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MULTIDENTATE LIGANDS BOUND VIA ALKYNE AND GROUP 15 OR 16 DONOR SITES

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CONTENTS

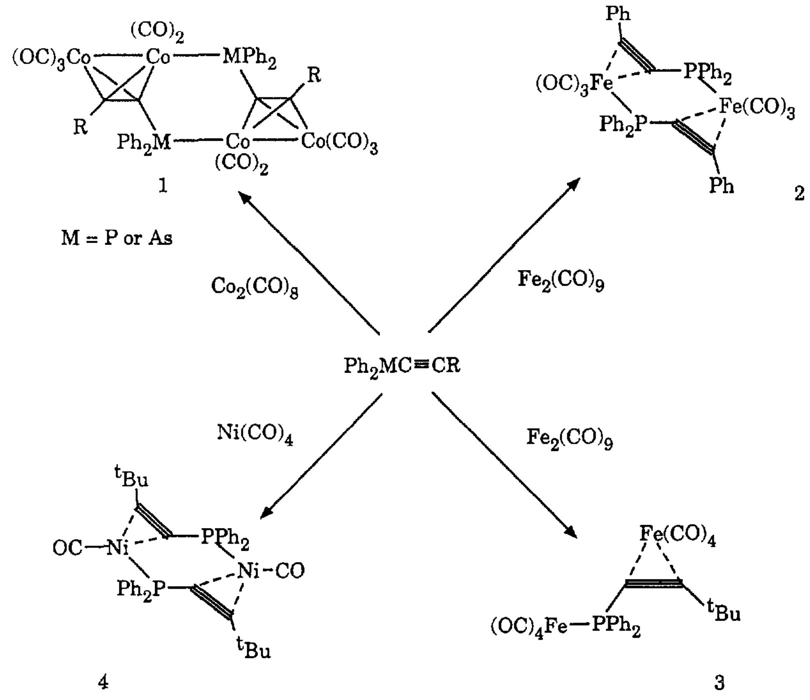
1. INTRODUCTION

This report concerns complexes containing ligands which are simultaneously bound through an alkyne and a group 15 or group 16 donor site. These multidentate, bifunctional ligands have played a variety of roles in organometallic chemistry. The majority of the reported investigations have concerned phosphinoalkyne ligands with the phosphine functionalities alpha to the carbon–carbon triple bond; however ligands with a more remote positioning of the heteroatom have also been studied. Thioether and ether alkynes, where the heteroatom is commonly beta to the alkyne, can also function as multidentate ligands.

2. DISCUSSION

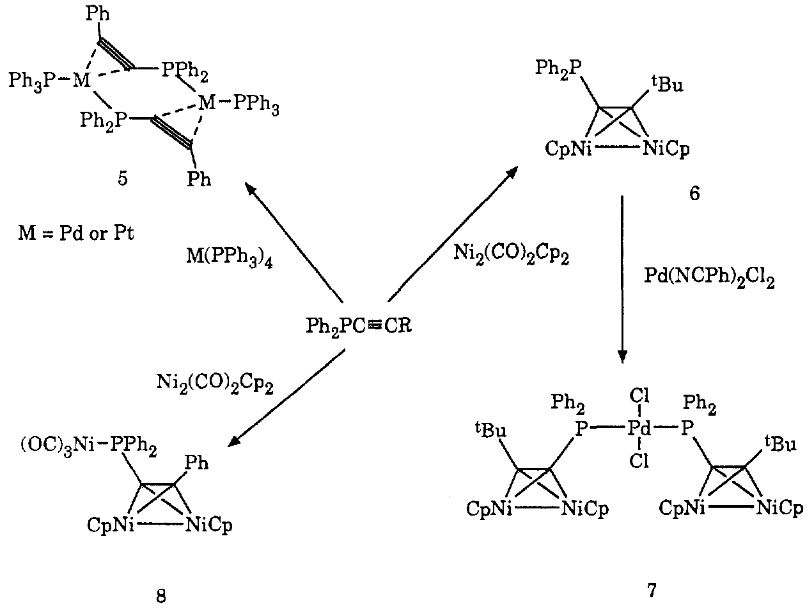
2.1. *Ligands bound via alkyne and phosphine or arsine donor sites*

Many of the first reactions of binary metal carbonyls to be reported concerned phosphines, arsines and alkynes and hence the early investigations explored the reactivity of bifunctional phosphinoalkynes and arsinoalkynes towards simple metal carbonyls. The first studies of phosphino or arsinoalkynes simultaneously coordinating transition metals with both the alkyne and the phosphine or arsine functionalities were reported by Carty *et al.* in 1971.[1] Reaction of $[Co_2(CO)_8]$ with $Ph_2MC{\equiv}CR$ ($M = P$, $R = H$, Me, ^iPr, CF_3; $M = As$, $R = CF_3$) affords compounds of the type $[Co_4(\mu_3\text{-}\eta^3\text{-}Ph_2MC{\equiv}CR)_2(CO)_{10}]$ (**1**) (Scheme 1) in which two dicobalt units are linked by the bidentate ligands. Previously, examples were known where only the alkyne, $[\{Co_2(CO)_6(\mu\text{-}HC{\equiv}C)\}_3As]$,[2] or only the phosphine centres, $[\{Co_2(CO)_7\}_2(\mu\text{-}Ph_2PC{\equiv}CPPh_2)]$,[3] were coordinated. Reaction of $[Fe_2(CO)_9]$ with $Ph_2PC{\equiv}CPh$ affords $[Fe_2(\mu_2\text{-}\eta^3\text{-}Ph_2PC{\equiv}CPh)_2(CO)_6]$ (**2**), which was the first example of a non-bridging two-electron donor alkyne bonded to iron, as well as $[Fe(CO)_3(\eta^1\text{-}Ph_2PC{\equiv}CPh)_2]$ and $[Fe_2(\mu\text{-}C{\equiv}CPh)(\mu\text{-}PPh_2)(CO)_6]$.[4] The latter compound illustrates a typical reaction of coordinated phoshinoalkynes, namely oxidative insertion into a P—C bond to afford a phosphido and an alkynyl ligand.[5] Reaction of $[Fe_2(CO)_9]$ with $Ph_2PC{\equiv}C^tBu$ affords $[Fe_2(\mu_2\text{-}\eta^3\text{-}$



Scheme 1.

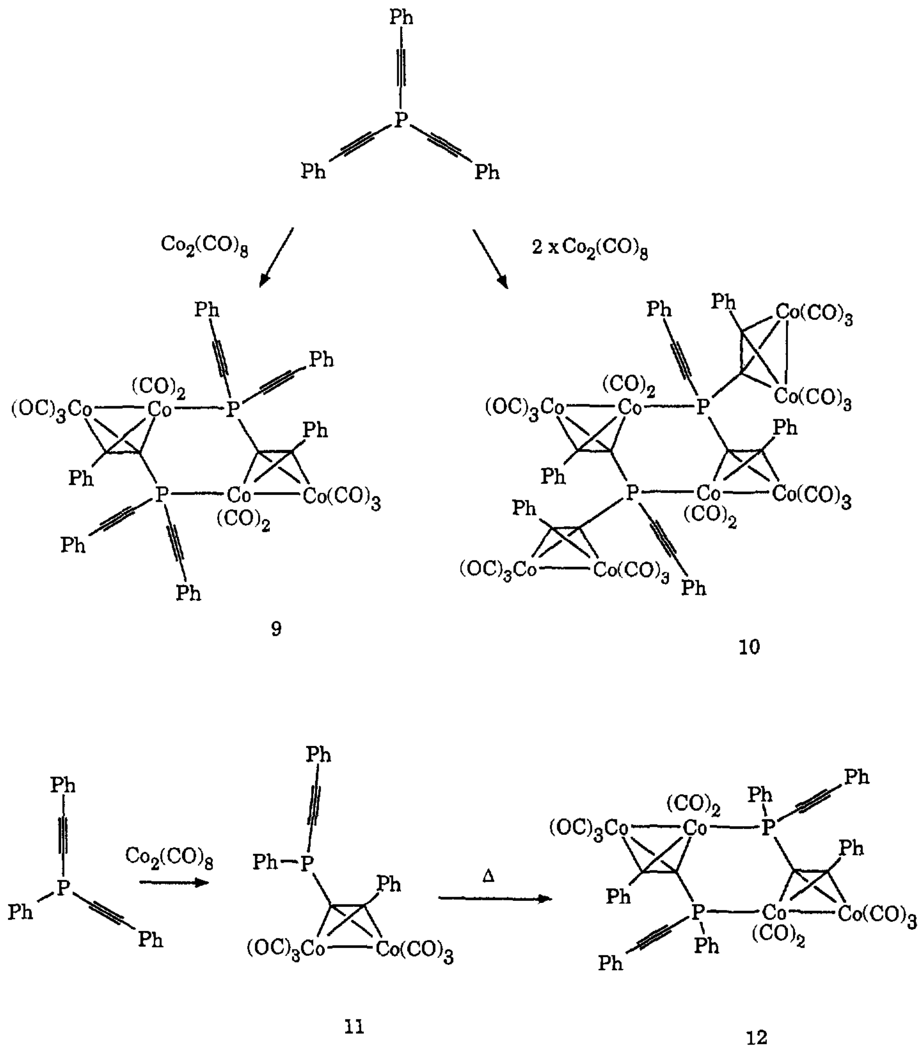
Ph$_2$PC≡C^{t}Bu)(CO)$_8$] (**3**) containing Fe(CO)$_4$(alkyne) and Fe(CO)$_4$(phosphine) moieties. The X-ray crystal of **3** provided the first structural parameters for a Fe(CO)$_4$(alkyne) fragment.[6] Reaction of [Ni(CO)$_4$] with Ph$_2$PC≡CPh gives [Ni$_2$(μ_2-η^3-Ph$_2$PC≡C^{t}Bu)$_2$(CO)$_2$] (**4**)[7] related to **2**. Similar MPPh$_3$ (M = 2Pd or Pt) derivatives [M$_2$(μ_2-η^3-Ph$_2$PC≡CPh)$_2$(PPh$_3$)$_2$] (**5**) are prepared by the reaction of [M(PPh$_3$)$_4$] with Ph$_2$PC≡CCF$_3$ (Scheme 2).[8] Reaction of Ph$_2$PC≡C^{t}Bu with [Ni$_2$(μ-CO)$_2$Cp$_2$] affords [Ni$_2$(μ_2-η^2-Ph$_2$PC≡C^{t}Bu)(Cp)$_2$] (**6**) which contains an uncoordinated phosphine functionality. A suitable metal-ligand fragment can be attached to the pendant functionality in such compounds and in this case **6** reacts with [Pd(NCPh)$_2$Cl$_2$] to afford [Ni$_4$(Cp)$_4$(μ_3-η^3-



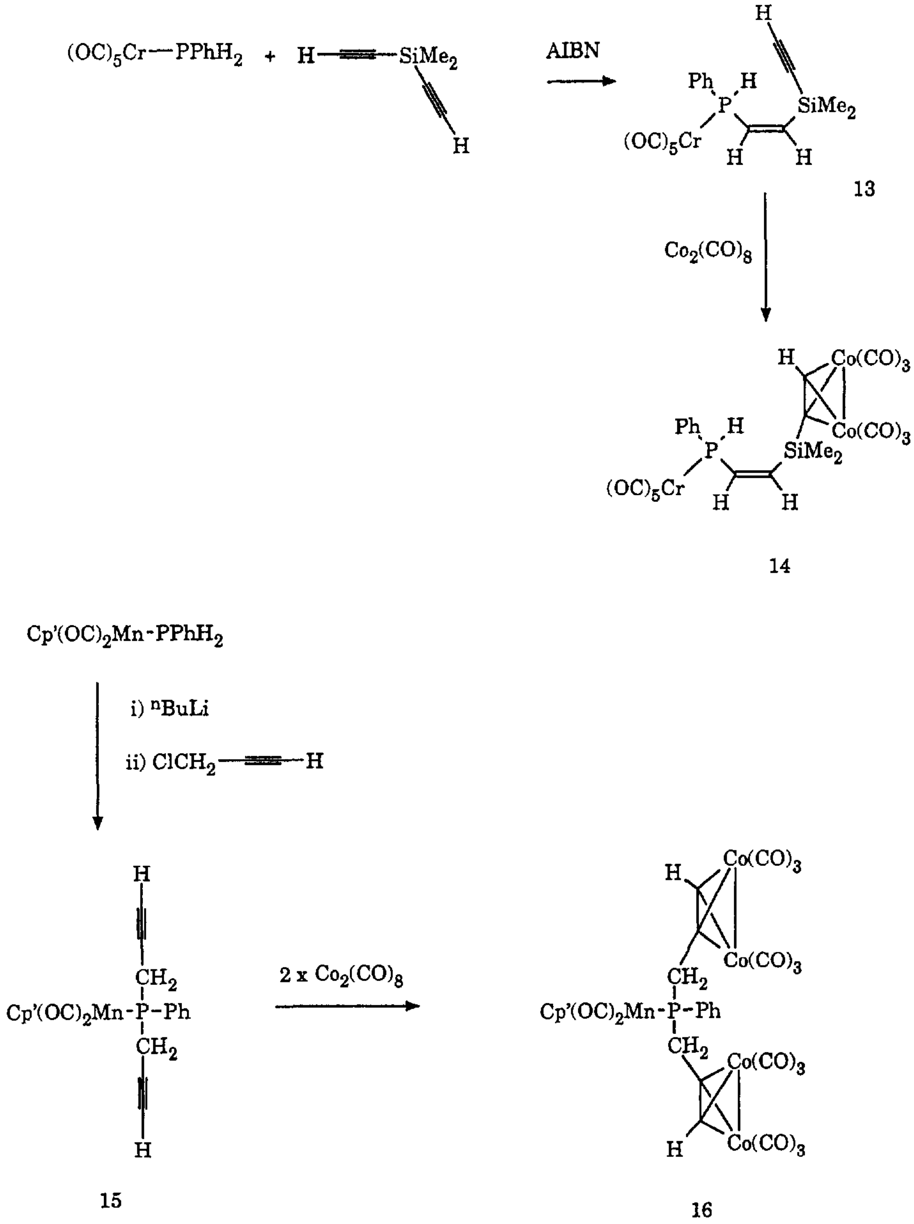
Scheme 2.

Ph$_2$PC≡C^{t}Bu)$_2$PdCl$_2$] (**7**) in which a PdCl$_2$ unit links two molecules of **6**.[9] Reaction of Ph$_2$PC≡CPh with [Ni$_2$(μ-CO)$_2$Cp$_2$] affords [Ni$_2$Cp$_2$(μ_3-η^3-Ph$_2$PC≡CPh)Ni(CO)$_3$] (**8**).[9]

Reaction of the trisalkyne phosphine P(C≡CPh)$_3$, containing four potential donor sites, with one equivalent of Co$_2$(CO)$_8$ affords [Co$_4${μ_3-η^3-P(C≡CPh)$_3$}$_2$(CO)$_{10}$] (**9**) analogous to compounds **1**, while addition of two equivalents of [Co$_2$(CO)$_8$] affords [Co$_8${μ_5-η^5-P(C≡CPh)$_3$}$_2$(CO)$_{22}$] (**10**), related to **9** but with two more alkyne donors attached to Co$_2$(CO)$_6$ units (Scheme 3).[10] The bisalkyne phosphine PPh(C≡CPh)$_2$ reacts with [Co$_2$(CO)$_8$] to afford [Co$_2${μ_2-η^2-PPh(C≡CPh)$_2$}(CO)$_6$] (**11**) with one of the acetylenic bonds coordinated, which when heated affords [Co$_4${μ_3-η^3-PPh(C≡CPh)$_2$}$_2$(CO)$_{10}$] (**12**) via carbonyl substitution by the phosphine functionality.[10] If a phosphinoalkyne is coordinated via only the phosphine functionality the pendant triple bond will normally coordinate further metal-ligand fragments such as Co$_2$(CO)$_6$. Scheme 4 depicts phosphinoalkyne complexes which are prepared with the phosphine functionality precoordinated and their subsequent reactions with [Co$_2$(CO)$_8$]. Reaction of [Cr(CO)$_5$(PPhH$_2$)] with SiMe$_2$(C≡CH)$_2$ in toluene with azo-bisisobutyronitrile (AIBN) affords [Cr(CO)$_5$(PhHPCH=CHSiMe$_2$C≡CH)] (**13**) by insertion of an alkyne into a P—H bond.[11] Treatment of **13** with [Co$_2$(CO)$_8$] affords [Cr(CO)$_5$(μ-PhHPCH=CHSiMe$_2$C≡CH)Co$_2$(CO)$_6$] (**14**) by addition of Co$_2$(CO)$_6$ to the remote alkyne. Propargylphosphines have been prepared by deprotonation of [Cp′(OC)$_2$Mn(PPhH$_2$)] (Cp′ = η^5-C$_5$H$_4$Me) with ^{n}BuLi followed by addition of ClCH$_2$C≡CH to afford [Cp′(OC)$_2$Mn{PPh(CH$_2$C≡CH)$_2$}] (**15**).[12] Both pendant triple bonds coordinate Co$_2$(CO)$_6$ fragments to afford [Cp′(OC)$_2$Mn{PPh(μ-(CH$_2$C≡CH)Co$_2$(CO)$_6$)$_2$}] (**16**). Stepwise coordination by



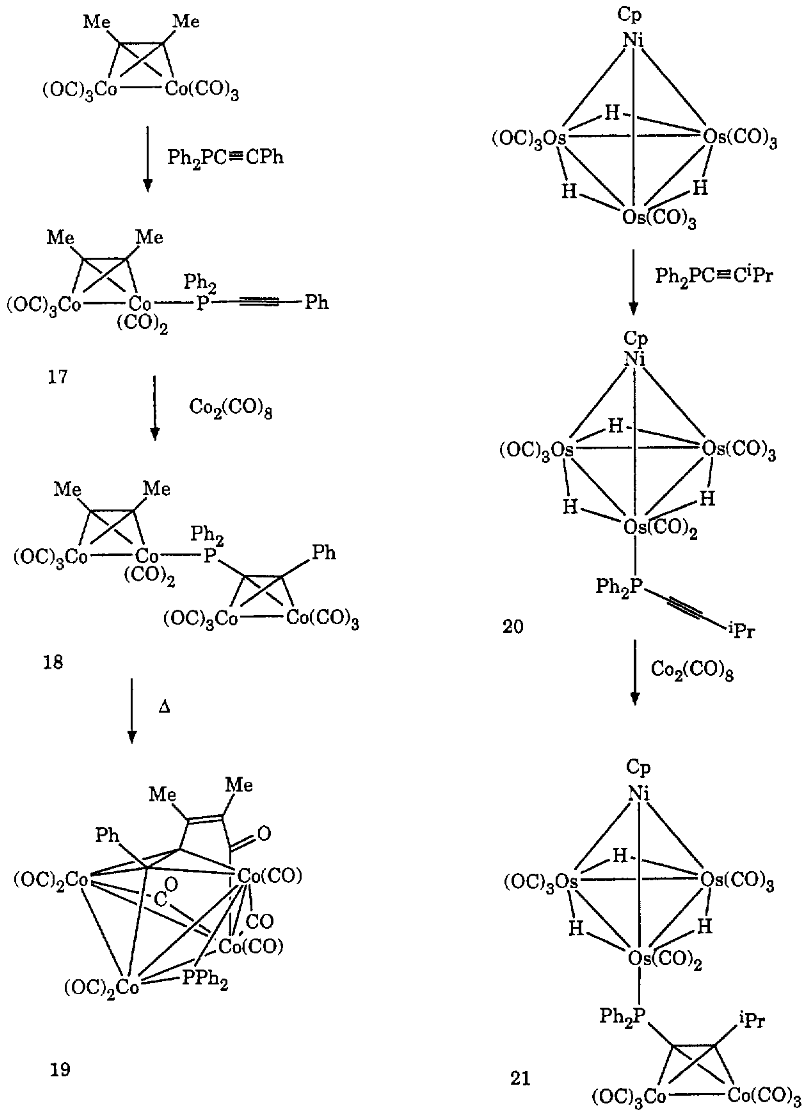
Scheme 3.



Scheme 4.

phosphinoalkynes has been used to build up clusters. For example, reaction of $[Co_2(\mu\text{-}MeC{\equiv}CMe)(CO)_6]$ and $Ph_2PC{\equiv}CPh$ affords $[Co_2(\mu\text{-}MeC{\equiv}CMe)(\eta^1\text{-}Ph_2PC{\equiv}CPh)(CO)_5]$ (**17**), which reacts with $[Co_2(CO)_8]$ to afford $[Co_2(\mu\text{-}MeC{\equiv}CMe)(CO)_5(\mu_3\text{-}\eta^3\text{-}Ph_2PC{\equiv}CPh)Co_2(CO)_6]$ (**18**), which upon thermolysis rearranges to give the butterfly tetracobalt cluster **19** illustrated in Scheme 5.[13]

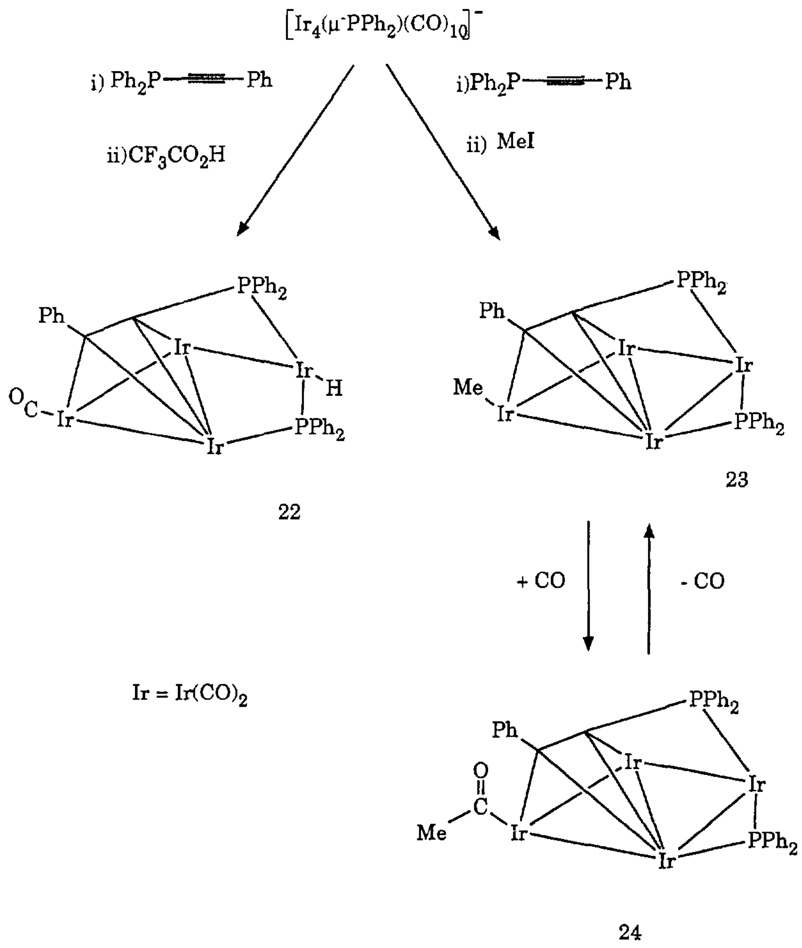
Phosphinoalkynes have also been added to preformed clusters. A cluster compound containing six metals has been prepared by sequential treatment of $[NiOs_3(\mu\text{-}H)_3(CO)_9Cp]$ with $Ph_2PC{\equiv}C^iPr$ to give $[NiOs_3(\mu\text{-}H)_3(Ph_2PC{\equiv}C^iPr)(CO)_8Cp]$ (**20**) and then with $[Co_2(CO)_8]$ to afford **21** illustrated in Scheme 5.[14] Reaction of $[Ir_4(\mu\text{-}PPh_2)(H)(CO)_{10}]$ with $Ph_2PC{\equiv}CPh$ affords $[Ir_4(\mu\text{-}PPh_2)(H)(\eta^1\text{-}Ph_2PC{\equiv}CPh)_n(CO)_{10-n}]$ ($n = 1$ or 2). The monosubstituted species undergoes facile P—C bond cleavage to give $[Ir_4(\mu\text{-}PPh_2)_2(\mu_3\text{-}\eta^2\text{-}HC{\equiv}CPh)(\mu\text{-}CO)(CO)_7]$ but under more forcing conditions $[Ir_4(H)(\mu\text{-}PPh_2)(\mu_4\text{-}\eta^3\text{-}Ph_2PC{\equiv}CPh)(CO)_9]$ (**22**) is formed in low yield.[15] Compound **22** can be prepared in higher yield by deprotonation of $[Ir_4(\mu\text{-}PPh_2)(H)(CO)_{10}]$ followed by reaction with $Ph_2PC{\equiv}CPh$ and then protonation (Scheme 6).[16] Alternatively methylation affords $[Ir_4(Me)(\mu\text{-}$



Scheme 5.

$PPh_2)(\mu_4\text{-}\eta^3\text{-}Ph_2PC{\equiv}CPh)(CO)_8]$ (**23**) which undergoes reversible two-step CO insertion to yield $[Ir_4\{MeC(O)\}(\mu\text{-}PPh_2)(\mu_4\text{-}\eta^3\text{-}Ph_2PC{\equiv}CPh)(CO)_8]$ (**24**).[17] In contrast to when the ligand is terminally bound, cleavage of the $\mu_4\text{-}\eta^3\text{-}Ph_2PC{\equiv}CPh$ ligand in compounds **22** and **23** was not observed. In these cases the $\mu_4\text{-}\eta^3$ ligand acts as an anchor holding the cluster together.

Reaction of $[Ru_3(CO)_{12}]$ with $Ph_2PC{\equiv}CPPh_2$ affords $[Ru_5(\mu\text{-}PPh_2)(\mu\text{-}C{\equiv}CPPh_2)(CO)_{13}]$, $[Ru_4(\mu\text{-}PPh_2)_2(\mu\text{-}C{\equiv}CPPh_2)_2(CO)_{10}]$ and **25**, which is illustrated in Scheme 7.[18] Compound **25** is a tetraruthenium cluster with a flattened butterfly geometry capped on one side by a $\mu_4\text{-}\eta^3\text{-}PhC{\equiv}CPPh_2$ ligand with the phosphine group making a three-membered Ru—P—C ring and on the other side by a phosphinidene group extracted from the original $Ph_2PC{\equiv}CPPh_2$. Hydrogenation of the alkynyl ligand in the pentaruthenium cluster **26**, which is obtained by thermolysis of $[\{Ru_3(CO)_{11}\}_2(\mu\text{-}Ph_2PC{\equiv}CPPh_2)_2]$, results in formation of compound **27** containing a $\mu_4\text{-}\eta^3\text{-}HC{\equiv}CPPh_2$ ligand.[19] Reaction of **26** with allene affords the cluster **28** which has a structure based on a tetraruthenium butterfly skeleton, which on one wing-tip has a fifth ruthenium atom attached.[20] The tetraruthenium skeleton is bonded to a $\mu_4\text{-}\eta^2$-alkyne ligand formed by combination of the Ph_2PC_2 alkynyl fragment in **26** with one of the CH_2 groups of the allene dimer. Thermolysis of $[Ru_3(\mu\text{-}H)(CO)_8$

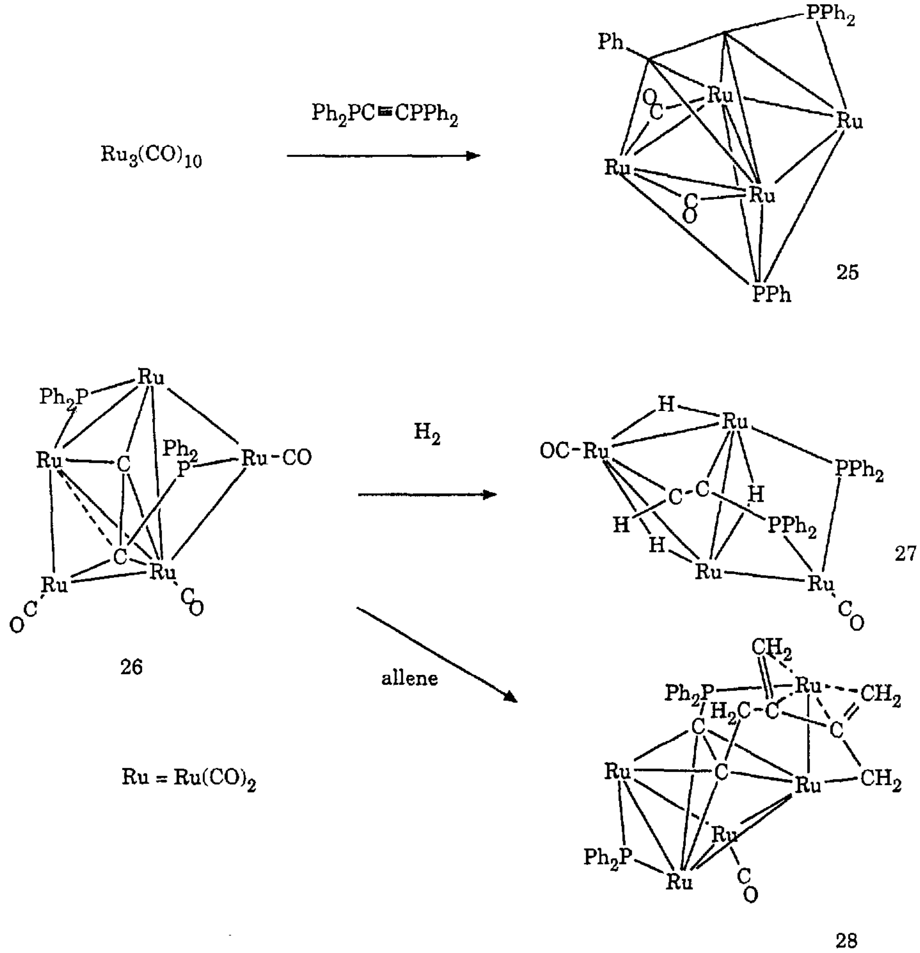


Scheme 6.

$(Ph_2PC{\equiv}CPh)(\mu_3\text{-}\eta^2\text{-}C{\equiv}C^tBu)]$ (**29**) affords $[Ru_3(CO)_8\{\mu_3\text{-}\eta^4\text{-}C(^tBu)CC(H)C(Ph)(PPh_2)\}]$ (**30**), in which the cluster-bound $C_2{}^tBu$ and the alkynyl ligand derived from the terminally bound phosphinoalkyne have coupled with a shift of a phenyl group (Scheme 8).[21] Thermolysis of **31** affords five products including **32** and **33** (illustrated in Scheme 8) containing phosphinoalkyne ligands formed by P—C bond cleavage and then addition of a cluster hydrogen atoms to the resulting alkynyl ligands.[22]

The coordinating ability of $Ph_2PC{\equiv}CPPh_2$ is usually dominated by the phosphine donor sites[23] and is often used as a bidentate phosphino donor to link two separate metal–ligand fragments or clusters[24] with the exception of $[Re_3(\mu\text{-}H)_3(\mu\text{-}Ph_2PC{\equiv}CPPh_2)(CO)_{10}]$ where the $Ph_2PC{\equiv}CPPh_2$ spans two rhenium centres.[25] Ward and Templeton[26] have shown that reaction of $[W(CO)_3(S_2CNEt_2)_2]$ with $Ph_2PC{\equiv}CPPh_2$ affords $[W(CO)_2(Ph_2PC{\equiv}CPPh_2)(S_2CNEt_2)_2]$ in which the $Ph_2PC{\equiv}CPPh_2$ acts as a monodentate phosphine donor. In solution, however, this compound loses carbon monoxide and rearranges to **34** (Scheme 9), which is a rare example of $Ph_2PC{\equiv}CPPh_2$ coordinated solely through the C≡C linkage and in this case acts as a four-electron donor. Reaction of **34** with $[Fe_2(CO)_9]$ affords **35** in which the phosphine sites coordinated iron tetracarbonyl fragments.[27] The distortion engendered skeleton of the alkyne through coordination of the triple bond enables **34** to bridge a Co—Co bond as observed in **36** or chelate to group 6 metal tetracarbonyl fragment as observed in compounds **37**.[27]

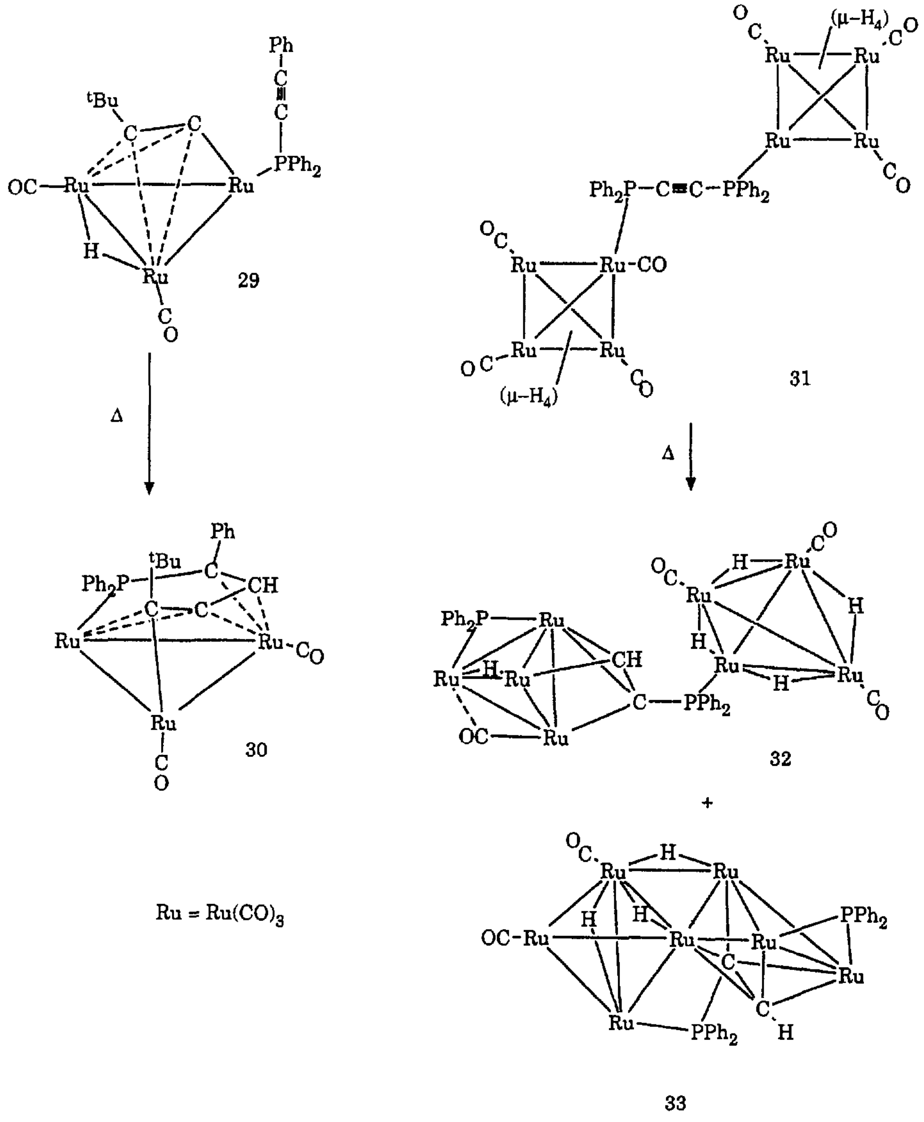
Reaction of $Ph_2PC{\equiv}C{-}C{\equiv}CPPh_2$ (bdpp) with $[M_3(CO)_{11}(NCMe)]$ (M = Ru or Os) affords the "barbell" complexes $[\{M_3(CO)_{11}\}_2(\mu\text{-bdpp})]$ (**38**) (Scheme 10).[28] Pyrolysis of these compounds affords the clusters $[\{M_3(\mu\text{-}PPh_2)(CO)_9\}_2(\mu_3:\mu_3\text{-}C_4)]$ (**39**) containing tetracarbon lig-



Scheme 7.

ands. A minor product from the pyrolysis when M = Ru is $[\{Ru_4(\mu\text{-}H)(CO)_{12}\}\{\mu_4\text{-}PPh(C_6H_4)C_2C_2PPh_2\}\{Ru_3(CO)_{11}\}]$ (**40**) containing a $Ru_3(CO)_{11}$ moiety linked via a $PPh_2C_2C_2PPh(C_6H_4)$ ligand to a Ru-spiked Ru_3 cluster. As indicated previously $Ph_2PC{\equiv}CPPh_2$ has been employed extensively in transition metal chemistry, but the acetylenic bond is seldom coordinated. Mixed metal clusters have been prepared using the less sterically hindered bdpp which more readily allows coordination to both phosphine and alkyne functionalities. Reaction of bdpp with $[Mo(CO)_5(NCMe)]$, $[W(CO)_5(thf)]$ or $[Fe_2(CO)_9]$ affords compounds **41** (Scheme 11) which react with $[Co_2(CO)_8]$ or $[Pt(C_2H_4)(PPh_3)_2]$ to afford **42** and **43**, respectively, in which one of the two triple bonds is used in coordination.[29] The same principle can be used with larger fragments coordinated to the phosphine donor sites. Compounds **44** contain tri and tetra nuclear clusters which react with $[Co_2(CO)_8]$ in a similar manner to afford compounds **45**.[30] Thermolysis of **45** (M = Ru) results in P—C bond cleavage to afford **46**. When M = Os, then thermolysis affords compound **47**. The $C{\equiv}CPPh_2\{Os_3(CO)_{11}\}$ fragment survives the reaction, while the $Co_2(CO)_6$ unit combines with the second Os_3 cluster to give a Co_2Os_3 unit. The mixed metal compound **48** (Scheme 12) also reacts with $[Co_2(CO)_8]$ and affords **49** which upon thermolysis gives **50** containing an Os_3 triangle bonded to a Co_2 unit, to which a single rhenium centre is attached.[30]

Reductive dehalogenation of $(2,4,6\text{-}{}^tBu_3C_6H_2O)(PhC{\equiv}C)PCl$ by $[Co_2(CO)_8]$ affords **51** illustrated in Scheme 13.[31] Similar treatment of $({}^tBu)(PhC{\equiv}C)PCl$ results in formation of cluster **52**. The postulated intermediates in the formation of **51** and **52**, $(OC)_3Co{=}C(R)C{\equiv}CPh$, were not isolated, but reactions of $(R)(PC{\equiv}C)PCl$ ($R = 2,6\text{-}{}^tBu\text{-}4\text{-}MeC_6H_2O$ or $2,4,6\text{-}{}^tBu_3C_6H_2O$) with $[Mo(CO)_3L]^-$ ($L = \eta^5\text{-}C_5H_5$ or $\eta^5\text{-}C_5Me_5$) form the analogous complexes **53**, illustrated in Scheme 14, which react



Scheme 8.

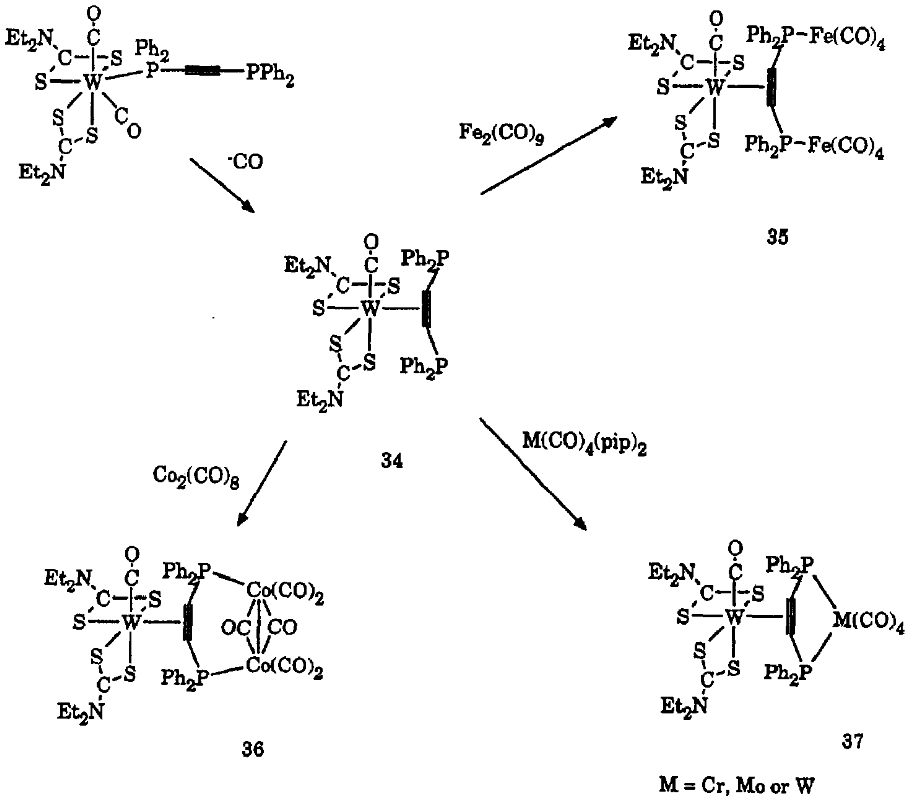
with $[Co_2(CO)_8]$ to afford complexes **54** or **55** depending on the nature of L.[32] 1,3-Dipolar addition reactions of complexes of type **53** have been explored and some representative reactions are illustrated in Scheme 15.[33]

2.2. *Ligands bound via alkyne and amine donor sites*

Most studies of transition metal complexes with aminoalkynes have involved transition metals in relatively low oxidation states and hence coordination has been dominated by the acetylenic functionality.[34]

2.3. *Ligands bound via alkyne and thioether donor sites*

Reaction of the μ-thiolate complex $[Fe_2(\mu\text{-SC}{\equiv}CC_6H_4Me\text{-}4)(\mu\text{-S}^iPr)(CO)_6]$ (**56**) with $[Co_2(CO)_8]$ attaches a $Co_2(CO)_6$ unit to the pendant alkyne to form **57** illustrated in Scheme 16.[35] Alkyne ligands containing thioether functionalities show a much stronger preference for alkyne coordination over heteroatom coordination compared with phosphinoalkyne ligands as illustrated by compounds **58**



34

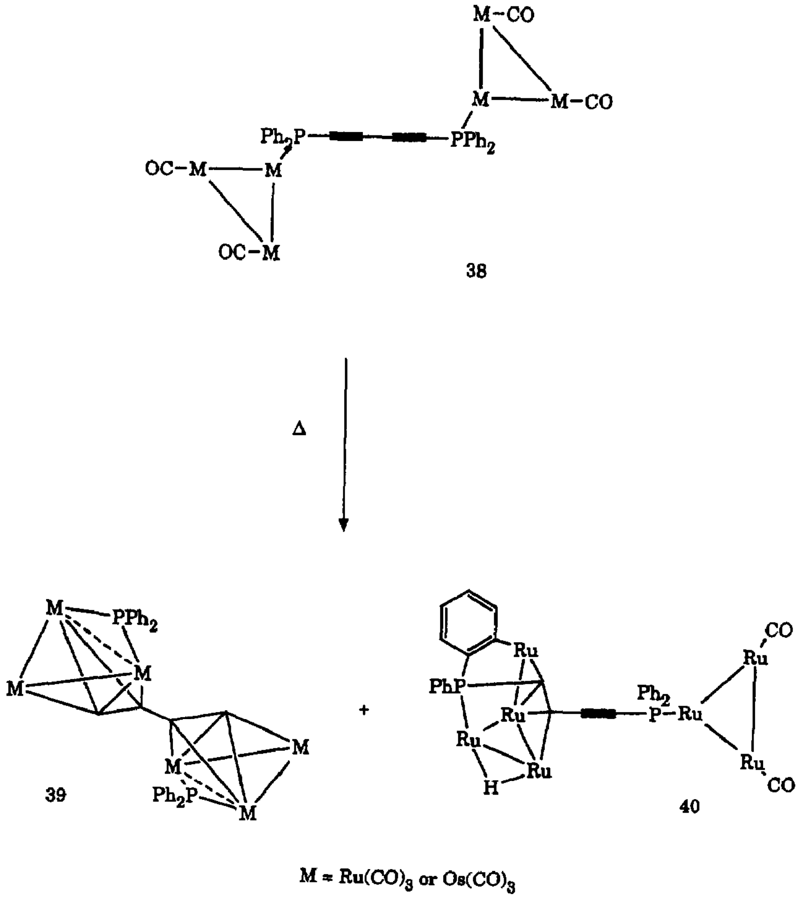
35

36

37

$M = Cr, Mo$ or W

Scheme 9.



38

39

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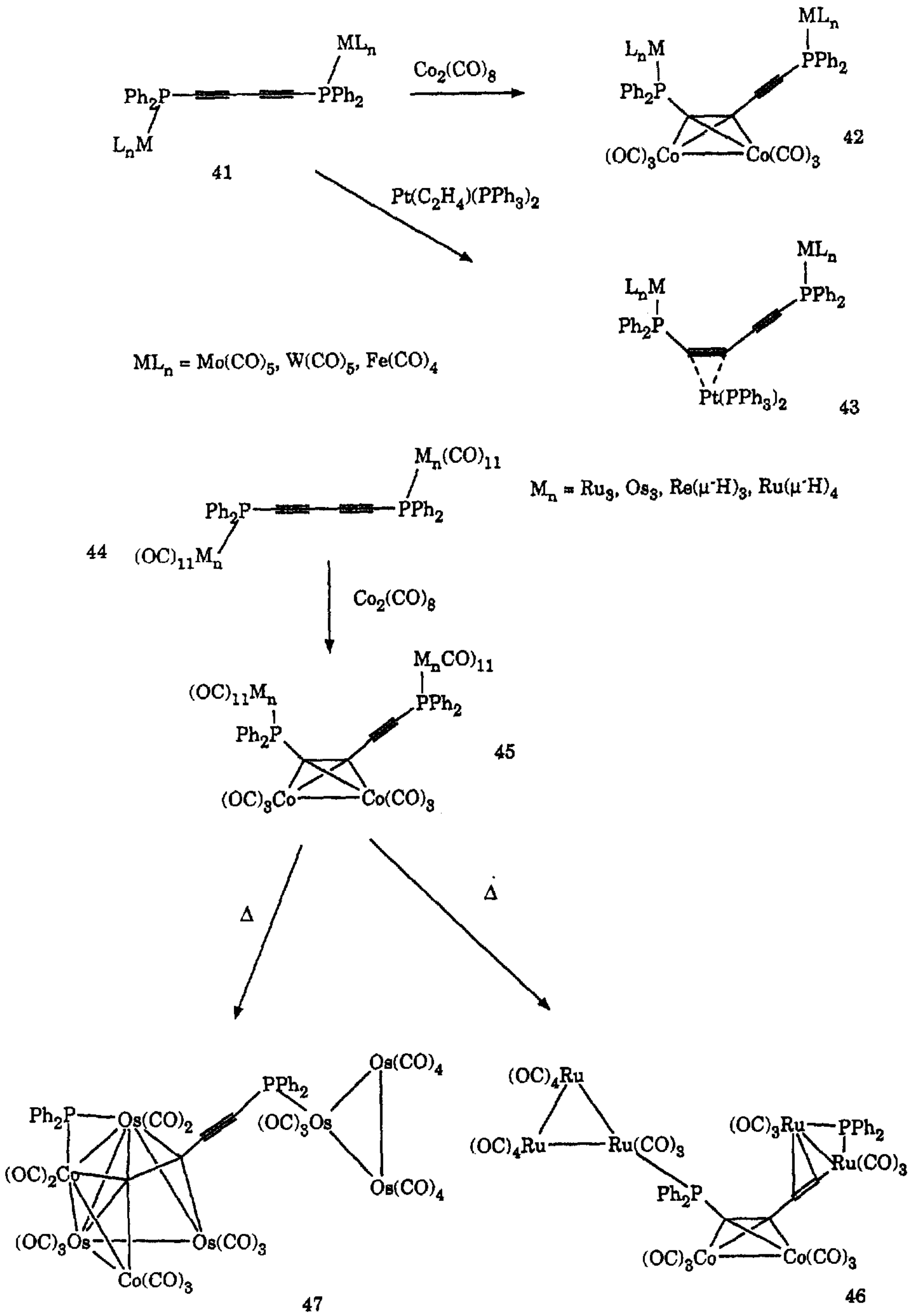
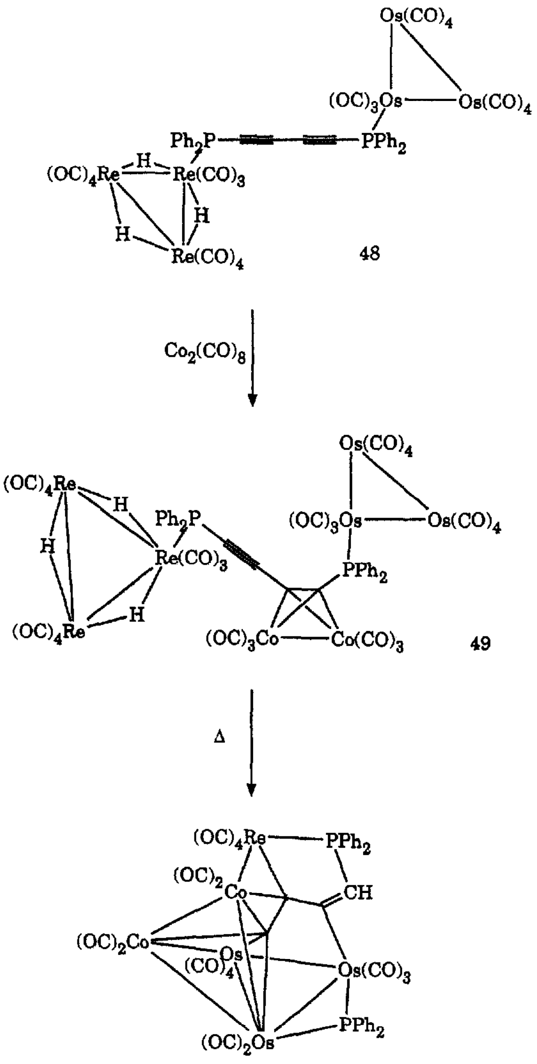
$M = Ru(CO)_3$ or $Os(CO)_3$

Scheme 10.


ML$_n$
Ph$_2$P
PPh$_2$
L$_n$M
41
Co$_2$(CO)$_8$
42
(OC)$_3$Co
Co(CO)$_3$
Pt(C$_2$H$_4$)(PPh$_3$)$_2$
ML$_n$ = Mo(CO)$_5$, W(CO)$_5$, Fe(CO)$_4$
Pt(PPh$_3$)$_2$
43
M$_n$(CO)$_{11}$
(OC)$_{11}$M$_n$
44
M$_n$ = Ru$_3$, Os$_3$, Re(μ-H)$_3$, Ru(μ-H)$_4$
Co$_2$(CO)$_8$
M$_n$CO)$_{11}$
45
Δ
Δ
Os(CO)$_2$
(OC)$_2$Co
(OC)$_3$Os
Os(CO)$_3$
Co(CO)$_3$
Os(CO)$_4$
(OC)$_3$Os
Os(CO)$_4$
47
(OC)$_4$Ru
(OC)$_4$Ru
Ru(CO)$_3$
(OC)$_3$Ru
Ru(CO)$_3$
46

Scheme 11.

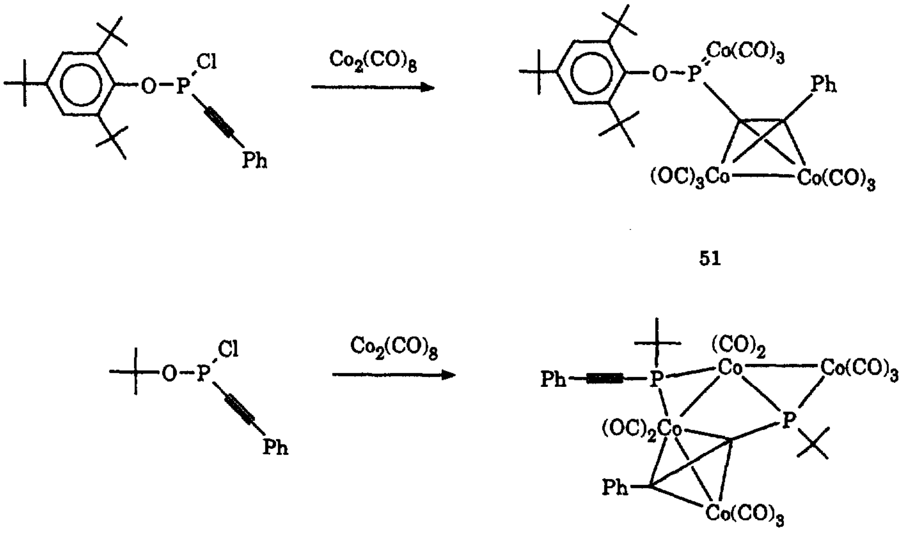


48

49

50

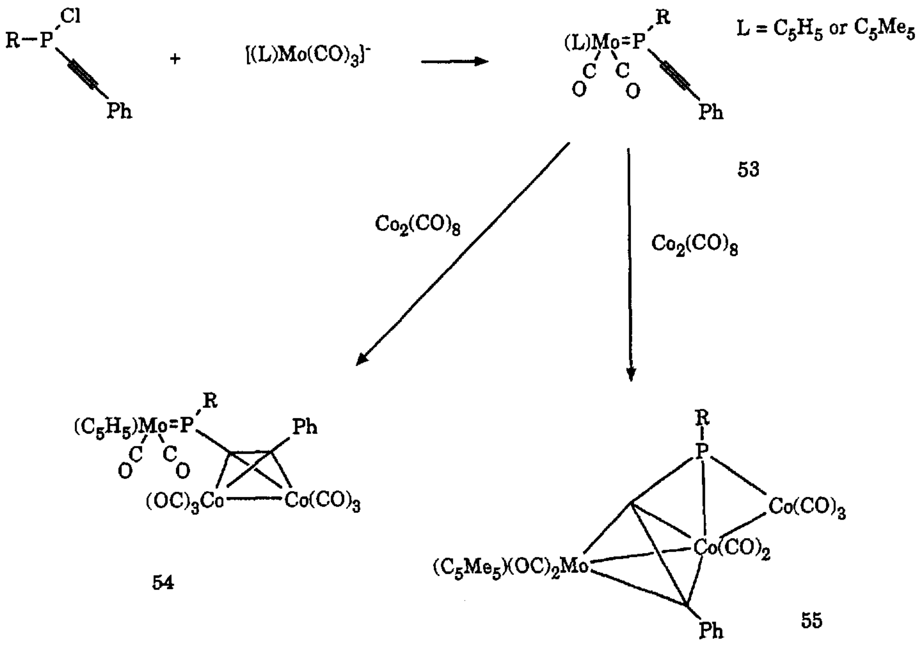
Scheme 12.



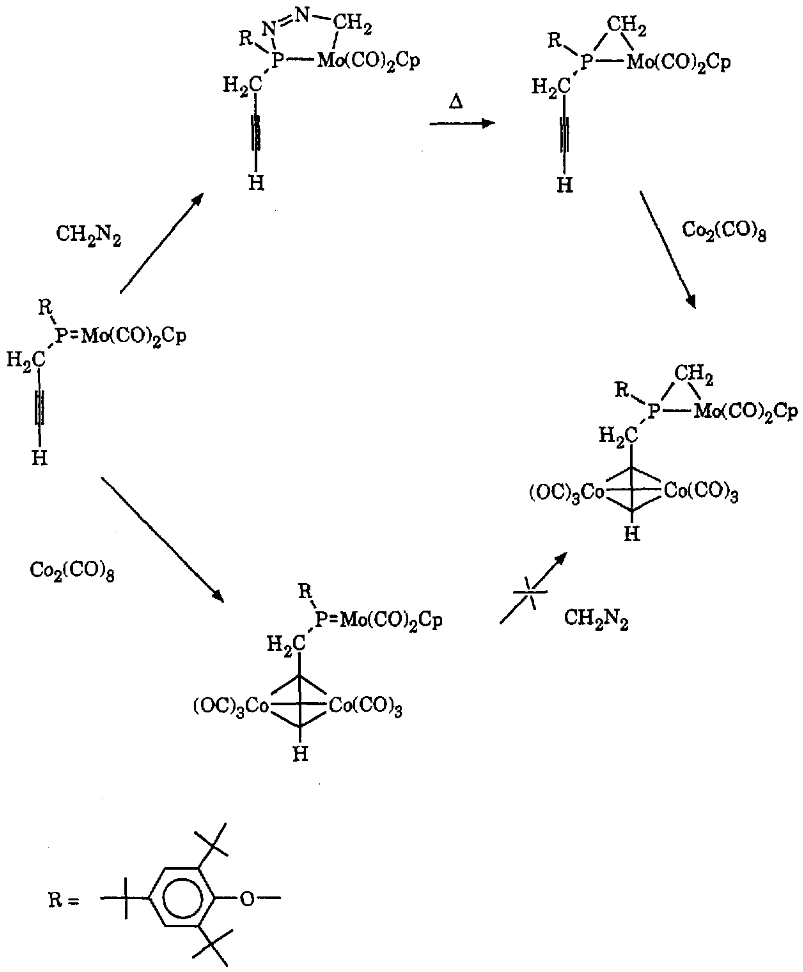
51

52

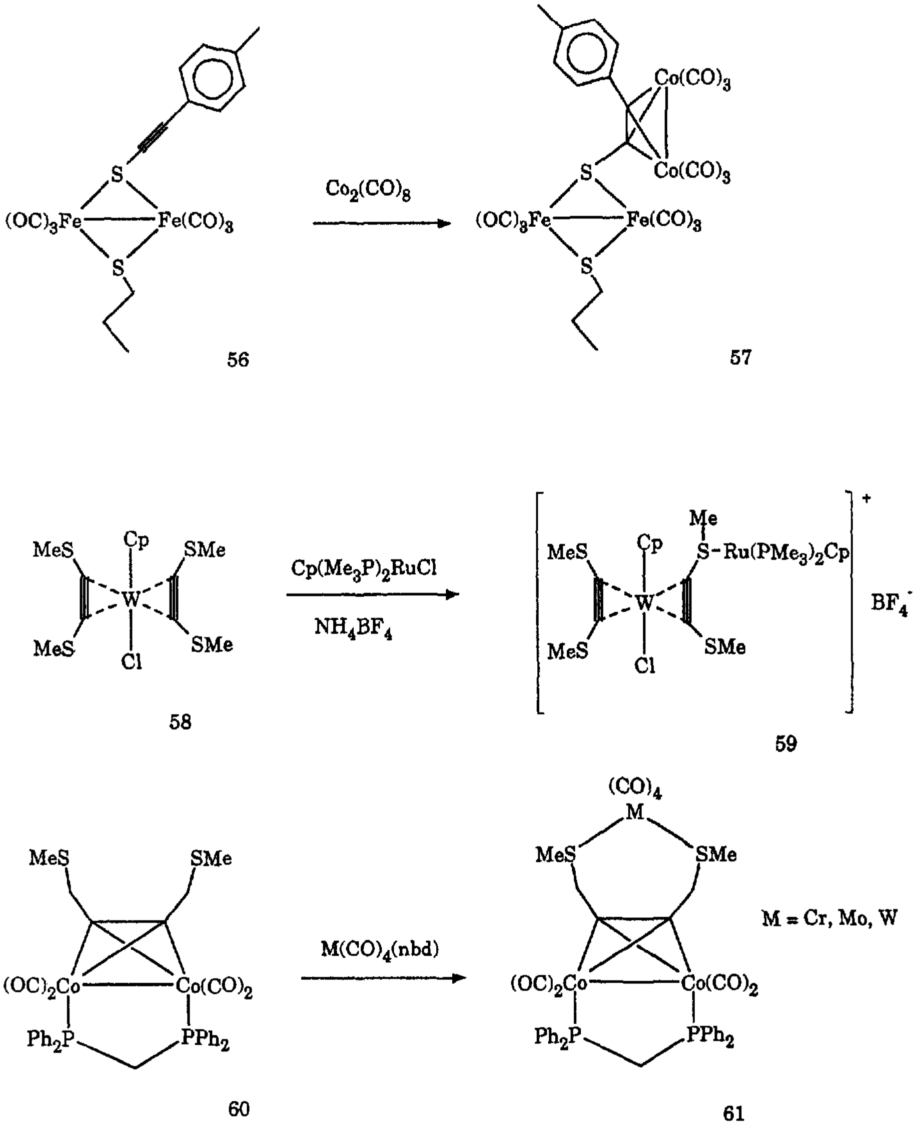
Scheme 13.



Scheme 14.



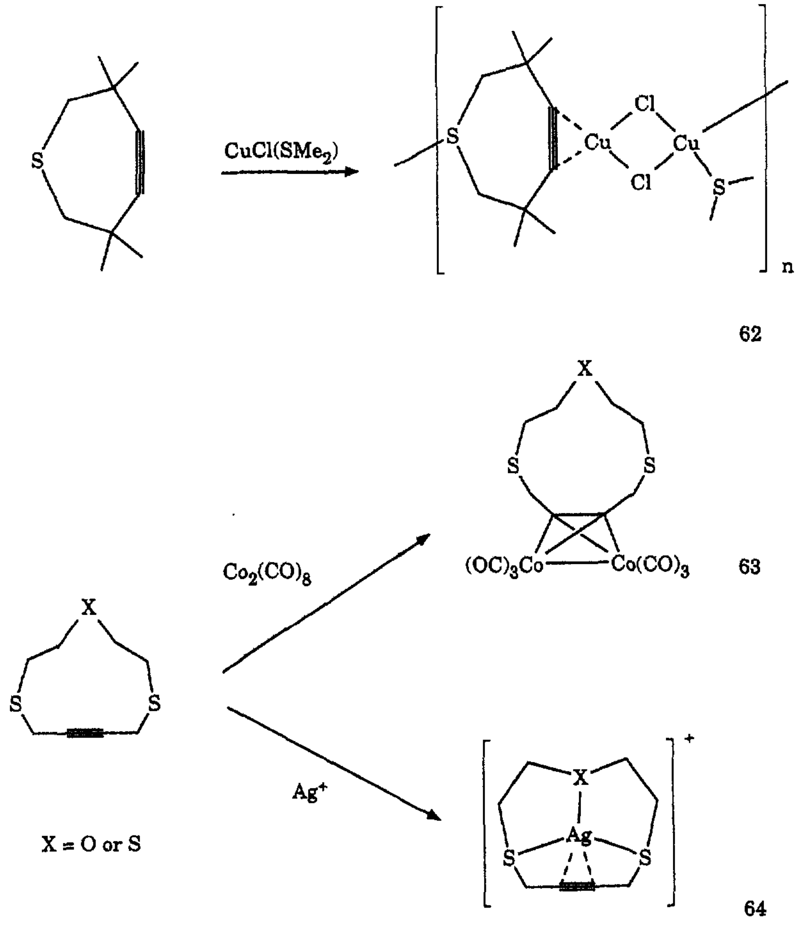
Scheme 15.



Scheme 16.

and **60**. The pendant thioethers in **58** and **60** can coordinate metal ligand fragments as exemplified by **59**[36] and **61**.[37] The formation of **61** illustrates the effect of the structural distortion engendered in an alkyne ligand upon coordination which enables 2,7-dithiooct-4-yne to act as a chelating ligand.

Some thiocycloalkynes are known and their coordination chemistry is beginning to be explored. In several cases there are examples of these cyclic ligands utilising the thioether and alkyne functionalities simultaneously. Reaction of 3,3,6,6-tetramethyl-1-thiacyclohept-4-yne with [CuCl(SMe$_2$)] affords the polymeric structure **62** depicted in Scheme 17.[38] 1,4,7-Trithiacycloundec-9-yne and 1,7-dithia-4-oxa-cycloundec-9-yne coordinate to Co$_2$(CO)$_6$ via the alkyne bond only (**63**), but with Ag$^+$ it is postulated that all four donor sites are used simultaneously to afford complexes **64** (Scheme 17).[39] Complex **63** (X = S), which can also be prepared by the acid catalysed reaction of bis(2-mercaptoethyl)sulfide with [Co$_2$(μ-HOCH$_2$C$\equiv$CCH$_2$OH)(CO)$_6$], coordinates Ag$^+$ and Cu$^+$ metal ligand fragments to afford compounds **65**–**68** (Scheme 18).[40] Bis(diphenylphosphino)methane substituted compounds **63** can also coordinate Mo(CO)$_3$ fragments to afford compound **70**.[40] The acid catalysed reaction of bis(2-mercaptoethyl)sulfide with [Co$_2$(μ-HOCH$_2$C$\equiv$CCH$_2$OH)(CO)$_6$] also affords the dimeric compound **71** which coordinates Ag$^+$ via four thioether groups to afford **72** (Scheme 19).[40]



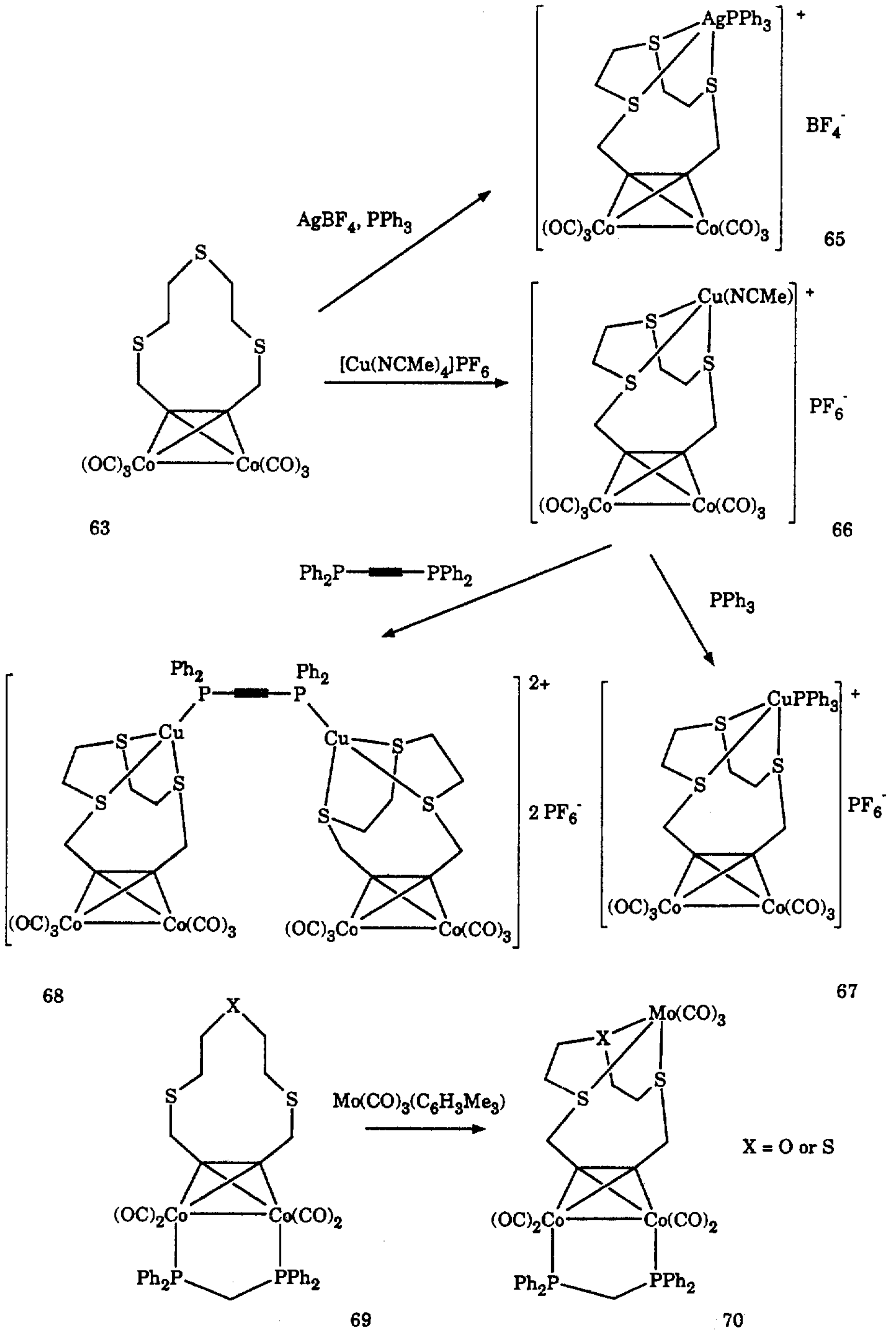
Scheme 17.

2.4. *Ligands bound via alkyne and ether donor sites*

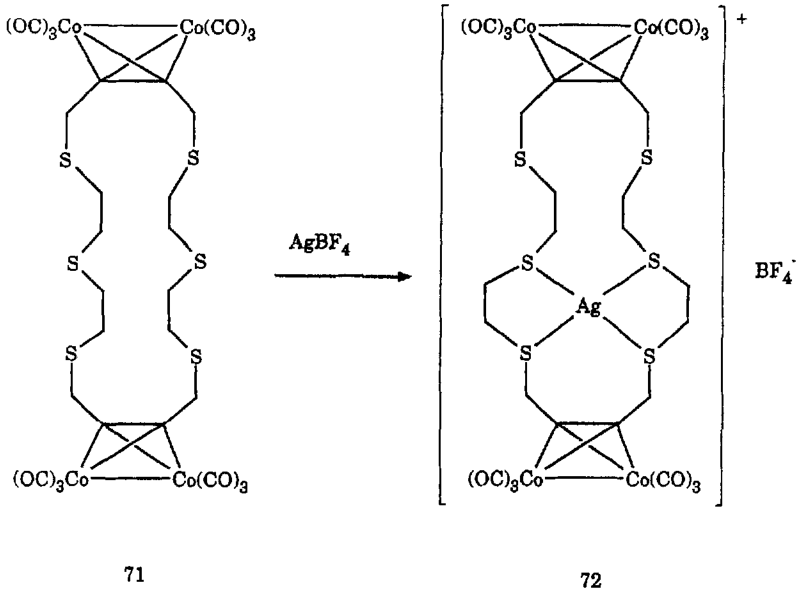
Crown ethers with alkyne functionalities already coordinated to dicobalt units can be prepared by reaction of $[Co_2(\mu\text{-}HOCH_2C{\equiv}CCH_2OH)(\mu\text{-dppm})(CO)_4]$ with triethylene or tetraethylene glycol in the presence of HBF_4 and $NaBF_4$ as a template. Compound **73** is obtained directly, but the Na^+ template is coordinated by **74** and washing with deionised water is necessary to remove it (Scheme 20).[41] Compound **73** can coordinate Li^+, while the large ring system in **74** can coordinate Li^+, Na^+ and K^+.

3. CONCLUSIONS

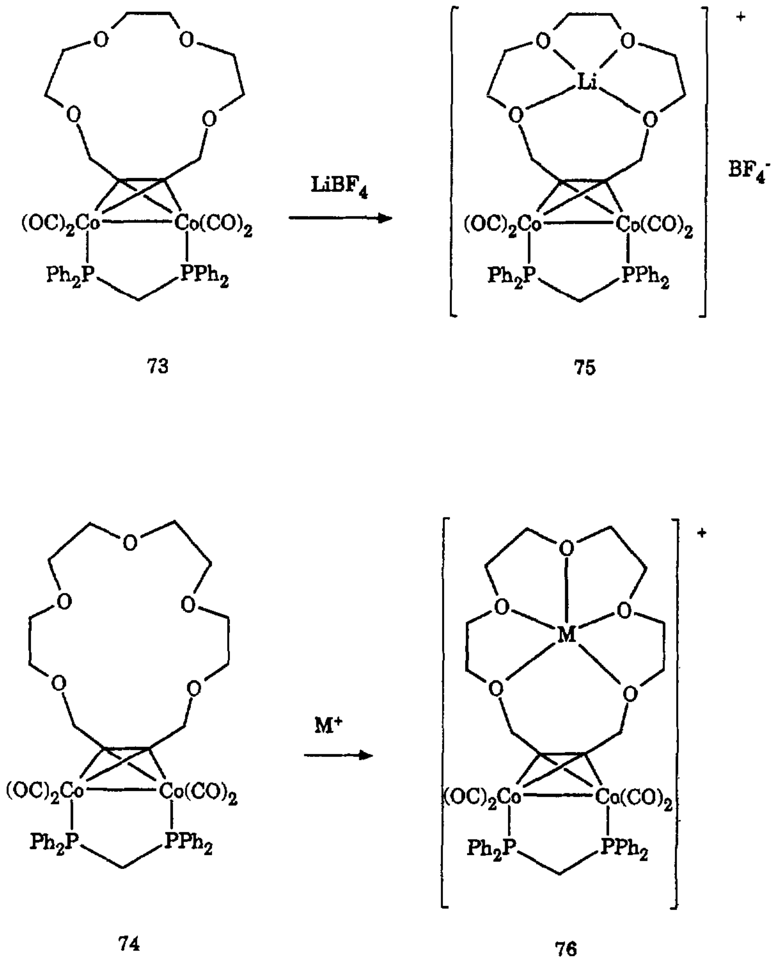
Phosphinoalkynes have been widely used in cluster chemistry due to their ability to bond several transition metal centres simultaneously and hence facilitate metal–metal formation and cluster build-up. Phosphorus–carbon bond cleavage results in formation of cluster stabilising phosphido ligands as well as hydrocarbon fragments. Alkynes with sulfur or oxygen donor atoms beta to the alkyne carbons have been incorporated into metallomacrocycles capable of binding hard or soft metal ions.[42]


AgBF$_4$, PPh$_3$
[Cu(NCMe)$_4$]PF$_6$
63
65
BF$_4^-$
66
PF$_6^-$
Ph$_2$P—≡—PPh$_2$
PPh$_3$
68
2+
2 PF$_6^-$
67
PF$_6^-$
Mo(CO)$_3$(C$_6$H$_3$Me$_3$)
X = O or S
69
70

Scheme 18.



Scheme 19.



M = Li, Na, K

Scheme 20.

REFERENCES

1. N. K. Hota, H. A. Patel, A. J. Carty, M. Mathew and G. J. Palenik, *J. Organomet. Chem.*, 1971, **32**, C55; H. A. Patel, A. J. Carty and N. K. Hota, *J. Organomet. Chem.*, 1971, **50**, 247.
2. P. H. Bird and A. R. Fraser, *J. Chem. Soc., Chem. Commun.*, 1970, 681.
3. A. J. Carty and T. W. Ng, *J. Chem. Soc., Chem. Commun.*, 1970, 149.
4. A. J. Carty, H. N. Paik and G. J. Palenik, *Inorg. Chem.*, 1977, **16**, 300.
5. A. J. Carty, *Pure and Appl. Chem.*, 1982, **54**, 113.
6. A. J. Carty, W. F. Smith and N. J. Taylor, *J. Organomet. Chem.*, 1978, **146**, C1.
7. H. N. Paik, A. J. Carty, K. Dymock and G. J. Palenik, *J. Organomet. Chem.*, 1974, **70**, C17.
8. S. Jacobsen, A. J. Carty, M. Mathew and G. J. Palenik, *J. Am. Chem. Soc.*, 1974, **96**, 4330.
9. A. J. Carty, H. N. Piak and T. W. Ng, *J. Organomet. Chem.*, 1974, **74**, 279.
10. H. Lang and L. Zsolnai, *J. Organomet. Chem.*, 1989, **369**, 131; *Chem. Ber.*, 1991, **124**, 259.
11. H. Lang and U. Lay, *J. Organomet. Chem.*, 1992, **441**, 389.
12. H. Lang, U. Lay, M. Leise and L. Zsolnai, *Z. Naturforsch., B*, 1993, **48**, 27.
13. J. C. Jeffery, R. M. S. Peirera, M. D. Vargas and M. J. Went, *J. Chem. Soc., Dalton Trans.*, in press.
14. E. Sappa, G. Prediera, A. Tiripicchio and M. Tiripicchio Camellini, *J. Organomet. Chem.*, 1985, **297**, 103.
15. M. H. A. Benvenutti, D. Braga, F. Grepioni and M. D. Vargas, *J. Chem. Soc., Chem. Commun.*, 1990, 1730; M. H. A. Benvenutti, M. D. Vargas, D. Braga, F. Greponi, B. E. Mann and S. Naylor, *Organometallics*, 1993, **12**, 2947.
16. M. H. A. Benvenutti, M. D. Vargas, D. Braga, F. Greponi, E. Parisini and B. E. Mann, *Organometallics*, 1993, **12**, 2955.
17. M. D. Vargas, R. M. S. Pereira, D. Braga and F. Grepioni, *J. Chem. Soc., Chem. Commun.*, 1993, 1008.
18. J. C. Daran, Y. Jeannin and O Kristiansson, *Organometallics*, 1985, **4**, 1882.
19. M. I. Bruce, M. L. Williams, B. W. Skelton and A. H. White, *J. Organomet. Chem.*, 1985, **282**, C53.
20. C. J. Adams, M. I. Bruce, B. W. Skelton and A. H. White, *J. Organomet. Chem.*, 1992, **423**, 119.
21. E. Sappa, G. Pasquinelli, A. Tiripicchio and M. Tiripicchio Camellini, *J. Chem. Soc., Dalton Trans.*, 1989, 601.
22. C. J. Adams, M. I. Bruce, B. W. Skelton and A. H. White, *J. Organomet. Chem.*, 1992, **423**, 83.
23. O. Orama, *J. Organomet. Chem.*, 1986, **314**, 273.
24. E. Sappa, *J. Organomet. Chem.*, 1988, **352**, 327.
25. C. J. Adams, M. I. Bruce, B. W. Skelton and A. H. White, *J. Organomet. Chem.*, 1993, **447**, 91.
26. B. C. Ward and J. L. Templeton, *J. Am. Chem. Soc.*, 1980, **102**, 1532.
27. A. K. Powell and M. J. Went, *J. Chem. Soc., Dalton Trans.*, 1992, 439.
28. C. J. Adams, M. I. Bruce, E. Horn, B. W. Skelton, E. R. T. Tiekink and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1993, 3299.
29. C. J. Adams, M. I. Bruce, E. Horn and E. R. T. Tiekink, *J. Chem. Soc., Dalton Trans.*, 1992, 1157.
30. C. J. Adams, M. I. Bruce, E. Horn, B. W. Skelton, E. R. T. Tiekink and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1993, 3313.
31. H. Lang and O. Orama, *J. Organomet. Chem.*, 1989, **371**, C48; H. Lang, M. Leise and L. Zsolnai, *J. Organomet. Chem.*, 1991, **410**, 379.
32. H. Lang, M. Leise and L. Zsolnai, *J. Organomet. Chem.*, 1990, **386**, 349.
33. H. Lang and M. Leise, *J. Organomet. Chem.*, 1993, **456**, C4; H. Lang, M. Leise and L. Zsolnai, *Organometallics*, 1993, **12**, 2394; H. Lang, M. Leise and W. Imhof, *Z. Naturforsch., B*, 1991, **46**, 1650.
34. G. Cetini, O. Gambino, R. Rossetti and E. Sappa, *J. Organomet. Chem.*, 1967, **8**, 149; L. P. Battaglia, D. Delledonne, N. Nardelli, G. Predieri, G. P. Chiusoli, M. Costa and C. Pelizzi, *J. Organomet. Chem.*, 1989, **363**, 209; B. Heim, J. C. Daran, Y. Jeannin, B. Eber, G. Huttner and W. Imhof, *J. Organomet. Chem.*, 1992, **441**, 81; R. D. Adams, G. Chen, Y. Chi, W. Wu and J. Yin, *Organometallics*, 1992, **11**, 1480.
35. R. J. Wang, L. C. Song, H. G. Wang, Z. X. Wang, J. T. Wang and H. Xuebao, *Acta Chim. Sinica*, 1989, **47**, 16.
36. D. C. Miller and R. J. Angelici, *J. Organomet. Chem.*, 1990, **394**, 235.
37. A. Gelling, M. J. Went and D. C. Povey, *J. Organomet. Chem.*, 1994, **455**, 203.
38. F. Olbrich, G. Schmidt, U. Behrens and E. Weiss, *J. Organomet. Chem.*, 1991, **418**, 421.
39. H. Meier and Y. Dai, *Tetrahedron Lett.*, 1993, **34**, 5277; G. F. Mohmand, K. Thiele and M. J. Went, *J. Organomet. Chem.*, 1994, **471**, 241; G. F. Mohmand and M. J. Went, unpublished results.
40. F. Demirhan, A. Gelling, S. Irişli, J. C. Jeffery, S. N. Salek, O. S. Şentürk and M. J. Went, *J. Chem. Soc., Dalton Trans.*, 1993, 2765.
41. S. C. Bennett, J. C. Jeffery and M. J. Went, *J. Chem. Soc., Dalton Trans.*, 1994, 3171.
42. F. C. J. M. van Veggel, W. Verboom and D. N. Reinhoudt, *Chem. Rev.*, 1994, **94**, 279.