separate molecules of \([\eta^5-C_5H_5]W(CO)_3(\text{CCPh})]\) through the acetylide group.

![Scheme 44.](image)

When \([\text{Fe}_2\text{Mo(CO)}_{10}(\mu_3-\text{S})_2]\) is made to interact with \([\eta^5-C_5\text{Me}_5]W(CO)_3(\text{C≡CPh})]\) under mild thermolytic condition in argon atmosphere, a mixed metal acetylide cluster \([\eta^5-C_5\text{Me}_5]\text{MoWFe}_4(\mu_3-\text{S})_3(\mu_4-\text{S})(\text{CO})_{14}(\text{CCPh})]\) \((\text{165})\) is isolated (Scheme 45).\(^70\) Molecular structure of 165 consists of a \{Fe\text{2MoS}_2\} distorted square pyramid unit in which the basal Mo atom is bonded to the two sulphur atoms of an open \{Fe\text{2S}_2\} butterfly unit and a \{\eta^5-C_5\text{H}_5\}W(CO)_2\} group. A single phenylacetylide ligand bridges the Mo-W bond in \(\mu-\eta^1,\eta^2\) fashion.

![Scheme 45.](image)

Photolysis of a benzene solution of a mixture of \([\text{Fe}_3(\text{CO})_9(\mu_3-\text{S})_2]\), \([\eta^5-C_5\text{Me}_5]\text{M(CO)}_3(\text{C≡CPh})\] (\(\text{M} = \text{Mo, W}\)) and \(\text{HC≡CR}\) (\(\text{R} = \text{Ph, n-Bu and Fc}\)) (\(\text{Fc} = \text{ferrocene}\)) forms two types of clusters depending on the nature of acetylene used. When
phenylacetylene or \(n\)-butyl acetylene are used, clusters \([(\eta^5-C_5Me_5)MFe_3(CO)_6(\mu_3-S)\{\mu_3-C(H)=C(R)S\}(\mu_3-CCPh)]\) \((166 - 169)\) are formed (Scheme 46).\(^7\) In these compounds a new C–S bond is formed yielding a \{HC=C(R)S\} ligand which bridges a \{MFe_2\} face of the cluster framework. Use of ferrocenylacetylene in the reaction medium results in the formation of \([(\eta^5-C_5Me_5)MFe_3(CO)\gamma(\mu_3-S)\{\mu_3-C(Fe)=C(H)S\}(\mu_3-CCPh)]\) \((170, 171)\) in which a formal switching of the \(\alpha\) and \(\beta\) carbons of the coordinated acetylide moiety is observed (Scheme 47). Nature of the sulfido-acetylene coupling may be an important factor in determining which cluster type is formed, with the bulky ferrocene group disfavouring the expected S–C\(_\text{subs}\) coupling. The structure of 166 can be described as consisting of a \{MoFe_3\} butterfly core in which the hinge is composed of the Mo and a Fe atom. One \{MoFe_2\} face is capped by \(\mu_3\)-S ligand as well as an unusual \{HC=C(Ph)S\} ligand. The second butterfly face is capped by a \{\eta^1: \eta^2: \eta^2-CCPh\} group. The wing-tip Fe atoms bear two and three carbonyl groups each and the hinge Fe atom has one terminal carbonyl bonded to it.

![Scheme 46](image-url)

Compound 170 consists of a Fe_3 triangle, which is capped by a sulfido ligand. One of the iron atoms is bonded to a \{\((\eta^5-C_5Me_5)W\)\} group, and the Fe–W bond is bridged by a ferrocenylacetylene group. A second sulfido ligand triply - bridges the terminal carbon atom of this acetylene with the tungsten and one of the iron atoms. A \{CCPh\} group forms an unusual quadruple bridge in which the \(\beta\) - carbon of the
acetylide is now $\eta^1$-bonded to the tungsten atom. Seven terminal carboxyls distributed on the three iron atoms and on the tungsten atom complete the ligand environment of the cluster.\footnote{72}

Scheme 47.

Reactions between $[\text{Ir}(\text{C}_2\text{Ph})(\text{CO})_2(\text{PPh}_3)_2]$ and iron carboxyls (Fe(CO)$_5$ or Fe$_2$(CO)$_9$) result in the formation of iron-iridium clusters $[\text{Fe}_2\text{Ir}(\mu_3-\text{C}_2\text{Ph})(\text{CO})_{9-n}(\text{PPh}_3)_n]$ ($n = 1$, \footnote{172} 2, \footnote{173}) and $[\text{FeIr}_2(\mu_3-\text{PhC}_2\text{C}_2\text{Ph})(\text{CO})_{12}(\text{PPh}_3)_2]$ (\footnote{174}). The Rh analogue of \footnote{172} has been obtained by a similar reaction (Scheme 48). Substitution of the iridium bound PPh$_3$ by PEt$_3$ and addition of PEt$_3$ to C$_\alpha$ of the acetylide ligand in \footnote{172} gives zwitterionic $[\text{Fe}_2\text{Ir}(\mu_3-\text{PhC}_2\text{PEt}_3)(\text{CO})_8(\text{PEt}_3)]$ (\footnote{177}), which on heating converts to $[\text{Fe}_2\text{Ir}(\mu_3-\text{C}_2\text{Ph})(\text{CO})_7(\text{PEt}_3)_2]$ (\footnote{179}) by migration of PEt$_3$ from carbon to iridium (Scheme 49).\footnote{73} Analogous complexes containing cluster-bound PMe$_2$Ph and P(OMe)$_3$ have also been obtained by such type of reaction.
Scheme 48.

Scheme 49.
Reaction of Fe$_2$Ir cluster (172) with dihydrogen gives complex 184, whereas, stepwise addition of H$^-$ and H$^+$ results in the formation of 184 and the isomeric hydrido alkyne derivative 185 (Scheme 50).^74

Scheme 50.

Treatment of the triruthenium imido complex [Ru$_3$(CO)$_{10}$(μ$_3$-NPh)] (186) with metal hydride complex [LW(CO)$_3$H] in refluxing toluene produces a trinuclear heterometallic imido cluster, [LWRu$_2$(CO)$_8$(μ-H)(μ$_3$-NPh)] (L=Cp, 187a; Cp*, 187b), which on reaction with tungsten acetylide [CpW(CO)$_3$CCPh] produces a tetranuclear imidoalkyne complex [LCpW$_2$Ru$_2$(CO)$_6$(μ-NPh)(μ-η$^2$-CH=CHPh)] (L=Cp, Cp*) (188a,b) (Scheme 51).^75
Convenient and widely applicable synthetic routes to trinuclear heterometallic acetylide complexes \([LMM'2(CO)\_8(CCR)]\) have been developed which involve the reaction of metal acetylide \([LM(CO)\_3(CCR)]\) (L = Cp or Cp*; M = W or Mo; R = Ph, C\(_5\)H\(_4\)F, C\(_5\)H\(_4\)OMe, \(^1\)Bu and \(^\text{n}\)Pr) with \([\text{Os}_3(CO)\_10(NCMe)]\) or \([\text{Ru}_3(CO)\_12]\). Thus, reaction of \([\text{CpW}(CO)\_3C\equiv CR]\) (R = Ph, \(^1\)Bu) with \([\text{Os}_3(CO)\_10(CH_3CN)_2]\) in refluxing toluene produces tetranuclear mixed-metal acetylide complexes \([\text{CpWOs}_3(CO)\_11(C\equiv CR)]\) (R = Ph, \(189a\); \(^1\)Bu, \(189b\)).\(^{76}\) The molybdenum analogue \([\text{MoOs}_3(CO)\_11(C\equiv CPh)(\eta_5-C_5H\_5)]\) (190) has also been prepared by a similar procedure. Carbylonylation of \(189a, b\) at 120 °C under pressurized CO induces cluster fragmentation, giving \([\text{CpWOs}_2(CO)\_6(C\equiv CR)]\) (191a,b) in 80-85 % yield. Hydrogenation of \(189b\) produces an alkylidyne complex, \([\text{CpWOs}_3(CO)\_11(\mu_3-CC_5H\_11)]\) (192), while treatment of \(189a\) with excess of ditolylacetylene affects the scission of the acetylide ligand to give \([\text{CpWOs}_3(CO)\_8(\mu_3-CPh){\mu_4-\eta^5-C(C_2Tol_2)\_2}]\) (193) (Scheme 52).\(^{77}\)
In contrast, treatment of complexes 189 a and b with alkynes containing electron-withdrawing groups produces the tetranuclear alkyne-acetylide coupling products [CpWOs3(CO)10{CR'CR'CCR}] (R = Ph and R' = CO2Me, 194a; R = Ph and R' = CO2Et, 194b; R = nBu and R' = CO2Et, 194c) and [CpWOs3(CO)9{CCRCR'CR'}] (R = Ph and R' = CO2Me, 195a; R = Ph and R' = CO2Et, 195b; R = nBu and R' = CO2Et, 195c) (Figure 13)."
The cluster acetylide complexes \([\text{MOs}_3(\text{CO})_{11}(C\equiv\text{CPh})(\eta_5-\text{C}_5\text{H}_5)]\) (M = Mo, 190; M = W, 189a) react with \([\text{Mo(CO)}_3(\text{C}\equiv\text{CPh})(\eta_5-\text{C}_5\text{H}_5)]\) to give planar pentanuclear complexes \([\text{MMoOs}_3(\text{CO})_{11}(\text{CCPhCCPh})(\eta_5-\text{C}_5\text{H}_5)_2]\) (M = Mo, 196; M = W, 197) which contain a C\(_4\) hydrocarbon fragment derived from head-to-tail coupling between the two acetylide fragments. Reaction of complex 190 with \([\text{W(CO)}_3(\text{C}\equiv\text{CPh})(\eta_5-\text{C}_5\text{H}_5)]\) does not produce the coupling product but induces C-C bond scission of \([\text{W(CO)}_3(\text{C}\equiv\text{CPh})(\eta_5-\text{C}_5\text{H}_5)]\) giving a novel carbide-alkylidyne complex \([\text{MoWOs}_3(\text{CO})_8(\mu_4-\text{C})(\mu_3-\text{CPh})(\text{CCPh})(\eta_5-\text{C}_5\text{H}_5)_2]\) (198) (Figure 14). 78

![Diagram](image1)

**Figure 14.**

Treatment of the acetylide complexes \([\text{CpWOs}_2(\text{CO})_8(\text{C}\equiv\text{CR})], (R = \text{Ph}, 191\text{a}; R = ^{n}\text{Bu}, 191\text{b})\) with Me\(_3\)NO in acetonitrile followed by reaction with various disubstituted alkynes, \(\text{C}_2\text{R'}_2\) in refluxing toluene facilitates acetylide-alkyne coupling and formation of two isomeric trinuclear complexes, \([\text{CpWOs}_2(\text{CO})_{12}\{\text{C(R')}\text{C(R')}\text{CCR}\}]\) (R = Ph and R' = Tol, 199; R = ^{n}\text{Bu} and R' = Tol, 200; R = Ph and R' = CO\(_2\text{Et}, 201; R = ^{n}\text{Bu} and R' = \text{CO}_2\text{Et}, 202; R = \text{Ph} and R' = \text{CF}_3, 203\) (Scheme 53). 79

![Diagram](image2)

**Scheme 53.**
When [Ru₃(CO)₁₂] has been used to react with [CpW(CO)₃C≡CPh] in refluxing toluene, [CpWRu₂(CO)₈(C≡CPh)] (204) is isolated. In solution the variable temperature NMR suggests that the acetylide ligand of 204 undergoes a 360° rotation on the face of the WRu₂ triangle.⁸⁰ With excess of [CpW(CO)₃C≡CR], 204 gives two heterometallic acetylide clusters [Cp₂W₂Ru₂(CO)₉(CCRCCR)] (R = Ph, 205a; R = p-C₆H₄F, 205b), with C-C bond coupling and [Cp₂W₂Ru₂(CO)₆(C≡CR)₂] (R = Ph, 206a; R = p-C₆H₄F, 206b), without C-C bond coupling (Scheme 54).⁸¹

![Scheme 54.](image)

In a similar reaction, thermolysis of a mixture of [Ru₃(CO)₁₂] and [CpMo(CO)₃C≡CPh] in a molar ratio 2:3 in refluxing toluene gives the trinuclear acetylide derivative [CpMoRu₂(CO)₈C≡CPh] (207) and a pentanuclear heterometallic acetylide complex [Cp₂Mo₂Ru₃(CO)₁₀(C≡CPh)₂] (208) (Figure 15).⁸²

![Figure 15.](image)

Condensation of triosmium alkyne complexes [Os₃(CO)₁₀(C₂R₂)] (R = Tol, 209a; R = Me, 209b) with mononuclear tungsten acetylide complexes [LW(CO)₃C≡CR'], (L =
Cp, Cp*, R’ = Ph, tBu) generates six WOs3 cluster complexes via 1:1 combination of the starting materials. Treatment of [Os3(CO)10(C2Me2)] with [CpW(CO)3C≡CPh] under refluxing toluene forms two heterometallic complexes

\[ \text{[CpWOs3(CO)9\{CC(Ph)C(Me)C(Me)\}] (210a)} \text{ and} \]
\[ \text{[CpWOs3(CO)10\{C(Me)C(Me)CC(Ph)\}] (211).} \] On the other hand, thermal reaction of

\[ \text{[Os3(CO)10(C2Tol2)] with [CpW(CO)3C≡CPh] gives} \]
\[ \text{[CpWOs3(CO)9\{CC(Ph)C(Tol)C(Tol)\} (210b) and [CpWOs3(CO)9(CCTolCTol)(\mu_3-CPh)] (212b), whereas only one heterometallic cluster,} \]
\[ \text{[LWOs3(CO)9\{CC(R’)C(Tol)C(Tol)\}] (L = Cp*, R’ = Ph, 210c; L = Cp and R’ = tBu, 210d) is obtained on thermolysis of [Os3(CO)10(C2Tol2)] with [LW(CO)3C≡CR’] (L = Cp*, R’ = Ph or L = Cp, R’ = tBu).} \] Addition of 1:1 molar equivalent of [Me3NO] to compound 211, followed by heating under refluxing toluene affords

\[ \text{[CpWOs3(CO)9(CCMeCMe)(\mu_3-CPh)] (212a).} \] When toluene solution of

\[ \text{[Os3(CO)10(C2Me2)] is thermally reacted with [Cp*W(CO)3C≡CPh], five heterometallic clusters are formed (210e, 212e, 213, 214 and 215) (Figure 16).} \]
Thermolysis of a toluene solution of complex 212b with ditolylacetylene yields the planar clusters \([\text{CpWOs}_3(\text{CO})_8(\mu_3-\text{CPh})\{\text{C(Tol)C(Tol)CC(Tol)C(Tol)}\}]\) (216a). On the other hand, reaction of 212e in refluxing xylene solvent gives \([\text{Cp}^*\text{WOs}_3(\text{CO})_8(\mu_3-\text{CPh})\{\text{C(Tol)C(Tol)CC(Me)C(Me)}\}]\) (216b), \([\text{WOs}_3(\text{C}_5\text{Me}_5)(\text{CO})_{12}(\mu_3-\text{CPh})\{\text{CMeCMeCC(Tol)C(Tol)}\}]\) (217) and 218 (Scheme 55). \(^8^4\)
Treatment of 211 with Me₃NO followed by thermolysis in refluxing toluene yields the spiked triangular cluster [WO₅Cp(CO)₉(μ-H){CMeCMChC(μ₂-η²-C₆H₄)}] (219) as a major product, which, on further thermolysis converts to a butterfly cluster [WO₅Cp(CO)₉{CMeCMChC(μ₂-η²-C₆H₄)}] (220) and then to a tetrahedral cluster [WO₅Cp(CO)₈{CMeCMChC(μ₂-η²-C₆H₄)}] (221) via hydride migration followed by loss of CO (Scheme 56).
The tetranuclear clusters 222-225 shown in Scheme 57 are formed in the reaction of \([\text{Cp}^*\text{W(CO)}_3\text{C}≡\text{CR}] (R = \text{Ph}, \text{^nBu}, \text{CH}_2\text{OMe}, \text{CH}_2\text{Ph})\) with \([\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]\). While 222 is stable in a single isomeric form, cluster 223-225 exist in two interconverting isomeric forms on heating. When 222 is treated with Me_3NO, followed by heating to reflux in toluene, 226 is obtained. On similar treatment, complex 223 affords two isomeric vinylidene clusters \([\text{Cp}^*\text{WOs}_3(\mu_4-C)(\mu-H)(\mu-C\text{CH}^\text{nPr})(\text{CO})_9]\) (227a,b) as an inseparable mixture, while thermal reaction of 224 a,b with Me_3NO forms two methoxy derivatives \([\text{Cp}^*\text{WOs}_3(\mu_4-C)(\mu-H)(\mu-C\text{CHO}Me)(\text{CO})_9]\) (228a,b) (Scheme 58).

Scheme 57.
Thermal reaction of 227 with CO in toluene leads to regeneration of 223a,b, while 228 gives 224a,b along with an alkenyl cluster [Cp*WOs3(μ₄-C)(μ-CHCHOME)(CO)₁₀] (229) (Scheme 59).[^86]

[^86]: Thermal reaction of 227 with CO in toluene leads to regeneration of 223a,b, while 228 gives 224a,b along with an alkenyl cluster [Cp*WOs3(μ₄-C)(μ-CHCHOME)(CO)₁₀] (229) (Scheme 59).[^86]

A mixture of two isomers (230 and 231) of a benzofuryl complex [Cp*WOs₃(μ₄-C)(μ-H)₂(μ-C₈H₅O)(CO)₉] is formed on thermolysis of 225. Clusters 230 and 231 have also been isolated on thermolysis of a 1:1 mixture of [Cp*W(CO)₃C≡CCH₂OPh] with [Os₃(CO)₁₀(NCMe)₂] in refluxing toluene (Scheme 60).[^86]
Scheme 60.

Hydrogenation of the CH₂OMe derivative, 224 affords four compounds (232-235) (Scheme 61).[^86]

Scheme 61.

When the carbide cluster complex \([\text{Cp}^*\text{WOs}_3(\mu_4-C)(\mu-H)(\text{CO})_{11}]\) (236) is treated with excess of Me₃NO and 4-ethynyltoluene, the formation of an alkylidyne compound \([\text{(C₅Me₅)WOs}_3(\mu_3-CCHCHTol)(\text{CO})_{11}]\) (237) is observed, while, the corresponding reaction of 236 with 3-phenyl-1-propyne affords alkenyl carbido cluster \([\text{(C₅Me₅)WOs}_3(\mu_4-C)(\text{CHCHCH₂Ph})(\text{CO})_{10}]\) (238) and an alkylidyne compound \([\text{(C₅Me₅)WOs}_3[\mu_3-\text{CC(CH₂Ph)(CH₂)}](\text{CO})_{10}]\) (239) (Scheme 62).[^87]
On the other hand, coupling of 236 with an electron deficient alkyne, diisopropyl acetylenedicarboxylate (DPAD) results in the formation of a dimetallaallyl cluster [Cp*WOs$_3$(CO)$_{10}$-C$_3$H(CO$_2$iPr)$_2$] (240), which undergoes C-C metathesis to afford a second dimetallaallyl cluster (241) (Scheme 63). Trace amount of a related vinyl-alkylidene cluster 242 has been observed in the reaction of 236 with DPAD in refluxing toluene solution.
Reaction of [CpWOs$_2$(CO)$_8$(C≡CPh)] with 1.2 equiv of Me$_3$NO in a mixture of dichloromethane-acetonitrile solvent at room temperature followed by in situ reaction with hydride complexes [LW(CO)$_3$H] (L = Cp and Cp*) in refluxing toluene produces the acetylide cluster complexes [CpLW$_2$Os$_2$(CO)$_9$(CCPh)(μ-H)] (L = Cp, 243a; L = Cp*, 243b) and vinylidene cluster complexes [CpLW$_2$Os$_2$(CO)$_9$(CCHPh)] (L = Cp, 244a; L = Cp*, 244b). Heating of the acetylide or vinylidene complex in refluxing toluene induces a reversible rearrangement giving a mixture of two isomeric complexes (Scheme 64).
Molybdenum analogue, \([\text{Cp}_2\text{Mo}_2\text{Os}_2(\text{CO})_9(\text{CCPh})(\mu-H)]\) (243c) has been obtained by the addition of \(\text{Me}_3\text{NO}\) to dichloromethane-acetonitrile solution of \([\text{CpMoOs}_2(\text{CO})_8(\text{CCPh})]\), followed by a thermolytic reaction with \([\text{CpW}(\text{CO})_3\text{H}]\).\(^{89}\)

Treatment of the carbido cluster \([\text{Ru}_5(\mu_5-C)(\text{CO})_{15}]\) with \(\text{Me}_3\text{NO}\) followed by addition of the tungsten acetylide complexes \([\text{LW}(\text{CO})_3(\text{CCPh})]\) (L=Cp, Cp*) affords the heterometallic cluster complexes \([\text{LWRu}_5(\mu_5-C)(\text{CCPh})(\text{CO})_{15}]\) (L=Cp, 245a; L=Cp*, 245b) and \([\text{LWRu}_5(\mu_5-C)(\text{CCPh})(\text{CO})_{13}]\) (L=Cp, 246a; L=Cp*, 246b). Thermolysis of 245 results in an irreversible formation of 246. Hydrogenation of 246b gives two cluster compounds \([\text{C}_5\text{Me}_5\text{WRu}_5(\mu_6-C)(\mu-C\text{CCH}_2\text{Ph})(\mu-H)_2(\text{CO})_{13}]\) (247) and \([\text{C}_5\text{Me}_5\text{WRu}_5(\mu_4-C)(\mu_3-C\text{CCH}_2\text{Ph})(\mu-H)_4(\text{CO})_{12}]\) (248), via 1,1-addition of \(\text{H}_2\) to the ligated acetylide and concurrent formation of two or four bridging hydrides (Scheme 65).\(^{90}\)
Heterometallic vinylacetylide clusters \([\text{Cp}^*\text{WRe}_2(\text{CO})_9(\text{CCR})]\) (R = C(Me)=CH\(_2\), 249; R = C\(_6\)H\(_9\), 250) have been obtained from the condensation of mononuclear tungsten acetylide complexes \([\text{Cp}^*\text{W}(\text{CO})_3(\text{C}≡\text{CR})]\) (R = -C(Me)=CH\(_2\), C\(_6\)H\(_9\)) and rhenium carbonyl complex \([\text{Re}_2(\text{CO})_8(\text{NMe}_2)]\). Treatment of the vinylacetylide complex \([\text{Cp}^*\text{WRe}_2(\text{CO})_9\{\text{C}≡\text{CC(Me)}\equiv\text{CH}_2\}]\) (249) with alcohols, ROH (R = Me, Et, Ph) in refluxing toluene solution afford complexes \([\text{Cp}^*\text{WRe}_2(\text{CO})_7(\mu\text{-OR})(\text{C}=\text{C}=\text{CMe}_2)]\) (R = Me, 251\(_a\); R = Et, 251\(_b\); R = Ph, 251\(_c\)), which contain an unusual \(\mu_3\)-allylidene ligand and a bridging alkoxide ligand, and show fluxional behavior in solution. When 249 is heated in the presence of hydrogen, a metallacyclopentadienyl complex \([\text{Cp}^*\text{WRe}_2(\text{CO})_7(\mu\text{-H})\{\text{CHCHC(Me)}\equiv\text{CH}\}]\) (252\(_a\),\(_b\)) is formed as a mixture of two non
interconvertible isomers (Scheme 66). On the other hand, hydrogenation of 250 in toluene under refluxing condition initially produces a dihydride cluster 
\[ \text{[Cp*WRe}_2\text{(CO)}_8(\mu-\text{H})_2\{\text{C}=\text{C(C}_6\text{H}_9)\}] \] (253) which on heating in toluene converts to 254 and 255 (Scheme 67).

Scheme 66.
The acetylide complex \([\text{Co}_2(\text{CO})_6\{\mu-\text{PhC}≡\text{CRe}(\text{CO})_5\}]\) (256) (obtained by the treatment of the binuclear acetylide-hydride carbonyl complex of rhenium \([\text{Re}_2(\text{CO})_8(\mu-H)(\mu-\text{C}≡\text{CPh})]\) with \([\text{Co}_2(\text{CO})_8]\)) undergoes nondestructive reaction with oxygen resulting in the net loss of one acetylide carbon atom together with a CO ligand and formation of the carbyne cluster complex \([\text{Co}_2\text{Re}(\text{CO})_{10}(\mu_3-\text{CPh})]\) (257) (Scheme 63).^{92}

A dichloromethane solution of rhenium ethynyl complex \([\eta^5-\text{C}_5\text{Me}_5]\text{Re(NO)(PPh}_3\){(\text{C}≡\text{C})_n\text{H}}\] (n = 1-3) (258a-c) and triosmium complex \([\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]\) react at room temperature to give \([\eta^5-\text{C}_5\text{Me}_5]\text{Re(NO)(PPh}_3\)(\text{CC})_n\text{Os}_3(\text{H})(\text{CO})_{10}\] (n = 1–3) (259a-c) (Scheme 69). Thermal reaction in hexane
converts 259b to the nonacarbonyl complex [(η⁵-C₅Me₅)Re(NO)(PPh₃)(CCCC)Os₃(CO)₉(H)] (260) (Scheme 70).⁹³, ⁹⁴
Synthesis of a \( \text{C}_3\text{OMe} \) complex \([(\eta^5-\text{C}_5\text{Me}_5)\text{Re(NO)(PPh}_3)(C≡\text{CC(OMe)})\text{Os}_3(\text{CO})_{11}] \) (262) from the reaction of \([(\eta^5-\text{C}_5\text{Me}_5)\text{Re(NO)(PPh}_3)(C≡\text{CLi})] \) with \([\text{Os}_3(\text{CO})_{12}] \) and \([\text{Me}_3\text{O}^+\text{BF}_4^-] \) has been reported.\(^93\)

On refluxing in heptane it forms 263 (Scheme 72).

Products obtained from the reaction between molybdenum dimer \([\text{Mo}_2(\text{CO})_4(\eta-\text{C}_5\text{H}_5)_2] \) and \([\text{M}(\text{CCR})(\text{CO})_2(\eta-\text{C}_5\text{H}_5)] \) (\(\text{M} = \text{Ru} \) or \(\text{Fe} \), \(\text{R} = \text{Me} \) or \(\text{Ph} \)) depends on the alkynyl metal used. The ruthenium containing reactant gives the dimolybdenum alkynyl adducts \([\text{Mo}_2\{\text{Ru}(\mu-\text{CCR})(\text{CO})_2(\eta-\text{C}_5\text{H}_5)]\}(\text{CO})_4(\eta-\text{C}_5\text{H}_5)_2] \) (\(\text{R} = \text{Me} \) (264a), \(\text{Ph} \) (264b)) as the only isolable product. In contrast, the iron alkynyls undergo Fe-C bond cleavage to give the alkyne adducts \([\text{Mo}_2(\mu-\eta^2-\text{HC}_2\text{R})(\text{CO})_4(\eta-\text{C}_5\text{H}_5)_2] \) (\(\text{R} = \text{Me} \), 265a; \(\text{R} = \text{Ph} \), 265b) (Scheme 73).\(^95\)
Scheme 73.

On the other hand, reaction of \([\{\text{Ru(CO)}_2(\eta_1-C_5H_5)\}_2(\mu-C\equiv C)\]\) with \([\text{Mo}_2(\text{CO})_4(\eta-C_5H_5)_2]\) gives \([\text{MoRu}_2(\mu_2-\text{CO})_3(\mu_3-C\equiv C\{\text{Ru(CO)}_2(\eta-C_5H_5)\}])(\eta-C_5H_5)_3]\) (266), but not the dimolybdenum ‘alkynyl’ adduct, 264a,b (Scheme 74).96

Scheme 74.

Reaction of \([((\text{OC})_4\text{Fe}(\eta^1\text{PPh}_2\text{C}\equiv\text{CPh}))]\) (267) with \([\text{Co}_2(\text{CO})_8]\) at room temperature affords the heterotrimetallic complex \([(\text{OC})_4\text{Fe}(\mu-\eta^1:\eta^2-\text{PPh}_2\text{C}\equiv\text{CPh})\text{Co}_2(\text{CO})_6]\) (268), in which the alkynic moiety is bound to a \(\text{Co}_2(\text{CO})_6\) unit. Both the mono- and di-substituted complexes, \([(\text{OC})_4\text{Fe}(\mu-\eta^1:\eta^2-\text{PPh}_2\text{C}\equiv\text{CPh})\text{Co}_2(\text{CO})_5\{\text{P(OMe)}_3\}]\) (269a) and \([(\text{OC})_4\text{Fe}(\mu-\eta^1:\eta^2-\text{PPh}_2\text{C}\equiv\text{CPh})\text{Co}_2(\text{CO})_4\{\text{P(OMe)}_3\}_2]\) (269b), have been obtained on reaction of 268 with an
excess of trimethylphosphite at elevated temperature. Thermolysis of 269a results in phosphorus-carbon bond cleavage and iron-cobalt bond formation to yield the acetylide bound mixed-metal triangular cluster [FeCo2(CO)₆{μ₃-η²-CCPh}{P(OMe)₃}{μ-PPh₂}] (270). Substitution of a Co-bound carbonyl ligand of 270 with triphenylphosphine gives [FeCo₂(CO)₅{μ₃-η²-CCPh}{P(OMe)₃}(PPh₃)(μ-PPh₂)] (271) (Scheme 75).⁹⁷

Scheme 75.

Reaction between [CpFe(CO)₂(C₂Me)] and [Co₂(CO₈)] which affords a μ-alkyne complex [CpFe(C₂Me)Co₂(CO)₈] (272a).⁹⁸ In contrast to the reaction of phenylacetylide complex [CpFe(CO)₂C₂Ph] and [Co₂(CO₈)] forms [(η-C₅H₅)Fe(C₂Ph)Co₂(CO)₆] (273) and [(η-C₅H₅)Fe(C₂Ph)Co₂(CO)₈] (272b) (Figure 17).⁹⁹
Tungsten-iridium tetrahedral cluster $[\text{WIr}_3(\mu-\text{CO})_3(\text{CO})_8(\text{η}-\text{C}_5\text{R}_5)]$ ($\text{R}_5 = \text{H}_5$, \textbf{274a}; $\text{R}_5 = \text{Me}_5$, \textbf{274b}; $\text{R}_5 = \text{H}_4\text{Me}$, \textbf{274c}), prepared from the reaction between [WH(\text{CO})_3(\text{η}-\text{C}_5\text{R}_5)] and [IrCl(\text{CO})_2(\rho\text{-toluidine})] under CO atmosphere, has been used extensively to synthesise several mixed metal acetylide complexes. Thermal reaction of $[\text{WIr}_3(\mu-\text{CO})_3(\text{CO})_8(\text{η}-\text{C}_5\text{Me}_5)]$ (\textbf{274b}) with $[\text{W(C≡CPh)(CO)}_3(\text{η}-\text{C}_5\text{H}_5)]$ resulted in the isolation of an edge-bridged tetrahedral cluster $[\text{W}_2\text{Ir}_3(\mu_4-\text{η}^2\text{-C}_2\text{Ph})(\mu-\text{CO})(\text{CO})_9(\text{η}-\text{C}_5\text{H}_5)(\text{η}-\text{C}_5\text{Me}_5)]$ (\textbf{275a}) and an edge-bridged trigonal-bipyramidal cluster $[\text{W}_3\text{Ir}_3(\mu_4-\text{η}^2\text{-C}_2\text{Ph})(\mu-\text{η}^2\text{-C=CHPh})(\text{Cl})(\text{CO})_8(\text{η}-\text{C}_5\text{Me}_5)(\text{η}-\text{C}_5\text{H}_5)_2]$ (\textbf{275b}) (Scheme 76). Cluster \textbf{275a} is formed by the insertion of $[\text{W(C≡CPh)(CO)}_3(\text{η}-\text{C}_5\text{H}_5)]$ into Ir-Ir and W-Ir bonds, and contains a $\mu_4-\text{η}^2$ alkynyl ligand. Cluster \textbf{275b} also contains an alkynyl ligand bonded to two iridium atoms and two tungsten atoms in a $\mu_4-\text{η}^2$ fashion and a vinylidene ligand bridge the W-W bond.
A similar reaction of a THF solution of W-Ir cluster, [WIr$_3$(CO)$_{11}$($\eta$-C$_5$R$_5$)] (R = H, 274a; R = Me, 274b) with [(C$_5$H$_5$)$_2$Ru(C≡C)Ru(CO)$_2$($\eta$-C$_5$H$_5$)] leads to cluster compound [Ru$_2$WIr$_3$(C$_2$)(CO)$_3$(CO)$_2$(CO)$_7$($\eta$-C$_5$H$_5$)$_2$($\eta$-C$_5$R$_5$)] [R = H, 276a; R = Me, 276b] containing WIr$_3$ butterfly core capped by Ru atoms. The reaction involves an insertion of a C$_2$ unit into a W-Ir bond and scission of Ru-C bond of the diruthenium ethynyl precursor (Scheme 77). Another mixed metal cluster with a butterfly W$_2$Ir$_2$ unit capped by a Ru($\eta$-C$_5$H$_5$) group, [RuW$_2$Ir$_2$($\eta$-C$_5$H$_5$)$_2$W(C≡C)W(CO)$_3$($\eta$-C$_5$H$_5$)$_3$] (277) has been isolated by the reaction of [W$_2$Ir$_2$(CO)$_{10}$($\eta$-C$_5$H$_5$)$_2$] (274d) with the diruthenium ethynyl reagent (Scheme 78). When the reaction between [WIr$_3$(CO)$_{11}$($\eta$-C$_5$R$_5$)] (R$_5$ = H$_5$, 274a; R$_5$ = Me$_5$, 274b; R$_5$ = H$_4$Me, 274c) and [(C$_5$H$_5$)$_2$W(C≡CC≡C)W(CO)$_3$($\eta$-C$_5$H$_5$)$_3$] is performed in refluxing toluene solution, metallaethynyl type of clusters [W$_2$Ir$_3$($\mu$$_4$-$\eta$)$^2$-(C$_2$C≡C)W(CO)$_3$($\eta$-C$_5$H$_5$)$_3$] (278a; R$_5$ = H$_4$Me, 278c) are obtained (Scheme 79).
Mixed group 6-9 transition metal complexes,

\[
\{\text{Cp(O)C}_3\text{W}\}C\equiv C\equiv C\{M(\text{CO})(\text{PPh}_3)_2\}\] (M = Ir, 279a; M = Rh, 279b) have been obtained from the reaction between \([\text{W}(C\equiv C\equiv CH)(\text{CO})_3\text{Cp}]\) and \([\text{M}(!\text{OTf})(\text{CO})(\text{PPh}_3)_2]\) (M = Ir, Rh) in presence of diethylamine. Thermal reaction of a THF solution of 279a or 279b with \([\text{Fe}_2(\text{CO})_9]\) gives \([\{\text{Cp(O)C}_3\text{W}\}C\equiv C\equiv C_2\{\text{Fe}_2\text{M}(\text{CO})_8(\text{PPh}_3)\}\] (M = Ir, 280a; M
Platinum-acetylide complexes have been used in reactions with copper, silver or gold salts to form heteropolynuclear Pt-Ag, Pt-Cu or Pt-Au complexes bridged by alkynyl ligands. A synthetic strategy for heterometallic complexes with bridging alkynyl ligands have been developed by Fornies and co-workers, in which alkynyl substrates containing linear acetylide units are allowed to react with electrophilic metal centres containing potential leaving groups. Reaction of alkynyl platinate(II) complexes \([\text{NBu}_4]_2[\text{Pt}(\equiv CR)_4].n\text{H}_2\text{O} (R = \text{Ph}, n = 0; R = ^4\text{Bu}, n = 2)\) and \(X_2\{\text{cis-Pt(C}_6\text{F}_5)_2(\equiv CR)_2\}\) \((X = \text{PMePh}_3, R = \text{Ph}; X = \text{NBu}_4, R = ^4\text{Bu})\) towards suitable electrophilic copper, silver and gold complexes has been investigated to obtain a variety types of heteropolynuclear platinum complexes, the type formed depending on the nature of the platinum starting material and on the molar ratio of the reactants. Treatment of \([\text{Pt}(\equiv CR)_4]^{2-} (39) (R = \text{Ph} (a), ^4\text{Bu} (b))\) with AgClO\(_4\), or with CuCl or [AuCl(tht)] (tht =
tetrahydrothiophene) in the presence of NaClO₄ in 1:2 molar ratio forms a hexanuclear complex [Pt₂M₄(C≡CR)₈] (M = Ag, Cu, Au) (R = Ph, nBu) (282a,b-284a,b). The Cu analogue, [Pt₂Cu₄(C≡CPh)₈] has been prepared by the reaction of [Pt{C₅H₄Fe(C₅H₅)}Cl(cod)] with an excess of phenylacetylene and CuI. An anionic tetranuclear complex [Pt₂M₂(C₆F₅)₄(C≡CR)₄]²⁻ (285a,b-286a,b) has been obtained from the reaction of [cis-Pt(C₆F₅)₂(C≡CR)₂]²⁻ (40) with AgClO₄, AgCl or CuCl in a 1:1 molar ratio. On treatment of complex 285a,b with AgClO₄ (1:2), the Pt-Ag mixed-metal acetylide complex [{PtAg₂(C₆F₅)₂(C≡CR)₂}ₙ] (287a,b) is obtained. An alternative reaction of [Pt(C₆F₅)₂(C≡CR)₂L₂] (288-290) with two equivalents of AgClO₄ also gives complex 287a,b. X-ray diffraction study of 301 (an acetone solvated derivative of 287) reveals a polymeric nature of the complex (Scheme 82). A trimetallic Pt-Ag complex [Pt₂Ag(C≡CR)₄L₄]ClO₄ (291-293) has been synthesized by the reaction of cis-[Pt(C≡CR)₂L₂] (288-290) with AgClO₄ (2:1 molar ratio) (Scheme 81).
39a; R = Ph
39b; R = nBu

\[ \text{[Pt(C≡CR)₄]²⁻} \xrightarrow{\text{AgClO₄ or CuCl or [AuCl(tht)].2NaClO₄}} \]

\begin{align*}
282a &: \text{Ag Ph} \\
282b &: \text{Ag nBu} \\
283a &: \text{Cu Ph} \\
283b &: \text{Cu nBu} \\
284a &: \text{Au Ph} \\
284b &: \text{Au nBu}
\end{align*}

\[ \text{cis-[Pt(C≡CR)₂L₂]} \xrightarrow{\frac{1}{2} \text{AgClO₄}} \]

\begin{align*}
288a &: \text{PPh₃ Ph} \\
288b &: \text{PPh₃ nBu} \\
289a &: \text{PEt₃ Ph} \\
289b &: \text{PEt₃ nBu} \\
290a &: \text{dppe Ph} \\
290b &: \text{dppe nBu} \\
291a &: \text{PPh₃ Ph} \\
291b &: \text{PPh₃ nBu} \\
292a &: \text{PEt₃ Ph} \\
292b &: \text{PEt₃ nBu} \\
293a &: \text{dppe Ph} \\
293b &: \text{dppe nBu}
\end{align*}

Scheme 81.
Treatment of complex \(285a,b\) with \(\text{PPh}_3\) or \(\text{PEt}_3\) (1:2 or 1:4 ratio) or with \(\text{dppe}\) results in the formation of anionic complexes \(294-295\) and dianionic complexes \(296\) respectively\(^{105}\). On the other hand, reaction of polymeric complex \(287\) with phosphines, tert-butylisocyanide or pyridine in a \(\text{Ag}:\text{L}\) molar ratio of 2:1 produces hexanuclear complexes \([\text{Pt}_2\text{Ag}_4(\text{C}_6\text{F}_5)_4(\text{C}≡\text{CR})_4\text{L}_2]\) \((297-300)\) which are structurally related to complex \(301\) (Scheme 76). The X-ray structure of \(297a\) reveals the tridentate behavior of the two \(\text{cis-}[\text{Pt}(\text{C}_6\text{F}_5)_2(\text{C}≡\text{CR})_2]\) fragments towards silver atoms. The alkynyl ligands exhibit an unsymmetrical \(\mu_3-\eta^2\) bonding mode. In contrast, trinuclear \([\text{PtAg}_2(\text{C}_6\text{F}_5)_2(\text{C}≡\text{CR})_2\text{L}_2]\) \((302-305)\) are isolated when higher proportion of the ligand \(\text{L}\) is used with complex \(287\). The tetranuclear \(285\) is obtained when \(287\) is reacted with \(\text{NBu}_4\text{Br}\) (Scheme 83).\(^{106,110}\)
Two different Pt-M (M = Ag, Cu) complexes (306-313) have been isolated when the hexanuclear complexes 282a,b-283a,b are reacted with anionic ligands X⁻ (X = Cl, Br) or neutral ligands L (L = ¹CNBu, pyridine). For instance, the reaction of
[Pt$_2$M$_4$(C≡CPh)$_8$] (M = Ag, 282a; M = Cu, 283a) with four equivalents of anionic (X = Cl, Br) or neutral ligands (L = CNBu$^t$, pyridine) gives the corresponding trinuclear anionic or neutral complexes (306-310), while, reaction of [Pt$_2$M$_4$(C≡C'Bu)$_8$] (M = Ag, 282b; M = Cu, 283b) with the same ligands gives hexanuclear complexes (311-313). Addition of 8 equivalents of the ligands to 282b or 283b afford the trinuclear complexes (306-310) (Scheme 84).

The platinum mononuclear complexes [Pt(C≡CR)$_4$]$^{2-}$ (39) and [Pt(C$_6$F$_5$)$_2$(C≡CR)$_2$]$^{2-}$ (40) have been used to synthesise di- and trinuclear complexes containing doubly bridged alkynyl systems. Their reactions with mercury halides afford 1:2 adducts (314-316) or 1:1 adducts (317-319) (Scheme 85).
The hexanuclear platinum-copper complex \([\text{Pt}_2\text{Cu}_4(\text{C}_6\text{F}_5)_4(\text{C}=\text{C}^\prime\text{Bu})_4(\text{acetone})_2]\) (320) and the polynuclear derivative \([\text{PtCu}_2(\text{C}_6\text{F}_5)_2(\text{C}=\text{CPh})_2]_x\) (321), which crystallizes in acetone as \([\text{Pt}_2\text{Cu}_4(\text{C}_6\text{F}_5)_4(\text{C}=\text{CPh})_4(\text{acetone})_4]\) (322), have been prepared from the reaction of \([\text{cis-Pt}(\text{C}_6\text{F}_5)_2(\text{THF})_2]\) with the corresponding copper-acetylide, \([\text{Cu}(\text{C}=\text{CR})]_x\) (R = Ph, \(^\prime\text{Bu}\)) (molar ratio 1:2) as starting materials. The Ag-analogues (323-325) have been synthesized similarly (Scheme 86).\(^{104,109}\)
Scheme 86.
Addition of four equivalents of 2,2'-bipyridine to a solution of 320 or 321 yields neutral trinuclear alkynyl bridged complexes \([\{\text{cis-Pt}(C_6F_5)_2(\mu-\text{C}≡\text{CR})_2\}\{\text{Cu(bipy)}\}_2]\) (R = \(^t\text{Bu}, 326; \text{R} = \text{Ph, 327}). An analogous trinuclear complex \([\{\text{cis-Pt}(C_6F_5)_2(\mu-\text{C}≡\text{C}^t\text{Bu})_2\}\{\text{Cu(dppe)}\}_2]\) (328) has been obtained by the reaction of 320 with four equivalents of dppe. In contrast, the reaction of 321 with dppe produces mixtures of mononuclear platinum or copper complexes (Scheme 87). A comparison of the photoluminescent spectra of 320 and 321 with those of the related platinum-silver species \([\text{PtAg}_2(C_6F_5)_2(C≡\text{CR})_2]_x\) and the monomeric \([\text{cis-Pt}(C_6F_5)_2(C≡\text{CR})_2]_x^–\) suggest the presence of emitting states bearing a large cluster \([\text{PtM}_2]_x^–\) -to-ligand (alkynide) charge transfer (CLCT).\(^{109}\)

\[
\begin{align*}
\text{Scheme 87.}
\end{align*}
\]

VII

OTHER MIXED METAL ACETYLIDE COMPLEXES

A variety of acetylide complexes have been reported with mixed early-late transition metal or mid-late transition metal complexes. The synthetic procedures either involve reactions of early transition metal acetylide complexes with late transition metal
complexes containing labile ligands or vice versa. Mixed early-mid transition metal acetylide complexes are rather rare.

The reaction of mononuclear \([\text{Cp}_2\text{Ti}(\equiv\text{C}^{\dagger}\text{Bu})_2]\) with \(\text{cis-}[\text{M}(\text{C}_6\text{F}_5)(\text{thf})_2]\) (\(\text{M} = \text{Pt}\)) results in the formation of dimetallic Pt-Ti acetylide complex \([\text{Cp}_2\text{Ti}(\mu-\eta^1-\text{C}≡\text{CtBu})(\mu-\eta^1-\text{C}≡\text{CtBu})\text{Pt}(\text{C}_6\text{F}_5)_2]\) (329) (Scheme 88).\(^{111}\)

\[
\text{cis-[Pt(C}_6\text{F}_5)_2(\text{thf})_2] \rightarrow [\text{Ti(Cp)}_2(\equiv\text{CtBu})_2]
\]

Scheme 88.

When \([\text{Pt(C}_2\text{H}_4)(\text{PPh}_3)_2]\) is added to \([\text{Ti}(\eta-\text{C}_5\text{H}_5)_2(\text{C}≡\text{CR})_2]\) (\(\text{R} = \text{Bu}^1, \text{Ph}\)), products \([\text{Cp}_2\text{Ti}(\mu-\eta^1,\eta^1-\text{C}≡\text{CBu}^1)(\mu-\eta^2,\eta^1-\text{C}≡\text{CBu}^1)\text{Pt(PPH}_3)_2]\) (330) and \([\text{Cp}_2\text{Ti}(\mu-\eta^2,\eta^1-\text{C}≡\text{CPh})_2\text{Pt(PPH}_3)_2]\) (331) are obtained (Scheme 89).\(^{112}\)

\[
[Ti(Cp)_2(\equiv\text{CR})_2] + [\text{Pt(C}_2\text{H}_4)(\text{PPh}_3)_2] \rightarrow \text{R = Ph, } \text{tBu}
\]

Scheme 89.

A solution of tetranuclear heteroleptic arylcopper aggregate \([\text{Cu}_4\text{R}_2\text{Br}_2]\) (\(\text{R} = \text{C}_5\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-2,6}\)) in diethylether reacts at room temperature with the titanium complex \([(\eta^5-\text{C}_5\text{H}_4\text{SiMe}_3)_2\text{Ti}(\equiv\text{CSiMe}_3)_2]\) (332), in 1:4 molar ratio, to give a 1,1-bis-metallaaalkenyl complex \([(\eta^5-\text{C}_5\text{H}_4\text{SiMe}_3)_2\text{Ti}(\equiv\text{CSiMe}_3)_2\{\mu-\text{C}=\text{C(SiMe}_3\text{(R)}}\text{Cu}\] (334)
resulting from an intramolecular addition of a Cu-C bond across the alkyne triple bond (Scheme 90). A probable formation of complex 333 as an intermediate has been proposed.

![Scheme 90](image)

**Scheme 90.**

Dinuclear Pt-Rh (336a-c, 339) and Pt-Ir (337a-c, 338) complexes with doubly alkynyl bridging systems have been isolated from the reactions between platinum alkynyl complex, 40 and from cyclooctadiene complexes of rhodium and iridium (Scheme 91).
Scheme 91.

The tetrannuclear mixed metal cluster $\left[\eta^5\text{C}_5\text{H}_5\right]_2\text{Ni}_2\text{Fe}_2(\text{CO})_5(\mu-\text{PPh}_2)(\mu_4-\eta^2-C≡\text{CPh})$ (340) has been synthesised in high yield via condensation of $[\text{Fe}_2(\text{CO})_6(\mu-\text{PPh}_2)(\mu_2-\eta^2-C≡\text{CPh})]$ and $[(\eta^5\text{C}_5\text{H}_5)_2\text{Ni}_2(\text{CO})_2]$ in benzene reflux.¹¹⁵ X-ray analysis has revealed a $\mu_4$-acetylide complex coordinated on a spiked triangular metal skeleton (Figure 18).

Figure 18.
A triangular Ni-Fe acetylide complex \([\text{Cp}_2\text{NiFe}_2(\text{CO})_6(\text{C}_2^t\text{Bu})]\) (341) has been obtained when \([\text{Cp}_2\text{Ni}_2(\text{HC}_2^t\text{Bu})]\) is reacted with \([\text{Fe}_3(\text{CO})_{12}]\) in refluxing heptane (Figure 19).\(^{116}\)

\[
\begin{align*}
\text{Bu}^t & \quad \text{C} \quad \text{NiCp} \\
\text{C} & \quad \text{Fe} \\
\text{C} & \quad \text{Fe} \\
\text{CO})_3 & \quad \text{CO})_3
\end{align*}
\]

Figure 19.

A pentanuclear Ni-Ru cluster \([\text{NiRu}_4(\text{CO})_9(\mu-\text{PPh}_2)_2(\mu_4-\text{C}≡\text{CiPr})_2]\) (342) has been synthesised by the addition of electron rich \([\eta-\text{Cp})\text{Ni}(\text{CO})_2]\) to a carbocationic \(\mu_3\)-acetylide group in \([\text{Ru}_3(\text{CO})_9(\mu_3-\text{C}≡\text{CiPr})(\text{PPh}_2)]\).\(^{117}\) Its structure consists of a Ru$_4$ butterfly, zipped up by a Ni(CO) group, with the two acetylide groups in \(\mu_4-\eta^2\)-bonding mode (Figure 20).

\[
\begin{align*}
\text{Me} & \quad \text{Me} \\
\text{Me} & \quad \text{Me} \\
\text{Ni(CO)} & \quad \text{Ru}_4(\text{CO})_2 \\
\text{Ph}_2\text{P} & \quad \text{Ru}(\text{CO})_2 \\
\text{Ru} & \quad \text{Ru}_4(\text{CO})_2 \\
\text{Ru}(\text{CO})_2 & \quad \text{Ru}_4(\text{CO})_2 \\
\text{Ru} & \quad \text{Ru}_4(\text{CO})_2 \\
\text{Ru}(\text{CO})_2 & \quad \text{Ru}_4(\text{CO})_2
\end{align*}
\]

Figure 20.

The reaction of the terminal alkyne, \([\text{HC}≡\text{C}^-\text{Pr}]\) with \([\text{Ru}_3(\text{CO})_{12}]\) in boiling heptane gives \([(\mu-H)\text{Ru}_3(\text{CO})_9(\mu_4-\eta^2-\text{C}≡\text{CH}^-\text{Pr})]\) (343) which on further reaction with an octane solution of \([[\eta^5-\text{C}_5\text{H}_5]\text{Ni}(\text{CO})_2]\) under reflux condition forms the vinylidene
cluster $[(\mu-H)(\eta^5-C_2H_5Ni)Ru_3(CO)_9(\mu_4-\eta^2-C=CH^iPr)]$ (344) (Figure 21). Structure of 344 consists of a butterfly arrangement of Ru$_3$Ni moiety, with the vinylidene ligand $\sigma$-bonded to two ruthenium and one nickel atoms and $\eta^2$-coordinated to the third ruthenium atom.

![Figure 21](image)

Reaction of a THF solution of [Ru$_2$(CO)$_6$(\mu-PPh$_2$)(\mu-\eta^1,\eta^2-C=C=CR)] (R = tBu, 345a; R = Ph, 345b) with [Pt(PPh$_3$)$_2$(\eta-C$_2$H$_4$)] leads to a trimetallic heteronuclear complex [Ru$_2$Pt(CO)$_7$(PPh$_3$)(\mu$_3$-\eta^1,\eta^1,\eta^1-C=C=CR)(\mu-PPh$_2$)] (346a,b) (Scheme 92). A THF solution of 345a also reacts under reflux condition with [Ni(cod)$_2$] or [Ni(CO)$_4$] to give a pentanuclear cluster, [Ru$_4$Ni(CO)$_{12}$(\mu-PPh$_2$)$_2$(\mu$_4$-\eta^1,\eta^1,\eta^2,\eta^4-tBuC=CC=C=CBu)] (347), resulting from stoichiometric coupling of two moieties of 345a and the incorporation of a nickel atom bonded to two Ru$_2$ units. The structure of 347 also shows a head-to-head coupling of two butadienyl ligands to form a C$_8$ chain.
A triangular triosmium-platinum cluster complex $\text{[Os}_3\text{Pt}(\mu-\text{H})(\mu_4-\eta^2-\text{C≡CPh})(\text{CO})_{10}(\text{PCy}_3)]$ (349) has been synthesised by the treatment of the unsaturated $\text{[Os}_3\text{Pt}(\mu-\text{H})_2(\text{CO})_{10}(\text{PCy}_3)]$ (348) with $\text{[LiC≡CPh]}$ followed by protonation.120 X-ray structural analysis reveals a $\mu_4-\eta^2-\text{C≡CPh}$ ligand about the triosmium framework with a platinum atom coordinated to one of the three osmium atoms in a spiked triangular arrangement (Figure 22).
To achieve alkyne oligomerization, bis(acetylide) Pt(II) complexes have been used to facilitate acyclic dimerization of alkynyls through head-to-head C-C bond coupling.\textsuperscript{121,122} Thermal reaction of a toluene solution of \([\text{cis-Pt(C≡CPh)}_2(\text{dppe})] (350a)\) with \([\text{Mn}_2(\text{CO})_9(\text{CH}_3\text{CN})]\) gives a mixed Mn-Pt compound, \([\text{Mn}_2\text{Pt(PhCCCCPh)(CO)}_6(\text{dppe})] (351)\),\textsuperscript{121} whereas reaction of \(350a\) with \([\text{Ru}_3(\text{CO})_{12}]\) in refluxing toluene forms two isomeric Ru/Pt compounds (352 a,b) (Scheme 93).\textsuperscript{122}

In refluxing toluene, compound \(350b\) reacts with \([\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3]\) to form the \(\mu\)-1,3-diyn compound \([\text{Pt(}\eta^{2-\text{PhCCCCPh}}\text{(PPh}_3)_2]\) (350c). Successive reaction of \(350c\) with \([\text{Fe}(\text{CO})_5]\) and \([\text{Ru}_3(\text{CO})_{12}]\) under benzene reflux lead to the isolation of a dimetallacyclic compound, \([\text{FePt(}\mu_2-\eta^1:\eta^1:\eta^2-\text{C(O)PhC=CC=CPh)}(\text{CO})_3(\text{PPh}_3)_2]\) (353) and a triangular cluster, \([\text{MPt}_2(\mu_3-\eta^1:\eta^1:\eta^2-\text{Ph-CCC}=\text{CPh)}(\text{CO})_5(\text{PPh}_3)_2]\) (M= Fe, 354a; M= Ru, 354b) (Scheme 94).\textsuperscript{121}
Addition of [(dppm)2RuCl2] to trans-[(PET3)2Pt(Ph)(C≡C-p-C6H4-C≡CH)] followed by treatment with DBU forms a heterometallic acetylide complex [(PET3)2Pt(C≡C-p-C6H4-C≡C)Ru(Cl)(dppm)2] (355). Thermal reaction of a methanol solution of [Cp(PPh3)2RuCl] with trans-[(PET3)2Pt(Ph)(C≡C-p-C6H4-C≡CH)] results in the formation of trans-[Cp(PPh3)2Ru(C≡C-p-C6H4-C≡C)Pt(Et3P)2(Ph)] (356) (Scheme 95).36b

Reduction of 172 with Na/Hg followed by addition of [O{Au(PPh3)}3][BF4] or [AuCl(PPh3)] gives complexes [AuFe2Ir(μ3-C2HPh)(CO)8(PPh3)2] (357a) and
[Au$_2$Fe$_2$Ir(μ$_4$-C$_2$Ph)(CO)$_7$(PPh$_3$)$_2$] (357b) (Scheme 96). Reaction of complex 172 with K[BH(CHMeEt)$_3$] followed by auration gives a Au$_3$FeIr cluster [Au$_3$Fe$_2$Ir(C$_2$HPh)(CO)$_{12}$(PPh$_3$)$_4$] (358). The Rh analogue of 357 has also been prepared by a similar procedure.$^{123}$

![Diagram of complex 357a and 357b](image)

Scheme 96.

Mono-, di- and tri-gold containing ruthenium clusters [Ru$_3$Au(μ$_3$-C$_2^1$Bu)(CO)$_9$(PPh$_3$)] (360), [Ru$_3$Au$_2$(μ$_3$-C=CH$^1$Bu)(CO)$_9$(PPh$_3$)$_2$] (361) and [Ru$_3$Au$_3$(C$_2^1$Bu)(CO)$_8$(PPh$_3$)$_3$] (362) have been isolated by a deprotonation reaction of [HRu$_3$(CO)$_9$C$_2^1$Bu] (359) with K[BH(CHMeEt)$_3$], followed by auration with [O{Au(PPh$_3$)}$_3$][BF$_4$] (Scheme 97).$^{124}$ Molecular structure of 361 contains a trigonal pyramidal Ru$_3$Au$_2$ core with the Ru$_3$ face bridged by a vinylidene ligand, σ-bonded to two ruthenium atoms and η$_2$-coordinated to the third ruthenium atom.
Addition of a THF solution of K[BH(CHMeEt)₃] to a solution of [Ru₃(μ-H)(μ₃-C₂H)(CO)₉] (363) in THF followed by auration with [AuCl(PPh₃)] results in the isolation of [AuRu₃(μ-H)(μ₃-C₂H₂)(CO)₉(PPh₃)] (364) and [Au₂Ru₃(μ₃-C=CH₂)(CO)₉(PPh₃)₂] (365) (Scheme 98). Complex 364 crystallises in a dark red form, in which the AuRu₃ core forms a tetrahedron (364a), and a yellow form, in which the AuRu₃ core has a butterfly structure (364b). The C₂H₂ ligand is 2η¹,η² coordinates to the Ru₃ face in both the isomeric forms. In cluster 365 the Au₂Ru₃ core has a distorted square pyramidal conformation with the CCH₂ ligand attached to the Ru₃ face.
Thermal reactions of a benzene solution of \([\text{RuCl}(\text{PPh}_3)_2(\text{C}_5\text{H}_5)]\) and \([\text{Cu}(\text{C}_2\text{Ph})]\) afford \([\text{RuCuCl}(\text{C}_2\text{Ph})(\text{PPh}_3)_2(\text{C}_5\text{H}_5)]_2\) \(366\) and \([\text{RuCuCl}(\text{C}_2\text{Ph})(\text{PPh}_3)_2(\text{C}_5\text{H}_5)]\) \(367\), whereas, similar reaction with \([\text{Cu}(\text{C}_2\text{C}_6\text{H}_4\text{Me}-p)]\) or \([\text{Cu}(\text{C}_2\text{C}_6\text{H}_4\text{F}-p)]\) results in the formation of a halogen free complex \([\text{RuCu}(\text{C}_2\text{R})(\text{PPh}_3)(\text{C}_5\text{H}_5)]\) \(368a,b\) \((\text{R} = p-\text{MeC}_6\text{H}_4 \text{ or } p-\text{FC}_6\text{H}_4)\) and \([\text{RuCuCl}(\text{C}_2\text{C}_6\text{H}_4\text{Me}-p)(\text{PPh}_3)_2(\text{C}_5\text{H}_5)]\) \(367b\) (Figure 23).\(^{126}\)

The Me-analogue, \([\text{RuCuCl}(\text{C}_2\text{Me})(\text{PPh}_3)_2(\text{C}_5\text{H}_5)]\) \(367c\) has been obtained by a heating reaction of \([\text{Cu}(\text{C}_2\text{Me})]\) and ruthenium chloride in benzene. On reflux, a benzene solution of \([\text{RuCl}(\text{PPh}_3)_2(\text{C}_5\text{H}_5)]\) and \([\text{Cu}(\text{C}_2\text{C}_6\text{F}_5)]\) gives a tetrannuclear complex \([\{\text{RuCu}(\text{C}_2\text{C}_6\text{F}_5)_2(\text{PPh}_3)(\text{C}_5\text{H}_5)\}_2\] \(369\). Room temperature reaction of a benzene solution of \([\text{Fe}_2(\text{CO})_9]\) and \(366\) gives the trinuclear cluster \([\text{Fe}_2\text{Ru}(\text{C}_2\text{Ph})(\text{CO})_6(\text{PPh}_3)(\text{C}_5\text{H}_5)]\) \(370\). Thermal reaction of a mixture of \(cis-\)[\(\text{ReCl}(\text{CO})_3(\text{PPh}_3)_2\)] and \([\text{Cu}(\text{C}_2\text{Ph})]\) in THF affords \([\text{ReCuCl}(\text{C}_2\text{Ph})(\text{CO})_3(\text{PPh}_3)_2]\) \(371\), while, thermolysis of \([\text{ReCl}(\text{CO})_3(\text{PPh}_3)_2]\) and \([\text{Cu}(\text{C}_2\text{C}_6\text{F}_5)]\) in benzene gives \([\text{ReCu}(\text{C}_2\text{C}_6\text{F}_5)_2(\text{CO})_3(\text{PPh}_3)_2]\) \(372\) (Figure 24).\(^{126}\)
The compounds $[\text{Ag}_3\{\text{Ru(CO)}_2(\eta^1-C_5H_4R)\}_2(\mu-C\equiv C)\}_3](\text{BF}_4)_3$ (R = H, 374a; R = Me, 374b), have been prepared from $[\{\text{Ru(CO)}_2(\eta^1-C_5H_4R)\}_2(\mu_2-C\equiv C)\}_2$ (R = H, 373a; R = Me, 373b) and AgBF$_4$ (Figure 25), and used in the reaction with [CpRuCl(CO)$_2$] to give $[\{\text{Ru(CO)}_2(\eta^1-C_5H_4R)\}_3(\eta^1,\eta^1-C\equiv C)][\text{BF}_4]$ (R = H, Me).$^{127}$
Addition reaction of dichloromethane solution of \([Au(C≡CPh)L](L = \text{PPh}_3 \text{ or PMe}_2\text{Ph})\) and \([\text{Os}_3(CO)_{10}(\text{MeCN})_2]\) gives \([\text{Os}_3(C≡CPh)(AuL)(CO)_{10}] (375\text{a,b})\) which contains a butterfly \(\text{Os}_3\text{Au}\) metal core and a \(\mu_2\text{-}\eta^2\text{-}\text{phenylethynyl}\) ligand bridging two osmium atoms. Decarbonylation of \(375\text{a,b}\) in refluxing heptane gives \([\text{Os}_3(\mu_3,\eta^2-C≡CPh)(\mu\text{-}AuL)(CO)_{9}] (376\text{a,b})\) (Scheme 99).  

Numerous examples exist of reactions between \([\text{M}(\text{C}_2\text{R})(\text{PR’}_3)] (\text{M} = \text{Au, Ag, Cu; R} = \text{Ph, C}_6\text{F}_5; \text{R’} = \text{Me, Ph})\) and \([\text{Os}_3(\mu\text{-}H)_2(CO)_{10}]\), which might be expected to proceed by oxidative addition of \([\text{RC}_2\text{M}(\text{PR’}_3)]\) and addition of the cluster-bound hydrogen to the acetylide moiety. In toluene at \(-11^\circ\text{C}, a\) rapid reaction occurs between \([\text{Os}_3(\mu\text{-}H)_2(CO)_{10}]\) and \([\text{M}(\text{C}_2\text{C}_6\text{F}_5)(\text{PPh}_3)] (\text{M}=\text{Au, Ag, Cu})\) to give \([\text{Os}_3\text{M}(\mu\text{-}CH=\text{CHC}_6\text{F}_5)(CO)_{10}(\text{PPh}_3)] (377\text{a-c})\) in quantitative yield,  while the reaction between
[H₂Os₃(CO)₁₀] and [M(C₂Ph)(PR₃)] (M = Cu, Ag, Au; R = Me or Ph) affords [HOs₃M(CO)₁₀(PR₃)] (M = Au, R = Me, Ph; M = Ag, Cu, R = Ph), [Os₃M(μ-CH=CHPh)(CO)₁₀(PR₃)] (M = Au and R = Me, 378a; M = Au and R = Ph, 378b; M = Ag and R = Ph, 378c; M = Cu and R = Ph, 378d), [Os₃M(μ-CH=CHPh)(CO)₉(PR₃)] (M = Au and R = Me, 379a; M = Au and R = Ph, 379b; M = Ag, R = Ph, 379c), [HOs₃M(μ₃-HCCPh)(CO)₈] (M = Au, 380a; M = Ag, 380b; M = Cu, 380c) and [Os₃M(μ-CH=CHPh)(CO)₉(PR₃)₂] (M = Au and R = Me, 381a; M = Au and R = Ph, 381b; M = Ag and R = Ph, 381c; M = Cu and R = Ph, 381d) (Figure 26).¹²⁹ X-ray crystallography of compounds 377a and 378b reveals the presence of a butterfly metal core and a μ-η¹,η²-vinyl ligand which is bonded to two osmium atoms of the Os₃Au core.

Thermal reaction of a THF solution of [AgC₂Ph] and [RhCl(PPh₃)₃] results in the formation of a hexanuclear cluster compound [Rh₂Ag₄(C₂Ph)₈(PPh₃)₂] (382a).¹³⁰ The analogous Ir₂Ag₄ compound, [Ir₂Ag₄(C₂Ph)₈(PPh₃)₂] (383a) has been obtained from AgC₂Ph and [trans-IrCl(CO)(PPh₃)₂] on toluene reflux. Thermolysis of a solution of [RhCl(PPh₃)₃] and [AgC₂C₆F₅] in 1,2-dimethoxyethane yields three compounds: [Rh₂Ag₄(C₂C₆F₅)₈(PPh₃)₂] (382b), [Ag(PPh₃)]⁺[Rh(C₂C₆F₅)₄(PPh₃)₂]⁻ (384a) and {[Ag(PPh₃)]₂⁺[Rh(C₂C₆F₅)₅(PPh₃)]²⁻} (385). The analogous iridium compound [Ir₂Ag₄(C₂C₆F₅)₈(PPh₃)₂] (383b) and [Ag(PPh₃)]⁺[Ir(C₂C₆F₅)₄(PPh₃)₂]⁻ (384b) are
obtained when a toluene solution of \([\text{trans-IrCl(CO)(PPh}_3\text{)}_2]\) and AgC\(_2\)C\(_6\)F\(_5\) are heated to reflux (Figure 27).

![Chemical structure](image1)

**Figure 27.**

Thermolytic reaction between \([\eta\text{-C}_5\text{H}_5\text{)Fe(CO)}_2\text{Cl}]\) and \([\text{CuC}_2\text{Ph}]\) affords a mixed metal complex \([\eta\text{-C}_5\text{H}_5\text{)Fe(CO)}_2(\text{C}_2\text{Ph})\text{CuCl}]_2\) (386) (Figure 28).\(^{131}\) Complex 386 contains a planar Cu\(_2\)Cl\(_2\) ring, and each copper atom is symmetrically bonded to a C\(_2\) unit of the phenylethynyl group.

![Chemical structure](image2)

**Figure 28.**
In toluene solution $[\text{trans-Pt(C≡CH)}_2(P\text{Me}_2\text{Ph})_2]$ and $[\text{W}_2(\text{O}^\text{tBu})_6]$ reacts at 30 ºC to give $[\text{trans-Pt(C≡CH)}][\text{C}_2\text{W}_2(\text{O}^\text{tBu})_5](\text{P}\text{Me}_2\text{Ph})_2]$ (387) and $[\text{trans-Pt}\{\text{C}_2\text{W}_2(\text{O}^\text{tBu})_5\}_2(\text{P}\text{Me}_2\text{Ph})_2]$ (388) (Figure 29).\textsuperscript{132,133a}

![Figure 29.](image)

Reaction of a THF solution of $[\text{Cp(CO)(NO)W(C≡CR)}]$ (\textit{R} = C\textsubscript{6}H\textsubscript{5}, 390\textit{a}; \textit{R} = C\textsubscript{6}H\textsubscript{4}CH\textsubscript{3}, 390\textit{b}; \textit{R} = C(CH\textsubscript{3})\textsubscript{3}, 390\textit{c}) with $[(\text{C}_6\text{H}_5)_3\text{PAuCl}]$ results in the formation of a tungsten-gold acetylide complex, $[\text{CpW(NO)(μ-CO)(μ-C≡CR)Au(P(\text{C}_6\text{H}_5)_3)}]$ (391) (Scheme 100).\textsuperscript{133b} Reaction of a THF solution of $[\text{Cp(CO)(NO)W(C≡CR)}]$ (\textit{R} = C\textsubscript{6}H\textsubscript{5}, 390\textit{a}; \textit{R} = C\textsubscript{6}H\textsubscript{4}CH\textsubscript{3}, 390\textit{b}; \textit{R} = C(CH\textsubscript{3})\textsubscript{3}, 390\textit{c}; \textit{R} = \text{SiMe}_3, 390\textit{d}) with $[\text{Cp(CO)\textsubscript{2}Fe(THF)}]\text{BF}_4$ as electrophile gives a bimetallic complex $[\{\text{Cp(CO)(NO)W}\} \eta^2-\{\text{Cp(CO)\textsubscript{2}FeC≡CR}\}]$ (392\textit{a-d}). Photolytic decarbonylation of complexes 392\textit{a-d} gives diastereomeric mixtures of heterometallic acetylides $[\{\text{Cp(CO)(NO)W}\} \eta^2-\{\text{Cp(CO)FeC≡CR}\}]$ (393\textit{a-d}/394\textit{a-d}) (Scheme 100).\textsuperscript{133c}
Reaction of fac-[Mn(CCR)(CO)₃(dppe)] (R = CH₂OMe, 395a; R = tBu, 395b; R = Ph, 395c) with a suspension of CuCl in dichloromethane affords [MnCuCl(μ-CCR)(CO)₃(dppe)] (396a-c). On the other hand, the reaction of 395a and 395b with [Au(C₆F₅)(tht)] (tht = tetrahydrothiophene) gives [MnAu(C₆F₅)(μ-CCR(CO)₃(dppe))] (R = CH₂OMe, 397a; R = Bu¹, 397b). Cationic mixed metal complexes [Mn₂Cu(μ-CCR)₂(CO)₆(dppe)₂]PF₆ (R = CH₂OMe, 398a; R = Bu¹, 398b) have been isolated from a dichloromethane solution of compound 396a or 396b on addition of TlPF₆ in presence of 395a or 395b respectively. The silver and gold complexes, [Mn₂M(μ-CCtBu)₂(CO)₆(dppe)₂]PF₆ (M = Ag, 399; Au, 400) are formed when [AgBF₄] or [AuCl(tht)] are reacted with TlPF₆ and two fold excess of 395b. Addition of TlPF₆ to
complex 396b in presence of [P(C₆H₄Me-2)] gives a cationic mixed metal complex

\[[\text{MnCu(μ-CC}t\text{Bu})(\text{CO})₃(\text{dppe})\{\text{P(C₆H₄Me-2)}\}_3]\]PF₆ (401) (Figure 30).\(^{133d}\)

\[
\begin{array}{c}
\text{(dppe)(CO)₃Mn} - \equiv \equiv C - R \\
\text{Cu} \\
\text{Cl}
\end{array}
\]

396a; \(R = \text{CH₂OMe}\)
396b; \(R = \text{tBu}\)
396c; \(R = \text{Ph}\)

\[
\begin{array}{c}
\text{(dppe)(CO)₃Mn} - \equiv \equiv C - R \\
\text{Au} \\
\text{(C₆F₅)}
\end{array}
\]

397a; \(R = \text{CH₂OMe}\)
397b; \(R = \text{tBu}\)

\[
\begin{array}{c}
\text{(dppe)(CO)₃Mn} - \equiv \equiv C - R \\
\text{M}
\end{array}
\]

398a \(\text{M = Cu, CH₂OMe}\)
398b \(\text{M = Cu, tBu}\)
399 \(\text{M = Ag, tBu}\)
400 \(\text{M = Au, tBu}\)

401; \(\text{M = Cu, tBu}\)

Figure 30.

Like organic alkynes or some monometalated acetylides (LₙMC≡CR), the
dirhenioethyne \([\text{(OC)₅ReC}≡\text{CRe(CO)₅}]\) (402) has been found to behave as an \(\eta^2\)-ligand
towards Cu\(^I\), Ag\(^I\), and Au\(^I\). Thus, when a THF solution of 402 reacts with CuCl, complex

\[
\left\{\left(\eta^2-C≡C\{\text{Re(CO)₅}\}_2\right)\text{Cu(μ-Cl)}\right\}_2 \hspace{1cm} (404)
\]
is isolated (Scheme 101).\(^{134}\)

\[
\begin{array}{c}
2 \text{(CO)₅Re} - \equiv \equiv C - \text{Re(CO)₅} \\
\text{402} \\
\text{2CuCl}
\end{array}
\]

\[
\begin{array}{c}
\text{(CO)₅Re} \\
\text{CuCl} \\
\text{CuCl} \\
\text{(CO)₅Re} \\
\text{Re(CO)₅}
\end{array}
\]

404

Scheme 101.

Reaction of 402 with [Cu(NCMe)₄]PF₆, [Ag(NCMe)₄]BF₄, [AgSbF₆] or
[AgO₂SOCF₃] gives cationic bis- (alkyne) complexes \([\left(\eta^2-C≡C\{\text{Re(CO)₅}\}_2\right)M]^+\)X⁻ (M
= Cu, Ag; X = PF$_6$, BF$_4$, SbF$_6$ or CF$_3$SO$_2$) (405a-d) and a cationic dimetallic tetrahedron [(μ-η$^2$:η$^2$-C≡C{Re(CO)$_5$})$_2$Cu$_2$(NCMe)$_4$]$^{2+}$ (406) (Figure 31).$^{134}$

$$\begin{align*}
\text{(CO)$_5$Re} & \equiv \text{Re(CO)$_5$} \\
\text{(CO)$_5$Re} & \equiv \text{Re(CO)$_5$} \\
\text{M}^+ & \text{X}^- \\
\text{H}_3\text{CCN} & \text{Cu} \equiv \text{NCCH}_3 \\
\text{H}_3\text{CCN} & \text{Cu} \equiv \text{NCCH}_3
\end{align*}$$

405a; M = Cu, X = PF$_6$
405b; M = Ag, X = BF$_4$
405c; M = Ag, X = SbF$_6$
405d; M = Ag, X = CF$_3$SO$_3$

Figure 31.

On the other hand, a dichloromethane solution of [(OC)$_5$ReC≡CSiMe$_3$] (403) on reaction with [Cu(NCMe)$_4$]PF$_6$ yields the cationic complex [(η$^2$-C≡CRe(CO)$_5$SiMe$_3$)$_2$Cu]$^+$ (407). Hydrolysis of [(μ-η$^2$:η$^2$-C≡C{Re(CO)$_5$})$_2$Cu$_2$(NCMe)$_4$](PF$_6$)$_2$ (406) or treatment of 403 with [Cu(MeCN)$_4$]PF$_6$ in moist CH$_2$Cl$_2$ affords the difluorophosphate-bridged complexes [(μ-η$^2$:η$^2$-[OC)$_5$ReC≡CR]}$_2$Cu$_4$(μ$_2$-O$_2$PF$_2$)$_4$ (R = Re(CO)$_5$, 410; R = SiMe$_3$, 411) (Scheme 102). The gold complex [(η$^2$-C≡C{Re(CO)$_5$})$_2$AuPPh$_3$]SbF$_6$ (408) obtained from the reaction of [Au(PPh$_3$)$_2$SbF$_6$] with 402, exists in equilibrium in solution with [Au(PPh$_3$)$_2$SbF$_6$] and [(η$^2$-C≡C{Re(CO)$_5$})$_2$Au]SbF$_6$ (409) (Scheme 103).$^{134}$

The gold complex [(η$^2$-C≡C{Re(CO)$_5$})$_2$AuPPh$_3$]SbF$_6$ (408) obtained from the reaction of [Au(PPh$_3$)$_2$SbF$_6$] with 402, exists in equilibrium in solution with [Au(PPh$_3$)$_2$SbF$_6$] and [(η$^2$-C≡C{Re(CO)$_5$})$_2$Au]SbF$_6$ (409) (Scheme 103).$^{134}$
Scheme 102.

Scheme 103.

VIII
ABBREVIATIONS

Cp = (η^5-C_5H_5)

Cp* = (η^5-C_5Me_5)

dppe = Diphenylphosphinoethane

dppm = Diphenylphosphinomethane

DPAD = Diisopropylacetylenedicarboxylate

DBU = 1,5-Diazabicyclo(5.4.0)undec-5-en
REFERENCES

(2) Nast, R. Angew. Chem. 1960, 72, 26.


(75) Adams, C. J.; Bruce, M. I.; Skelton, B. W.; White, A. H. *Polyhedron* 1998, 17, 2795.


