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Mixed Metal Acetylide Complexes

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References

I
INTRODUCTION

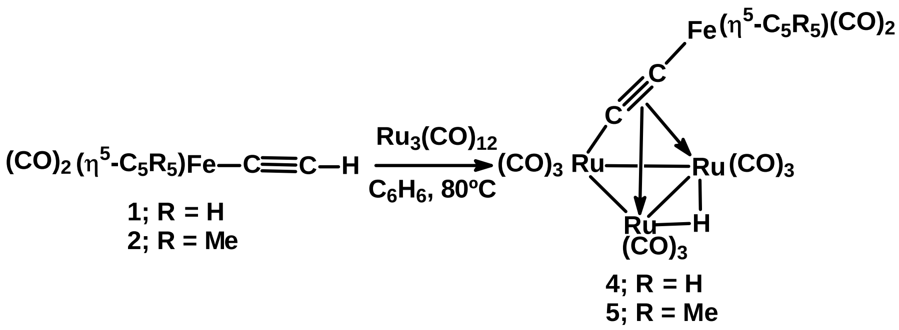
Complexes containing C_2 hydrocarbyl ligands occupy a very important position in the development of di-, tri- and polynuclear organometallic chemistry. Recognition that monovalent anions of alk-1-ynes, $[RC\equiv C]^-$ are isoelectronic to cyanide ion and CO prompted the first preparation of metal alkynyl 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.

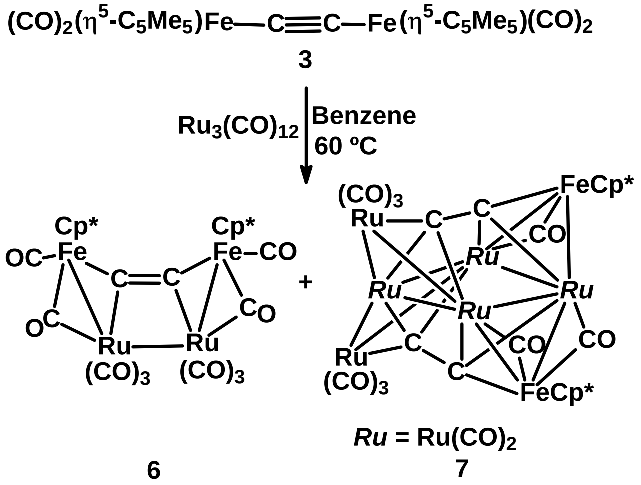
II

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 C_2 complexes derived from ethynyl and diethynediyl iron complexes. Reaction of the ethynyliron complexes $[\{(\eta^5\text{-}C_5R_5)Fe(CO)_2\}\text{-}C\equiv C\text{-}H]$ (R = H, **1**; R = Me, **2**) with $[Ru_3(CO)_{12}]$ in refluxing benzene affords triruthenium $\mu\text{-}\eta^1,\eta^2,\eta^2$-acetylide cluster compounds $[Ru_3(CO)_9(\mu\text{-}H)\ (\mu_3\text{-}\eta^1\text{:}\eta^2\text{:}\eta^2\text{-}C\equiv C\text{-}\{(\eta^5\text{-}C_5R_5)Fe(CO)_2\})]$ (R = H, **4**; R = Me, **5**) (Scheme 1).[32] On the other hand, the reaction of the ethynediyldiiron complex, $[\{(\eta^5\text{-}C_5Me_5)Fe(CO)_2\}\text{-}C\equiv C\text{-}\{(\eta^5\text{-}C_5Me_5)Fe(CO)_2\}]$ (**3**) with $[Ru_3(CO)_{12}]$, gives a complicated mixture of products, from which $[Cp^*_2Fe_2Ru_2(\mu_4\text{-}C_2)(CO)_{10}]$ (**6**) and $[Cp^*_2Fe_2Ru_6(\mu_6\text{-}C_2)(CO)_{17}]$ **(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 C_2 ligand. Compound **7** is an octanuclear compound with two C_2 units above and below a Ru_4 plane arranged perpendicular to each other. Two of the edges of the central Ru_4 plane are bridged by $Ru(CO)_3$ groups and the other two by FeCp* moieties.

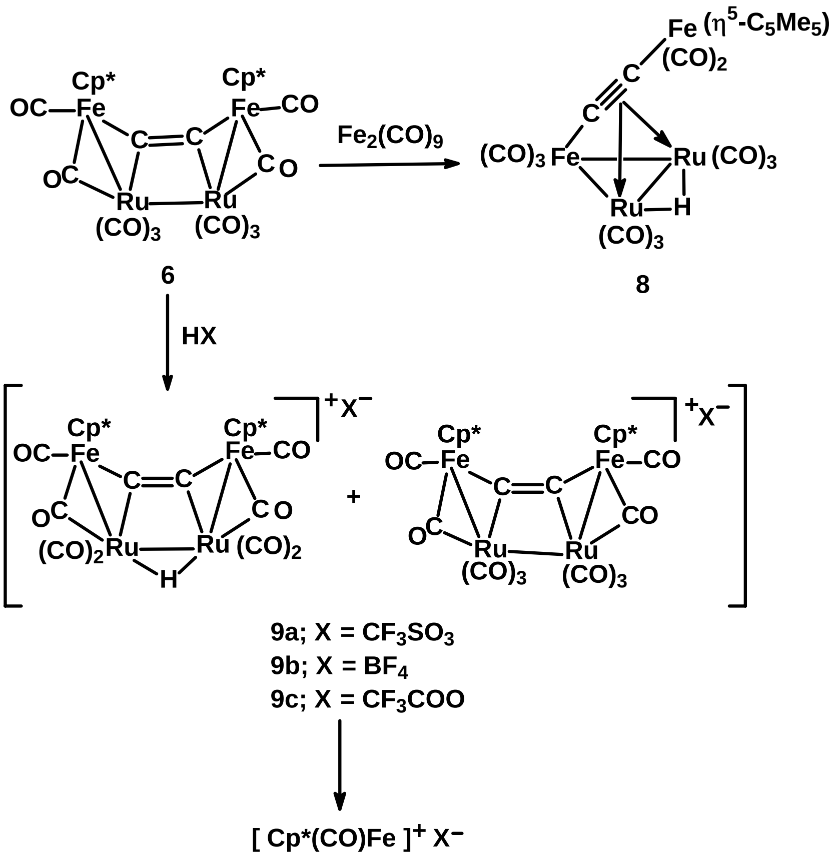


Scheme 1.



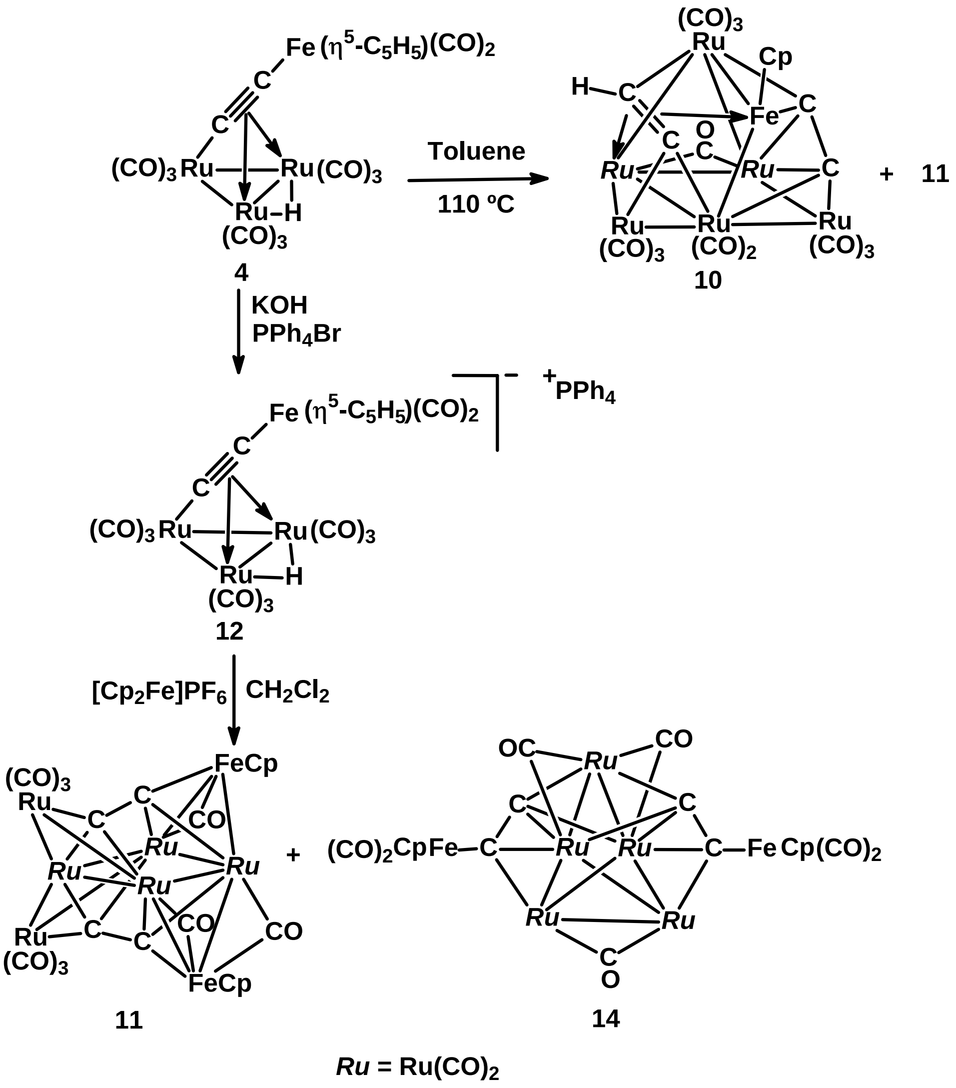
Scheme 2.

On reflux of a THF solution of a mixture of $[Fe_2(CO)_9]$ and **6**, iron-substituted derivative of **5,** complex $[Ru_2Fe(\mu\text{-}H)(CO)_9(\mu_3\text{-}C{\equiv}C\text{-}\{(\eta^5\text{-}C_5Me_5)Fe(CO)_2\})]$ (**8**) is formed. Treatment of **6** with CF_3SO_3H, $HBF_4.OEt_2$ or CF_3COOH forms an unstable cationic species **9**,which has been characterised solely by spectroscopy, as it readily converts to $[\{(\eta^5\text{-}C_5Me_5)Fe(CO)]^+ X^-$ (Scheme 3).[32]



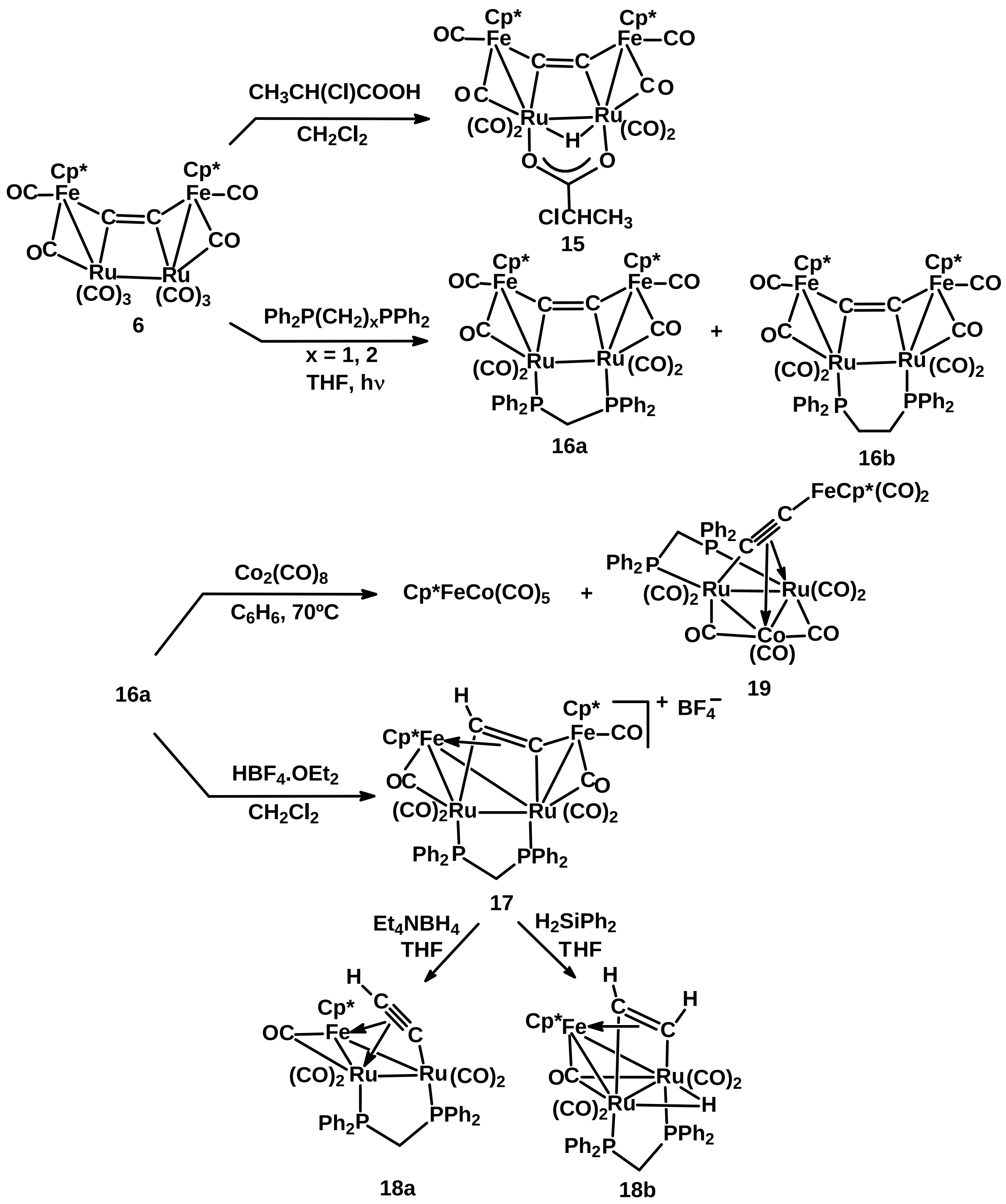
Scheme 3.

Thermolysis of the mixed-metal tetranuclear cluster [(μ_3-C≡C-{(η^5-C_5H_5)Fe(CO)$_2$})Ru$_3$(μ-H)(CO)$_9$] (**4**) affords two products: [CpFeRu$_6$(μ_5-C$_2$)(μ_5-C$_2$H)(CO)$_{16}$] (**10**) and [Cp$_2$Fe$_2$Ru$_6$(μ_6-C$_2$)$_2$(CO)$_{17}$] (**11**) (Scheme 4).[33] The anion [(μ_3-C≡C-{(η^5-C_5H_5)Fe(CO)$_2$})Ru$_3$(CO)$_9$]$^-$ (**12**) derived from **4** undergoes coupling of the {(C$_2$)FeRu$_3$} core to give compound **11** and a heptanuclear cluster [Cp$_2$Fe$_2$Ru$_5$(μ_5-C$_2$)$_2$(CO)$_{17}$] (**14**), a coordinatively saturated compound with 112 cluster valence electrons bearing two six-electron donating C$_2$ ligands.



Scheme 4.

Treatment of **6** with *R*-chloropropionic acid results in an addition reaction yielding a μ-hydrido μ-carboxylato derivative, $[(\mu_4\text{-C=C})(\mu\text{-H})(\mu\text{-}\kappa^1,\kappa^1\text{-CH}_3\text{CHClCOO})\text{Fe}_2\text{Ru}_2\text{Cp*}_2(\text{CO})_8]$ (**15**). On irradiation of a THF solution of **6**, in presence of diphosphines, $[\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2]$ (n= 1, 2), the substituted products $[(\mu_4\text{-C=C})\text{Fe}_2\text{Ru}_2\text{Cp*}_2(\text{CO})_8\{\mu\text{-Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2\}]$ (n = 1, **16a**; n = 2, **16b**) are formed. Treatment of **16** with $\text{HBF}_4\text{.OEt}_2$ results in protonation at the C=C unit to give the cationic $\mu_4\text{-C}_2\text{H}$ complex, $[(\mu_4\text{-C=CH})\text{Fe}_2\text{Ru}_2\text{Cp*}_2(\text{CO})_{12}(\text{dppm})]\text{BF}_4$ (**17**) which on reduction with $[\text{NEt}_4]\ \text{BH}_4$ results in elimination of one of the iron fragments to afford a trinuclear acetylide cluster, [(μ_3-C≡CH)FeRu$_2$Cp*(CO)$_5$(dppm)] (**18a**). On the other hand, treatment of **17** with H$_2$SiPh$_2$ leads to hydrogen addition to give the trinuclear μ_3-HC=CH complex [(μ_3-HC=CH)(μ-H)FeRu$_2$Cp*(CO)$_5$(dppm)] (**18b**). Thus, the μ_3-HC=CH ligand in **18b** arises from formal hydrogenation of the μ_4-C=C ligand in **16a** and the ligand transformations are realized by the flexible coordination capability of the C$_2$ ligand. Cluster expansion of **16a** with [Co$_2$(CO)$_8$] gives [(μ_3-C≡CFe(CO)$_2$Cp*)FeRu$_2$CoCp*(CO)$_{12}$(dppm)] (**19**) (Scheme 5).[34a]



Scheme 5.

Thermal reaction of a THF solution of ethynediyl complex $[\{Cp_2Ru(CO)_2\}_2(\mu\text{-}C\equiv C)]$ (**20**) with diiron nonacarbonyl gives $[Cp_2Fe_2Ru_2(\mu_4\text{-}C\equiv C)(\mu\text{-}CO)(CO)_8)]$ **(21)** (Figure 1).[34b]

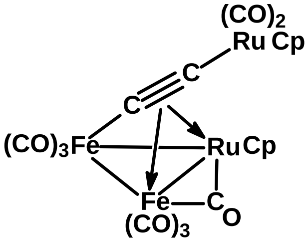


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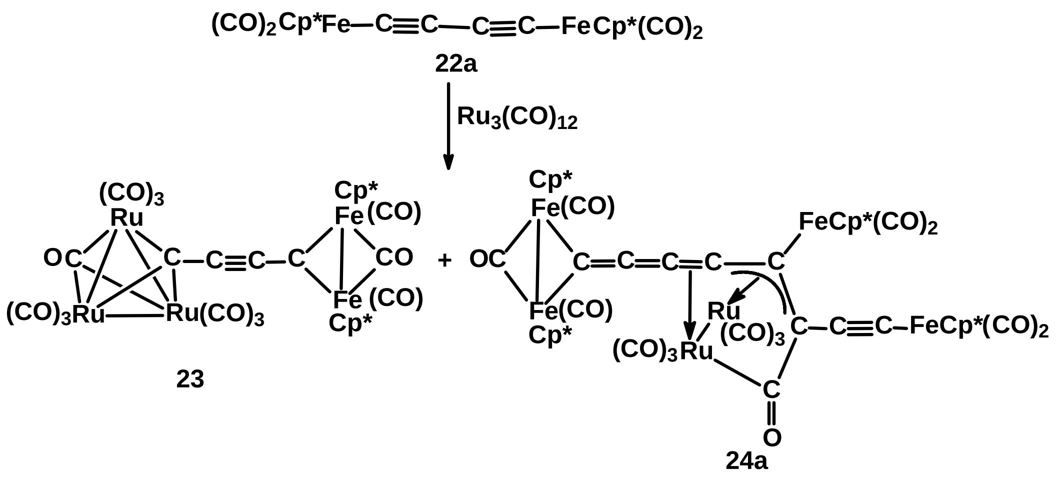
Figure 1.

Highly conjugated polycarbon–metal systems, the zwitterionic μ-but-2-yn-1-ylidene-4-ylidyne complex [$Ru_3(CO)_{10}(\mu_3$-C–C≡C–μ-C)$Fe_2Cp^*_2(CO)_3$] (**23**) and the dimerized product with a cumulenic μ-C_8 ligand, [$(Cp^*Fe)_4Ru_2(CO)_{13}[\mu_6$-$C_8$–C(=O)] (**24a**) have been isolated from the reactions of butadiynediyldimetal complex, [{(η^5-C_5Me_5)$Fe(CO)_2$}–C≡C–C≡C–Fe(η^5-C_5Me_5)$(CO)_2$] (**22a**) with [$Ru_3(CO)_{12}$] (Scheme 6). An isostructural C_8 complex **24b** is obtained on reaction of the Fe-Ru mixed metal complex [{(η^5-C_5Me_5)$Fe(CO)_2$}–C≡C–C≡C–Ru(η^5-C_5Me_5)$(CO)_2$] (**22b**) with [$Ru_3(CO)_{12}$]. A zwitterionic acetylide cluster-type product {(η^5-C_5Me_5)$Fe(CO)_2$}$^+$[Cp$(CO)_2$Ru(η^2-C≡C)–(μ_3-C≡C)$Fe_3(CO)_9$]$^-$ (**25**) is formed by the reaction of butadiynediyldimetal complex, [{(η^5-C_5Me_5)$Fe(CO)_2$}–C≡C–C≡C–Ru(η^5-C_5H_5)$(CO)_2$] (**22c**) with [$Fe_2(CO)_9$] (Figure 2).[35a] X-ray crystallography reveals a pentanuclear structure containing a dinuclear μ-η^1,η^2-acetylide cationic species and a trinuclear μ_3-acetylide anionic species.



Scheme 6.

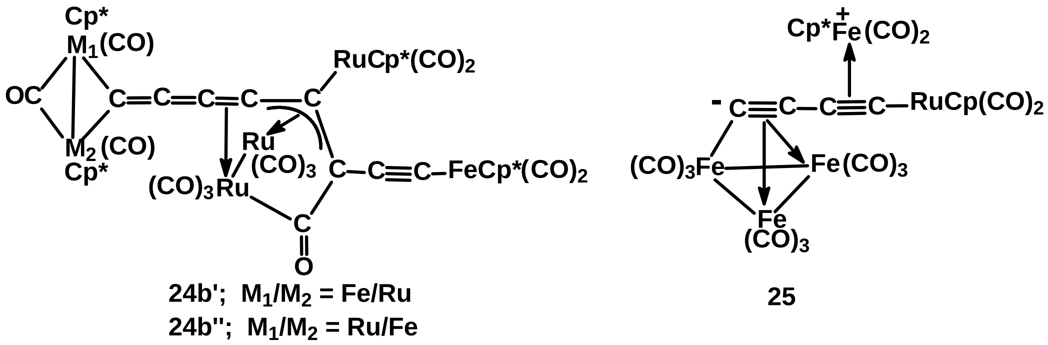
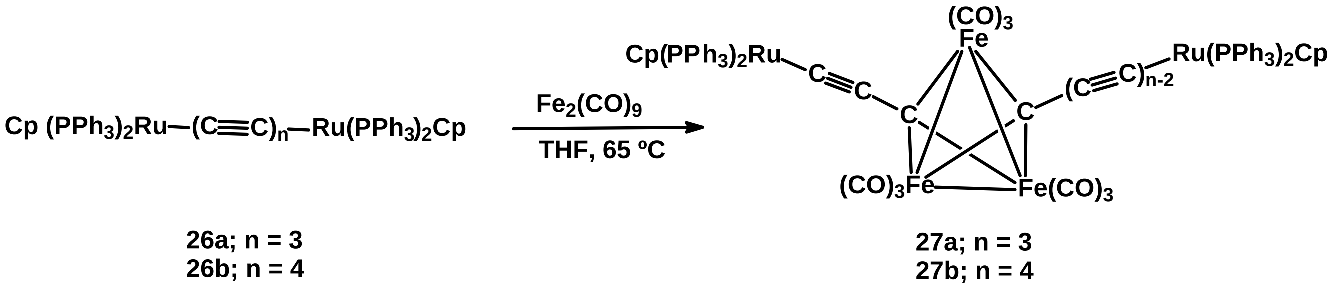


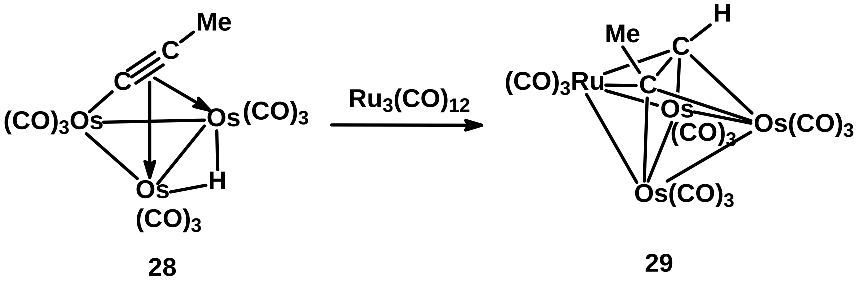
Figure 2.

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



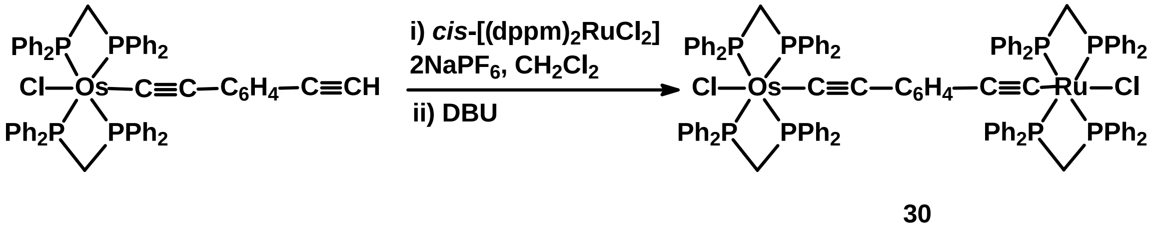
Scheme 7.

The triosmium acetylide cluster, $[Os_3(\mu\text{-}H)(\mu_3\text{-}C{\equiv}CMe)(CO)_9]$ (**28**) reacts with $[Ru_3(CO)_{12}]$ in refluxing hexane to give the tetranuclear $[RuOs_3(\mu_4\text{-}HC_2Me)(CO)_{12}]$ (**29**) (Scheme 8).[36a]



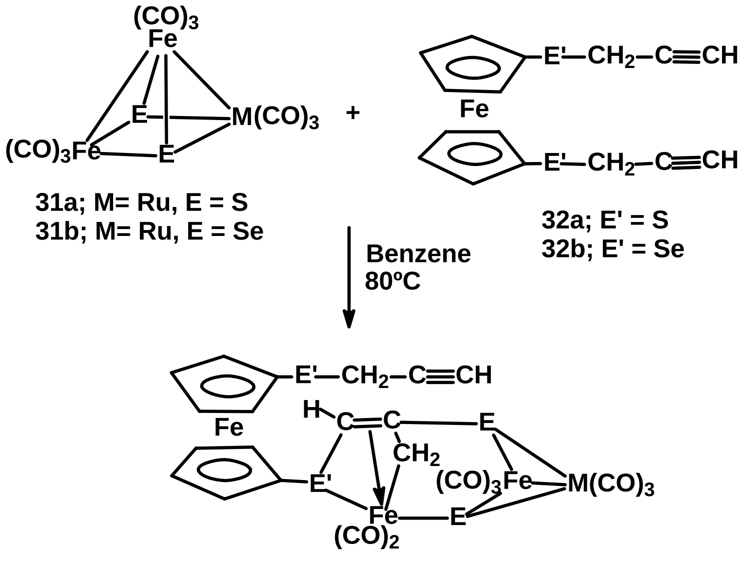
Scheme 8.

Reaction of a dichloromethane solution of *cis*-$[(dppm)_2RuCl_2]$ with *trans*-$[(dppm)_2(Cl)Os(C{\equiv}C\text{-}p\text{-}C_6H_4\text{-}C{\equiv}CH)]$ and $NaPF_6$ gives a vinylidene complex, which converts to *trans*-$[(dppm)_2(Cl)Os(C{\equiv}C\text{-}p\text{-}C_6H_4\text{-}C{\equiv}C\text{-}Ru(Cl)(dppm)_2]$ (**30**) on addition of DBU in the reaction mixture (Scheme 9).[36b]



Scheme 9.

On reflux of a benzene solution containing $[Fe_2M(CO)_9(\mu_3\text{-}E)_2]$ (M = Ru; E = S, Se) (**31a, b**) and $[Fe(\eta^5\text{-}C_5H_4E'CH_2C{\equiv}CH)_2]$ (E' = S, **32a**; Se, **32b**) unusual ferrocenyl containing heterometal clusters $[Fe(\eta^5\text{-}C_5H_4E'CH_2C{\equiv}CH)(\eta^5\text{-}C_5H_4\{Fe_2M(CO)_8(\mu\text{-}E)(\mu_3\text{-}E)(E'CHCCH_2)\})]$ (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 $\{(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_4SeCH_2C{\equiv}CH)Fe\}$ unit.



31a; M= Ru, E = S
31b; M= Ru, E = Se

32a; E' = S
32b; E' = Se

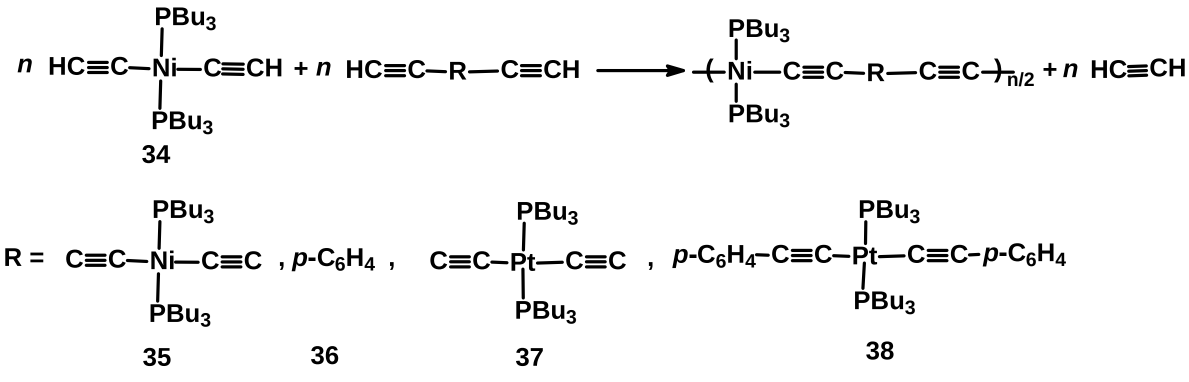
33a; M = Ru, E = Se, E' = Se
33b; M = Ru, E = S, E' = Se

Scheme 10.

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).

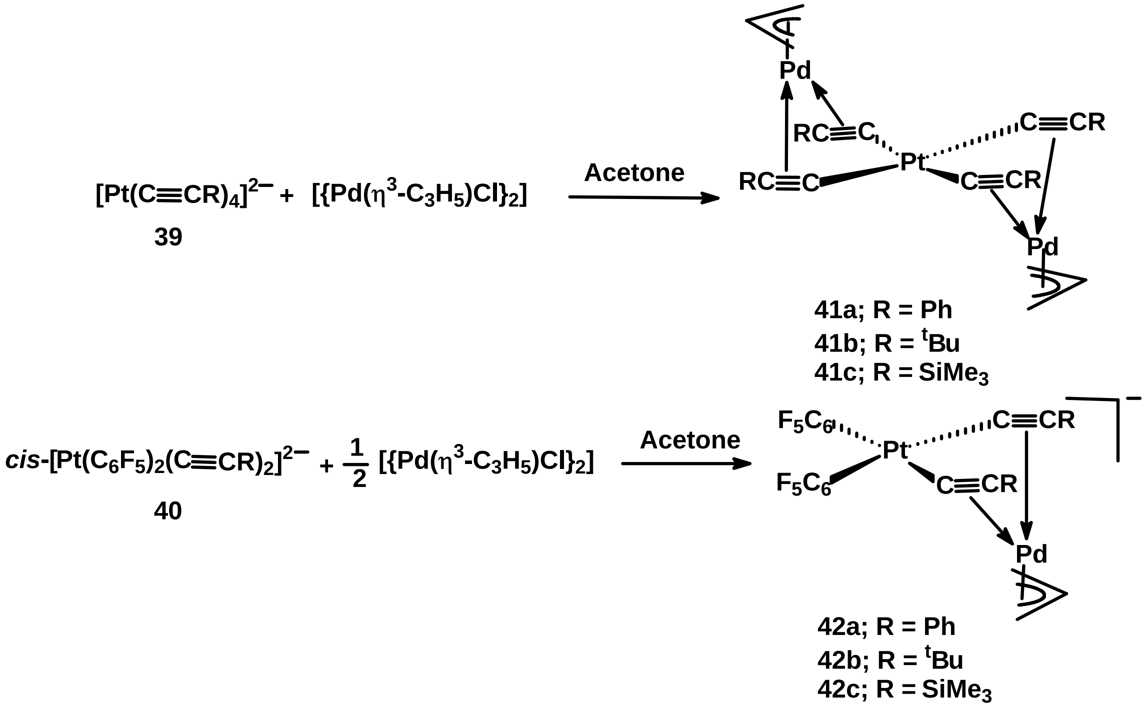


34

35 36 37 38

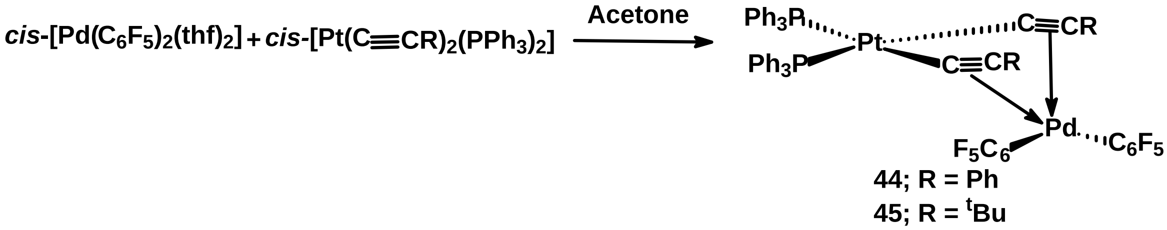
Scheme 11.

Formation of heterodinuclear Pt-Pd anionic complexes $[(C_6F_5)_2Pt(CCR)_2Pd(\eta^3\text{-}C_3H_5)]^-$ (R = Ph, ^{t}Bu, $SiMe_3$) (**42a-c**) and neutral trinuclear complexes $[\{(\eta^3\text{-}C_3H_5)Pd\}_2\{Pt(CCR)_4\}]$ (R = Ph, ^{t}Bu, $SiMe_3$) (**41a-c**) have been reported from the reactions of anionic substrates **39**, $[Pt(C{\equiv}CR)_4]^{2-}$ or **40**, *cis*-$[Pt(C_6F_5)_2(C{\equiv}CR)_2]^{2-}$ with $[\{Pd\ (\eta^3\text{-}C_3H_5)Cl\}_2]$ complex (Scheme 12).[39]



Scheme 12.

The reaction of mononuclear platinum acetylide complexes [*cis*-$Pt(CCR)_2L_2$] (R = Ph, ^{t}Bu; L = PPh_3) towards *cis*-$[Pd(C_6F_5)(thf)_2]$ (**43**) results in the formation of dimetallic Pt-Pd (R =Ph, **44**; R = ^{t}Bu, **45**) complexes (Scheme 13).[40]



Scheme 13.

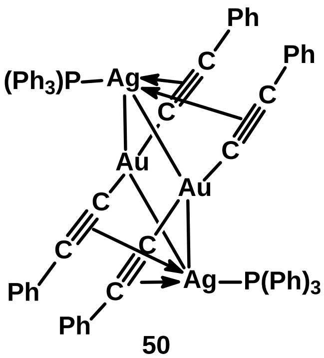
IV

MIXED GROUP 11 METAL ACETYLIDE COMPLEXES

New aspects of chemistry and bonding have emerged from reactions of the anionic linear metal acetylide complexes $[M(C_2Ph)_2]^-$ with metal phenylacetylide polymers $[M(C_2Ph)]_n$ (M = Cu, Ag, Au). The reactions involve depolymerization, ethynylation and condensation to form novel clusters. Thus, the homonuclear $[Ag_5(C_2Ph)_6]^-$ and heteronuclear $[Au_2Cu(C_2Ph)_4]^-$, $[Au_3M_2(C_2Ph)_6]^-$ (M = Cu, Ag), $[Ag_6Cu_7(C_2Ph)_{14}]^-$, and $[AuAg_6Cu_6(C_2Ph)_{14}]^-$ complexes have been obtained. Extension of ethynylation reactions to neutral complexes resulted in formation of $[Au_2Ag_2(C_2Ph)_4(PPh_3)_2]$, $[Ag_2Cu_2(C_2Ph)_4(PPh_3)_4]$, $[AuAg(C_2Ph)_2]_n$, $[AuCu(C_2Ph)_2]_n$, and $[AgCu(C_2Ph)_2]_n$.

Mixed gold-silver and gold-copper phenylacetylide polymers $[\{AuM(C_2Ph)_2\}_n]$ (M = Ag, **46**; M = Cu, **47**) have been made by the reaction of $[Au(C_2Ph)L]$ (L = $AsPh_3$, $P(OPh)_3$) with $[\{Ag(C_2Ph)\}_n]$ (**48**) and $[\{Cu(C_2Ph)\}_n]$ (**49**) respectively. The gold-silver polymer **46** has also been prepared by the reaction of $[AuClPPh_3]$ with $[\{Ag(C_2Ph)\}_n]$.[41]

Another heterometallic gold-silver cluster, $[Au_2Ag_2(C_2Ph)_4(PPh_3)_2]$ (**50**) has been prepared by the reaction of $[(PPh_3)AuC_2Ph]$ and $[AgC_2Ph]_n$ and also by the reaction of PPh_3 with the polymer $[AuAg(C_2Ph)_2]_n$ (**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 π-bonded to two triple bonds and one phosphine ligand (Figure 3).



50

Figure 3.

$$\begin{tikzcd}
Ph_3PAuC_2Ph + AgC_2Ph \arrow[r] & \underset{\mathbf{50}}{[AuAg(C_2Ph)_2PPh_3]_2} \arrow[d, shift left] \\
Ph_3PAuCl + 2AgC_2Ph \arrow[r] & \underset{\mathbf{46}}{[AuAg(C_2Ph)_2]_n} \arrow[u, shift left, "PPh_3"]
\end{tikzcd}$$

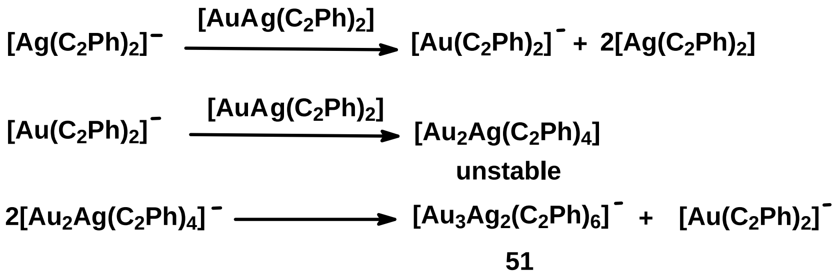
Scheme 14.

Reaction of $[Au_2(C_2Ph)_3]^-$ and $[AgC_2Ph]$ gives a gold-silver pentanuclear cluster $[Au_3Ag_2(C_2Ph)_6]^-$ (**51**) (Scheme 15).[43]

$$[N(PPh_3)_2][Au_2(C_2Ph)_3] \xrightarrow{[AgC_2Ph]} \underset{\mathbf{51}}{1/2[N(PPh_3)_2][Au_3Ag_2(C_2Ph)_6]} + 1/2[N(PPh_3)_2][Au(C_2Ph)_2]$$

Scheme 15.

The pentanuclear cluster $[Au_3Ag_2(C_2Ph)_6]^-$ (**51**) has also been obtained from the reaction between $[Ag(C_2Ph)_2]^-$ and the polymer complex $[\{AuAg(C_2Ph)_2\}_n]$ (**46**) (Scheme 16).[44]



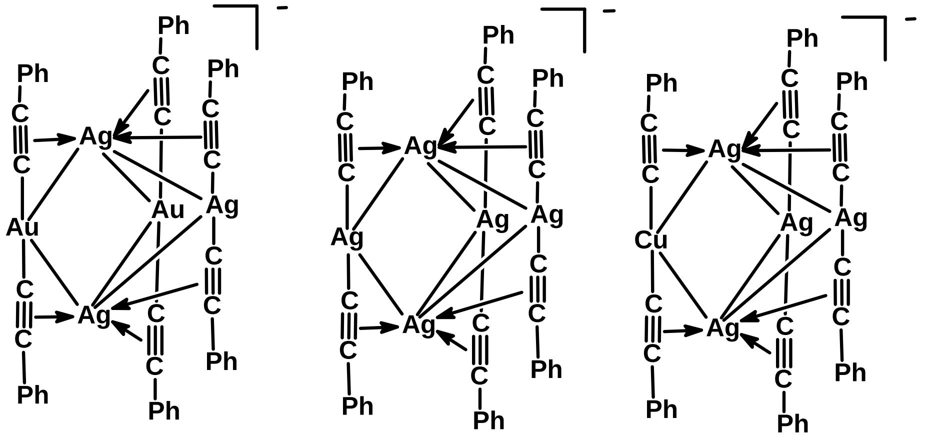
$$[Ag(C_2Ph)_2]^- \xrightarrow{[AuAg(C_2Ph)_2]} [Au(C_2Ph)_2]^- + 2[Ag(C_2Ph)_2]$$

$$[Au(C_2Ph)_2]^- \xrightarrow{[AuAg(C_2Ph)_2]} \underset{\text{unstable}}{[Au_2Ag(C_2Ph)_4]}$$

$$2[Au_2Ag(C_2Ph)_4]^- \longrightarrow \underset{\mathbf{51}}{[Au_3Ag_2(C_2Ph)_6]^-} + [Au(C_2Ph)_2]^-$$

Scheme 16.

Homonuclear silver complex $[Ag_5(C_2Ph)_6]^-$ (**52**) and heteronuclear silver-copper complex $[Ag_4Cu(C_2Ph)_6]^-$ (**53**) have been obtained by the reactions of silver phenylacetylide with the linear complex anions $[Ag(C_2Ph)_2]^-$ and $[Cu(C_2Ph)_2]^-$, respectively (Figure 4).[43]



51 **52** **53**

Figure 4.

The reaction of $[Cu(C_2Ph)_2]^-$ and $[\{AuCu(C_2Ph)_2\}_n]$ (**47**) affords the cluster $[Au_2Cu(C_2Ph)_4]^-$ (**54**) or $[Au_3Cu_2(C_2Ph)_6]^-$ (**55**) depending on the molar ratio of the reactants. The pentanuclear cluster $[N^nBu_4][Au_3Cu_2(C_2Ph)_6]$ (**55**) is also obtained by the reaction of $[N^nBu_4][Au(C_2Ph)_2]$ with a mixture of $[AuC_2Ph]_n$ and $[CuC_2Ph]_n$.[45] 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 σ-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 $[Cu(C_2Ph)_2]^-$ and $[\{AuAg(C_2Ph)_2\}_n]$ (**46**) gives the expected complex $[Au_3Ag_2(C_2Ph)_6]^-$ (**51**) and the trimetallic $[AuAg_6Cu_6(C_2Ph)_{14}]^-$ (**56**) (Scheme 17).[46]

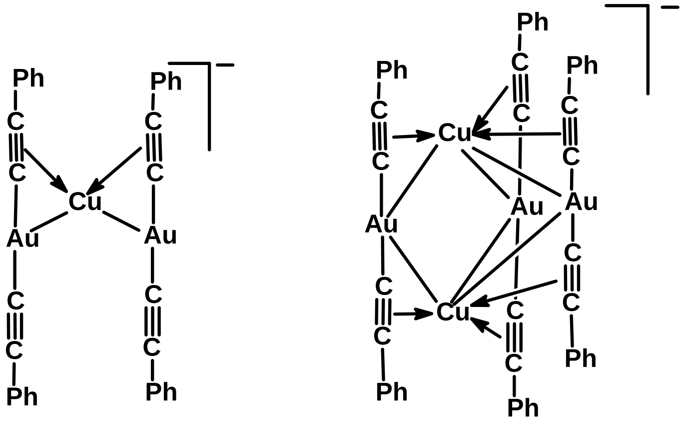
$$[Cu(C_2Ph)_2]^- + 2[AuAg(C_2Ph)_2] \longrightarrow \underset{\text{unstable}}{[Au_2Ag_2Cu(C_2Ph)_6]^-}$$

$$[Au_2Ag_2Cu(C_2Ph)_6]^- \longrightarrow [AgCu(C_2Ph)_2] + [Au_2Ag(C_2Ph)_4]^-$$

$$2[Au_2Ag(C_2Ph)_4]^- \longrightarrow \underset{\mathbf{51}}{[Au_3Ag_2(C_2Ph)_6]^-} + [Au(C_2Ph)_2]^-$$

$$[Au(C_2Ph)_2]^- + 6[AgCu(C_2Ph)_2] \longrightarrow \underset{\mathbf{56}}{[AuAg_6Cu_6(C_2Ph)_{14}]^-}$$

Scheme 17.

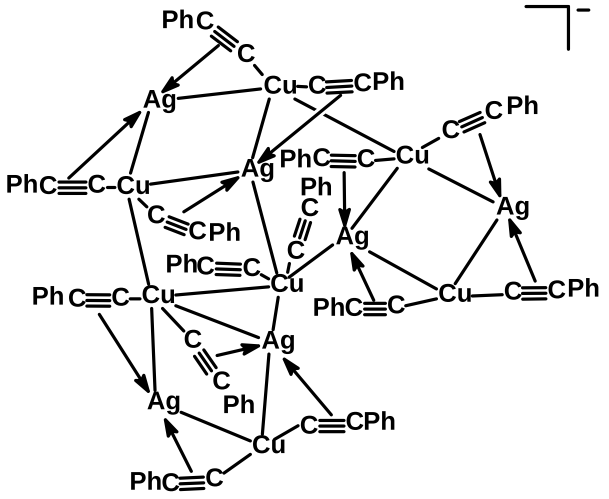


54 **55**

Figure 5.

A trimetallic cluster, $[Au_3AgCu(C_2Ph)_6]^-$ (**57**) has been prepared by the reaction of $[Au_3Cu_2(C_2Ph)_6]^-$ (**55**) with a mixture of gold phenylacetylide and silver phenylacetylide. Complex **57** is also obtained by the addition of $[Au_3Ag_2(C_2Ph)_6]^-$ (**51**) to $[\{AuCu(C_2Ph)_2\}_n]$ (**47**) or by the reaction of $[Au_2Cu(C_2Ph)_4]^-$ (**54**) with $[\{AuAg(C_2Ph)_2\}_n]$ (**46**). High nuclearity heterometallic cluster $[AuAg_6Cu_6(C_2Ph)_{14}]^-$ (**56**) has been synthesized by the reaction of a dichloromethane solution of polymeric $[\{Ag(C_2Ph)\}_n]$, $[\{Cu(C_2Ph)\}_n]$ and $[Ag(C_2Ph)_2]^-$. Other synthetic methods to prepare **56** include reaction of $[Au_3Cu_2(C_2Ph)_6]^-$ (**55**) or $[Au_3Ag_2(C_2Ph)_6]^-$ (**51**) with a mixture of $[\{Ag(C_2Ph)\}_n]$ and $[\{Cu(C_2Ph)\}_n]$.[48] Room temperature reaction of the linear complex $[Ag(C_2Ph)_2]^-$ and a mixture of $[\{Cu(C_2Ph)\}_n]$ and $[\{Ag(C_2Ph)\}_n]$ in dichloromethane affords the silver-copper heteronuclear cluster $[Ag_6Cu_7(C_2Ph)_{14}]^-$**(57)**. When $[Cu(C_2Ph)_2]^-$ or halide ions, X^- (X = Cl, Br, I) are treated with $[\{Ag(C_2Ph)\}_n]$ and $[\{Cu(C_2Ph)\}_n]$, cluster **57** is obtained.[47]

An X-ray diffraction study of cluster **57** 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_2Ph groups in addition to six Cu-Ag bonding interactions and three tetranuclear $[Ag_2Cu_2(C_2Ph)_4]$ subclusters (Figure 6).[49]



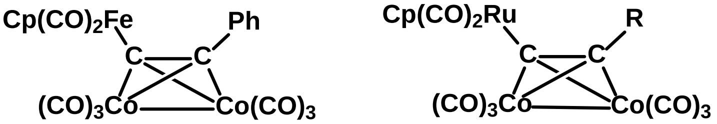
57

Figure 6.

V

MIXED GROUP 6 - 9 METAL ACETYLIDE COMPLEXES

The metal acetylides $[Cp(CO)_2MC\equiv CR]$ (**58a**, M = Fe, R = Ph and **58b-c**, M = Ru, R = Ph, ^tBu, Me) react with $[Co_2(CO)_8]$ to form the acetylide-bridged trinuclear mixed metal complexes [$Co_2(CO)_6$-μ-($Cp(CO)_2MC{\equiv}CR$)] (M = Fe and R = Ph, **59**;, M = Ru and R = Ph, ^{t}Bu, Me, **60a-c**) (Figure 7).[50]

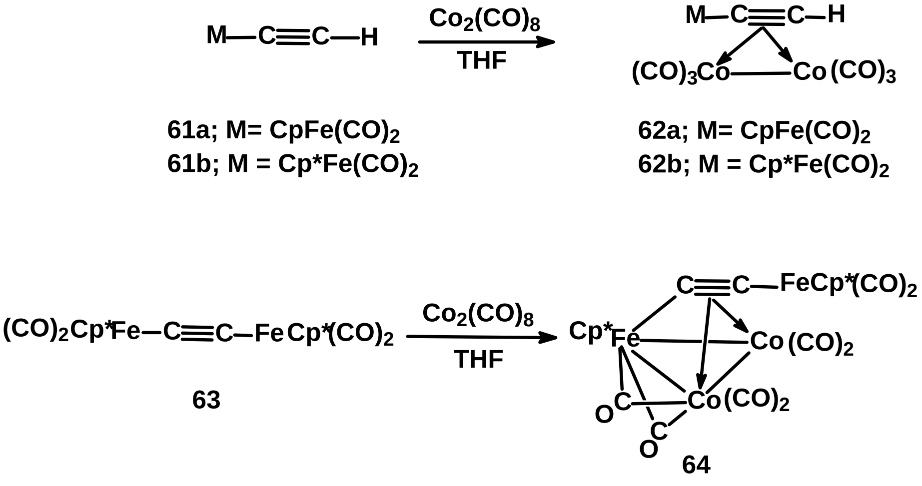


59a

60a; R = Ph
60b; R = ^{t}Bu
60c; R = Me

Figure 7.

Compounds with a tetrahedral C_2Co_2 core, [$Co_2(CO)_6$(μ-η^2,η^2-MCCH)] (M = $CpFe(CO)_2$, **62a;** M = $Cp^*Fe(CO)_2$, **62b**) have been obtained by the interaction of THF solution of ethynyliron complexes [{$CpFe(CO)_2$}-C≡CH] (**61a**) and [{$Cp^*Fe(CO)_2$}-C≡CH] (**61b**) with [$Co_2(CO)_8$] respectively. The reaction of the ethynyldiiron complex [{$Cp^*Fe(CO)_2$}-C≡C-{$Cp^*Fe(CO)_2$}] (**63**) with [$Co_2(CO)_8$] similarly affords the deep green adduct [$Cp^*Fe[Co(CO)_2]_2$(μ-CO)$_2$(μ-η^1,η^2,η^2-CC-Fp*)] (**64**), which shows fluxional properties at ambient temperature (Scheme 18).[51]

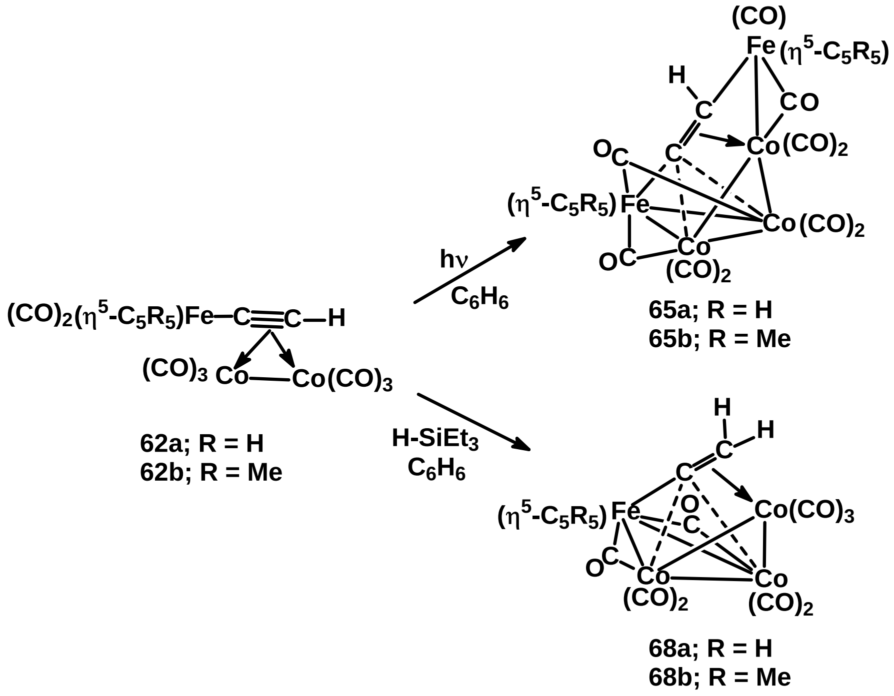


61a; M= CpFe(CO)2
61b; M = Cp*Fe(CO)2
62a; M= CpFe(CO)2
62b; M = Cp*Fe(CO)2
63
64

Scheme 18.

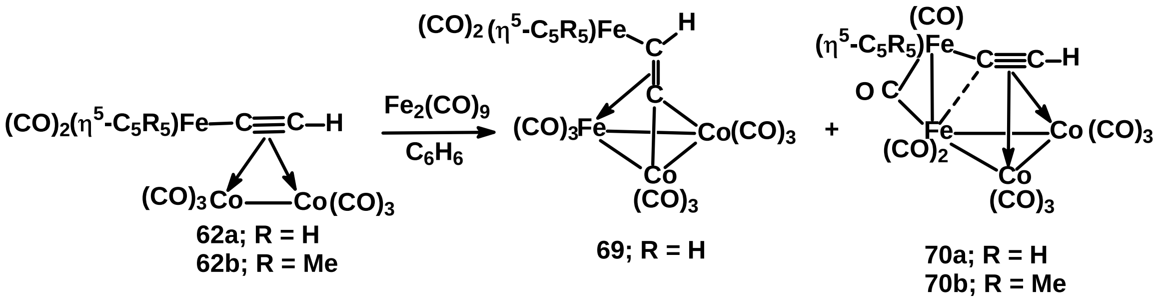
Photolytic reaction of [(μ-η^2,η^2-M-C≡C-H)$Co_2(CO)_6$] (M = $CpFe(CO)_2$, **62a;** M = $Cp^*Fe(CO)_2$, **62b**) produces pentanuclear clusters [(η^5-C_5R_5)$_2Fe_2Co_3$(μ_5-CCH)(CO)$_{10}$]

(R = H, **65a;** R = Me, **65b**), respectively, via an apparent addition reaction of a (η^5-C_5R_5)FeCo(CO)$_n$ fragment to **62**. On the other hand, thermolysis of **62a** gives the Fe-free hexacobalt cluster compound [(μ-CH=CH){(μ_3-C)$Co_3(CO)_9$}$_2$] (**66**), whereas when **62b** is thermolyzed, the Fe-Co dimer without the C_2H 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)$FeCo_3$(μ_4-C=CH_2)$(CO)_9$] (R = H, **68a**; R = Me, **68b**) by hydrosilylation and hydrometallation of the C_2H ligand, respectively (Scheme 19).[52]

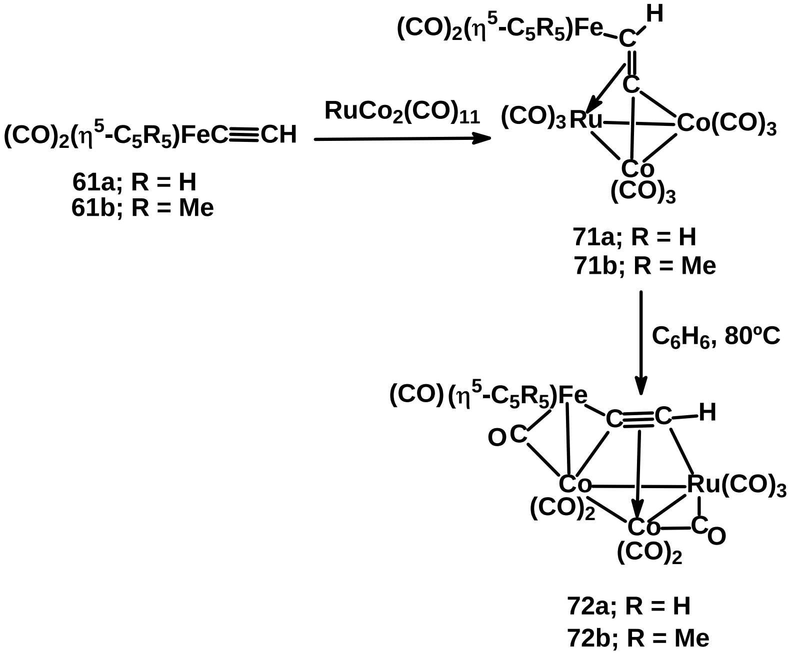


Scheme 19.

Interaction of the trinuclear ethynyl complexes [$Co_2(CO)_6$[(μ-(η^5-C_5R_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 [$Co_2Fe(CO)_9$[μ_3-C=C(H)Fe(η^5-C_5R_5)$(CO)_2$] (**69**) which undergo thermal decarbonylation to produce the tetranuclear acetylide clusters [(μ_4-C_2H)[(η^5-C_5R_5)Fe]Fe$Co_2(CO)_{10}$] (**70 a,b**) (Scheme 20). Similarly, the addition reaction of [(η^5-C_5R_5)Fe$(CO)_2$C≡CH] (**61a,b**) to the trimetallic species $RuCO_2(CO)_{11}$ affords the ruthenium analogue of the vinylidene complex $[Co_2Ru(CO)_9[\mu_3\text{-}C{=}C(H)Fe(\eta^5\text{-}C_5R_5)(CO)_2]$ (**71a,b**), which decarbonylates to $[(\mu_4\text{-}C_2H)[(\eta^5\text{-}C_5R_5)Fe]RuCo_2(CO)_{10}]$ (**72a,b**) (Scheme 21).[53]

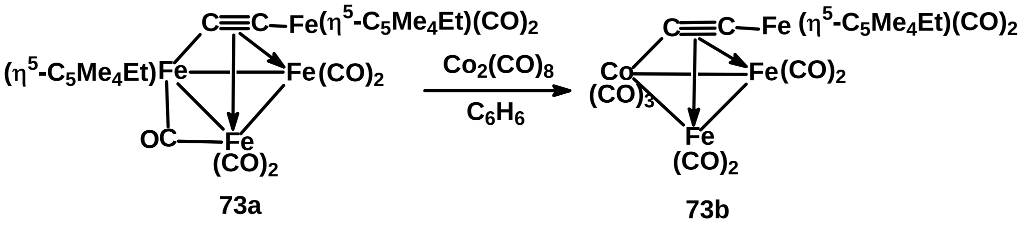


Scheme 20.



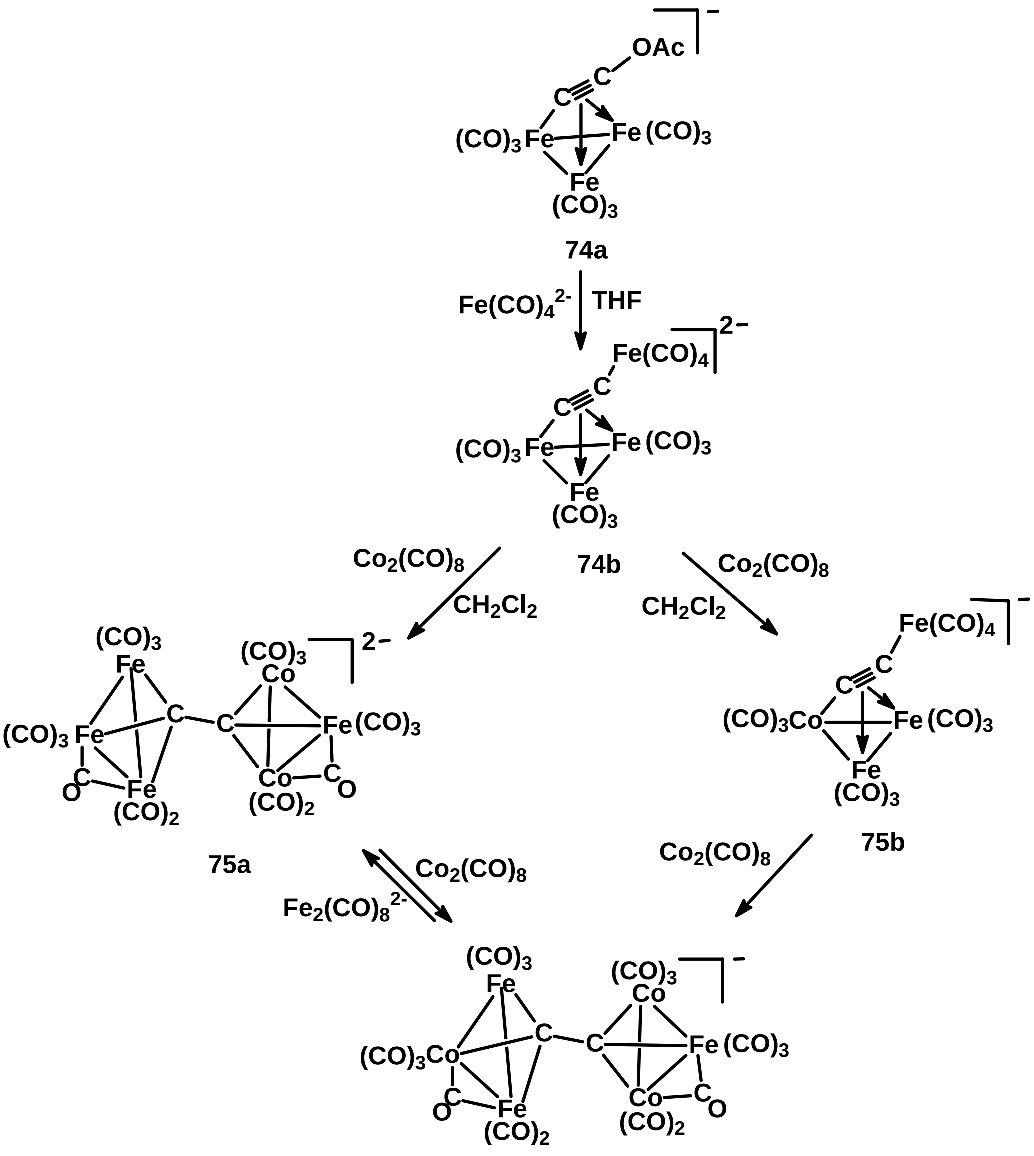
Scheme 21.

A formal replacement of $(\eta^5\text{-}C_5Me_4Et)Fe(CO)$ moiety of a triiron $\mu_3,\eta^1,\eta^2,\eta^2$-acetylide cluster compound **73a** by an isolobal $Co(CO)_3$ fragment occurs when cluster **73a** reacts with $[Co_2(CO)_8]$ (Scheme 22).[54a]



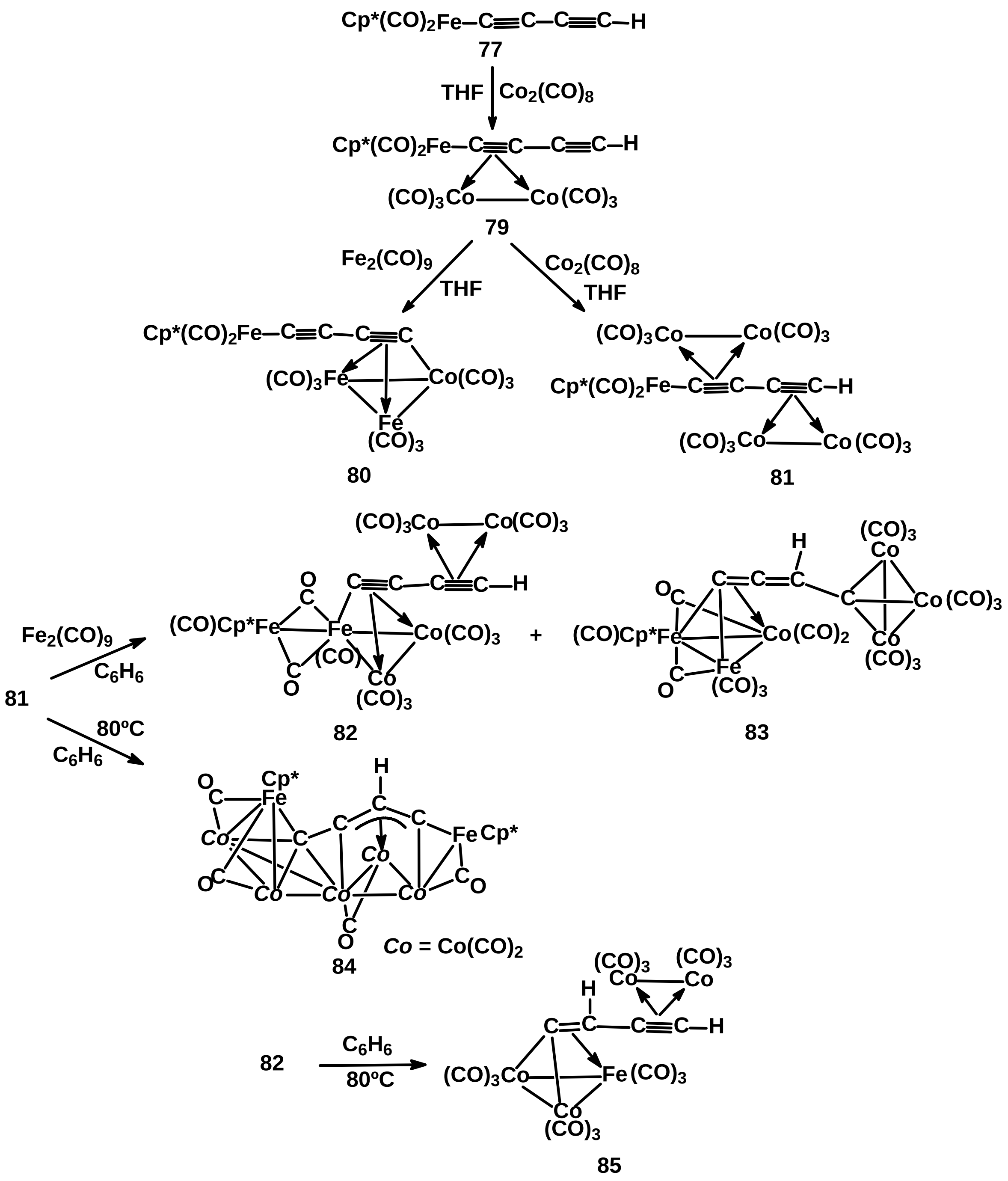
Scheme 22.

The triiron acetylide cluster compound [PPN] [$Fe_3(CO)_9C{\equiv}C(OAc)$] **(74a)** [PPN = $(Ph_3P)_2N^+$] reacts with $[Fe(CO)_4]^{2-}$ at room temperature to produce the metalated acetylide cluster $[PPN]_2[Fe_3(CO)_9C{\equiv}CFe(CO)_4]$ (**74b**). Further metalation of **74b** with excess $[Co_2(CO)_8]$ produces a hexametallic cluster [PPN] [$Fe_3Co_3(C_2)(CO)_{18}$] **(76).** The reaction proceeds by formation of two intermediate compounds, the dicarbide-containing cluster compound $[PPN]_2[Fe_4Co_2(C_2)(CO)_{18}]$ **(75a)** and the acetylide [PPN] [$Fe_2Co(CO)_9CCFe(CO)_4$] **(75b)** (Scheme 23)**.**[54b]



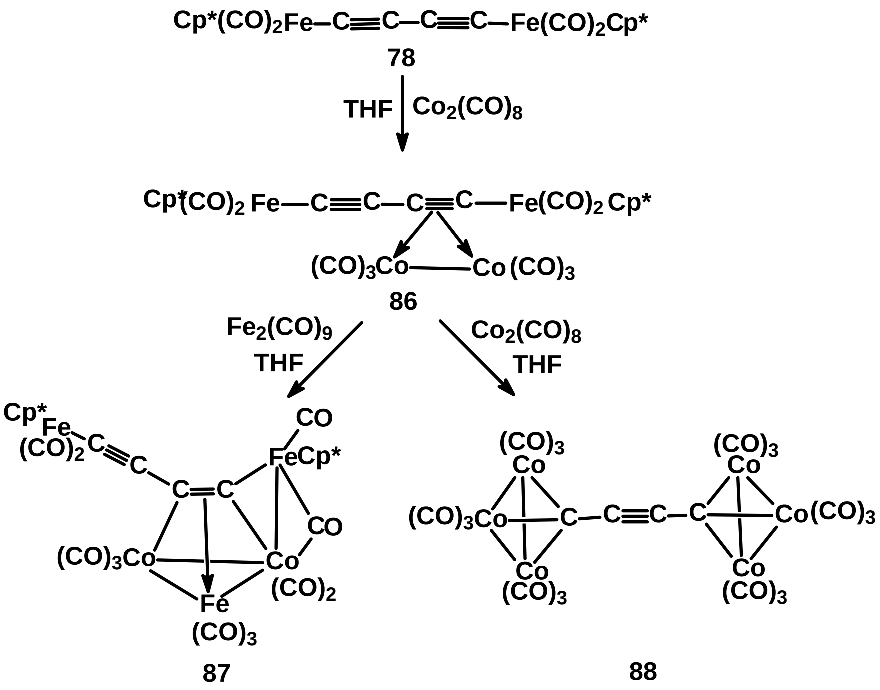
Scheme 23.

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≡C-H] (**77**) (Scheme 24).[55] 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_4H ligand.



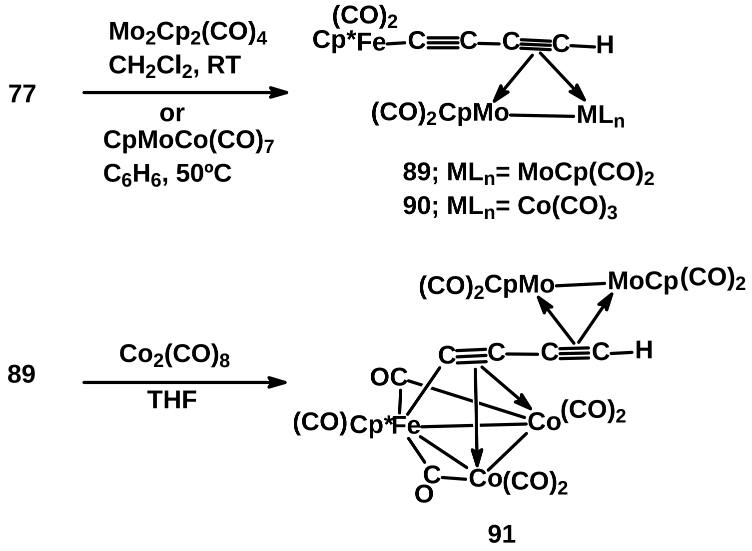
Scheme 24.

Sequential addition of [$Co_2(CO)_8$] and [$Fe_2(CO)_9$] to the butadiynediyl iron complex (**78**) results in formation of the mixed Fe/Co complexes **86** and **87** and the C_4-bridged Co_6 cluster **88** (Scheme 25).[55]



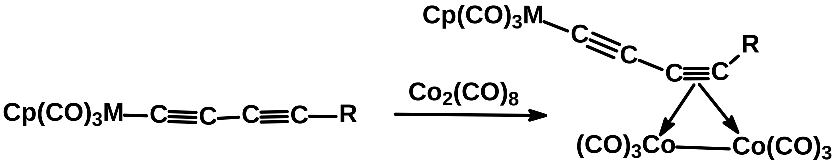
Scheme 25.

Compound **77** also reacts with [$Mo_2Cp_2(CO)_4$] at room temperature or with [$CpMoCo(CO)_7$] at 50 °C to yield mixed metal acetylide complexes **89**, [$Cp^*Fe(CO)_2C_4H\{Cp_2Mo_2(CO)_4\}$] and **90**, [$Cp^*Fe(CO)_2C_4H\{CpMoCo(CO)_5\}$]. On further reaction with [$Co_2(CO)_8$], **89** gives **91** (Scheme 26).[55]



Scheme 26.

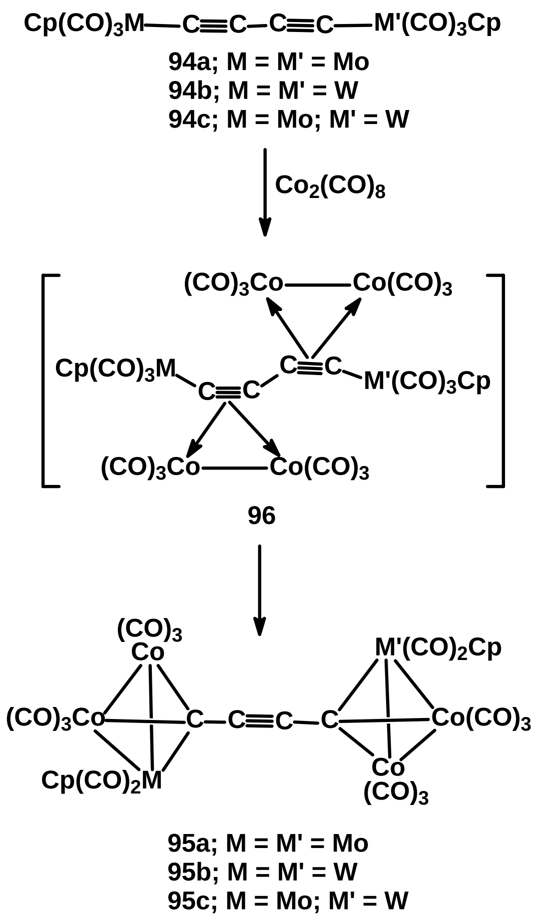
Reaction of $[Co_2(CO)_8]$ with the acetylide complexes, $[M(C{\equiv}CC{\equiv}CR)(CO)_3Cp]$ (M = Mo, W; R = H, $Fe(CO)_2Cp$) (**92a-c**) afford simple adducts (**93a-c**) containing a $Co_2(CO)_6$ group attached to the least sterically-hindered C≡C triple bond (Scheme 27). In contrast, bis-cluster complexes $[\{Cp(OC)_8Co_2M(\mu_3\text{-}C)\}C{\equiv}C\{(\mu_3\text{-}C)Co_2M'(CO)_8Cp\}]$ (M = M' = Mo, W; M = Mo, M' = W) (**95a-c**) have been obtained when $[M(C{\equiv}CC{\equiv}CR)(CO)_3Cp]$ (M = Mo, W; R = $M(CO)_3Cp$ (M = Mo, W), $Fe(CO)_2Cp$) (**94a-c**) are used to react with $[Co_2(CO)_8]$ (Scheme 28). Reaction between $[Co_2(\mu\text{-dppm})(CO)_6]$ and $[\{W(CO)_3Cp\}_2(\mu\text{-}C_4)]$ affords $[Co_2(\mu\text{-dppm})\{\mu\text{-}[Cp(OC)_3W]C_2C{\equiv}C[W(CO)_3Cp](CO)_4]$ (**97**).[56a]



92a; M = Mo; R = H
92b; M = W; R = H
92c; M = W; R = Fe(CO)$_2$Cp

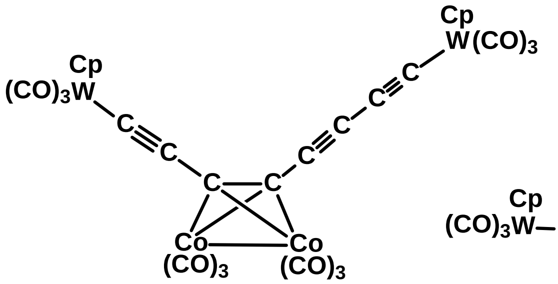
93a; M = Mo; R = H
93b; M = W; R = H
93c; M = W; R = Fe(CO)$_2$Cp

Scheme 27.

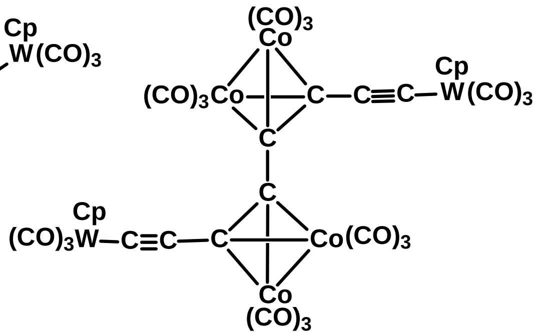


Scheme 28.

Reaction of a THF solution of [$\{W(CO)_3Cp\}_2(\mu\text{-}C_8)$] and [$Co_2CO_8$] gives mono and di-adducts, [$\{W(CO)_3Cp\}_2\{\mu\text{-}C_8[Co_2(CO)_6]\}$] (**98a**) and [$\{W(CO)_3Cp\}_2\{\mu\text{-}C_8\text{-}[Co_2(CO)_6]_2\}$] (**98b**) (Figure 8). Thermolytic reaction between [$\{W(CO)_3Cp\}_2(\mu\text{-}C_8)$] and [$Co_2(\mu\text{-dppm})(CO)_6$] under benzene reflux affords [$\{W(CO)_3Cp\}_2\{\mu\text{-}C_8[Co_2(\mu\text{-dppm})(CO)_4]\}$] (**99a**) and two isomeric products, [$\{W(CO)_3Cp\}_2\{\mu\text{-}C_8[Co_2(\mu\text{-dppm})(CO)_4]_2\}$] (**99b**) and [$\{W(CO)_3Cp\}_2\{\mu\text{-}C_8[Co_2(\mu\text{-dppm})(CO)_4]_2\}$] (**99c**) (Figure 9).[56b]

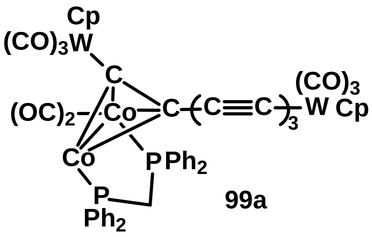


98a

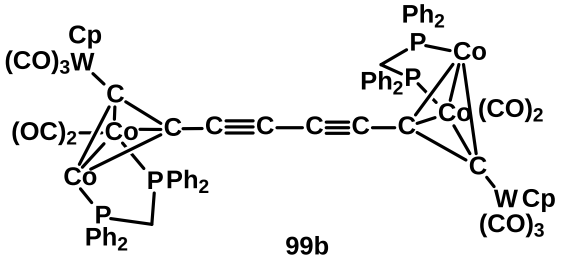


98b

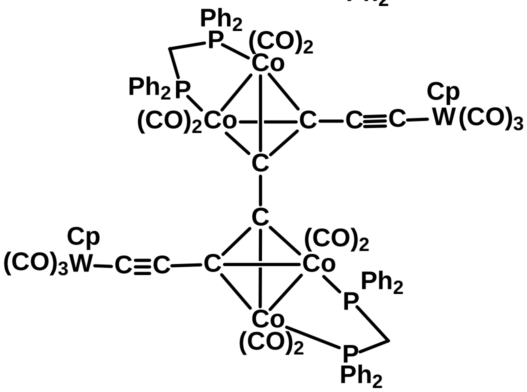
Figure 8.



99a



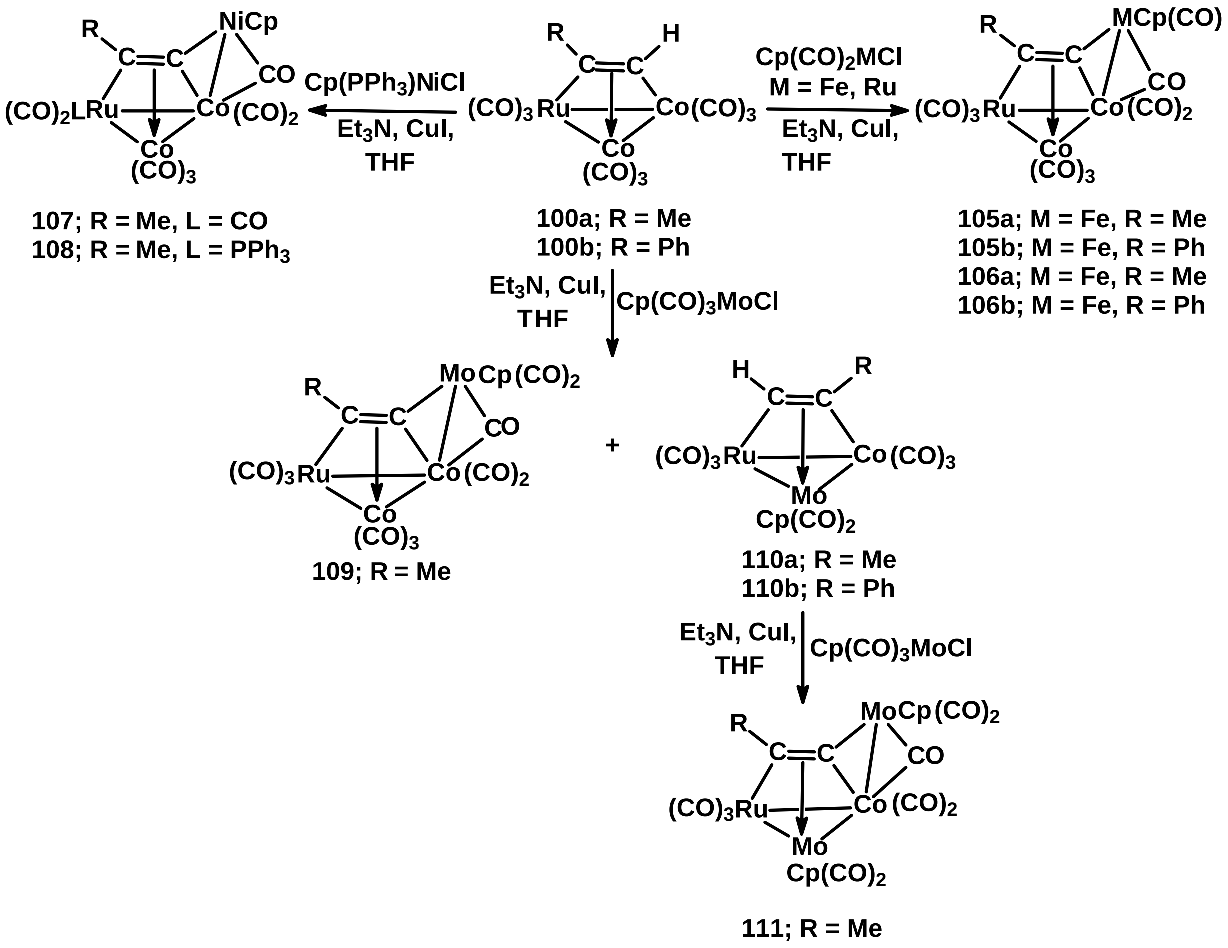
99b



99c

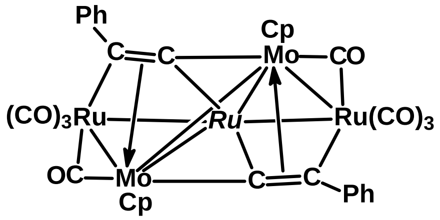
Figure 9.

Deprotonation of the alkyne-bridged clusters [$RuCo_2(CO)_9(\mu_3\text{-}RC{\equiv}CH)$] (**100a-d**) with triethylamine and further reaction with the organometallic halides [$Cp(CO)_2FeCl$] (**101**), [$Cp(CO)_2RuCl$] (**102**), [$Cp(PPh_3)NiCl$] (**103**), and [$Cp(CO)_3MoCl$] (**104**) in presence of catalytic amounts of copper(I) iodide results in incorporation of the metal species as organometallic acetylides MC≡CR into the $RuCo_2M$ metal frameworks (**105-111**) (Scheme 29). With acids, the resulting acetylide-bridged clusters are reconverted to the starting materials.[57]



Scheme 29.

A pentanuclear heterometallic acetylide complex [$Cp_2Mo_2Ru_3(CO)_{10}(C{\equiv}CPh)_2$] (**113**) has been prepared by the thermolysis reaction of a toluene solution of metal acetylide [$CpMo(CO)_3(C{\equiv}CPh)$] with [$Ru_3(CO)_{12}$] (Figure 10).[58]

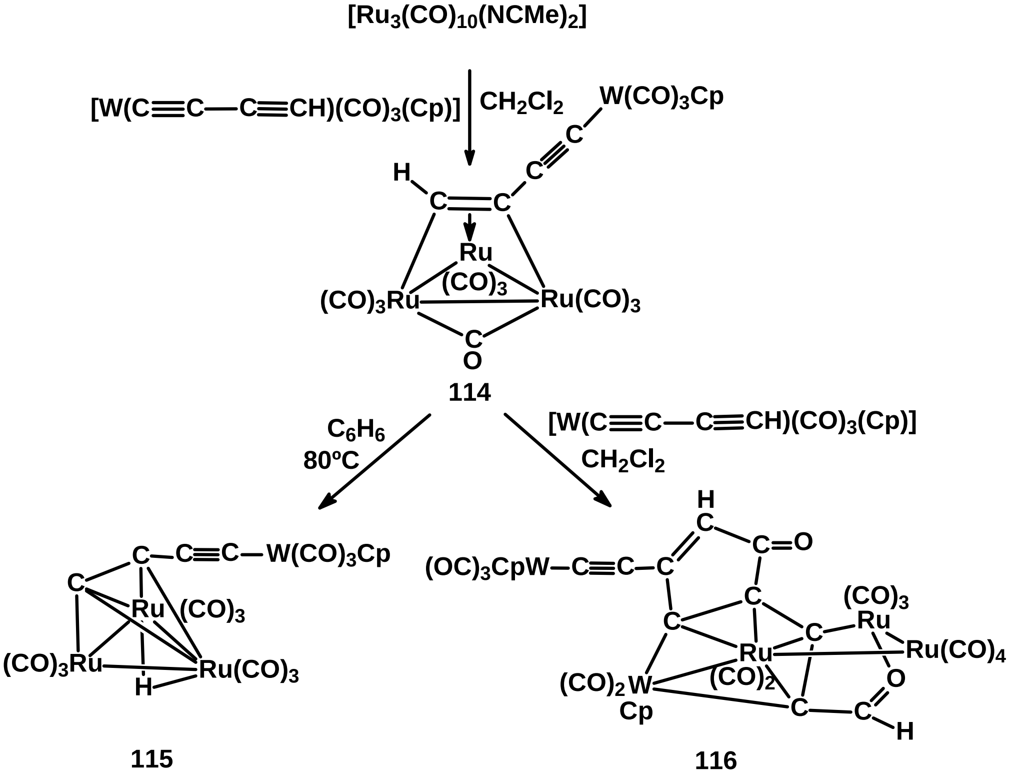


Ru = $Ru(CO)_2$

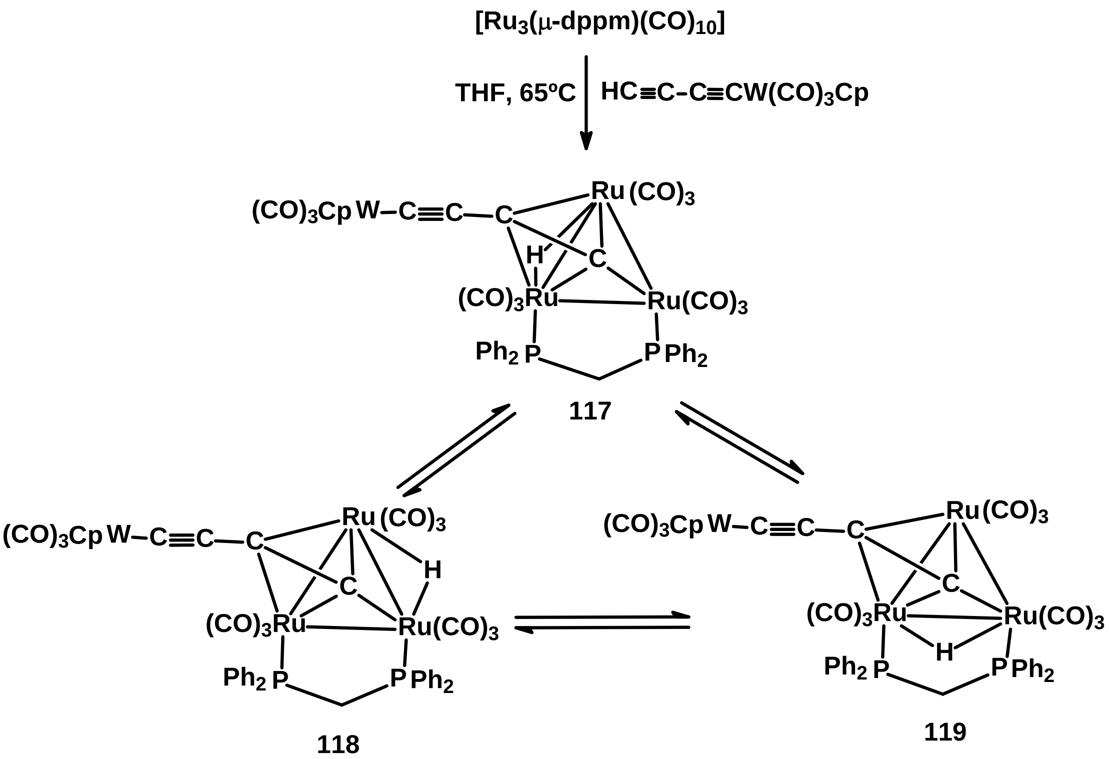
113

Figure 10.

Room temperature reaction of [W(C≡CC≡CH)(CO)$_3$Cp] with the reactive [Ru$_3$(CO)$_{10}$(NCMe)$_2$] forms initially [Ru$_3${μ$_3$-HC$_2$C≡C[W(CO)$_3$Cp]}(μ-CO)(CO)$_9$] **(114)**, which readily transforms to [Ru$_3$(μ-H){μ$_3$-C$_2$C≡C[W(CO)$_3$Cp]}(CO)$_9$] **(115)** on benzene reflux and to **116** on reaction with excess of [W(C≡CC≡CH)(CO)$_3$Cp] (Scheme 30).[59] Similarly, reaction with [Ru$_3$(μ-dppm)(CO)$_{10}$] forms three interconverting isomers of [Ru$_3$(μ-H){μ$_3$-C$_2$C≡C[W(CO)$_3$Cp]}(μ-dppm)(CO)$_{12}$] (**117-119**) (Scheme 31).

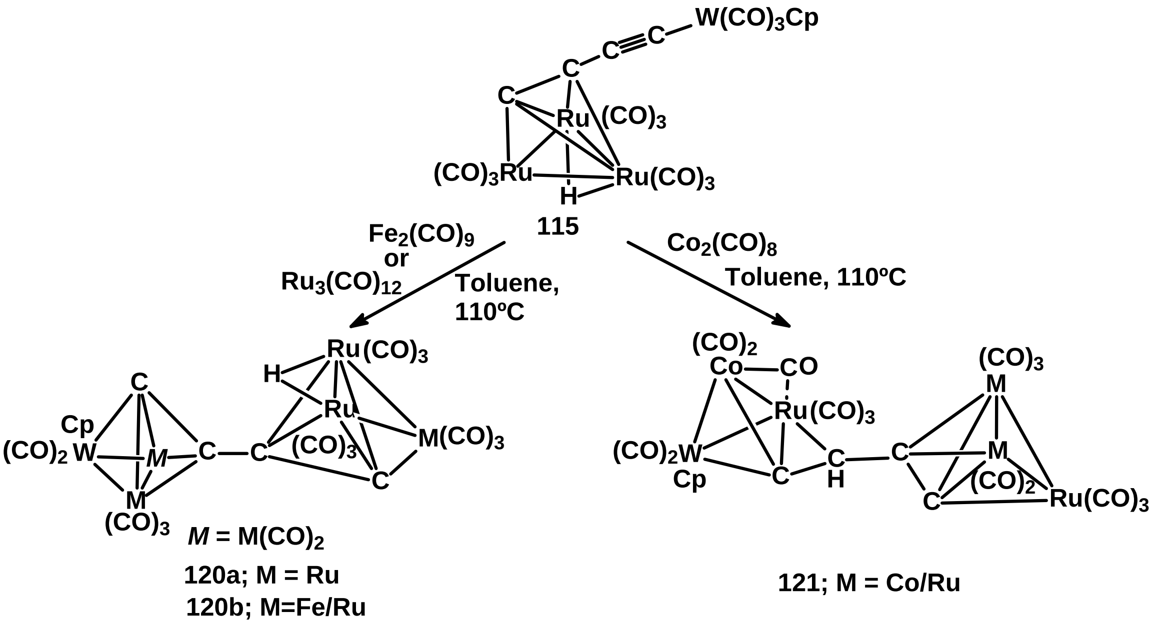


Scheme 30.



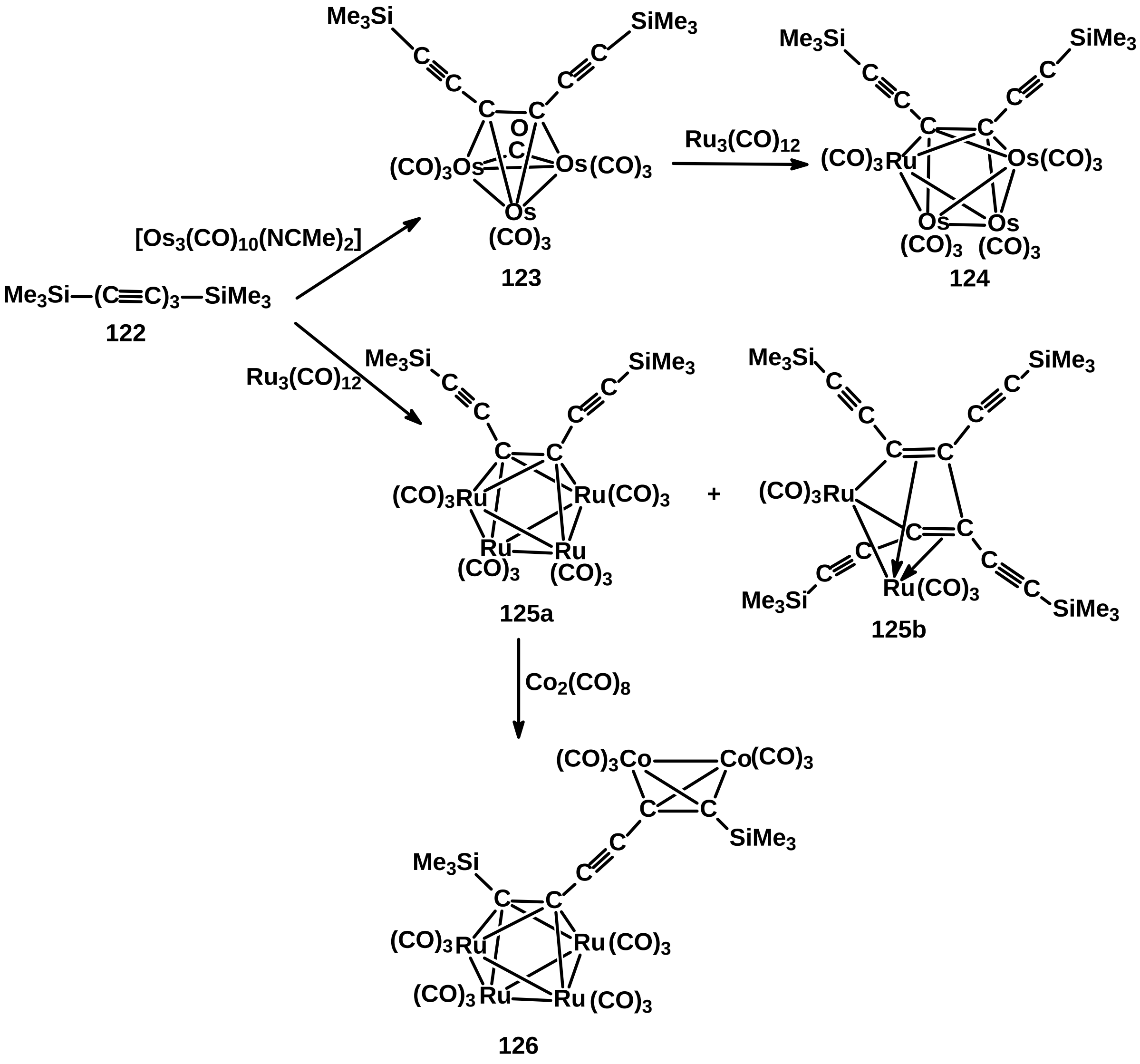
Scheme 31.

Further reaction of [Ru_3(μ-H){μ_3-C_2C≡C[W$(CO)_3$Cp]}$(CO)_9$] (**115**) with [$Ru_3(CO)_{12}$] affords [{Ru_3(μ-H)$(CO)_9$}(μ_3-η^2,μ_3-η^2-C_2C_2){$Ru_2W(CO)_8Cp$}] (**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_2C≡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,μ_3-η^2-$CCHC_2$){$CoRuW(CO)_8Cp$}] (**121**) by a process involving the transfer of cluster-bound hydride to the C_4 ligand.[59]



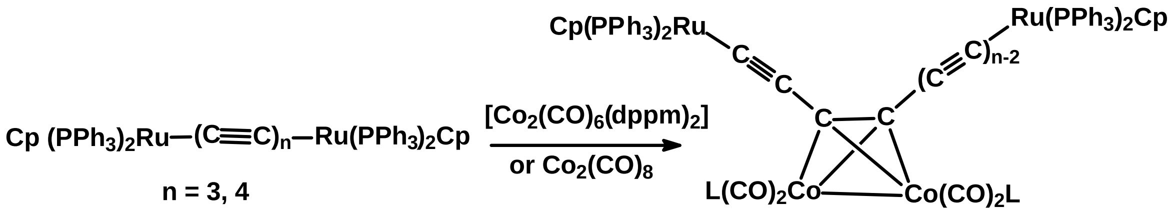
Scheme 32.

Reaction of a dichloromethane solution of 1,6-bis(trimethylsilyl)hexa-1,3,5-triyne (**122**) with $[Os_3(CO)_{10}(NCMe)_2]$ yields $[Os_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}\eta^1,\eta^1,\eta^2\text{-}Me_3SiC{\equiv}CC_2C{\equiv}CSiMe_3)]$ (**123**), which on reflux in heptane with $[Ru_3(CO)_{12}]$ gives $[Os_3Ru(CO)_{12}(\mu_4\text{-}\eta^1,\eta^2,\eta^1,\eta^2\text{-}Me_3SiC{\equiv}CC_2C{\equiv}CSiMe_3)]$ (**124**). However, thermal reaction between **122** and $[Ru_3(CO)_{12}]$ forms a butterfly cluster $[Ru_4(CO)_{12}(\mu_4\text{-}\eta^1,\eta^2,\eta^1,\eta^2\text{-}Me_3SiC{\equiv}CC_2C{\equiv}CSiMe_3)]$ (**125a**) and the ruthenole complex $[Ru_2(CO)_6\{\mu\text{-}\eta^2,\eta^5\text{-}C(C{\equiv}CSiMe_3)C(C{\equiv}CSiMe_3)C(C{\equiv}CSiMe_3)C(C{\equiv}CSiMe_3)\}]$ (**125b**). In the room temperature reaction between cluster **125a** and $[Co_2(CO)_8]$, a slippage of the butterfly cluster core along the hexatriyne chain occurs and $[\{Ru_4(CO)_{12}\}\{Co_2(CO)_6\}(\mu_4\text{-}\eta^1,\eta^2,\eta^1,\eta^2\text{:}\mu\text{-}\eta^2,\eta^2\text{-}Me_3SiC_2C{\equiv}CC_2SiMe_3)]$ (**126**) is obtained (Scheme 33).[60]



Scheme 33.

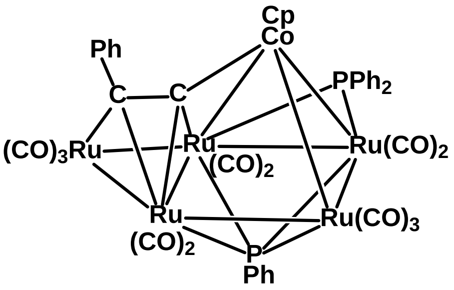
Reaction of a benzene solution of $[\{Cp(PPh_3)_2Ru\}_2(\mu\text{-}C\equiv C)_3\}]$ with $[Co_2(CO)_8]$ or $[Co_2(\mu\text{-dppm})(CO)_6]$ gives $[\{Ru(PPh_3)_2Cp\}_2\{\text{-}C\equiv CC_2\{Co_2(CO)_6\}(C\equiv C)\}]$ (**127a**) and $[\{Ru(PPh_3)_2Cp\}_2\{\mu\text{-}C\equiv CC_2\{Co_2(\mu\text{-dppm})(CO)_4\}C\equiv CC\equiv C\}]$ (**127b**), while $[\{Ru(PPh_3)_2Cp\}_2\{\mu\text{-}C\equiv CC_2\{Co_2(\mu\text{-dppm})(CO)_4\}C\equiv CC\equiv C\}]$ (**127c**) has been obtained from a thermal reaction of $[\{Cp(PPh_3)_2Ru\}_2(\mu\text{-}C\equiv C)_4\}]$ with $[Co_2(\mu\text{-dppm})(CO)_6]$ (Scheme 34).[35b]



127a; n = 3, L = CO
127b; n = 3, L_2 = dppm
127c; n = 4, L_2 = dppm

Scheme 34.

A heterometallic $CoRu_5$ cluster, $[CoRu_5(\mu_4\text{-PPh})(\mu_4\text{-}C_2Ph)(\mu\text{-}PPh_2)(CO)_{12}(\eta^5\text{-}C_5H_5)]$ (**129**) has been isolated from the reaction between $[Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}]$ (**128**) and $[Co(CO)_2(\eta\text{-}C_5H_5)]$ (Figure 11).[61] Its structure consists of a square pyramidal Ru_5Co unit, and a $Ru(Ph)C_2$-group attached to it through two ruthenium and one cobalt atoms.



129

Figure 11.

The reaction between $[Ru_3(\mu_3\text{-}\eta^2\text{-}PhC_2C_2Ph)(\mu\text{-}CO)(CO)_9]$ and $[Co_2(CO)_8]$ affords a pentametallic cluster $[Co_2Ru_3(\mu_5\text{-}\eta^2,\eta^2\text{-}PhC_2C_2Ph)(CO)_{14}]$ (**130**) in quantitative yield.[62a] The X-ray determined molecular structure consists of a Co_2Ru_3 bow-tie cluster straddled by the PhC_2C_2Ph ligand, the two C≡C triple bonds are attached to the five metal atoms by 2σ(2Ru) and π(Co) bonding modes (Figure 12).

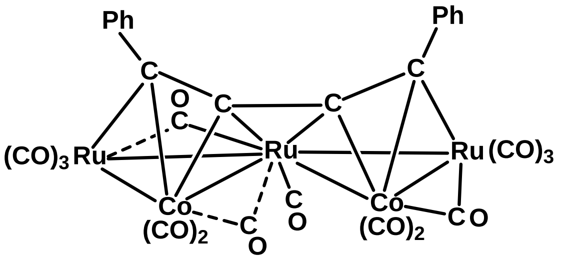


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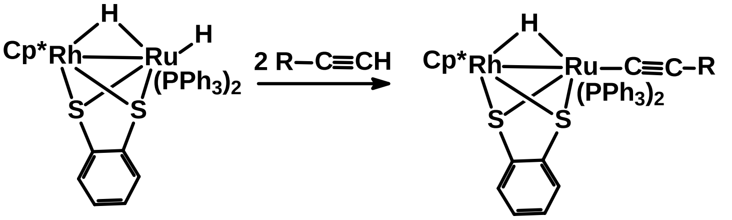
Figure 12.

A dihydride complex [Cp*Rh(μ_2-1,2-$S_2C_6H_4$)(μ_2-H)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, [Cp*Rh(μ_2-1,2-$S_2C_6H_4$)(μ_2-H)Ru(C≡CTol-*p*)(PPh_3)$_2$] (**132a**). On the other hand, reaction of **131** with trimethylsilylacetylene gives, exclusively the *cis* isomer of [Cp*Rh(μ_2-1,2-$S_2C_6H_4$)(μ_2-H)Ru(C≡CSiMe$_3$)(PPh_3)$_2$] (**132b**) (Scheme 35).[62b] 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 [Cp*Rh(μ_2-1,2-$S_2C_6H_4$)Ru(PPh_3)$_2$] unit.

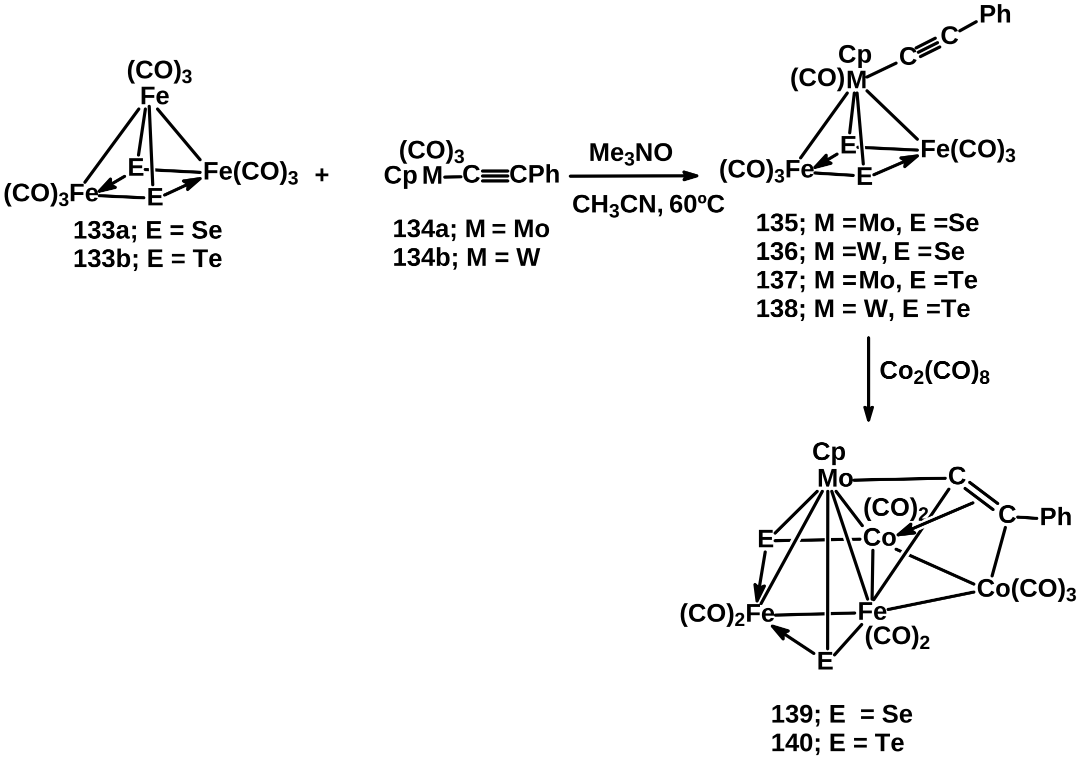


131

132a; R = *p*-tolyl (*cis:trans* = 8:2)
132b; R = SiMe$_3$ (*cis*)

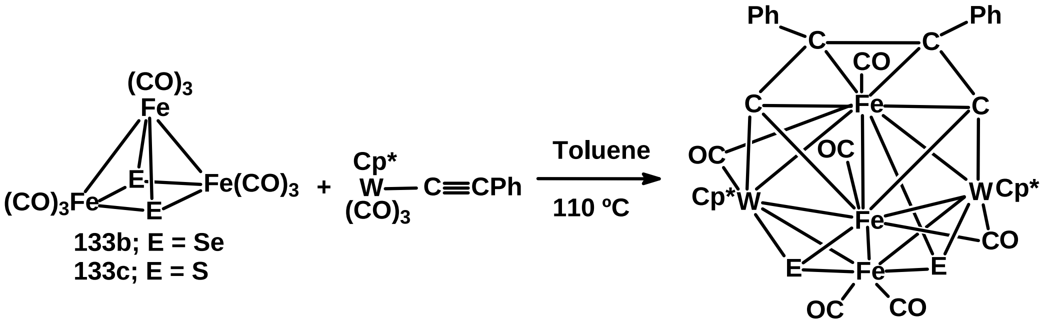
Scheme 35.

Thermal reaction of [$Fe_3(CO)_9(\mu_3\text{-}E)_2$], (E=Se, **133a**; Te, **133b**) with [(η^5-C_5H_5)M(CO)$_3$(C≡CPh)] (M =Mo, W) (**134a, b**) in the presence of trimethylamine-N-oxide (TMNO), in acetonitrile solvent yield the mixed-metal clusters [(η^5-C_5H_5)MFe$_2$(μ_3-E)$_2$(CO)$_7$(η^1-CCPh)] (E = Se and M = Mo, **135**; E = Se and M = W, **136**; E = Te and M = Mo, **137**; E = Te and M = W, **138**) bearing η^1-acetylide groups. Further reaction of **135** or **137** with dicobaltoctacarbonyl at room temperature gives the mixed-metal cluster compound $[(\eta^5\text{-}C_5H_5)MoFe_2Co_2(\mu_3\text{-}E)_2(CO)_9(\eta\text{-}CCPh)]$ (**139, 140**) (Scheme 36).[63]



Scheme 36.

When a toluene solution containing $[Fe_3(CO)_9(\mu_3\text{-}E)_2]$ (E = S, Se or Te) and $[W(\eta^5\text{-}C_5Me_5)(CO)_3(CCPh)]$ is subjected to reflux, mixed metal clusters $[W_2Fe_3(\eta^5\text{-}C_5Me_5)_2(\mu_3\text{-}E)_2\{\mu_4\text{-}CC(Ph)C(Ph)C\}]$ (E = S, **141**; Se, **142**) are formed.[64] The molecule is made up of a Fe_3W_2 metal core which is enveloped by terminal and bridging carbonyl ligands and a μ_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).

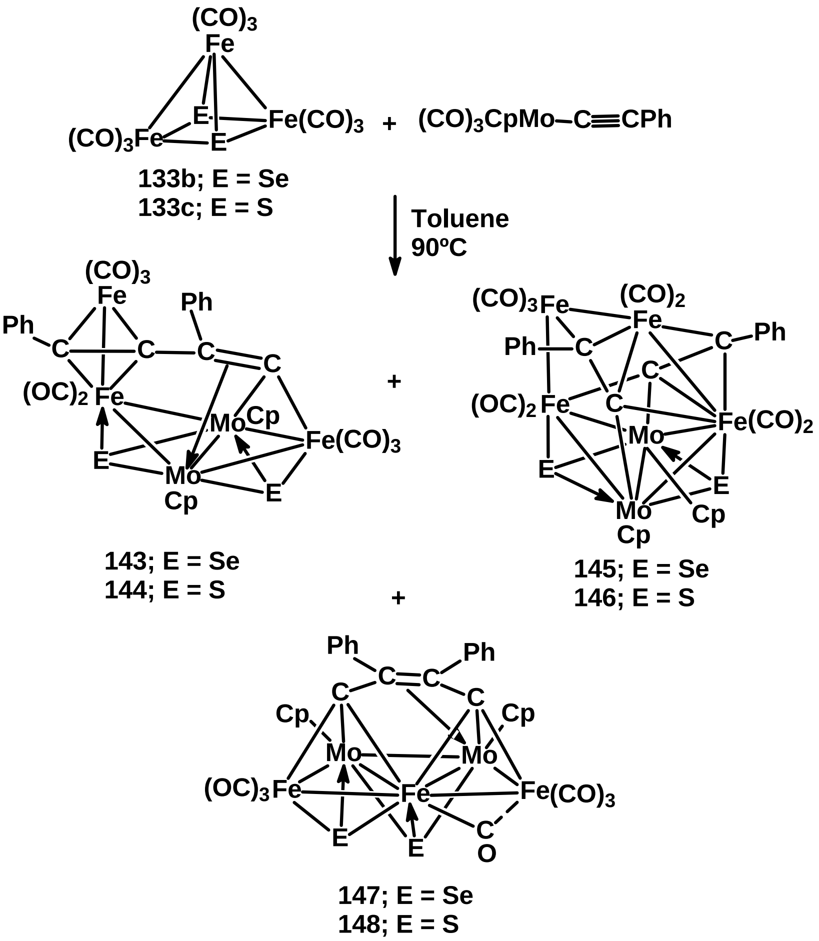


133b; E = Se
133c; E = S

141; E = Se
142; E = S

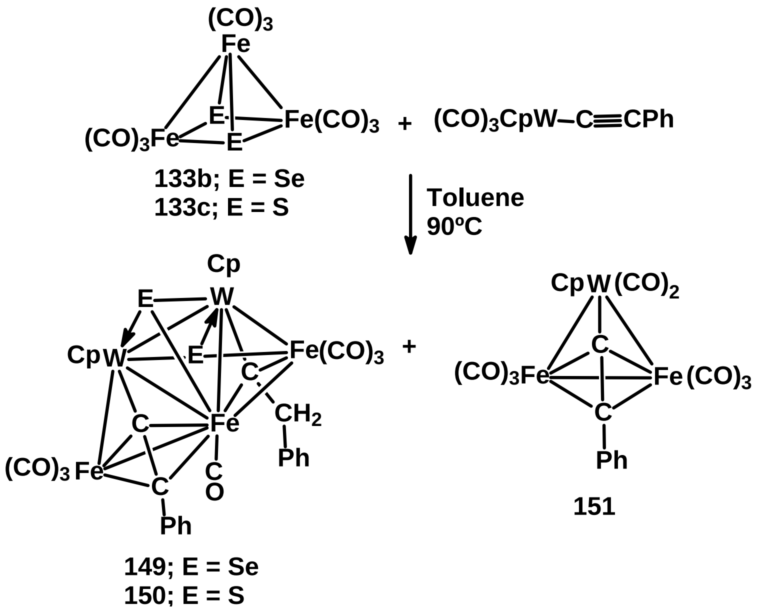
Scheme 37.

When a toluene solution of the acetylide complex, [Mo(η^5-C_5H_5)$(CO)_3$(C≡CPh)] is thermally reacted with [$Fe_3(CO)_9(\mu_3$-$E)_2$] (E = S, Se), formation of mixed metal clusters, [(η^5-$C_5H_5)_2Mo_2Fe_3(CO)_8(\mu_3$-$E)_2\{\mu_5$-CC(Ph)CC(Ph)}] (E = S, **143**; Se, **144**), [(η^5-$C_5H_5)_2Mo_2Fe_4$ $(CO)_9(\mu_3$-$E)_2(\mu_4$-$CCPh)_2$] (E = S, **145**; Se**, 146**) and [(η^5-$C_5H_5)_2Mo_2Fe_3$ $(CO)_7(\mu_3$-$E)_2\{\mu_5$-CC(Ph)C(Ph)C}] (E = S, **147**; 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).[65] The head-to-tail acetylide -coupled μ_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 Fe_3MoE 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.



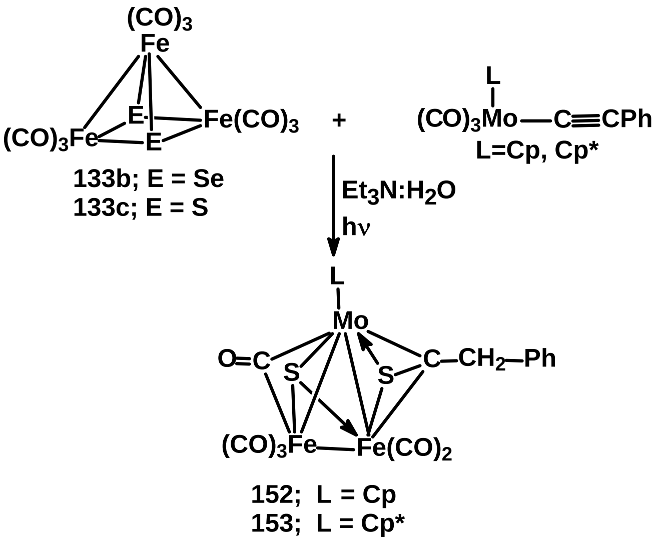
Scheme 38.

Under similar thermolytic conditions, formation of clusters [(η^5-C_5H_5)$_2$$W_2Fe_3$ $(CO)_7$(μ_3-E)$_2$(μ_3-η^2-CCPh)(μ_3-η^1-CCH_2Ph)] (E = S, **149**; Se, **150**) and [(η^5-C_5H_5)$WFe_2(CO)_8$(μ-CCPh)] (**151**) has been observed in reactions of [W(η^5-C_5H_5)$(CO)_3$(C≡CPh)] with [$Fe_3(CO)_9$(μ_3-E)$_2$] (E = S, Se) (Scheme 39).[65]



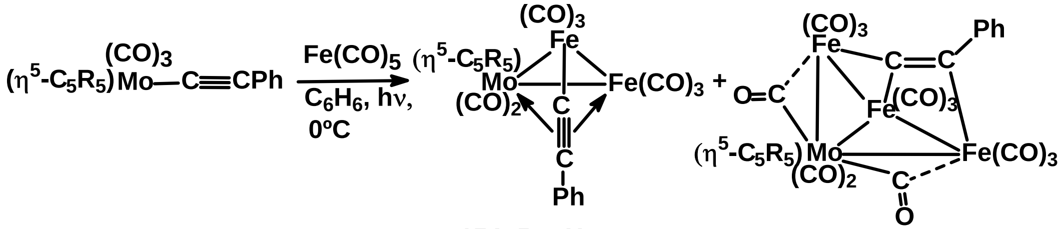
Scheme 39.

When a benzene solution containing [$Fe_3(CO)_9(\mu_3\text{-}S)_2$], [($\eta^5$-$C_5R_5$)$Mo(CO)_3(C{\equiv}CPh)$] (R = H, Me), H_2O and Et_3N are photolysed with continuous bubbling of argon a rapid formation of cluster [(η^5-C_5R_5)$MoFe_2(CO)_6(\mu_3\text{-}S)(\mu\text{-}SCCH_2Ph)$] (R = H, **152**; R = Me, **153**) is observed (Scheme 40).[66] The H_2O molecule acts as a source of protons as confirmed by labeling experiment, and Et_3N works as a phase transfer catalyst



Scheme 40.

Photolytic reaction of metal acetylide complexes with simple metal carbonyls has been used to form heterometallic acetylide bridged complexes. For instance, photolytic reaction of a benzene solution of [Fe(CO)$_5$] and [(η^5-C$_5$R$_5$)Mo(CO)$_3$(C≡CPh)] (R = H, Me) under continuous bubbling of argon results in a rapid formation of [(η^5-C$_5$R$_5$)Fe$_2$Mo(CO)$_8$(μ_3-η^1:η^2:η^2-CCPh)] (R = H, **154**; Me, **155**) and [(η^5-C$_5$H$_5$)Fe$_3$Mo(CO)$_{11}$(μ_4-η^1:η^1: η^2:η^1-CCPh)] (**156**) (Scheme 41).[67] The structure of **154** consists of a MoFe triangle and a μ_3-η^1,η^2,η^2 acetylide ligand. The molecular structure of **156** comprises of an open Fe$_3$Mo butterfly arrangement with a acetylide group bonded in μ_3-η^1 mode.

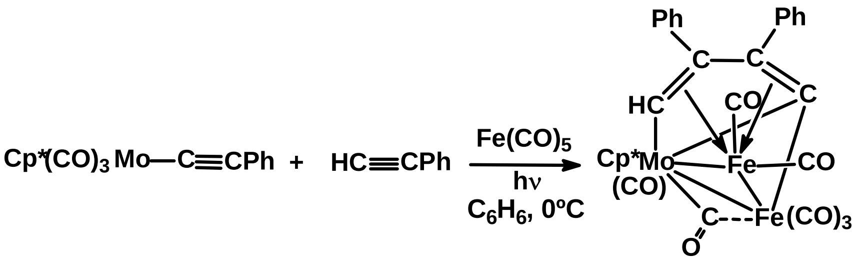


154; R = H
155; R = Me

156; R = H

Scheme 41.

However, when a benzene solution containing a mixture of [(η^5-C$_5$Me$_5$)Mo(CO)$_3$(C≡CPh)], [Fe(CO)$_5$] and [PhC≡CH] are photolysed, formation of alkyne-acetylide coupled mixed metal cluster [(η^5-C$_5$Me$_5$)Fe$_2$Mo(CO)$_7$(μ_3-C(H)C(Ph)C(Ph)C)] (**157**) is obtained in moderate yield (Scheme 42).[67] The molecular structure of **157** consists of a Fe$_2$Mo triangle with a {C(H)=C(Ph)C(Ph)=C} ligand triply bridging the Fe$_2$Mo face.



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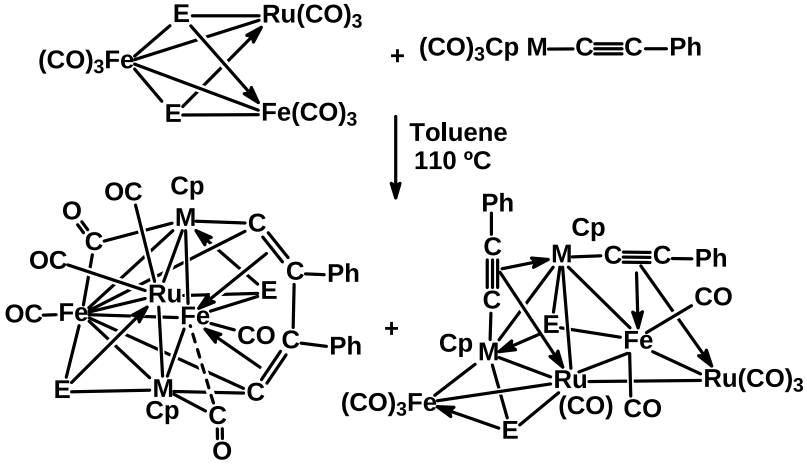
Scheme 42.

When a mixed metal cluster $[Fe_2Ru(CO)_9(\mu_3\text{-}E)_2]$ (E = S or Se) has been reacted with $[(\eta^5\text{-}C_5H_5)M(CO)_3(C{\equiv}CPh)]$ (M = Mo or W) in toluene reflux condition, heterometallic clusters $[(\eta^5\text{-}C_5H_5)_2Fe_2RuM_2(CO)_6(\mu_3\text{-}E)_2\{\mu_4\text{-}CC(Ph)C(Ph)C\}]$ (M = Mo and E = S, **158**; M = Mo and E = Se, **159**; M = W and E = S, **160**; M = W and E = Se, **161**) and $[(\eta^5\text{-}C_5H_5)_2Fe_2Ru_2M_2(CO)_9(\mu_3\text{-}E)_2\{\mu_3\text{-}CCPh\}_2]$ (M = W and E = S, **162;** M = W and E = Se, **163**), have been isolated from the reaction mixtures (Scheme 43).[68] The molecular structure of **158** consists of an open trigonal bipyramidal Fe_2RuMo_2 metal core enveloped by terminal and bridging carbonyl ligands and a μ_4-{CC(Ph)C(Ph)C} unit. Structure of **162** can be described as a $FeRuW_2S$ distorted square pyramid core, in which the WRu edge is bridged by a $Fe(CO)_3S$ and the RuFe edge by a $Ru(CO)_3$ unit. One acetylide group caps the W_2Ru face in a η^1, η^2, η^2 fashion and another caps the open FeRuW face in a similar bonding mode.

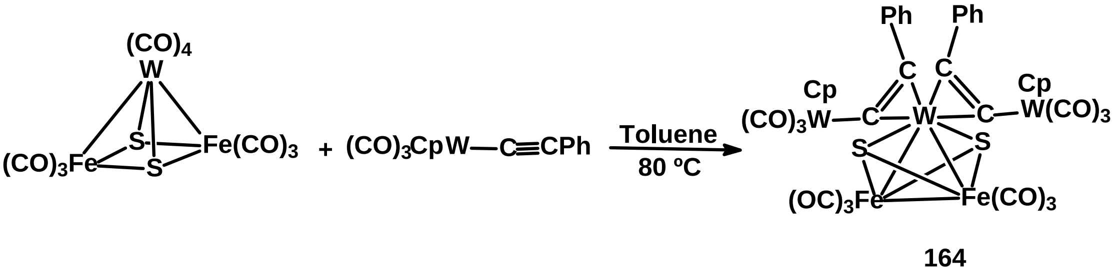


158; M = Mo, E = S
159; M = Mo, E = Se
160; M = W, E = S
161; M = W, E = Se

162; M = W, E = S
163; M = W, E = Se

Scheme 43.

When a toluene solution of a Fe/W mixed metal cluster, $[Fe_2W(CO)_{10}(\mu_3\text{-}S)_2]$ is heated at 80 °C with the tungsten acetylide complex $[(\eta^5\text{-}C_5H_5)W(CO)_3(CCPh)]$, the Fe_2W_3 mixed metal $[(\eta^5\text{-}C_5H_5)_2W_3Fe_2S_2(CO)_{12}(CCPh)_2]$ (**164**) was isolated (Scheme 44).[69] Its structure consists of a Fe_2WS_2 trigonal bipyramidal unit in which the W atom is attached to two separate molecules of [(η^5-C_5H_5)W(CO)$_3$(CCPh)] through the acetylide group.



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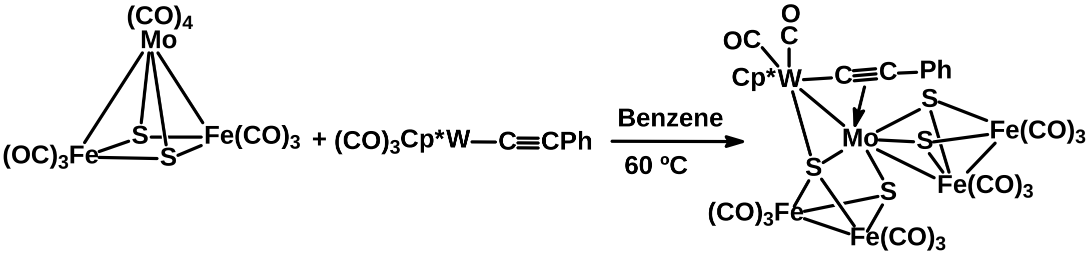
Scheme 44.

When [$Fe_2Mo(CO)_{10}(\mu_3\text{-}S)_2$] is made to interact with [(η^5-C_5Me_5)W(CO)$_3$(C≡CPh)] under mild thermolytic condition in argon atmosphere, a mixed metal acetylide cluster [(η^5-C_5Me_5)MoWFe$_4$(μ_3-S)$_3$(μ_4-S)(CO)$_{14}$(CCPh)] (**165**) is isolated (Scheme 45).[70] Molecular structure of **165** consists of a {Fe_2MoS_2} distorted square pyramid unit in which the basal Mo atom is bonded to the two sulphur atoms of an open {Fe_2S_2} butterfly unit and a {(η^5-C_5H_5)W(CO)$_2$} group. A single phenylacetylide ligand bridges the Mo-W bond in μ-η^1,η^2 fashion.



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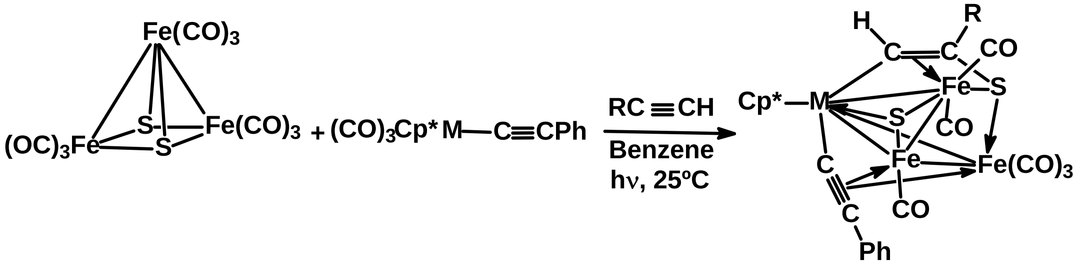
Scheme 45.

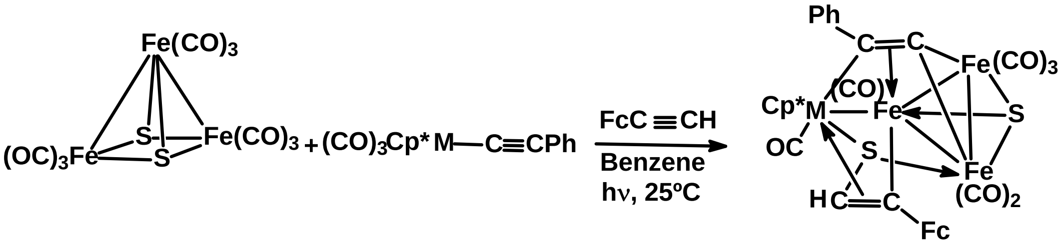
Photolysis of a benzene solution of a mixture of [$Fe_3(CO)_9(\mu_3\text{-}S)_2$], [($\eta^5$-$C_5Me_5$)M(CO)$_3$(C≡CPh)] (M = Mo, W) and HC≡CR (R = Ph, *n*-Bu and Fc) (Fc = ferrocene) forms two types of clusters depending on the nature of acetylene used. When phenylacetylene or *n*-butyl acetylene are used, clusters [(η^5-C_5Me_5)$MFe_3(CO)_6$(μ_3-S){(μ_3-C(H)=C(R)S}(μ_3-CCPh)] (**166** - **169**) are formed (Scheme 46).[71] 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 [(η^5-C_5Me_5)$MFe_3(CO)_7$(μ_3-S){μ_3-C(Fc)=C(H)S}(μ_3-CCPh)] (**170, 171**) in which a formal switching of the α and β 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_{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 μ_3-S ligand as well as an unusual {HC=C(Ph)S} ligand. The second butterfly face is capped by a {η^1: η^2: η^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.



166; M = Mo, R = Ph
167; M = Mo, R = ^{n}Bu
168; M = W, R = Ph
169; M = W, R = ^{n}Bu

Scheme 46.

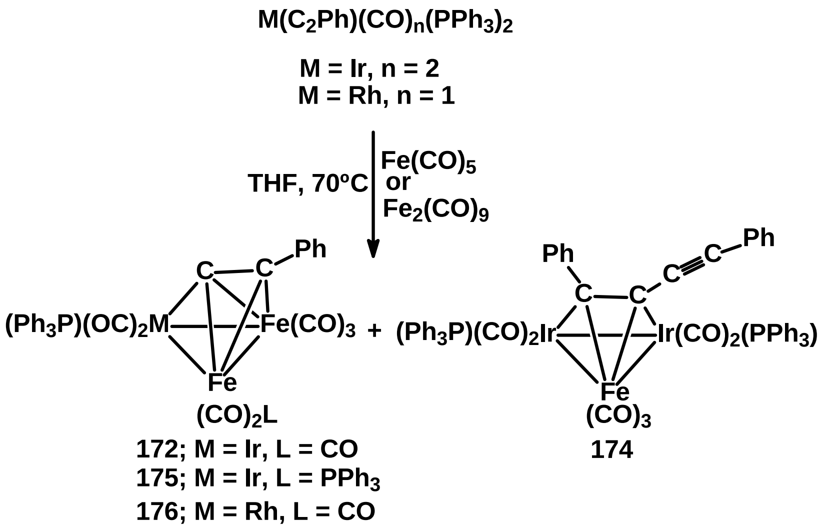
Compound **170** consists of a Fe_3 triangle, which is capped by a sulfido ligand. One of the iron atoms is bonded to a {(η^5-C_5Me_5)W} group, and the Fe–W bond is bridged by a ferrocenylacetylene group. A second sulfido ligand triply - bridges the terminal carbon atom of this acetylene with the tungsten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



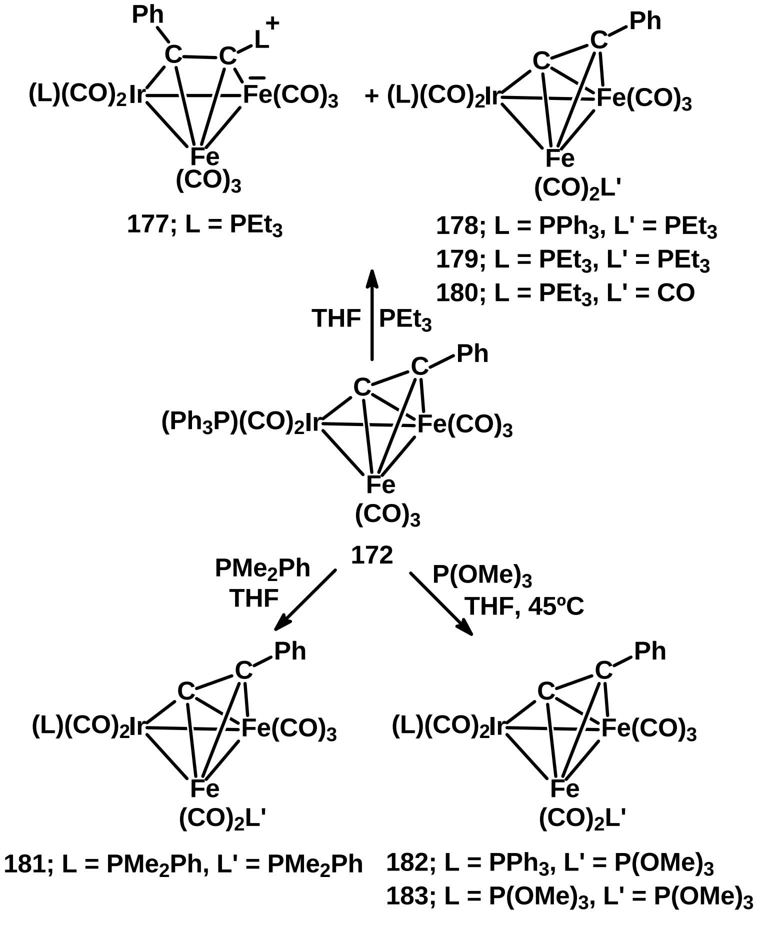
170 M = Mo
171 M = W

Scheme 47.

Reactions between [Ir(C_2Ph)(CO)$_2$(PPh$_3$)$_2$] and iron carbonyls (Fe(CO)$_5$ or Fe$_2$(CO)$_9$) result in the formation of iron-iridium clusters [Fe$_2$Ir(μ_3-C$_2$Ph)(CO)$_{9-n}$(PPh$_3$)$_n$] (n =1, **172**; 2 ,**173**) and [FeIr$_2$(μ_3-PhC$_2$C$_2$Ph)(CO)$_{12}$(PPh$_3$)$_2$] (**174**). The Rh analogue of **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_α of the acetylide ligand in **172** gives zwitterionic [Fe$_2$Ir(μ_3-PhC$_2$PEt$_3$)(CO)$_8$(PEt$_3$)] (**177**), which on heating converts to [Fe$_2$Ir(μ_3-C$_2$Ph)(CO)$_7$(PEt$_3$)$_2$] (**179**) by migration of PEt$_3$ from carbon to iridium (Scheme 49).[73] Analogous complexes containing cluster-bound PMe$_2$Ph and P(OMe)$_3$ have also been obtained by such type of reaction.

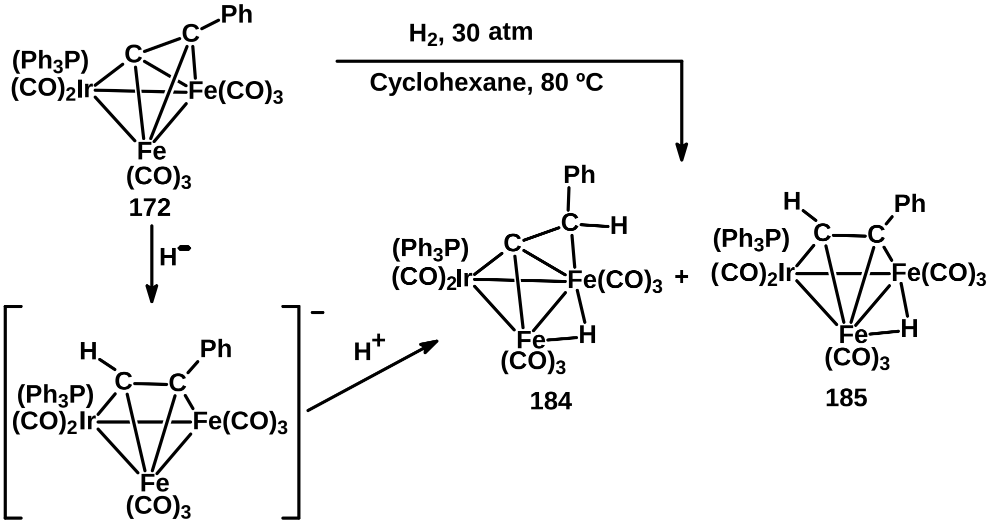


Scheme 48.



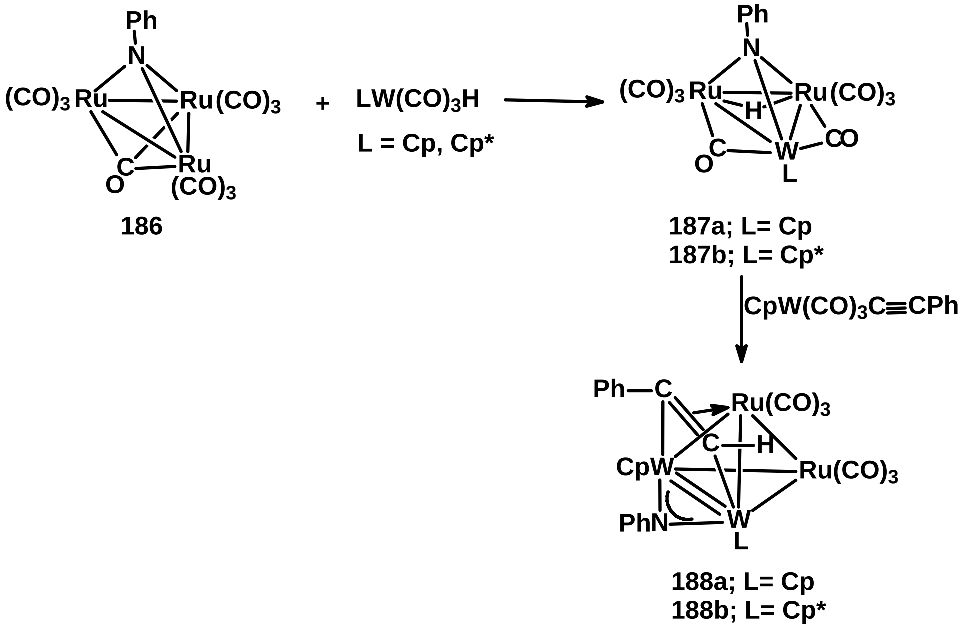
Scheme 49.

Reaction of Fe_2Ir 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]



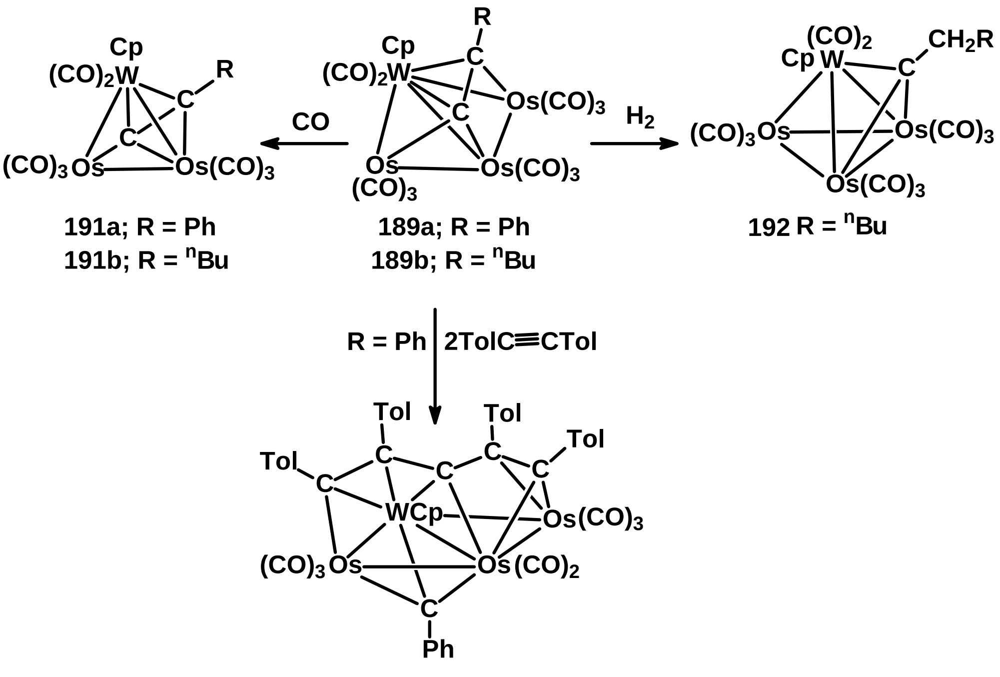
Scheme 50.

Treatment of the triruthenium imido complex $[Ru_3(CO)_{10}(\mu_3\text{-NPh})]$ (**186**) with metal hydride complex $[LW(CO)_3H]$ in refluxing toluene produces a trinuclear heterometallic imido cluster, $[LWRu_2(CO)_8(\mu\text{-H})(\mu_3\text{-NPh})]$ (L=Cp, **187a**; Cp*, **187b**), which on reaction with tungsten acetylide $[CpW(CO)_3CCPh]$ produces a tetranuclear imidoalkyne complex $[LCpW_2Ru_2(CO)_6(\mu\text{-NPh})(\mu\text{-}\eta^2\text{-CH=CPh})]$ (L=Cp, Cp*) (**188a,b**) (Scheme 51).[75]



Scheme 51.

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_5H_4F, C_5H_4OMe, ^{t}Bu and ^{n}Pr) with [Os$_3$(CO)$_{10}$(NCMe)] or [Ru$_3$(CO)$_{12}$]. Thus, reaction of [CpW(CO)$_3$C≡CR] (R = Ph, ^{t}Bu) with [Os$_3$(CO)$_{10}$(CH$_3$CN)$_2$] in refluxing toluene produces tetranuclear mixed-metal acetylide complexes [CpWOs$_3$(CO)$_{11}$(C≡CR)] (R = Ph, **189a**; ^{t}Bu, **189b**).[76] The molybdenum analogue [MoOs$_3$(CO)$_{11}$(C≡CPh)(η-C$_5$H$_5$)] (**190**) has also been prepared by a similar procedure. Carbonylation of **189a, b** at 120 °C under pressurized CO induces cluster fragmentation, giving [CpWOs$_2$(CO)$_8$(C≡CR)] **(191a,b**) in 80-85 % yield. Hydrogenation of **189b** produces an alkylidyne complex, [CpWOs$_3$(CO)$_{11}$(μ_3-CC$_5$H$_{11}$)] **(192)**, while treatment of **189a** with excess of ditolylacetylene affects the scission of the acetylide ligand to give [CpWOs$_3$(CO)$_8$(μ_3-CPh){μ_4-η^5-C(C$_2$Tol$_2$)$_2$}] (**193**) (Scheme 52).[77]



191a; R = Ph
191b; R = ^{n}Bu

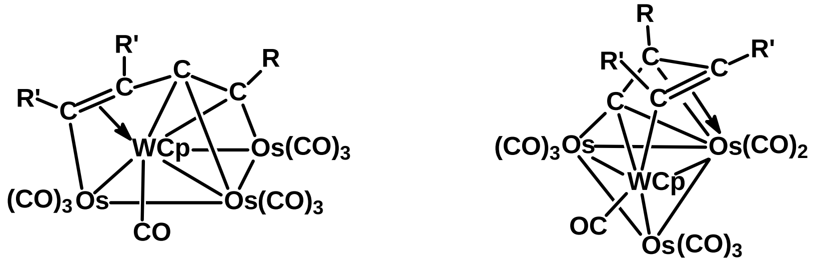
189a; R = Ph
189b; R = ^{n}Bu

192 R = ^{n}Bu

193

Scheme 52.

In contrast, treatment of complexes **189 a** and **b** with alkynes containing electron-withdrawing groups produces the tetranuclear alkyne-acetylide coupling products [CpWOs$_3$(CO)$_{10}${CR'CR'CCR}] (R = Ph and R' = CO$_2$Me, **194a**; R = Ph and R' = CO$_2$Et, **194b**; R = ^{n}Bu and R' = CO$_2$Et, **194c**) and [CpWOs$_3$(CO)$_9${CCRCR'CR'}] (R = Ph and R' = CO$_2$Me, **195a**; R = Ph and R' = CO$_2$Et, **195b**; R = ^{n}Bu and R' = CO$_2$Et, **195c**) (Figure 13).[76]

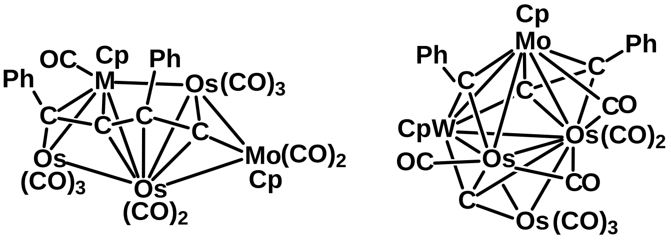


194a; R = Ph, R' = CO$_2$Me
194b; R = Ph, R' = CO$_2$Et
194c; R = ^{n}Bu, R' = CO$_2$Me

195a; R = Ph, R' = CO$_2$Me
195b; R = Ph, R' = CO$_2$Et
195c; R = ^{n}Bu, R' = CO$_2$Me

Figure 13.

The cluster acetylide complexes [$MOs_3(CO)_{11}(C{\equiv}CPh)(\eta\text{-}C_5H_5)$] (M = Mo, **190**; M = W, **189a**) react with [$Mo(CO)_3(C{\equiv}CPh)(\eta\text{-}C_5H_5)$] to give planar pentanuclear complexes [$MMoOs_3(CO)_{11}(CCPhCCPh)(\eta\text{-}C_5H_5)_2$] (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 [$W(CO)_3(C{\equiv}CPh)(\eta\text{-}C_5H_5)$] does not produce the coupling product but induces C-C bond scission of [$W(CO)_3(C{\equiv}CPh)(\eta\text{-}C_5H_5)$] giving a novel carbide-alkylidyne complex [$MoWOs_3(CO)_8(\mu_4\text{-}C)(\mu_3\text{-}CPh)(CCPh)(\eta\text{-}C_5H_5)_2$] (**198**) (Figure 14).[78]

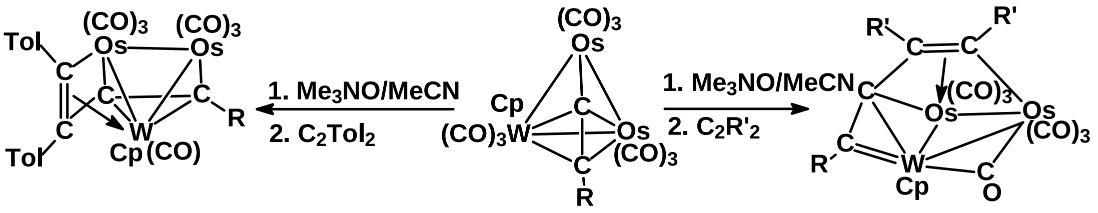


196; M = Mo
197; M = W

198

Figure 14.

Treatment of the acetylide complexes [$CpWOs_2(CO)_8(C{\equiv}CR)$], (R = Ph, **191a**; R =^{n}Bu, **191b**) with Me_3NO in acetonitrile followed by reaction with various disubstituted alkynes, $C_2R'_2$ in refluxing toluene facilitates acetylide-alkyne coupling and formation of two isomeric trinuclear complexes, [$CpWOs_2(CO)_{12}\{C(R')C(R')CCR\}$] (R = Ph and R' = Tol, **199**; R = ^{n}Bu and R' = Tol, **200**; R = Ph and R' = CO_2Et, **201**; R = ^{n}Bu and R' = CO_2Et, **202**; R = Ph and R' = CF_3, **203**) (Scheme 53).[79]



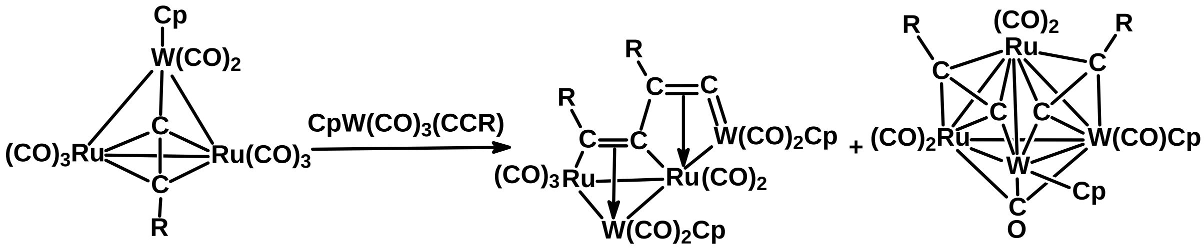
199; R = Ph
200; R = ^{n}Bu

191a; R = Ph
191a; R = ^{n}Bu

201; R = Ph, R' = Co2Et
202; R =^{n}Bu, R = Co2Et
203; R = Ph, R = CF3

Scheme 53.

When $[Ru_3(CO)_{12}]$ has been used to react with $[CpW(CO)_3C{\equiv}CPh]$ in refluxing toluene, $[CpWRu_2(CO)_8(C{\equiv}CPh)]$ (**204**) is isolated. In solution the variable temperature NMR suggests that the acetylide ligand of **204** undergoes a 360º rotation on the face of the WRu_2 triangle.[80] With excess of $[CpW(CO)_3C{\equiv}CR]$, **204** gives two heterometallic acetylide clusters $[Cp_2W_2Ru_2(CO)_9(CCRCCR)]$ (R = Ph, **205a**; R = *p*-C_6H_4F, **205b**), with C-C bond coupling and $[Cp_2W_2Ru_2(CO)_6(C{\equiv}CR)_2]$ (R = Ph, **206a**; R = *p*-C_6H_4F, **206b**), without C-C bond coupling (Scheme 54).[81]



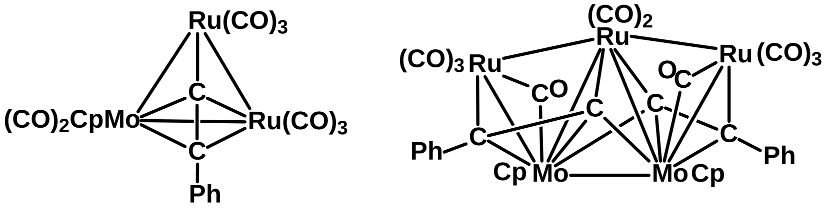
204a;R = Ph
204b;R = C_6H_4F-*p*

205a;R = Ph
205b;R = C_6H_4F-*p*

206a;R = Ph
206b;R = C_6H_4F-*p*

Scheme 54.

In a similar reaction, thermolysis of a mixture of $[Ru_3(CO)_{12}]$ and $[CpMo(CO)_3C{\equiv}CPh]$ in a molar ratio 2:3 in refluxing toluene gives the trinuclear acetylide derivative $[CpMoRu_2(CO)_8C{\equiv}CPh]$ (**207**) and a pentanuclear heterometallic acetylide complex $[Cp_2Mo_2Ru_3(CO)_{10}(C{\equiv}CPh)_2]$ (**208**) (Figure 15).[82]



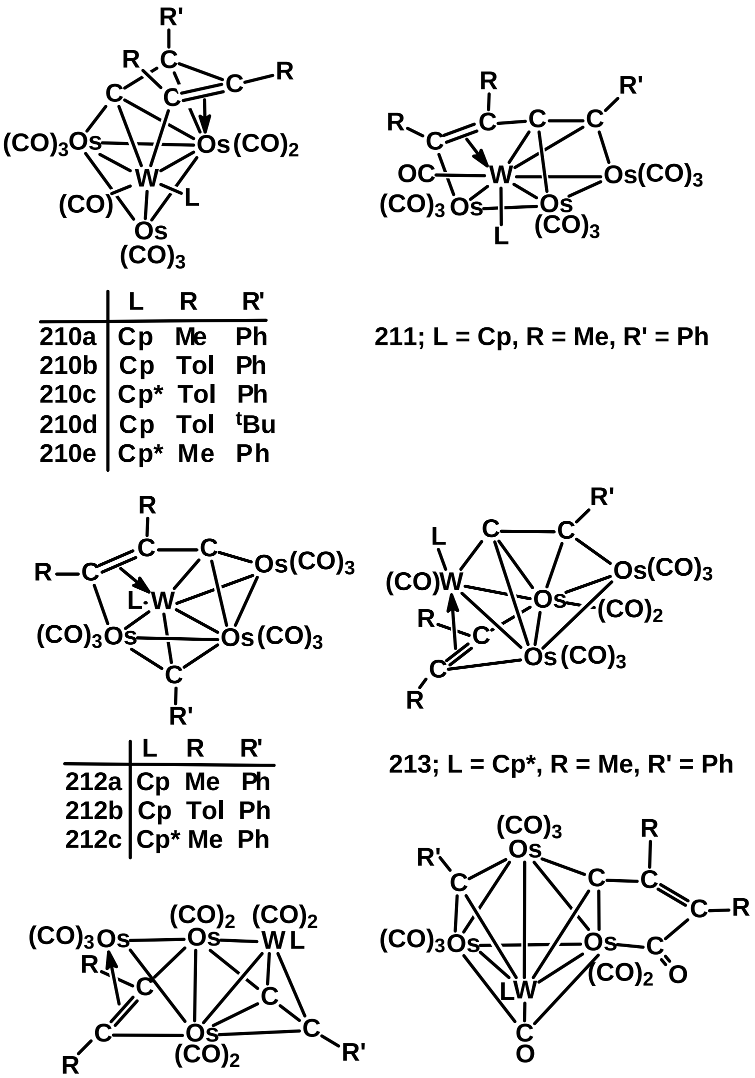
207

208

Figure 15.

Condensation of triosmium alkyne complexes $[Os_3(CO)_{10}(C_2R_2)]$ (R = Tol, **209a**; R = Me, **209b**) with mononuclear tungsten acetylide complexes $[LW(CO)_3C{\equiv}CR']$, (L =

Cp, Cp*, R' = Ph, ^{t}Bu) generates six WOs_3 cluster complexes via 1: 1 combination of the starting materials. Treatment of $[Os_3(CO)_{10}(C_2Me_2)]$ with $[CpW(CO)_3C{\equiv}CPh]$ under refluxing toluene forms two heterometallic complexes $[CpWOs_3(CO)_9\{CC(Ph)C(Me)C(Me)\}]$ (**210a**) and $[CpWOs_3(CO)_{10}\{C(Me)C(Me)CC(Ph)\}]$ (**211**). On the other hand, thermal reaction of $[Os_3(CO)_{10}(C_2Tol_2)]$ with $[CpW(CO)_3C{\equiv}CPh]$ gives $[CpWOs_3(CO)_9\{CC(Ph)C(Tol)C(Tol)\}$ (**210b**) and $[CpWOs_3(CO)_9(CCTolCTol)(\mu_3\text{-}CPh)]$ (**212b**), whereas only one heterometallic cluster, $[LWOs_3(CO)_9\{CC(R')C(Tol)C(Tol)\}]$ (L = Cp* and R' = Ph, **210c**; L = Cp and R' = ^{t}Bu, **210d**) is obtained on thermolysis of $[Os_3(CO)_{10}(C_2Tol_2)]$ with $[LW(CO)_3C{\equiv}CR']$ (L = Cp*, R' = Ph or L = Cp, R' = ^{t}Bu). Addition of 1:1 molar equivalent of $[Me_3NO]$ to compound **211**, followed by heating under refluxing toluene affords $[CpWOs_3(CO)_9(CCMeCMe)(\mu_3\text{-}CPh)]$ (**212a**). When toluene solution of $[Os_3(CO)_{10}(C_2Me_2)]$ is thermally reacted with $[Cp^*W(CO)_3C{\equiv}CPh]$, five heterometallic clusters are formed (**210e**, **212e**, **213**, **214** and **215**) (Figure 16).[83]



	L	R	R'
210a	Cp	Me	Ph
210b	Cp	Tol	Ph
210c	Cp*	Tol	Ph
210d	Cp	Tol	^{t}Bu
210e	Cp*	Me	Ph

211; L = Cp, R = Me, R' = Ph

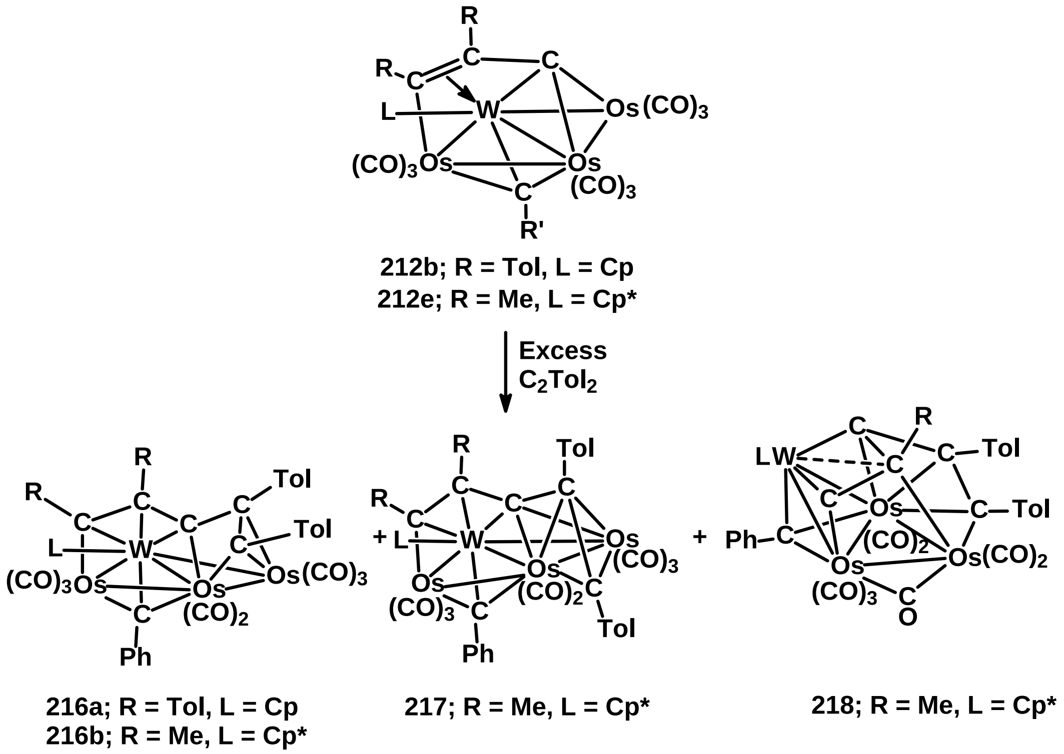
	L	R	R'
212a	Cp	Me	Ph
212b	Cp	Tol	Ph
212c	Cp*	Me	Ph

213; L = Cp*, R = Me, R' = Ph

214; L = Cp*, R = Me, R' = Ph   215; L = Cp*, R = Me, R' = Ph

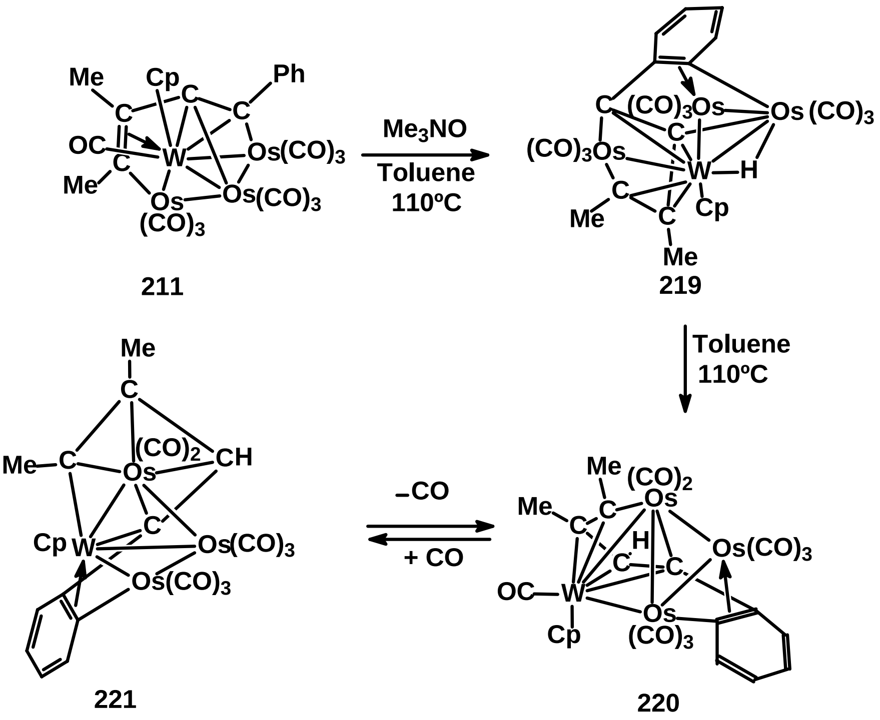
Figure 16.

Thermolysis of a toluene solution of complex **212b** with ditolylacetylene yields the planar clusters [CpWOs$_3$(CO)$_8$(μ_3-CPh){C(Tol)C(Tol)CC(Tol)C(Tol)}] (**216a**). On the other hand, reaction of **212e** in refluxing xylene solvent gives [Cp*WOs$_3$(CO)$_8$(μ_3-CPh){C(Tol)C(Tol)CC(Me)C(Me)}] (**216b**), [WOs$_3$(C$_5$Me$_5$)(CO)$_{12}$(μ_3-CPh){CMeCMeCC(Tol)C(Tol)}] (**217**) and **218** (Scheme 55).[84]



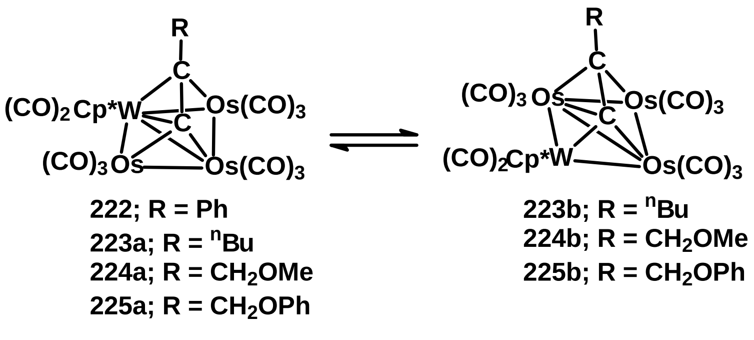
Scheme 55.

Treatment of **211** with Me_3NO followed by thermolysis in refluxing toluene yields the spiked triangular cluster $[WOs_3Cp(CO)_9(\mu\text{-}H)\{CMeCMeCC(\mu_2\text{-}\eta^2\text{-}C_6H_4)\}]$ (**219**) as a major product, which, on further thermolysis converts to a butterfly cluster $[WOs_3Cp(CO)_9\{CMeCMeCHC(\mu_2\text{-}\eta^2\text{-}C_6H_4)\}]$ (**220**) and then to a tetrahedral cluster $[WOs_3Cp(CO)_8\{CMeCMeCHC(\mu_2\text{-}\eta^2\text{-}C_6H_4)\}]$ (**221**) via hydride migration followed by loss of CO (Scheme 56).[85]

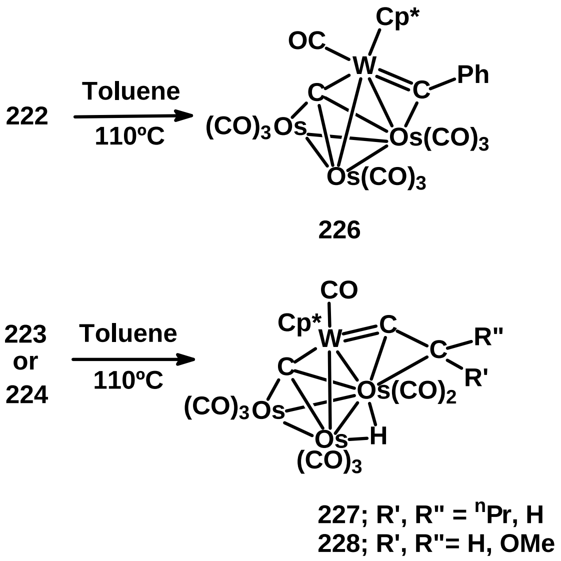


Scheme 56.

The tetranuclear clusters **222-225** shown in Scheme 57 are formed in the reaction of $[Cp^*W(CO)_3C\equiv CR]$ (R = Ph, ^{n}Bu, CH_2OMe, CH_2Ph) with $[Os_3(CO)_{10}(NCMe)_2]$. 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 $[Cp^*WOs_3(\mu_4\text{-}C)(\mu\text{-}H)(\mu\text{-}CCH^nPr)(CO)_9]$ (**227a,b**) as an inseparable mixture, while thermal reaction of **224 a,b** with Me_3NO forms two methoxy derivatives $[Cp^*WOs_3(\mu_4\text{-}C)(\mu\text{-}H)(\mu\text{-}CCHOMe)(CO)_9]$ (**228a,b**) (Scheme 58).[86]

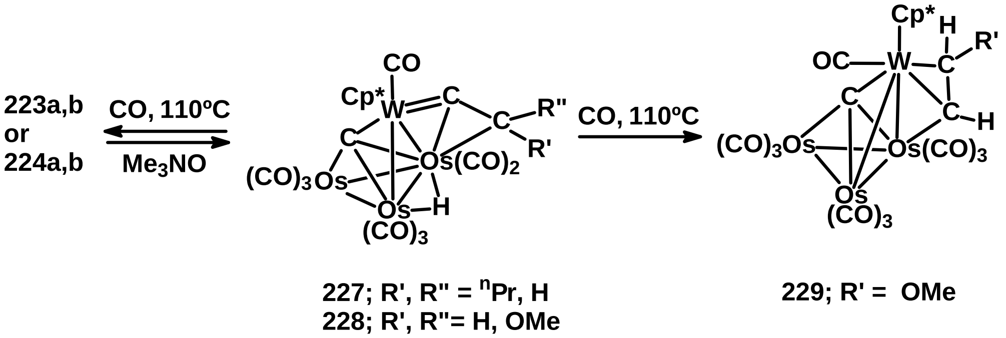


Scheme 57.



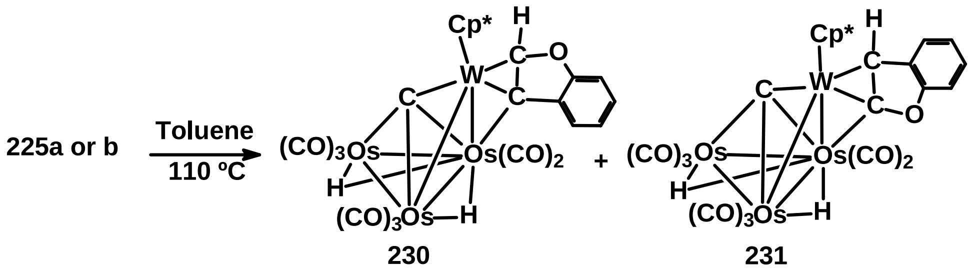
Scheme 58.

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*WOs$_3$(μ_4-C)(μ-CHCHOMe)(CO)$_{10}$] (**229**) (Scheme 59).[86]



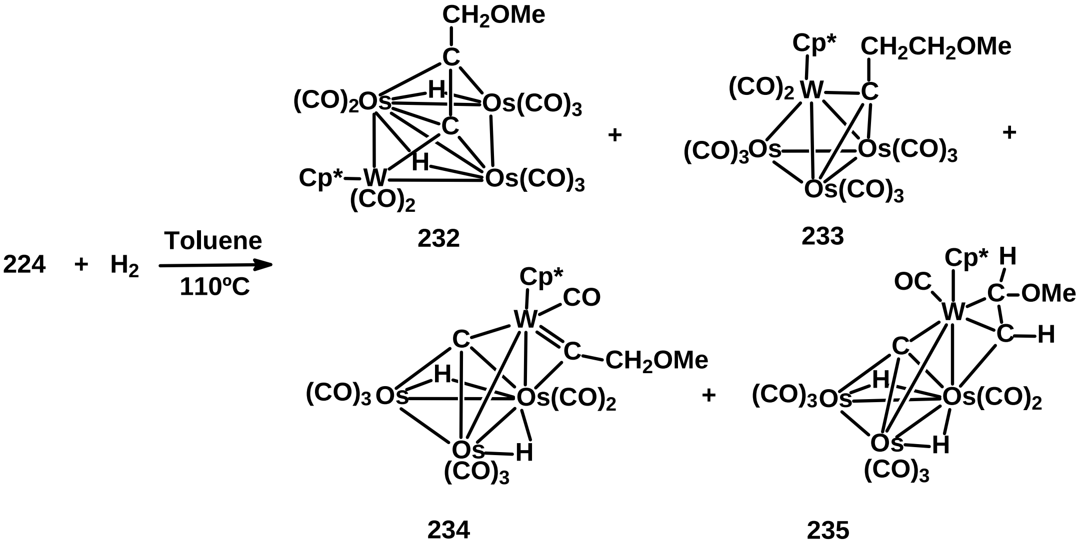
Scheme 59.

A mixture of two isomers (**230** and **231**) of a benzofuryl complex [Cp*WOs$_3$(μ_4-C)(μ-H)$_2$(μ-C$_8$H$_5$O)(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)$_3$C≡CCH$_2$OPh] with [Os$_3$(CO)$_{10}$(NCMe)$_2$] in refluxing toluene (Scheme 60).[86]



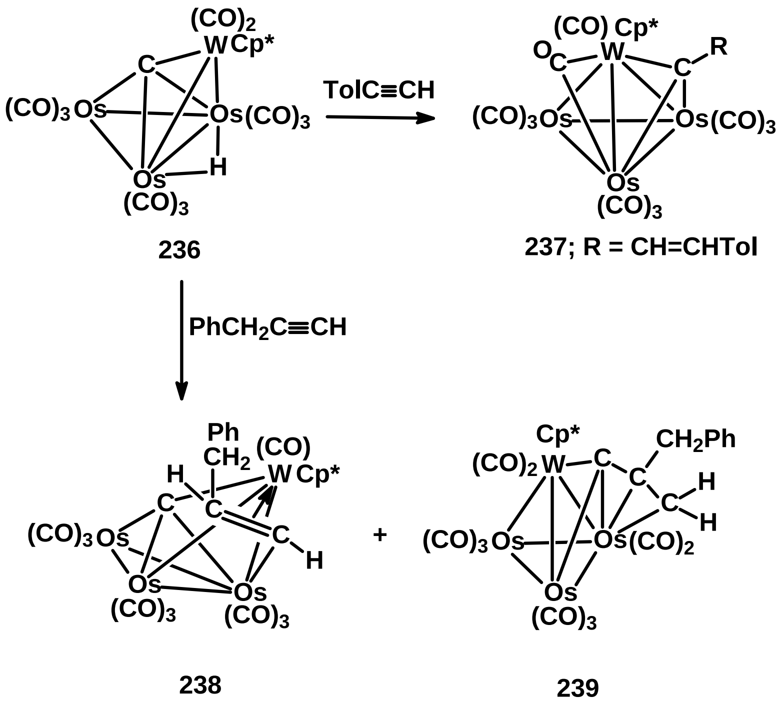
Scheme 60.

Hydrogenation of the CH_2OMe derivative, **224** affords four compounds (**232-235**) (Scheme 61).[86]



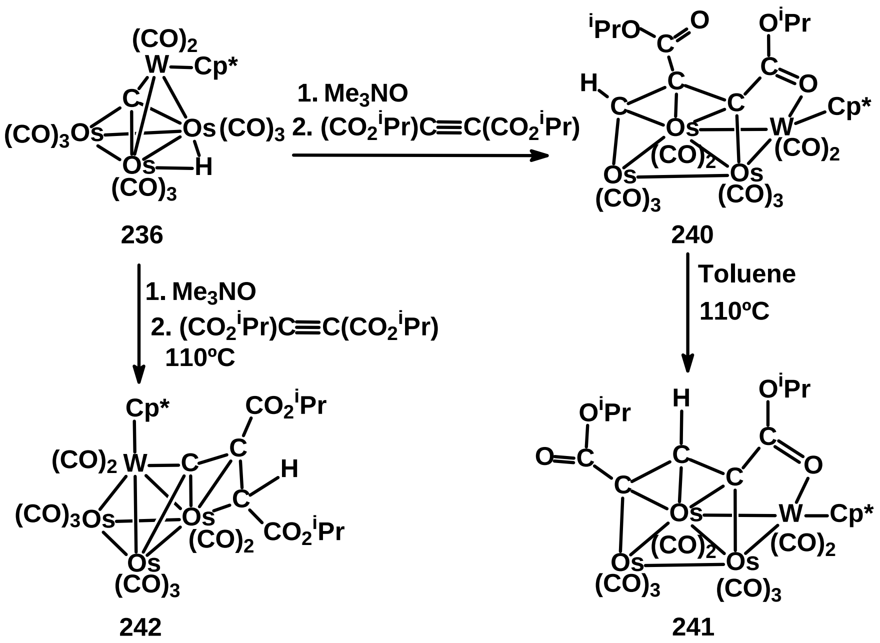
Scheme 61.

When the carbide cluster complex [$Cp^*WOs_3(\mu_4\text{-}C)(\mu\text{-}H)(CO)_{11}$] **(236)** is treated with excess of Me_3NO and 4-ethynyltoluene, the formation of an alkylidyne compound [$(C_5Me_5)WOs_3(\mu_3\text{-}CCHCHTol)(CO)_{11}$] (**237**) is observed, while, the corresponding reaction of **236** with 3-phenyl-1-propyne affords alkenyl carbido cluster [$(C_5Me_5)WOs_3(\mu_4\text{-}C)(CHCHCH_2Ph)(CO)_{10}$] (**238**) and an alkylidyne compound [$(C_5Me_5)WOs_3[\mu_3\text{-}CC(CH_2Ph)(CH_2)](CO)_{10}$] (**239**) (Scheme 62).[87]



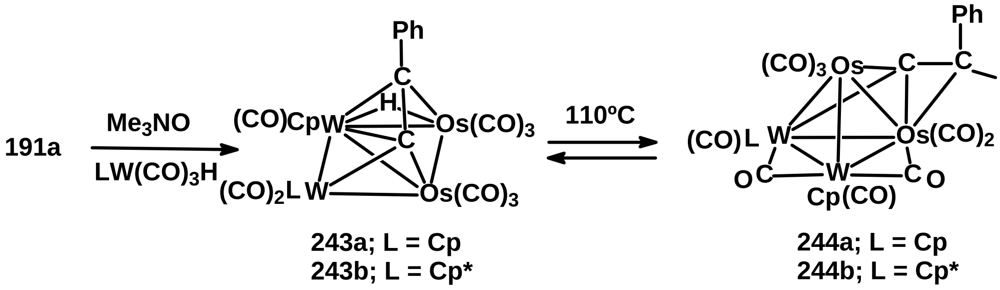
Scheme 62.

On the other hand, coupling of **236** with an electron deficient alkyne, diisopropyl acetylenedicarboxylate (DPAD) results in the formation of a dimetallaallyl cluster $[Cp^*WOs_3(CO)_{10}\{C_3H(CO_2{}^iPr)_2\}]$ (**240**), which undergoes C-C metathesis to afford a second dimetallaallyl cluster (**241**) (Scheme 63).[88] Trace amount of a related vinyl-alkylidene cluster **242** has been observed in the reaction of **236** with DPAD in refluxing toluene solution.



Scheme 63.

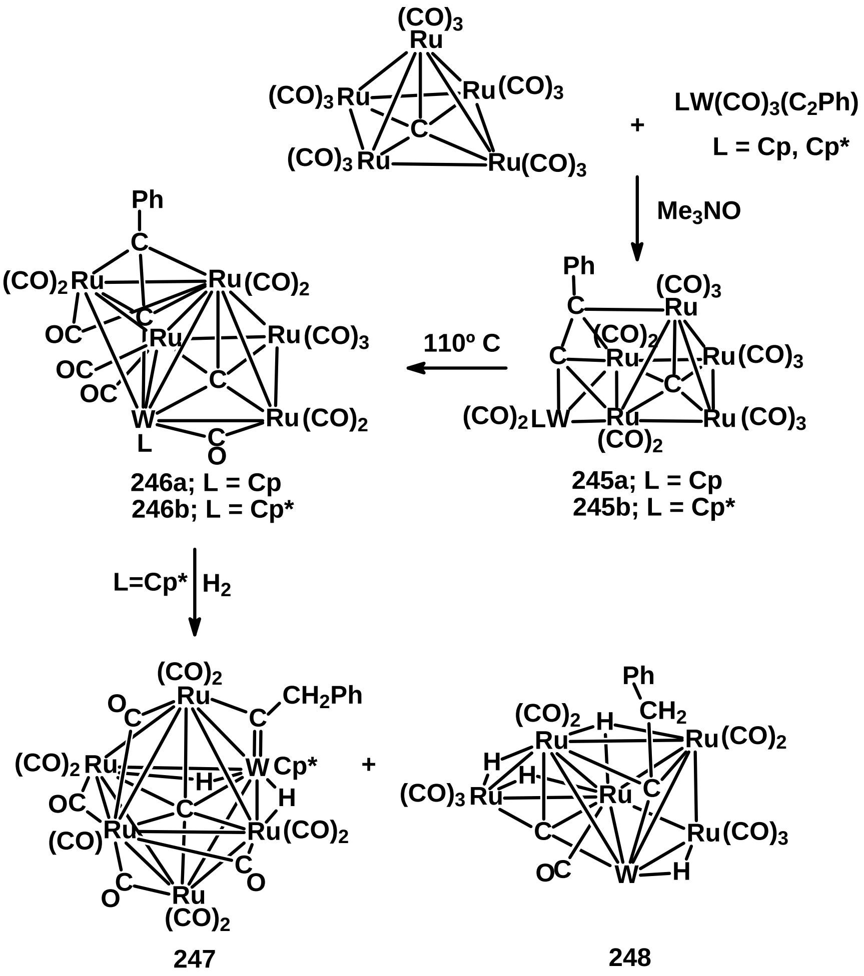
Reaction of [$CpWOs_2(CO)_8(C{\equiv}CPh)$] with 1.2 equiv of Me_3NO in a mixture of dichloromethane-acetonitrile solvent at room temperature followed by in situ reaction with hydride complexes [$LW(CO)_3H$] (L = Cp and Cp*) in refluxing toluene produces the acetylide cluster complexes [$CpLW_2Os_2(CO)_9(CCPh)(\mu\text{-}H)$] (L = Cp, **243a**; L = Cp*, **243b**) and vinylidene cluster complexes [$CpLW_2Os_2(CO)_9(CCHPh)$] **(**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).[78]



Scheme 64.

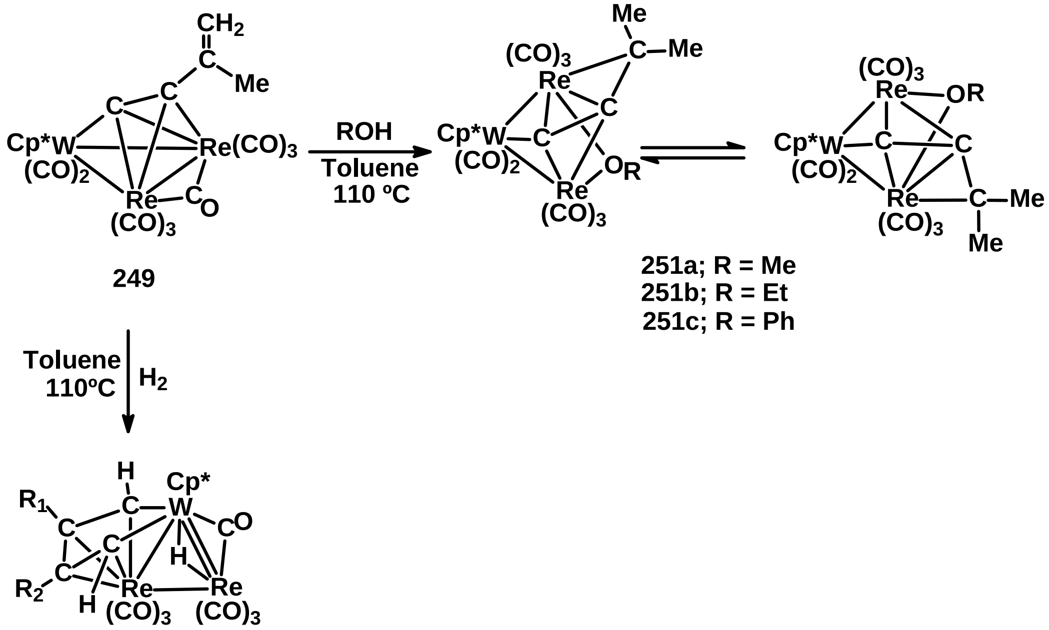
Molybdenum analogue, [$Cp_2Mo_2Os_2(CO)_9(CCPh)(\mu\text{-}H)$] (**243c)** has been obtained by the addition of Me_3NO to dichloromethane-acetonitrile solution of [$CpMoOs_2(CO)_8(CCPh)$], followed by a thermolytic reaction with [$CpW(CO)_3H$].[89]

Treatment of the carbido cluster [$Ru_5(\mu_5\text{-}C)(CO)_{15}$] with Me_3NO followed by addition of the tungsten acetylide complexes [$LW(CO)_3(CCPh)$] (L=Cp, Cp*) affords the heterometallic cluster complexes [$LWRu_5(\mu_5\text{-}C)(CCPh)(CO)_{15}$] (L=Cp, **245a**; L=Cp*, **245b**) and [$LWRu_5(\mu_5\text{-}C)(CCPh)(CO)_{13}$] (L=Cp, **246a**; L=Cp*, **246b**). Thermolysis of **245** results in an irreversible formation of **246**. Hydrogenation of **246b** gives two cluster compounds [$(C_5Me_5)WRu_5(\mu_6\text{-}C)(\mu\text{-}CCH_2Ph)(\mu\text{-}H)_2(CO)_{13}$] (**247**) and [$(C_5Me_5)WRu_5(\mu_4\text{-}C)(\mu_3\text{-}CCH_2Ph)(\mu\text{-}H)_4(CO)_{12}$] (**248**), via 1,1-addition of H_2 to the ligated acetylide and concurrent formation of two or four bridging hydrides (Scheme 65).[90]



Scheme 65.

Heterometallic vinylacetylide clusters [Cp*$WRe_2(CO)_9(CCR)$] (R = C(Me)=CH_2, **249**;R = C_6H_9, **250**) have been obtained from the condensation of mononuclear tungsten acetylide complexes [Cp*$W(CO)_3$(C≡CR)] (R = -C(Me)=CH_2, C_6H_9) and rhenium carbonyl complex [$Re_2(CO)_8(NCMe)_2$]. Treatment of the vinylacetylide complex [Cp*$WRe_2(CO)_9${C=CC(Me)=CH_2}] **(249)** with alcohols, ROH (R = Me, Et, Ph) in refluxing toluene solution afford complexes [Cp*$WRe_2(CO)_8$(μ-OR)(C=C=CMe_2)] **(**R = Me, **251a**; R = Et, **251b**; R = Ph, **251c**), which contain an unusual μ_3-η^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 [Cp*$WRe_2(CO)_7$(μ-H){CHCHC(Me)CH}] (**252a,b**) is formed as a mixture of two non interconvertible isomers (Scheme 66).[91] On the other hand, hydrogenation of **250** in toluene under refluxing condition initially produces a dihydride cluster $[Cp^*WRe_2(CO)_8(\mu\text{-}H)_2\{C{=}C(C_6H_9)\}]$ **(253)** which on heating in toluene converts to **254** and **255** (Scheme 67).[91]

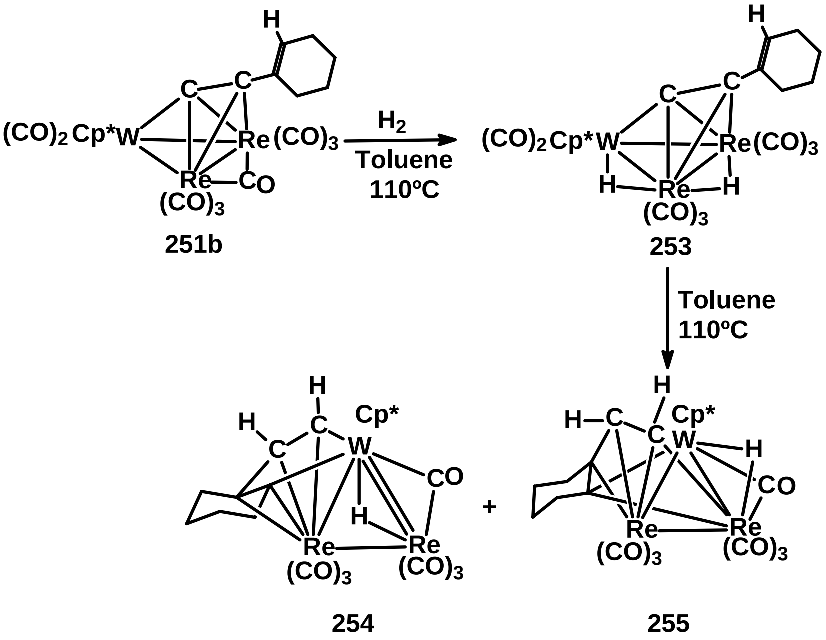


249

251a; R = Me
251b; R = Et
251c; R = Ph

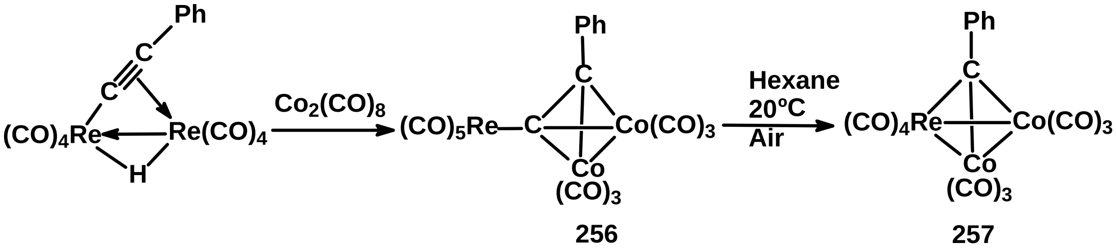
252a; R$_1$ = H, R$_2$ = Me
252b; R$_1$ = Me, R$_2$ = H

Scheme 66.



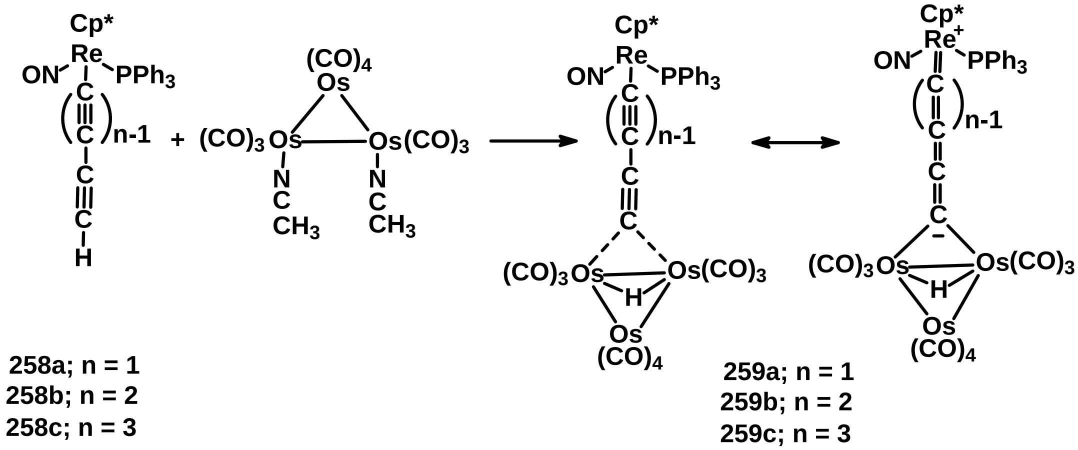
Scheme 67.

The acetylide complex $[Co_2(CO)_6\{\mu\text{-}PhC{=}CRe(CO)_5\}]$ (**256**) (obtained by the treatment of the binuclear acetylide-hydride carbonyl complex of rhenium $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}C{\equiv}CPh)]$with $[Co_2(CO)_8]$) 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 $[Co_2Re(CO)_{10}(\mu_3\text{-}CPh)]$ **(257)** (Scheme 63).[92]

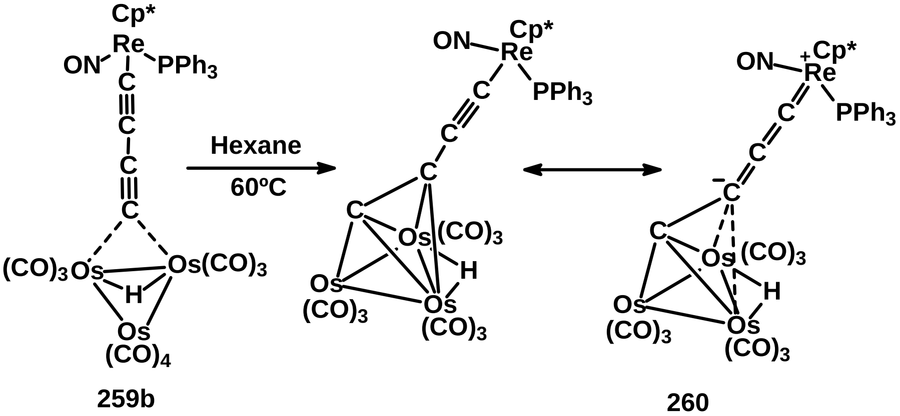


Scheme 68.

A dichloromethane solution of rhenium ethynyl complex $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)\{(C{\equiv}C)_nH\}]$ (n = 1-3) (**258a-c**) and triosmium complex $[Os_3(CO)_{10}(NCMe)_2]$ react at room temperature to give $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(CC)_nOs_3(H)(CO)_{10}]$ (n = 1–3) (**259a-c**) (Scheme 69). Thermal reaction in hexane converts **259b** to the nonacarbonyl complex [(η^5-C_5Me_5)Re(NO)(PPh_3)(CCCC)$Os_3(CO)_9$(H)] (**260**) (Scheme 70).[93, 94]

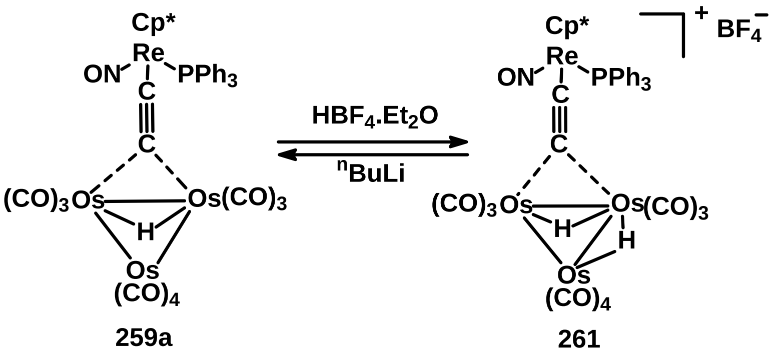


Scheme 69.



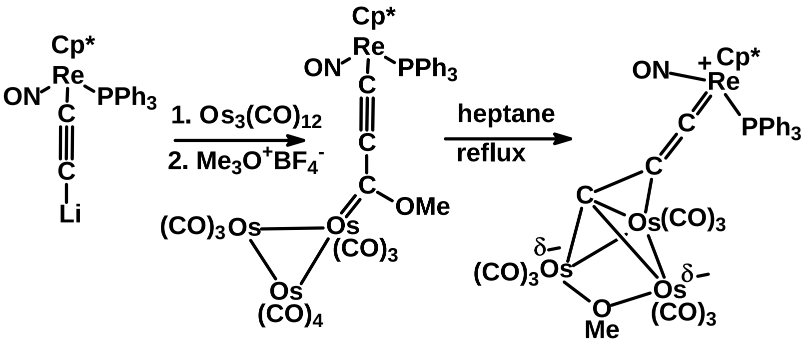
Scheme 70.

Addition of HBF_4. Et_2O (1 equiv.) to compound **259a** gives the cationic dihydride complex [(η^5-C_5Me_5)Re(NO)(PPh_3)(CC)$Os_3(CO)_{10}(H)_2$]$^+$ BF_4^- (**261**) (Scheme 71).[93]



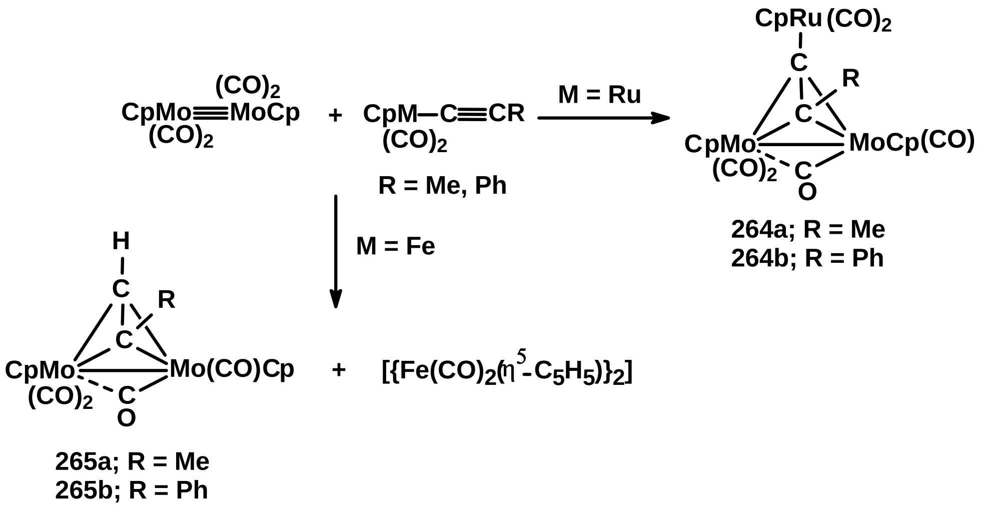
Scheme 71.

Synthesis of a C$_3$OMe complex [(η^5-C$_5$Me$_5$)Re(NO)(PPh$_3$)(C≡CC(OMe))Os$_3$(CO)$_{11}$] (**262**) from the reaction of [(η^5-C$_5$Me$_5$)Re(NO)(PPh$_3$)(C≡CLi)] with [Os$_3$(CO)$_{12}$] and [Me$_3$O$^+$BF$_4^-$] has been reported.[93] On refluxing in heptane it forms **263** (Scheme 72).



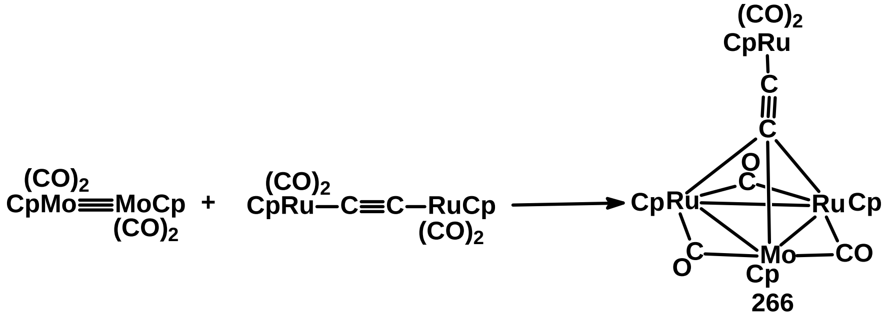
Scheme 72.

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



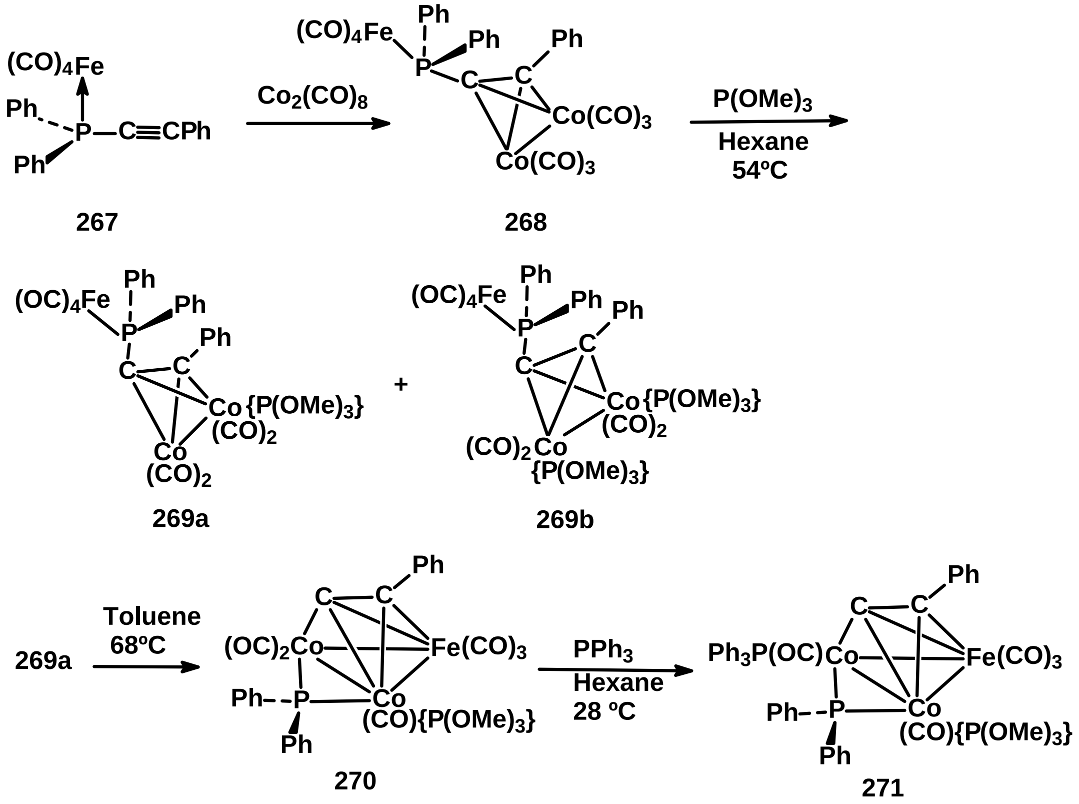
Scheme 73.

On the other hand, reaction of $[\{Ru(CO)_2(\eta\text{-}C_5H_5)\}_2(\mu\text{-}C\equiv C)]$ with $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$ gives $[MoRu_2(\mu_2\text{-}CO)_3[\mu_3\text{-}C\equiv C\{Ru(CO)_2(\eta\text{-}C_5H_5)\}](\eta\text{-}C_5H_5)_3]$ (**266**), but not the dimolybdenum 'alkynyl' adduct, **264a,b** (Scheme 74).[96]



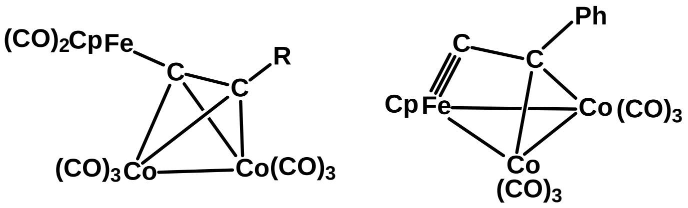
Scheme 74.

Reaction of $[(OC)_4Fe(\eta^1\text{-}PPh_2C\equiv CPh)]$ (**267**) with $[Co_2(CO)_8]$ at room temperature affords the heterotrimetallic complex $[(OC)_4Fe(\mu\text{-}\eta^1\text{:}\eta^2\text{-}PPh_2CCPh)Co_2(CO)_6]$ (**268**), in which the alkynic moiety is bound to a $Co_2(CO)_6$ unit. Both the mono- and di-substituted complexes, $[(OC)_4Fe(\mu\text{-}\eta^1\text{:}\eta^2\text{-}PPh_2C\equiv CPh)Co_2(CO)_5\{P(OMe)_3\}]$ (**269a**) and $[(OC)_4Fe(\mu\text{-}\eta^1\text{:}\eta^2\text{-}PPh_2CCPh)Co_2(CO)_4\{P(OMe)_3\}_2]$ (**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 [$FeCo_2(CO)_6\{\mu_3\text{-}\eta^2\text{-}CCPh\}\{P(OMe)_3\}(\mu\text{-}PPh_2)$] (**270**). Substitution of a Co - bound carbonyl ligand of **270** with triphenylphosphine gives [$FeCo_2(CO)_5\{\mu_3\text{-}\eta^2\text{-}CCPh\}\{P(OMe)_3\}(PPh_3)(\mu\text{-}PPh_2)$] (**271**) (Scheme 75).[97]



Scheme 75.

Reaction between [$CpFe(CO)_2(C_2Me)$] and [$Co_2(CO_8)$] which affords a μ-alkyne complex [$CpFe(C_2Me)Co_2(CO)_8$] (**272a**).[98] In contrast to the reaction of phenylacetylide complex [$CpFe(CO)_2C_2Ph$] and [$Co_2(CO_8)$] forms [$(\eta\text{-}C_5H_5)Fe(C_2Ph)Co_2(CO)_6$] (**273**) and [$(\eta\text{-}C_5H_5)Fe(C_2Ph)Co_2(CO)_8$] (**272b**) (Figure 17).[99]

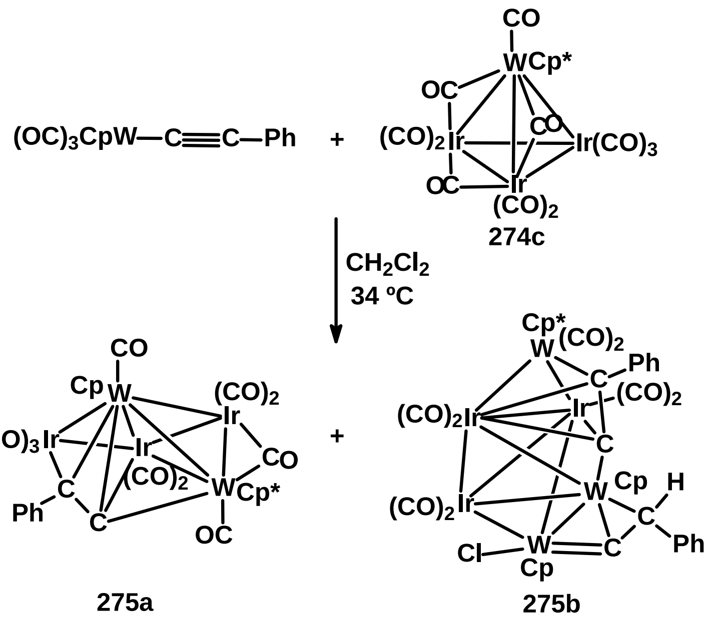


272a; R = Me
272b; R = Ph

273; R = Ph

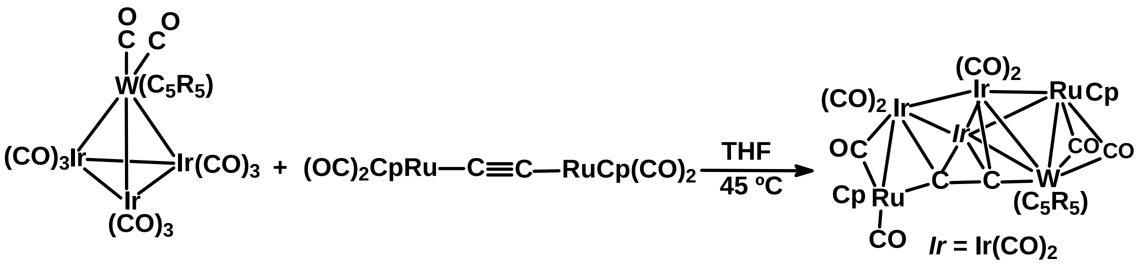
Figure 17.

Tungsten-iridium tetrahedral cluster [$WIr_3(\mu\text{-}CO)_3(CO)_8(\eta\text{-}C_5R_5)$] ($R_5 = H_5$, **274a**; $R_5 = Me_5$**, 274b**; $R_5 = H_4Me$**, 274c**), prepared from the reaction between [$WH(CO)_3(\eta\text{-}C_5R_5)$] and [$IrCl(CO)_2$(*p*-toluidine)] under CO atmosphere, has been used extensively to synthesise several mixed metal acetylide complexes. Thermal reaction of [$WIr_3(\mu\text{-}CO)_3(CO)_8(\eta\text{-}C_5Me_5)$] (**274b**) with [$W(C\equiv CPh)(CO)_3(\eta\text{-}C_5H_5)$] results in the isolation of an edge-bridged tetrahedral cluster [$W_2Ir_3(\mu_4\text{-}\eta^2\text{-}C_2Ph)(\mu\text{-}CO)(CO)_9(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)$] (**275a**) and an edge-bridged trigonal-bipyramidal cluster [$W_3Ir_3(\mu_4\text{-}\eta^2\text{-}C_2Ph)(\mu\text{-}\eta^2\text{-}C{=}CHPh)(Cl)(CO)_8(\eta\text{-}C_5Me_5)(\eta\text{-}C_5H_5)_2$] (**275b**) (Scheme 76).[100] Cluster **275a** is formed by the insertion of [$W(C\equiv CPh)(CO)_3(\eta\text{-}C_5H_5)$] into Ir-Ir and W-Ir bonds, and contains a μ_4-η^2 alkynyl ligand. Cluster **275b** also contains an alkynyl ligand bonded to two iridium atoms and two tungsten atoms in a μ_4-η^2 fashion and a vinylidene ligand bridge the W-W bond.



Scheme 76.

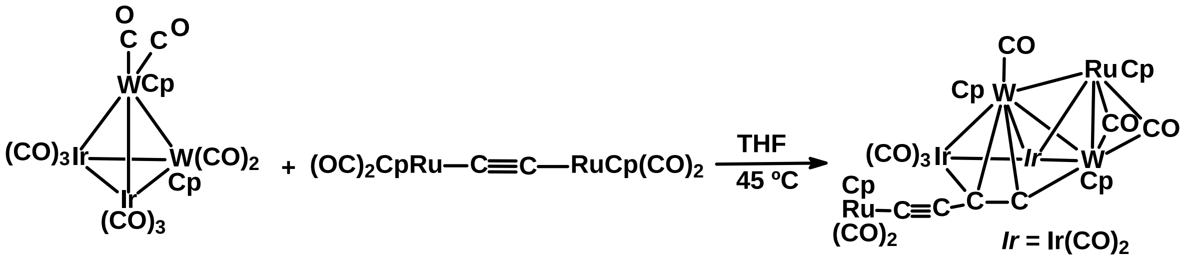
A similar reaction of a THF solution of W-Ir cluster, $[WIr_3(CO)_{11}(\eta\text{-}C_5R_5)]$ (R = H, **274a**; R = Me, **274b**) with $[(\eta\text{-}C_5H_5)(CO)_2Ru(C{\equiv}C)Ru(CO)_2(\eta\text{-}C_5H_5)]$ leads to cluster compound $[Ru_2WIr_3(\mu_5\text{-}\eta^2\text{-}C_2)(\mu\text{-}CO)_3(CO)_7(\eta\text{-}C_5H_5)_2(\eta\text{-}C_5R_5)]$ [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 ethyndiyl precursor (Scheme 77). Another mixed metal cluster with a butterfly W_2Ir_2 unit capped by a $Ru(\eta\text{-}C_5H_5)$ group, $[RuW_2Ir_2\{\mu_4\text{-}\eta^2\text{-}(C_2C{\equiv}C)Ru(CO)_2(\eta\text{-}C_5H_5)\}(\mu\text{-}CO)_2(CO)_6(\eta\text{-}C_5H_5)_3]$ (**277**) has been isolated by the reaction of $[W_2Ir_2(CO)_{10}(\eta\text{-}C_5H_5)_2]$ (**274d**) with the diruthenium ethyndiyl reagent (Scheme 78). When the reaction between $[WIr_3(CO)_{11}(\eta\text{-}C_5R_5)]$ ($R_5 = H_5$, **274a**; $R_5 = Me_5$, **274b**; $R_5 = H_4Me$, **274c)** and $[(\eta\text{-}C_5H_5)(CO)_3W(C{\equiv}CC{\equiv}C)W(CO)_3(\eta\text{-}C_5H_5)]$ is performed in refluxing toluene solution, metallaethynyl type of clusters $[W_2Ir_3\{\mu_4\text{-}\eta^2\text{-}(C_2C{\equiv}C)W(CO)_3(\eta\text{-}C_5H_5)\}(\mu\text{-}CO)_2(CO)_2(\eta\text{-}C_5H_5)(\eta\text{-}C_5R_5)]$ (R = H, **278a**; R = Me, **278b**; $R_5 = H_4Me$, **278c**) are obtained (Scheme 79).[100a]



274a; R = H
274b; R = Me

276a; R = H
276b; R = Me

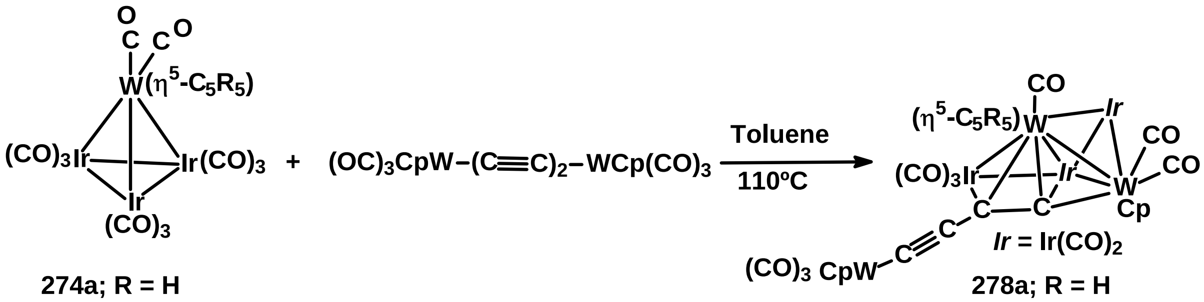
Scheme 77.



274d

277

Scheme 78.



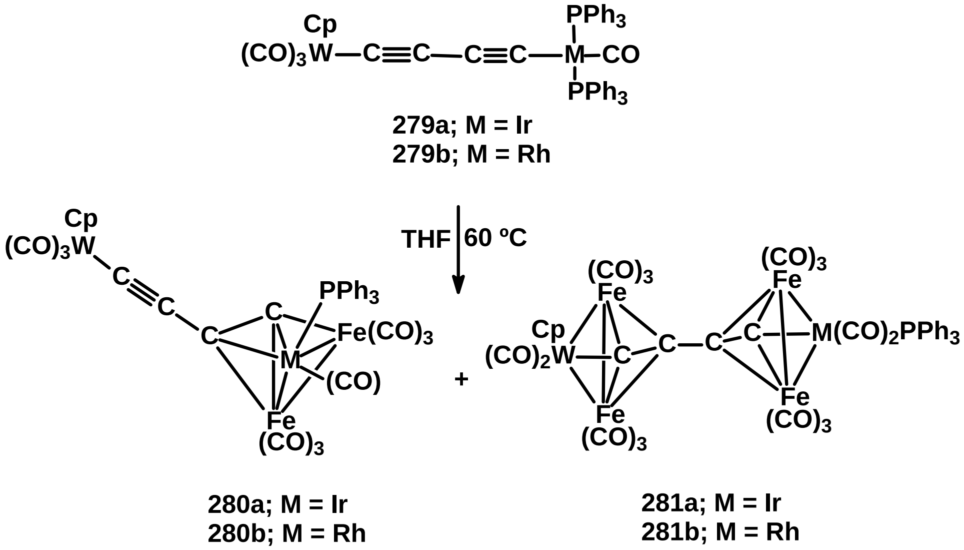
274a; R = H
274b; R = Me
274c; R5 = H4Me

278a; R = H
278b; R = Me
278c; R5 = H4Me

Scheme 79.

Mixed group 6-9 transition metal complexes, [{Cp(OC)$_3$W}C≡CC≡C{M(CO)(PPh$_3$)$_2$}] (M = Ir, **279a**; M = Rh, **279b**) have been obtained from the reaction between [W(C≡CC≡CH)(CO)$_3$Cp] and [M(OTf)(CO)(PPh$_3$)$_2$] (M = Ir, Rh) in presence of diethylamine. Thermal reaction of a THF solution of **279a** or **279b** with [Fe$_2$(CO)$_9$] gives [{Cp(OC)$_3$W}C≡CC$_2${Fe$_2$M(CO)$_8$(PPh$_3$)}] (M = Ir, **280a**; M

= Rh, **280b**) and [{$Cp(OC)_8Fe_2W$}C_2C_2{$Fe_2M(CO)_8(PPh_3)$}] (M = Ir, **281a**; M = Rh, **281b**) (Scheme 80).[100b]



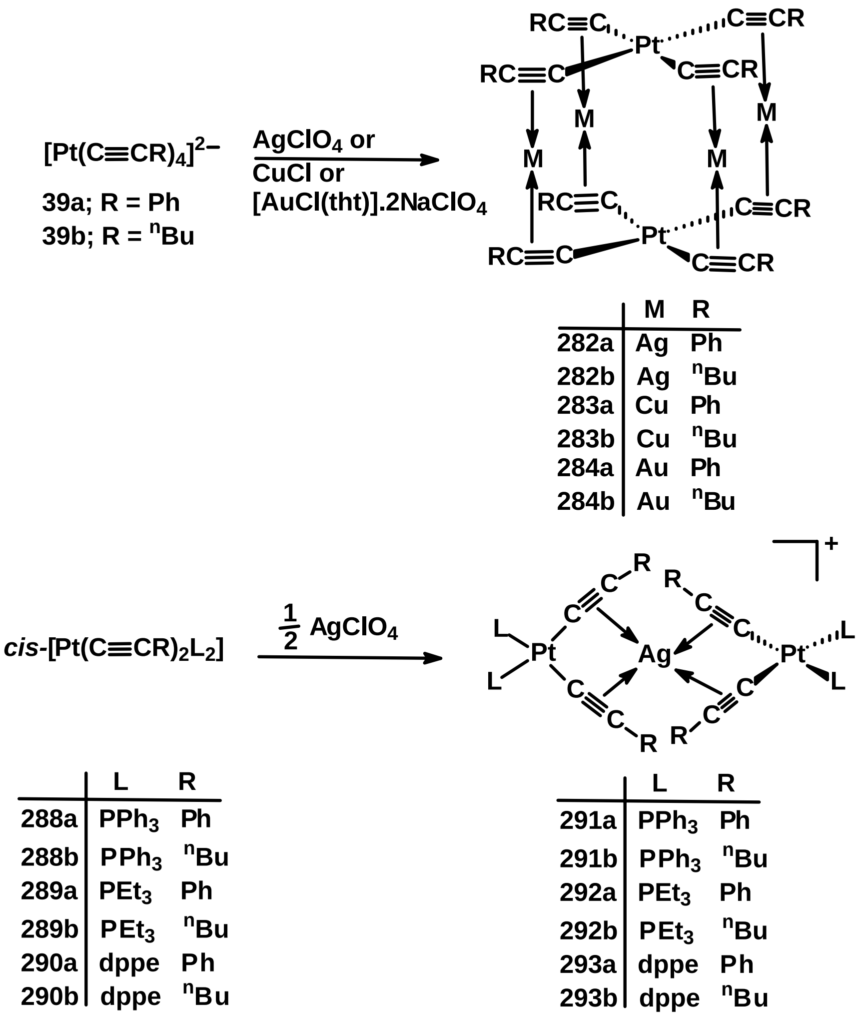
Scheme 80.

VI

MIXED GROUP 10 - 12 METAL ACETYLIDE COMPLEXES

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,[102-110] 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 $[NBu_4]_2[Pt(C{\equiv}CR)_4].nH_2O$ (R = Ph, n = 0; R = ^tBu, n = 2) and X_2[*cis*-$Pt(C_6F_5)_2(C{\equiv}CR)_2$] (X = $PMePh_3$, R = Ph; X = NBu_4, R = ^tBu) 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 $[Pt(C{\equiv}CR)_4]^{2-}$ (**39**) (R = Ph (**a**), ^tBu (**b**)) with $AgClO_4$, or with CuCl or [AuCl(tht)] (tht =

tetrahydrothiophene) in the presence of $NaClO_4$ in 1:2 molar ratio forms a hexanuclear complex $[Pt_2M_4(C{\equiv}CR)_8]$ (M = Ag, Cu, Au) (R = Ph, ^nBu) (**282a,b-284a,b**).[102] The Cu analogue, $[Pt_2Cu_4(C{\equiv}CPh)_8]$ has been prepared by the reaction of $[Pt\{C_5H_4Fe(C_5H_5)\}Cl(cod)]$ with an excess of phenylacetylene and CuI.[101] An anionic tetranuclear complex $[Pt_2M_2(C_6F_5)_4(C{\equiv}CR)_4]^{2-}$ (**285a,b-286a,b**) has been obtained from the reaction of [*cis*-$Pt(C_6F_5)_2(C{\equiv}CR)_2]^{2-}$ (**40**) with $AgClO_4$, AgCl or CuCl in a 1:1 molar ratio.[103] On treatment of complex **285a,b** with $AgClO_4$ (1:2), the Pt-Ag mixed-metal acetylide complex $[\{PtAg_2(C_6F_5)_2(C{\equiv}CR)_2\}_n]$ (**287a,b**) is obtained.[104] An alternative reaction of $[Pt(C_6F_5)_2(C{\equiv}CR)_2]^{2-}$ (**40**) with two equivalents of $AgClO_4$ 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 $[Pt_2Ag(C{\equiv}CR)_4L_4]ClO_4$ (**291-293**) has been synthesized by the reaction of *cis*-$[Pt(C{\equiv}CR)_2L_2]$ (**288-290**) with $AgClO_4$ (2:1 molar ratio) (Scheme 81).[102]



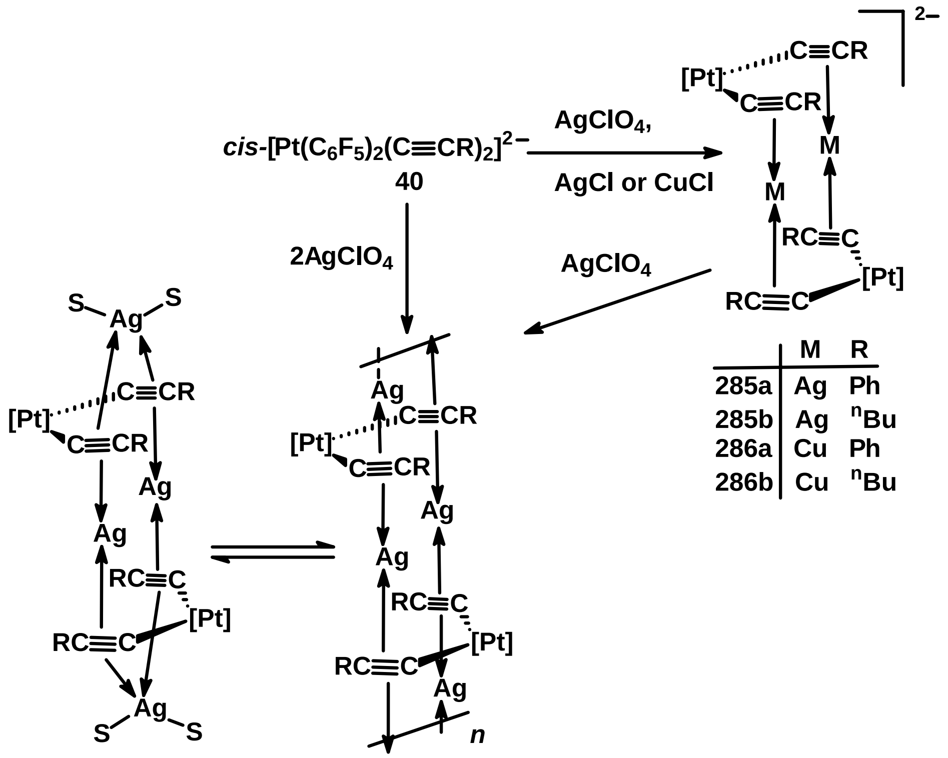
39a; R = Ph
39b; R = ^{n}Bu

	M	R
282a	Ag	Ph
282b	Ag	^{n}Bu
283a	Cu	Ph
283b	Cu	^{n}Bu
284a	Au	Ph
284b	Au	^{n}Bu

	L	R
288a	PPh$_3$	Ph
288b	PPh$_3$	^{n}Bu
289a	PEt$_3$	Ph
289b	PEt$_3$	^{n}Bu
290a	dppe	Ph
290b	dppe	^{n}Bu

	L	R
291a	PPh$_3$	Ph
291b	PPh$_3$	^{n}Bu
292a	PEt$_3$	Ph
292b	PEt$_3$	^{n}Bu
293a	dppe	Ph
293b	dppe	^{n}Bu

Scheme 81.



	M	R
285a	Ag	Ph
285b	Ag	ⁿBu
286a	Cu	Ph
286b	Cu	ⁿBu

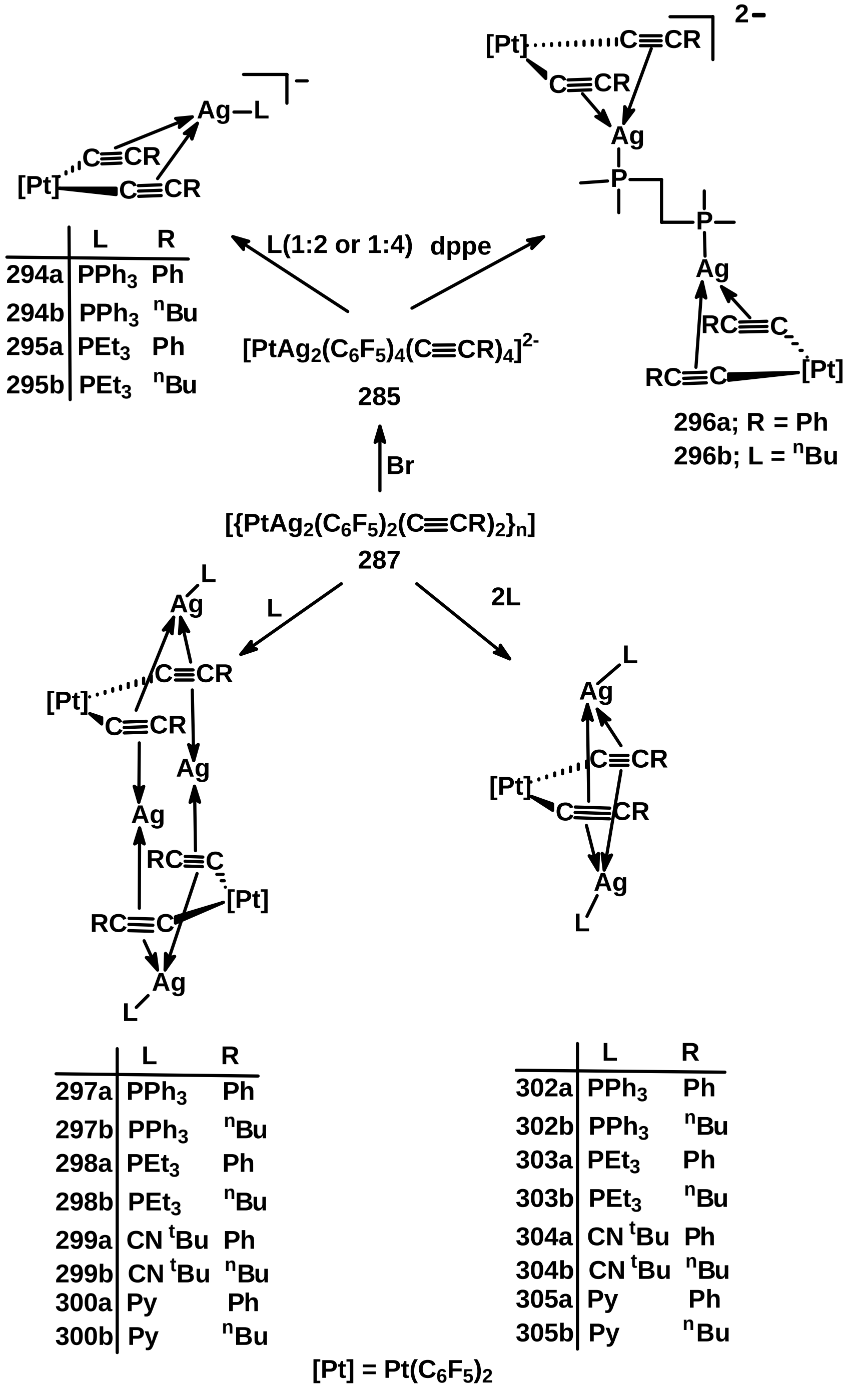
301a; M = Ag, R = Ph
301b; M = Ag, R = ⁿBu

287a; M = Ag, R = Ph
287b; M = Ag, R = ⁿBu

S = Acetone
[Pt] = Pt $(C_6F_5)_2$

Scheme 82.

Treatment of complex **285a,b** with PPh_3 or PEt_3 (1:2 or 1:4 ratio) or with 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 Ag:L molar ratio of 2:1 produces hexanuclear complexes $[Pt_2Ag_4(C_6F_5)_4(C{\equiv}CR)_4L_2]$ (**297-300**) which are structurally related to complex **301** (Scheme 76). The X-ray structure of **297a** reveals the tridentate behavior of the two *cis*-$[Pt(C_6F_5)_2(C{\equiv}CR)_2]$ fragments towards silver atoms. The alkynyl ligands exhibit an unsymmetrical μ_3-η^2 bonding mode. In contrast, trinuclear $[PtAg_2(C_6F_5)_2(C{\equiv}CR)_2L_2]$ (**302-305**) are isolated when higher proportion of the ligand L is used with complex **287**. The tetranuclear **285** is obtained when **287** is reacted with NBu_4Br (Scheme 83).[106,110]



	L	R
294a	PPh_3	Ph
294b	PPh_3	^nBu
295a	PEt_3	Ph
295b	PEt_3	^nBu

	L	R
297a	PPh_3	Ph
297b	PPh_3	^nBu
298a	PEt_3	Ph
298b	PEt_3	^nBu
299a	CN^tBu	Ph
299b	CN^tBu	^nBu
300a	Py	Ph
300b	Py	^nBu

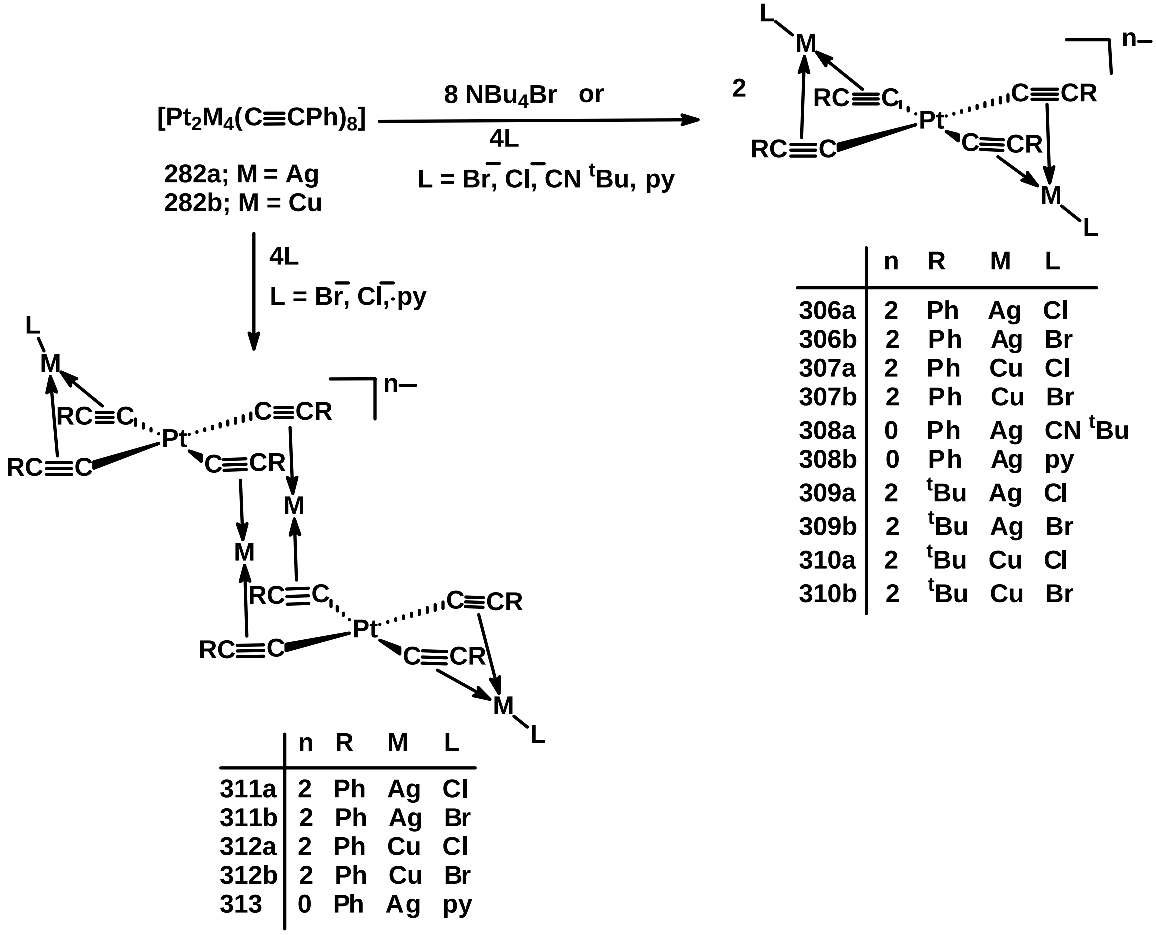
	L	R
302a	PPh_3	Ph
302b	PPh_3	^nBu
303a	PEt_3	Ph
303b	PEt_3	^nBu
304a	CN^tBu	Ph
304b	CN^tBu	^nBu
305a	Py	Ph
305b	Py	^nBu

[Pt] = $Pt(C_6F_5)_2$

Scheme 83.

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 = ^{t}CNBu, pyridine). For instance, the reaction of

$[Pt_2M_4(C{\equiv}CPh)_8]$ (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 $[Pt_2M_4(C{\equiv}C^tBu)_8]$ (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).[107]

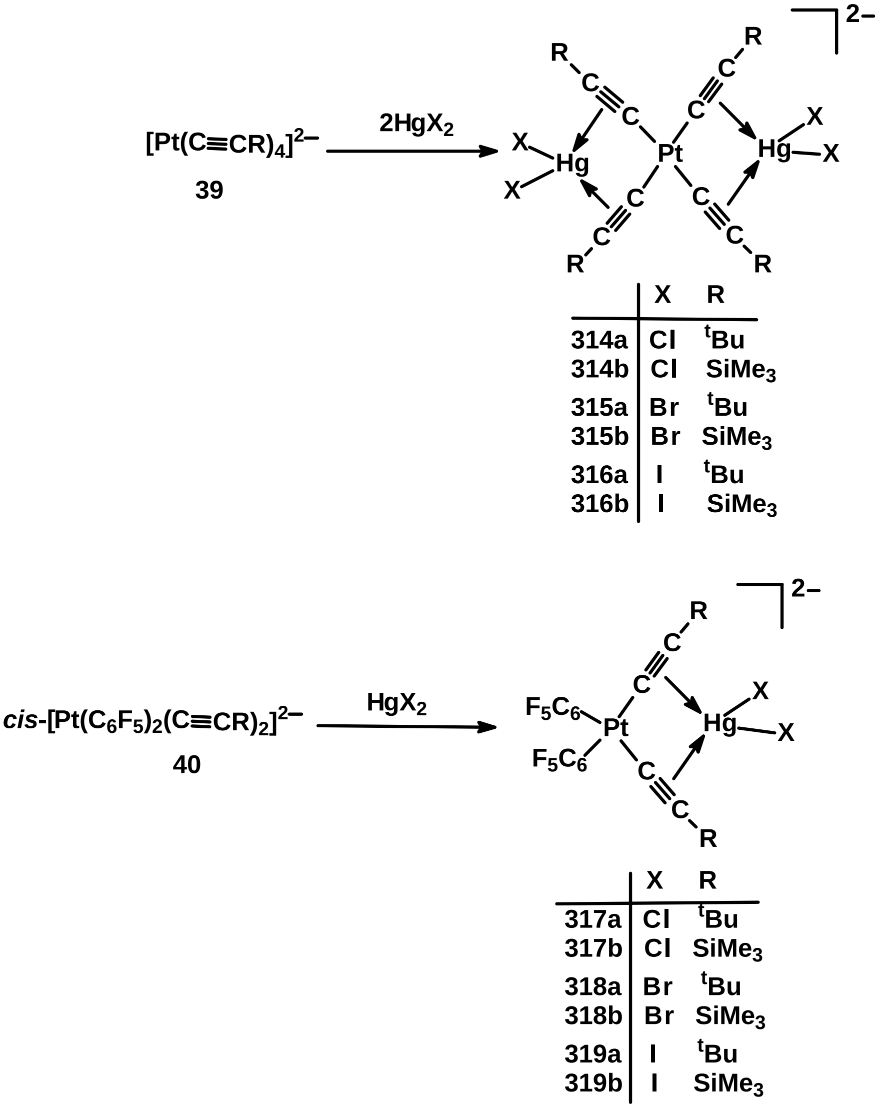


	n	R	M	L
306a	2	Ph	Ag	Cl
306b	2	Ph	Ag	Br
307a	2	Ph	Cu	Cl
307b	2	Ph	Cu	Br
308a	0	Ph	Ag	CN ^{t}Bu
308b	0	Ph	Ag	py
309a	2	^{t}Bu	Ag	Cl
309b	2	^{t}Bu	Ag	Br
310a	2	^{t}Bu	Cu	Cl
310b	2	^{t}Bu	Cu	Br

	n	R	M	L
311a	2	Ph	Ag	Cl
311b	2	Ph	Ag	Br
312a	2	Ph	Cu	Cl
312b	2	Ph	Cu	Br
313	0	Ph	Ag	py

Scheme 84.

The platinum mononuclear complexes $[Pt(C{\equiv}CR)_4]^{2-}$ (**39**) and $[Pt(C_6F_5)_2(C{\equiv}CR)_2]^{2-}$ (**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).[108]

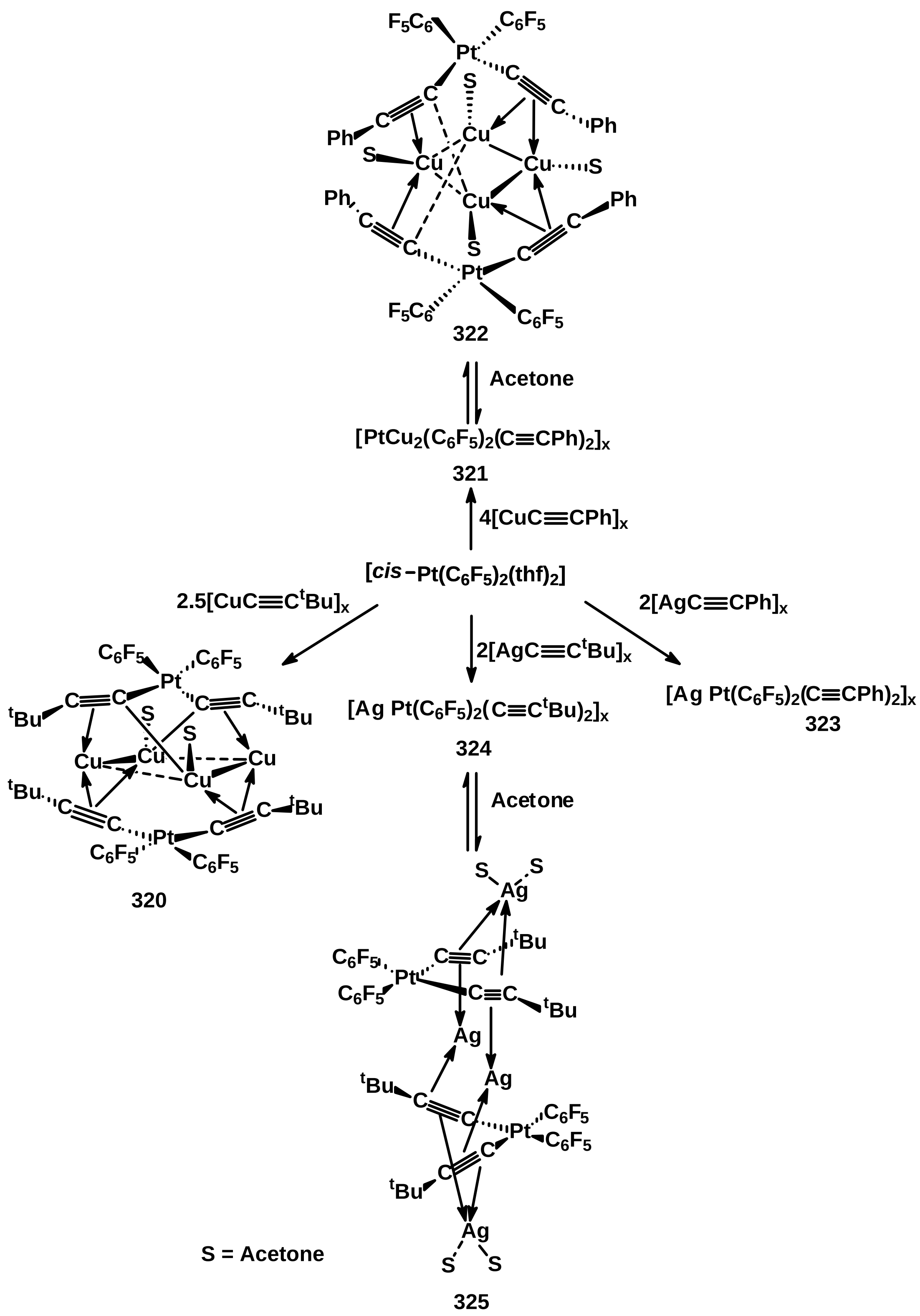


	X	R
314a	Cl	^tBu
314b	Cl	$SiMe_3$
315a	Br	^tBu
315b	Br	$SiMe_3$
316a	I	^tBu
316b	I	$SiMe_3$

	X	R
317a	Cl	^tBu
317b	Cl	$SiMe_3$
318a	Br	^tBu
318b	Br	$SiMe_3$
319a	I	^tBu
319b	I	$SiMe_3$

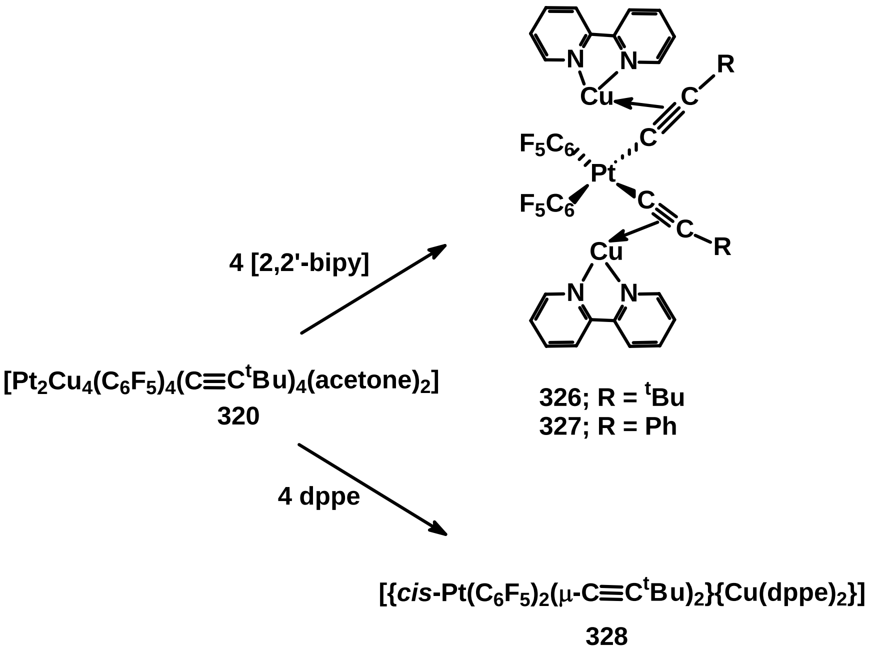
Scheme 85.

The hexanuclear platinum-copper complex $[Pt_2Cu_4(C_6F_5)_4(C{\equiv}C^tBu)_4(acetone)_2]$ (**320**) and the polynuclear derivative $[PtCu_2(C_6F_5)_2(C{\equiv}CPh)_2]_x$ (**321**), which crystallizes in acetone as $[Pt_2Cu_4(C_6F_5)_4(C{\equiv}CPh)_4(acetone)_4]$ (**322**), have been prepared from the reaction of [*cis*-$Pt(C_6F_5)_2(THF)_2$] with the corresponding copper-acetylide, $[Cu(C{\equiv}CR)]_x$ (R = Ph, ^{t}Bu) (molar ratio 1:2) as starting materials. The Ag-analogues (**323-325**) have been synthesized similarly (Scheme 86).[104,109]


322
Acetone
[PtCu2(C6F5)2(C≡CPh)2]x
321
4[CuC≡CPh]x
[cis-Pt(C6F5)2(thf)2]
2.5[CuC≡CtBu]x
2[AgC≡CtBu]x
2[AgC≡CPh]x
[Ag Pt(C6F5)2(C≡CtBu)2]x
324
[Ag Pt(C6F5)2(C≡CPh)2]x
323
320
Acetone
325
S = Acetone

Scheme 86.

Addition of four equivalents of 2,2'-bipyridine to a solution of **320** or **321** yields neutral trinuclear alkynyl bridged complexes [{*cis*-Pt(C_6F_5)$_2$(μ-C≡CR)$_2$}{Cu(bipy)}$_2$] (R = ^{t}Bu, **326**; R = Ph, **327**). An analogous trinuclear complex [{*cis*-Pt(C_6F_5)$_2$(μ-C≡C^{t}Bu)$_2$}{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 [PtAg$_2$(C_6F_5)$_2$(C≡CR)$_2$]$_x$ and the monomeric [*cis*-Pt(C_6F_5)$_2$(C≡CR)$_2$]$_2^-$ suggest the presence of emitting states bearing a large cluster [PtM$_2$]$_x$ -to-ligand (alkynide) charge transfer (CLCT).[109]

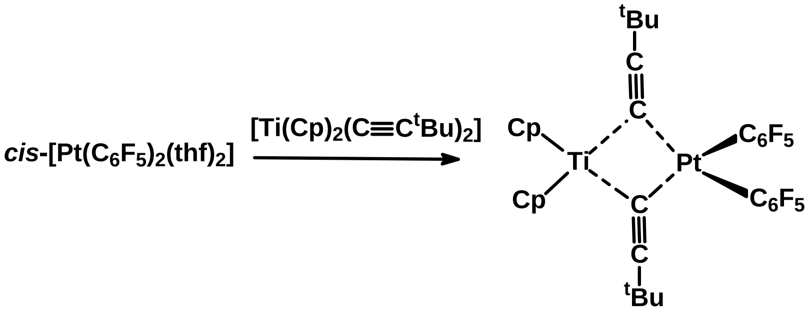


Scheme 87.

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.

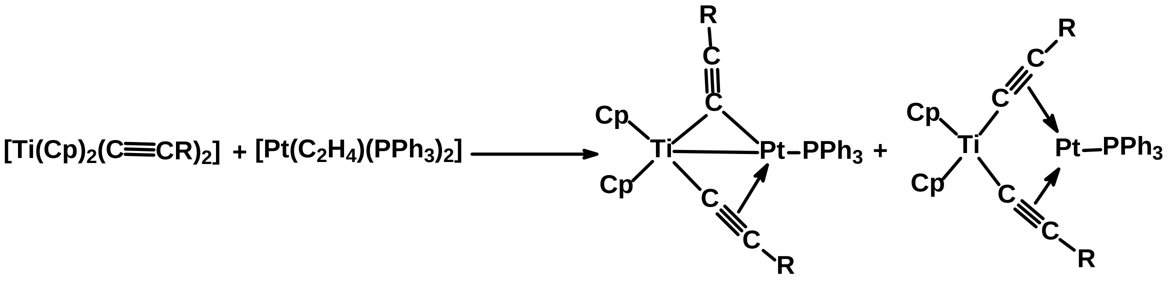
The reaction of mononuclear $[Cp_2Ti(C{\equiv}C^tBu)_2]$ with *cis*-$[M(C_6F_5)(thf)_2]$ (M = Pt) results in the formation of dimetallic Pt-Ti acetylide complex $[Cp_2Ti(\mu\text{-}\eta^1\text{-}C{\equiv}CBu^t)_2Pt(C_6F_5)_2]$ (**329**) (Scheme 88).[111]



329

Scheme 88.

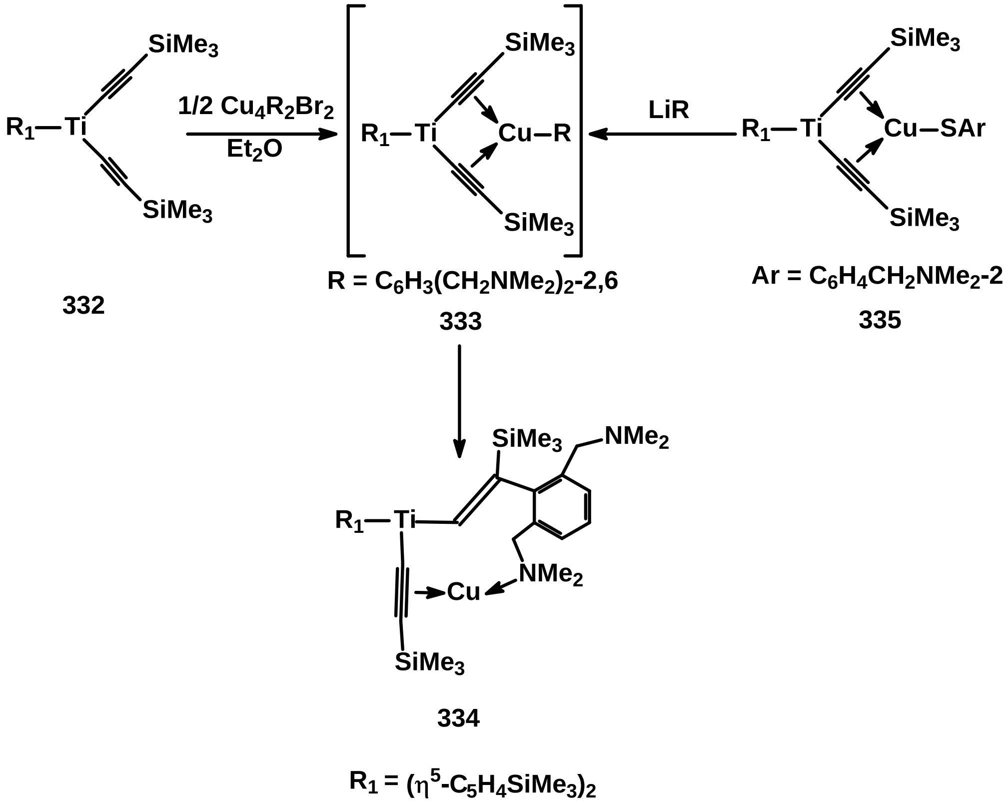
When $[Pt(C_2H_4)(PPh_3)_2]$ is added to $[Ti(\eta\text{-}C_5H_5)_2(C{\equiv}CR)_2]$ (R = Bu^t, Ph), products $[Cp_2Ti(\mu\text{-}\eta^1,\eta^1\text{-}C{\equiv}CBu^t)(\mu\text{-}\eta^2,\eta^1\text{-}C{\equiv}CBu^t)Pt(PPh_3)]$ (**330**) and $[Cp_2Ti(\mu\text{-}\eta^2,\eta^1\text{-}C{\equiv}CPh)_2Pt(PPh_3)]$ (**331)** are obtained (Scheme 89).[112]



R = Ph, ^{t}Bu **330; R = ^{t}Bu** **331; R = Ph**

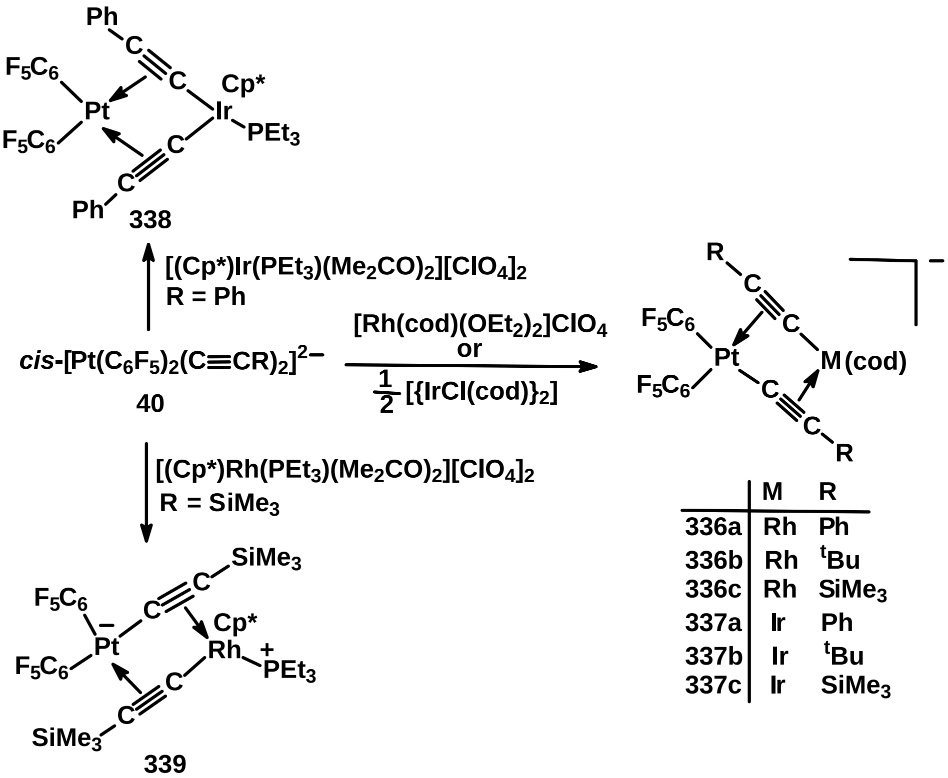
Scheme 89.

A solution of tetranuclear heteroleptic arylcopper aggregate $[Cu_4R_2Br_2]$ (R = $C_6H_3(CH_2NMe_2)_2$-2,6) in diethylether reacts at room temperature with the titanium complex $[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CSiMe_3)_2]$ (**332**), in 1:4 molar ratio, to give a 1,1-bis-metallaalkenyl complex $[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CSiMe_3)\{\mu\text{-}C{=}C(SiMe_3)(R)\}Cu]$ (**334**) resulting from an intramolecular addition of a Cu-C bond across the alkyne triple bond (Scheme 90).[113] A probable formation of complex **333** as an intermediate has been proposed.



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).[114]



	M	R
336a	Rh	Ph
336b	Rh	^{t}Bu
336c	Rh	SiMe$_3$
337a	Ir	Ph
337b	Ir	^{t}Bu
337c	Ir	SiMe$_3$

Scheme 91.

The tetranuclear mixed metal cluster $[(\eta^5\text{-}C_5H_5)_2Ni_2Fe_2(CO)_5(\mu\text{-}PPh_2)(\mu_4\text{-}\eta^2\text{-}C{\equiv}CPh)]$ (**340**) has been synthesised in high yield via condensation of $[Fe_2(CO)_6(\mu\text{-}PPh_2)(\mu_2\text{-}\eta^2\text{-}C{\equiv}CPh)]$ and $[(\eta^5\text{-}C_5H_5)_2Ni_2(CO)_2]$ in benzene reflux.[115] X-ray analysis has revealed a μ_4-acetylide complex coordinated on a spiked triangular metal skeleton (Figure 18).

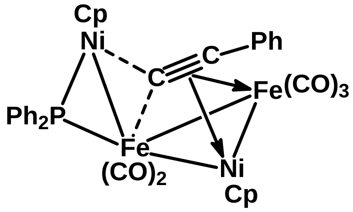


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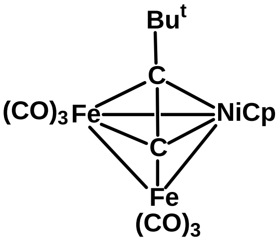
Figure 18.

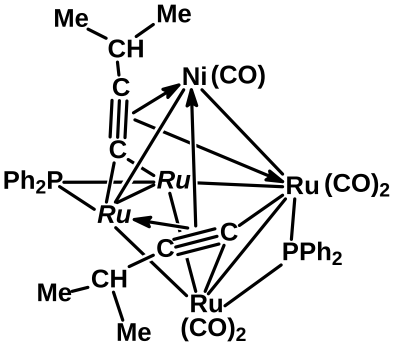
A triangular Ni-Fe acetylide complex $[Cp_2NiFe_2(CO)_6(C_2{}^tBu)]$ (**341**) has been obtained when $[Cp_2Ni_2(HC_2{}^tBu)]$ is reacted with $[Fe_3(CO)_{12}]$ in refluxing heptane (Figure 19).[116]



341

Figure 19.

A pentanuclear Ni-Ru cluster $[NiRu_4(CO)_9(\mu\text{-}PPh_2)_2(\mu_4\text{-}C{\equiv}C^iPr)_2]$ (**342**) has been synthesised by the addition of electron rich $[(\eta\text{-}Cp)Ni(CO)]_2$ to a carbocationic μ_3-acetylide group in $[Ru_3(CO)_9(\mu_3\text{-}C{\equiv}C^iPr)(PPh_2)]$.[117] Its structure consists of a Ru_4 butterfly, zipped up by a Ni(CO) group, with the two acetylide groups in μ_4-η^2-bonding mode (Figure 20).

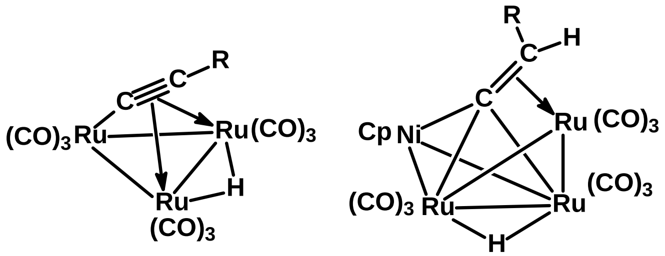


Ru = Ru(CO)$_2$

342

Figure 20.

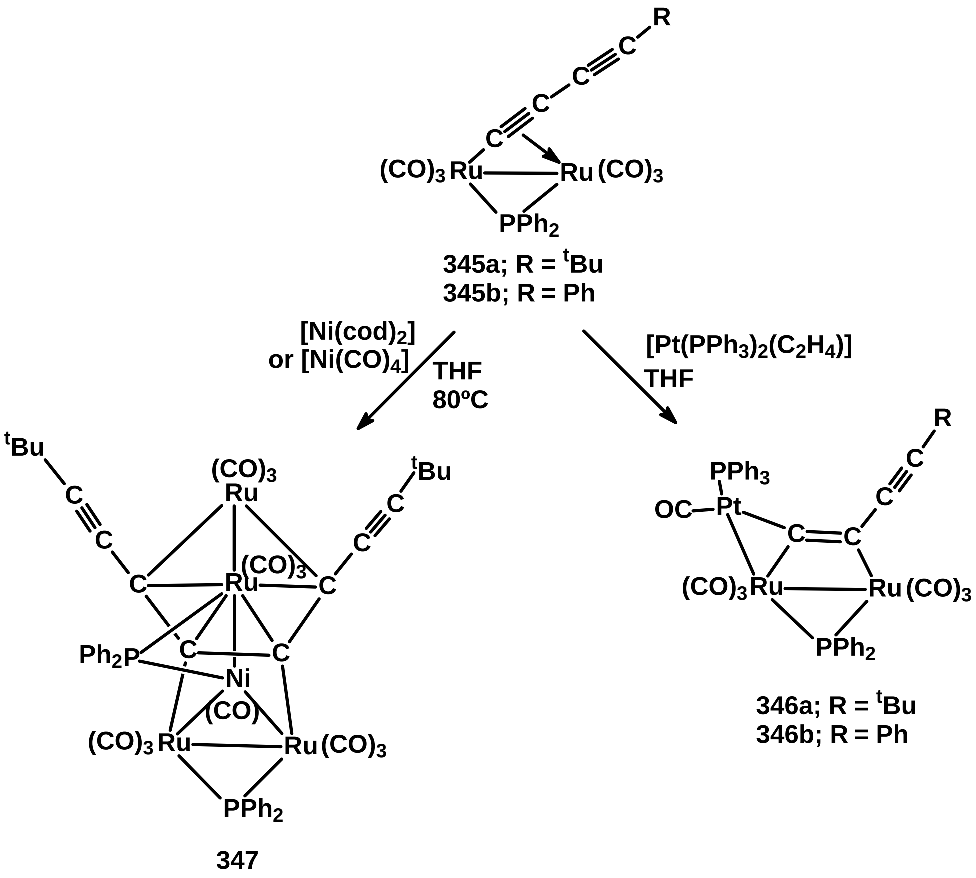
The reaction of the terminal alkyne, $[HC{\equiv}C\text{-}{}^iPr]$ with $[Ru_3(CO)_{12}]$ in boiling heptane gives $[(\mu\text{-}H)Ru_3(CO)_9(\mu_4\text{-}\eta^2\text{-}C{=}CH^iPr)]$ (**343**) which on further reaction with an octane solution of $[(\eta^5\text{-}C_5H_5)Ni(CO)]_2$ under reflux condition forms the vinylidene cluster [(μ-H)(η^5-C_5H_5Ni)$Ru_3(CO)_9$(μ_4-η^2-C=CH^{i}Pr)] (**344**) (Figure 21).[118] Structure of **344** consists of a butterfly arrangement of Ru_3Ni moiety, with the vinylidene ligand σ - bonded to two ruthenium and one nickel atoms and η^2- coordinated to the third ruthenium atom.



343 **344**

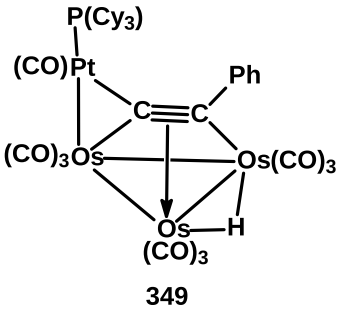
Figure 21.

Reaction of a THF solution of [$Ru_2(CO)_6$(μ-PPh_2)(μ-η^1,η^2-C≡C–C≡CR)] (R= ^{t}Bu, **345a**;R = Ph, **345b**) with [$Pt(PPh_3)_2$(η-C_2H_4)] leads to a trimetallic heteronuclear complex [$Ru_2Pt(CO)_7(PPh_3)$(μ_3-η^1,η^1,η^1-C=C–C≡CR)(μ-PPh_2)] (**346a,b**) (Scheme 92).[119] A THF solution of **345a** also reacts under reflux condition with [Ni(cod)$_2$] or [Ni(CO)$_4$] to give a pentanuclear cluster, [$Ru_4Ni(CO)_{12}$(μ-PPh_2)$_2$(μ_4-η^1,η^1,η^2,η^4-^{t}BuC≡CC$_4$C≡C^{t}Bu)] (**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.



Scheme 92.

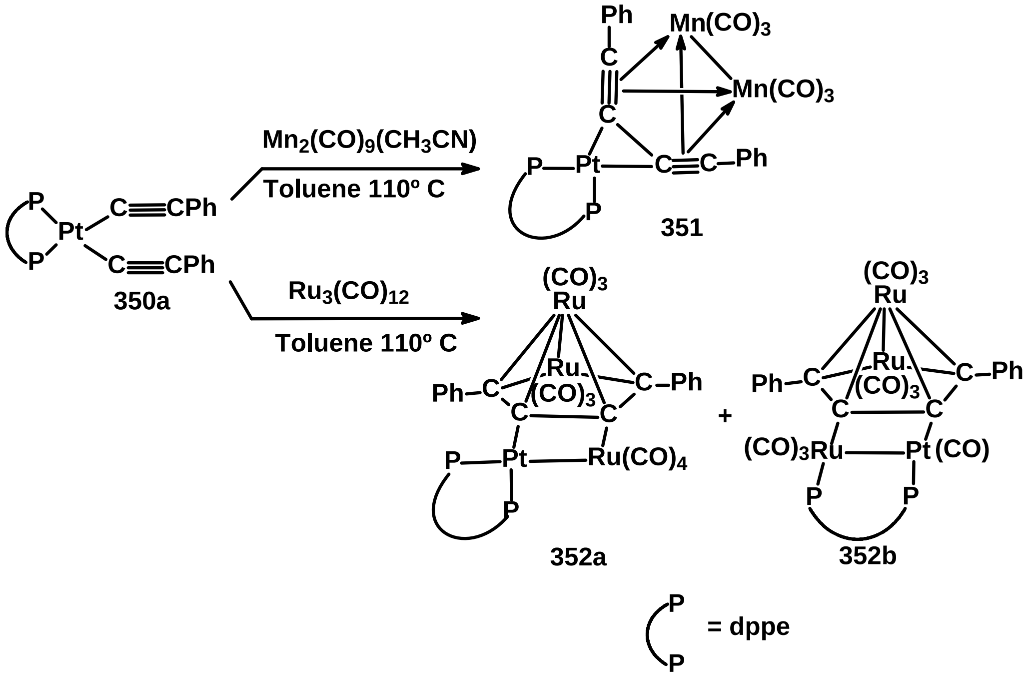
A triangular triosmium-platinum cluster complex [$Os_3Pt(\mu\text{-}H)(\mu_4\text{-}\eta^2\text{-}C{\equiv}CPh)(CO)_{10}(PCy_3)$] (**349**) has been synthesised by the treatment of the unsaturated [$Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PCy_3)$] (**348**) with [LiC≡CPh] followed by protonation.[120] X-ray structural analysis reveals a μ_4-η^2-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).



349

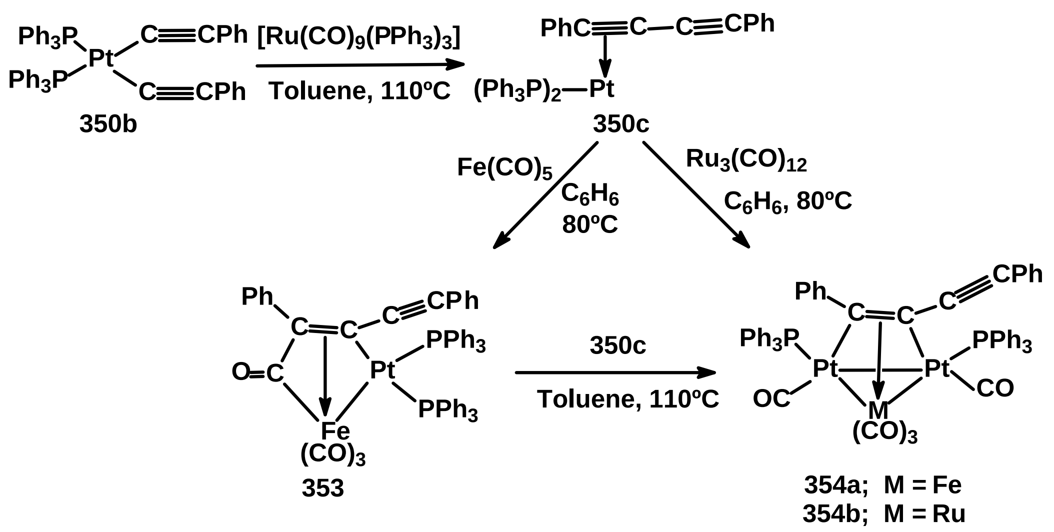
Figure 22.

To achieve alkyne oligomerization, bis(acetylide) Pt(II) complexes have been used to facilitate acyclic dimeriztion of alkynyls through head-to-head C-C bond coupling.[121,122] Thermal reaction of a toluene solution of [*cis*-$Pt(C\equiv CPh)_2(dppe)$] (**350a**) with $[Mn_2(CO)_9(CH_3CN)]$ gives a mixed Mn-Pt compound, $[Mn_2Pt(PhCCCCPh)(CO)_6(dppe)]$ (**351**),[121] whereas reaction of **350a** with $[Ru_3(CO)_{12}]$ in refluxing toluene forms two isomeric Ru/Pt compounds (**352 a,b**) (Scheme 93).[122]



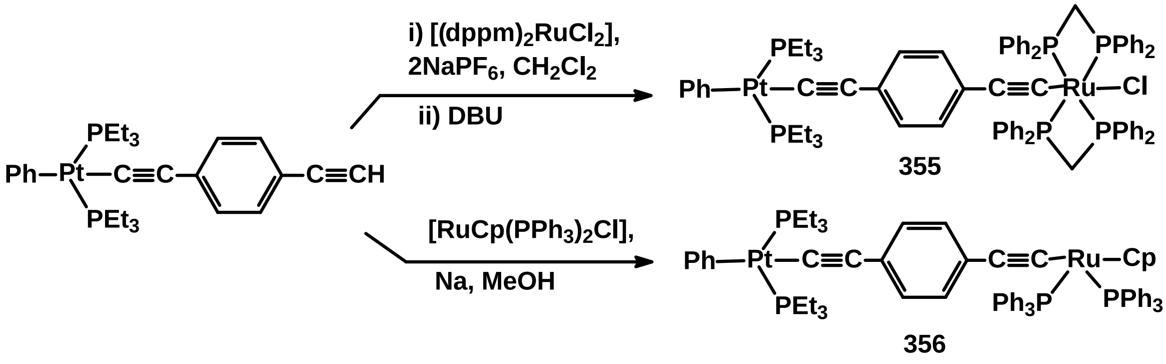
Scheme 93.

In refluxing toluene, compound **350b** reacts with $[Ru_3(CO)_9(PPh_3)_3]$ to form the μ-1,3-diyne compound $[Pt(\eta^2\text{-}PhCCCCPh)(PPh_3)_2]$ (**350c**). Successive reaction of **350c** with $[Fe(CO)_5]$ and $[Ru_3(CO)_{12}]$ under benzene reflux lead to the isolation of a dimetallacyclic compound, $[FePt(\mu_2\text{-}\eta^1\text{:}\eta^1\text{: }\eta^2\text{-}C(O)PhC{=}CC\equiv CPh)(CO)_3(PPh_3)_2]$ (**353**) and a triangular cluster, $[MPt_2(\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^2\text{-}Ph\text{-}CCC\equiv CPh)(CO)_5(PPh_3)_2]$ (M= Fe, **354a**; M= Ru, **354b**) (Scheme 94).[121]



Scheme 94.

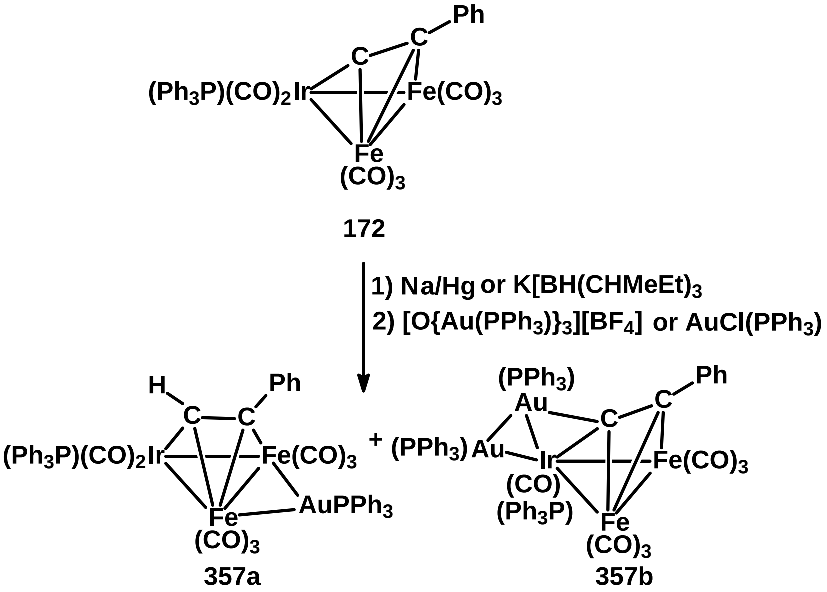
Addition of [$(dppm)_2RuCl_2$] to *trans*-[$(PEt_3)_2Pt(Ph)(C{\equiv}C$-*p*-$C_6H_4$-$C{\equiv}CH)$] followed by treatment with DBU forms a heterometallic acetylide complex [$(PEt_3)_2Pt(C{\equiv}C$-*p*-C_6H_4-$C{\equiv}C)Ru(Cl)(dppm)_2)$] (**355**). Thermal reaction of a methanol solution of [$Cp(PPh_3)_2RuCl$] with *trans*-[$(PEt_3)_2Pt(Ph)(C{\equiv}C$-*p*-$C_6H_4$-$C{\equiv}CH)$] results in the formation of *trans*-[$Cp(PPh_3)_2Ru(C{\equiv}C$-*p*-C_6H_4-$C{\equiv}C)Pt(Et_3P)_2(Ph)$] (**356**) (Scheme 95).[36b]



Scheme 95.

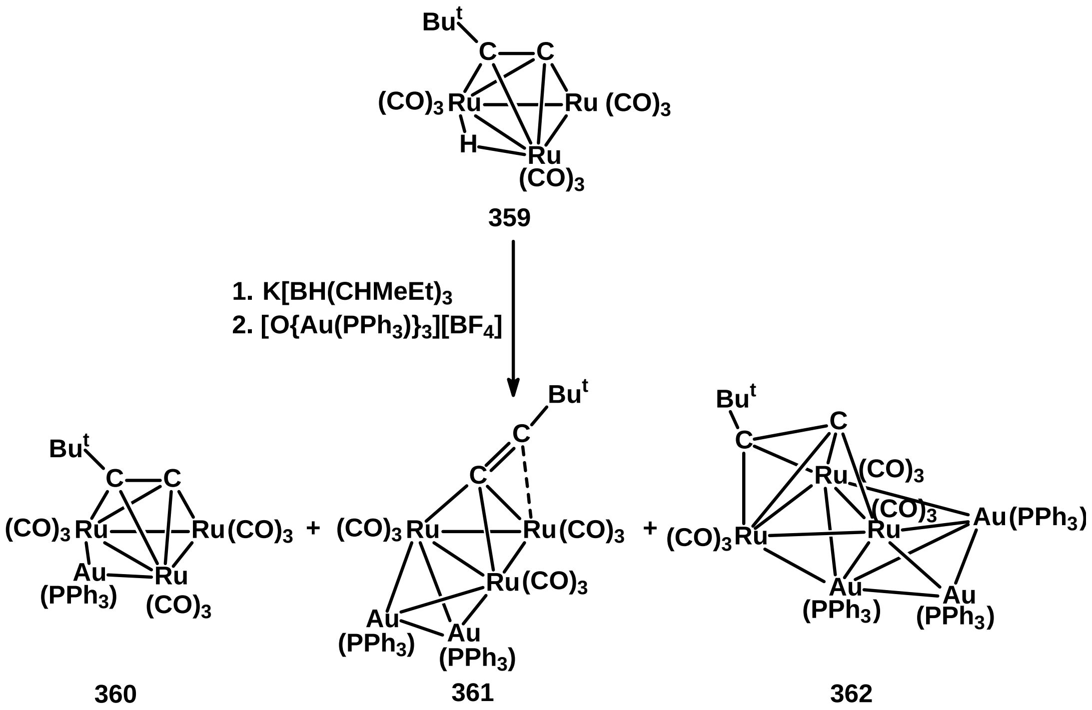
Reduction of **172** with Na/Hg followed by addition of [$O\{Au(PPh_3)\}_3$][BF_4] or [$AuCl(PPh_3)$] gives complexes [$AuFe_2Ir(\mu_3$-$C_2HPh)(CO)_8(PPh_3)_2$] (**357a**) and

$[Au_2Fe_2Ir(\mu_4\text{-}C_2Ph)(CO)_7(PPh_3)_2]$ (**357b**) (Scheme 96). Reaction of complex **172** with $K[BH(CHMeEt)_3]$ followed by auration gives a Au_3FeIr cluster $[Au_3Fe_2Ir(C_2HPh)(CO)_{12}(PPh_3)_4]$ (**358**). The Rh analogue of **357** has also been prepared by a similar procedure.[123]



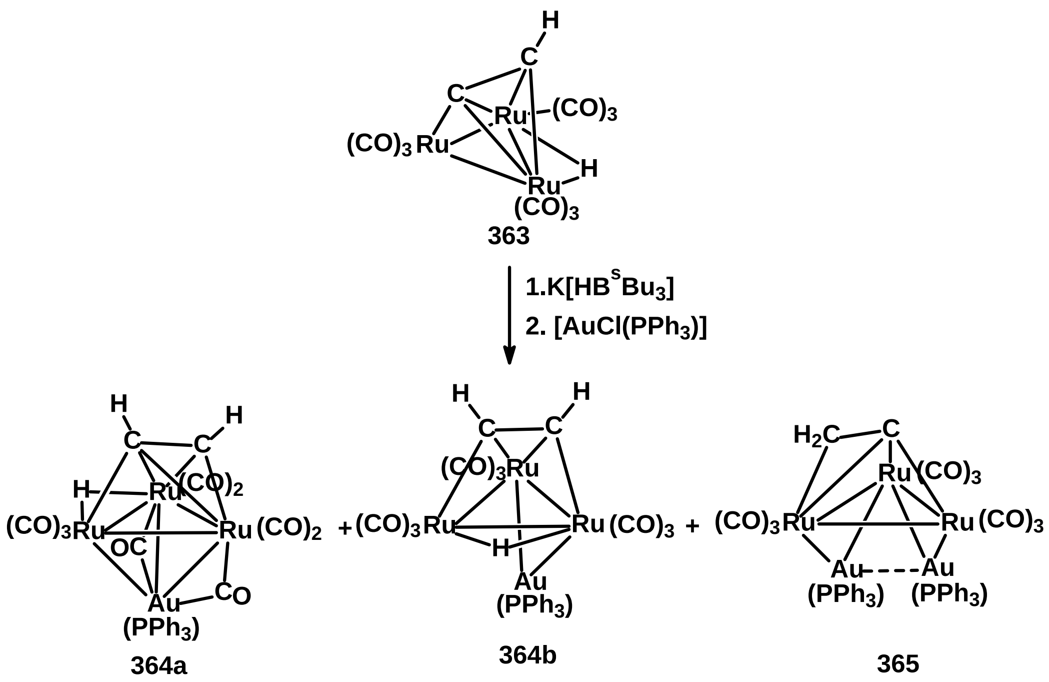
Scheme 96.

Mono-, di- and tri-gold containing ruthenium clusters $[Ru_3Au(\mu_3\text{-}C_2{}^tBu)(CO)_9(PPh_3)]$ (**360**), $[Ru_3Au_2(\mu_3\text{-}C{=}CH^tBu)(CO)_9(PPh_3)_2]$ (**361**) and $[Ru_3Au_3(C_2{}^tBu)(CO)_8(PPh_3)_3]$ (**362**) have been isolated by a deprotonation reaction of $[HRu_3(CO)_9C_2{}^tBu]$ (**359**) with $K[HB(CHMeEt)_3]$, followed by auration with $[O\{Au(PPh_3)\}_3][BF_4]$ (Scheme 97).[124] Molecular structure of **361** contains a trigonal pyramidal Ru_3Au_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.



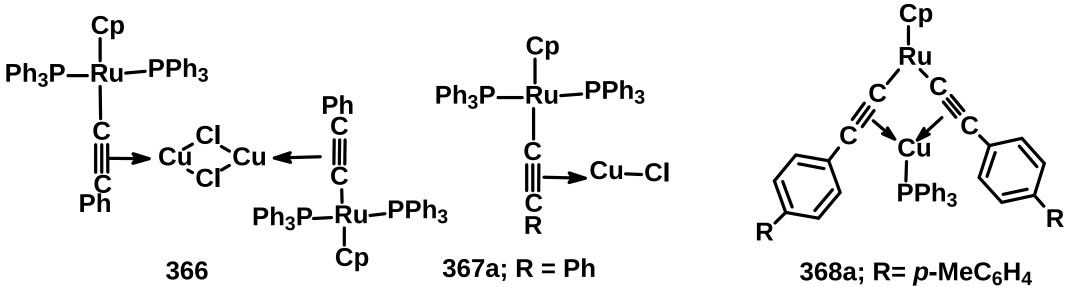
Scheme 97.

Addition of a THF solution of K[BH^{s}Bu$_3$] to a solution of [Ru$_3$(μ-H)(μ$_3$-C$_2$H)(CO)$_9$] (**363**) in THF followed by auration with [AuCl(PPh$_3$)] results in the isolation of [AuRu$_3$(μ-H)(μ$_3$-C$_2$H$_2$)(CO)$_9$(PPh$_3$)] (**364**) and [Au$_2$Ru$_3$(μ$_3$-C=CH$_2$)(CO)$_9$(PPh$_3$)$_2$] (**365**) (Scheme 98).[125] Complex **364** crystallises in a dark red form, in which the AuRu$_3$ core forms a tetrahedron (**364a**), and a yellow form, in which the AuRu$_3$ core has a butterfly structure (**364b**). The C$_2$H$_2$ ligand is $2\eta^1,\eta^2$ coordinates to the Ru$_3$ face in both the isomeric forms. In cluster **365** the Au$_2$Ru$_3$ core has a distorted square pyramidal conformation with the CCH$_2$ ligand attached to the Ru$_3$ face.



Scheme 98.

Thermal reactions of a benzene solution of [RuCl(PPh$_3$)$_2$(C$_5$H$_5$)] and [Cu(C$_2$Ph)] afford [RuCuCl(C$_2$Ph)(PPh$_3$)$_2$(C$_5$H$_5$)]$_2$ (**366**) and [RuCuCl(C$_2$Ph)(PPh$_3$)$_2$(C$_5$H$_5$)] (**367a**), whereas, similar reaction with [Cu(C$_2$C$_6$H$_4$Me-*p*)] or [Cu(C$_2$C$_6$H$_4$F-*p*)] results in the formation of a halogen free complex [RuCu(C$_2$R)$_2$(PPh$_3$)(C$_5$H$_5$)] (**368a,b**) (R = *p*-MeC$_6$H$_4$ or *p*-FC$_6$H$_4$) and [RuCuCl(C$_2$C$_6$H$_4$Me-*p*)(PPh$_3$)$_2$(C$_5$H$_5$)] (**367b**) (Figure 23).[126] The Me-analogue, [RuCuCl(C$_2$Me)(PPh$_3$)$_2$(C$_5$H$_5$)] (**367c**) has been obtained by a heating reaction of [Cu(C$_2$Me)] and ruthenium chloride in benzene. On reflux, a benzene solution of [RuCl(PPh$_3$)$_2$(C$_5$H$_5$)] and [Cu(C$_2$C$_6$F$_5$)] gives a tetranuclear complex [{RuCu(C$_2$C$_6$F$_5$)$_2$(PPh$_3$)(C$_5$H$_5$)}$_2$] **(369)**. Room temperature reaction of a benzene solution of [Fe$_2$(CO)$_9$] and **366** gives the trinuclear cluster [Fe$_2$Ru(C$_2$Ph)(CO)$_6$(PPh$_3$)(C$_5$H$_5$)] (**370**). Thermal reaction of a mixture of *cis*-[ReCl(CO)$_3$(PPh$_3$)$_2$] and Cu(C$_2$Ph) in THF affords [ReCuCl(C$_2$Ph)(CO)$_3$(PPh$_3$)$_2$] (**371**), while, thermolysis of [ReCl(CO)$_3$(PPh$_3$)$_2$] and Cu(C$_2$C$_6$F$_5$) in benzene gives [ReCu(C$_2$C$_6$F$_5$)$_2$(CO)$_3$(PPh$_3$)$_2$] (**372**) (Figure 24).[126]

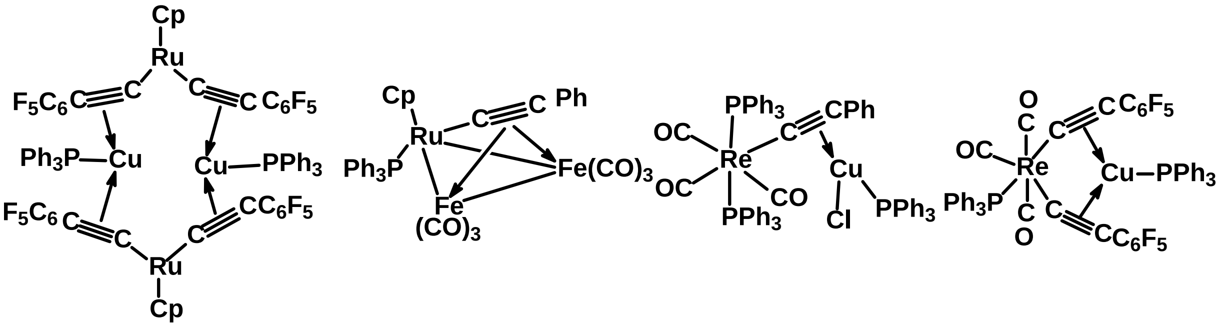


366

367a; R = Ph
367b; R= *p*-MeC$_6$H$_4$
367c; R = Me

368a; R= *p*-MeC$_6$H$_4$
368b; R= *p*-FC$_6$H$_4$

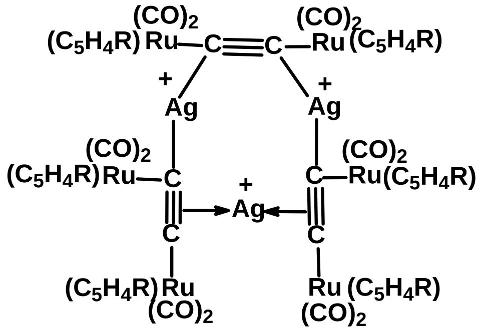
Figure 23.



369 **370** **371** **372**

Figure 24.

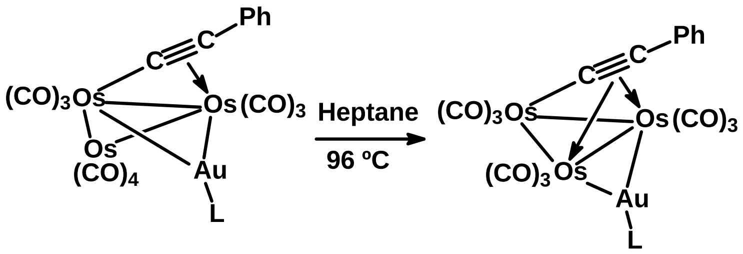
The compounds [Ag$_3$({Ru(CO)$_2$(η-C$_5$H$_4$R)}$_2$(μ-C≡C))$_3$](BF$_4$)$_3$ (R = H, **374a**; R = Me, **374b**), have been prepared from [{Ru(CO)$_2$(η-C$_5$H$_4$R)}$_2$(μ$_2$-C≡C)] (R = H, **373a**; Me, **373b**) and AgBF$_4$ (Figure 25), and used in the reaction with [CpRuCl(CO)$_2$] to give [{Ru(CO)$_2$(η-C$_5$H$_4$R)}$_3$(η^1,η^1-C≡C)][BF$_4$] (R = H, Me).[127]



374a; R = H
374b; R = Me

Figure 25.

Addition reaction of dichloromethane solution of $[Au(C{\equiv}CPh)L]$ (L = PPh_3 or PMe_2Ph) and $[Os_3(CO)_{10}(MeCN)_2]$ gives $[Os_3(C{\equiv}CPh)(AuL)(CO)_{10}]$ (**375a,b**) which contains a butterfly Os_3Au metal core and a μ-η^2-phenylethynyl ligand bridging two osmium atoms. Decarbonylation of **375a,b** in refluxing heptane gives $[Os_3(\mu_3,\eta^2\text{-}C{\equiv}CPh)(\mu\text{-}AuL)(CO)_9]$ (**376a,b**) (Scheme 99).[128]



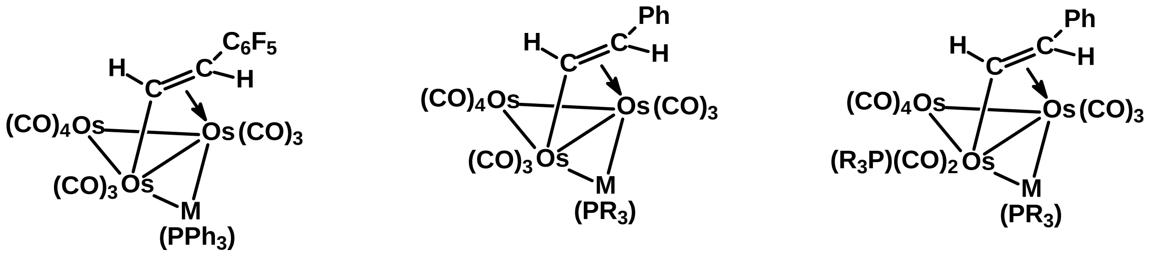
375a; L = PPh$_3$
375b; L = PMe$_2$Ph

376a; L = PPh$_3$
376b; L = PMe$_2$Ph

Scheme 99.

Numerous examples exist of reactions between $[M(C_2R)(PR'_3)]$ (M = Au, Ag, Cu; R = Ph, C_6F_5; R' = Me, Ph) and $[Os_3(\mu\text{-}H)_2(CO)_{10}]$, which might be expected to proceed by oxidative addition of $[RC_2M(PR'_3)]$ and addition of the cluster-bound hydrogen to the acetylide moiety. In toluene at –11 ºC, a rapid reaction occurs between $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ and $[M(C_2C_6F_5)(PPh_3)]$ (M=Au, Ag, Cu) to give $[Os_3M(\mu\text{-}CH{=}CHC_6F_5)(CO)_{10}(PPh_3)]$ (**377a-c**) in quantitative yield,[129] while the reaction between

$[H_2Os_3(CO)_{10}]$ and $[M(C_2Ph)(PR_3)]$ (M = Cu, Ag, Au;R= Me or Ph) affords $[HOs_3M(CO)_{10}(PR_3)]$ (M = Au, R = Me, Ph; M = Ag, Cu, R = Ph), $[Os_3M(\mu\text{-}CH{=}CHPh)(CO)_{10}(PR_3)]$ (M = Au and R = Me, **378a**; M = Au and R = Ph, **378b**; M = Ag and R = Ph, **378c**; M = Cu and R = Ph, **378d**), $[Os_3M(\mu\text{-}CH{=}CHPh)(CO)_9(PR_3)]$ (M = Au and R = Me, **379a**; M = Au and R = Ph, **379b**; M = Ag, R = Ph, **379c**), $[HOs_3M(\mu_3\text{-}HCCPh)(CO)_8]$ (M = Au, **380a**; M = Ag, **380b**; M = Cu, **380c**) and $[Os_3M(\eta\text{-}CH{=}CHPh)(CO)_9(PR_3)_2]$ (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-η^1,η^2-vinyl ligand which is bonded to two osmium atoms of the Os_3Au core.



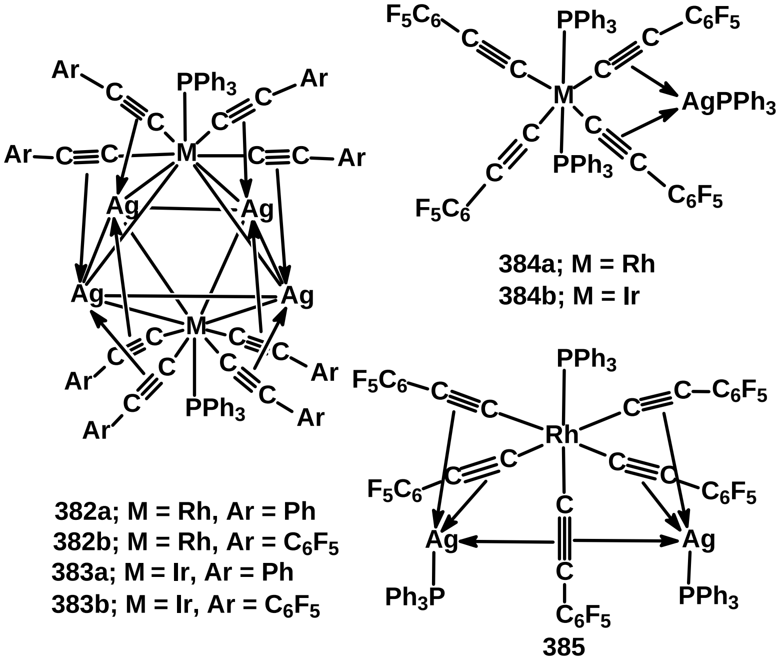
377a; M = Au
377b; M = Ag
377c; M = Cu

	M	R
378a	Au	Me
378b	Au	Ph
378c	Ag	Ph
378d	Cu	Ph

	M	R
381a	Au	Me
381b	Au	Ph
381c	Ag	Ph
381d	Cu	Ph

Figure 26.

Thermal reaction of a THF solution of $[AgC_2Ph]$ and $[RhCl(PPh_3)_3]$ results in the formation of a hexanuclear cluster compound $[Rh_2Ag_4(C_2Ph)_8(PPh_3)_2]$ (**382a**).[130] The analogous Ir_2Ag_4 compound, $[Ir_2Ag_4(C_2Ph)_8(PPh_3)_2]$ (**383a**) has been obtained from AgC_2Ph and [*trans*-$IrCl(CO)(PPh_3)_2$] on toluene reflux. Thermolysis of a solution of $[RhCl(PPh_3)_3]$ and $[AgC_2C_6F_5]$ in 1,2-dimethoxyethane yields three compounds: $[Rh_2Ag_4(C_2C_6F_5)_8(PPh_3)_2]$ (**382b**), $[Ag(PPh_3)]^+[Rh(C_2C_6F_5)_4(PPh_3)_2]^-$ (**384a**) and $\{[Ag(PPh_3)]_2{}^+[Rh(C_2C_6F_5)_5(PPh_3)]^{2-}\}$ (**385**). The analogous iridium compound $[Ir_2Ag_4(C_2C_6F_5)_8(PPh_3)_2]$ (**383b**) and $[Ag(PPh_3)]^+[Ir(C_2C_6F_5)_4(PPh_3)_2]^-$ (**384b**) are obtained when a toluene solution of [*trans*-IrCl(CO)(PPh$_3$)$_2$] and AgC$_2$C$_6$F$_5$ are heated to reflux (Figure 27).



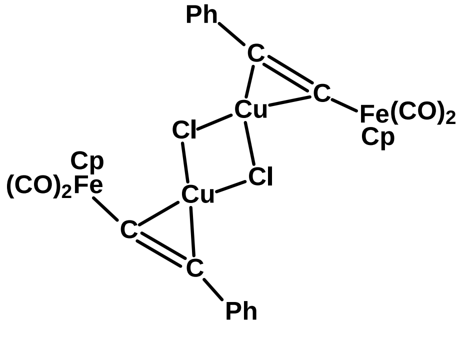
382a; M = Rh, Ar = Ph
382b; M = Rh, Ar = C$_6$F$_5$
383a; M = Ir, Ar = Ph
383b; M = Ir, Ar = C$_6$F$_5$

384a; M = Rh
384b; M = Ir

385

Figure 27.

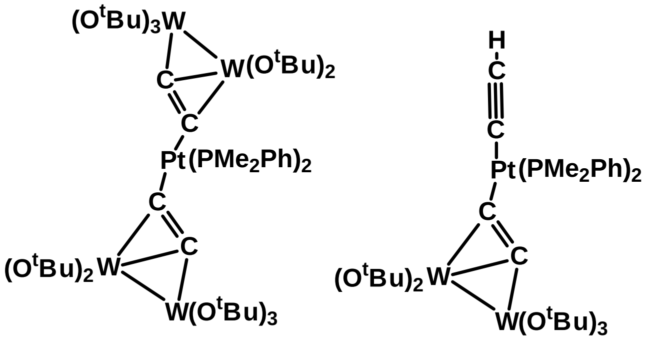
Thermolytic reaction between [(η-C$_5$H$_5$)Fe(CO)$_2$Cl] and [CuC$_2$Ph] affords a mixed metal complex [(η-C$_5$H$_5$)Fe(CO)$_2$(C$_2$Ph)CuCl]$_2$ (**386**) (Figure 28).[131] Complex **386** contains a planar Cu$_2$Cl$_2$ ring, and each copper atom is symmetrically bonded to a C$_2$ unit of the phenylethynyl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



386

Figure 28.

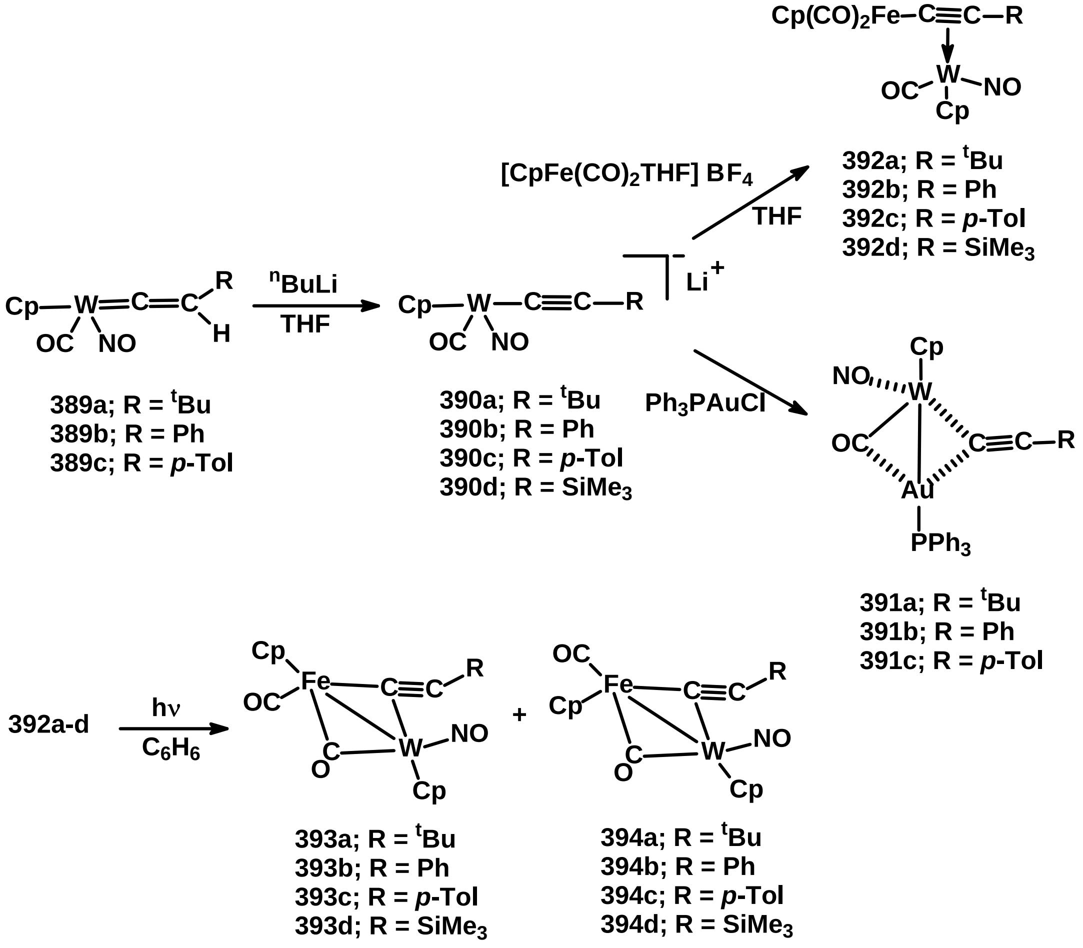
In toluene solution [*trans*-Pt(C≡CH)$_2$(PMe$_2$Ph)$_2$] and [W$_2$(O^{t}Bu)$_6$] reacts at 30 ºC to give [*trans*-Pt(C≡CH)[C$_2$W$_2$(O^{t}Bu)$_5$](PMe$_2$Ph)$_2$] (**387**) and [*trans*-Pt{C$_2$W$_2$(O^{t}Bu)$_5$}$_2$(PMe$_2$Ph)$_2$] (**388**) (Figure 29).[132,133a]



388 **387**

Figure 29.

Reaction of a THF solution of [Cp(CO)(NO)W(C≡CR)]$^-$ (R = C$_6$H$_5$, **390a**; R = C$_6$H$_4$CH$_3$, **390b**; R = C(CH$_3$)$_3$, **390c**) with [(C$_6$H$_5$)$_3$PAuCl] results in the formation of a tungsten-gold acetylide complex, [CpW(NO)(μ-CO)(μ-C≡CR)Au(P(C$_6$H$_5$)$_3$)] (**391**) (Scheme 100).[133b] Reaction of a THF solution of [Cp(CO)(NO)W(C≡CR)]$^-$ (R = C$_6$H$_5$, **390a**; R = C$_6$H$_4$CH$_3$, **390b**; R = C(CH$_3$)$_3$, **390c**; R = SiMe$_3$, **390d**) with [Cp(CO)$_2$Fe(THF)]BF$_4$ as electrophile gives a bimetallic complex [{Cp(CO)(NO)W} η^2-{Cp(CO)$_2$FeC≡CR}] (**392a-d**). Photolytic decarbonylation of complexes **392a-d** gives diastereomeric mixtures of heterometallic acetylides [{Cp(CO)(NO)W}η^2-{Cp(CO)FeC≡CR}] (**393a-d/394a-d**) (Scheme 100).[133c]



Scheme 100.

Reaction of *fac*-[Mn(CCR)(CO)$_3$(dppe)] (R = CH$_2$OMe, **395a**; R = ^{t}Bu, **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(C$_6$F$_5$)(tht)] (tht = tetrahydrothiophene) gives [MnAu(C$_6$F$_5$)(μ-CCR(CO)$_3$(dppe)] (R = CH$_2$OMe, **397a**; R = Bu^t, **397b**). Cationic mixed metal complexes [Mn$_2$Cu(μ-CCR)$_2$(CO)$_6$(dppe)$_2$]PF$_6$ (R = CH$_2$OMe, **398a**; R = Bu^t, **398b**) have been isolated from a dichloromethane solution of compound **396a** or **396b** on addition of TlPF$_6$ in presence of **395a** or **395b** respectively. The silver and gold complexes, [Mn$_2$M(μ-CC^{t}Bu)$_2$(CO)$_6$(dppe)$_2$]PF$_6$ (M = Ag, **399**; Au, **400**) are formed when [AgBF$_4$] or [AuCl(tht)] are reacted with TlPF$_6$ and two fold excess of **395b**. Addition of TlPF$_6$ to complex **396b** in presence of [P(C_6H_4Me-2)$_3$] gives a cationic mixed metal complex [MnCu(μ-CC^{t}Bu)(CO)$_3$(dppe){P(C_6H_4Me-2)$_3$}]PF_6 (**401**) (Figure 30).[133d]

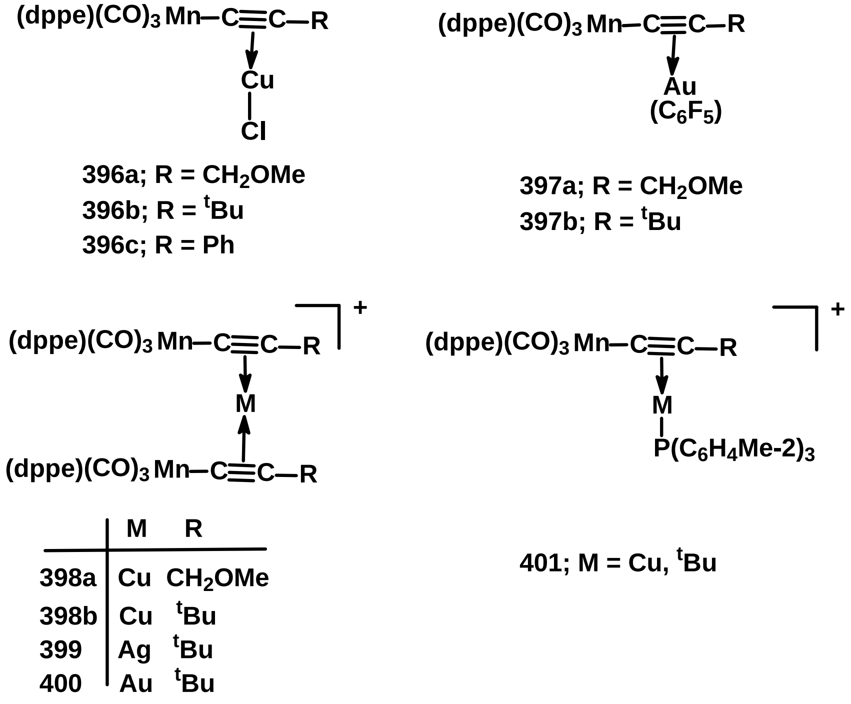
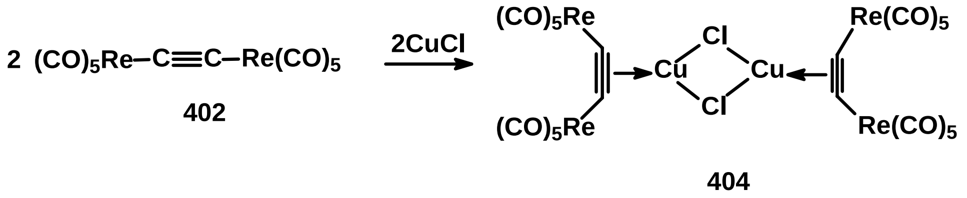


Figure 30.

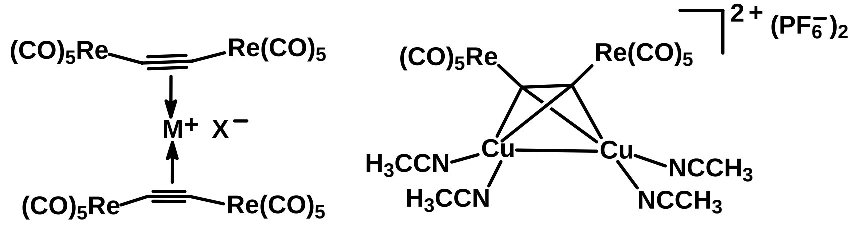
Like organic alkynes or some monometalated acetylides (L_nMC≡CR), the dirhenioethyne [(OC)$_5$ReC≡CRe(CO)$_5$] (**402**) has been found to behave as an η^2-ligand towards Cu^I, Ag^I, and Au^I. Thus, when a THF solution of **402** reacts with CuCl, complex [{(η^2-C≡C{Re(CO)$_5$}$_2$)Cu(μ-Cl)}$_2$] (**404**) is isolated (Scheme 101).[134]



Scheme 101.

Reaction of **402** with [Cu(NCMe)$_4$]PF_6, [Ag(NCMe)$_4$]BF_4, [AgSbF_6] or [AgO_2SOCF_3] gives cationic bis- (alkyne) complexes [(η^2-C≡C{Re(CO)$_5$}$_2$)$_2$M]$^+$X$^-$ (M

= Cu, Ag; X = PF_6, BF_4, SbF_6 or CF_3SO_2) (**405a-d**) and a cationic dimetallic tetrahedron $[(\mu\text{-}\eta^2,\eta^2\text{-}C\equiv C\{Re(CO)_5\}_2)Cu_2(NCMe)_4]^{2+}$ (**406**) (Figure 31).[134]

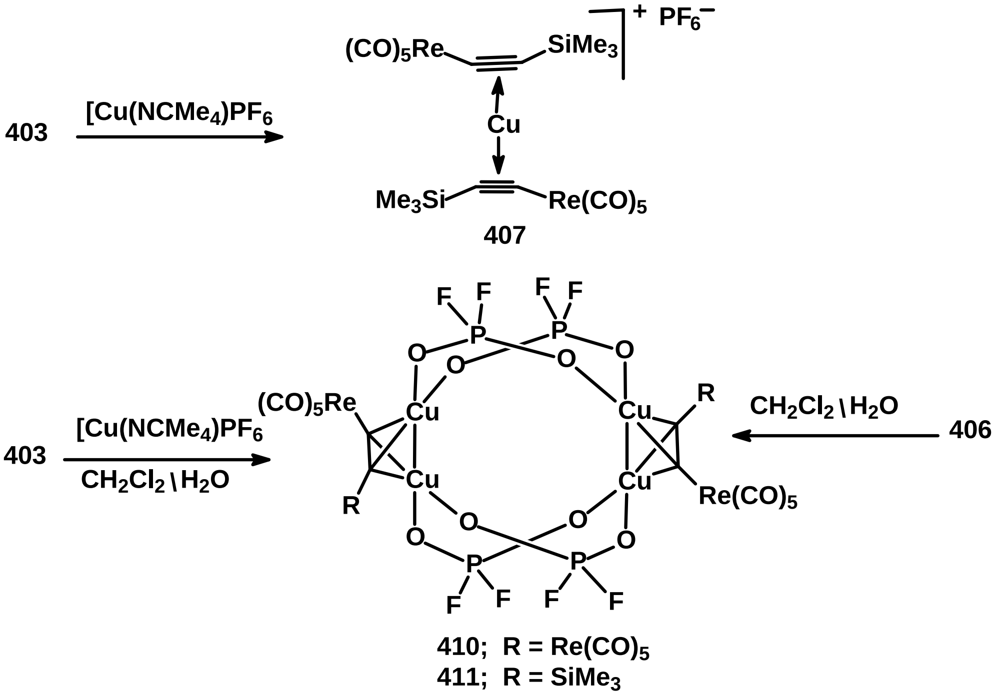


405a; M = Cu, X = PF_6
405b; M = Ag, X = BF_4
405c; M = Ag, X = SbF_6
405d; M = Ag, X = CF_3SO_3

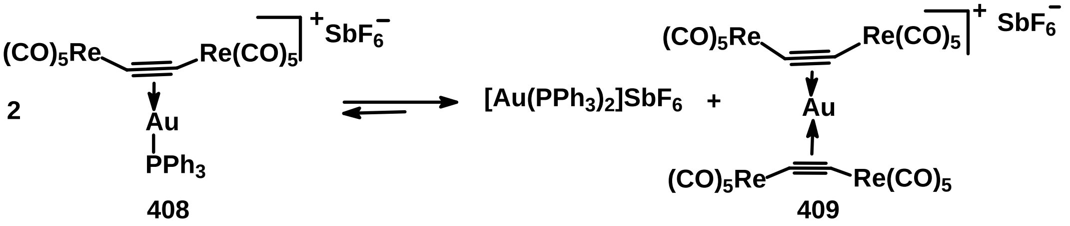
406

Figure 31.

On the other hand, a dichloromethane solution of $[(OC)_5ReC\equiv CSiMe_3]$ (**403**) on reaction with $[Cu(NCMe)_4]PF_6$ yields the cationic complex $[(\eta^2\text{-}C\equiv CRe(CO)_5SiMe_3)_2Cu]^+$ (**407**). Hydrolysis of $[(\mu\text{-}\eta^2\text{:}\eta^2\text{-}C\equiv C\{Re(CO)_5\}_2)Cu_2(NCMe)_4](PF_6)_2$ (**406**) or treatment of **403** with $[Cu(MeCN)_4]PF_6$ in moist CH_2Cl_2 affords the difluorphosphate-bridged complexes $[\{\mu\text{-}\eta^2\text{:}\eta^2\text{-}[(OC)_5ReC\equiv CR]\}_2Cu_4(\mu_2\text{-}O_2PF_2)_4]$ (R = $Re(CO)_5$, **410**; R = $SiMe_3$, **411**) (Scheme 102). The gold complex $[(\eta^2\text{-}C\equiv C\{Re(CO)_5\}_2)AuPPh_3]SbF_6$ (**408**) obtained from the reaction of $[Au(PPh_3)SbF_6]$ with **402**, exists in equilibrium in solution with $[Au(PPh_3)_2SbF_6]$ and $[(\eta^2\text{-}C\equiv C\{Re(CO)_5\}_2)_2Au]SbF_6$ (**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

Fc = Ferrocene

PPN = Bis(triphenylphosphine)nitrogen(l+), $[(Ph_3P)_2N^+]$

tht = Tetrahydrothiophene

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