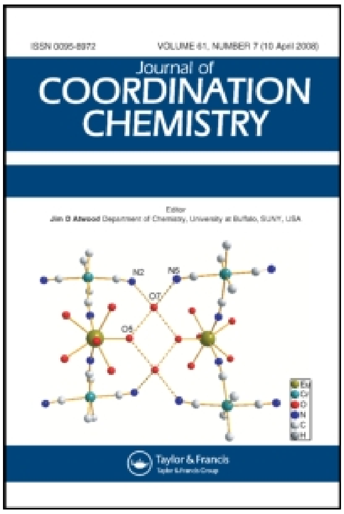

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THE INTERFACE OF MAIN GROUP AND TRANSITION METAL CLUSTER CHEMISTRY

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THE INTERFACE OF MAIN GROUP AND TRANSITION METAL CLUSTER CHEMISTRY

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The literature concerning cluster complexes which contain both main group element and transition metal vertices is reviewed. Synthetic methods and general reactivity patterns are summarized. Emphasis is placed on structural comparisons of cluster geometries for a wide variety of element combinations. Relationships between these mixed clusters and the main group element clusters known as Zintl ions are discussed.

Keywords: Cluster, main group element, transition metal, Zintl, carbonyl, carbide, phosphide, sulfide, nitride.

1. INTRODUCTION

While the phenomenon of cluster formation has been recognized only recently it is now known to be widespread and can be observed for almost any area of the periodic table. Lithium alkyls are known to aggregate in solution forming tetramers and higher order species, the early transition metals are recognized for their ability to form halide and oxo bridged high oxidation state clusters, and the later transition metals for their propensity to exist in low oxidation state carbonyl clusters. Recently, polynuclear gold-phosphine clusters have generated considerable interest. Transition metal cluster chemists have discovered the facility of adding gold-phosphine fragments to carbonyl clusters and some quite interesting results have been obtained. One of the major emphases of that work has been to stress the analogy of a $AuPR_3$ fragment to a hydride ligand, but in many cases where more than one gold unit is present bonding occurs between the gold atoms reminiscent of the homometallic gold-phosphine clusters. Main group element clusters are also known with the most famous examples being the now classical studies in the boron hydrides, but cluster anions of the heavier main group elements are represented, too. These latter species derive in large part from work of the German chemist Zintl after whom many of the solid state phases and cluster anions are named. More recently, work by Corbett's research group has enabled the structural characterization of a number of these main group clusters by sequestering the alkali metal counterion with cryptands.[1,2] It is quite reasonable to expect that hybrids of these various cluster groups should exist as precedented by studies on the metalloboranes; however, it has been less well recognized for other areas of main group cluster chemistry.

The incorporation of main group elements into transition metal carbonyl clusters has been known for over thirty years. Much of the early work was performed in the laboratories of W. Hieber, but many of the compounds were poorly characterized because of the inavailability of definitive structural data from techniques such as X-ray crystallography and multinuclear nuclear magnetic resonance. Many of the clusters studied since then have been viewed as derivatives of a transition metal framework in which the main group element is thought of as a ligand donating a number of electrons to the cluster. This simple approach may not be sufficient to deal with more complex structures which result as the relative sizes and orbital energies of the main group element and transition metals change. Even among the lighter p-block-containing species there is some indication that this may be true and mounting evidence suggests that the former approach is not adequate. In many cases the electron counting rules are satisfied by viewing the p-block element as a ligand or as a cluster vertex, but in a number of cluster examples it is becoming increasingly difficult not to consider the main group atom as being intrinsically involved in the cluster bonding scheme as more than a simple donor atom. It is due to some of these more recent findings that this review can be attributed. A review of somewhat different scope has recently appeared describing transition metal complexes containing naked main group atoms.[3] In order to limit the scope of topic we will concentrate our comments on mixed p-block/d-block compounds containing at least four such atoms. Emphasis will be placed on mixed compounds which include main group elements that are known to form Zintl ions and related compounds. While the group 13 and 16 elements do not form complexes which have traditionally been classified as Zintl ions, some of their compounds bear very obvious structural and reactivity relationships to those compounds in groups 14 and 15 and they will be covered briefly.

2. GENERAL SYNTHETIC CONSIDERATIONS

Before beginning a discussion of syntheses of specific compounds, it should be noted that a number of these reaction schemes can be generalized to p-block elements of different groups. Some methods for generating the main group/transition metal bonds can be summarized:

1. Substitution reactions
2. Lewis acid-base interactions
3. Reaction of main group halo complexes with anionic or neutral transition metal complexes.
4. Reaction of anionic main group reagents with transition metal compounds.
5. Reaction of transition metal hydrides with main group alkyl complexes.
6. Pyrolyses of organo–main group complexes with transition metal compounds.
7. Deoxygenation of main group oxides by transition metal carbonyls.
8. Direct reaction of main group elements with transition metal compounds.

The simplest method of forming main group element–transition metal bonds is via substitution reactions in which dative bonds are formed between a lone pair of electrons on the main group atom and a transition metal. Application of this method does not produce compounds which are topical to this review; however, it is probably an important first process involved in the synthesis of a number of the more complex compounds to be discussed. It is obviously most important for the group 15 ER_3 ($E = N$, P, As, Sb, Bi; $R =$ alkyl, aryl, alkoxy, aryloxy) species which are historically good donor ligands contributing a lone pair of electrons. Substitution processes are, of course, governed by the nature of the main group element and in general the heavier members of the group are poorer donors. Lone pairs on some of these atoms may be present even after cluster formation and may provide an avenue for attaching other metal fragments to the cluster.

The opposite case to the substitution products are the Lewis acid adducts of the group 13 elements. For a number of examples, electron rich transition metal centers can act as electron donors to conventional six electron, Lewis acid ER_3 species such as $InBr_3$. This method sometimes produces adducts of the type $L_nM \rightarrow ER_3$ which are not going to be covered by this review, but as in the case of the substitution chemistry, this type of reactivity may be important in the mechanism by which more complicated higher nuclearity species are built up. In other cases these interactions lead to substitution of an R group by the ML_n moiety and the ultimate production of $E[ML_n]_3$ species in which the transition metal fragments function as pseudo halides. In these complexes, the group 13 atom is still a Lewis acid site and, therefore, can be used for further cluster building. Complexes of this type are particularly prevalent in systems where the ML_n species has a formal -1 charge. Ionic displacement reactions of ER_3 species where $R =$ halide in reaction with metal carbonyl anions are prone to yield such complexes. ML_n fragments having higher negative charge lead to more complex products as will be seen for the Tl/Fe system. Alternatively, main group anions such as $[Ph_3Sn]^-$ can displace halide atoms from transition metal centers.

These products possess E–M bonds which may be described as normal 2-center-2-electron coordinate covalent bonds. The extent of these ionic displacement reactions appears to be solvent dependent and, in the case of group 13 complexes especially, redistribution reactions can be important. The driving force in a number of these cases is the production of insoluble alkali metal halides in suitable organic solvents or the formation of neutral metal–main group clusters which precipitate readily from aqueous solution. Similar to these methods is the reaction of metal hydrides with main group alkyls in which the formation of alkane drives the reaction.

Pyrolysis reactions are probably the least desirable of the reaction methods listed above as these are most likely to yield complex mixtures of products in low isolated yields. However, in a few cases where a particularly thermodynamically-favored product is formed, this approach may result in a convenient synthesis. Often E–carbon bonds of the heavier main group elements are easily ruptured, and under pyrolysis conditions ER and naked E groups can be generated and trapped with metal fragments.

A large number of transition metal clusters containing main group atoms have been generated by what appears to be a general reaction in which E–O bonds are reduced by CO. The driving force for this reaction is the production of gaseous CO_2. This is especially important in the production of the cluster carbides, nitrides and bismuthides, and probably is also important for the chalcogenides.

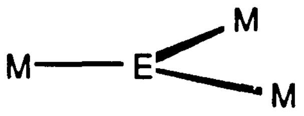
In a few cases, main group elements will react directly with metal compounds to produce E–M bonds, but there are fewer of these reactions reported and the method may be less general than some of those listed above. Other less general methods will be discussed in connection with specific reactions, and it is not improbable that more than one of the methods listed may be important in the formation of the ultimate products.

3. GENERAL STRUCTURAL FEATURES

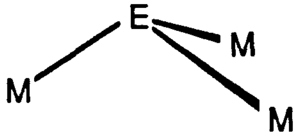
Many of the more traditional carbonyl cluster complexes possess geometries consistent with the EAN rule and/or with Wade's rules. A number of frequently-encountered structural types are observed and these will now be discussed. We will begin with the simplest systems incorporating only one main group atom following increasing numbers of transition metals, and thereafter complexes with larger numbers of main group atoms will be considered in order. Structural data for a number of compounds belonging to these various classifications are given in Tables I–XIII.

3.1 EM_3 and EM_4 Complexes Without Transition Metal–Transition Metal Bonds

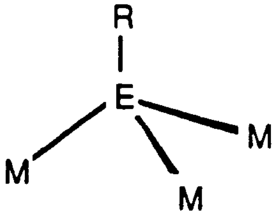
In compounds of group 13 to 16 elements, the main group element begins with an atomic electronic configuration of s^2p^x where $x = 1$–4. These elements wish to acquire a noble gas inert shell configuration which will put eight electrons around the main group atom, although electron deficient bonding where that atom is surrounded by only six electrons is not unusual, especially for group 13. Many complexes adopt structures which are analogues to those which these elements form with halides and alkyl or aryl substituents.[4–6, 265–272] The most common formal oxidation states are +3 for groups 13 and 15 and +4 for group 14. Thus group 13 and 15 elements tend to form EM_3 complexes. For group 13 the only examples of this type observed to date are planar molecules with 6 electrons around the main group atom,[4–6] while group 14 and 15[7] examples exhibit both planar and pyramidal geometries depending on whether six or eight electrons are available. A planar, tellurium-centered complex[8] is also known. In the structurally characterized examples, the transition metals almost invariably obey the eighteen electron rule. The planar and pyramidal geometries are illustrated as structures **A** and **B**. Multiple bonding between the main group element and the transition metals has been proposed for the planar As,[7] Sb[7] and Te[8] molecules. This has recently been reviewed for group 14 elements and is discussed in terms of the divalent main group fragments behaving similarly to carbene groups.[273] EM_4 compounds are known which are tetrahedral as illustrated in **D**. Structural data for complexes of these three types are given in Table 1. Halides and alkyl groups may replace one or more of the metal atoms giving rise to structures such as that illustrated in **C** for EM_3R. Higher numbers of such substitutions are possible but lead to compounds which will not be covered in this review although they have obvious structural and reactivity relationships to the compounds discussed herein. The reader is also referred to two earlier reviews on group 13[274] and group 14[275] -element-containing clusters.



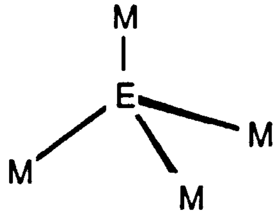
A



B



C



D

The most common way of generating these compounds for either planar or pyramidal geometries is by reaction of a main group halide with a monoanionic metal complex as illustrated below.

$$InCl_3 + 3[Co(CO)_4]^- \rightarrow In\{Co(CO)_4\}_3 + 3\,Cl^- \qquad (1)^{5}$$

$$TlCl_3 + 3[CpMo(CO)_3]^- \rightarrow Tl\{CpMo(CO)_3\}_3 + 3\,Cl^- \qquad (2)^{6}$$

$$2Pb(NO_3)_2 + 4[Co(CO)_4]^- \rightarrow Pb\{Co(CO)_4\}_4 + Pb^{\circ} + 4\,NO_3{}^- \qquad (3)^{270}$$

$$2Pb(NO_3)_2 + 4[Fe(CO)_3(NO)]^- \rightarrow Pb\{Fe(CO)_3(NO)\}_4 + Pb^{\circ} + 4\,NO_3{}^- \qquad (4)^{277}$$

$$2Pb(OAc)_2 + 4\,Na[Co(CO)_3PR_3] \rightarrow Pb\{Co(CO)_3PR_3\}_4 + Pb^{\circ} + 4\,NaOAc \qquad (5)^{277}$$

$$BiCl_3 + 3[Co(CO)_4]^- \rightarrow Bi\{Co(CO)_4\}_3 + 3\,Cl^- \qquad (6)^{10}$$

It is significant that in many cases, where low oxidation state main group halides are used, the ultimate metal carbonyl product contains the main group element in its higher oxidation state. Often this redox is achieved by disproportionation, forming the neutral main group element, as can be seen in equations 3–5. Reactions of neutral metal carbonyls directly with the elements also afford clusters of this type (eqn 7). They can undergo substitution reactions to produce complexes similar to those in which substituted metal carbonyl anions are employed (eqn 8). Reducing $Pb\{Co(CO)_4\}_4$, $Sn\{Co(CO)_4\}_4$, and $Bi\{Co(CO)_4\}_3$ with alkali metals leads to the production of $[Co(CO)_4]^-$.

$$E + 2Co_2(CO)_8 \rightarrow E\{Co(CO)_4\}_4 \quad E = Sn, Pb \qquad (7)^{276}$$

$$PbCo_4(CO)_{16} + xPPh_3 \rightarrow PbCo_4(CO)_{16-x}(PPh_3)_x + x\,CO \quad x = 3, 4 \qquad (8)^{276}$$

$$M\{Co(CO)_4\}_x \xrightarrow{Na/Hg} x[Co(CO)_4]^- + M \qquad (9)^{276}$$

(M = Sn, Pb; x = 4; M = Bi, x = 3)

Efforts to induce the formation of M–M bonds between the isolated $Co(CO)_4$ units were not successful and this was attributed to the steric requirements of the Sn and Pb atoms. This needs to be reexamined in light of more recent results, however.

Planar P, As, and Sb complexes have been generated by similar methods but involve the use of an intermediate transition metal/main group halide complex of general formula $(L_nM)_2EX$ in reaction with metal carbonyl anions. The Te compound was generated from TeH_2 (generated *in situ*) and $CpMn(CO)_2(THF)$.[8]

$$E\{Cr(CO)_5\}_2Cl + [Mn(CO)_5]^- \rightarrow E\{Cr(CO)_5\}_2\{Mn(CO)_5\} + Cl^-$$
$$(E = As, Sb) \qquad (10)^{7}$$

$$Sb\{Cr(CO)_5\}_2Cl + [CpMo(CO)_3]^- \rightarrow Sb\{Cr(CO)_5\}_2\{CpMo(CO)_3\} + Cl^- \qquad (11)^{7}$$

$$Sb\{Cr(CO)_5\}_2Cl + Na_2M_2(CO)_{10} \rightarrow [Na(THF)_2][Sb\{Cr(CO)_5\}_2\{M(CO)_5\}] \qquad (12)^{7}$$
THF, M = Cr, Mo, W

$$\left.\begin{array}{l}\mathrm{Al_2Te_3} \xrightarrow{\mathrm{HCl}} \mathrm{TeH_2} + \\ \mathrm{CpMn(CO)_3} \xrightarrow{h\nu} \mathrm{CpMn(CO)_2(THF)}\end{array}\right\} \longrightarrow \mathrm{Te\{CpMn(CO)_2\}_3}$$

(*13*)[8]

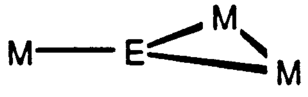
The six electron complexes $\mathrm{In\{Co(CO)_4\}_3}$ and $\mathrm{Tl\{Co(CO)_4\}_3}$ function as Lewis acids toward $\mathrm{[Co(CO)_4]^-}$ giving $\mathrm{[M\{Co(CO)_4\}_4]^-}$ ions[278] which have been spectroscopically characterized but no X-ray diffraction data have been reported on these or the presumably isostructural $\mathrm{Sn\{Co(CO)_4\}_4}$, $\mathrm{Pb\{Co(CO)_4\}_4}$ and $\mathrm{Pb\{Fe(CO)_3(NO)\}_4}$. A structural model does exist in the isoelectronic $\mathrm{[Bi\{Fe(CO)_4\}_4]^{3-}}$ whose crystal structure has been determined.[12] This compound was obtained in high yield by a deoxygenation process in the reaction of $\mathrm{Fe(CO)_5/KOH/MeOH}$ solutions with $\mathrm{NaBiO_3}$.

$$\mathrm{Fe(CO)_5} \xrightarrow[\mathrm{MeOH}]{\mathrm{KOH}} \mathrm{[HFe(CO)_4]^-} \xrightarrow{\mathrm{NaBiO_3}} \mathrm{[Bi\{Fe(CO)_4\}_4]^{3-}}$$

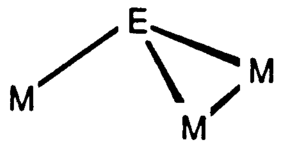
(*14*)[12]

3.2 EM_3 and EM_4 Complexes Containing Transition Metal–Transition Metal Bonds

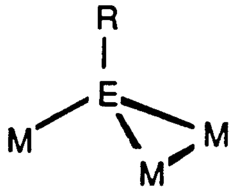
Unlike halides and alkyl or aryl groups, transition metal fragments offer the additional complication that there may be interactions between the metals giving rise to one or more metal–metal bonds. They are illustrated as follows: Structural types **E**, **F**, **G** and **H** with one metal–metal bond (Table II); two metal–metal bonds of type **I** and **J** (spirocyclics, Table III); three metal–metal bonds of types **K**, **L** and **M** (Table IV); and butterfly complexes of type **N** and **O** (Table V).



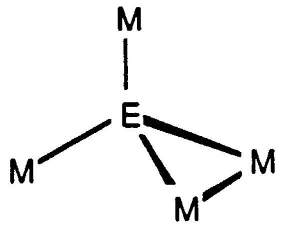
E



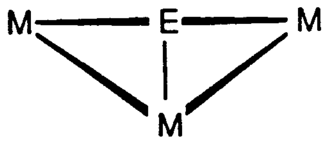
F



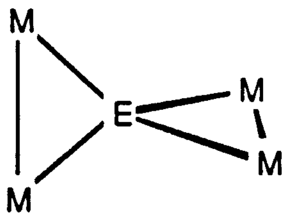
G



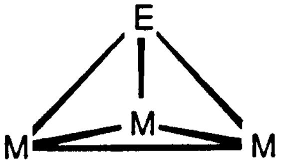
H



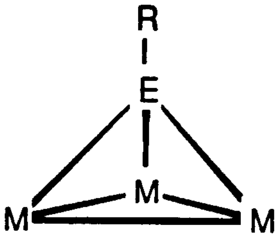
I



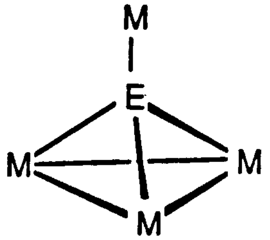
J



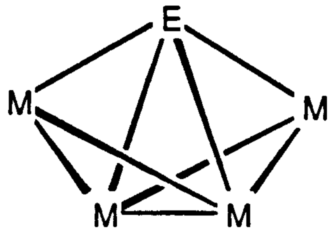
K



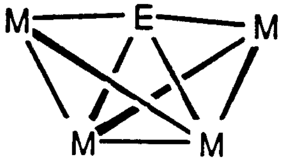
L



M



N



O

As required by electron counting considerations, formation of one metal–metal bond gives complexes which have two less electrons than the parent which has one less M–M bond. Planar complexes (**E**, Table II) arise directly from reactions similar to those producing planar complexes with no metal–metal bonds. They may also be obtained by loss of a ligand from compounds with no M–M bond. Unfortunately, the yields of many of these reactions are low. While the thermal elimination of CO described in equation 20 does proceed in 90% yield and reactions of $Sb\{Cr(CO)_5\}_2Cl$ with $Na_2M_2(CO)_{10}$ gave 72 to 83% yields, the other reactions gave less than 50% with many giving less than 10%. A planar selenium compound, $[Se\{Cp_2Cr_2(CO)_4\}\{CpCr(CO)_2\}]^-$, has been generated by treating $Se\{CpCr(CO)_2\}_2$ with cobaltocene.[14]

$$MCl_4 + Na_2W_2(CO)_{10} \rightarrow M\{W(CO)_5\}\{W_2(CO)_{10}\}\ M = Ge, Sn \qquad (15)^7$$

$$P\{Cr(CO)_5\}_2Br + [CpW(CO)_3]^- \rightarrow P\{Cr(CO)_5\}\{CpWCr(CO)_7\} + CO + Br^- \qquad (16)^7$$

$$As\{W(CO)_5\}_2\{PPh_3\}Cl + [CpM(CO)_3] \rightarrow AS\{W(CO)_5\}\{CpMW(CO)_7\} + PPh_3 + CO \qquad (17)^7$$

$M = Mo, W$

$$\mathrm{As\{Cr(CO)_5\}\{CpMn(CO)_2\}Cl + [CpMo(CO)_3]^- \rightarrow}$$
$$\mathrm{As\{CpMn(CO)_2\}\{CpMoCr(CO)_7\} + CO + Cl^-} \qquad (18)^{7}$$

$$\mathrm{As\{Cr(CO)_5\}_2Cl + [Mn(CO)_5]^- \rightarrow As\{Cr(CO)_5\}_2Mn(CO)_5 + Cl^-} \qquad (19)^{7}$$

$$\mathrm{As\{Cr(CO)_5\}_2Mn(CO)_5 \rightarrow As\{Mn(CO)_5\}\{Cr_2(CO)_9\} + CO} \qquad (20)^{7}$$

Pyramidal complexes behave similarly. Thus $\mathrm{PhGe[Co(CO)_4]_3}$ thermally eliminates CO to generate first $\mathrm{PhGe\{Co(CO)_4\}\{Co_2(CO)_7\}}$ and then $\mathrm{PhGeCo_3(CO)_9}$, the formation of each M–M bond requiring the loss of one CO.[15,279] The cobalt–germanium system has been the best example of the flexibility of the $\mathrm{EM_x}$ compounds to adopt either open or closed geometries due to the appropriateness of its size. Thus, in addition to the compounds just described, $\mathrm{Ge\{Co(CO)_4\}_4}$,[43] $\mathrm{Ge\{Co_2(CO)_7\}_2}$,[22] $\mathrm{Co_3(CO)_9\{\mu_3\text{-}GeCo(CO)_4\}}$,[280] $\mathrm{Co_3(CO)_9\{\mu_3\text{-}GeMn(CO)_5\}}$[281] and $\mathrm{[Co_3(CO)_9\{\mu_3\text{-}GeCo_2(CO)_6\}]^-}$ [43] are known which contain zero, two, three and four M–M bonds around Ge, respectively. A mixed metal complex containing only one metal–metal bond, $\mathrm{\{Co_2(CO)_7\}\{Mn(CO)_5\}GeMe}$ is formed directly by treating $\mathrm{Mn(CO)_5GeMeH_2}$ with $\mathrm{Co_2(CO)_8}$.[281] Open $\mathrm{RSn(ML_n)_3}$ compounds have been prepared from the Sn IV halides and $\mathrm{Co_2(CO)_8}$.[282] Similar complexes containing a PH group bonded to three osmium atoms with only one Os–Os bond between them arise from the reaction of $\mathrm{HOs_3(CO)_{10}(\mu\text{-}PH_2)}$ with the activated osmium clusters $\mathrm{Os_3(CO)_{12-x}(NCMe)_x}$.[16] The compounds so produced have the formulations $\mathrm{H_2Os_6(CO)_{21}(\mu_3\text{-}PH)}$, $\mathrm{[PPN][H_2Os_6(CO)_2(CO_2Me)(\mu_3\text{-}PH)]}$, $\mathrm{[H_2Os_6(CO)_2(NCMe)(\mu_3\text{-}PH)]}$,$\mathrm{[PPN][HOs_6(CO)_{21}(\mu_3\text{-}PH)]}$, $\mathrm{[PPN][H_2Os_6(CO)_{19}(CO_2Me)(\mu_3\text{-}PH)]}$, and $\mathrm{H_3Os_6(CO)_{19}(CO_2Me)(\mu_3\text{-}PH)}$. Of these, the complexes $\mathrm{H_2Os_6(CO)_{20}(NCMe)(\mu_3\text{-}PH)}$ and $\mathrm{H_3Os_6(CO)_{19}(CO_2Me)(\mu_3\text{-}PH)}$ have been structurally characterized. They both contain two osmium triangles, one of which has the P atom bridging two of the metals while the P atom is ligated to only one osmium of the other triangle.

Examples of pyramidal antimony, bismuth and selenium compounds are also known (Table II).

Reversible ligand addition has been observed from the μ_3-PPh compound $\mathrm{CpMnFe_2(CO)_9(\mu_3\text{-}PPh)}$.[283] One CO can be added at 20°C and 2 bar CO, while two more will add at 40°C and 40 bar CO pressure. At 80°C under $\mathrm{N_2}$, the process is reversed to give the starting material. In the case of equation 22, displacement of the $\mathrm{PPh_3}$ from the antimony complex generates a planar structure which obtains its electrons for donation to the incoming $\mathrm{W(CO)_5}$ unit from metal–metal bond formation. This ability to pump electrons in and out of M–M, E–M and E–E bonds is an important feature of these complexes which will appear repeatedly in this review.

$$\mathrm{PhGe\{Co(CO)_4\}_3 \underset{+\,CO}{\overset{-CO}{\rightleftharpoons}} PhGe\{Co(CO)_4\}\{Co_2(CO)_7\} \underset{+2CO}{\overset{-2CO}{\rightleftharpoons}} GeCo_3(CO)_9} \qquad (21)^{15}$$

$$\mathrm{{}^tBuSb\{W(CO)_5\}_2\{PPh_3\} + W(CO)_5(THF) \rightarrow {}^tBuSb\{W(CO)_5\}\{W_2(CO)_{10}\}} \qquad (22)^{17}$$

$$\mathrm{Se\{CpFe(CO)_2\}_2 + CpMn(CO)_2(THF) \rightarrow Se\{CpFe(CO)_2\}_2\{CpMn(CO)_2\}}$$
$$\mathrm{+\ THF} \qquad (23)^{11}$$

$$\mathrm{Se\{CpFe(CO)_2\}_2\{CpMn(CO)_2\} \rightarrow Se\{Cp_2Fe_2(CO)_3\}\{CpMn(CO)_2\} + CO} \qquad (24)^{11}$$

Redox processes can give rise to similar M–M bond formation and cleavage as reported for the reversible oxidation of $[PbFe_4(CO)_{16}]^{2-}$ (with only one metal bond) to $PbFe_4(CO)_{16}$ which has a spirocyclic Pb atom connected to two $Fe_2(CO)_8$ fragments.[19,26] Similar reactivity is observed for the analogous Sn complexes. It is interesting that attempts to produce a germanium compound of type **H** by similar reaction methods led instead to isolation of $[GeFe_4(CO)_{14}]^{2-}$ (type **M**). The smaller size of germanium may tend to promote the more closed structure with three M–M bonds as opposed to just one. It should be noted, however, that the same spirocyclic geometry is obtained for the neutral Ge compound $GeFe_4(CO)_{16}$ when the dianion is oxidized.[20,21,40] Molecules containing multiple spirocyclic main group atoms are known. Addition of $Co_2(CO)_8$ to $Fe_2(CO)_8(\mu\text{-}GeH_2(_2$ results in addition of cobalt across the Ge–H bonds producing $Fe_2(CO)_6(\mu\text{-}CO)\{\mu\text{-}GeCo_2(CO)_6(\mu\text{-}CO)\}_2$ which contains two spirocyclic germanium atoms each connected to two iron atoms and two cobalt atoms.[23] A spirocyclic complex containing cobalt as the only transition metal has been isolated from the reaction of Ge_3H_8 along with spirocyclic $Ge\{Co_2(CO)_6(\mu\text{-}CO)\}_2$ and $Ge_2Co_6(CO)_{20}$. The compound is $Ge_3Co_8(CO)_{26}$ and it contains a chain-like linkage of three spirocyclic germanium atoms connected as $\{Co_2(CO)_7\}Ge\{Co_2(CO)_6\}Ge\{Co_2(CO)_6\}Ge\{Co_2(CO)_7\}$.[23] This chain-like structure has been observed for $Sb_2Fe_6(CO)_{22}$ which contains two spirocyclic antimony atoms with a $Fe_2SbFe_2SbFe_2$ core geometry.[30] Additional CO is not necessary for this reaction but it markedly increases the yield. More complicated redox processes are observed for the bismuth–iron system. Upon oxidation, $[Bi\{Fe(CO)_4\}_4]^{3-}$ is converted into $[BiFe_3(CO)_{10}]^-$ or $[Bi_2Fe_4(CO)_{13}]^{2-}$ (depending upon conditions) which contain three and two iron–iron bonds, respectively.[64] Protonation of $[Bi\{Fe(CO)_4\}_4]^{3-}$ leads to oxidation with the formation of low yields of $Bi_2Fe_3(CO)_9$ (*ca.* 10%).[238] The neutral hydride $H_3BiFe_3(CO)_9$ is a minor product of that reaction.[65]

$$Fe(CO)_5 \xrightarrow[MeOH]{KOH} [HFe(CO)_4]^- \xrightarrow[-2Pb^\circ]{+3PbX_2} [PbFe_4(CO)_{16}]^{2-} \xrightarrow[-2Cu^0]{+2Cu^+} PbFe_4(CO)_{16} \qquad (25)^{19}$$

$$2[Fe_2(CO)_8]^{2-} + PbX_2 \rightarrow [PbFe_4(CO)_{16}]^{2-} + 2X^- \qquad (26)^{17}$$

$$2[Fe_2(CO)_8]^{2-} + SnX_2 \longrightarrow \begin{matrix}[SnFe_4(CO)_{16}]^{2-}\\ + 2X^-\end{matrix} \xrightarrow[-2Cu^0]{2Cu^+} SnFe_4(CO)_{16} \qquad (27)^{40}$$

$$2[Fe_2(CO)_8]^{2-} + GeI_2 \longrightarrow [GeFe_4(CO)_{14}]^{2-} \xrightarrow[2CO]{2Cu^+} GeFe_4(CO)_{16} \qquad (28)^{40}$$

3.3 Steric Requirements of the Main Group Atom

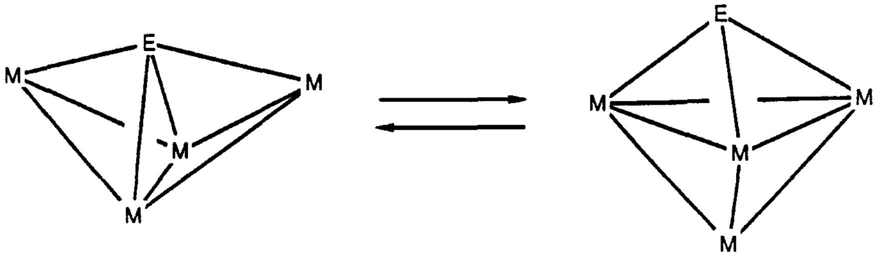
The ease with which these compounds form M–M bonds is related to the steric bulk of the central main group element. This has recently been discussed by Schmid.[284] The smaller main group elements show a strong tendency to have as much M–M bonding as possible, while the heavier homologues form more open structures. Intermediate sized atoms can accommodate either the open or closed forms as discussed for the germanium–cobalt compounds. This argument breaks down with some of the heavier elements as will be seen shortly.

This size argument may be important in the observation that the butterfly type structures **N** and **O** are known only for elements of the first row i.e. the borides, carbides, nitrides and oxides. The one silicon compound which has been characterized by X-ray diffraction shows a $M_3(\mu_3\text{-}EM)$ geometry (type **M**) as do several GeM_4 complexes (see Table IV). Indeed the μ_3-E geometry is perhaps the most prevalent bonding mode for main group elements attached to transition metal clusters for elements of any size. Metal–metal bond formation is not precluded for the compounds containing larger main group elements such as $[PbFe_4(CO)_{16}]^{2-}$,[19] $PbFe_4(CO)_{16}$,[40] $[BiFe_3(CO)_{10}]^{-}$,[64] $H_3BiFe_3(CO)_9$,[65] $BiFe_3(CO)_9(\mu_3\text{-}COMe)$,[65] etc. which have been structurally characterized since Schmid's review was published. In the Bi compounds the presence of bridging ligands may help to stabilize the more closed configurations.

3.4 Basicity of μ_3-E Main Group Atoms Incorporated into Transition Metal Clusters

The μ_3-E atom may be bonded to any external one-electron group such as halide, alkyl or aryl or it may possess a lone pair of electrons which may be donated to an external transition naked μ_3-E clusters have been reported for groups 13 or 14, while the heavier group 15 atoms can adopt this configuration as can all of the group 16 elements. For the group 15 examples, the tendency to form the naked μ_3-E atoms may be related to the basicity of the lone pairs on the main group atom which becomes more diffuse and less basic as one goes down the periodic table. Thus, examples of nitride-like atoms in clusters have a four coordinate nitrogen atom either in a butterfly or $(\mu_3\text{-}NR)M_3$ configuration. Three examples of a T-shaped $(\mu_3\text{-}N)M_3$ structural type are known but are proposed to be stabilized by π-bonding between the nitrogen and the two trans metal atoms.[95,285,286] Descending to phosphorus one finds two compounds which have the naked μ_3-P group. One is the highly reactive $PCo_3(CO)_9$ which very readily acts as a ligand to other transition metal groups such as $Fe(CO)_4$.[287,288] If no transition metal is available to complex the lone pair on phosphorus, then the molecule undergoes cyclic trimerization by displacement of CO to give $[PCo_3(CO)_8]_3$ in which each phosphorus coordinates to the cobalt of an external Co_3 triangle. More recently, a sterically protected μ_3-P group has been characterized in $Fe_3(CO)_6\{P(O\text{–}{}^{i}C_3H_7)_3\}_3(\mu_3\text{-}PMn(CO)_2Cp)(\mu_3\text{-}P)$.[28] For arsenic, μ_3-AsR, μ_3-AsM and μ_3-As are known. The compound $Co_3(CO)_9As$ also undergoes cyclic trimerization to give $[Co_3(CO)_8As]_3$.[288] Very few antimony compounds are known, but in two the antimony atoms are four coordinate. These include the double spiro cluster $Sb_2Fe_6(CO)_{22}$[30] and $[Et_4N][Fe_3(CO)_{10}\{\mu_3\text{-}SbFe(CO)_4\}]$.[61] In the latter the antimony atom functions as a donor ligand to a fourth metal atom. For bismuth the lone pair is only observed to donate to an external M unit when the cluster has a 2- charge or greater. Thus the only examples of bismuth in an iron cluster acting as a donor ligand to a fourth metal center are $[Bi\{Fe(CO)_4\}_4]^{3-}$,[12] $[Bi_2Fe_4(CO)_{13}]^{2-}$[221] and $[Bi_4Fe_4(CO)_{13}]^{2-}$.[289,290] Except for $MeBi\{W(CO)_5\}\{W_2(CO)_8Bi_2\}$,[18] μ_3-BiR (R = halide, alkyl, aryl) fragments have not been observed coordinated to transition metals.

The non-observance of naked μ_3-C or μ_3-N on a closed triangle of metal atoms does not preclude their involvement as intermediates in the reactions of more encapsulated geometries. One can envision an equilibrium process as shown below.



(29)

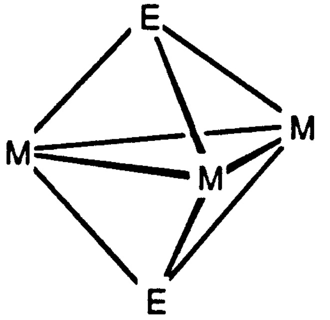
Calculations on the butterfly configuration of the carbide cluster suggest a high charge exists at carbon but the available reactive molecular orbitals are metal centered.[291,292] The reaction of MeI with $[Fe_4(CO)_{12}C]^{2-}$ gives an acyl group bonded to the carbide atom, $[Fe_4(CO)_{12}CC(O)Me]^-$, which may imply initial attack at the metal center followed by CO insertion and acyl migration; however, if $MeSO_3CF_3$ is used instead, the product is the tetrahedral $[Fe_4(CO)_{12}(\mu_3\text{-}CMe)]^-$ in which alkylation of the carbide has occurred.[293] Two reaction pathways, one involving metal attack in the butterfly and the other involving attack at the μ_3-C group of the tetrahedral form, could explain this difference in reactivity. The μ_3-C would be expected to be extremely basic as it would be formally a carbanion. The rapid interconversion between butterfly and tetrahedral geometries has recently been documented by Shriver and coworkers for $[HFe_4(CO)_{13}]^-$, the first known butterfly cluster.[29] Molecular mechanics calculations have been carried out on the strain induced by various types of groups attached to the carbido carbon in the tetra-iron butterfly series, $Fe_4(CO)_{12}(CR)$.[295] Orientation of the R group to minimize nonbonding repulsions to the carbonyls was found to be important. That paper, however, used only a fixed metal core and CO ligand geometry which is not reasonable considering real situations since it has been shown that carbonyl reorganization and metal framework motions are relatively low energy processes. The effect of metal reorganization on the strain energy induced by direct attack of CH_3^+ and $AuPPh_3^+$ has been probed.[296] Small changes in the framework structure were found to lower significantly the nonbonding repulsion energy.

An additional structural type has been reported for some M_3N clusters shown as I.[94,285] Instead of having a μ_3-E group on a triangle of metal atoms, they possess a T-shaped configuration. Structurally this unit can be viewed as a fragment of an M_4E butterfly cluster. Calculations suggest that π-bonding of the main group atom to the metals which are trans to each other is important in stabilizing this structure.

3.5 Electron Counting and Structural Relationships in Clusters Containing Main Group Elements

With increasing numbers of metal-metal bonds, complexes become more and more universally categorized as cluster compounds. Main group element fragments are readily involved in cluster bonding and many of the observed compounds obey classical counting rules such as the EAN rule or Wade's rules. The number of electrons which can be contributed to the cluster by a main group atom fragment can vary depending on the presence of substituents on the main group atom. In general, the main group elements will have one external pair of electrons which are not part of the cluster count, unless the atom is interstitial in which case all of its electrons are contributed. The external electrons may be present as a "naked" lone pair, a lone pair complexed to an external metal center, or a covalent pair made of one electron from the main group atom plus one electron from some one electron group such as halogen, alkyl, aryl or metal fragment (e.g. $Co(CO)_4$, $Mn(CO)_5$, etc.) Thus naked group 13 atoms would be expected to donate one electron to the cluster count, group 14 atoms would contribute 2, group 15 three and group 16 four. The number of electrons donated obviously does not change if the lone pair is simply complexed to some external metal acceptor, usually a 16 electron metal fragment such as $Fe(CO)_4$ or $Cr(CO)_5$. External bonds to groups such as halide, alkyl, aryl or 17 electron metal fragments will, however, increase the donation by one electron. Thus a CR fragment provides three electrons, an NR four electrons, etc.

The four vertex, tetrahedral clusters can have the full range of stoichiometries for main group/transition metal content. Thus clusters range from M_4, through M_3E, M_2E_2, and ME_3 to E_4. These clusters generally possess six skeletal electron pairs which is consistent with edge-localized bonding (a tetrahedron has six edges) or with treatment of the cluster as a nido trigonal bipyramid (six skeletal pairs, five vertex cluster with one vertex missing). Trigonal bipyramidal E_2M_3 clusters such as $As_2Fe_3(CO)_9$ and $Bi_2Fe_3(CO)_9$ have the same observed numbers of skeletal electron pairs.



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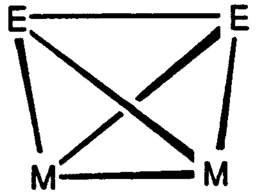

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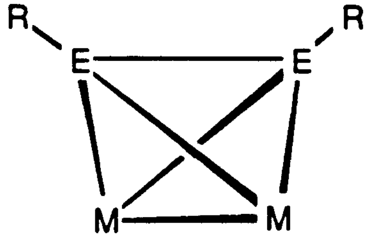

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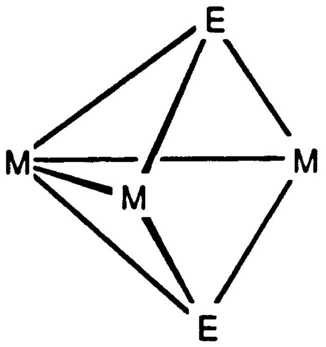

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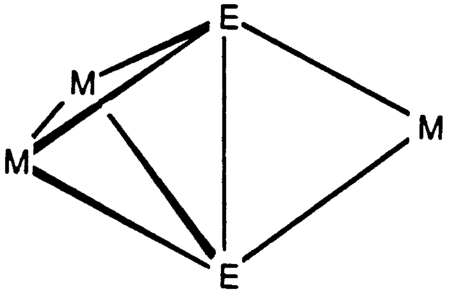


T

Alternatively, one can count cluster valence electrons. By this approach tetrahedral M_4 clusters are expected to have 60 electrons, EM_3 (**K**, **L**, or **M**) or E_2M_3 (**P**) to have 48 electrons and E_2M_2 clusters (**Q**, **R**) 34 electrons. All the simple EM_3 complexes listed in Table III have 48 cluster valence electrons. As an example, consider $Co_3(CO)_9\{SiCo(CO)_4\}$. The three cobalt atoms donate nine electrons each, each CO donates two and the $SiCo(CO)_4$ fragment is a three electron donor for a total count of 48 electrons. Likewise the electron count of $As_2Fe_3(CO)_9$ is 48 electrons and a *closo*-trigonal bipyramidal geometry is observed. Other examples are given in the first part of Table X. Changing the electron count to 50 by converting the three electron donor As's into AsPh's (four electron donors) causes the disruption of one Fe–Fe bond resulting in a square pyramidal geometry (**S**). The number of skeletal pairs is now seven, so it could be considered as a *nido*-cluster with one vertex missing from a parent octahedron. Examples of structurally characterized molecules of this type are given in the second part of Table X.

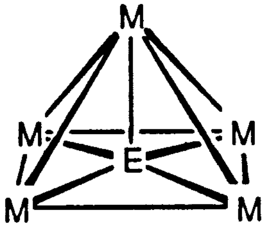
Addition of one more pair of electrons to E_2M_3 clusters might be expected to break yet another M–M (or E–M) bond. The molecules so formed deviate somewhat yielding structures similar to what is expected except that there is significant interaction postulated between the main group atoms (**T**). The electron counts derived in the above manner are consistent with the presence of only one M–M bond but do not account for the E–E bonding. If one takes a different view, however, in which these clusters are seen as M_2E_2 tetrahedra with the extra bridging metal functioning as an acceptor or donor, depending on the situation, then the electron counting agrees with the geometry. Thus, $[Bi_2Fe_2(CO)_6\{\mu\text{-}Co(CO)_4\}]^-$ has six skeletal pairs if the $[Co(CO)_4]^-$ fragment is considered as a simple two electron donor to the cluster core.[221] The Bi–Bi distance is 3.092Å which is comparable to other Bi–Bi single bond distances. The distances between Te atoms in the complexes synthesized by Rauchfuss and coworkers are about the same but indicative of a bond order of *ca.* two-thirds.[92]

More encapsulated structures are observed for M_4E, M_5E and M_6E stoichiometries. The accessibility of the main group atom for doing chemistry is inhibited by being surrounded by metals but this is not quite so severe as once believed, and the lower nuclearity butterfly complexes have been shown to have an extensive chemistry. All of these structures have a demonstrated importance for only the first row main group elements of boron, carbon, nitrogen and oxygen. Larger main group elements are evidently too large to exist in the required cavities. The best structurally documented example is $[PCo_6(CO)_{16}]^-$ where the six metals can be viewed as being splayed open from a distorted octahedron or trigonal prism by the size of the P atom.[297] In the M_4E, M_5E and M_6E clusters, the main group is most often considered interstitial and consequently donates all of its electrons to the cluster valence electron count (see Tables V, VI and VIII).

The butterfly geometry has become a very well established structural prototype for iron, ruthenium and osmium. Some mixed metal complexes have been obtained by vertex substitution and by addition of metal fragments to the iron ketenylidene compound $[Fe_3(CO)_9(CCO)]^{2-}$.[102] Structural data for a number of them are given in Table V. These clusters have 62 cluster valence electrons which is two more than the corresponding tetrahedral species. They possess seven skeletal electron pairs, making them most appropriately viewed as *arachno*-octahedral compounds. This is chemically reasonable since they can be derived from the parent $[Fe_6(CO)_{16}C]^{2-}$ cluster by a series of vertex elimination reactions.

Interconversion of tetrahedral↔butterfly structures depending on the ability of a ligand to adopt either a two or four electron donating configuration is now well-documented and equilibria between the two forms may be very important in the chemistry of these molecules (eqn 29). Two exceptions to this counting formalism are $[Fe_4(CO)_{12}CC(O)OCH_3]^-$ [95] and $[Fe_4(CO)_{12}C{=}C(OCH_3)_2]$[96] which possess only 60 electrons but do not adopt a tetrahedral configuration. At first glance, they are still butterfly arrangements although somewhat distorted. The structural parameters are such that the carbide atoms are much more prominent and can be considered as cluster vertices. This is most apparent from the wingtip Fe–C–wingtip Fe angles which are 148° and 149° for these two exceptions, while for the other iron butterfly carbides and nitrides those angles are more nearly linear, ranging from 170° to 179°. The two 60-electron clusters can be viewed as trigonal bipyramids having six skeletal electron pairs with the iron-iron distances in these two examples notably shorter (*ca.* 0.1Å) than those observed in the 62-electron molecules. The subtle electronic factors influencing the adoption of this geometry rather than a tetrahedral one are not clearly understood. A butterfly oxide cluster has recently been synthesized starting from $[Fe_3(CO)_9(\mu_3\text{-}O)]^{2-}$.[298] It is $[PPN][Fe_3Mn(CO)_{12}O]$ generated when the iron oxo cluster is treated with $[Mn(CO)_3(NCMe)_3]PF_6$.

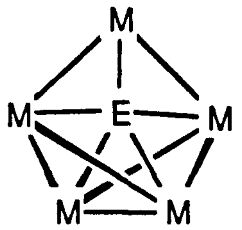
Two independent molecular orbital studies on the Fe_4C clusters have been reported and show similar results which attempt to explain the reactivity of this series of compounds.[291,292] One important aspect of the bonding appears to be the ability of the carbide to π-bond to the wing-tip metals. Reactivity tends to be greater when the $\text{metal}_{\text{wingtip}}\text{–C–metal}_{\text{wingtip}}$ angle deviates from 180°, a situation that tends to disrupt the M–C–M π-bonding overlap. A high negative charge is found at carbon, but the chemistry appears to be directed more by the HOMO and LUMO which are not centered at carbon but rather on the metals. An anomaly to this predicted behaviour is the reaction of $[Fe_4(CO)_{12}C]^{2-}$ with $MeSO_3CF_3$ which has already been discussed in the section on the basicity of μ_3-E main group atoms.[293]



U

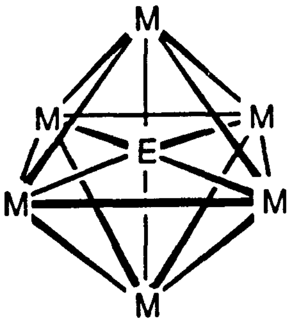
Clusters of the next higher nuclearity series, M_5E, often adopt a square pyramidal configuration of metal atoms with the main group element sitting in the center of the square base, structure type **U**, having seven skeletal pairs and are considered to be *nido*-octahedral molecules. Structural data are given in Table VI for the known carbides and nitrides. One interesting feature of these clusters is the position of the main group atom which generally sits slightly below the square of metal atoms away from the apical metal. How far below the plane it sits appears to be sensitive to charge effects. Thus substituted or reduced clusters which are expected to have a higher electron density concentrated at the metal centers show a significant movement of the main group atom farther away from the square base. Thus the carbide lies 0.09Å below the square base in $Fe_5(CO)_{15}C$ but 0.18Å below it in $[Fe_5(CO)_{14}C]^{2-}$. The corresponding osmium complexes show distances of 0.12Å and 0.21Å, respectively. For the series of compounds $Ru_5(CO)_{15-x}(PPh_3)_xC$ the values are 0.11Å for x = 0, 0.19Å for x = 1 and 0.23Å for x = 2.

Metal–nitride stretching frequencies for a series of the butterfly clusters $M_4(CO)_{12}(\mu\text{-}L)$ N where M = Ru, L = H, NCO, NO; M = Os, L = H have been reported[299] and range from 591 cm^{-1} to 863 cm^{-1}. Assignments made for $[Co_6(CO)_{15}N]^-$ (698 cm^{-1}(e′), 722(a$_2''$)) and for $[Rh_6(CO)_{15}N]^-$ (622(e″), 645 (a$_2'$)) fall in the same region.[300] An infrared spectroscopic analysis of three isostructural square pyramidal compounds—$Fe_5(CO)_{15}C$, $Ru_5(CO)_{15}C$ and $Os_5(CO)_{15}C$—has been done.[301] For $Fe_5(CO)_{15}C$, two Fe-carbide stretching frequencies have been observed at 790 cm^{-1} and 770 cm^{-1} in cyclohexane. For KBr disks, the following data have been reported (cm^{-1}): $Fe_5(CO)_{15}C$, Fe-C$_{str}$; 805vs, 775sh, 766s; $Ru_5(CO)_{15}C$, Ru-C$_{str}$: 757s, 738s, 730vs; $Os_5(CO)_{15}C$, OS-C$_{str}$: 793s, 769vs, 757s. The presence of an extra strong M–C stretch for Ru and Os is thought to arise from the presence of two crystallographically distinct molecules in the solid state. What is unexpected is that the ordering of M-C frequencies is Fe > Os > Ru. This is believed to arise because of the opposing nature of the effect of the M–C$_{str}$ force constant (k_{M-C}) and the effect of the mass of M. A steady increase in k_{M-C} with metal mass is obtained from the data. These values can be compared to the Co–C stretching frequencies found for $Co_6(CO)_{12}(\mu_3\text{-}S)_2C$: 819 cm^{-1} (A$_2''$) and 535.5 cm^{-1} (E′).[302] Assignments have also been made for $[Co_6(CO)_{15}C]^{2-}$ (719 (e′), 722 (a$_2''$)) and for $[Rh(CO)_{15}C]^{2-}$ (653 (e′), 689 (a$_2''$)).[300]

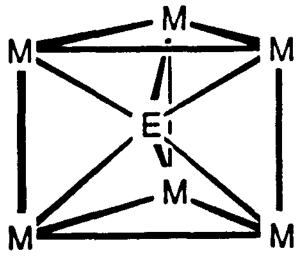


V

Addition of two electrons to a square pyramidal cluster may be expected to result in breakage of a M–M bond and this is exactly the reactivity observed for a number of the carbido clusters mentioned in Table VI. The resultant structure is known as a "bridged-butterfly" and is illustrated as **V** with structural data for known compounds given in Table V. It is obvious from looking at the molecules that they contain a rather normal looking butterfly unit to which another metal has been added to the main group atom and is also connected to the wing-tip metals. This structural type is an apparently important, logical intermediate in the conversion of the hexanuclear iron carbide dianion $[Fe_6(CO)_{16}C]^{2-}$ to $[Fe_4(CO)_{12}CC(O)CH_3]^{2-}$.



W



X

Structural data for clusters containing carbide and nitride atoms in octahedral or trigonal prismatic M_6E cavities are listed in Table VIII (**W**, **X**). It is interesting to note that these two very common structural types are the basic building blocks of the solid phase metal carbides represented by NbC (octahedral cavities about C) and WC (trigonal prismatic cavities about C). Calculations relating the discrete molecular clusters to the solid phases have been reported and apparently the metal–metal bonding situation is key in determining the geometry of these complexes. The metal–carbon bonding is very strong and lies well under the M–M bonding orbitals in energy. In both discrete clusters and the solid phases the addition of the carbide atom has the effect of increasing the size of the HOMO–LUMO gap relative to the non-carbide-containing metal fragments.[303]

Simple M_6E clusters with the trigonal prismatic geometry are observed to possess nine pairs of skeletal electrons which is sufficient for localized edge-bonding. Octahedral clusters would require twelve skeletal pairs for localized edge bonding which is clearly many more than observed. Wade's rules for *closo* clusters, a delocalized bonding approach, predicts that the number of skeletal bond pairs should be equal to $N + 1$ ($N =$ the number of vertices) and this is observed. Substantiating the electron counting formalisms developed to date is the observation that the M_6C cobalt–carbide can adopt either configuration by reversible addition/elimination of CO.[184]

$$\underset{\text{trigonal prismatic}}{[Co_6(CO)_{15}C]^{2-}} \rightleftharpoons \underset{\text{octahedral}}{[Co_6(CO)_{13}C]^{2-}} + 2CO \qquad (30)$$

The higher nuclearity clusters can be derived by similar electron counting procedures. Thus $[Os_{10}(CO)_{24}C]^{2-}$ can be thought of as a derivative of octahedral $[Os_6(CO)_{16}C]^{2-}$ in which four carbonyls are replaced with four $Os(CO)_3$ units which are also two electron donor groups. This gives $[Os_6(CO)_{12}\{\mu_3\text{-}Os(CO)_3\}_4C]^{2-}$ which is the observed structure. Similarly, $[Re_7(CO)_{21}C]^{3-}$ can be built up from a hypothetical octahedral parent $[Re_6(CO)_{19}C]^{2-}$ by replacement of a CO with a two electron donor $\{Re(CO)_3\}^-$ fragment. Trigonal prismatic clusters behave similarly. Thus, $Rh_8(CO)_{19}C$ can be viewed as $Rh_6(CO)_{16}C$ in which one carbonyl has been replaced by 2 one-electron donating $Rh(CO)_2$ moieties. This approach breaks down for $[Os_{11}(CO)_{27}(CuNCCH_3)C]^-$ which does not fit nicely into Wade's rules but does appear to obey the EAN rule overall.

4. SYNTHESIS AND CHEMISTRY OF CLUSTERS CONTAINING A μ_3-E MOIETY ATTACHED TO A CLOSED TRIANGLE OF METAL ATOMS

4.1 The First Row: Boron, Carbon, Nitrogen and Oxygen

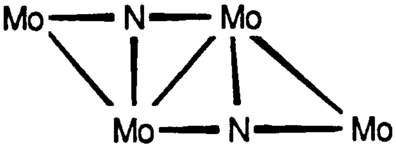
4.1.1 Boron: From the reaction of $[Fe(CO)_4\{C(=O)CH_3\}]^-$ with two equivalents of $BH_3{\cdot}THF$ and two equivalents of $Fe(CO)_5$, a series of clusters can be obtained including $(\mu\text{-H})Fe_3(CO)_9(BH_2)$, $[PPN][Fe_3(CO)_9(\mu\text{-CO})(BH_2)]$, $[PPN][Fe_3(CO)_9(BH_4)]$ and $(\mu\text{-H})Fe_3(CO)_9(BH_4)$.[304] As is obvious from the structural and spectroscopic data on these molecules, boron exhibits a high tendency to form multicenter electron deficient bonds just as it does in the boron clusters. A related M_3B cluster has been isolated from the reaction of $H_2Os_3(CO)_{10}$ and $BH_3{\cdot}NEt_3$ in

CH_2Cl_2 and has the formula $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-BCO})$.[36] The boron atom in this molecule exhibits transition metal-like vertex reactivity in that the CO can be replaced by PPh_3 in a simple substitution process, which is very similar to the reactivity patterns seen for the analogous carbon-based ketenylidene cluster $[Fe_3(CO)_9(\mu_3\text{-CCO})]^{2-}$. The reaction of BBr_3 with $[Co(CO)_4]^-$ in the presence of stoichiometric amounts of triethylamine yields the isoelectronic $Co_3(CO)_9\{\mu\text{-BNEt}_3\}$.[305]

4.1.2 Carbon: Many complexes of the type $M_3L_n(\mu_3\text{-CR})$ have been prepared since the first was synthesized in 1958.[306] We will make no attempt to review this particular compound type since the volume of data available would constitute a review article in itself. It should be noted that the synthetic methods for obtaining compounds of that type are well-known at this time and these complexes exhibit many of the same types of chemistry seen for other μ_3-E type clusters. For example, they undergo metal substitution reactions to give mixed metal species.

4.1.3 Nitrogen: Complexes containing the μ_3-NR unit are also documented but they are not as common as the alkylidyne clusters. A low yield of $Fe_3(CO)_{10}(\mu_3\text{-NH})$ was reported as one of several products that resulted upon protonation of reaction mixtures of $Na[Fe(CO)_3(NO)]$ and $Fe_3(CO)_{12}$.[103] Higher nuclearity nitride clusters were also produced in that reaction. Treatment of nitro and azo compounds with $Fe_3(CO)_{12}$ at elevated temperatures produces the isoelectronic molecules $Fe_3(CO)_{10}(NR)$ (R = Et,[304] $SiMe_3$).[308] X-ray analysis of the R = $SiMe_3$ complex[47] has been reported and that compound reacts with H_2 upon photolysis replacing the μ_3-CO to give $(\mu\text{-H})_2Fe_3(CO)_9(\mu_3\text{-NSiMe}_3)$.[309] This cluster has been reported to catalyze the photochemical hydrogenation of olefins and dienes.[309]

We have already mentioned that a few compounds containing a naked nitrogen atom bonded to only three metals do not adopt the $(\mu_3\text{-N})M_3$ geometry where the M_3 portion is a closed triangle. Instead, a T-shaped geometry is observed in which the ability of the nitrogen to π-bond to the metals may be the driving force for stabilizing this configuration. Such molecules include $Cp_3Mo_3(CO)_4(O)(\mu_3\text{-N})$,[285] $(C_5Me_5)_3Mo_3(CO)_4(O)(\mu_3\text{-N})$.[286] This first was obtained in only *ca.* 0.5% yield from the reaction of $Cp_2Mo_2(CO)_4$ with ethyldiazoacetate while the second is formed from the reaction of $(C_5Me_5)_2Mo_2(CO)_4$ with nitrosyl-containing molecules. The other known molecule having this general structural feature is $Mo_4(O\text{-}^i\text{Pr})_{12}(\mu_3\text{-N})_2$ obtained from the reaction of $(^t\text{Bu-O})_3MoN$ and $Mo_2(O\text{-}^i\text{Pr})_6$.[94] This planar array of metals and nitrogen atoms contains two T-shaped NMo_3 groups which share a common Mo–Mo edge, **Y**.



Y

Clusters of the general formula $Fe_3(CO)_9\{\mu_3\text{-NR}\}_2$ are known but are different from the molecules discussed above in that the iron triangle is not closed.[239] The geometry is perhaps better described as a square pyramid with the NR groups occupying trans basal sites. The loss of an Fe–Fe bond is due to the presence of an extra pair of electrons giving a 50 e count whereas the closed clusters of E_2M_3

structure have only 48 e's. The R = Me complex has been structurally characterized.[239]

Ruthenium complexes containing a μ_3-NR group include $Ru_3(CO)_{10}(\mu_3\text{-}NOMe)$[45] and $Ru_3(CO)_7(C_6H_6)(\mu_3\text{-}NPh)$.[46] The first of these arises from alkylation of $[Ru_3(CO)_{10}(NO)]^-$ while the second obtains from $PhNO_2$ and $Ru_3(CO)_{12}$ in the presence of $Co_2(CO)_8$ with benzene as solvent. Similar reactions with $Fe_3(CO)_{12}$ yield $FeCo_2(CO)_9(NPh)$. These reactions are typical of main group element deoxygenation reactions mentioned earlier.

Osmium complexes containing a μ_3-NR function have been reported.[50,310] Aniline and $Os_3(CO)_{12}$ yield $(\mu\text{-}H)_2Os_3(CO)_9(\mu_3\text{-}NPh)$.[310] The other established route to these complexes is the reaction of $H_2Os_3(CO)_{10}$ with organic azides and proceeds through the intermediacy of $HOs_3(CO)_{10}(HN_3R)$ complexes which upon thermolysis eliminate N_2 and CO.[50]

4.1.4 Oxygen: Oxygen is also known to adopt a μ_3 geometry in a number of low valent transition metal complexes. These complexes include $[Et_4N][H_3Re_3(CO)_9(\mu_3\text{-}O)]$,[65] $[Me_3NCH_2Ph][Fe_3(CO)_9(\mu_3\text{-}O)]$,[66] $Ru_3(CO)_6\{Ph_2AsCH_2CH_2AsPh_2\}_2(\mu_3\text{-}O)$[67] and $Os_6(CO)_{19}(\mu_3\text{-}O)$.[68] All except the rhenium compound, for which the origin of the oxygen atom has not been studied, are generated from the reaction of molecular O_2 with the appropriate metal carbonyl cluster. Alkylation of the oxide in the iron compound is reported to produce $[Fe_3(CO)_9(\mu_3\text{-}OR)]^-$ but details have not yet appeared.

4.2 *μ_3-E Clusters of the Larger Main Group Elements*

4.2.1 Group 13: Reports of $AlCo_3(CO)_{12}$[311] and $GaCo_3(CO)_{12}$[312] from the reactions of the main group trichlorides and $[Co(CO)_4]^-$ have been made but the compounds are not structurally characterized and perhaps a bit dubious. If they do exist with pyramidal main group elements as proposed, then they will almost certainly have some donor group coordinated to the main group atom. On the other hand planar EM_3 type structures with no Co–Co bonds are a reasonable alternative to the pyramidal structures suggested for these molecules. Attempts in our laboratories to reproduce the aluminium reaction have not yet been successful.

The only structurally characterized group 13 compound in which one of the heavier main group atoms adopts a μ_3 geometry is $Re_4(CO)_{12}\{InRe(CO)_5\}_4$ in which the four $InRe(CO)_5$ groups cap four faces of a Re tetrahedron.[37] It was obtained along with $Re_2(CO)_8\{\mu\text{-}InRe(CO)_5\}_2$ by the reaction of In metal with $Re_2(CO)_{10}$ in xylene at 220–230° C (bomb reaction, 41% yield). At lower temperatures (175–185° C) only $Re_2(CO)_8\{InRe(CO)_5\}_2$ was observed. The analogous Ga compound $Re_4(CO)_{12}\{GaRe(CO)_5\}_4$ has been synthesized but not structurally characterized.[313] It arises from the reaction of gallium halides and $Re_2(CO)_{10}$. An intermediate is $Re_2(CO)_8\{\mu\text{-}GaRe(CO)_5\}_2$ which is converted to $Re_4(CO)_{12}\{GaRe(CO)_5\}_4$ at 300° C.

4.2.2 Group 14: One example of a μ_3-Si complex has been reported and it arises from the reaction of SiI_4 with $[Co(CO)_4]^-$.[38] The product is $Co_3(CO)_9\{\mu_3\text{-}SiCo(CO)_4\}$ and has been characterized by X-ray analysis. Silicon, as a number of other main group atoms, poses certain synthetic problems since it has a strong tendency to bind to oxygen and interactions with carbonyl ligands may complicate desired metal-centered reactions.

Clusters containing the $Co_3(\mu_3\text{-}SiR)$ function are also known but they do not appear suitable to metal substitution reactions as observed for a number of other

μ_3-E clusters.[312] Mixed metal silylidene clusters can be obtained, however, from the reaction of $L_nM{-}SiRH_2$ complexes ($L_nM = Cp(CO)_3Mo$, $Cp(CO)_3W$, $Cp(CO)_2Fe$) with $Co_2(CO)_8$. In some cases complexes with only one metal–metal bond were formed initially but these yielded closed $M_3(\mu_3\text{-}E)$ geometries upon thermolysis.

One of the major methods of creating μ_3-GeM_3 clusters is via ionic displacement reactions. Thus, GeI_2 when treated with $[Fe_2(CO)_8]^{2-}$ yields $[Fe_3(CO)_{10}\{\mu_3\text{-}GeFe(CO)_4\}]^{2-}$.[39] Similarly, reaction of $GeCl_4$ with $[Co(CO)_4]^-$ gives $Co_3(CO)_9\{\mu_3\text{-}GeCo(CO)_4\}$.[280] Both of these compounds are of similar structure to $Co_3(CO)_9\{\mu_3\text{-}SiCo(CO)_4\}$ except that the iron complex contains an added μ_3-CO ligand. Similarly $K[Co(CO)_4]$ and organogermanium trihalides react to produce $Co_3(CO)_9\{\mu_3\text{-}GeR\}$ complexes where R = Me, Ph or ^{t}Bu.[41]

Germanium diiodide will insert into the metal–metal bonds of $\{CpFe(CO)_2\}_2$, $Co_2(CO)_8$ or $\{CpNiCO\}_2$ giving L_2GeI_2 where $L = CpFe(CO)_2, Co(CO)_4$ or CpNiCO.[41] These complexes can in turn be converted into the μ_3-GeM_3 species bytreatment with $[Co(CO)_4]^-$. The complexes $Co_3(CO)_9\{\mu_3\text{-}GeML_n\}$ where $ML_n = CpFe(CO)_2, Co(CO)_4$ or CpNiCO have been prepared.

Germanium hydrides can be employed to produce *closo* GeM_3 clusters as evidenced by the reaction of $Mn(CO)_5GeH_3$ with $Co_2(CO)_8$ giving $Co_3(CO)_9\{\mu_3\text{-}GeMn(CO)_5\}$[281] and reaction of $PhGeH_3$ with $Co_2(CO)_8$ making $PhGe\text{-}Co_3(CO)_{11}$.[15]

Other mixed-metal μ_3-GeM_3 compounds can be generated from the above-mentioned compounds by metal substitution reactions.[40] Thus, reaction of $Co_3(CO)_9(\mu_3\text{-}GeR)$ (R = Me, Ph or ^{t}Bu) with $\{CpMo(CO)_3\}_2$, $\{CpW(CO)_3\}_2$ or $Na_2[Fe(CO)_4]$ results in formation of $CpMoCo_2(CO)_8\{\mu_3\text{-}GeR\}$, $CpWCo_2(CO)_8\{\mu_3\text{-}GeR\}$ or $(\mu_3\text{-}H)FeCo_2(CO)_9\{\mu_3\text{-}GeR\}$, respectively. Further, metal substitution reactions are reported for the product $CpMCo_2(CO)_8(\mu_3\text{-}Ge^tBu\}$ (M = Mo, W) which produce $Cp_2Mo_2Co(CO)_7\{\mu_3\text{-}Ge^tBu\}$, $Cp_2MoWCo(CO)_7\{\mu_3\text{-}Ge^tBu\}$, $Cp_2MoCoNi(CO)_5\{\mu_3\text{-}Ge^tBu\}$, and $(\mu_3\text{-}H)CpMoFeCo(CO)_8\{\mu_3\text{-}Ge^tBu\}$. The anion $[Mn(CO)_5]^-$ has been reported to displace the external $Co(CO)_4$ fragment in $Co_3(CO)_9\{\mu_3\text{-}GeCo(CO)_4\}$ giving $Co_3(CO)_9\{\mu_3\text{-}GeMn(CO)_5$.[281] The tetrametal germanium complexes $Co_3(CO)_9\{\mu_3\text{-}GeML_n\}$ ($ML_n = CpMo(CO)_3$, $CpW(CO)_3$ or $CpFe(CO)_2$) undergo metal substitution reactions giving $CpMoCo_2(CO)_8\{\mu_3\text{-}GeML_n\}$.

$$Mn(CO)_5GeH_3 + 1.5\ Co_2(CO)_8 \rightarrow 1.5H_2 + 3CO + Co_3(CO)_9\{\mu\text{-}GeMn(CO)_5\} \qquad (31)^{281}$$

$$X_3GeR + 3K[Co(CO)_4] \rightarrow Co_3(CO)_9\{\mu_3\text{-}GeR\} + 3CO + 3KX \qquad (32)^{41}$$

Structural data are available for $[Et_4N]_2[Fe_3(CO)_9(\mu_3\text{-}CO)\{\mu_3\text{-}GeFe(\mu_3CO)_4\}]$,[39] $(\mu_3\text{-}H)CpMoCoFe(CO)_8\{\mu_3\text{-}Ge^tBu\}$,[40] $CpMoCo_2(CO)_8(\mu_3\text{-}GeW(CO)_3Cp\}$[40] and $Co_3(CO)_9\{\mu_3\text{-}GeFe(CO)_2Cp\}$[41] with pertinent structural parameters collected in Table IV.

Addition of ligands to the closed $Co_3(CO)_9\{\mu_3\text{-}GeR\}$ clusters opens two of the metal–metal bonds.[279] The products are $\{Co_2(CO)_5(\mu\text{-}CO)PPh_3\}\{Co(CO)_3PPh_3\}GeR$ (R = Me, Ph), but subsequent loss of CO generates the disubstituted closed compounds $Co_3(CO)_7(PPh_3)_2\{\mu_3\text{-}GeR\}$ in the case of R = ^{t}Bu. The nature of the added ligands can be complex and includes things such as $CpM(CO)_3AsMe_2$ (M = Cr, Mo, W).

No simple μ_3-SnM_3 or μ_3-PbM_3 complexes have been reported; however, a couple of $(\mu_3\text{-Sn})_2M_3$ complexes are known. Thermal decomposition of $\{\eta^1\text{-CpSnFe(CO)}_4\}_2$ gives $Fe_3(CO)_9\{\mu_3\text{-SnFe(CO)}_2Cp\}_2$ which is degraded by Br_2 to $CpFe(CO)_2Br$ and $SnBr_4$.[235] Clusters of a completely different type giving $(\mu_3\text{-Sn})_2M_3$ cores are observed when $SnCl_2$ and $PtCl_2$ are dissolved in dilute HCl.[236,315] The products are $[Pt_3(SnCl_3)_3(\mu_3\text{-SnCl})_2]^{4-}$ and $Pt_3(C_8H_{12})_3(\mu_3\text{-SnCl}_3)_2$. The latter complex is obtained from the former upon treating it with 1,5-cyclooctadiene. The structure of the cyclooctadiene derivative has been confirmed by X-ray analysis.[236]

4.2.3 Group 15: Several molecules containing a single μ_3-P group attached to aclosed triangle of metal atoms are known. Among these is $Re_5(CO)_{14}(\mu_4\text{-PMe})(\mu\text{-PMe}_2)\{\mu_3\text{-PRe(CO)}_5\}$ generated from the pyrolysis of $Re_4Cl_2(CO)_{15}\{\text{MePP(Me)PMe}\}$ in the presence of $Re_2(CO)_{10}$.[49] Also known is $[PPh_4][Fe_3(CO)_9(\mu\text{-CO})\{\mu_3\text{-PFe(CO)}_4\}]$ generated from the reaction of PCl_3 and $[Fe_4(CO)_{13}]^{2-}$.[51] The reactive $Co_3(CO)_9P$ has been generated from P_4 and $Co_2(CO)_8$, PI_3 and $Co_2(CO)_8$ or PX_3 (X = Cl, Br, I) and $[Co(CO)_4]^-$, but the complex undergoes cyclic trimerization by loss of CO to give $[Co_3(CO)_8(\mu_3\text{-P})]_3$.[287,288] In the presence of $Fe(CO)_4$ fragments the naked phosphorus complex can be trapped as $Co_3(CO)_9\{\mu_3\text{-PFe(CO)}_4\}$. The cluster $Co_3(CO)_9\{\mu_3\text{-PMn(CO)}_2Cp\}$ was produced similarly from the reaction of $CpMn(CO)_2(PX_3)$ with $Co_2(CO)_8$ and it undergoes simple substitution reactions with a variety of phosphorus donor ligands.[58]

A general route to mixed metal complexes begins with $Fe(CO)_4PRH_2$ (R = Me, ^{t}Bu, Ph) and makes use of the facile insertion of transition metals into P–H bonds. Reaction of the above complexes with $Co_2(CO)_8$ produces intermediate dinuclear bridging phosphido clusters $(\mu\text{-PRH})FeCo(CO)_7$, which react further with transitionmetal moieties to give μ_3-PR capped trimetal clusters.[316] These include $FeCo_2(CO)_9(\mu_3\text{-PR})$, $HFe_2Co(CO)_9(\mu_3\text{-PMe})$, $HFeRuCo(CO)_9(\mu_3\text{-PMe})$, $HFe_2Co(CO)_9(\mu_3\text{-P}^t\text{Bu})$ and $HRu_2Co(CO)_9(\mu_3\text{-PMe})$.

Other PRH_2 metal complexes used as precursors to clusters of this type include $CpMn(CO)_2(PPhH_2)$ which reacts with $Fe_3(CO)_{12}$ to give $CpMnFe_2(CO)_8(\mu_3\text{-PPh})$ and $Cr(CO)_5(PPhH_2)$ which reacts with $Fe_3(CO)_{12}$ producing $CrFe_2(CO)_{11}(\mu_3\text{-PR})$.[49] The activation of PH bonds is directly achieved by reaction of $Fe_3(CO)_{12}$ and PRH_2[49] and probably proceeds through a substitution process as demonstrated for some ruthenium and osmium clusters.[54,55,57]

Deprotonation of cluster hydrides by base followed by addition of other metal-complexes results in cluster building reactions. Thus addition of $[Rh(CO)_3(PEt_3)_2]BF_4$ to basic solutions of $(\mu\text{-H})_2Ru_3(CO)_9(\mu_3\text{-PPh})$ generates $(\mu\text{-H})Ru_3Rh(CO)_{10}(PEt_3)(\mu_3\text{-PPh})$ as the major product.[56] The $[HRu_3(CO)_9(\mu_3\text{-PPh})]^-$ anion so generated may also be treated with $[M(PEt_3)I]_4$ (M = Cu, Ag) or with $(Au(PR_3)_2]\,PF_6$ giving $(\mu\text{-H})Ru_3(MPR_3)(CO)_9(\mu_3\text{-PPh})$ clusters. The $Au(PMe_2Ph)$ derivative has been structurally characterized.[56]

Molecules with two μ_3-P or μ_3-PR functionalities are a bit more well-known. An entire series of such compounds has been obtained from the reaction of $L_nM \leftarrow PX_3$ (L_nM = $CpMn(CO)_2$, $Cr(CO)_5$, $Mo(CO)_5$, $W(CO)_5$) with $Fe_2(CO)_9$ and they have the general formula $Fe_3(CO)_9\{\mu_3\text{-PML}_n\}_2$.[28] These complexes exhibit closed trigonal bipyramidal geometries with the μ_3-P units capping opposite sides of the iron triangle and functioning as two-electron-donor ligands to the external metals. Several of these have been structurally characterized as shown in Table X. A more complicated cluster is observed in the case where ML_n = $CpMn(CO)_2$ and it has the formula $Fe_3(CO)_8\{\mu_3\text{-PMn(CO)}_2Cp\}\{\mu_3\text{-PFe}_2(CO)_8\}$. Like the other examples, both phosphorus atoms act as donors to external metals, but the Fe_2 fragment is further bound to the Fe_3 triangle.

$L_nM \leftarrow PX_3 + Fe_2(CO)_9 \rightarrow Fe_3(CO)_9\{\mu_3\text{-}PML_n\}_2$ *(33)*[28]
$(ML_n = CpMn(CO)_2, Cr(CO)_5, Mo(CO)_5, W(CO)_5)$

$(OC)_5CrPX_3 + Fe_2(CO)_9 \rightarrow Fe_3(CO)_9\{\mu_3\text{-}PCr(CO)_5\}\{\mu_3\text{-}PFe(CO)_4\}$ *(34)*[28]
$(X = Cl, Br)$

Another route to these clusters is the reaction of phosphinidene complexes $(L_nM)_2PX$ with $Na_2[Fe(CO)_4]$.[28] This approach also works for the production of arsinidene and stibinidene compounds.

$[(OC)_5Cr]_2PCl + Na_2[Fe(CO)_4] \rightarrow Fe_3(CO)_9\{\mu_3\text{-}PCr(CO)_5\}\{\mu_3\text{-}PFe(CO)_4\}$ *(35)*

These clusters undergo substitution reactions and for one compound displacement of a ML_n fragment has been observed resulting in a naked μ_3-P atom which is sterically protected by bulky phosphine ligands.[28]

$Fe_3(CO)_9\{\mu_3\text{-}PMn(CO)_2Cp\}_2 + P(^iPr)_3 \rightarrow$
$Fe_3(CO)_6\{P(^iPr)_3\}_3\{\mu_3\text{-}PMn(CO)_2Cp\}\{\mu_3\text{-}P\}$ *(36)*[28]

Triiron dodecacarbonyl reacts with $PPhH_2$ in refluxing toluene to give $Fe_3(CO)_9\{\mu_3\text{-}PPh\}_2$ which is isoelectronic and isostructural with the $Fe_3(CO)_9\{\mu_3\text{-}NR\}_2$ complexes.[240] This cluster has been the subject of an electrochemical study which shows that it undergoes facile one-electron reduction giving $Fe_3(CO)_9\{\mu_3\text{-}PPh\}_2^-$.[241] This chemistry gives rise to facile electron-transfer-catalyzed substitution reactions producing $Fe_3(CO)_{9-x}\{P(OMe)_3\}_x\{\mu_3\text{-}PPh\}_2$ (X = 1, 2, 3). The trisubstituted derivative has a phosphite attached to each iron atom.

Two different types of reactions have been used to prepare $Ru_3(\mu_3\text{-}P)$ complexes. The more general of these is the treatment of $Ru_3(CO)_{12}$ with PRH_2 and products have the general formula $H_2Ru_3(CO)_9(\mu_3\text{-}PR)$.[54,55] This route proceeds through the formation of the substituted complexes $Ru_3(CO)_{11}PRH_2$ which then undergo metal insertion into a PH bond to give $HRu_3(CO)_{10}(\mu\text{-}PRH)$. These bridging complexes are then converted into the $(\mu\text{-}H_2(Ru_3(CO)_9(\mu_3\text{-}PR)$ complexes. This is also true for osmium clusters of the same structural type.[57] More recently it has been shown that $(\mu\text{-}H)_2Ru_3(CO)_9(PH_2PCH_2PPh_2)$ reacts with H_2 producing $(\mu\text{-}H)_2Ru_3(CO)_8(PMePh_2)(\mu_3\text{-}PPh)$ where the PPh and $PMePh_2$ groups are derived from the $Ph_2PCH_2PPh_2$ ligand.[52] This cluster is a substituted version of $(\mu\text{-}H)_2Ru_3(CO)_9(\mu_3\text{-}PR)$. Substituted products can be obtained directly.[53]

The chemistry above can be extended to the production of "double clusters"—two clusters which are linked by a sigma bonding network. Clusters have the form $M_3P\text{–}R\text{–}PM_3$ and are generated from the phosphanes $X_2P\text{–}R\text{–}PX_2$ ($X = NEt_2$, Cl, H; $R = p\text{-}C_6H_4, 4,4'\text{-}C_6H_4\text{–}C_6H_4$). The M_3 groups so made include $Co_3(CO)_9$, $FeCo_2(CO)_9$, $HFe_2Co(CO)_9$ and $H_2Fe_3(CO)_9$. The hydrides in the last cluster could be replaced by $AuPPh_3$ groups.[317]

Arsenic atoms bridging three metals are found in a number of clusters. A single naked arsenic atom caps a closed triangle of molybdenum or tungsten atoms in the 48 e complexes $Cp_3M_3(CO)_6(\mu_3\text{-}As)$ (M = Mo, W).[59] The complexes are synthesized by the reaction of $[CpM(CO)_3]_2$ with arsenic metal. The arsenic atom where M = Mo has been found to function as a donor ligand to the metal of a $(MeC_5H_4)Mn(CO)_2$ fragment. The isoelectronic $Co_3(CO)_9(\mu_3\text{-}As)$ is known from the reaction of $[Co(CO)_4]^-$ with $AsCl_3$ (1.4% yield) or from $Co_2(CO)_8$ and AsI_3

(30% yield). Like the phosphorus analogue it undergoes cyclic trimerization with CO loss to produce $[Co_3(CO)_8(\mu_3\text{-}As)]_3$.[288] Treatment of $[Cr(CO)_5]_2AsCl$ with $Na[Co(CO)_4]$ produces $Co_3(CO)_9\{\mu_3\text{-}AsCr(CO)_5\}$.[58] A similar compound with the arsenic ligated to an external metal, $Co_3(CO)_9\{\mu_3\text{-}AsCo_4(CO)_{11}\}$, arises when $Cr(CO)_5AsPhH_2$ is treated with $Co_2(CO)_8$ (6.6% yield).[58]

An AsMe group caps a mixed metal $FeCo_2$ triangle in $FeCo_2(CO)_9(\mu_3\text{-}AsMe)$.[318] It is generated via the reaction of $Fe(CO)_4AsMeH_2$ with $Co_2(CO)_8$ or $(C_3H_5)Co(CO)_3$. A higher order oligomeric cubane-like compound, $[MeAsFe(CO)_3]_4$ is obtained from $Fe(CO)_4AsMeH_2$. The cluster $FeCo_2(CO)_9(\mu_3\text{-}AsMe)$ undergoes metal exchange reactions with $CpMo(CO)_2$ fragments giving $CpMoFeCo(CO)_8(\mu_3\text{-}AsMe)$ which has a closed metal triangle as well. Addition of phosphines results in breakage of metal–metal bonds producing an adduct believed to be $\{FeCo(CO)_6(PPhMe_2)\}\{Co(CO)_3PMe_2Ph\}AsMe$ with only one M–M bond.[319] No simple, stable, substituted product was observed. This can be compared to the reactivity of the analogous phosphorus complex $FeCo_2(CO)_9\{\mu_3\text{-}PMe)$ which undergoes substitution presumably via an open intermediate. The steric strain imposed by the larger arsenic atom was proposed to account for the difference in the reactivity patterns.

Molecules containing more than one arsenic atom capping a closed metal triangle are known. These include $Fe_3(CO)_9(\mu_3\text{-}As)_2$[237] and $Fe_3(CO)_9\{\mu_3\text{-}AsCr(CO)_5\}_2$. The first of these was obtained in very low yield (2%) from the reaction of AsF_3 with $Fe(CO)_5$, the second by treating the arsinidene compound $[Cr(CO)_5]_2AsCl$ with $Na_2[Fe(CO)_4]$ (26% yield).

An iron cluster containing two μ_3-AsPh groups, $Fe_3(CO)_9(\mu_3\text{-}AsPh)_2$ adopts the expected open, square pyramidal geometry as observed for the μ_3-NR and μ_3-PR complexes. It can be obtained from the reaction of $Cp(CO)_2MnAsPhCl_2$ with $Fe_2(CO)_9$[242] or from the reaction of $Na_2[Fe(CO)_4]$ with $PhAsCl_2$.[243] The open structure is also observed for $CrCo_2(CO)_{10}\{\mu_3\text{-}AsCr(CO)_5\}$ which is another product of the reaction of $[Cr(CO)_5]_2AsCl$ with $[Co(CO)_4]^-$ (14% yield).[58]

Very few antimony-containing clusters are known. One of the ones reported to date contains two μ_3-Sb atoms and is generated from the stibinidene complex $[Cr(CO)_5]_2SbCl$ and $Na_2[Fe(CO)_4]$ as are the corresponding phosphorus and arsenic complexes.[27] The product is $Fe_3(CO)_9\{\mu_3\text{-}SbCr(CO)_5\}_2$ (20%). In addition, we have found in our laboratory that $SbCl_3$ reacts with $[Fe_4(CO)_{13}]^{2-}$ similarly to PCl_3 and produces a product isostructural to $[Fe_3(CO)_8(\mu\text{-}CO)\{\mu_3\text{-}PFe(CO)_4\}]^-$.

The exploration of the μ_3-BiM_3 chemistry has proven to be a fruitful field although original indications from the literature were not promising. The complex $(\mu_3\text{-}Bi)Ir_3(CO)_9$[62] was known but the cobalt analogue was not observed to lose CO to form a similar species.[9] This was thought to be due to the steric strain imposed by the large Bi atom on the cobalts of a closed framework. Recently, however, we have isolated $BiCo_3(CO)_9$ which does show the closed geometry but unlike the iridium complex it has three bridging carbonyls around the cobalt triangle.[320] These bridging ligands may be necessary to stabilize the strained configuration.

$$BiCl_3 + 3[Ir(CO)_4]^- \rightarrow BiIr_3(CO)_9 + 3CO + 3Cl^- \qquad (37)^{62}$$

This observation was not unexpected in light of the iron system where a number of closed BiM_3 clusters are known. Among these are $[(\mu_3\text{-}Bi)Fe_3(CO)_9(\mu_3\text{-}CO)]^-$ generated from $NaBiO_3$ and $Fe(CO)_5$ in methanol,[63] and $(\mu\text{-}H)_3(\mu_3\text{-}Bi)Fe_3(CO)_9$ and $(\mu_3\text{-}Bi)_2Fe_3(CO)_9$ obtained in low yield from the protonation of

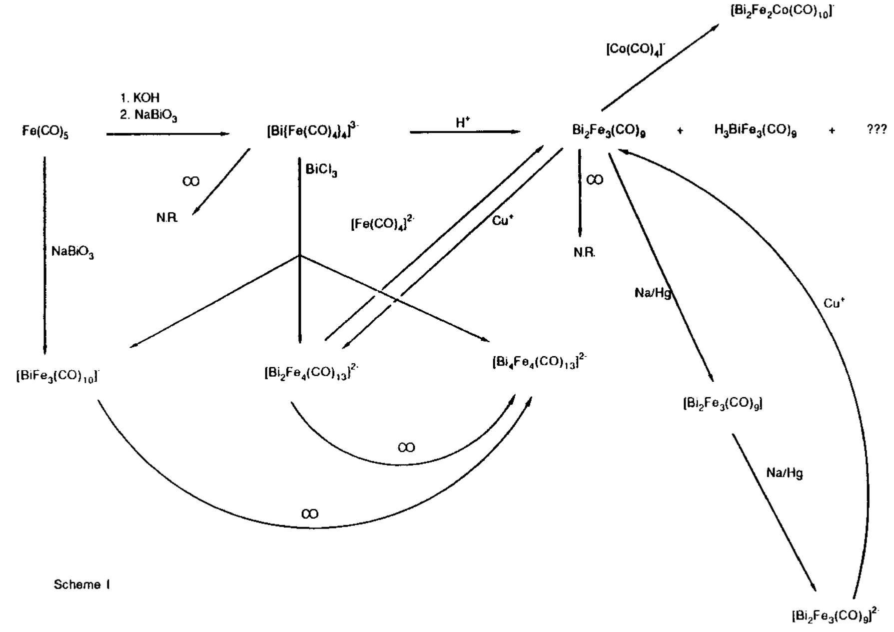
$[BiFe_4(CO)_{16}]^{3-}$ solutions.[64,238] A better synthesis of $Bi_2Fe_3(CO)_9$ is via the Cu^+ oxidation of the open, square pyramidal $[Fe_3(CO)_9\{\mu_3\text{-}Bi\}\{\mu_3\text{-}BiFe(CO)_4\}]^{2-}$ cluster which can be generated in reasonable yield (75%) from the reaction of $[BiFe_4(CO)_{16}]^{3-}$ and $BiCl_3$ in refluxing acetonitrile. On the other hand $[Fe_3(CO)_9\{\mu_3\text{-}Bi\}\{\mu_3\text{-}BiFe(CO)_4\}]^{2-}$ can be obtained from $Bi_2Fe_3(CO)_9$ by addition of $Na_2[Fe(CO)_4]$.

$$[Fe_3(CO)_9\{\mu_3\text{-}Bi\}\{\mu_3\text{-}BiFe(CO)_4\}]^{2-} + \text{xs}\,Cu^+ \rightarrow \underset{(75\%)}{Bi_2Fe_3(CO)_9} \qquad (38)$$

$$Bi_2Fe_3(CO)_9 + [Fe(CO)_4]^{2-} \rightarrow \underset{(85\%)}{[Fe_3(CO)_9\{\mu_3\text{-}Bi\}\{\mu_3\text{-}BiFe(CO)_4\}]^{2-}} \qquad (39)$$

Alkylation of $[(\mu_3\text{-}Bi)Fe_3(CO)_9(\mu_3\text{-}CO)]^-$ with methyl triflate produces the mixed methoxy alkylidyne/bismuth cluster $(\mu_3\text{-}Bi)Fe_3(CO)_9(\mu_3\text{-}COMe)$.[64] This illustrates the low basicity of the bismuth in low charged clusters. Coordination of μ_3-Bi to an external group is known only for the clusters which have a charge of 2- or greater.

Reversible reduction of $Bi_2Fe_3(CO)_9$ has been observed by both chemical and electrochemical means. The electrochemical process gives rise to a reversible one-electron reduction ($E_{1/2} = -0.39$ V) in which the electron appears localized on the iron atoms. This would suggest a structure intermediate between the closed trigonal-bipyramidal geometry and the open square pyramidal configuration. Chemically, one-electron and two-electron reduction products are observed. The two-electron product $[Bi_2Fe_3(CO)_9]^{2-}$ is thought to be very similar to $[Fe_3(CO)_9\{\mu_3\text{-}Bi\}\{\mu_3\text{-}BiFe(CO)_4\}]^{2-}$, its structure only missing the external $Fe(CO)_4$ unit. Cobaltocene is an effective reducing agent for these systems as well. The chemical oxidation of $[BiFe_3(CO)_{10}]^-$ with Cu^+ produces $Bi_2Fe_3(CO)_9$ (26% yield) while the electrochemical oxidation is very messy with fouling of the electrodes observed. The results of a number of these Bi/Fe carbonyl interconversions are summarized in Scheme I.



Scheme I

Treating $[BiFe_3(CO)_{10}]^-$ or $[Fe_3(CO)_9\{\mu_3\text{-}Bi\}\{\mu_3\text{-}BiFe(CO)_4\}]^{2-}$ with CO produces the unusual Zintl-metal carbonylate $[Bi_4Fe_4(CO)_{13}]^{2-}$ which will be discussed later.

4.2.4 Group 16: The triply bridging configuration is a very commonly observed structure type for sulfur, selenium and tellurium. The sulfur complexes are very readily obtained by a variety of reactions which can employ almost any type of sulfur compound and transition metal complex. Table IV contains parameters for a number of these which have been structurally characterized. In addition to those in which the sulfur caps a closed triangle of metals, there are numerous examples in which the M_3 unit contains only two metal–metal bonds.

Elemental sulfur, thiols, sulfite, hydrogen sulfide, ethylene sulfide and carbon disulfide have all been observed to give up their sulfur atoms to form sulfido-clusters

$Co_2(CO)_8 + EtSH \rightarrow Co_6(CO)_{11}(SEt)_4(\mu_3\text{-}S)$ (*40*)[89]

$Co_2(CO)_8 + S \rightarrow [SCo_3(CO)_7]_2S_2$ (*41*)[88]

$[Co(CO)_4]^- + Na_2SO_3 \rightarrow [SCo_3(CO)_7]_2S_2$ (*42*)[88]

$Co_2(CO)_8 + PhSH \rightarrow Co_3(CO)_9S$ (*43*)[86]

$Co_2(CO)_8 + Fe(CO)_5 + PhSH \rightarrow Co_2Fe(CO)_9S$ (*44*)[321]

$Co_2(CO)_8 + CS_2 \rightarrow Co_6(CO)_{16}C(\mu_3\text{-}S)_2 + [Co_3(CO)_7CS]_2$ (*45*)[87]

$Fe(CO)_5/KOH \xrightarrow[2.\ H^+]{1.\ SO_3^{2-}} Fe_3(CO)_9S_2 + Fe_2(CO)_6S_2$ (*46*)[322,320]

$[HFe_3(CO)_{11}]^- \xrightarrow[2.\ H^+]{1.\ SO_3^{2-}} Fe_3(CO)_9S(SO)$ (*47*)[246]

$Ru_3(CO)_{12} + C_2H_4S \longrightarrow Ru_3(CO)_{10}(\mu_3\text{-}S)$ (*48*)[152]

$Ru_3(CO)_{10}(\mu_3\text{-}S) + C_2H_4S \longrightarrow Ru_3(CO)_9(\mu_3\text{-}S)_2$ (*49*)[152]

$Ru_3(CO)_{12} \xrightarrow[3.\ H^+]{\substack{1.\ KOH \\ 2.\ SO_3^{2-}}} H_2Ru_3(CO)_9S$ (*50*)[324]

$Ru_3(CO)_{12} + S \xrightarrow{\Delta} H_2Ru_3(CO)_9S$ (low yield) (*51*)[324]

$Os_3(CO)_{12} + H_2S \longrightarrow H_2Os_3(CO)_9(\mu_3\text{-}S)$ (*52*)[75]

In one case, the triply-binding SR fragment has been observed. Reaction of anionic clusters with halide complexes of main group elements has been reported (eqn 53) but the chemistry of the anions in general is underexplored. This is true of most of the main group containing cluster anions.

$$[Fe_3(CO)_9(\mu_3\text{-}SR')]^- + XCl \longrightarrow Fe_3(CO)_9(\mu\text{-}X)(\mu_3\text{-}SR') \qquad (53)^{325}$$

$$X = PR_2, AsR_2, SbR_2, SR, SeR$$

Reactions of clusters which already contain a sulfur moiety can also lead to μ_3-S ligands. In equation 54 a cluster building reaction is used while in equations 55–58 thermolysis of μ-SR complexes leads to a variety of sulfur containing clusters many of which are derived from μ_3-S clusters.

$$[Fe_2(CO)_6S_2]^{2-} + CpCo(CO)_2I_2 \longrightarrow CpCoFe_2(CO)_6(\mu_3\text{-}S)_2 \qquad (54)^{326}$$

$$HRu_3(CO)_9(SPh) \xrightarrow[\text{or } h\nu]{\Delta} Ru_3(CO)_{10}(\mu_3\text{-}S) \qquad (55)^{152}$$

$$\begin{aligned} HOs_3(CO)_{10}(SPh) \xrightarrow{\Delta} {} & H_2Os_3(CO)_9(\mu_3\text{-}S) + \\ & Os_3(CO)_9(\mu_3\text{-}S)_2 + \\ & Os_4(CO)_{12}(\mu_3\text{-}S) + \\ & Os_4(CO)_{12}(\mu_3\text{-}S)_2 + \\ & Os_6(CO)_{16}(\mu_4\text{-}S)(\mu_3\text{-}S) \end{aligned} \qquad (56)^{82}$$

$$\begin{aligned} HOs_3(CO)_{10}(SCH_2Ph) \xrightarrow{\Delta} {} & Os_3(CO)_9(\mu_3\text{-}S)_2 + \\ & Os_6(CO)_{16}(\mu_4\text{-}S)(\mu_3\text{-}S) + \\ & H_2Os_6(CO)_{17}(\mu_4\text{-}S)(\mu_3\text{-}S) + \\ & Os_7(CO)_{20}(\mu_4\text{-}S)_2 \end{aligned} \qquad (57)^{327}$$

$$\begin{aligned} HOs_3(CO)_{10}(SPh) \xrightarrow[150^\circ C]{CO,\ 200psi} {} & Os_3(CO)_9(\mu_3\text{-}S)_2 + \\ & Os_4(CO)_{13}(\mu_3\text{-}S) + \\ & Os_5(CO)_{15}(\mu_4\text{-}S) + \\ & Os_3(CO)_{12} \end{aligned} \qquad (58)^{78}$$

Varying the conditions under which these pyrolyses take place can alter the products formed. These processes can be promoted photochemically. As may be expected, the presence of other sulfur-containing compounds such as H_2S or COS, or CS_2 results in the cluster ending up with additional sulfido-ligands in the products.

$$HOs_3(CO)_{10}(SPh) \xrightarrow[CO]{h\nu} Os_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}S) \qquad (59)^{74}$$

$$HOs_3(CO)_{10}(SPh) \xrightarrow[H_2]{h\nu} H_2Os_3(CO)_9(\mu_3\text{-}S) \qquad (60)^{74}$$

$$HOs_3(CO)_{10}(SPh) \xrightarrow[COS]{h\nu} Os_3(CO)_9(\mu_3\text{-}S)_2 \qquad (61)^{74}$$

$$HOs_3(CO)_{10}(SPh) \xrightarrow[CS_2]{h\nu} Os_3(CO)_9(CS)(\mu_3\text{-}S)_2 \qquad (62)^{74}$$

$$HOs_3(CO)_{10}(SPh) \xrightarrow[H_2S]{h\nu} H_2Os_3(CO)_9(\mu_3\text{-}S)_2 \qquad (63)^{74}$$

$$Os_4(CO)_{12}(\mu_3\text{-}S) + H_2S \longrightarrow H_2Os_4(CO)_{12}(\mu_3\text{-}S)_2 \qquad (64)^{85}$$

$$Os_5(CO)_{15}(\mu_4\text{-}S) + H_2S \longrightarrow H_2Os_5(CO)_{14}(\mu_3\text{-}S)_2 \qquad (65)^{85}$$

$$H_2Os_3(CO)_8(NCMe)S + CS_2 \longrightarrow H_2Os_3(CO)_7(CS)S_2 \qquad (66)^{249}$$

The μ_3-sulfur atom possesses a lone pair of electrons which may be used for donation to other metal fragments. This capability can lead to the formation of higher nuclearity clusters.

$$Co_2Fe(CO)_9(\mu_3\text{-}S) + Cr(CO)_5(THF) \rightarrow Co_2Fe(CO)_9(\mu_3\text{-}SCr(CO)_5) \qquad (67)^{72}$$

$$H_2Ru_3(CO)_9S \xrightarrow[\text{or } h\nu]{\Delta} [H_2Ru_3(CO)_8S]_3 \qquad (68)^{73}$$

Addition of metal fragments, however, does not always occur at sulfur, or at least addition to the sulfur atom is not obvious by inspection of the observed products. Metal substitution may occur as may reactions in which the metal framework is expanded by the addition of the metal moiety. Cluster substitution has been extensively studied for $Co_2Fe(CO)_9S$, $Co_2Ru(CO)_9S$, $Fe_2Co(CO)_9S$, $HFe_2Co(CO)_9S$, $H_2Fe_3(CO)_9S$ as well as some of their other chemistry.[70,71,328,329] As in many cluster reactions, the mechanisms of many of these cluster building processes are unknown. It would be wise to bear in mind that even though the sulfur does not always end up attached to the added metal fragment, an interaction between the sulfur atom and that metal group may be significant in directing the chemistry observed. Often extensive structural reorganization accompanies these reactions.

$$Co_2Fe_2(CO)_{11}S_2 + [CpMo(CO)_3]_2 \rightarrow CpMoCoFe(CO)_8(\mu_3\text{-}S) \qquad (69)^{330}$$

$$H_2Ru_3(CO)_9S + SnCl_4 \rightarrow H_2Ru_3(CO)_8(\mu\text{-}Cl)(SnCl_3)(\mu_3\text{-}S) \qquad (70)^{331}$$

$$Os_3(CO)_{10}(\mu_3\text{-}S) + Pt(PMe_2Ph)_4 \rightarrow PtOs_3(CO)_8(PMe_2Ph)_3(\mu_3\text{-}S) \qquad (71)^{80,81}$$

$$Os_3(CO)_{10}(\mu_3\text{-}S) + W(CO)_5(PMe_2Ph) \rightarrow WOs_3(CO)_{11}(PMe_2Ph)_2(\mu_3\text{-}S) \qquad (72)^{81}$$

$$Os_3(CO)_9(\mu_3\text{-}S)_2 + Pt(PMe_2Ph)_4 \rightarrow PtOs_3(CO)_9(PMe_2Ph)_2(\mu_3\text{-}S)_2 \qquad (73)^{332}$$

$$Os_3(CO)_{10}(\mu_3\text{-}S) + Pt(PPh_3)_2(C_2H_4) \rightarrow PtOs_3(CO)_9L(PPh_3)(\mu_3\text{-}S)_2 \qquad (74)^{333}$$
$$L = CO, PPh_3$$

$$Os_3(CO)_9(\mu_3\text{-}S)_2 + W(CO)_6 \rightarrow Os_3(CO)_9(\mu_3\text{-}S)(\mu_3\text{-}SW(CO)_5) \qquad (75)^{250}$$

$$Os_4(CO)_{12}(\mu_3\text{-}S)_2 + Pt(PMe_2Ph)_4 \longrightarrow \qquad (76)^{84}$$
$$PtOs_4(CO)_{11}(PMe_2Ph)_2(\mu_3\text{-}S)_2 + PtOs_3(CO)_9(PMe_2Ph)_2(\mu_3\text{-}S)_2$$

$$Os_3(CO)_9(\mu_3\text{-}S)_2 + Os(CO)_5 \xrightarrow{h\nu} Os_4(CO)_{13}(\mu_3\text{-}S) \qquad (77)^{334}$$

$$Os_3(CO)_9(\mu_3\text{-}S)_2 \xrightarrow[N_2\text{ purge}]{h\nu} Os_6(CO)_{16}(\mu_3\text{-}S)_4 \qquad (78)^{251}$$

$$\begin{array}{l} HOs_3(CO)_9(\mu\text{-}HC{=}NPh)(\mu_3\text{-}S) \xrightarrow{\Delta} \\ H_2Os_6(CO)_{16}\ (\mu\text{-}HC{=}NPh)(\mu_4\text{-}S)(\mu_3\text{-}S) \end{array} \qquad (79)^{309}$$

$$\begin{array}{r} Os_3(CO)_{10}(\mu_3\text{-}S) + Os_3(CO)_{10}(NCMe) \rightarrow Os_6(CO)_{19}(\mu_3\text{-}S) + \\ Os_5(CO)_{15}(\mu_4\text{-}S) \end{array} \qquad (80)^{154}$$

$$\begin{array}{rl} Os_3(CO)_{10}(\mu_3\text{-}S) + Me_3NO \longrightarrow & HOs_3(CO)_8(NMe_3)(\mu\text{-}OH)(\mu_3\text{-}S) \\ & \quad \downarrow Os_3(CO)_{10}(\mu_3\text{-}S) \\ & HOs_6(CO)_{18}(\mu\text{-}OH)(\mu_4\text{-}S)(\mu_3\text{-}S) \end{array} \qquad (81)^{335}$$

Addition of donor ligands can result in a number of outcomes. Simple addition as well as substitution is observed. In some cases, however, more extensive reaction occurs as evidenced for some of the amine compounds where N–H bonds can be activated. Insertion into a C–H bond of a methyl group on trimethylamine has been reported.

$$Fe_3(CO)_9S_2 + Me_2NH \longrightarrow Fe_3(CO)_8(NMe_2H)(\mu_3\text{-}S) \qquad (82)^{336}$$

$$Os_3(CO)_{10}(\mu_3\text{-}S) + NMe_3 \longrightarrow H_2Os_3(CO)_8[C(H)NMe_2](\mu_3\text{-}S) \qquad (83)^{76}$$

$$Os_3(CO)_9(\mu_3\text{-}S)_2 + Me_2NH \longrightarrow HOs_3(CO)_8(\mu\text{-}Me_2NCO)(\mu_3\text{-}S)_2 \qquad (84)^{336}$$

$$Os_4(CO)_{12}(\mu_3\text{-}S) + Me_2NH \longrightarrow Os_4(CO)_{12}(Me_2NH)(\mu_3\text{-}S) \qquad (85)^{79}$$

$$Os_4(CO)_{12}(\mu_3\text{-}S) + CO \rightarrow Os_4(CO)_{13}(\mu_3\text{-}S) \qquad (86)^{79}$$

$$Os_4(CO)_{12}(\mu_3\text{-}S)_2 \xrightarrow{L} Os_4(CO)_{12}L(\mu_3\text{-}S)_2 \rightarrow Os_4(CO)_{11}L(\mu_3\text{-}S)_2 \qquad (87)^{337}$$

$L = PMe_2Ph, CN\text{-}{}^tBu$

Dihydrogen is activated by these clusters. It can either add directly to the cluster or displace some other ligand such as CO.

$$Ru_3(CO)_{10}(\mu_3\text{-}S) + H_2 \rightarrow H_2Ru_3(CO)_9(\mu_3\text{-}S) + CO \qquad (88)^{152}$$

$$Ru_3(CO)_9(\mu_3\text{-}S)_2 + H_2 \rightarrow H_2Ru_3(CO)_8(\mu_3\text{-}S)_2 + CO \qquad (89)^{152}$$

$$Os_4(CO)_{12}(\mu_3\text{-}S) + H_2 \rightarrow H_2Os_4(CO)_{12}(\mu_3\text{-}S) \qquad (90)^{79}$$

$$HOs_3(CO)_9(HC{=}NPh) \xrightarrow[\Delta]{H_2} H_4Os_6(CO)_{15}(\mu\text{-}HC{=}NPh)_2(\mu_4\text{-}S)(\mu_3\text{-}S) + H_2Os_6(CO)_{14}(\mu\text{-}HC{=}NPh)_2(\mu_4\text{-}S)(\mu_3\text{-}S) \qquad (91)^{338}$$

Clusters containing selenium or tellurium atoms capping either a closed triangle of metals or three metals connected by only two metal–metal bonds are much less well-known than those for sulfur, but well-characterized examples do exist. The naked μ_3-Se and Te atoms donate four electrons to the cluster count. To date, no μ_3-SeR or μ_3-TeR complexes have been reported. The methods of synthesis are similar to those employed for sulfur.

$$3\ Co_2(CO)_8 + 2\ H_2Se \xrightarrow[\text{Co, 100 atm}]{150^\circ C} 2\ Co_3(CO)_9(\mu_3\text{-}Se) \qquad (92)^{90}$$

$$3\ Co_2(CO)_8 + Fe_3(CO)_{12} + 3\ H_2Se \xrightarrow[\text{CO, 100 atm}]{150^\circ C} 3\ FeCo_2(CO)_9(\mu_3\text{-}Se) \qquad (93)^{90}$$

$$Co_2(CO)_8 + Fe_3(CO)_{12} + Et_2Te \longrightarrow Co_2Fe(CO)_9(\mu_3\text{-}Te) \qquad (94)^{90}$$

$$\begin{tikzcd}
HOs_3(CO)_{10}(SePh) \arrow[r, "160^\circ C", "\text{CO, 3000 psi}"'] & Os_3(CO)_9(\mu_3\text{-}Se)_2 \arrow[d, "h\nu"', "Os(CO)_5"] & (95)^{339} \\
& Os_4(CO)_{13}(\mu_3\text{-}Se)_2 \arrow[d, "-CO"] & \\
& Os_3(CO)_{12}(\mu_3\text{-}Se)_2 \arrow[d, "+H_2"] & \\
& H_2Os_4(CO)_{12}(\mu_3\text{-}Se)_2 &
\end{tikzcd}$$

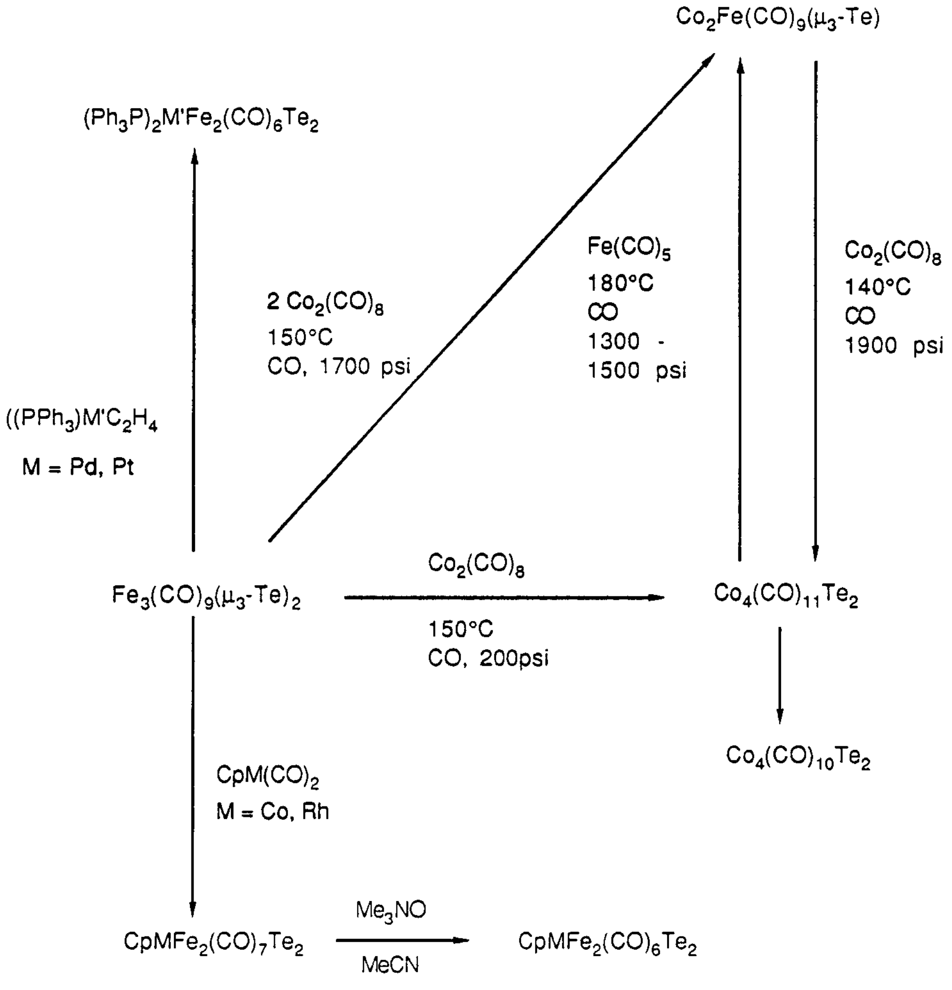
$$HOs_3(CO)_{10}(SePh) \xrightarrow{h\nu} Os_3(CO)_{10}(\mu_3\text{-}Se) \xrightarrow{H_2} H_2Os_3(CO)_9(\mu_3\text{-}Se) \qquad (96)^{339}$$

$$Fe(CO)_5/KOH + K_2TeO_3 \rightarrow Fe_3(CO)_9(\mu_3\text{-}Te)_2 + Fe_2(CO)_6Te_2 \qquad (97)^{323,340}$$

The cluster $Co_3(CO)_9(\mu_3\text{-}Se)$ is paramagnetic while the $Co_2Fe(CO)_9(\mu_3\text{-}E)$ (E = Se, Te) are diamagnetic. Single crystal ESR studies of $Co_3(CO)_9(\mu_3\text{-}Se)$ doped into crystals of $Co_2Fe(CO)_9(\mu_3\text{-}Se)$ were consistent with the postulate that the unpaired electron resides in a metal–metal antibonding orbital. Molecules in which Se and Te cap three metals with only two metal–metal bonds include $Fe_3(CO)_9(\mu_3\text{-}Se)_2$ and $Fe_3(CO)_9(\mu_3\text{-}Te)_2$. The structure of the selenium compound has been reported and it is isostructural with $Fe_3(CO)_9(\mu_3\text{-}S)_2$.[252]

The tellurium compound $Fe_3(CO)_9(\mu_3\text{-}Te)_2$ differs from the S and Se analogues in that it undergoes substitution processes via an associative mechanism.[234] For the S and Se complexes, substitution occurs, but by a dissociative pathway. Adducts of the type $Fe_3(CO)_9(L)Te_2$ have been isolated and structurally characterized and show addition of L to one metal with breakage of an Fe–Fe bond. There is now thought to be a significant interaction between the tellurium atoms in these adducts. This makes the adducts more appropriately described as tetrahedral M_2E_2 clusters with an edge bridged by a third metal.[92] As such they will be discussed in more detail in the section on M_2E_2 clusters. $Fe_3(CO)_9(\mu_3\text{-}Te)_2$ will react with a number of metal complexes giving metal addition, metal substitution and cluster building reactions. These reactions are summarized in Scheme II.[331,341,342] The ^{13}C NMR spectra of the $Fe_3(CO)_9X_2$ ($X = S, Se, Te$) complexes have been examined.[343]

Scheme II



5. CHEMISTRY OF THE CLUSTERS $EM_X(x \geq 4)$

5.1 *The First Row: Boron, Carbon and Nitrogen*

5.1.1 Boron: The structure of only one boron compound which is pertinent to this section has been reported to date. It is $HFe_4(CO)_{12}BH_2$ which is synthesized via the reaction of $Fe_2(CO)_6B_2H_6$ and $Fe_2(CO)_9$ and possesses two three center-two electron Fe–H–B bonds.[93] Structurally it is very similar to the isoelectronic $\mathrm{HFe_4(CO)_{12}(\eta^2\text{-CH})}$.[98] A higher order interstitial boride cluster has been reported from the reaction of $\mathrm{Co_2(CO)_8}$ with $\mathrm{BBr_3}$ (43% yield) or from treating $\mathrm{Co_2(CO)_8}$ with 8–10 atm of $\mathrm{B_2H_6}$ in an autoclave (ca. 14% yield). The product is $\mathrm{Co_6(CO)_{18}B}$ but has not been characterized by X-ray analysis.[305]

5.1.2 Carbon: Rhenium carbido-clusters are known but are not as well studied as the iron and cobalt subgroup complexes to be discussed shortly. The known molecules all contain the carbide atom in the octahedral cavity. Pyrolysis of $\mathrm{[Et_4N][H_2Re(CO)_4]}$ at 235° C affords $\mathrm{[Et_4N]_2[(\mu_3\text{-H})_2Re_6(CO)_{18}C]}$[157] but raising the temperature to 250° C affords $\mathrm{[Et_4N]_3[Re_7(CO)_{21}C]}$ (yields up to 50%) and $\mathrm{[Et_4N]_2[Re_8(CO)_{24}C]}$ (yields up to 30%).[158,159] The hydrido cluster having seven skeletal electron pairs is a simple octahedron with three terminal carbonyls on each Re and a Re-carbide distance of 2.136 Å. The heptanuclear cluster can be derived by replacing the two hydrides with a $\mathrm{[Re(CO)_3]^-}$ fragment to give a monocapped octahedral cluster also showing seven skeletal electron pairs. Each rhenium is still ligated by three terminal carbonyls. The octarhenium cluster is similarly derived by replacing one of the negative charges by a one-electron donor neutral $\mathrm{[Re(CO)_3]}$ moiety to give an octahedron in which opposite faces are capped. It has seven skeletal electron pairs and three terminal carbonyls per rhenium.

Little chemistry of these clusters has been reported, but $\mathrm{[(\mu_3\text{-H})_2Re_6(CO)_{18}C]^{2-}}$ is known to undergo protonation to $\mathrm{[H_3Re_6(CO)_{18}C]^-}$,[157] while $\mathrm{[Re_7(CO)_{21}C]^{3-}}$ reacts with group 11 salts namely $\mathrm{AuClPPh_3}$, $\mathrm{(AgClPPh_3)_4}$, $\mathrm{AgBF_4}$ or $\mathrm{[Cu(NCMe)_4]PF_6}$ to give adducts in which the group 11 metal caps the face of the octahedron opposite to the capping Re atom. The X-ray structure analysis of $\mathrm{[\{Re_7(CO)_{21}C(\mu_3\text{-Ag})\}_2Br]^{5-}}$ has been performed and has two bicapped octahedral units dimerized via coordination of the μ_3-Ag's to a $\mathrm{Br^-}$ ion.[160] The average Re-carbide distances for $\mathrm{[Re_7(CO)_{21}C]^{3-}}$, $\mathrm{[\{Re_7(CO)_{21}C(\mu_3\text{-Ag})\}_2Br]^{5-}}$ and $\mathrm{[Re_8(CO)_{24}C]^{2-}}$ are very close to those of $\mathrm{[(\mu_3\text{-H})_2Re_6(CO)_{18}C]^{2-}}$ being 2.13 Å, 2.13 Å and 2.116 Å, respectively. The silver atoms appear to cause little structural perturbation of the M–M bonds in the triangular faces to which they are attached, while the capping Re atoms tend to cause shortening of the M–M bonds in the capped faces. The $\mathrm{[Re_7(CO)_{21}C]^{3-}}$ anion is oxidized by $\mathrm{I_2}$ in $\mathrm{CH_3CN}$ to yield the $\mathrm{[Re_4(CO)_{15}(I)C]^-}$ ion of unique structure.[133] Further reaction with $\mathrm{I_2}$ leads to monometal iodo/acetonitrile complexes of rhenium. The $\mathrm{[Re_4(CO)_{15}(I)C]^-}$ cluster contains a μ_4-carbide atom sitting in a distorted square of rhenium atoms. The Re–C distances are 2.08 Å(ave) which is slightly shorter than those observed for the octahedral Re carbide clusters (2.12–2.14 Å). The carbide atom is closest to the iodine-coordinated Re as might be expected based on charge arguments. The cluster is a 64 e system obeying the EAN rule having two electrons more than the iron group tetrametal butterfly carbides and can be viewed as being derived from that structural type by breakage of the M–M hinge bond.

An extensive chemistry has been found for the iron group carbides. The pentametal complex $\mathrm{Fe_5(CO)_{15}C}$ was the first known carbido cluster being structurally characterized in 1962.[123] It was observed in low yield (<0.5%) from the pyrolysis of 1-pentyne and $\mathrm{Fe_3(CO)_{12}}$. As one can see from Tables V and VI, many more carbide complexes are now known and the $\mathrm{Fe_5C}$ is available in improved yields from the oxidation of $\mathrm{[Fe_6(CO)_{16}C]^{2-}}$ [161] by $\mathrm{H_2SO_4}$[344] or, even better, by ferric ion.[346] The production of $\mathrm{[Fe_6(CO)_{16}C]^{2-}}$ occurs in reasonable yields from $\mathrm{Fe(CO)_5}$ and $\mathrm{[Fe(CO)_4]^{2-}}$ (or other metal carbonyl anions) at a temperature in excess of *ca.* 160°

which evidently is necessary for the formation of the carbido atom and which probably occurs by the reduction of CO with the concomitant production of CO_2. Reduction of $Fe_5(CO)_{15}C$ with $[Fe(CO)_4]^{2-}$ produces $[Fe_5(CO)_{14}C]^{2-}$ [307] which upon protonation by gaseous HCl in toluene yields the η^2-methyne cluster $HFe_4(CO)_{12}CH$ having a butterfly geometry.[98] This methyne is also produced upon protonation of $[Fe_4(CO_{13}]^{2-}$ in concentrated triflic acid as observed in part of the studies on the proton-induced reduction of CO in the tetranuclear iron system.[99] The methyne carbon was derived from CO in that reaction.

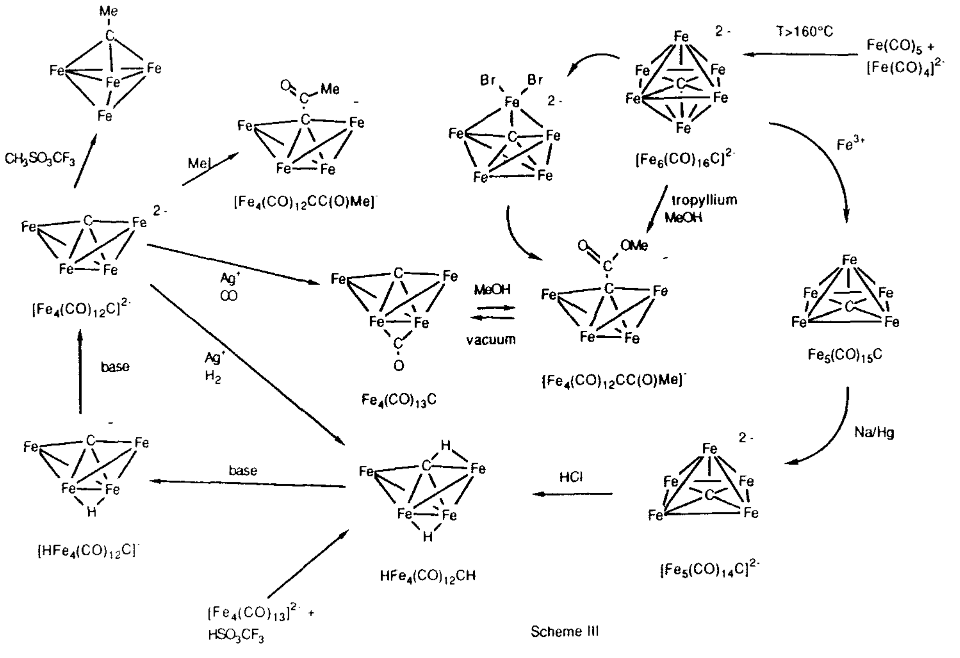
The protonation route to a carbide was also employed successfully after first treating $[Fe_4(CO)_{13}]^{2-}$ with $AuClPR_3$.[110] The product was $(\mu\text{-H})Fe_4\{AuPR_3\}(CO)_{12}C$ which has a bridged butterfly geometry in which the $AuPR_3$ unit spans the wingtips of the basic Fe_4C butterfly core. The hydrido ligand bridges the Fe–Fe hinge bond. Structural data are available for the R = Ph derivative. The cluster can be deprotonated with base and further derivatized with $AuClPR_3$ giving $Fe_4(AuPR_3)_2(CO)_{12}C$ which is an octahedral cluster with adjacent gold atoms joined by a Au–Au bond (3.017Å).[163] The gold atoms are both bonded to the carbide as are all the iron atoms. This contrasts to the structure observed for the $Ru_4\{AuPR_3\}_2(CO)_{12}C$ complexes in which the bridged butterfly geometry is retained but in which the other $AuPR_3$ unit bridges the Ru–Ru hinge bond.[113]

The neutral methyne is acidic and easily deprotonated to give $[HFe_4(CO)_{12}C]^-$ and $[Fe_4(CO)_{12}C]^{2-}$ which have both been structurally characterized.[99,100] Oxidation of the dianion leads to $Fe_4(CO)_{13}C$ in the presence of CO and the regeneration of $HFe_4(CO)_{12}CH$ in the presence of H_2.[100] Alkylation of the dianion with $MeSO_3CF_3$ occurs at the carbide to produce a tetrahedral μ_3-ethylidyne cluster $[Fe_4(CO)_{12}(\mu_3\text{-CMe})]^-$ [293] While use of MeI as alkylating agent results in the production of a butterfly cluster with an acyl ligand attached to the carbide atom: $[Fe_4(CO)_{12}CC(O)Me]^-$.[96]

Another way to access the butterfly series of iron carbides is oxidation of $[Fe_6(CO)_{16}C]^{2-}$ with tropyllium bromide in methanol which forms $[Fe_4(CO)_{12}C\text{-}C(O)OMe]^-$.[97] Upon protonation, this cluster is converted into $Fe_4(CO)_{13}C$ which is reconverted into $[Fe_4(CO)_{12}CC(O)Me]^-$ by dissolution in methanol. An intermediate in the oxidation appears to be the pentanuclear, bridged-butterfly cluster $[Fe_5(CO)_{12}(Br)_2C]^{2-}$ which provides a very rational pathway for the production of the lower nuclearity clusters.[109] These findings are summarized in Scheme III.

A Mössbauer study of the iron butterfly clusters has been reported and shows that calculated values for the effective nuclear charge at iron using Slater's method correlate well with the Mössbauer isomer shifts.[347] These studies tend to support the molecular orbital calculations on these carbides that show a relatively high localized charge on the carbide atom.

The ^{13}C NMR data for the carbonyls of the tetranuclear iron clusters also support the localization of charge at carbon. If one compares the average $\delta^{13}C$ for $[Fe_4(CO)_{13}]^{2-}$, $[HFe_4(CO)_{13}]^-$ and $[Fe_4(CO)_{12}(COMe)]^-$, one observes that there is an eight to ten ppm shift to lower field on addition of a net negative charge. These general trends are observed for a wide variety of iron, ruthenium and osmium mononuclear and cluster species. The same trends are seen for the average $\delta^{13}C$ of the CO's of $Fe_4(CO)_{13}C$, $HFe_4(CO)_{12}CH$, $[HFe_4(CO)_{12}C]^-$ and $[Fe_4(CO)_{12}C]^{2-}$ which give values of 208 ppm, 207.3 ppm, 216.3 ppm and 223.4 ppm, respectively. What is key to note is that these values are all consistently about 7–10 ppm to higher field of the non-carbido clusters. This implies that the CO's in the carbide clusters see less electron density than those in the non-carbide-containing species, which further implies that the carbide atom is acting as an electron sink to pull electron density away from the metal centers.



Scheme III

When treated with transition metal complexes that are coordinatively unsaturated or which contain labile ligands, the pentanuclear dianion $[Fe_5(CO)_{14}C]^{2-}$ is converted into mixed metal octahedral clusters.[126,127,345,346] Clusters produced by this method include:

$[CrFe_5(CO)_{17}C]^{2-}$, $[MoFe_5(CO)_{17}C]^{2-}$, $[WFe_5(CO)_{17}C]^{2-}$, $[Fe_6(CO)_{16}C]^{2-}$, $[RhFe_5(CO)_{16}C]^-$,$[RhFe_5(CO)_{14}(COD)C]^-$,$[IrFe_5(CO)_{14}(COD)C]^-$,$[NiFe_5(CO)_{13}(COD)C]^{2-}$, $[NiFe_5(CO)_{15}C]^{2-}$, $[CoFe_5(CO)_{16}C]^-$, $[PdFe_5(CO)_{14}(C_3H_5)C]^-$ and $[CuFe_5(CO)_{14}(MeCN)C]^-$. Oxidation of several of these by ferric ion led to the formation of square pyramidal carbide clusters including $CrFe_4(CO)_{16}C$, $MoFe_4(CO)_{16}C$ and $[RhFe_4(CO)_{14}C]^-$. An exception to this trend was the formation of $NiFe_5(CO)_{16}C$ upon oxidation of $[NiFe_5(CO)_{15}C]^{2-}$. It has already been mentioned that the carbide-mimic ketenylidene ligand in $[Fe_3(CO)_9CCO]^{2-}$ is a useful starting point for the synthesis of higher nuclearity mixed-metal carbides.[102]

Reaction of $[Fe_5(CO)_{14}C]^{2-}$ with $Au(PEt_3)Cl$ proceeds similarly giving an octahedral Fe_5Au_2 cluster in which the gold atom is bonded to the carbide carbon and four iron atoms. The other gold atom bridges two of the iron atoms which are bonded to the μ_4-Au moiety.[163] The iron–iron distances are normal except that doubly bridged by the $Au(PEt_3)$ unit which is longer (2.941Å *vs.* 2.633Å ave). Air oxidation of $Fe_5\{\mu_4\text{-}AuPEt_3\}\{\mu\text{-}AuPEt_3\}(CO)_{14}C$ leads to low yields of $Fe_4\{AuPEt_3\}(CO)_{12}C$.

A short review of some of the ruthenium and osmium carbide cluster chemistry has appeared.[348] Lower nuclearity ruthenium carbide clusters can be accessed through a hexanuclear carbide cluster, in this case $Ru_6(CO)_{17}C$ which is generated along with $Ru_6(CO)_{14}(arene)C$ from the pyrolysis of $Ru_3(CO)_{12}$ in high boiling organic aromatic solvents such as mesitylene.[164,172,349,350] The mesitylene adduct has been structurally characterized as has the all carbonyl compound. Pyrolysis *in vacuo* also gives $Ru_6(CO)_{17}C$ suggesting that the carbide source is CO.[351] Reaction of $Ru_3(CO)_{12}$ with ethylene produces a hexanuclear carbide cluster, $Ru_6(CO)_{15}(CH_3CH{=}CHCH{=}CHCH_3)C$ in which three molecules of ethylene have evidently been coupled to give a 2,4-hexadiene ligand.[171] Formation of $Ru_6(CO)_{17}C$ also appears to be promoted by the addition of ethylene. Treatment of $Ru_6(CO)_{17}C$ with CO under moderate pressures causes elimination of $Ru(CO)_5$ and production of $Ru_5(CO)_{15}C$.[111] $Ru_6(CO)_{17}C$ undergoes substitution with phosphines giving $Ru_6(CO)_{17-n}L_nC$ ($L = PPh_2Et$, $n = 1, 2$; $L = P(OMe)_3$, $n = 1$–4). The structure of the PPh_2Et, $n = 1$ derivative has been reported.[169]

$$Ru_3(CO)_{12} \xrightarrow{\Delta} Ru_6(CO)_{17}C \xrightarrow{CO} Ru_5(CO)_{15}C \qquad (98)^{351,111}$$

The reduced form of the hexanuclear cluster $[Ru_6(CO)_{16}C]^{2-}$ is produced on treating $Ru_3(CO)_{12}$ with $[Mn(CO)_5]^-$ or with Na in refluxing diglyme.[165,352] It is the starting material along with $[C_7H_7]^+$ for producing $Ru_6(CO)_{14}(bitropyl)C$ in high yield.[170]

Substitution is observed when $Ru_5(CO)_{15}C$ is treated with phosphines and the derivatives $Ru_5(CO_{14}(PPh_3)C$ and $Ru_5(CO)_{13}(PPh_3)_2C$ have been structurally characterized.[111] On the other hand, addition of some ligands such as acetonitrile does not result in substitution but rather in addition to produce the bridged-butterfly structures given in Table V.[111] Similar structures are obtained by the oxidative-addition of $(PPh_3)Au$ halides to these clusters which formally adds two electrons to the metal framework. Structural data are available for the chloride and bromide complexes.[112] The gold atoms bridge the two hinge metals. In the bromide case, further loss of CO occurs readily to allow the bromide to coordinate to a hinge ruthenium atom as well. The bridging position of the bromide between the unique bridging ruthenium and a hinge ruthenium causes some distortion of the unique bridging metal towards the Br-side of the molecule as might be expected. Cyclopentadienide ion will add with the replacement of two carbonyls giving $[CpRu_5(CO)_{13}C]^-$ which has been characterized as the $[AuPPh_3]^+$ derivative.[114] The Cp ring is η^5-coordinated to the unique bridging ruthenium while the $AuPPh_3$ group bridges the hinge Ru–Ru bond.

Chemical reduction employing NaK alloy in THF or Na_2CO_3 in CH_3OH or electrochemical reduction of $Ru_5(CO)_{15}C$ leads to $[Ru_5(CO)_{14}C]^{2-}$ which can be isolated as its $[PPN]^+$ salt.[116] It reacts with $[AuPPh_3]Cl$ to give $Ru_5\{AuPR_3\}_2(CO)_{14}C$ ($PR_3 = PEt_3$, PPh_3, PMe_2Ph).[113] Treatment of these clusters with CO (80 atm, 60° C) results in loss of a ruthenium atom giving $Ru_4(CO)_{12}\{AuPR_3\}_2C$ in high yield (>80%). X-ray analysis has confirmed the structure of the PMe_2Ph derivative as a bridged butterfly with a $AuPR_3$ group acting as the unique bridging metal to a normal Ru_4C butterfly core. The other $AuPR_3$ bridges the hinge Ru–Ru bond. This contrasts with the structure of the iron complex of the same general formula which adopts an octahedral Fe_4Au_2 geometry with adjacent gold atoms. The hinge-bridging Au can be replaced in the ruthenium cluster with iodine by treating the complex with I_2 or with H by treating the complex with HI. These derivatives are isostructural with the parent digold cluster. Treatment of

$HRu_4\{AuPR_3\}(CO)_{12}C$ (R = Et or Ph) with [PPN][BH_4] produces $H_2Ru_4(CO)_{12}C$ whose structure is not yet known but does appear to be different from (μ-H)$Fe_4(CO)_{12}(\eta^2$-CH).[113] In the ruthenium case, the butterfly geometry is probably retained but with the hydrides associated only with the metals and not with the carbide as expected with the higher M–H bond energy for ruthenium as compared to iron.

The dianion $[PPN]_2[Ru_5(CO)_{14}C]$ reacts with $[Ru(\eta^6\text{-}C_6H_6)(NCPh)_3][ClO_4]$ in CH_2Cl_2 to give $Ru_6(CO)_{14}(\eta^6\text{-}C_6H_6)C$ in high yield.[173] This compound is related to the previously mentioned $Ru_6(CO)_{14}$(mesitylene)C cluster formed by pyrolysis of $Ru_3(CO)_{12}$ in mesitylene, and it can be reduced with Na_2CO_3 in CH_3OH to give $[Ru_6(CO)_{12}(C_6H_6)C]^{2-}$ which on further treatment with $[Ru(\eta^6\text{-}C_6H_6)(NCPh)_3][ClO_4]$ gives $Ru_6(CO)_{11}(C_6H_6)_2C$.[173] Mixed metal ions of formula $[Ru_5M(CO)_{17}C]^{2-}$ (M = Cr, Mo, W) have also been generated from $[Ru_5(CO)_{14}C]^{2-}$.[175] These clusters react with $Au(PR_3)X$ reagents to give neutral Ru_5CAu_2 clusters.

Reduction of $Ru_5(CO)_{15}C$ can be accomplished with LiMe giving the dianion $[Ru_5(CO)_{14}C]^{2-}$ in situ which upon addition of $AuPPh_3Cl$ produces a bridged-butterfly structure having the $AuPPh_3$ unit bridging the hinge bond[114] and a MeC(O)-group is sigma bonded to a hinge ruthenium. The oxygen of the acetyl donates to the unique bridging ruthenium atom. It is similar in structure to $Ru_5(CO)_{14}\{AuPPh_3\}(\mu\text{-Br})C$ where the μ-Br is replaced by the η^2-MeC(O)-. Structures of the same kind are known for some pentanuclear osmium clusters such as $HOs_5(CO)_{14}\{EtOC(O)\}C$.[123]

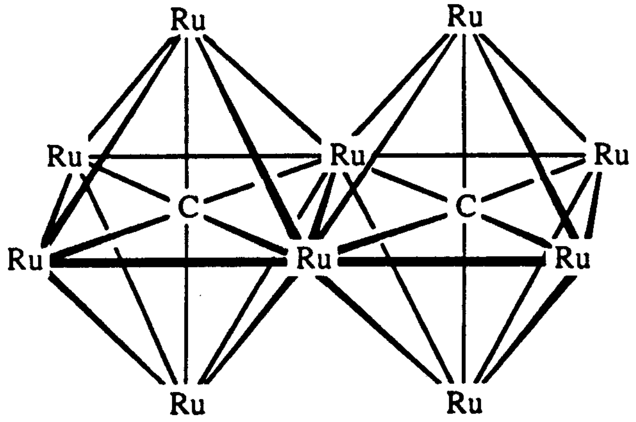
Nitrosyl ligated Ru_5C clusters can be obtained by treating $Ru_5(CO)_{15}C$ with $[NO_2]^-$ giving $[Ru_5(CO)_{13}(NO)C]^-$.[129] The simple $[AuPPh_3]^+$ derivative is known and exists in two isomeric forms. In one the gold atom bridges a triangular face of the square pyramidal Ru_5C core, while in the other the gold atom bridges an apical-basal Ru–Ru bond.

A square pyramidal Ru_5C cluster core is observed for a product of the reaction of $Ru_5(CO)_{13}(\mu\text{-}PPh_2)(\mu_5\text{-}C_2PPh_2)$ with dihydrogen.[131] The product is $(\mu\text{-H})_3Ru_5(CO)_{11}(\mu\text{-}PPh_2)(PMePh_2)C$. The carbide and $PMePh_2$ ligand are derived from hydrogenation of the C_2PPh_2 group in the starting material.

Reaction of $Ru_6(CO)_{17}C$ with $P(OMe)_3$ results in substitution where up to four CO ligands can be replaced by the phosphite.[115] Addition of HSEt, however, causes rearrangement of the cluster to a bridged butterfly geometry of formula $HRu_6(CO)_{15}(SEt)_3C$.[115] The structure of this molecule shows it to be like that of $Ru_5(CO)_{15}(NCMe)C$ but with the MeCN replaced by an $\{Ru(SMe)_3\}$ function which bridges a wingtip Ru to unique bridging Ru bond. The sulfido groups are all bridging. There is one bridge between the sixth ruthenium and the wingtip ruthenium and two between the unique bridging ruthenium and the sixth ruthenium atom. Yield data were not reported.

Extended pyrolysis of $[Ru_6(CO)_{16}C]^{2-}$ induces a coupling reaction giving $[Ru_{10}(CO)_{24}C_2]^{2-}$ (**Z**) in 35% yield.[176] The reaction is cation dependent and works best for $[Et_4N]^+$, $[Et_3NCH_2Ph]^+$ and $[Bu_4N]^+$ while Na^+, $[Me_3NCH_2Ph]^+$ and $[PPN]^+$ result only in decomposition. The molecule is composed of two octahedral cavities both containing six-coordinate carbide atoms. These two octahedra possess a common edge. The Ru–carbide and Ru–Ru distances are very similar to those in other Ru_6C clusters, although there is a considerable variation in metal–metal bond lengths (2.814 Å to 3.098 Å).

The lowest nuclearity osmium carbides known are pentametal clusters based on structures which have already been discussed for the ruthenium system. Thus $Os_5(CO)_{15}C$, a square pyramidal cluster with the carbide in the center of the square base, is obtained from the pyrolysis of $Os_6(CO)_{18}$ in 40% yield in an evacuated Carius tube at 255°C or from the pyrolysis of $Os_3(CO)_{12}$ in $\sim$10% yield.[117] In the $Os_3(CO)_{12}$ reaction other higher nuclearity carbonyls are produced such as $Os_6(CO)_{18}$, $Os_7(CO)_{21}$ and $Os_8(CO)_{23}$. Another carbido cluster, $Os_8(CO)_{21}C$, was identified from that reaction but its structure is unknown. Its electron count is the same as $[Re_8(CO)_{24}C]^{2-}$ suggesting that it might have a bicapped octahedral geometry.



Z

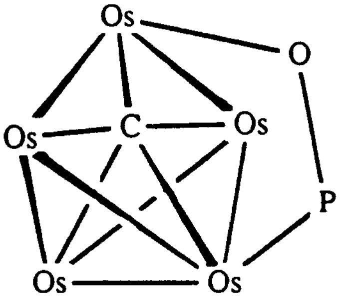
The basic Os_5C square pyramidal unit is also present in $[Os_6(CO)_{16}(MeC{=}CMe)C]$ produced from the pyrolysis of $Os_6(CO)_{18}$ with ethylene at 165°C.[132] The sixth osmium atom and the alkyne ligand bridge one of the basal Os–Os bonds in the square pyramid.

The reactivity of $Os_5(CO)_{15}C$ has been explored and shows similarities to $Ru_5(CO)_{15}C$. Reaction of I^- or CO (50 atm, 70°C) with $Os_5(CO)_{15}C$ results in addition to the cluster framework producing $[Os_5(CO)_{15}(I)C]^-$ or $Os_5(CO)_{16}C$, respectively, which adopt bridged-butterfly geometries like $Ru_5(CO)_{15}(NCMe)C$.[118,116] The iodide ion and added CO are observed by X-ray analysis to be attached to the unique bridging metal as is the MeCN in the ruthenium complex. Similarly, 1,2-bis(diphenylphosphino)ethane (dppe) adds to $Os_5(CO)_{15}C$ to give a monodentate coordination of the phosphine in the bridged butterfly geometry.[117] This is unlike the ruthenium system for which reaction with phosphines has been observed only to yield substituted products. Presumably that substitution process proceeds by an initial adduct formation with fast subsequent loss of CO to generate the substituted products. Addition of H_2 (75 atm, 90°C) to $Os_5(CO)_{15}C$ gives $H_2Os_5(CO)_{15}C$ of undetermined structure.[116]

Alcohols and I_2 also add to $Os_5(CO)_{15}C$ giving bridged-butterfly based geometries. Addition of ROH results in protonation of the Os–Os hinge bond and RO^- attack at a CO producing a $C(O)OR^-$ ligand in which the carbon of the carbonyl function is attached to an osmium hinge atom and the oxygen of the carbonyl is attached to the unique bridging metal atom. Structural data is available for the compound for which R = Et.[123] Iodine addition to $Os_5(CO)_{15}C$ gives $I_2Os_5(CO)_{15}C$ in which one I bridges the Os–Os hinge bond and the other is coordinated in a terminal fashion to the unique bridging metal in much the same manner as seen for $Ru_5(CO)_{15}(AuPPh_3)(Cl)C$. Addition of ROH to $I_2Os_5(CO)_{15}C$ causes the loss of HI and production of $(\mu\text{-}I)Os_5(CO)_{14}\{C(O)OR\}C$. X-ray analysis of the R=Me derivative shows it to be essentially isostructural to $HOs_5(CO)_{14}\{C(O)OEt\}C$.[123] The major difference is that the bridging I ligand appears to function as a three electron donor which causes breakage of the bridged Os–Os hinge bond. Loss of the alkoxy group results upon treatment of $HOs_5(CO)_{14}\{C(O)Et\}C$ with H_2 or CO and leads to the formation of $H_2Os_5(CO)_{15}C$. $Os_5(CO)_{16}C$ was also isolated when R = Et. Protonation by concentrated H_2SO_4 similarly causes loss of the alkoxy function.

Electrochemical 2e reduction of $Os_5(CO)_{15}C$ occurs at −1.50 V (scan rate $1\ Vs^{-1}$, 25°C) which can be compared to the value of −1.78 V observed for $Ru_5(CO)_{15}C$ under the same conditions.[116] Controlled potential electrolysis produces $[Os_5(CO)_{14}C]^{2-}$ which can be obtained by reduction of $Os_5(CO)_{15}C$ with NaK alloy in THF, with KOH or Na_2CO_3 (75% yield) in CH_3OH or with $[Et_4N][BH_4]$ in CH_2Cl_2 (57% yield). The structure of the product is square pyramidal. It can be protonated but gives the pentadecacarbonyl product $H_2Os_5(CO)_{15}C$ identical to that obtained from reaction of H_2 and $Os_5(CO)_{15}C$.

Reaction of $[Os_5(CO)_{14}C]^{2-}$ with $AuClPPh_3$ in the presence of $TlPF_6$ produces an intermediate monoanion $[Os_5(CO)_{14}(AuPPh_3)C]^-$ which reacts further giving $Os_5(CO)_{14}(\mu\text{-}AuPPh_3)_2C$ whose X-ray structure shows it to be similar to the parent but has $AuPPh_3$ groups bridging opposite apical to basal Os–Os edges.[116] The Tl salt is present to promote the abstraction of halide from the gold reagent, but it should be noted that thallium is not "innocent" in metal carbonyl anion systems as will be discussed later. The bridged edges of $Os_5(CO)_{14}(\mu\text{-}AuPPh_3)_2C$ are *ca.* 0.2Å longer than the corresponding nonbridged distances. Usually the carbide atom lies below the square basal plane in molecules of this type but here it is 0.04Å above that plane.



AA

The bridged-butterfly geometry is observed for a series of products arising from the pyrolysis of $Os_3(CO)_{11}\{P(OMe)_3\}$. Those clusters are $HOs_5(CO)_{13}\{OP(OMe)OP(OMe)_2\}C$,[120] $HOs_5(CO)_{14}\{OP(OMe)_2\}$[119] and $HOs_5(CO)_{13}\{OP(OMe)_2\}\{P(OMe)_3\}C$.[121] The metal core of $HOs_5(CO)_{14}\{OP(OMe)_2\}C$ is represented as **AA**. In these compounds the phosphorus atom of what was originally a phosphite ligand is coordinated to one of the hinge Os atoms. A phosphite oxygen from which the methyl group has been removed is attached to the unique bridging metal. The hydride ligands are thought to bridge the two hinge Os atoms. For the case where two phosphite ligands have coupled to give $OP(OMe)OP(OMe)_2$, the second phosphorus displaces a carbonyl on a wingtip osmium giving an intramolecularly substituted cluster. The location of substitution is different from that seen in $HOs_5(CO)_{13}\{OP(OMe)_2\}\{P(OMe)_3\}C$ where the $P(OMe)_3$ is found in place of CO on the unique bridging metal atom. The choice of metal may be influenced by steric requirements where the coupled ligand is present. The presence of the P–O bridge between the unique bridging metal does not sit symmetrically above the Os–Os hinge bond but is displaced towards the side of the PO bridging group as expected. This type of distortion is also present in $Ru_5(CO)_{14}(\mu\text{-}AuPPh_3)(\mu\text{-}Br)C$ where the bromide bridges the corresponding ruthenium atoms. The pyrolysis of $Os_3(CO)_{11}\{P(OMe)_3\}$ also yields a non-carbido product, $Os_5(CO)_{15}(\mu_4\text{-}POMe)$ which will be discussed later.

Some mixed osmium–platinum carbide compounds have been generated by addition of $Pt(C_2H_4)_2\{P(\textit{cyclo}\text{-}C_6H_{11})_3\}$ across the CH bond of $(\mu\text{-}H)Os_3(CO)_{10}(\mu_3\text{-}CH)$.[353] One product is a four metal cluster of formula $(\mu\text{-}H)_2Os_3\{PtP(C_6H_{11})_3\}(CO)_{10}C$ in which the Pt atom bridges an Os–carbide bond of a tetrahedral Os_3C cluster. In the other, there are three osmium and two platinum atoms: $(\mu\text{-}H)_2Os_3\{PtP(C_6H_{11})_3\}_2(CO)_{10}C$. This compound has a five-coordinate carbon sitting on a triangle of osmium atoms with the two platinum atoms each bridging an Os–C bond. One could view the structure as being derived from an Os_3Pt_2C square pyramid with the two platinums as adjacent basal metals. To get the observed structure the Pt-to-apical Os bonds are broken. These two products could also be obtained from the reaction of the ketenylidene cluster $(\mu\text{-}H)Os_3(CO)_9(\mu_3\text{-}CCO)$ with the same platinum reagent.

A similar five metal complex is obtained when $(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}COMe)$ is treated with $Pt(C_2H_4)_2\{P(\textit{cyclco}\text{-}C_6H_{11})_3\}$.[353] In this case the platinum atoms have inserted into the μ_3-C–O bond of the starting material, with the methoxy group adopting a bridging configuration between two osmium atoms. The structure is very similar to that of $(\mu\text{-}H)_2Os_3\{PtP(C_6H_{11})_3\}_2(CO)_{10}C$ except one μ-H ligand is replaced by μ-OMe and the other bridges a Pt–Os rather than an Os–Os bond in the new structure.

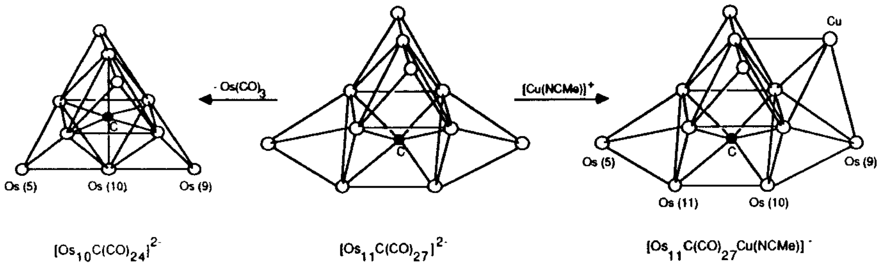
The next higher nuclearity carbide cluster $Os_6(CO)_{17}C$ is prepared by treating $Os_3(CO)_{12}$ first with one equivalent of Na in refluxing diglyme.[352] The intermediate anion $[Os_6(CO)_{16}C]^{2-}$ is then oxidized in the presence of CO by ferric ion to give the neutral heptadecacarbonyl cluster.

The Os_6 carbide dianion is difficult to isolate from pyrolysis reactions of $Os_3(CO)_{12}$ owing to the formation of the very stable $[Os_{10}(CO)_{24}C]^{2-}$ cluster which is obtained in 63% yield as the $[Et_4N]^+$ salt when $Os_3(CO)_{12}$ and *ca.* 1 equivalent of Na are heated in tetraglyme to 230°C.[352] It can also be prepared by pyrolysis of $Os_3(CO)_{11}$(pyridine) *in vacuo* giving 80% yield,[122] but that method suffers from the necessity of making the pyridine substituted complex first. X-ray analysis shows the carbide to reside in an octahedral Os_6 cavity capped on four faces with $\mu_3\text{-}Os(CO)_3$ groups having approximate overall Td symmetry,[122,177] obeying Wade's rules with seven skeletal electron pairs as expected for an octahedron. X-ray absorption fine structure (EXAFS) data are available for $[Os_{10}(CO)_{24}C]^{2-}$.[354]

Numerous derivatives of $[Os_{10}(CO)_{24}C]^{2-}$ are known. Addition of $[Cu(NCMe)_4]BF_4$ to $[Os_{10}(CO)_{24}C]^{2-}$ results in capping one Os_3 triangle not involved as a face of the octahedron.[179,180] In contrast addition of $Au(PPh_3)Cl$ gives a product having an Os–Os bond bridged by the gold atom.[179,180] The Os–C(carbide) distances do not seem to be affected by those derivatizations (Table VIII). Addition of PPh_3AuBr and $AgClO_4$ to $[Os_{10}(CO)_{24}C]^{2-}$ produces $[Os_3(CO)_{24}(\mu_3\text{-}AuBr)C]^{2-}$ in which the μ_3-AuBr moiety caps a face similarly to $AuPPh_3$ in the $[Os_{10}(CO)_{24}(\mu_3\text{-}$

$AuPPh_3)C]^-$ cluster.[181] Mercury reagents XHgY, X = C_6F_5, C_6Cl_5, CF_3CO_2 or Cl; Y = Cl, CF_3CO_2 behave similarly in reaction with $[Os_{10}(CO)_{24}C]^{2-}$ Ultimately, however, both the AuBr and HgR complexes dimerize to give the very large clusters $[Os_{20}(CO)_{48}M(C)_2]^{2-}$ (M = Au, Hg) in which the octahedral carbide groups are retained.[181] Addition of a proton, however, produces $[HOs_{10}(CO)_{24}C]^-$ for which the X-ray data imply the hydrogen to reside in an interstitial tetrahedral Os_4 cavity.[178] Two nitrosyl derivatives from the reaction of $[Os_{10}(CO)_{24}C]^{2-}$ with $[NO]BF_4$ have been structurally characterized.[182] The first arises from the simple addition of NO^+ across an Os–Os bond of one of the tetrahedral μ_3-$Os(CO)_3$ units giving $[Os_{10}(CO)_{24}(NO)C]^-$ in which the NO ligand acts as a three electron donor and bridges two osmium atoms which are no longer bonded to each other. Upon standing in solution it loses CO to give $[Os_{10}(CO)_{23}(NO)C]^-$ which is isostructural with the all-carbonyl compound. The Os–carbide carbon distances show little sensitivity to these structural changes, but the Os–Os bonds in the octahedral fragment show some distortion. As expected $[Os_{10}(CO)_{23}(NO)C]^-$ is virtually identical to the all-carbonyl parent, while the derivatives possessing an NO or I bridged Os–Os bond show some average lengthening of the metal–metal bonds within the octahedron.

Similar results obtain for the reaction of I_2 with $[Os_{10}(CO)_{24}C]^{2-}$.[183] The products are $[(\mu\text{-}I)Os_{10}(CO)_{24}C]^-$, which is isostructural with the twenty-four carbonyl-containing nitrosyl compound, and $(\mu\text{-}I)_2Os_{10}(CO)_{24}C$. In the latter, the second iodine adds similarly to the first but across the Os–Os bond of one of the other capping μ_3-Os groups.



Scheme IV

The higher nuclearity osmium carbonyl carbide anion $[Os_{11}(CO)_{27}C]^{2-}$ is obtained in low yield from the vacuum pyrolysis of $Os_3(CO)_{12}$.[187] It has not been successfully structurally characterized owing to crystal disorder problems, but the $Cu(NCMe)^+$ derivative has been made and shown to possess a trigonal prismatic arrangement of osmium atoms about the carbide. The Os–C distances are considerably longer (~0.12Å than in the octahedral-centered structures) while the Os–Os interactions seem to be slightly shorter in the trigonal prism than in the octahedral compounds. It is the only iron group metal cluster known to adopt a trigonal prismatic structure about the carbide. In the structure the two triangular faces of the prism are capped by μ_3-$Os(CO)_3$ units and one of the square faces by a linear Os_3

fragment perpendicular to the C_3 axis of the prism. The Cu is bonded to four osmium atoms as an equatorial vertex in a trigonal bipyramidal array. These osmium atoms include one of the capping μ_3-Os atoms, two osmium atoms of the triangle to which that capping osmium is attached and the central osmium of the linear, square face-capping Os_3 fragment. The $[Os_{11}(CO)_{27}C]^{2-}$ anion will undergo reactions similar to $[Os_{10}(CO)_{24}C]^{2-}$ with I_2 giving $[(I)Os_{11}(CO)_{27}C]^-$ and with $AuPR_3{}^+$ reagents giving $[Os_{11}(CO)_{27}(AuPR_3)C]^-$. All of these clusters undergo loss of an osmium atom to generate $[Os_{10}(CO)_{24}C]^{2-}$. The structural conversion can be easily envisioned as illustrated in Scheme IV.

Cobalt and rhodium also form a series of high nuclearity carbido-cluster compounds, and both metals show a marked preference for putting the carbide atom in a trigonal prismatic cavity in contrast to the iron group metals where the preference appears to be for the octahedron. The metal to carbido–carbon distances are slightly longer in the trigonal prismatic cavities as seen in Table VIII. Some of the cobalt cluster interconversions are illustrated in Scheme V. The parent compound for the cobalt series is the $[Co_6(CO)_{15}C]^{2-}$ anion which is synthesized by the reaction of $Co_3(CO)_9CCl$ with $[Co(CO)_4]^-$ in 40–50% yields.[188] The direct reaction of CCl_4 with $[Co(CO)_4]^-$ produces the same cluster in much lower yields. The structure of the cluster is a trigonal prism of cobalt atoms surrounding an interstitial carbide with nine skeletal electron pairs available for cluster bonding as expected. In general, it appears for the trigonal prismatic clusters that the M–M bonds within the two triangular faces are slightly shorter than the bonds between the two triangles. A mixed Co–Rh cluster $[Co_2Rh_4(CO)_{15}C]^{2-}$ is generated similarly by treating the $Co_3(CO)_9CCl$ cluster with $[Rh(CO)_4]^-$ but it has not been structurally characterized.[186]

$$Co_3(CO)_9CCl + 3Na[Co(CO)_4] \xrightarrow{60^\circ C} Na_2[Co_6(CO)_{15}C] + NaCl + CO \qquad (99)^{186,188}$$

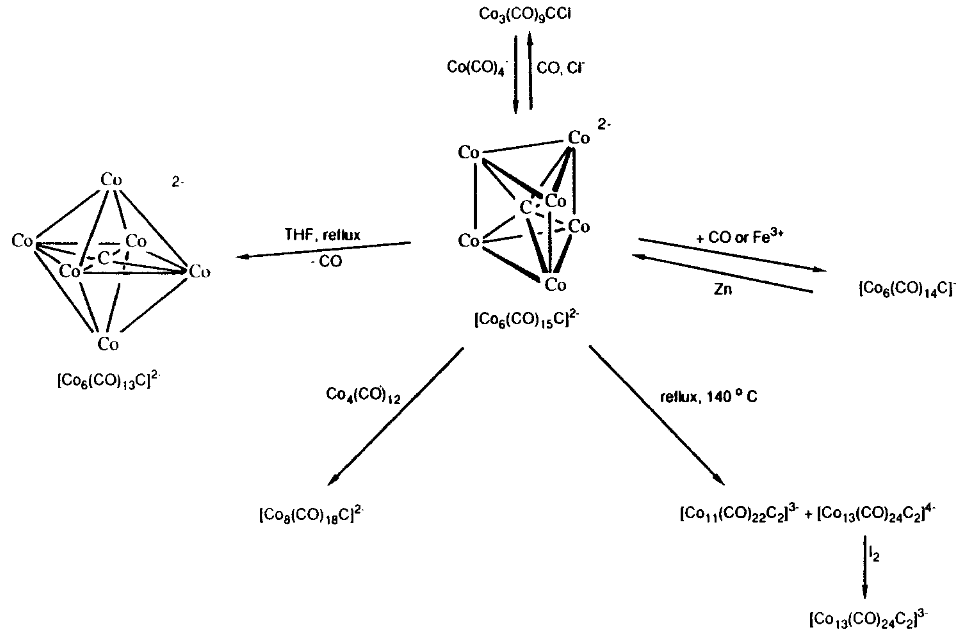
$[Co_6(CO)_{15}C]^{2-}$ is degraded in the presence of CO and Cl^- to $Co_3(CO)_9CCl$ and $[Co(CO)_4]^-$ but with only CO added it is converted to the octahedral, paramagnetic cluster $[Co_6(CO)_{14}C]^-$. A more efficient synthesis of the paramagnetic species arises from the oxidation of $[Co_6(CO)_{15}C]^{2-}$ by ferric ion (75–80%).[188] Reduction of $[Co_6(CO)_{14}C]^-$ in the presence of CO under appropriate conditions affords the parent $[Co_6(CO_{15}C]^{2-}$.

$$[Co_6(CO)_{15}C]^{2-} + Fe^{3+} \xrightarrow[Et_4NBr]{\text{diisopropyl ether}} [Co_6(CO)_{14}C]^- + Fe^{2+} + CO \qquad (100)^{188}$$

$$[Et_4N][Co_6(CO)_{14}C] + Zn \longrightarrow \underset{\text{(ppt, quantitative)}}{[Et_4N]_2[Co_6(CO)_{15}C]} \qquad (101)$$

Reaction of $[Co_6(CO)_{15}C]^{2-}$ with $Co_4(CO)_{12}$ leads to $[Co_8(CO)_{18}C]^{2-}$ which has the carbide centered in a rare square antiprismatic array of cobalt atoms. The octacobalt cluster also reacts with CO to produce $[Co_6(CO)_{14}C]^-$.[188]

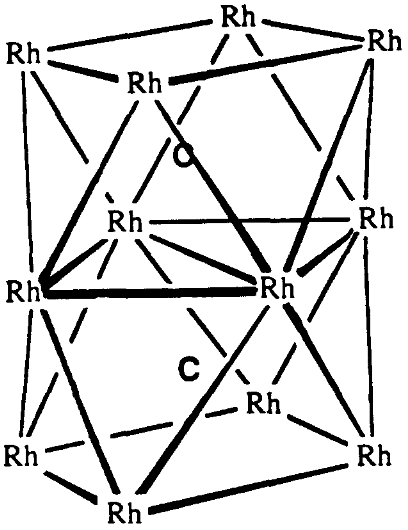
Refluxing $[Co_6(CO)_{15}C]^{2-}$ in THF causes the elimination of CO and the formation of $[Co_6(CO)_{13}C]^{2-}$ in which the cobalt framework has rearranged from trigonal prismatic to octahedral to accommodate the presence of two less skeletal electron pairs.[184] The Co–C distances are slightly shorter in the octahedral cluster (1.87Å, ave) than in the trigonal prismatic form (1.95Å, ave). At higher temperatures the pyrolysis reaction leads to $[Co_{11}(CO)_{22}C_2]^{3-}$ and $[Co_{13}(CO)_{24}C_2]^{4-}$.[355] An X-ray analysis of $[Co_{11}(CO)_{22}C_2]^{3-}$ has been performed and shows that it belongs to the small class of clusters containing an interstitial dicarbide group (d_{C-C} = 1.62Å). The metal geometry can be viewed as a tricapped cube or as a trigonal prism with a capped square face fused onto a square antiprism through a square face. On the other hand, the crystal structure of $[Co_{13}(CO)_{24}C_2]^{4-}$ shows it to be a complex arrangement of metal atoms with the two carbido atoms well-separated but both sit in trigonal prismatic cavities for which the Co–C distances (1.98Å, ave) are similar to those in the hexanuclear parent.[196] Oxidation of $[Co_{13}(CO)_{24}C_2]^{4-}$ with I_2 leads to $[Co_{13}(CO)_{24}C_2]^{3-}$ which has been structurally characterized and is isostructural with the tetraanion.[195] The average Co–Co bond distances are the same for both. The Co–C (Carbide) distances are slightly shorter in the trianion overall (1.97Å, ave.). This difference was interpreted as implying that the extra electron is present to help widen the trigonal prismatic cavity to accommodate the carbide atom.



Scheme V

Treating $Co_2(CO)_8$ with CS_2 results in the formation of a trigonal prismatic hexacobalt carbide cluster $Co_6(CO)_{12}(\mu_3\text{-}S)_2C$ that is capped on the two triangular faces by sulfur atoms.[87] The sulfur atoms are formally four electron donors so that $Co_6(CO)_{12}(\mu_3\text{-}S)_2C$ is isoelectronic with $[Co_6(CO)_{15}C]^-$. The Co–carbide distances are comparable for the two molecules, but the M–M bond distances show some differences. The effect of the μ_3-S atoms is to shorten the Co–Co bonds within the triangular faces by *ca.* 0.1Å. The average of all metal–metal bond distances for the disulfide carbide cluster, however, is about the same for the overall average of the Co–Co bonds in $[Co_6(CO)_{15}C]^-$ (2.51Å *vs.* 2.55Å). The origin of the carbide atom has been confirmed by isotope labelling studies. The Co–C stretching frequencies were located in that study at 819 cm^{-1} and 548 cm^{-1} (790 cm^{-1} and 535.5 cm^{-1}) for ^{13}C and have been assigned to the A_2'' and E' modes, respectively. The frequency of the A_2'' mode corresponds well with the values seen for the iron carbide $Fe_5(CO)_{15}C$.[294]

The rhodium carbide complexes are similar to their cobalt counterparts. Treatment of $Rh_4(CO)_{12}$ with NaOH in CH_3OH under CO produces $[Rh_7(CO)_{13}]^{3-}$ which reacts with $CHCl_3$ to produce $[Rh_6(CO)_{15}C]^{2-}$ and which is isostructural and isoelectronic with the cobalt compound. The potassium salt is obtained in 70% yield from this method. This anion can be oxidized with ferric ion to $Rh_8(CO)_{19}C$,[186,194] $[Rh_{15}(CO)_{28}C_2]^-$ [356] and $Rh_{12}(CO)_{25}C_2$.[357] The neutral $Rh_{12}(CO)_{25}C_2$ is interesting in possessing a dicarbide ligand (d_{C-C} = 1.48Å) like $[Co_{11}(CO)_{22}C_2]^{3-}$.



AB

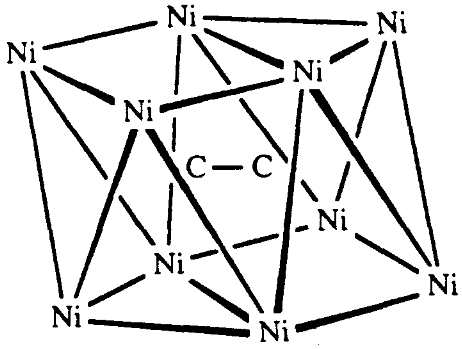
Addition of H_2SO_4 to $[Rh_6(CO)_{15}C]^{2-}$ generates $[Rh_{12}(CO)_{24}C_2]^{2-}$ perhaps via the intermediacy of a reactive hydride $[HRh_6(CO)_{15}C]^-$ which dimerizes with elimination of H_2. The structure of this cluster shows it to be composed of two trigonal prismatic Rh_6C units which share an intertriangle edge **AB**.[198] Two capping rhodium atoms are situated symmetrically over both sides of this common edge and are bonded to six rhodium atoms each. A detailed ^{13}C NMR investigation of the $[Rh_6(CO)_{15}C]^{2-}$ ion and its monohydride has been reported.[358]

Reduction of $[Rh_{12}(CO)_{24}C_2]^{2-}$ by alkali metal hydroxides in MeOH produces paramagnetic $[Rh_{12}(CO)_{23}C_2]^{3-}$ and diamagnetic $[Rh_{12}(CO)_{23}C_2]^{4-}$ for which the arrangements of metal atoms are almost identical to those of the parent.[199,200] While the Rh–C distances in all three of these dicarbide clusters are very similar, the Rh–Rh distance with the Rh_3 triangles seem to be greater upon reduction (Table VIII).

Nickel carbonyl complexes form carbido clusters via the reaction of $[Ni_6(CO)_{12}]^{2-}$ with CCl_4. Depending on conditions, the clusters generated include $[Ni_{10}(CO)_{18}C]^{2-}$ (34.5%), $[Ni_9(CO)_{17}C]^{2-}$ (80%) or $[Ni_8(CO)_{16}C]^{2-}$ (69%).[359] The octa- and nonanickel complexes have been structurally characterized. Both are based on a square antiprismatic array of nickel atoms. In the nine metal cluster, the added metal caps one of the square faces. The suggested geometry for the ten metal system is quite reasonably the bicapped square antiprism geometry. This structural array is observed for $[Bi_8]^{2+}$ which has the same number of skeletal electron pairs for cluster bonding. The Ni–carbide distances are 2.084Å in $[Ni_8(CO)_{16}C]^{2-}$ which has only one unique Ni–carbide distance as imposed by crystallographic symmetry, while the reported values for $[Ni_9(CO)_{17}C]^{2-}$ are 2.03Å and 2.15Å within the square antiprism and the capping Ni is 2.81Å from the carbide. The Ni–Ni distances average 2.55Å for both compounds with the inter-square planar distances being somewhat longer (2.627Å for Ni_8C^{2-}, 2.612Å for Ni_9C^{2-}) than the distance within the planes (2.477Å for Ni_8C^{2-}, 2.489Å for Ni_9C^{2-}).

The decanuclear cluster was not characterized by X-ray due to lack of suitable single crystals. It is not surprisingly converted into the nine nickel cluster under CO. In the presence of Cl^-, another product observed is $[Ni(CO)_3Cl]^-$. Under CO alone, the mononuclear product is $Ni(CO)_4$. Consequently, $[Ni_{10}(CO)_{18}C]^{2-}$ is best obtained when the reactions are run under a purge of N_2 to remove by-product CO. The $[Ni_9(CO)_{17}C]^{2-}$ cluster is further degraded to $[Ni_8(CO)_{16}C]^{2-}$ in the presence of CO.

A related cluster is the dicarbide anion $[Ni_{10}(CO)_{16}C_2]^{2-}$ which arises when $[Ni_6(CO)_{12}]^{2-}$ is treated with C_2Cl_6 or C_2Cl_4.[360] In this cluster, the carbon atoms are within bonding distance (1.40Å). Each carbon atom is, on the average, 2.08Å from the seven nearest nickel atoms. The nickel skeleton can be described as two square-face sharing trigonal prisms which are each capped by μ_4-Ni groups. Alternatively, the geometry can be viewed as based on two distorted edge-sharing octahedra which are further linked via the apical metal atoms. $[Ru_{10}(CO)_{24}C_2]^{2-}$ has a similar arrangement of metal atoms.[176] The Ni–Ni distances show a considerable range (2.38Å to 3.00Å) with the largest distances being seen around the shared square face. One could envision the C atoms originally being centered in the trigonal prisms but having been pulled towards each other by the bonding interaction. This results in the opening of the shared square metal face (**AC**).



AC

Mixed metal carbido clusters are obtained if $[Ni_6(CO)_{12}]^{2-}$ is treated with $Co_3(CO)_9CCl$ (2 : 1 ratio). The observed product along with $Ni(CO)_4$ is $[Co_3Ni_9(CO)_{20}C]^{3-}$ which is a tetracapped square antiprism of nickel atoms.[360] Its reactivity with CO is unusual when compared to other metal carbonyl carbides in that it is completely degraded, the products being $[Co(CO)_4]^-$ and $Ni(CO)_4$. Under a mixture of H_2 and CO (1:1, 1 atm, 25°C) the carbide is converted selectively into ethane. Under different conditions the cluster product obtained is a dicarbide, $[Co_6Ni_2(CO)_{16}C_2]^{2-}$, which can also be generated by addition of $Co_3(CO)_9CCl$ to $[Co_3Ni_9(CO)_{20}C]^{3-}$. This cluster is composed of two square face-sharing trigonal prisms with a carbide atom in the center of each. The C–C distance is only 1.49Å and in that regard is similar to several other clusters which have been noted as having an interstitial dicarbide. Data for the C–C separation for a number of these complexes are summarized in Table XIII.

If the starting nickel cluster is $[Ni_9(CO)_{17}C]^{2-}$, the reaction with $Co_3(CO)_9CCl$ yields the dicarbide cluster $[Co_3Ni_7(CO)_{16}C_2]^{2-}$ which can be reduced by Na in THF to $[Co_3Ni_7(CO)_{16}C_2]^{3-}$ or with NaOH in CH_3OH to $[Co_3Ni_7(CO)_{15}C_2]^{3-}$.

The dicarbide dianion $[Co_3Ni_7(CO)_{16}C_2]^{2-}$ has been structurally characterized and shows a coupled, interstitial C_2 moiety ($d_{C-C} = 1.48$Å).[362] The metal framework bears close relationship to $[Ni_{10}(CO)_{16}C_2]^{2-}$ except that the distortions from the ideal trigonal prismatic geometry are greater. The metal atoms are apparently disordered as often happens in the mixed metal systems. The metal–carbide distances range from 1.90Å to 2.15Å (2.07 ave) which is not very different from that seen in $[Ni_{10}(CO)_{16}C_2]^{2-}$. The cobalt–nickel cluster contains three fewer electrons than the all nickel one, a condition that is the cause of the observed structural distortions. In fact, the extra electrons in $[Co_3Ni_7(CO)_{15}C_2]^{3-}$ (which has one more electron pair than $[Ru_{10}(CO)_{24}C_2]^{2-}$) are thought to reside in the C–C bonding orbital. The close C–C distance is lacking in $[Ru_{10}(CO)_{24}C_2]^{2-}$.

The structure of $[Co_3Ni_7(CO)_{15}C_2]^{3-}$ (which has one less electron than $[Co_3Ni_7(CO)_{16}C_2]^{2-}$) has been done and shows that the C–C distance (1.41Å) is shorter than in the dianion, presumably because the extra electron in $[Co_3Ni_7(CO)_{16}C_2]^{2-}$ lies in the C–C antibonding orbital: the metal–metal frameworks show almost identical parameters. Treatment of $[Co_3Ni_7(CO)_{15}C_2]^{3-}$ with H_2 and CO liberates the C_2 moiety as ethane, and this cluster may be an intermediate in the generation of ethane from $[Co_3Ni_9(CO)_{20}C]^{3-}$ under H_2. The chemistry of some of these carbido–cobalt and nickel clusters has been previously reviewed.[364]

When treated with PPh_3, the dicarbido cluster $[Ni_{10}(CO)_{16}C_2]^{2-}$ is converted into $[Ni_{16}(CO)_{23}C_4]^{4-}$ which contains two interstitial C_2 groups.[365] The C–C distance of 1.38Å is the shortest observed for dicarbide type clusters but the two dicarbide groups do not bond to each other even though they reside in the same, large cavity of the cluster.

5.1.3 Nitrogen: Similar butterfly, square pyramidal and octahedral structures are observed for the nitrido clusters, a topic which has recently been reviewed.[366] A variety of approaches are available which use NO, NO^+, NO_2^- and NCO^- as nitride sources. The reaction of $[NO_2]^-$ with metal carbonyls produces CO_2 and a nitrosyl ligand.[103]

$$Fe(CO)_5 + [NO_2]^- \rightarrow [Fe(CO)_3(NO)]^- + CO + CO_2 \qquad (102)$$

Further reaction of $[Fe(CO)_3(NO)]^-$ with $Fe_3(CO)_{12}$ produces $Fe(CO)_5$ and $[Fe_4(CO)_{12}N]^-$.[103,104] The overall stoichiometry has been determined to be:

$$2[Fe(CO)_3NO]^- + 3Fe_3(CO_{12} \rightarrow 2[Fe_4(CO)_{12}N]^- + 3Fe(CO)_5 + 2CO_2 + CO \qquad (103)$$

Protonation of $[Fe_4(CO)_{12}N]^-$ yields $HFe_4(CO)_{12}N$.[104] No further interaction of the nitrogen with protons to give NH or M–H–N bonds has been observed unlike the carbide system. Similar chemistry employing $Ru_3(CO)_{12}$, however, led first to $[FeRu_3(CO)_{12}(NO)]^-$ but upon protonation the nitrido-mixed-metal cluster $HFeRu_3(CO)_{12}N$ was obtained.[43] Apparently, the intermediate production of a nitrosyl ligand is important to this chemistry. The NO ligand can then be reduced by reaction with coordinated CO (producing CO_2) or some other reducing agent such as metal bound hydride ligands. Similarly, when $Ru_3(CO)_{12}$ is treated with $[Ru(CO)_3NO]^-$ the product is $[Ru_4(CO)_{12}N]^-$ obtained in 40% yield.[128]

Pre-coordinated nitrosyl ligands are evidently converted to nitrides when $Ru_3(CO)_{10}(\mu\text{-}NO)_2$ is treated with CO.[108] A mixture of products results which includes $Ru_3(CO)_{12}$, $Ru_3(CO)_{10}(\mu\text{-}NO)(\mu\text{-}NCO)$, $Ru_4(CO)_{12}(\mu\text{-}NO)N$ and $Ru_4(CO)_{12}(\mu\text{-}NCO)N$. The two tetranuclear nitrides adopt butterfly geometries with the hinge bond bridged in one case by NO and in the other by NCO. The Ru–Ru hinge distances are long suggesting that the two bridging ligands function as three electron donors to break that metal–metal bond. The iron nitride cluster $[Fe_4(CO)_{12}N]^-$ will react with $[NO]^+$ to give $Fe_4(CO)_{11}(NO)N$.[104]

Another method which generates intermediate nitrosyl ligands is the reaction of $[NO]^+$ salts with transition metal cluster anions. Thus treatment of $[H_3Ru_4(CO)_{12}]^-$ with $[NO]BF_4$ produces $HRu_4(CO)_{12}N$ in low yield presumably via a $Ru_4(NO)$ intermediate.[106] Structural data is available for the trimethylphosphite derivative of this cluster. $H_3Ru_4(CO)_{11}N$ is also known from this route.[107] Reaction of NO^+, $Fe(CO)_5$ and $[Fe_2(CO)_8]^{2-}$ produces the previously mentioned $[Fe_4(CO)_{12}N]^-$ along with $[Fe_5(CO)_{14}N]^-$.[105] The structures of these complexes are analogous to the corresponding carbido clusters. The pentanuclear nitride can also be protonated giving $HFe_5(CO)_{14}N$ where, as before, the proton is associated with the metal centers and not the nitrogen atom.

Isocyanate ligands can function as a source of nitride atoms. These ligands are generated via attack on CO by azide ion, N_3^-, with the liberation of dinitrogen. Addition of $[PPN][N_3]$ to $Ru_3(CO)_{12}$ produces $[PPN][Ru_6(CO)_{16}N]$ in 90% yield presumably via an intermediate isocyanate. The production of a nitride ligand from coordinated isocyanate is directly observed for $[Ru_4(CO)_{13}(NCO)]^-$ which slowly converts into $[Ru_4(CO)_{12}N]^-$ in solution.[128]

Cluster building reactions are known but less has been reported for the nitrides than for the carbides. One reaction that has been reported is the generation of $[FeRu_4(CO)_{14}N]^-$ from $[FeRu_3(CO)_{12}N]^-$ and $Ru_3(CO)_{12}$.

As in the case of some of the ruthenium carbide clusters, degradation of the hexanuclear nitride under pressures of CO occurs producing $Ru(CO)_5$ (which rapidly converts to $Ru_3(CO)_{12}$) and the pentanuclear ruthenium nitrido cluster in 95% yield. The conditions are, interestingly, less severe than those used for the similar degradation of the $Ru_6(CO)_{17}C$ cluster. Charge differences may be an important factor influencing the reactivity pattern differences between the carbido and nitrido systems.[128]

$$[Ru_6(CO)_{16}N]^- \longrightarrow [Ru_5(CO)_{14}N]^- + 1/3\ Ru_3(CO)_{12} \qquad (104)$$

A butterfly cluster containing a nitride-like function bonded to only three of the metals has been observed for $[HOs_4(CO)_{12}\{\mu_3\text{-}N(CO)Me\}MPPh_3]$ (M = Au, Cu) obtained from the reaction of $[H_3Os_4(CO)_{12}(NCMe)_2]^+$ and $[NO_2]^-$ followed by addition of $MPPh_3{}^+$ reagents. The nitride-like ligand is derived from the acetonitrile ligand of the parent.[367]

Cobalt and rhodium nitrides have been obtained via similar reactions employing NO^+, NO_2^-, or NO.[189,191]

$$[Co_6(CO)_{15}]^{2-} + NO^+ \rightarrow [Co_6(CO)_{15}N]^- + Co^{2+} + Co(CO)_3NO + Co_4(CO)_{12} \qquad (105)$$

$$[Rh_6(CO)_{15}]^{2-} + NO^+ \rightarrow [Rh_6(CO)_{15}N]^- \qquad (106)$$

$$M_4(CO)_{12} + NO_2^- \rightarrow [M_6(CO)_{15}N]^- \quad (M = Co, Rh) \qquad (107)$$

The yields in these reactions span a considerable range with NO^+ and $[Co_6(CO)_{15}]^{2-}$ giving 40–50% yields while the reaction of NO_2^- and $Co_4(CO)_{12}$ gives the same product in 12% yield. In contrast the rhodium reactions appear to produce the nitride in higher yield from the NO_2^- route. Thus NO^+ and $[Rh_6(CO)_{15}]^{2-}$ yields the hexanuclear nitride in less than 10% yields while the NO_2^- treatment of $Rh_4(CO)_{12}$ gives 30% and $Rh_6(CO)_{16}$ gives 74%. A 1 : 1 mixture of NO and CO reacts with $[Rh_7(CO)_{16}]^{3-}$ producing the same nitrido cluster in 40–60% yields.

Reaction of $[Rh_6(CO)_{15}N]^-$ and $[PtRh_4(CO)_{14}]^{2-}$ results in a cluster building reaction where one of the products has been characterized as $[PtRh_{10}(CO)_{21}N]^{3-}$.[368] The nitride is interstitial and resides in an unusual five-coordinate cavity. The metal framework is not readily described in terms of a common structure but appears to be based approximately on a fragment of a hexagonal close-packed array of metal atoms. Only one complex containing more than one encapsulated nitride atom has been reported to date. It is obtained from the pyrolysis of $[Rh_6(CO)_{15}N]^-$ in basic media and has the formula $[HRh_{12}(CO)_{23}(N)_2]^{3-}$.[369] One nitrogen occupies a distorted trigonal prismatic cavity, while the other sits at the center of a distorted square antiprism.

5.2 Interstitial Geometries for the Heavier Main Group Elements

Encapsulation of atoms larger than boron, carbon and nitrogen is much less observed and is partially attributable to the steric requirements of the larger atoms. Two clusters showing incomplete encapsulation of phosphorus are known. The cluster $[Co_6(CO)_{15}P]^-$ has already been discussed.[297] It resembles an octahedral cluster of metals which has been forced open by the size of the main group atom. A ruthenium cluster, $Ru_5(CO)_{16}(\mu\text{-}PPh)(\mu_5\text{-}P)$, has been generated from pyrolysis of $HRu_3(CO)_9(\mu\text{-}PPh_2)$.[370] Benzene is eliminated in that reaction. The phosphorus appears to be bonded to all five metals although one of those interactions is quite long compared to the others. (2.632(2) *vs.* 2.383(2), 2.332(1), 2.332(1), 2.327(2) and 2.496(2)Å). If one neglects the longest Ru–P bond, then the coordination about phosphorus is a distorted spirocyclic array $P(Ru_2)_2$ in which the extra ruthenium bridges one of the Ru–Ru bonds and is bonded also to one of the rutheniums of the other Ru_2 unit.

Very few structures are known which show complete encapsulation of main group atoms larger than those in the first row. Only one completely encapsulated group 14 atom cluster structure is known. It is the $[SiCo_9(CO)_{21}]^{2-}$ anion made from the reaction of $[Co(CO)_4]^-$ with $Si\{Co_2(CO)_7\}_2$.[371] The silicon atom sits in a square antiprismatic cavity of eight cobalts. The ninth cobalt atom caps one of the square faces of the Co_8 antiprism. Besides this cluster, the others that are known are members of a series of high nuclearity anionic rhodium carbonyl clusters synthesized by pyrolysis reactions.

$$\mathrm{Rh(CO)_2(acac)} + \mathrm{PPh_3} \xrightarrow[\substack{140\text{–}160^\circ\mathrm{C}\\ \mathrm{Cs\ benzoate}\\ \mathrm{CsBH_4}}]{\substack{\mathrm{CO/H_2}\ (1:1)\\ 400\ \mathrm{atm}}} [\mathrm{Rh_9(CO)_{22}P}]^{3-} \qquad (108)^{372}$$

$$\mathrm{Rh(CO)_2(acac)} + \mathrm{PPh_3} \xrightarrow[\substack{140\text{–}160^\circ\mathrm{C}\\ \mathrm{Cs\ benzoate}}]{\substack{\mathrm{CO/H_2}\ (1:1)\\ 400\ \mathrm{atm}}} [\mathrm{Rh_9(CO)_{21}P}]^{2-} \qquad (109)^{373}$$

$$\mathrm{Rh(CO)_2(acac)} + \mathrm{AsPh_3} \xrightarrow[140\text{–}160^\circ\mathrm{C}]{\substack{\mathrm{CO/H_2}\ (1:1)\\ 300\ \mathrm{atm}}} [\mathrm{Rh_{10}(CO)_{22}As}]^{3-} \qquad (110)^{374}$$

$$\mathrm{Rh(CO)_2(acac)} + \mathrm{SbPh_3} \xrightarrow[150^\circ\mathrm{C}]{\substack{\mathrm{CO/H_2}\ (1:1)\\ 400\ \mathrm{atm}}} [\mathrm{Rh_{12}(CO)_{27}Sb}]^{3-} \qquad (111)^{375}$$

$$\mathrm{Rh(CO)_2(acac)} + \mathrm{H_2S} \xrightarrow[140\text{–}160^\circ\mathrm{C}]{\mathrm{CO/H_2}\ (1:1)} [\mathrm{Rh_{17}(CO)_{32}(S)_2}]^{3-} \qquad (112)^{376}$$

$$[\mathrm{Rh_{10}(CO)_{22}As}]^{3-} \xrightarrow[150^\circ\mathrm{C}]{\substack{\mathrm{CO/H_2}\ (1:1)\\ 862\ \mathrm{atm}}} [\mathrm{Rh_9(CO)_{21}As}]^{2-} + [\mathrm{Rh(CO)_4}]^{-} \qquad (113)^{374}$$

$$[\mathrm{Rh_{10}(CO)_{22}P}]^{3-} + 4\,\mathrm{CO} \xrightarrow[240^\circ\mathrm{C}]{\substack{\mathrm{CO/H_2}\ (1:1)\\ 12{,}500\ \mathrm{psi}}} [\mathrm{Rh_9(CO)_{21}P}]^{2-} + [\mathrm{Rh(CO)_4}]^{-} \qquad (114)^{372}$$

The structures of both phosphorus-containing compounds (eqns 108, 109) are known and show reasonably similar bond parameters for both Rh–P and Rh–Rh bonds. An important feature is that some of the Rh–Rh distances are longer than expected, probably due to the steric requirements of the phosphorus atom. This is also true of the arsenic-containing cluster. The rhodium-phosphorus and -arsenic compounds are all based on a square antiprismatic array of metals with the main group atom in the center. The extra metals cap the square faces. In the case of antimony, however, the rhodium atoms adopt a distorted icosahedral array with the Sb atom in the center of the cluster. The disulfur complex is structurally more difficult to describe. The sulfur atoms are in similar coordination sites with each bonded to seven rhodium atoms which are arranged in four layers of $\mathrm{Rh_4}$ squares with an interstitial Rh between the second and third layers. The interstitial rhodium is bonded to both sulfur atoms in a nearly linear S–Rh–S chain while all other rhodium atoms bond to only one sulfur.

Very little chemistry of these complexes has been reported, but some of their reactivity towards high pressures of CO and H_2 is known. Thus the $[Rh_{10}P]^{3-}$ and $[Rh_{10}As]^{3-}$ clusters lost only one rhodium as $[Rh(CO)_4]^-$ upon treatment with CO/H_2 mixtures. The antimony and sulfur complexes, however, were shown to be inert under the conditions employed.

5.3 Clusters Containing a μ_4-E Group on a Square of Metal Atoms

In addition to capping triangular metal faces, main group fragments can cap square faces. In all known cases for groups 14 and 15 the main group atom is bonded to an external R group or metal atom in addition to the four metals of the square, while for the group 16 complexes the μ_4-E atoms are "naked". Structurally characterized examples include a number of Ge, P, S and Te compounds as listed in Table VII. A number of clusters in which the main group atom is technically considered μ_4 are known but the metals are not arranged in a square. These include spiro-$E(M_2)_2$ and $M_3(\mu_3\text{-}EM)$ clusters. In the latter case, examples where the M_3 unit contains three or only two metal–metal bonds are known. The discussion of μ_4-complexes in this section will be restricted to groups capping square arrays of metal atoms.

The germanium complexes $Co_4(CO)_{11}(\mu_4\text{-}GeR)_2$ can be obtained along with $Co_3(CO)_9(\mu_3\text{-}GeR)$ clusters from the reaction of $[Co(CO)_4]^-$ with $RGeCl_3$.[41] These clusters undergo metal substitution reactions as evidenced by the formation of $(^tBuGe)_2Co_3(CO)_8ML_n$ ($ML_n = CpMo(CO)_2$, CpNi). The disubstituted cluster $(^tBuGe)_2Co_2(CO)_7(NiCp)_2$ has been reported. An alternative route to these clusters is the reaction of germanium hydrides with $Co_2(CO)_8$. Thus Ge_2H_6 reacts with $Co_2(CO)_8$ to give a complex formulated as $Ge_2Co_6(CO)_{20}$ of unknown structure which loses CO producing $Co_4(CO)_{11}(\mu_4\text{-}GeCo(CO)_4)_2$.[134]

Reports of PR groups capping square faces of metal clusters are more numerous than those of germanium and can be accessed by a number of routes. The rhenium clusters $Re_6(CO)_{18}(\mu_4\text{-}PMe)_3$ and $Re_5(CO)_{14}(\mu_4\text{-}PMe)(\mu\text{-}PMe_2)(\mu_3\text{-}PRe(CO)_5)$ are obtained from the reaction of $Re_4Cl_2(CO)_{15}\{MePP(Me)PMe\}$ with $Re_2(CO)_{10}$ at 230–250°C.[48]

Cobalt complexes with μ_4-PR fragments can be synthesized by treating solutions of $Co_2(CO)_8$ which have been reduced by Zn powder under CO with $RPCl_2$ (35% yield for R = Ph).[144] A significant aspect of the structure of $Co_4(CO)_{10}(\mu_4\text{-}PPh)_2$ is the short distance between the two phosphorus atoms of 2.544(3)Å which suggests some type of bonding interaction. Such interactions are not observed in analogous sulfur clusters.

A similar non-carbonyl cluster is generated from the reaction of Li_2PPh and $Rh_2(\mu\text{-}Cl)_2(cod)_2$ (cod = cyclooctadiene) or the reaction of $Rh_2(\mu\text{-}PPh_2)(\mu\text{-}Cl)(cod)_2$ with $Li[BHEt_3]$.[150] The product is $Rh_4(cod)_2(\mu_4\text{-}PPh)_2$ and is electron deficient by four electrons. The $P\cdots P$ distance is 2.679(4)Å and is somewhat longer than that of the cobalt case mentioned above as might be expected based on the steric requirements of the larger rhodium atoms.

Taking advantage of metal reactions with reactive P–H bonds,[136,137] a strategy employing reaction of $Fe_2(CO)_6(\mu\text{-}PRH)_2$ with $Fe_3(CO)_{12}$ was successful in producing $Fe_4(CO)_{11}(\mu_4\text{-}PR)_2$ and $Fe_4(CO)_{12}(\mu_4\text{-}PR)_2$ along with some trinuclear derivatives (R = Me, Ph, p-tolyl). The undeca- and dodecacarbonyl derivatives are interconvertible by reversible CO addition/elimination. The properties of these clusters and their substitution chemistry have been studied in detail.[139] Proton, ^{13}C and ^{31}P NMR data suggest aromatic-like electron delocalization in the Fe_4 system.

The P· · ·P contacts in $Fe_4(CO)_{11}[P(OMe)_3](\mu_4\text{-}PTol)_2$ and $Fe_4(CO)_{10}[P(OMe)_3](\mu_4\text{-}PTol)_2$ are 2.598(3)Å and 2.646(8)Å, respectively. They are in the same range as those for the Co and Rh clusters mentioned earlier.

Ruthenium clusters with μ_4-PR groups are generated via a strategy similar to that used for the iron clusters. Thus reaction of $Ru_3(CO)_{12}$ with $PPhH_2$ produces, in addition to $(\mu\text{-}H)Ru_3(CO)_{10}(\mu\text{-}PHPh)$ and $(\mu\text{-}H)_2Ru_3(CO)_9(\mu_3\text{-}PPh)$, $Ru_4(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}PPh)_2$ and $Ru_5(CO)_{15}(\mu_4\text{-}Ph)$.[141] An alternative, low yield route to clusters of the type $Ru_5(CO)_{15}(\mu_4\text{-}PR)$ has been observed in the reaction of $Ru_3(CO)_{12}$ with $CpMn(CO)_2(PRCl_2)$ for R = CH_3, CH_2–Ph, Ph and Et.[140] Several mixed Ru/Os–μ_4-PR clusters have been reported to arise from the reaction of $(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}PRH)$ and $Ru_3(CO)_{12}$ or $Os_3(CO)_{12}$. They include $Os_5(CO)_{15}(\mu_4\text{-}PPh)$, $Os_5(CO)_5(\mu_4\text{-}PC_6H_{11})$, $Ru_2Os_3(CO)_{15}(\mu_4\text{-}PPh)$ and $Ru_2Os_3(CO)_{15}(\mu_4\text{-}PC_6H_{11})$.[377] A related mixed metal cluster deserves mention at this point. It is $Ni_2Ru_3(Cp)_2(CO)_9(\mu_5\text{-}PPh)$ obtained from the reaction of $(\mu\text{-}H)Ru_3(CO)_9(\mu\text{-}PPh_2)$ and $Cp_2Ni_2(CO)_2$.[378] It has the same general shape as a number of $M_5(\mu_4\text{-}E)$ clusters with two Ni's and two Ru's occupying the sites around the square base of the square pyramidal array of metals. In this case, however, this square base is lacking one metal–metal bond (that between the adjacent nickel atoms) and does seem to have an interaction between the phosphorus atom and the apical ruthenium (d_{Ru-P} = 2.689(5)Å). The other Ru–P distances are 2.400(5)Å and 2.404(5)Å. Ni–P distances are 2.139(5)Å and 2.141(5)Å.

Likewise, $Co_4(CO)_{10}(\mu_4\text{-}PPh_4)_2$ undergoes a ligand substitution/addition reaction with $F_2PN(Me)PF_2$ to give $Co_4(CO)_3[(F_2P)_2NMe]_4(\mu_4\text{-}PPh)_2$. This cluster has one more electron pair donated to the electron count and has one less Co–Co bond as in the Ru/Ni cluster just discussed.[379] The structure of this complex is interesting in light of the kinetics of substitution reactions of these clusters which indicate for the first two substitutions an associative mechanism proceeding via reversible Co–Co bond cleavage.[146]

Pyrolysis of $Os_3(CO)_{11}P(OMe)_3$ at 210°C yields a mixture of products among which was $Os_5(CO)_{15}(\mu_4\text{-}POMe)$ which contains a square pyramid of osmium atoms with the P atom bridging the square face.[142] The eighteen electron rule is obeyed about each metal and the cluster is isoelectronic with $Fe_5(CO)_{15}C$.

Another route to M_4E_2 clusters is the reaction of $[Fe_3(CO)_9(\mu_3\text{-}PPh)_2]^{2-}$ with metal halides. Thus, this cluster reacts with $[(C_5Me_5)RhCl_2]_2$ to give $(C_5Me_5)RhFe_3(CO)_8(\mu_4\text{-}PPh)_2$ in 15% yield.[149] Like the other M_4E_2 clusters, it shows reversible CO addition producing $(C_5Me_5)RhFe_3(CO)_9(\mu_4\text{-}PPh)_2$. The structures of both the saturated and unsaturated species are known and show parameters similar to those of other members of this series with P· · ·P distances of 2.579 (nine carbonyls) and 2.666Å (eight carbonyls). The unsaturated cluster $(C_5Me_5)RhFe_3(CO)_8(\mu_4\text{-}PPh)_2$ undergoes two successive one-electron reductions giving a mono- and dianion while the saturated cluster undergoes two, one-electron oxidations. The ESR spectra of the radical one-electron reduction and oxidation products both show coupling to two phosphorus atoms indicating that the unpaired electron is delocalized over the entire cluster framework. The anion radical $[(C_5Me_5)RhFe_3(CO)_9(\mu_4\text{-}PPh)_2]^-$ undergoes rapid CO loss with formation of $[(C_5Me_5)RhFe_3(CO)_8(\mu_4\text{-}PPh)_2]^-$. One M_4E_2 cluster with different E groups has been reported. It is $Co_4(CO)_{10}\{\mu_4\text{-}PCH(SiMe_3)_2\}\{\mu_4\text{-}PCH_2SiMe_3\}$.[147]

A cube of Ni atoms capped on its six faces with μ_4-PPh groups arises from the reaction of $PhPCl_2$ with $[NMe_4]_2[Ni_3(CO)_3(\mu\text{-}CO)_3]_2$.[143] Each nickel atom is also ligated by one terminal CO to give a compound with a molecular formula of $Ni_8(CO)_8(\mu_4\text{-PPh})_6$. The distance between P atoms is long (4.9Å) and shows no interaction like that which may be present in the $M_4(\mu_4\text{-E})$ clusters.

As can be seen from Table VII, a number of sulfide complexes having naked sulfur atoms capping square faces of metal clusters have been structurally characterized. The most prevalent method of synthesis is thermal conversion of clusters already containing sulfido-atoms. Often these clusters are obtained as mixtures with a number of other sulfur-containing metal cluster products. Hydrogen sulfide and elemental sulfur can be used directly to produce clusters with the μ_4-S functionality. Examples are detailed below.

$$\begin{aligned} HOs_3(CO)_{10}(\mu\text{-SPh}) \xrightarrow{\Delta} & H_2Os_3(CO)_9(\mu_3\text{-S}) \\ & Os_3(CO)_9(\mu_3\text{-S})_2 \\ & Os_4(CO)_{12}(\mu_3\text{-S}) \\ & Os_4(CO)_{12}(\mu_3\text{-S})_2 \\ & Os_6(CO)_{16}(\mu_4\text{-S})(\mu_3\text{-S}) \end{aligned} \qquad (115)^{78}$$

$$Os_4(CO)_{12}[\mu_4\text{-SC}(CO_2Me)CH] \xrightarrow{\Delta} Os_4(CO)_{11}(\mu_4\text{-S})(\mu_4\text{-HC}_2CO_2Me) \qquad (116)^{380}$$

$$\begin{aligned} Os_3(CO)_{12} + \text{elemental S} \xrightarrow{\Delta} & Os_3(CO)_9(\mu_3\text{-S})_2 \\ & Os_5(CO)_{15}S \\ & Os_6(CO)_{18} \\ & Os_7(CO)_{20}S_2 \\ & Os_{10}(CO)_{23}(\mu_4\text{-S})_2 \end{aligned} \qquad (117)^{381}$$

$$Co_2(CO)_8 + \text{elemental S} \longrightarrow Co_4(CO)_{10}(\mu_4\text{-S})_2 \qquad (118)^{144,151,382,383}$$

$$Co_2(CO)_8 + H_2S \longrightarrow Co_4(CO)_{10}(\mu_4\text{-S})_2 \qquad (119)^{384}$$

Preliminary structural data for a tellurium-containing cluster, $Co_4(CO)_{10}(\mu_4\text{-Te})_2$, which is isostructural with the sulfur compound of the same general formula has been reported.[144]

Some cases of cluster building reactions beginning with preformed sulfido clusters have been noted. Examples are given in equations 120–127.

$$Fe_2(CO)_6S_2 + Co_2(CO)_8 \longrightarrow Fe_2Co_2(CO)_{11}(\mu_4\text{-S})_2 \qquad (120)^{148}$$

$$Ru_3(CO)_9(\mu_3CO)(\mu_3\text{-S}) + Ru_3(CO)_{12} \longrightarrow Ru_8(CO)_{15}(\text{tolyl})(\mu_4\text{-S}) \qquad (121)^{153}$$

$$\begin{aligned} Ru_3(CO)_9(\mu_3CO)(\mu_3\text{-S}) + Ru(CO)_5 \xrightarrow{h\nu} & Ru_4(CO)_{11}(\mu_4\text{-S})_2 \\ & \downarrow PMe_2Ph \\ & Ru_4(CO)_{11-n}(PMe_2Ph)_n(\mu_4\text{-S}) \\ & \quad n = 1, 2 \end{aligned} \qquad (122)^{152}$$

$$Os_4(CO)_{12}(\mu_3\text{-S}) + Os_3(CO)_{10}(NCMe)_2 \longrightarrow Os_7(CO)_{19}(\mu_4\text{-S}) \qquad (123)^{77}$$

$$\mathrm{Os_3(CO)_9(\mu_3\text{-}S)_2 + Os_3(CO)_{10}(NCMe)_2 \longrightarrow Os_6(CO)_{17}(\mu_4\text{-}S)_2} \qquad (124)^{83}$$

$$\mathrm{Os_4(CO)_{12}(\mu_3\text{-}S)_2 + Os_3(CO)_{10}(NCMe)_2 \longrightarrow Os_7(CO)_{20}(\mu_4\text{-}S)_2} \qquad (125)^{334}$$

$$\mathrm{Os_3(CO)_{10}(\mu_3\text{-}S) + Os_3(CO)_{10}(NCMe)_2 \longrightarrow Os_6(CO)_{19}(\mu_3\text{-}S) + Os_5(CO)_{15}(\mu_4\text{-}S)} \qquad (126)^{154}$$

$$\mathrm{Os_6(CO)_{19}(\mu_3\text{-}S) \xrightarrow{\Delta} Os_6(CO)_{17}(\mu_4\text{-}S)} \qquad (127)^{154}$$

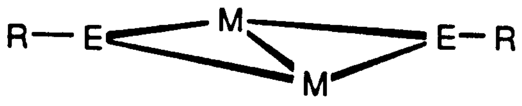
Metal exchange reactions and addition reactions producing this structural type are also known as in equation 128.

$$\begin{aligned}\mathrm{Os_5(CO)_{15}(\mu_4\text{-}S) + Pt(PPh_3)_2C_2H_4 \longrightarrow} &\ \mathrm{Os_5(CO)_{14}(PPh_3)(\mu_4\text{-}S)\ +} \\ &\ \mathrm{PtOs_4(CO)_{13}(PPh_3)(\mu_4\text{-}S)\ +} \\ &\ \mathrm{PtOs_5(CO)_{15}(PPh_3)(\mu_4\text{-}S)\ +} \\ &\ \mathrm{PtOs_5(CO)_{15}(PPh_3)_2(\mu_4\text{-}S)}\end{aligned} \qquad (128)^{155}$$

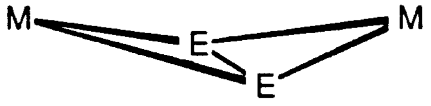
6. M_2E_2 CLUSTERS

Clusters containing two main group atoms and two transition metals are well-known and fall generally into three categories. The most studied is the closed-M_2E_2 tetrahedral geometry which often shows the expected six skeletal electron pairs for cluster bonding (**Q, R**). The other general category exhibits a metal–metal bond bridged by two μ-E groups which are not bonded to each other. In this second category the $M_2(\mu\text{-}E)_2$ framework may be planar or butterfly (**AD, AE**). It is most often observed to be planar for group 13 complexes in which the group 13 atom is electron deficient. The group 15–16 elements generally adopt as their most stable form the butterfly type geometry. These molecules may pass through planar intermediates in some of their fluxional processes. The last category is the least observed. Here the two hinge atoms are main group elements with the transition metals present as bridging functions (**AF**).

AD



AE



AF

6.1 *Planar M_2E_2 Complexes*

The group 13 element-containing clusters are prepared by treating the main group halides with metal carbonyl anions or the main group element with neutral metal carbonyls. The complexes $M_2(CO)_8\{\mu\text{-}EMn(CO)_5\}_2$ where M = Mn or Re and E = Ga or In have been structurally characterized and comparative data are presented in Table IX along with parameters for other molecules in this general class.[203,205] All of the Ga and In complexes contain planar M_2E_2 cores and have an M–M bond. The iron complex $Fe_2(CO)_8\{\mu\text{-}InMn(CO)_5\}_2$ also has a planar Fe_2In_2 framework but shows no Fe–Fe bond as expected as it has two more electrons than the Mn and Re clusters.[206] This is also true of $[Tl_2\{Fe(CO)_4\}_4]^{2-}$ which is composed of a planar Fe_2Tl_2 parallelogram with two external $Fe(CO)_4$ groups—one attached to each Tl.[207] The complex $Re_2(CO)_8\{TlRe(CO)_5\}_2$ which is prepared by the thermal decomposition of $Tl\{Re(CO)_5\}_3$ has been prepared but not structurally characterized. The group 13 atoms in these clusters can act as Lewis acid sites as evidenced by the reaction of $Mn_2(CO)_8\{\mu\text{-}GaMn(CO)_5\}_2$ with $[PPh_4]X$ which replaces the external $Mn(CO)_5$ fragments to give $[PPh_4]_2[Mn_2(CO)_8\{\mu\text{-}GaX_2\}_2]$.[385]

$$2\,Ga + 2\,Mn_2(CO)_{10} \longrightarrow Mn_2(CO)_8\{\mu\text{-}GaMn(CO)_5\}_2 + 2\,CO \qquad (115)^{205}$$

$$Mn_2(CO)_8\{\mu\text{-}GaMn(CO)_5\}_2 + 4[PPh_4]X \longrightarrow [PPh_4]_2[Mn_2(CO)_8\{\mu\text{-}GaX_2\}_2] + 2[PPh_4][Mn(CO)_5] \qquad (116)^{385}$$

$$TlCl + NaRe(CO)_5 \xrightarrow{\Delta} NaCl + TlRe(CO)_5 \rightarrow Re_2(CO)_8\{\mu\text{-}TlRe(CO)_5\}_2 \qquad (117)^{270}$$

$$SnX_2 + Mn_2(CO)_{10} \xrightarrow{\Delta} Mn_2(CO)_8\{\mu\text{-}SnXMn(CO)_5\}_2 \qquad (118)^{386}$$

Group 14 halides behave similarly, but the planar M_2E_2 arrays are formed with the main group atom having two external units attached. These may be halides, alkyls, aryls or metal fragments. Thus $Mn_2(CO)_8\{\mu\text{-}EXMn(CO)_5\}_2$ clusters are known (eqn *118*) where E = Ge, X = Br, E = Sn, X = Cl, Br.[386] More complicated systems arise for organotin halides in reaction with pentacarbonyl iron. Two of the products observed are $[R_2SnFe(CO)_4]_2$ and $[R_2SnFe(CO)_4]_2Sn$ which both possess E_2M_2 arrays. The latter complex contains two such co-joined groups sharing a spirocyclic tin atom.[387]

Tin(II) chloride has been observed to add to $Os_3(CO)_{11}(\mu\text{-}CH_2)$ producing the related $Os_3(CO)_{11}(CH_2)(SnCl_2)$ which is a butterfly cluster that contains only one main group atom. The molecule is nearly planar with the tin and one osmium acting as hinge atoms.[388]

6.2 *Butterfly and Tetrahedral M_2E_2 Clusters*

There is a strong chemical relationship between many of the butterfly and tetrahedral M_2E_2 clusters and the two forms may be interconverted by addition and removal of electrons. The fluctionality of the butterfly clusters has been examined in solution by

NMR[389] and calculations describing the bonding in a series of butterfly and tetrahedral E_2M_2 clusters have been reported.[390]

6.2.1 Group 15: The tetrahedral geometry with an Fe_2N_2 core is observed for $Fe_2(CO)_6(NR)_2$ from the reaction of $Fe_2(CO)_9$ and organic azo compounds such as azobenzene, azomethane and azoethane.[210,304] The N–N distance is 1.366(8)Å in agreement with an N–N single bond. An isoelectronic phosphorus derivative, $Fe_2(CO)_6(\mu\text{-}P^tBu)_2$, has been synthesized from the reaction shown in equation *120*. The P–P bond distance of 2.06Å, however, appears shorter than expected for a P–P single bond and is thought to have considerable double bond character.[211]

$$Fe_2(CO)_6(\mu\text{-}PH^tBu)_2 \xrightarrow[2.\ C_2H_4Br_2]{1.\ 2\,LiMe/Et_2O} Fe_2(CO)_6(P^tBu)_2 \qquad (119)$$

Since cobalt has one more electron than iron, clusters with the Co_2P_2 core are isoelectronic with $Fe_2(PR)_2$ compounds and show the same tetrahedral geometry. As in the iron clusters, $Co_2(CO)_5(PPh_3)P_2$ shows a short P–P bond distance of 2.019Å which is typical of P=P double bonds. A noticeable difference between the iron and cobalt systems is that the phosphorus is not bonded to an external unit but has a lone pair instead. These lone pairs are basic and are observed to donate to other metal fragments (eqn *122*).[213] The phosphorus-phosphorus bond distance is slightly longer when the phosphorus is complexed to an external metal fragment.

An alternative way of viewing these molecules is to consider the main group fragment P_2 as analogous to dinitrogen, N_2. From this viewpoint, the two π bonds between the P atoms can donate two electrons each to the cobalt atoms in a fashion similar to acetylenes. Arsenic exhibits similar chemistry to phosphorus. X-ray structural characterization of $Co_2(CO)_5(PPh_3)As_2$ shows the As–As bond distance to be only 2.372(5)Å indicative of multiple bonding in this system as well.[215,216] Phosphine substitution for CO in the cobalt clusters appears to increase the basicity of the lone pairs on arsenic making them better donors to external metal fragments (eqns *124–128*). Other metals besides Fe and Co are known to form M_2E_2 tetrahedral clusters as shown in equations *129–132*.

$$[Co(CO)_4]^- + PCl_3 \longrightarrow Co_2(CO)_6P_2 \qquad (120)^{212}$$

$$Co_2(CO)_6P_2 + PPh_3 \longrightarrow Co_2(CO)_5(PPh_3)P_2 + CO \qquad (121)^{212}$$

$$\begin{array}{l} Co_2(CO)_5(L)P_2 + ML'_n \xrightarrow{h\nu} Co_2(CO)_5(L)\{PML_{n-1}\}P + CO \qquad (122)^{213} \\ \qquad\qquad\qquad\qquad\qquad\qquad \downarrow ML'_n \\ \qquad\qquad\qquad\qquad\qquad\qquad Co_2(CO)_5(L)\{PML_{n-1}\}_2 + CO \end{array}$$

$L = CO, PBu_3, PPh_3;\ ML'_n = Cr(CO)_6, Mo(CO)_6, W(CO)_6, Fe(CO)_5$

$$Co_2(CO)_8 + AsCl_3 \longrightarrow Co_2(CO)_6As_2 \qquad (123)^{215}$$

$$Co_2(CO)_6As_2 + L \longrightarrow Co_2(CO)_{6-n}(L)_nAs_2 \qquad (124)^{216}$$

$L = PPh_3, n = 1;\ L = PMe_3, n = 1, 2;\ L = P(OMe)_3, n = 1\text{–}4$

$$\begin{array}{l}\mathrm{Co_2(CO)_5(PMe_3)As_2 + 2\,M(CO)_5(THF) \longrightarrow}\\ \mathrm{Co_2(CO)_5(PMe_3)\{AsM(CO)_5\}_2}\\ \mathrm{M = Cr, Mo, W}\end{array} \qquad (125)^{217}$$

$$\begin{array}{l}\mathrm{Co_2(CO)_4L_2As_2 + 2\,M(CO)_5(THF) \longrightarrow Co_2(CO)_4L_2\{AsM(CO)_5\}_2}\\ \mathrm{M = Cr, Mo, W}\end{array} \qquad (126)^{217}$$

$$\begin{array}{l}\mathrm{Co_2(CO)_3\{P(OMe)_3\}_3As_2 + 2\,M(CO)_5(THF) \longrightarrow}\\ \mathrm{Co_2(CO)_3\{P(OMe)_3\}_3\{AsM(CO)_5\}_2}\\ \mathrm{M = Cr, Mo, W}\end{array} \qquad (127)^{217}$$

$$\begin{array}{l}\mathrm{As\{CpMCr(CO)_7\}\{Cr(CO)_5\} \xrightarrow[-n\,M(CO)_5(PPh_3)]{n\,PPh_3} CpM_2(CO)_4\{AsCr(CO)_5\}_2 +}\\ \qquad\qquad\qquad\qquad\qquad\qquad\quad \mathrm{CpM_2(CO)_4\{AsCr(CO)_5\}As +}\\ \qquad\qquad\qquad\qquad\qquad\qquad\quad \mathrm{CpM_2(CO)_4As_4}\\ \qquad\qquad\qquad\qquad\qquad \mathrm{M = Cr, Mo, W}\end{array} \qquad (128)^{218}$$

$$\mathrm{CpM_2(CO)_4As_2 \underset{\substack{+\,2\,PPh_3\\ -\,2\,Cr(CO)_5(PPh_3)}}{\overset{\substack{+\,2\,Cr(CO)_5(THF)\\ -\,2\,THF}}{\rightleftarrows}} Cp_2Mo_2(CO)_4\{AsCr(CO)_5\}_2} \qquad (129)^{218}$$

$$\mathrm{As_2\{W(CO)_5\}_3 \xrightarrow{I_2} W_2(CO)_7(\mu\text{-}I)As_2} \qquad (130)^{218}$$

6.2.2 Group 16: $\mathrm{Fe_2(CO)_6S_2}$ adopts a tetrahedral geometry as determined by X-ray crystallography on both the pure compound and as a 1 : 1 mixture with $\mathrm{Fe_3(CO)_9S_2}$.[222,223] The S–S bond distance of 2.007(5)Å is in general agreement with other known S–S single bonds and therefore does not show the possible multiple bond character of the P and As complexes. It can be reduced to a dianion which is believed to have a butterfly geometry with the S–S bond cleaved.[326] This is supported by its reactivity (summarized in Scheme VI) with a number of reagents such as MeI which alkylates at sulfur to give the butterfly cluster $\mathrm{Fe_2(CO)_6(\mu\text{-}SMe)_2}$ (31% yield). It should be remembered that S and SR donate different numbers of electrons to the cluster count, S being a four-electron donor and SR being a five-electron donor. Similar situations arise for the group 14 (E, two e donor; ER, three e donor) and group 15 (E, three e donor; ER, four e donor). Further support for the addition of electrons to an antibonding S–S orbital has recently been present based on solution EXAFS data.[391] This appears to be the case for the $\mathrm{Fe_2(CO)_6Se_2}$ reduction as well.[391] The butterfly cluster $\mathrm{Fe_2(CO)_6(\mu\text{-}SMe)_2}$ exists as geometrical isomers in solution. This isomerism comes about because the S atoms also possess lone pairs of electrons so that each methyl group can occupy one of two locations on each sulfur atom (Scheme VII). Better yields of alkylated product are obtained if $\mathrm{Li[AlH_4]}$ or $\mathrm{Li[BHEt_3]}$ are used in place of Na/Hg to reduce $\mathrm{Fe_2(CO)_6S_2}$. The $\mathrm{Fe_2(CO)_6(SR)_2}$ molecules have no direct S–S bonding, however, a number of the derivatives have the sulfur atoms bridged by one or more atoms. In the nonbridged complexes such as $\mathrm{Fe_2(CO)_6(SEt)_2}$, the molecule can exist as one of three possible isomers (Scheme

VII). When the sulfur groups are bridged, that effectively locks the molecule into the axial–axial form. Such bridges are present where the sulfur atoms are linked by carbon as in $Fe_2(CO)_6(S_2CH_2)$ and $[Fe_2(CO)_6S_2C]_2$, by C_2 as in $Fe_2(CO)_6S_2C_2Ph_2$ and $Fe_2(CO)_6Fe_2(CO)_6S_2C_2H_4$, by metals as in $Fe_2S_2ML_n$ ($ML_n = Pd(PPh_3)_2$, CoCp, Ni(diphos)), or main group elements as in $Fe_2(CO)_6S_2ER_2$ (E = Ge, R = alkyl, Cl; E = Sn, R = alkyl) and $[Fe_2(CO)_6S_2]_2Ge$.

Butterfly compounds of the general formula $Fe_2(CO)_6(SR)_2$ can be obtained from the direct reaction of iron carbonyls with various organic sulfur compounds (eqns 131–134 and Schemes VIII and IX).[31,32,224–228,392–394] Use of iron pentacarbonyl tends to give lower yields than use of $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$. The "naked" sulfide clusters $Fe_3(CO)_9S_2$ and $Fe_2(CO)_6S_2$ are often obtained in addition to the complexes where the sulfur retains an R group.

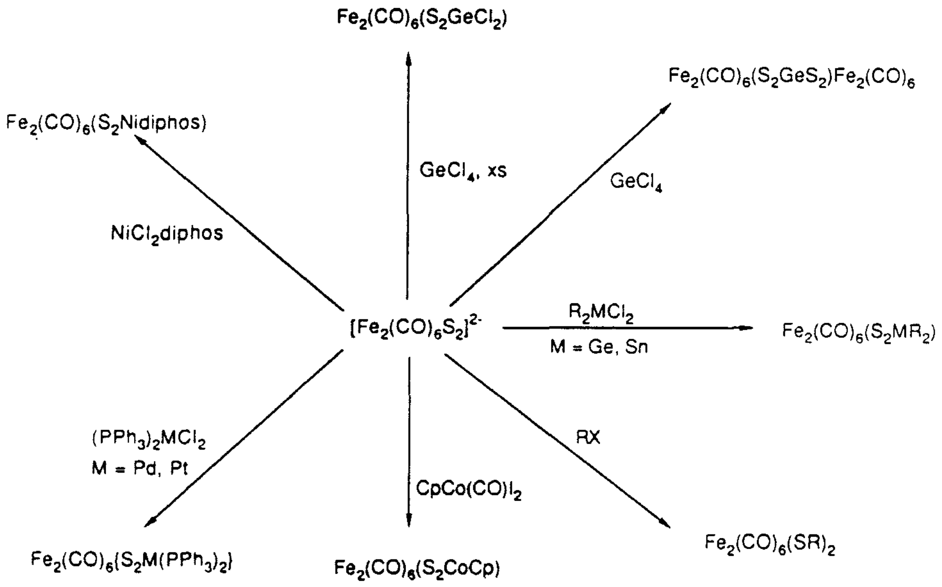
$$\mathrm{Fe(CO)_5 + Na_2S_5 \longrightarrow Fe_2(CO)_6S_2} \qquad (131)^{149}$$

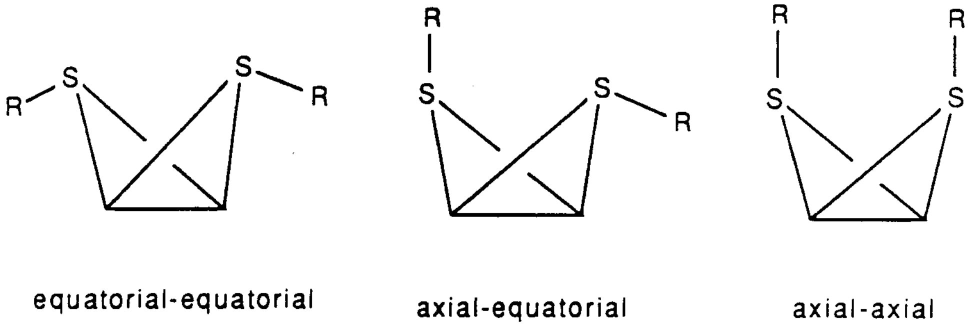
$$\mathrm{Fe_2(CO)_6S_2 \xrightarrow{Na/Hg} [Fe_2(CO)_6S_2]^{2-} \xrightarrow{2\,MeI} Fe_2(CO)_6(\mu\text{-}SMe)_2} \qquad (132)^{149}$$

$$\mathrm{Fe_3(CO)_{12} + C_5H_4(SH)N \longrightarrow Fe_2(CO)_6(\mu\text{-}SC_5H_4N)(\mu\text{-}SFe_2(CO)_6C_5H_4N)} \qquad (133)^{32}$$

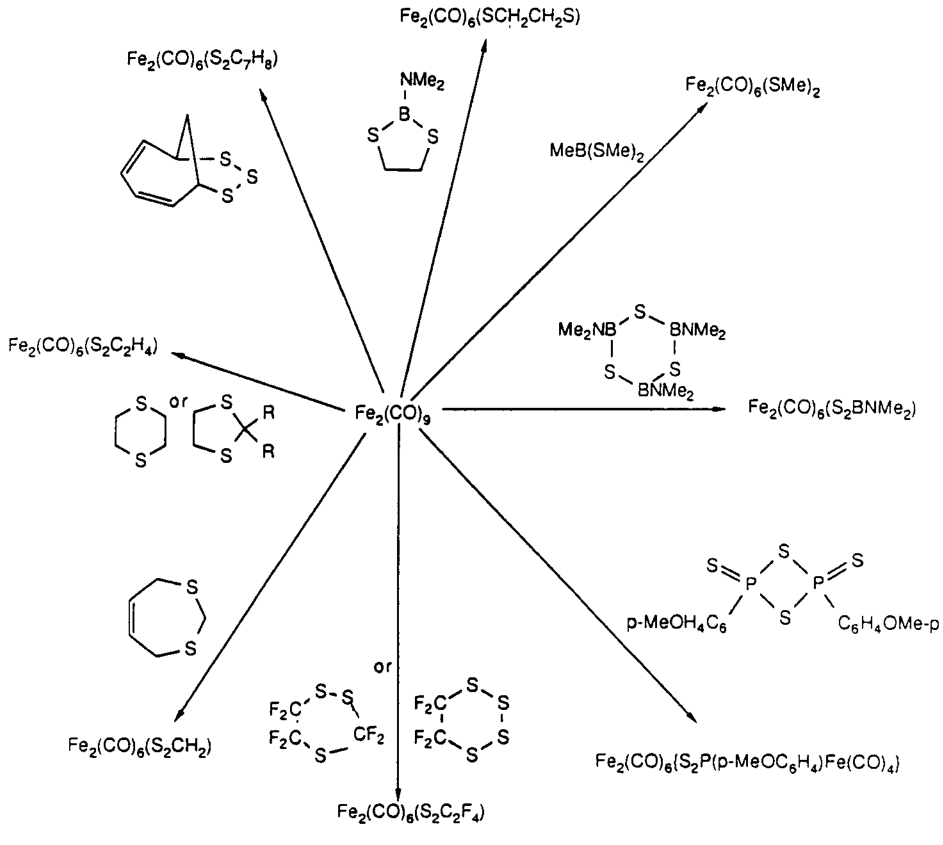
$$\mathrm{Fe_2(CO)_4(PPh_3)_2(\eta^2\text{-}SC\text{-}Me_2C_6H_6) + Me_4C_6H_6CS} \qquad (134)^{228}$$
$$\downarrow$$
$$\mathrm{Fe_2(CO)_3(PPh_3)(PPh_3)({=}C{=}C_6H_4Me_4)(S_2C{=}C_6H_6Me_4)}$$

Scheme VI

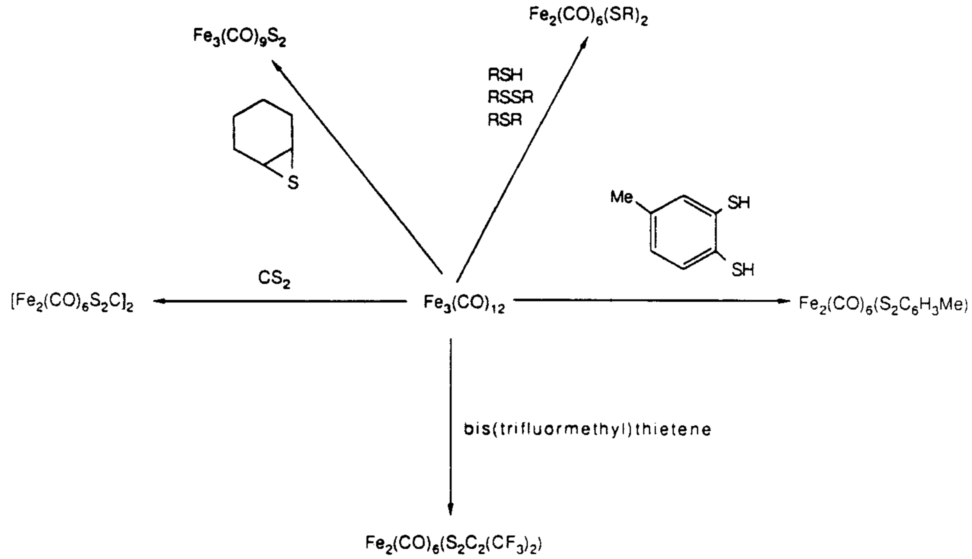




Scheme VII



Scheme VIII



Scheme IX

Selenium and tellurium analogues of $Fe_2(CO)_6S_2$ are known.[229,340] The selenium compound has been structurally characterized. The tellurium complex is less stable than the others and has not been isolated and structurally characterized. Upon removal of solvent it tends to form species which are insoluble and may be polymers or have cubane-like structures. Heterometal clusters can be obtained from all three $Fe_2(CO)_6X_2$ (X = S, Se, Te) compounds by addition of metal fragments such as $CpRh(CO)_2$[341] or $M(PPh_3)_2(C_2H_4)$ (M = Pd, Pt).[342] Also known is a cationic, tetrahedral cluster $[FeW(CO)_8Se_2]^{2+}$ made from the reaction of $W(CO)_6$, $Fe_2(CO)_9$ (1 : 2) with Se_4^{2+} in SO_2(l). The Se–Se bond distances of 2.281 Å indicate a bond order of *ca.* 1.5.[231]

One very important aspect of the reactivity of these clusters may be the ability of the main group atom to become "hypervalent." This type of bonding situation has recently been identified for $CpMoFe(CO)_5(Te_2Br)$ and $(MeC_5H_4)MoFe(CO)_5(Te_2S_2CNEt_2)$ (eqn *135*).[233]

$$\begin{array}{ll} CpMo_2Fe(CO)_7Te_2 \xrightarrow{Br_2} CpMo(CO)_3Br + CpMoFe(CO)_5(Te_2Br) & (135)^{205} \\ \qquad\qquad\qquad\qquad\qquad + NaS_2CNEt_2 \downarrow - NaBr & \\ \qquad\qquad\qquad\qquad\qquad CpMoFe(CO)_5(Te_2S_2CNEt_2) & \end{array}$$

The Te–Te–Br bond angle is 201° suggesting that the Te possesses a lone pair in addition to bonding to the other Te, Mo and Fe atoms. The Br ion can be displaced by other nucleophiles such as $S_2CNEt_2^-$. Some evidence also suggests that it is possible to oxidatively add this Te–Br bond to other metal centers such as Ir.[233]

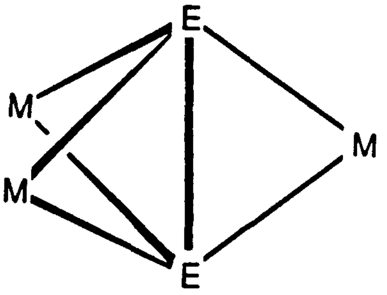
Two butterfly clusters are known in which both hinge atoms are main group elements. The first compound is $[CpCr(CO)_2Se]_2$ and is formed as per equation *136*.

$[CpCr(CO)_2]_2 + Se \rightarrow [\mu\text{-}Cp(CO)_2Cr]_2Se_2 + [Cp(CO)_2Cr]_2Se$ (*136*)[230]

The pentamethylcyclopentadienyl chromium tricarbonyl anion reacts with Se_2Cl_2 to form similar compounds of composition $[(Me_5C_5)(OC)_2Cr]_2Se$ and $(Me_5C_5)Cr_2(CO)_5Se$.[395] The second example is the arsenic compound $[(C_5Me_5)Mn(CO)_2]_2As_2$ formed from the solid state thermolysis of $[(C_5Me_5)Mn(CO)_2]_2AsH$.[219,220] The As–As bond distance (2.225Å) indicates some multiple bond character. The complex $\{(diphos)Ni\}_2Te_2$ is planar with an alternating Ni–Te–Ni–Te parallelogram and a Te–Te bond. The Te–Te bond distance is 2.802(1)Å and is considerably longer than in some Te–Te singly bonded complexes.[232]

6.3 *E_2M_3 Clusters*

Clusters containing two main group elements and three transition metals have been observed to yield four different structural types shown as **P**, **S**, **T** and **AG**. Types **P** and **S** have already been discussed in the section on μ_3-E complexes. In looking at these structural types it is interesting to note the progression from maximum M–M bonding (**P**) to maximum E–E bonding (**AG**). A small E–E interaction is thought to be present in several molecules of type **S**. These include $Fe_3(CO)_9(\mu_3\text{-}PPh)_2$ (P···P, 2.587Å),[240] $Fe_3(CO)_6\{P(OMe)_3\}_3(\mu_3\text{-}PPh)_2$ (P···P, 2.566Å),[241] $Fe_3(CO)_9(\mu_3\text{-}AsPh)_2$ (As···As, 2.798Å),[243] $Fe_3(CO)_9(\mu_3\text{-}PPh)(\mu_3\text{-}S)$ (P···S, 2.713Å),[240] $Fe_3(CO)_9(\mu_3\text{-}AsPh)(\mu_3\text{-}S)$ (As···S, 2.816Å),[245] and $Fe_3(CO)_9(\mu_3\text{-}S)(\mu_3\text{-}SO)$ (S···S, 2.72Å).[246]



AG

Such interactions are much more pronounced for clusters of type **T**. In the Te examples, the Te–Te bond distances ($CpMo_2Fe(CO)_7Te_2$, 3.146Å; $Fe_3(CO)_9(PPh_3)Te_2$, 3.138Å) are thought to represent bonds of about order = 2/3, while in the known Bi complex the value is consistent with a Bi–Bi single bond (3.08Å). The syntheses of these compounds are shown in equations *137–139*. The formation of the E–E bonding interaction may be a key driving force in these reactions.

$Fe_3(CO)_9(\mu_3\text{-}Bi)_2 + [Co(CO)_4]^- \longrightarrow [Bi_2Fe_2Co(CO)_{10}]^-$ (*137*)[221]

$$Fe_3(CO)_9(\mu_3\text{-}Te)_2 + Cp_2Mo_2(CO)_6 \xrightarrow{CO} Cp_2Mo_2Fe(CO)_7Te_2 \qquad (138)^{92}$$

$$Fe_3(CO)_9(\mu_3\text{-}Te)_2 \xrightarrow{L} Fe_3(CO)_9LTe_2\ (L = CO,\ \text{phosphine}) \qquad (139)^{234}$$

Even more surprising are the compounds of type **AG** which have been generated from the main group halide ECl_3 (E = As,[253] Sb,[254] Bi)[255] and $[W_2(CO)_{10}]^{2-}$. The structures of all three are known (Table XI). The E–E distances are very short and suggestive of multiple bonding. It should be noted that for all known compounds of both types **T** and **AG** that it is not necessary to have any E–E interaction to satisfy electron counting rules. The important thing to note is that significant E–E interactions can occur and may dominate the bonding picture for main group/transition metal clusters.

7. $(\mu_3\text{-}M)E_3$ MOLECULES

We have already seen molecules belonging to the general tetrahedral class $E_{4-x}(ML_n)_x$. The pure main group prototypes are P_4 and As_4, and at the other extreme are pure transition metal clusters such as $Co_4(CO)_{12}$. The $(\mu_3\text{-}E)M_3$ and the E_2M_2 clusters have been discussed. The last general classification in this series is the E_3M clusters which are also well-documented. Structural data for a number of these molecules are found in Table XII. A good review of them has recently appeared.[396] "Double sandwich" complexes of the type $(\mu_3\text{-}M)_2E_3$ which have a trigonal bipyramidal core have been structurally characterized. Some of this work derives from attempts to make complexes having P_4 as a ligand.[397] This has been successful in the case of $P_4Ni(np_3)$ (np_3 = tris(diphenylphosphinoethyl)amine) directly from P_4.[398] A palladium P_4 compound has been reported as well,[399] but in other reactions of P_4 the products are the $(\mu_3\text{-}M)E_3$ or $(\mu_3\text{-}M)_2E_3$ types of products.[396] One or two metals can be attached to the E_3 triangle depending on the stoichiometry of the reaction. Using this knowledge, mixed complexes of the type $(\mu_3\text{-}M)(\mu_3\text{-}M')E_3$ can be obtained by first isolating the single metal-containing product and then treating it with an appropriate metal complex and ligand.[263] The $(\mu_3\text{-}M)E_3$ molecules can be looked at as derivatives of P_4 in which an "isolobal" three-electron-donating metal fragment replaces one of the phosphorus atoms.

$$Ni(np_3) + P_4 \xrightarrow{THF} Ni(np_3)(\eta^1\text{-}P_4) \qquad (140)^{398}$$

$$[Co(H_2O)_6][BF_4]_2 + P_4(xs) \xrightarrow{\text{triphos}} (\text{triphos})CoP_3 \qquad (141)^{257}$$

$$[Rh(C_2H_4)_2Cl]_2 + P_4 \xrightarrow{\text{triphos}} (\text{triphos})RhP_3 \qquad (142)^{400}$$

$$Ir(PPh_3)_2(CO)Cl + P_4 \xrightarrow{\text{triphos}} (\text{triphos})IrP_3 \qquad (143)^{400}$$

$$[MCl_2(PBu_3)]_2 + P_4 \xrightarrow[M\, =\, Pd,\, Pt]{\text{triphos}} [(\text{triphos})MP_3]^+ \qquad (144)^{259}$$

$$[M(H_2O)_6][BF_4]_2 + P_4\,(1:1) \xrightarrow[M\,=\,Co,\,Ni]{\text{triphos}} [\{(\text{triphos})M\}_2P_3]^{2+}$$
(*145*)[263]

$$[M(H_2O)_6][BF_4]_2 + (\text{triphos})CoP_3 \xrightarrow[M\,=\,Co,\,Ni]{\text{triphos}} [(\text{triphos}M)(\text{triphos}M')P_3]^{2+}$$
(*146*)[263]

$$(\text{triphos})CoP_3 + [M(H_2O)_6][BF_4]_2 \xrightarrow[\substack{M\,=\,Fe,\\ Co,\,Ni}]{\text{etriphos}} [(\text{triphos})CoP_3M(\text{etriphos})]^{2+}$$
(*147*)[401]

Similar complexes containing arsenic in place of phosphorus have been prepared as shown in equations *148–150*. Equation *151* illustrates the synthesis of a more complex molecule which has a As_3 group, but in this molecule the arsenic triangle is attached to a triangle of cobalt atoms giving rise to a Co_3As_3 octahedron.

$$[Co(H_2O)_6][BF_4]_2 + As_4 \xrightarrow{\text{triphos}} [\{(\text{triphos})Co\}_2As_3]^{2+}$$
(*148*)[263,264]

$$Co_2(CO)_8 + (AsMe)_5 \xrightarrow[\substack{200°C\\ 100\ \text{atm CO}}]{\text{hexane}} As_3Co(CO)_3$$
(*149*)[261]

$$(C_5Me_5)_2Mo_2(CO)_4 + As_4S_4 \longrightarrow (C_5Me_5)(CO)_2MoAs_3$$
(*150*)[262]

$$CoCl_2(PPh_3)_2 + PhAs(SiMe_3)_2 \rightarrow Co_4(\mu_3\text{-}As)_3(\mu_3,\eta^3\text{-}As_3)(PPh_3)_4$$
(*151*)[60]

The phosphorus atoms in the $(\mu_3\text{-}M)E_3$ complexes can function as donor ligands as evidenced by the formation of $(\text{triphos})CoP_3\{Cr(CO)_5\}_n$ (n = 1, 2).[261,402] The X-ray structure of the n = 2 complex shows that adduct formation leaves the bonding parameters of the P_3 unit essentially unchanged. A much more complicated adduct is formed between $(\text{triphos})CoP_3$ and CuBr.[260] The product has two $(\text{triphos})CoP_3$ groups capping opposite sides of a bromide bridged Cu_6 hexagon.

$$(\text{triphos})CoP_3 + Cr(CO)_6 \xrightarrow[n\,=\,1,2]{h\nu} (\text{triphos})CoP_3\{Cr(CO)_5\}_n$$
(*152*)[261,402]

$$(\text{triphos})CoP_3 + CuBr \longrightarrow [(\text{triphos})CoP_3]_2Cu_6Br_6$$
(*153*)[260]

The structures of the ME_3 and M_2E_2 clusters are interesting in that the E–E distances are *shorter* than those in the pure element E_4 form (E = P, As). This has been attributed to the metal's ability to accept electrons and thereby reduce E–E antibonding interactions.

The redox chemistry of some of the M_2E_3 clusters shows that a number of redox states are accessible which give total electron counts ranging from 30 to 33 electrons. For example, $[\{(\text{triphos})Co\}_2P_3]^{2+}$ has 31 electrons and undergoes a one-electron oxidation and two one-electron reduction processes. Comparisons of the redox chemistry of the $[\{(\text{triphos})M\}_2E_3]^{2+}$ where M = Co, Ni; E = P, As show that the cobalt complexes are more easily oxidized than the nickel ones and that the arsenic ones are more easily oxidized than the phosphorus complexes in agreement with the ionization potentials for the metals and main group atoms.

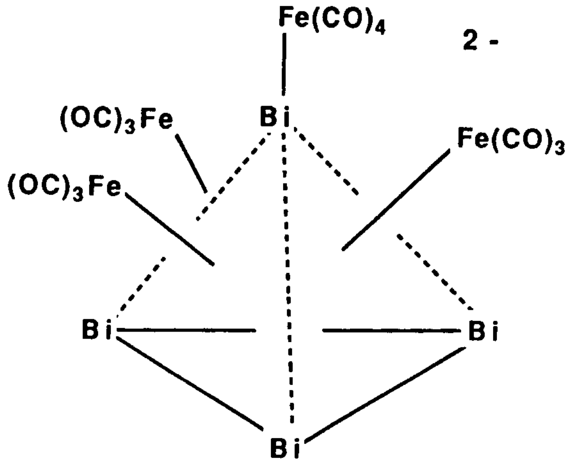
This same type of electron flexibility can be achieved chemically by varying the metals attached to the E_3 triangle. Thus the series {(triphos)M}{(triphos)M′}P_3 where M = Fe, M′ = Co (30 electrons); M = M′ = Co (31 electrons); M = Co, M′ = Ni (32 electrons) and M = M′ = Ni (33 electrons) has been studied. A steady increase in both M–P and P–P distances are seen with an increase in the number of electrons. This trend is opposite of what one would expect based on the metal atomic radii. The factors influencing this observation are complex and involve the interplay of a number of interrelated phenomena.

8. "ZINTL"-METAL CLUSTERS

The last section we will present could easily be classified as a "miscellaneous" section because the complexes discussed are more complex and exhibit less obvious relationship to each other. Certain common characteristics, however, are important features of main group/transition metal cluster compounds which have prompted this review. The idea of "Zintl"-metal clusters is a natural extension of the progression of cluster types that we have been examining up to this point. Clearly, as the clusters become more and more complicated it is less and less appropriate to consider them as main group derivatives of transition metal clusters. Indeed, in many the main group atom is not easily relegated to the simple position of "ligand" but occupies a much more fundamental structural function in the cluster. This is apparent in considering the known (μ_3-M)E_3 species which beg to be thought of as derivatives of P_4 and As_4. Thus, we are led to the analogy between these clusters and the Zintl ions which have been known for some time. The Zintl ions are naked cluster anions and cations of the main group elements. By using the term Zintl-metal cluster we mean to emphasize the importance of the main group atoms to the cluster structure and function.

Even in the simpler complexes we have already discussed there exist some parallels to Zintl ion chemistry. Anions such as $SnTe_4^{4-}$ which contains a central tin atom tetrahedrally surrounded by four tellurium atoms is comparable to $[Bi\{Fe(CO)_4\}_4]^{3-}$. These are both highly charged anionic species. One might generalize that it should be possible to replace electron-rich main group vertices in Zintl ions by electron-rich transition metal fragments.

A more interesting example is the anion $[Bi_4Fe_4(CO)_{13}]^{2-}$ shown in **AH**.[289,290] It is produced from the reaction of $[BiFe_3(CO)_{10}]^-$ or $[Bi_2Fe_4(CO)_{13}]^{2-}$ with CO. It is an unexpected hybrid based on a tetrahedral array of bismuth atoms which are capped on three faces by $Fe(CO)_3$ groups. The Bi which is mutually attached to all three $Fe(CO)_3$ groups also coordinated to the external $Fe(CO)_4$ moiety in a typical donor fashion. In some ways the structure is related to that of the main group cage cluster P_4S_3. The apical Bi is 3.45Å from those in the triangular base of the molecule—a distance considered non-bonding. The Bi–Bi distance in the base is about 3.08Å which is comparable to accepted values of a Bi–Bi single bond. It is interesting to note that the two closest neighbor contacts in elemental Bi are roughly 3.1 and 3.45Å. A key feature of the molecule is the interaction between molecules in the solid state. While the interaction is weak, there are short intermolecular contacts between Bi atoms in the triangular bases of adjacent molecules. These give rise to a semi-polymeric network of the molecules in the crystal lattice. It is exactly these types of interactions that are suggestive of applications to synthesis of solids of designed stoichiometry and structure.



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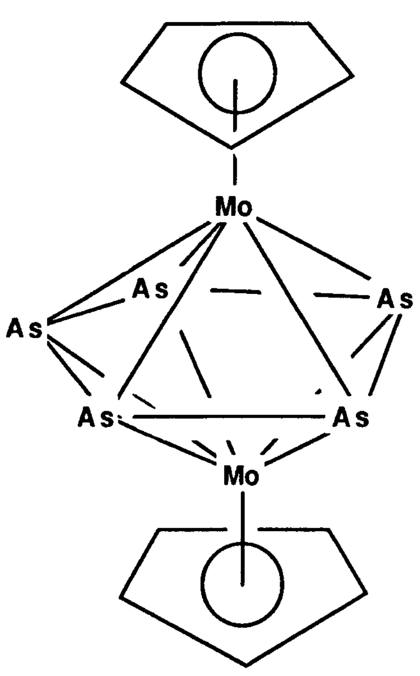

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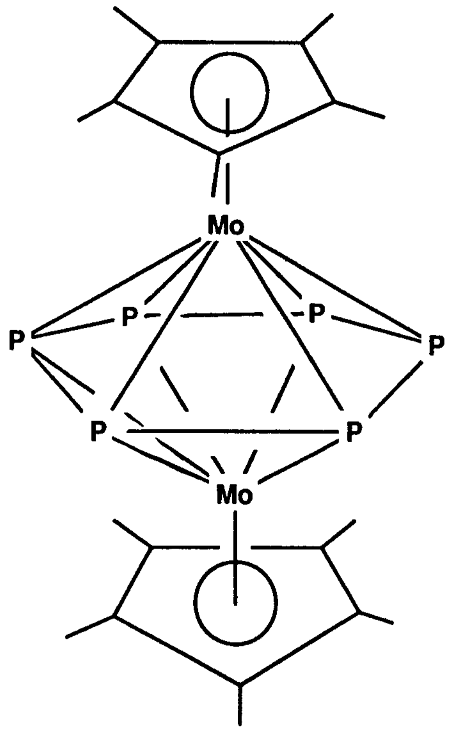
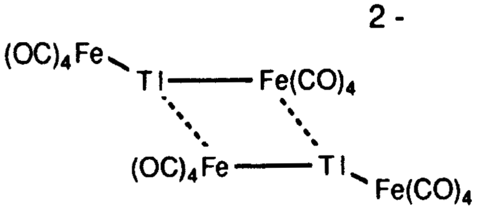


AJ

The interaction of main group atoms and transition metals often leads to structural types which may not be common among either the Zintl ions or the pure transition metal clusters. This is obviously true of $[Bi_4Fe_4(CO)_{13}]^{2-}$. It is also the case with $(CpMo)_2As_5$[403] (**AI**) and $(C_5Me_5Mo)_2P_6$[404] (**AJ**). The arsenic complex is generated from $Cp_2Mo_2(CO)_4$ and $(AsMe)_5$ while the phosphorus-containing molecule is derived from $(C_5Me_5)_2Mo_2(CO)_4$ and P_4. These molecules, however, do not show the longer range main group–main group interactions seen for $[Bi_4Fe_4(CO)_{13}]^{2-}$. It is interesting to compare them to the less cluster-like transition metal complexes derived from organo-phosphorus and arsenic complexes which still retain a fair amount of the organic functionalities.[405–407] What is unexpected is that an organo-complex $[CpMo(CO)_2]_2]\mu\text{-}(AsMe)_5]$ is *not* a precursor to $[CpMo]_2As_5$.[403]

$$(C_5Me_5)_2Mo(CO)_4 + P_4 \longrightarrow [(C_5Me_5)Mo]_2P_6 \qquad (154)^{404}$$

$$\begin{array}{l} (Cp)_2Mo_2(CO)_4 + (AsMe)_5 \xrightarrow{190^\circ C} (CpMo)_2As_5 \qquad (155)^{403} \\ \quad \downarrow 140^\circ C \\ [CpMo(CO)_2]_2[\mu\text{-}(AsMe)_5] \\ \quad\quad \downarrow 190^\circ C \\ \quad\quad Cp_4Mo_4As_4 \end{array}$$



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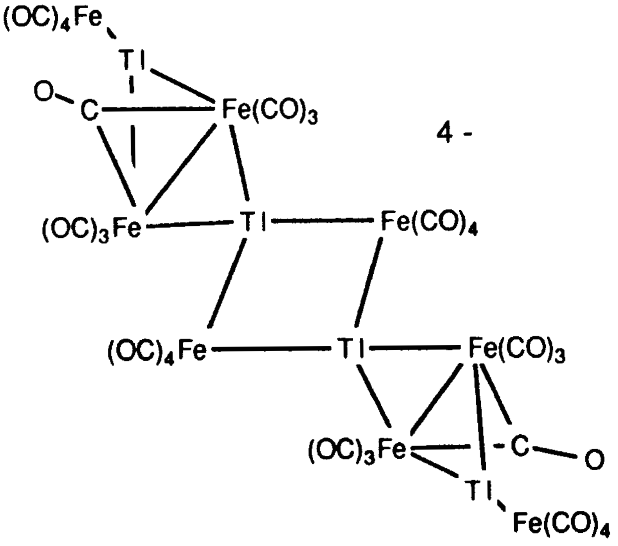

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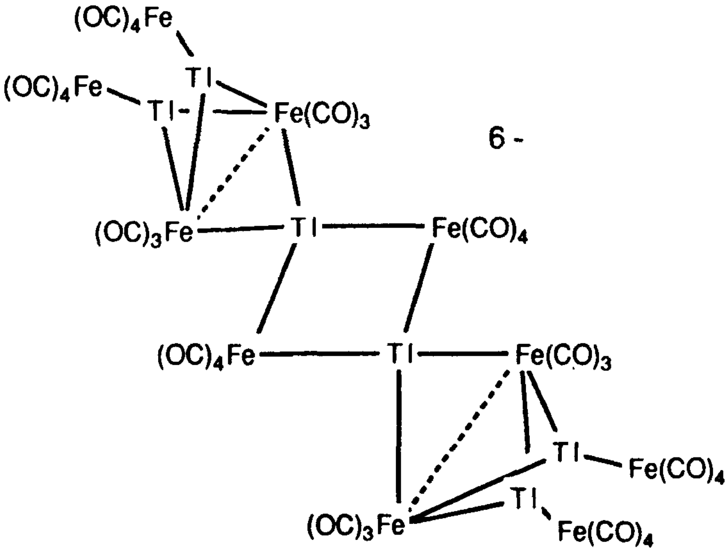
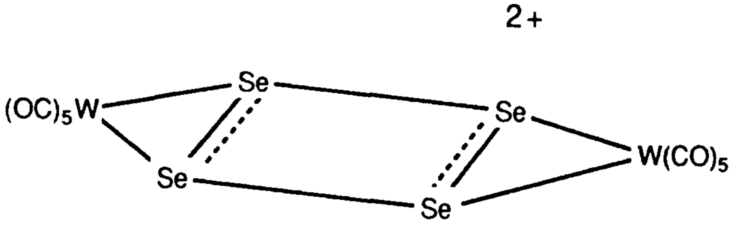


AM

In Zintl ion chemistry, one does not find homoatomic clusters for group 13 because the low electron count is insufficient to stabilize cluster bonding. When coupled with electron rich main group elements, however, thallium can be incorporated into the Zintl ion clusters. Examples include $[TlSn_8]^{3-}$,[408] $[TlSn_9]^{3-}$ [408] and $[Tl_2Te_2]^{2-}$.[409] The same thing is true of thallium metal carbonylates. When treated with solutions of $Fe(CO)_5$/KOH/MeOH, a simple complex results which has the empirical formula $[Et_4N][Tl\{Fe(CO)_4\}_2]$ but X-ray analysis shows it to be a dimer composed of a planar $Tl_2Fe_2{}^{2-}$ core (**AK**) which has striking resemblances to $[Tl_2Te_2]^{2-}$. A trigonal bipyramidal $Fe(CO)_4$ group is attached externally to each Tl as well. The driving force for the dimerization is probably the ability to relieve some of the electron deficiency at thallium which in the monomer would have only four electrons while in the dimer it has six. This situation is still electron poor but not uncommon for group 13 elements. This complex undergoes further oligomerization with loss of CO to give $[Tl_4Fe_8(CO)_{30}]^{4-}$ (**AL**) which can be viewed as a dimer of $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}TlFe(CO)_4)_2]^{2-}$. The bridging portion of the molecule is reminiscent of the parent complex but is more symmetrical. A further molecule in this series is known and has the formula $[Tl_6Fe_{10}(CO)_{36}]^{6-}$ (**AM**) which can be viewed as a dimer of $[Fe_2(CO)_6(\mu\text{-}TlFe(CO)_4)_3]^{3-}$ ions.[410] It can be derived from $Tl_4Fe_6{}^{4-}$ by replacing the bridging carbonyls with bridging $[TlFe(CO)_4]^-$ groups. The striking structural difference between $Tl_4Fe_8{}^{4-}$ and $Tl_6Fe_{10}{}^{6-}$ is the difference in Fe–Fe distances in the $Fe_2(CO)_6$ portion of the molecule. In $Tl_4Fe_8{}^{4-}$ the distance is about 2.77Å while in $Tl_6Fe_{10}{}^{6-}$ it is 3.08Å. The presence of the bridging carbonyl evidently helps to hold the two iron atoms together. As in $Fe_2(CO)_9$ with which the two monomers are isoelectronic, the bonding between metals is not believed to be direct but largely occurs through the bridging groups. In all of these molecules the thallium–thallium distances are long (*ca.* 3.7Å) and considered non-bonding. The important aspect of this series of molecules is the evident tendency to oligomerize which is a key property for potential solid state synthesis applications.

Another rather complicated aggregate has been observed for the Co/As system. Instead of building up the cluster by means of electron deficiency as in the thallium case, for $[Co_8(\mu_6\text{-}As)(\mu_4\text{-}As)(\mu_4\text{-}AsPh)_2(CO)_{16}]_2$ the expansion of the cluster arises from the donor ability of the arsenic atoms.[411] Such clusters have the appearance of being very closely related to an extended solid network.



AN

A metal derivative of a cationic Zintl-like ion is known. The compound is $[W_2(CO)_{10}Se_4][SbF_6]_2$ (AN) generated from the reaction of $W(CO)_6$ with $Se_4(Sb_2F_{11})_2$ in SO_2.[412,413] It can be viewed as two $W(CO)_5Se_2{}^+$ cations which are dimerized through the four selenium atoms. The Se–Se distance between selenium atoms attached to the same tungsten atom is 2.208Å while the Se–Se distance between the two metal fragments is 3.017Å. The shorter of the two distances suggests a Se–Se bond order of about 1.7. The $W(CO)_5$ groups are roughly symmetrically bridging the short Se–Se bond.

9. FINAL REMARKS

The incorporation of main group elements into transition metal clusters can often stabilize the bonding network and lead to the ability to add or remove ligands or electrons while retaining the basic cluster integrity. Main group element incorporation, however, should not be considered simply as a ligand-to-metal interaction. The main group atoms have key structural and chemical importance in the cluster make-up. For the larger main group atoms, their size may profoundly influence the chemistry observed as they may place a strain on the metal–metal bonding network.

Zintl ions have been known for some time, but their chemistry, especially as connected to transition metal species has been little explored. It is now apparent that main group/transition metal hybrids are an important interfacial region between the pure transition metal clusters and the Zintl ions. These mixed clusters fall into the same type of structural classes that the Zintl ions do. Classical type bonding in ions such as $SnTe_4^{4-}$ is paralleled by that of $[Bi\{Fe(CO)_4\}_4]^{3-}$ while $[Bi_4Fe_4(CO)_{13}]^{2-}$ represents a non-classical, cluster-type hybrid. The ability to form Zintl ions incorporating the electron deficient group 13 elements by using more electron-rich co-cluster atoms is paralleled by the chemistry observed for the Tl–Fe clusters.

Not only are these clusters interesting from their theoretical importance to main group/transition metal bonding, but they also have a potential for application to synthesis of solids of designed stoichiometry and structure. The synthetic problems of making that possibility a reality are formidable, but nevertheless, represent a very exciting and hopeful area for further exploration.

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TABLE I

Structural data for EM_3 and EM_4 complexes containing no transition metal–metal bonds. Distances are in Å.

Compound	E–M	References
planar complexes:		
$Ga\{CpW(CO)_3\}_3$	2.744(3) 2.758(3) 2.716(3)	4
$In\{Co(CO)_4\}_3$	2.597(3) 2.595(3) 2.590(3)	5
$Tl\{CpMo(CO)_3\}_3$	3.001(3) 2.955(3) 2.938(2)	6
$As\{Cr(CO)_5\}_2\{Mn(CO)_5\}$	Mn: 2.511(4) Cr: 2.440(3) 2.418(4)	7
$[Na(THF)_2][Sb\{Cr(CO)_5\}_3]$	2.636(3) 2.624(3)	7
$Te\{Mn(CO)_2Cp\}_3$	2.47 2.47 2.51	8
pyramidal complexes:		
$BrSn\{Mn(CO)_5\}_3$	2.739(2) 2.722(2) 2.758(2)	9
$Bi\{Co(CO)_4\}_3$	2.770(2) 2.767(2) 2.760(2)	10
$Se\{CpMn(CO)_2\}\{CpFe(CO)_2\}_2$	Mn: 2.421(1) Fe: 2.445(1) 2.443(1)	11
tetrahedral EM_4 complexes:		
$[Et_4N]_3[Bi\{Fe(CO)_4\}_4]$	2.753(3) 2.748(2) 2.751(3) 2.749(3)	12

TABLE II

Structural data for EM_3 and EM_4 complexes containing one transition metal–transition metal bond and related complexes. Distances are in Å and angles in degrees.

Compound E–M (EM_2)	E–M′	M–M	<M–E–M	References
planar EM_3 complexes:				
$Ge\{W(CO)_5\}\{W_2(CO)_{10}\}$				
2.589(1) 2.579(2)	2.505(2)	3.278(1)	78.8(1)	7
$Sn\{W(CO)_5\}\{W_2(CO)_{10}\}$				
2.789(2) 2.776(2)	2.702(2)	3.354(2)	74.1(1)	7
$P\{Cr(CO)_5\}\{CpWCr(CO)_7\}$				
Cr: 2.428(5) W: 2.268(4)	2.305(5)	3.085(3)	82.1(2)	7
$As\{Mn(CO)_5\}\{Cr_2(CO)_8(\mu\text{-}CO)\}$				
2.345(5) 2.353(5)	2.347(4)	3.001(6)	79.4(2)	7
$\{(Me_3Si)_2C(H)\}Sb\{Fe_2(CO)_8\}$				
2.633(1) 2.641(1)		2.801(1)	64.15(2)	13
$[Cp_2Co][Se\{Cp_2Cr_2(CO)_4\}\{CpCr(CO)_2\}]$				
2.333(2) 2.345(2)	2.279(2)	3.083(2)	82.6(1)	14
pyramidal EM_3 complexes:				
$PhGe\{Co(CO)_4\}\{Co_2(CO)_6(\mu\text{-}CO)\}$				
2.375(3) 2.392(3)	2.456(3)	2.546(3)	64.6(1)	15
$HP\{\mu\text{-}Os_3(CO)_{10}H_2\}\{Os_3(CO)_{10}NCMe\}$				
2.425(10) 2.420(10)	2.411(12)	2.888(2)	73.2(3)	16
$HP\{\mu\text{-}Os_3(CO)_{10}H_2\}\{Os_3(CO)_{10}(CO_2Me)H\}$				
2.401(14) 2.387(14)	2.372(13)	2.904(4)	74.7(4)	16
${}^{t}BuSb\{W(CO)_5\}\{W_2(CO)_{10}\}$				
2.817(4) 2.854(4)	2.805(5)	3.306(3)	71.3(1)	17
$MeBi\{W(CO)_5\}\{W_2(CO)_8Bi_2\}$				
2.881(1) 2.864(1)	2.851(1)	3.142(3)	66.33(2)	18
$Se\{CpMn(CO)_2\}\{Cp_2Fe_2(CO)_2(\mu\text{-}CO)\}$				
2.348(1) 2.341(1)	2.434(1)	2.667(1)	69.3(0)	11
EM_4 complexes:				
$[Et_4N]_2[Pb\{Fe(CO)_4\}_2\{Fe_2(CO)_8\}]$				
2.832(4) 2.823(4)	2.651(5) 2.659(5)	2.617(5)	55.13(12)	19

TABLE III
Spiro M_4E clusters.

M–E	M–M	<M–E–M	<M–M–E	References
$Ge\{Fe_2(CO)_8\}_2$				
I. A. 2.409(2)	2.829(3)	71.4(1)	54.8(1)	20
2.378(2)	2.810(3)	71.9(1)	54.6(1)	
2.411(2)			53.5(1)	
2.438(2)			53.8(1)	
B. 2.420(2)	2.837(3)	71.9(1)	53.9(1)	
2.411(2)	2.816(2)	72.1(1)	54.2(1)	
2.413(2)			53.3(1)	
2.374(2)			54.6(1)	
II. 2.388(1)	2.825(1)	72.20(3)	54.21(2)	21
2.407(1)	2.821(1)	71.94(3)	53.60(2)	
2.406(1)			54.16(2)	
2.398(1)			53.90(2)	
$Ge\{Fe_2(CO)_8\}\{(MeC_5H_4)MnFe(CO)_6\}$				
Fe: 2.394(1)	Fe–Fe: 2.796(1)	70.5	53.0	20
2.416(1)	Fe–Mn: 2.865(1)	72.9	54.2	
2.427(1)			54.9	
Mn: 2.431(1)			54.6	
$Ge\{Co_2(CO)_6(\mu\text{-}CO)\}_2$				
A. 2.372(3)	2.570(3)	66.0(1)	56.5(1)	22
2.344(2)	2.564(3)	65.7(1)	57.5(1)	
2.348(2)			57.8(1)	
2.381(3)			56.5(1)	
B. 2.379(3)	2.559(3)	65.7(1)	56.4(1)	
2.341(3)	2.552(3)	65.4(1)	57.9(1)	
2.339(2)			58.2(1)	
2.387(2)			56.4(1)	
$Ge_3Co_8(CO)_{26}$				
2.361(1)	2.664(2)			23
2.393(2)	2.519(2)			
2.388(2)				
2.338(2)				
2.407(2)				
2.357(2)				
$Fe_2(CO)_6(\mu\text{-}CO)\{\mu\text{-}GeCo_2(CO)_6(\mu\text{-}CO)\}_2$				
Fe: 2.365(1)	Fe–Fe: 2.678(1)			23
2.437(1)	Co–Co: 2.528(1)			
2.421(1)	2.491(1)			
Co: 2.383(1)				
2.351(1)				
2.309(1)				
2.400(1)				
$Ge\{Co_2(CO)_6(\mu\text{-}CO)\}\{Co_2(CO)_6(\mu\text{-}HgCo(CO)_4)\}$				
2.432(2)	2.536(3)	63.4(1)	57.7(1)	24
2.397(2)	Hg bridged: 2.751(2)	72.7(1)	59.0(1)	
2.317(2)			53.5(1)	
2.325(2)			53.8(1)	
$Sn\{Fe_2(CO)_8\}_2$				
2.54(ave)	2.87	69		25

TABLE III (*cont.*)

Compound				
M–E	M–M	<M–E–M	<M–M–M	References
$Pb\{Fe_2(CO)_8\}_2$				
2.606(3)	2.911(4)	67.49(9)	56.73(8)	26
2.635(3)	2.890(4)	66.95(9)	55.78(8)	
2.606(3)			56.99(8)	
			56.07(8)	
$P\{Fe_2(CO)_8\}\{Fe_2(CO)_6(\mu\text{-}Cl)\}$				
2.28	2.73	68.8(1)		27
2.28	2.54*	73.8(1)		
2.24				
2.25				
*halide bridged				
$P\{Fe_2(CO)_6(\mu\text{-}Br)\}\{FeW(CO)_9\}$				
2.236–2.242	Fe–Fe: 2.553(4)	Fe_2P: 69.5(1)		28
	Fe–W: 2.957(2)	FeWP: 74.6(1)		
$As\{Fe_2(CO_8)\}\{Fe_2(CO)_6(\mu\text{-}Cl)\}$				
2.37	2.80	72.5(1)		27
2.37	2.56*	66.1(1)		
2.35				
2.35				
*halide bridged				
$[As\{Cp_2Co_2(CO)_2\}_2][BF_4]\cdot 1/2$ benzene				
2.263(3)	2.596(3)	69.8(1)		29
2.273(3)	2.607(3)	70.3(1)		
2.271(3)				
2.255(3)				
$Sb_2\{Fe_2(CO)_6\}\{Fe_2(CO)_8\}_2$				
2.498(1)	2.841(1)	69.2(1)	55.5(1)	30
2.503(1)	2.841(1)	67.2(1)	55.3(1)	
2.567(1)	2.822(2)	69.3(1)	56.4(1)	
2.565(1)		67.2(1)	56.4(1)	
2.494(1)			55.5(1)	
2.502(1)			55.2(1)	
2.548(1)			56.5(1)	
2.554(1)			56.3(1)	
$S\{Fe_2(CO)_6(\mu\text{-}SMe)\}_2$				
2.247(7)	2.543(6)	68.8(2)	55.7(2)	31
2.253(7)	2.536(7)	68.7(2)	55.5(2)	
2.254(7)			55.4(2)	
2.239(7)			55.9(2)	
$S\{Fe_2(CO)_6(C_5H_4N)\}\{Fe_2(CO)_6(SC_5H_4N)\}$				
2.236(2)	2.598(1)	70.83(9)	56.14(5)	32
2.248(2)	2.532(1)	68.32(6)	55.54(6)	
2.247(2)			54.37(7)	
2.263(2)			54.80(7)	
$Os_2(CO)_6[\mu\text{-}S\{Os_2(CO)_6(\mu\text{-}HC{=}NPh)\}]_2$				
2.411(4)	2.752(1)	69.6(1)	55.2(1)	33
2.413(5)	2.752(1)	69.2(1)	55.5(1)	
2.420(4)	2.756(1)	69.4(1)	55.1(1)	
2.426(5)		69.2(1)	55.3(1)	

TABLE III (*cont.*)

Compound M–E	M–M	<M–E–M	<M–M–M	References
2.424(4)			55.6(1)	
2.411(5)			55.6(1)	
2.421(4)			55.2(1)	
2.433(5)			55.3(1)	
$H_2Os_6(CO)_{17}(\mu_4\text{-S})(\mu_3\text{-S})(\mu\text{-HC=N-}p\text{-C}_6H_4F)_2$				
2.447(4)	2.803(1)	92.54(13)		34
2.481(3)		68.96(10)		
2.441(4)				
2.509(4)				
$H_2Os_6(CO)_{16}(\mu_4\text{-S})(\mu_3\text{-S})(\mu\text{-HC=N-}p\text{-C}_6H_4F)_2$				
2.372(8)	2.839(2)	72.7		34
2.417(7)	2.769(2)	70.0(2)		
2.425(7)				
2.403(8)				

TABLE IV

Structural data on complexes containing a tetrahedral $(\mu_3\text{-E})M_3$ unit. For the more complicated examples, parameters listed are only for the $(\mu_3\text{-E})M_3$ portion of the molecule.

Compound E–M	M–M	<M–E–M	<M–M–E	References
$HFe_3(CO)_9BH_4$				
2.199(8)	2.674(2)			35
2.130(8)	2.602(2)			
2.176(9)	2.591(2)			
$(\mu\text{-H})_3Os_3(CO)_9BCO$				
	2.913(1)			36
	2.917(1)			
	2.919(1)			
$Re_4(CO)_{12}(\mu_3\text{-InRe}(CO)_5)_4$				
2.735(7)	3.028(5)			37
2.818(7)*				
*distance to external rhenium				
$Co_3(CO)_9\{\mu_3\text{-SiCo}(CO)_4\}$				
2.217	2.604	71.9	60	38
2.222	2.611	72.2		
2.216	2.596	71.6		
2.288*				
*distance to external cobalt				
$[Et_4N]_2[Fe_3(CO)_9(\mu_3\text{-CO})\{\mu_3\text{-GeFe}(CO)_4\}]$				
2.400(4)	2.643	66.91(11)	59.98(11)	39
2.394(4)	2.657	67.41(11)	60.28(11)	
2.389(3)	2.649	67.26(10)	59.74(11)	
$H(Cp)MoCoFe(CO)_8(\mu_3\text{-Ge}^t\text{Bu})$				
2.556(3)(Mo)	2.905(8)(MoFe)	72.9(3)(MoFe)	55.0(1)(FeMoCo)	40
2.321(10)(Fe)	2.903(8)(MoCo)	73.6(3)(MoCo)	62.4(3)(MoFeCo)	
2.277(9)(Co)	2.684(6)(FeCo)	71.4(2)(FeCo)	62.5(3)(MoCoFe)	

TABLE IV (*cont.*)

Compound E–M	M–M	<M–E–M	<M–M–E	References
$CpMoCo_2(CO)_8(\mu_3\text{-}GeW(CO)_3Cp)$				
2.565(4)(Mo)	2.784(6)(MoCo)	69.6(2)(MoCo)	63.3(2)(MoCoCo)	40
2.298(6)(Co)	2.824(6)(MoCo)	70.3(2)(MoCo)	61.8(2)(MoCoCo)	
2.328(6)(Co)	2.585(7)(CoCo)	67.9(2)(CoCo)	54.9(2)(CoMoCo)	
2.589(4)(W)				
$Co_3(CO)_9(\mu_3\text{-}GeFe(CO)_2Cp)$				
2.308(1)	2.590(1)	68.1(1)	60.0(1)	41
2.320(1)	2.589(1)	68.1(1)	60.0(1)	
2.315(1)	2.590(1)	68.0(1)	60.0(1)	
2.303(1)(Fe)				
$[Et_4N][Co_3(CO)_6(\mu\text{-}CO)_3(\mu_3\text{-}GeCo_2(CO)_8)]$				
A. 2.46(1)	2.52(1)	63	60	42
2.35(1)	2.54(1)	62	59	
2.51(1)	2.55(1)	63	61	
2.43(1)*	2.53(1)*	62*		
2.47(1)*				
B. 2.48(1)	2.51(1)	63	60	
2.33(1)	2.52(1)	62	60	
2.44(1)	2.52(1)	64	60	
2.48(1)*	2.54(1)*	62*		
2.45(1)*				
*parameters involving the $GeCo_2$ group				
$FeRu_2(CO)_9[P(OMe)_3](\mu_3\text{-}NH)$				
1.960(5)*	2.657(1)	85.3(3)	60.88(1)	43
2.031(6)	2.729(1)	86.3(2)	58.25(3)	
*Fe and one Ru disordered				
$FeCo_2(CO)_9(\mu_3\text{-}NH)$				
1.867(2)	2.479(1)	83.69(9)	59.79(1)	44
1.850(2)	2.476(1)	84.26(9)	59.91(1)	
1.861(2)	2.489(1)	83.26(9)	60.31(1)	
$Ru_3(CO)_{10}(\mu_3\text{-}NOMe)$				
2.027(3)	2.740(1)	86.5(2)		45
2.006(4)	2.762(1)			
$Ru_3(CO)_7(C_6H_6)(\mu_3\text{-}NPh)$				
2.016(9)	2.695(2)			46
2.029(9)	2.726(2)			
2.043(9)	2.704(2)			
$Fe_3(CO)_9(\mu_3\text{-}NSiMe_3)$				
1.870	2.528	84.2	60.2	47
1.920	2.535	82.7	60.0	
1.907	2.541	84.3	59.7	
$Re_5(CO)_{14}(\mu_4\text{-}PMe)(\mu\text{-}PMe_2)\{\mu_3\text{-}PRe(CO)_5\}$				
2.465(7)	2.983(1)			48
2.281(7)	2.973(1)			
2.488(7)	2.960(1)			
2.486(7)				
*distance to external Re				

TABLE IV (*cont.*)

Compound E–M	M–M	<M–E–M	<M–M–E	References
$(\mu\text{-H})_2Fe_3(CO)_9(\mu_3\text{-PPh})$				
2.199(2)	2.729(1)			49
2.146(2)	2.727(1)			
2.153(2)	2.692(1)			
$(\mu\text{-H})_2Os_3(CO)_9(\mu_3\text{-NPh})$				
2.099(8)	2.848(2)	86.1(3)	61.6(1)	50
2.074(8)	2.846(2)	81.7(3)	61.5(1)	
2.078(8)	2.715(2)	85.9(3)	57.0(1)	
$[Ph_4P][Fe_3(CO)_{10}\{\mu_3\text{-PFe(CO)}_4\}]$				
2.156(2)	2.620(2)			51
2.245(2)	2.641(2)			
2.237(2)	2.593(2)			
$(\mu\text{-H})_2Ru_3(CO)_8(PMePh_2)(\mu_3\text{-PPh})$				
2.310(2)	2.934(1)			52
2.296(2)	2.942(1)			
2.303(2)	2.841(1)			
$(\mu\text{-H})_2Ru_3(CO)_8(PPh_3)(\mu_3\text{-PPh})$				
2.304(1)	2.959(1)	77.0(1)	61.3(1)	53
2.282(1)	2.958(1)	80.4(1)	61.3(1)	
2.284(1)	2.842(1)	80.3(1)	57.4(1)	
$(\mu\text{-H})_2Ru_3(CO)_9(\mu\text{-PC}_6H_4OMe\text{-p})$				
2.320(4)	2.937(2)	79.2(1)	61.2(1)	54
2.275(4)	2.928(2)	79.5(1)	60.9	
2.273(4)	2.844(2)	77.4(1)	58.0	
$(\mu\text{-H})_2Ru_3(CO)_9(\mu_3\text{-PPh})$				
2.333(5)	2.938(3)	76.8(2)	61.0(1)	55
2.296(5)	2.947(3)	79.1(2)	61.3(1)	
2.279(5)	2.842(3)	79.1(2)	57.8(1)	
$(\mu\text{-H})Ru_3(CO)_9\{\mu\text{-AuPMe}_2Ph\}(\mu_3\text{-PPh})$				
2.347(12)	3.002(5)			56
2.258(12)	2.972(5)			
2.279(11)	2.869(5)			
$(\mu\text{-H})_2Os_3(CO)_9(\mu_3\text{-PPh})$				
2.358(10)	2.972(3)	78.9(2)	61.3(1)	57
2.320(7)	2.967(3)	79.0(3)	61.5(1)	
2.309(8)	2.845(2)	75.9(2)	57.2(1)	
$Co_3(CO)_9(\mu_3\text{-PMn(CO)}_2Cp)$				
Co: 2.189(4) to	2.533(5) to	59.8(1)–60.2(1)		58
2.211(4)	2.544(4)			
Mn: 2.141(4)				
$Co_3(CO)_7\{P(OMe)_3\}_2(\mu_3\text{-PMn(CO)}_2Cp)$				
Co: 2.170(3) to	2.542(3) to	59.5(1)–60.5(1)		58
2.206(3)	2.568(3)			
Mn: 2.183(3)				
$Cp_3Mo_3(CO)_6(\mu_3\text{-As})$				
2.553(1)	3.122(1)	75.6		59
2.540(1)	3.125(1)	76.2		
2.509(1)	3.101(1)	75.8		

TABLE IV (*cont.*)

Compound E–M	M–M	<M–E–M	<M–M–E	References
$Co_3(CO)_9(\mu_3\text{-}AsCr(CO)_5)$				
Co: 2.261(1) to	2.548(1) to	59.81(1)–60.24(4)		58
2.284(1)	2.560(1)			
Cr: 2.376(1)				
$Co_3(CO)_9(\mu_3\text{-}AsCo_4(CO)_{11})$				
2.268(2)	2.563(3) to	68.6(1)	59.8(1)	59
2.261(2)	2.575(3)	68.7(1)		
2.279(2)		69.3(1)		
$[Co_4(\mu_3\text{-}As)_3(\mu_3, \eta\text{-}As_3)(PPh_3)_4]$				
2.294	2.616	64.2–69.8	55.4–62.2	60
2.274	2.438			
$[Et_4N][Fe_3(CO)_9(\mu\text{-}CO)\{SbFe(CO)_4\}]$				
2.515	2.660	63.8	60.2	61
2.518	2.680	65.2	59.4	
2.460	2.685	65.3	60.4	
$Ir_3(CO)_9(\mu_3\text{-}Bi)$				
2.733(1)	2.757(1)	59.8	60.0	62
2.736(2)	2.760(2)	59.7	60.0	
2.734(2)	2.760(1)	59.7	60.0	
$[Et_4N][Fe_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}Bi)]$				
2.648(2)	2.646(2)	59.88(4)	60.13(5)	63
2.652(1)	2.634(2)	59.61(4)	60.16(5)	
2.650(2)	2.645(2)	59.85(4)	59.71(5)	
$Fe_3(CO)_9(\mu_3\text{-}Bi)(\mu_3\text{-}COMe)$				
2.644(1)	2.649(2)	60	60	64
2.650(1)	2.612(2)			
2.657(1)	2.606(2)			
$H_3BiFe_3(CO)_9$				
2.638(1)	2.772(2)	63.3(ave)	59.9(ave)	64
2.639(1)	2.774(1)			
2.641(1)	2.776(2)			
$[Et_4N]_2[H_3Re_3(CO)_9(\mu_3\text{-}O)]$				
2.12(ave)	2.973(1)			65
	2.963(1)			
$[Me_3NCH_2Ph][Fe_3(CO)_9(\mu_3\text{-}O)]$				
1.895(3)	2.480(1)			66
1.891(3)	2.492(1)			
1.890(3)	2.480(1)			
$Ru_3(CO)_6(Ph_2AsCH_2AsPh_2)(\mu_3\text{-}O)$				
2.06(1)	2.750(2)			67
2.07(1)	2.723(2)			
2.11(1)	2.670(2)			
$[Os_6(\mu_3\text{-}O)(\mu_3\text{-}CO)(CO)_{18}]$				
2.06(2)	2.706(2)			68
2.07(2)				
$FeCo_2(CO)_9S$				
2.159(ave)	2.554(ave)	72.6(ave)		69

TABLE IV (*cont.*)

Compound E–M	M–M	<M–E–M	<M–M–E	References
$Fe_2Co(CO)_8(NO)S$				
2.164(ave)	2.558(ave)	72.5(ave)		70
$[Fe_3(CO)_9S]^{2-}$				
2.190(ave)	2.584(ave)			see 70
$Fe_3(CO)_9(Au_2(PPh_3)_2)S$				
2.218(8)	2.642(5)			70
2.194(5)	2.864(4)			
2.198(6)	2.750(4)			
$CpMoCo_2(CO)_6\{Fe(CO)_4AsMe_2\}S$				
Mo: 2.360(s)	Mo–Co: 2.777(1)			71
Co: 2.171(2)	2.749(2)			
2.177(2)	Co–Co: 2.474(2)			
$FeCo_2(CO)_9\{\mu_3\text{-}SCr(CO)_5\}$				
2.145(5)	2.557(3)			72
2.351(Cr)				
$[(\mu\text{-}H)_2(\mu_3\text{-}S)Ru_3(CO)_8]_3$				
2.373(2)	2.885(1)	75.49(8)	56.70(3)	73
2.341(2)	2.921(1)	76.09(8)	62.30(3)	
2.367(3)	2.758(1)	71.71(7)	61.00(3)	
2.372(2)	2.888(1)	75.82(7)	56.62(3)	
2.328(3)	2.922(1)	76.22(7)	62.30(3)	
2.362(2)	2.756(1)	71.96(7)	61.08(3)	
2.354(2)	2.768(1)	71.76(7)	62.14(3)	
2.368(2)	2.866(1)	74.59(7)	60.59(3)	
2.376(3)	2.909(1)	75.63(7)	57.27(3)	
2.423(2)*				
2.399(2)*				
2.413(3)*				
*S–Ru bonds connecting the μ_3-SRu_3 units				
$Os_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}S)$				
2.386(3)	2.826(1)	72.82(9)	59.80(2)	74
2.375(3)	2.825(1)	72.83(9)	59.85(2)	
2.372(3)	2.840(1)	73.49(9)	60.35(2)	
$H_2Os_3(CO)_9(\mu_3\text{-}S)$				
2.393(2)	2.908(1)	74.8(1)	62.0(1)	75
2.395(2)	2.764(1)	70.8(1)	56.6(1)	
2.383(2)	2.922(1)	75.4(1)	61.4(1)	
$Os_3(CO)_8[C(H)NMe_2](\mu\text{-}H)_2(\mu_3\text{-}S)$				
A.	2.768(1)			76
	2.911(1)			
	2.922(1)			
B.	2.920(1)			
	2.918(1)			
	2.773(1)			
$Os_4(CO)_{12}(\mu_3\text{-}S)$				
2.386(4)	2.870(1)	73.9(11)	59.79(2)	77
2.386(4)	2.864(1)	73.83(10)	60.00(2)	
2.383(3)	2.858(1)	73.65(11)	60.21(2)	

TABLE IV (*cont.*)

Compound E–M	M–M	<M–E–M	<M–M–E	References
$Os_4(CO)_{13}(\mu_3\text{-}S)$				
A. 2.427(4)	2.807(1)	71.4(1)	60.55(2)	78
2.382(4)	2.752(1)	69.2(1)	58.75(2)	
2.418(4)	2.899(1)	71.4(1)	60.70(2)	
B. 2.414(4)	2.793(1)	70.9(1)	60.06(2)	
2.398(4)	2.769(1)	69.9(1)	59.55(2)	
2.418(4)	2.877(1)	70.6(1)	60.39(2)	
$Os_4(CO)_{12}(NHMe_2)(\mu_3\text{-}S)$				
2.418(3)	2.770(1)	70.43(7)	60.69(2)	79
2.386(2)	2.750(1)	69.27(1)	59.30(2)	
2.422(3)	2.789(1)	70.91(7)	60.0(2)	
$PtOs_3(CO)_{10}(PMe_2Ph)_2(\mu_3\text{-}S)$				
Pt: 2.337(4)	Os–Os: 2.869(1)	72.87(10)	60.37(2)	80
Os: 2.416(4)	Pt–Os: 2.768(1)	71.21(10)	61.57(2)	
2.414(4)	2.836(1)	73.27(10)	58.06(2)	
$PtOs_3(CO)_9(PMe_2Ph)_3(\mu_3\text{-}S)$				
A.				
Pt: 2.339(4)	Os–Os: 2.833(1)	72.15(12)	60.49(2)	80
Os: 2.406(4)	Os–Pt: 2.789(1)	72.01(13)	60.56(2)	
2.405(4)	2.835(1)	73.37(13)	58.96(2)	
B.				
Pt: 2.354(4)	Os–Os: 2.907(1)	74.63(13)	62.73(2)	80
Os: 2.403(5)	Os–Pt: 2.803(1)	72.20(13)	59.00(2)	
2.392(4)	2.782(1)	71.75(12)	58.27(2)	
$PtOs_3(CO)_8(PMe_2Ph)_3(\mu_3\text{-}S)$				
2.406(2)	2.816(1)	73.22(6)	66.52(2)	80, 81
2.315(2)	2.770(1)	71.25(6)	56.02(1)	
2.350(2)	3.064(1)	82.12(7)	57.46(1)	
$HPtOs_3(CO)_7(PMe_2Ph)_2(PMe_2C_6H_4)(\mu_3\text{-}S)$				
2.440(3)	2.920(1)	75.69(8)	65.12(5)	80
2.317(3)	2.837(1)	71.84(8)	57.54(2)	
2.395(3)	2.972(1)	78.20(8)	60.31(2)	
$Os_3W(CO)_{11}(PMe_2Ph)_2(\mu_3\text{-}S)$				
2.311(4)	Os–Os: 2.831(1)			81
2.396(4)	Os–W: 2.947(1)			
2.37(4)	2.913(1)			
$Os_6(CO)_{16}(\mu_4\text{-}S)(\mu_3\text{-}S)$				
2.352(4)	2.686(1)	69.32(12)	61.43(2)	82, 83
2.372(4)	2.844(1)	75.67(13)	62.04(3)	
2.285(4)	2.828(1)	74.76(13)	56.53(2)	
$PtOs_4(CO)_{11}(PMe_2Ph)_2(\mu_3\text{-}S)_2$ Os_3S:				
2.28(2)	2.882(1)	75.8(5)	58.01(4)	84
2.41(2)	2.809(1)	76.1(6)	59.66(4)	
2.28(2)	2.760(2)	72.0(5)	62.33(4)	
Os_2PtS:				
Pt: 2.20(2)	Os–Pt: 2.762(1)	75.3(6)	55.29(3)	
Os: 2.32(2)	Os–Os: 2.967(1)	80.7(6)	66.26(4)	
2.38(2)	2.665(1)	69.0(4)	58.45(3)	

TABLE IV (*cont.*)

Compound E–M	M–M	<M–E–M	<M–M–M	References
$H_2Os_5(CO)_{14}(\mu_3\text{-}S)_2$				
values not reported				85
$Co_3(CO)_9S$				
A. 2.143(10)	2.633(7)	76.1(3)	60.4(2)	86
2.131(10)	2.649(7)	76.6(3)	59.5(2)	
2.141(10)	2.655(5)	76.6(3)	60.1(2)	
B. 2.147(10)	2.612(6)	75.4(3)	60.6(2)	
2.122(9)	2.627(7)	75.9(3)	59.4(2)	
2.148(10)	2.641(6)	75.9(3)	60.0(2)	
$Co_6(CO)_{12}(\mu_3\text{-}S)_2C$				
2.194	2.437	67.4		87
	2.669			
$[(\mu_3\text{-}S)Co_3(CO)_7]_2S_2$				
2.160	2.485	70.2	60.6	88
2.162	2.463	70.7	60.4	
2.134	2.524	71.5	60.7	
2.122	2.521	71.7	61.2	
2.152	2.531	73.3	59.0	
2.139	2.544	72.6	58.1	
$(\mu_3\text{-}S)Co_6(CO)_{11}(SEt)_4$				
2.159	2.459	69.3	59.6	89
2.166	2.450	69.6	60.0	
2.163	2.471	69.1	60.4	
$Co_3(CO)_9Se$				
2.83(2)	2.609(2)	69.70(6)	59.72(6)	90
2.83(2)	2.624(2)	69.94(6)	59.98(6)	
2.81(2)	2.616(2)	70.21(6)	60.30(6)	
$FeCo_2(CO)_9Se$				
2.287(1)	2.570(1)	68.44(4)	59.71(3)	90
2.283(1)	2.583(1)	68.71(4)	60.08(3)	
2.284(1)	2.580(1)	68.88(4)	60.21(3)	
$FeCo_2(CO)_9Te$				
2.466(4)	2.599(6)	63.59(16)	60.05(13)	90
2.467(5)	2.595(4)	63.62(4)	60.07(7)	
2.466(4)	2.600(4)	63.47(8)	59.88(11)	
$(C_5Me_5)MnFe_2(CO)_8Te$				
Mn: 2.518(1)	Fe–Fe: 2.677(2)	Fe–Te–Fe: 65.5(0)	Fe–Mn–Fe: 58.5(0)	91
2.472(1)	Mn–Fe: 2.743(2)	Mn–Te–Fe: 66.7(0)	Mn–Fe–Fe: 60.9(0)	
Fe: 2.476(1)	2.736(2)	66.4(0)	60.6(0)	
$Cp_2Mo_2Fe_2(CO)_7(\mu_3\text{-}Te)_2$				
Mo: 2.684(1)	Fe–Fe: 2.433(2)	65.1(0)	Mo–Mo–Fe: 59.9(0)	92
2.683(1)	Fe–Mo: 2.861(2)	67.3(0)	60.3(0)	
2.681(1)	2.863(2)	67.6(0)	59.6(0)	
2.673(1)	2.872(2)	65.3(0)	59.4(0)	
Fe: 2.472(2)	2.889(2)	67.4(0)	Mo–Fe–Mo: 60.5(0)	
2.468(2)	Mo–Mo: 2.888(1)	68.2(0)	60.3(0)	

TABLE IV (*cont.*)

Compound E–M	M–M	<M–E–M	<M–M–E	References
			Mo–Fe–Fe: 64.9(0)	
			65.4(1)	
			64.8(0)	
			64.7(1)	
			Fe–Mo–Fe: 50.3(0)	
			50.0(0)	

TABLE V

Structural comparisons of butterfly M_4E and bridged-butterfly M_5E clusters. Distances in Å and angles in degrees.

Compound M_{ap}-E	M_{bas}-E	M_{ap}-M_{bas}	M_{bas}-M_{bas}	Dihedral angle	<M_{ap}-E-M_{ap}	M_5-M	M_5-C	References
Butterfly:								
$HFe_4(CO)_{12}(BH_2)$								
1.966(6)	2.044(6)	2.666(1)	2.637(1)	114	162			93
1.974(6)	2.047(6)	2.672(1)						
		2.671(1)						
		2.662(1)						
$W_4(O\text{-}i\text{Pr})_{12}(NMe)C$								
1.914(14)	2.251(14)	2.799(2)	2.795(2)		163.5			94
1.956(15)	2.241(14)	2.814(2)						
		2.822(1)						
		2.747(1)						
$[Et_4N][Fe_4(CO)_{12}(CCO_2CH_3)]$								
2.022(3)	1.951(9)	2.489	2.553	130	148			95
2.022(3)	1.958(9)	2.427						
		2.442						
		2.430						
$Fe_4(CO)_{12}\{C{=}C(OMe)_2\}$								
2.026(9)	1.976(9)	2.491(3)	2.532(3)	127	149			96
2.028(9)	1.960(9)	2.555(2)						
$Fe_4(CO)_{13}C$								
1.797(4)	1.999(4)	2.642(1)	2.545(1)	101	175			97
1.800(4)	1.988(4)	2.637(1)						
		2.647(1)						
		2.640(1)						
$Fe_4(CO)_{10}\{PMe_3\}_3C$								
1.785(4)	1.979(4)	2.644(ave)	2.528(1)	102.4	174			96
1.838(4)	2.014(4)							
$HFe_4(CO)_{12}(CH)$								
1.828(5)	1.946(5)	2.6160(9)	2.6053(8)	110.6	170.5(1)			98
1.926(5)	1.939(4)	2.6118(9)						
		2.6251(9)						
		2.6361(8)						

TABLE V (*cont.*)

Compound M_{ap}-E	M_{bas}-E	M_{ap}-M_{bas}	M_{bas}-M_{bas}	Dihedral angle	<M_{ap}-E-M_{ap}	M_5-M	M_5-C	References
$[PPN][HFe_4(CO)_{12}C]$								
1.79(5)	1.99(4)	2.627(9)	2.608(10)	104	174(2)			99
1.79(5)	1.99(4)	2.618(9)						
		2.631(9)						
		2.619(9)						
$[Zn(NH_3)_4][Fe_4(CO)_{12}C]\cdot H_2O$								
1.810(7)	1.969(5)	2.637(1)	2.534(1)	101.5	177.6(5)			100
1.786(7)		2.653(1)						
$[Et_4N]_2[Fe_4(CO)_{12}C]$								
1.772(11)	1.969(12)	2.640(2)	2.521(2)	101	178			96
1.803(12)	1.936(12)	2.641(3)						
$[PhCH_2NMe_3]_2[Fe_4(CO)_{12}C]$								
1.784(7)	1.941(7)	2.621(2)	2.533(2)	102.4	176.3			101
1.820(7)	1.980(7)	2.637(2)						
		2.630(2)						
		2.654(2)						
$[PPN][RhFe_3(CO)_{12}C]\cdot CH_2Cl_2$								
1.73(2)	2.12(1)	2.681(3)	2.630(2)	98	173.2(8)			102
1.80(2)	2.06(1)	2.675(3)						
		2.659(3)						
		2.676(3)						
$[PPN][Fe_4(CO)_{12}N]$								
1.774(5)	1.904(5)	2.596(1)	2.512(1)	101.8	179.0			103, 104
1.767(5)	1.896(5)	2.612(1)						
		2.605(1)						
		2.604(1)						
$HFe_4(CO)_{12}N$								
1.77(1)ave	1.92(2)ave	2.62(1)ave	2.54(2)	101	178.4(6)			105
$HRu_4(CO)_{11}\{P(OMe)_3\}N$								
1.913(5)	2.105(5)	2.832(1)	2.804(1)		173.2(3)			106
1.941(5)	2.114(4)	2.801(1)						
		2.773(1)						
		2.770(1)						
$[Et_4N][FeRu_3(CO)_{10}\{P(OMe)_3\}_2N]$								
1.944(1)	2.03(1)	2.721(2)	2.605(4)	107.6	172.0(4)			43
		2.746(2)						
$H_3Ru_4(CO)_{11}N$								
1.972(4)	2.020(4)	2.783(1)	2.811(1)	108.6	174.0(2)			107
1.953(4)	2.092(4)	2.794(1)						
		2.794(1)						
		2.798(1)						
$Ru_4(CO)_{12}(\mu\text{-}NO)N$								
A.								
1.906(5)	2.163(5)	2.823(1)	3.249(1)	69.6	173.0(3)			108
1.896(5)	2.171(6)	2.827(1)						
		2.821(1)						
		2.826(1)						

TABLE V (*cont.*)

Compound								
M_{ap}-E	M_{bas}-E	M_{ap}-M_{bas}	M_{bas}-M_{bas}	Dihedral angle	$<M_{ap}$-E-M_{ap}	M_5-M	M_5-C	References
B.								
1.909(5) 1.894(5)	2.169(5) 2.152(3)	2.831(1) 2.814(1) 2.826(1) 2.825(1)	3.244(1)	69.6	173.5(2)			
$Ru_4(CO)_{12}(\mu$-NCO)N								
1.903(3) 1.901(3)	2.132(2) 2.132(3)	2.817(1) 2.814(1) 2.826(1) 2.807(1)	3.239(1)	68.9	174.9(2)			108
$[PPN][Os_4(CO)_{12}N]$								
1.93(2) 1.98(2)	2.13(2) 2.10(2)	2.811(2) 2.816(2) 2.811(2) 2.793(2)	2.728(2)	105.4				107
Bridged-Butterfly:								
$[Et_4N]_2[Fe_5(CO)_{12}(Br)_2C]$								
1.839(10) 1.841(10)	1.974(9) 1.951(11)	2.654(2) 2.661(2) 2.651(2) 2.674(2)	2.531(2)	103.6	177.4	2.681(2)	1.938(11)	109
$(\mu$-H)$Fe_4(AuPPh_3)(CO)_{12}C$								
1.844(5) 1.868(5)	1.957(4) 1.951(5)	2.626(1) 2.638(1) 2.644(1) 2.628(1)	2.618(1)	71.70	173.1	2.880(1) 2.854(1)	2.077(5)	110
$Ru_5(CO)_{15}(MeCN)C$								
1.968(17) 1.961(17)	2.076(18) 2.068(18)	2.886(3) 2.888(3) 2.873(3) 2.887(3)	2.720(3)	101(1)	176.8	2.873(3) 2.886(3)	2.158(18)	111
$Ru_5(CO)_{15}C(AuPPh_3)Cl$								
A.								
1.91(2) 1.93(2)	2.10(2) 2.05(3)	2.772(4) 2.866(4) 2.961(4) 2.830(5)	2.965(4)		176.0	2.915(4) 2.819(4)	2.20(2)	112
B.								
1.91(3) 1.92(3)	2.17(2) 2.10(2)	2.867(4) 2.895(4) 2.785(4) 2.863(5)	2.970(4)		178.2	2.890(4) 2.810(4)	2.08(2)	
$Ru_5(CO)_{14}C(AuPPh_3)Br$								
1.99(1) 1.98(1)	2.06(1) 2.02(1)	2.849(3) 2.866(3) 2.826(3) 2.829(3)	2.951(3)		179.4	2.892(3) 2.877(3)	2.09(1)	112

TABLE V (*cont.*)

Compound								
M_{ap}-E	M_{bas}-E	M_{ap}-M_{bas}	M_{bas}-M_{bas}	Dihedral angle	$<M_{ap}$-E-M_{ap}	M_5-M	M_5-C	References
$(\mu\text{-H})Ru_4\{AuPPh_3\}(CO)_{12}C$								
1.98	2.09	2.82	2.856(1)			2.95	2.066(6)	113
$\{\mu\text{-AuPMe}_2Ph\}Ru_4\{AuPMe_2Ph\}(CO)_{12}C$								
1.81	2.22	2.80	3.252(3)			2.86	2.104(25)	113
$(\mu\text{-I})Ru_4\{AuPEt_5)_3\}(CO)_{12}C$								
1.96	2.14	2.86	3.427(1)			2.92	2.078(10)	113
$\{\mu\text{-AuPPh}_3\}Ru_5(CO)_{14}\{\mu\text{-}\eta^2\text{-C(O)Me}\}C$								
1.906(24) 1.977(18)	2.035(19) 2.080(18)	2.817(3) 2.822(3) 2.867(3) 2.879(3)	2.989(3)	71		2.880(3)	2.087(18)	114
$(\mu\text{-AuPPh}_3)Ru_5(CO)_{13}(Cp)C$								
1.980(5) 2.001(5)	2.115(6) 2.111(6)	2.839(1) 2.867(1) 2.880(1) 2.844(1)	2.894(1)	72		2.905(1) 2.890(1)	2.023(6)	114
$HRu_5(CO)_{15}(SEt)_3C$								
1.956(4)	2.150(4) 2.001(4)	2.840(1) 2.132(4) 2.875(1) 2.816(1)	2.855(1) 2.903(1)			3.049(1)	2.130(4) 2.908(1)	115
$Os_5(CO)_{16}C$								
A.								
1.96(2) 2.00(2)	2.11(3) 2.13(2)	2.915(2) 2.900(1) 2.912(1) 2.910(2)	2.757(1)	101.2	178.4	2.916(1) 2.917(1)	2.15(2)	116
B.								
1.93(2) 2.03(2)	2.13(2) 2.12(2)	2.910(2) 2.901(2) 2.915(1) 2.917(1)	2.746(1)	101.8	178.8	2.915(1) 2.917(2)	2.16(2)	
$Os_5(CO)_{15}C\{Ph_2P(CH_2)_2PPh_2\}$								
1.97(1) 1.99(1)	2.14(1) 2.09(1)	2.897(1) 2.884(1) 2.909(1) 2.897(1)	2.761(1)		178.4	2.996(1) 2.947(1)	2.20(1)	117
$[PPN][Os_5(CO)_{15}(I)C]$								
1.978 1.995	2.108 2.108	2.903 2.899 2.896 2.921	2.748			2.934 2.933	2.174	118
$HOs_5(CO)_{14}[OP(OMe)_2]C$								
1.988(12) 1.988(12)	2.086(14) 2.121(12)	2.870(2) 2.889(2) 2.879(2) 2.876(2)	2.914(2)	177.6(8)		2.928(2) 2.937(2)	2.121(14)	119

TABLE V (*cont.*)

Compound M_{ap}-E	 M_{bas}-E	 M_{ap}-M_{bas}	 M_{bas}-M_{bas}	Dihedral angle	 $<M_{ap}$-E-M_{ap}	 M_5-M	 M_5-C	 References
$HOs_5(CO)_{13}[OP(OMe)OP(OMe)_2]C$								
A.								
1.983(24)	2.096(23)	2.831(3)	2.927(3)		176.6	2.911(3)	2.141(24)	120
2.004(24)	2.064(24)	2.920(3)				2.951(3)		
		2.861(3)						
		2.866(4)						
B.								
1.992(22)	2.078(22)	2.843(3)	2.902(3)		176.6	2.899(3)	2.120(26)	
1.998(22)	2.107(26)	2.903(4)				2.963(3)		
		2.857(3)						
		2.890(4)						
$HOs_5(CO)_{13}\{OP(OMe)_2\}\{P(OMe)_3\}C$								
A.								
2.148(18)	1.988(17)	2.872(2)	2.893(2)		175.1	2.969(2)	2.096(18)	121
2.096(18)	2.002(17)	2.873(2)				2.939(2)		
		2.881(2)						
		2.868(2)						
B.								
2.148(18)	1.972(18)	2.867(2)	2.903(2)		175.5	2.960(2)	2.101(19)	
2.101(18)	2.015(15)	2.879(2)				2.946(2)		
		2.887(2)						
		2.879(2)						
$HOs_5(CO)_{14}(NC_5H_4)C$								
1.97(3)	2.11(3)	2.896(1)	2.927(1)		179.5	2.912(1)	2.12(3)	122
2.01(3)	2.06(3)	2.860(1)				2.908(1)		
		2.902(1)						
		2.853(1)						
$HOs_5(CO)_{14}(CO_2Et)C$								
1.96–2.11		2.889(1)	2.921(1)			2.931(1)		123
		2.857(1)				2.916(1)		
		2.865(1)						
		2.885(1)						
$IOs_5(CO)_{14}(CO_2Me)C$								
1.88–2.21		2.922(2)				2.905(2)		123
		2.927(2)				2.915(2)		
		2.916(2)						
		2.906(2)						

TABLE VI
Structural comparisons for square pyramidal M_5E clusters.

Compound	M_{apical}–E	M_{basal}–E	M_{apical}–M_{basal}	M_{basal}–M_{basal}	M_4-plane–E	References
$Fe_5(CO)_{15}C$						
	1.96(3)	1.87(3)	2.650(6)	2.667(7)		124
		1.89(3)	2.587(6)	2.636(7)		
		1.88(3)	2.666(7)	2.675(6)		
		1.90(3)	2.600(7)	2.652(7)		

TABLE VI (*cont.*)

Compound	M_{apical}-E	M_{basal}-E	M_{apical}-M_{basal}	M_{basal}-M_{basal}	M_4-plane-E	References
$Fe_5(CO)_{15}C$						
	1.953(5)	1.903(4)	2.615(2)	2.650(2)	0.09(1)	125
		1.877(5)	2.714(2)	2.671(1)		
		1.911(5)	2.624(1)	2.683(1)		
		1.873(5)	2.636(2)	2.682(2)		
$[(n\text{-}Bu)_4N]_2[Fe_5(CO)_{14}C]$						
	2.00(1)	1.88(2)	2.597(4)	2.553(3)	0.18(1)	126
		1.84(2)	2.616(4)	2.597(4)		
		1.87(2)	2.590(2)	2.670(4)		
		1.87(2)	2.591(2)	2.680(4)		
$[PPN][Fe_4Co(CO)_{14}C]$						
	1.962(5)	1.870(5)	2.575(1)	2.533(1)	0.15	102
		1.854(5)	2.572(1)	2.643(1)		
		1.865(5)	2.630(1)	2.626(1)		
		1.838(5)	2.581(1)	2.666(1)		
$[Et_4N][Fe_4Co(CO)_{14}C]$						
	1.97(1)	1.866(8)	2.568(2)	2.538(2)	0.17	126
		1.855(7)	2.594(2)	2.649(2)		
				2.642(2)		
$[Et_4N][Fe_4Rh(CO)_{14}C]$						
	1.980(12)	1.868(8)	2.616(ave)		0.19	127
		1.941(8)	2.633(ave)			
			2.779(ave)			
$[PPN][Fe_5(CO)_{14}N]$						
	1.916(8)	1.84(1)	2.611(3)	2.599(3)	0.11(1)	125
		1.882(9)	2.585(2)	2.646(3)		
		1.83(1)	2.579(3)	2.550(3)		
		1.826(8)	2.564(4)	2.629(3)		
$HFe_5(CO)_{14}N$						
	1.913(2)	1.836(3)	2.58(ave)		0.093	105
$Ru_5(CO)_{15}C$						
A.	2.101(18)	2.005(18)	2.853(2)	2.836(2)	0.11(2)	111
		2.017(17)	2.829(2)	2.843(2)		
		2.041(18)	2.804(2)	2.858(2)		
		2.028(17)	2.800(2)	2.882(2)		
B.	2.078(17)	2.030(17)	2.811(2)	2.838(2)	0.11(2)	
		2.029(17)	2.872(2)	2.847(2)		
		2.019(17)	2.800(2)	2.859(2)		
		2.004(18)	2.838(2)	2.876(2)		
$Ru_5(CO)_{14}(PPh_3)C$						
	2.123(5)	2.023(5)	2.819(1)	2.892(1)	0.19(1)	111
		2.022(5)	2.813(1)	2.815(1)		
		2.077(5)	2.830(1)	2.940(1)		
		2.026(5)	2.800(1)	2.830(1)		
$Ru_5(CO)_{13}(PPh_3)_2C$						
	2.163(8)	2.070(8)	2.787(2)	2.919(2)	0.23(1)	111
		2.044(7)	2.804(2)	2.889(2)		
		2.076(8)	2.832(2)	2.845(2)		
		2.004(7)	2.815(2)	2.864(2)		

TABLE VI (*cont.*)

Compound	M_{apical}-E	M_{basal}-E	M_{apical}-M_{basal}	M_{basal}-M_{basal}	M_4-plane-E	References
$[PhCH_2NEt_3][Ru_5(CO)_{14}N]$						
	2.14(2)	2.01(2)	2.747(3)	2.868(4)	0.21(2)	128
		2.06(2)	2.817(3)	2.818(3)		
		2.07(2)	2.848(3)	2.809(3)		
		1.97(2)	2.751(4)	2.911(4)		
$Ru_5(\mu\text{-}AuPPh_3)(CO)_{13}(NO)C$						
	2.03		2.789(2)	2.851(2)		129
			2.839(2)	2.847(2)		
			2.829(2)	2.760(2)		
			2.905(2)	2.866(2)		
$Ru_5(\mu_3\text{-}AuPPh_3)(CO)_{13}(NO)C$						
	2.04		2.907(2)	2.883(4)		129
			2.858(2)	2.830(2)		
			2.788(2)	2.776(2)		
			2.769(2)	2.838(2)		
$(\mu\text{-}H)Ru_5(CO)_{13}(\mu\text{-}PPh_2)C$						
	2.17(1)	2.02(1)	2.882(1)	2.721(1)	0.12	130
		2.00(1)	2.944(1)	2.873(1)		
		2.01(1)	2.786(1)	2.886(1)		
		2.03(1)	2.866(1)	2.878(1)		
$(\mu\text{-}H)_3Ru_5(CO)_{11}(\mu\text{-}PPh_2)(PMePh_2)C$						
	2.075(2)	2.022(3)	2.8934(6)	2.9170(6)		131
		2.065(2)	2.8347(5)	2.9014(7)		
		1.971(3)	2.8820(6)	2.7705(6)		
		2.060(2)	2.8391(6)	2.8948(7)		
$Os_5(CO)_{15}C$						
	2.06(ave)	2.85(3)(ave)	2.88(2)(ave)		0.12	118
$[PPN]_2[Os_5(CO)_{14}C]$						
	2.22(2)	2.06(2)	2.913(2)	2.768(2)	0.21	116
		2.04(2)	2.897(3)	2.921(2)		
		2.03(2)	2.817(3)	2.917(2)		
		2.05(2)	2.813(2)	2.904(2)		
$Os_5(CO)_{13}\{\mu\text{-}Os(CO)_2(MeCCMe)\}C$						
	2.20(2)	2.05(2)	2.823(4)	2.881(4)	0.20	132
		2.05(2)	2.828(4)	2.964(4)		
		2.02(2)	2.847(4)	2.893(4)		
		2.04(2)	2.881(4)	2.745(4)		
$Os_5(CO)_{14}\{AuPPh_3\}_2C$						
	2.038(14)	2.072(17)	3.019(1)	2.912(1)	−0.04(2)	116
		2.026(18)	2.793(1)	2.897(1)		
		2.019(17)	3.038(1)	2.894(1)		
		2.056(18)	2.796(1)	2.892(1)		

TABLE VII
Structural data on compounds containing μ_4-E groups. In this context, μ_4-E is used to refer to a main group element which is capping a square of metal atoms.

Compound M–E	M–M	<M–E–M	<M–M–M	References
[PPN][$Re_4(CO)_{15}$(I)C]				
2.08(ave)	3.007(2)	92.1(cis, ave)		133
	3.012(1)	157.4(trans, ave)		
	2.992(2)			
	2.986(1)			
$Co_4(CO)_{11}\{\mu_4\text{-}GeCo(CO)_4\}_2$				
2.406(4)	2.671(7)	67.2(2)	90.3(2)	134
2.423(4)	2.604(7)	103.5(1)	90.8(2)	
2.434(5)	2.693(8)	65.8(2)	87.9(2)	
2.390(5)	2.735(7)	67.4(2)	91.1(2)	
2.405(4)(terminal Co)		103.0(1)		
		69.1(2)		
$Co_4(CO)_{11}(\mu_4\text{-}GeMe)_2$				
2.390(ave)	2.580			135
2.926(Ge· · ·Ge)	2.692			
	2.692			
	2.721			
$Co_3(CO)_8NiCp\{\mu_4\text{-}Ge^tBu\}_2$				
Co: 2.406(9)	Co–Co: 2.609(6)	Co–Ge–Co: 102.2(3)	Co–Co–Co: 89.6(1)	41
2.381(9)	2.707(6)	103.7(3)	Co–Co–Ni: 89.1(2)	
2.389(8)	Ni–Co: 2.600(6)	Ni–Ge–Co: 99.9(3)	88.0(2)	
2.361(8)	2.552(5)	103.3(3)	Co–Ni–Co: 93.3(1)	
2.407(8)				
2.384(9)				
Ni: 2.385(8)				
2.300(8)				
$Re_4(CO)_{18}(\mu_4\text{-}PMe)_3$				
2.432(6)	3.156(1)			48
2.474(6)	3.092(1)			
$Re_5(CO)_{14}(\mu_4\text{-}PMe)(\mu\text{-}PMe_2)(\mu_3\text{-}PRe(CO)_5)$				
2.437(7)	3.067(2)			48
2.436(7)	3.101(1)			
2.450(7)	3.024(1)			
2.411(7)	2.983(1)			
$Fe_4(CO)_{11}(\mu_4\text{-}Ptolyl)_2$				
2.242(3)	2.685(2)		87.28(7)	136, 137
2.244(3)	2.694(3)		92.72(7)	
2.316(3)	2.440(3)			
2.321(3)				
2.637(4)(P· · ·P)				
$Fe_4(CO)_{10}[P(OMe)_3]\{\mu_4\text{-}Ptolyl\}_2$				
2.264(5)	2.755(3)	108.5(2)		138, 139
2.256(5)	2.642(3)	107.6(2)		
2.346(5)	2.671(3)	109.1(2)		
2.323(5)	2.458(3)	110.0(2)		
2.253(5)				
2.232(5)				
2.301(5)				
2.319(5)				

TABLE VII (*cont.*)

Compound M–E	M–M	<M–E–M	<M–M–M	References
$Fe_4(CO)_{11}[P(OMe)_3]\{\mu_4\text{-Ptolyl}\}_2$				
2.215(2)	2.710(2)	117.2(1)		138, 139
2.351(2)	2.666(2)	105.5(1)		
2.377(2)	2.687(2)	105.2(1)		
2.215(3)	2.668(2)	116.5(1)		
2.355(2)				
2.197(2)				
2.234(2)				
2.406(2)				
$Ru_5(CO)_{15}(\mu_4\text{-PPh})$				
A. 2.350(7)	2.837(3)			140
2.375(7)	2.900(3)			
2.370(7)	2.838(3)			
2.407(7)	2.882(3)			
B. 2.366(6)	2.848(3)			
2.384(6)	2.886(3)			
2.339(6)	2.835(3)			
2.391(6)	2.896(3)			
$Ru_3Rh_2(CO)_{13}(PEt_3)(\mu_4\text{-PPh})$				
Ru: 2.355(2)	Ru–Ru: 2.837(1)			56
2.340(2)	Rh–Rh: 2.775(1)			
Rh: 2.362(2)	Ru–Rh: 2.930(1)			
2.383(2)	2.862(1)			
$Ru_5(CO)_{15}(\mu_4\text{-PEt})$				
2.373(8)	2.882(2)			140
2.380(6)	2.817(2)			
2.360(7)	2.873(3)			
2.372(6)	2.910(3)			
$Ru_4(CO)_{10}(\mu\text{-CO})(\mu_4\text{-PPh})_2$				
2.39(1)	2.874(5)		91.5	140
2.48(1)	2.878(5)		91.6(1)	
2.45(1)	2.717(5)		88.7(1)	
2.42(1)	2.854(5)		88.0(1)	
2.39(1)				
2.46(1)				
2.52(1)				
2.38(1)				
$Os_5(CO)_{15}(\mu_4\text{-POMe})$				
2.338(9)	2.878(3)	74.9(3)		142
2.393(8)	2.896(3)	121.0(4)		
2.357(8)	2.887(3)	74.9(2)		
2.381(8)	2.932(3)	75.7(3)		
		118.9(4)		
		76.5(2)		
$Ni_8(CO)_8(\mu_4\text{-PPh})_6$				
2.183(ave)	2.648(ave)	75(ave)		143
$Co_4(CO)_8(\mu\text{-CO})_2(\mu_4\text{-PPh})_2$				
2.227(6)	2.521(4)(CO bridged)	68.7(2)	89.7(1)	144, 145
2.239(6)	2.519(4)(CO bridged)	68.7(2)	90.3(1)	
2.243(6)	2.710(4)	68.0(2)	90.3(1)	

TABLE VII (*cont.*)

Compound M–E	M–M	<M–E–M	<M–M–M	References
2.219(6)	2.685(4)	68.4(2)	89.7(1)	
2.244(6)		75.1(2)		
2.266(6)		73.6(2)		
2.244(6)		74.5(2)		
2.234(6)		73.1(1)		
2.537(6)(P···P)				
$Co_4(CO)_8[P(OMe)_3]_2(\mu_4\text{-}PPh)_2$				
2.250(1)	2.524(1)	68.39(3)	90.25(2)	146
2.254(1)	2.713(1)	74.09(3)	89.75(2)	
2.169(1)				
2.534(2)(P···P)				
$Co_4(CO)_8[P(OMe)_3]_2(\mu_4\text{-}PPh)_2$				
2.259(2)	2.518(1)	68.12(6)	89.91(4)	146
2.249(2)	2.727(1)	74.55(6)	90.09(4)	
2.246(2)	2.521(1)	110.97(8)	90.12(4)	
2.255(2)	2.726(1)	110.89(8)	89.88(4)	
		110.91(7)		
		111.03(7)		
		67.91(6)		
		74.36(6)		
$Co_4(CO)_6(PPh_3)_2(\mu\text{-}CO)_2(\mu_4\text{-}PPh)_2$				
2.254(4)	2.552(2)(CO bridged)	68.8(1)	91.24(8)	145
2.258(3)	2.551(1)(CO bridged)	67.3(1)	91.44(7)	
2.261(4)	2.785(2)	76.9(1)	88.58(8)	
2.225(4)	2.777(2)	75.8(1)	88.44(8)	
2.249(3)		67.8(1)		
2.255(3)		67.0(1)		
2.323(4)		74.1(1)		
2.366(4)		74.6(1)		
2.540(5)(P···P)				
$Co_4(CO)_{10}\{\mu_4\text{-}PCH(SiMe_3)_2\}\{\mu_4\text{-}PCH_2SiMe_3\}$				
2.333(1)				147
2.270(1)				
2.210(1)				
2.264(1)				
2.306(1)				
2.286(1)				
2.309(1)				
2.231(1)				
$Fe_2Co_2(CO)_{11}(\mu_4\text{-}PPh)_2$				
Fe: 2.23(ave)	Fe–Fe: 2.724(3)			148
Co: 2.27(ave)	Co–Co: 2.515(3)			
	Co–Fe: 2.62(ave)			
2.544(3)(P···P)				
$(C_5Me_5)RhFe_3(CO)_8(\mu_4\text{-}PPh)_2$				
Rh: 2.270(1)	Fe–Fe: 2.551(1)		83.42(1)	149
2.272(1)	2.506(1)		91.01(1)	
Fe: 2.312(1)	Fe–Rh: 2.769(1)		93.61(1)	
2.271(1)	2.772(1)		91.91(1)	
2.353(1)				
2.387(1)				

TABLE VII (*cont.*)

Compound M–E	M–M	<M–E–M	<M–M–M	References
2.292(1)				
2.271(1)				
2.666(1)(P···P)				
$(C_5Me_5)RhFe_3(CO)_9(\mu_4\text{-}PPh)_2$				
Rh: 2.264(2)	Fe–Fe: 2.659(1)		88.44(3)	149
2.275(2)	2.657(1)		89.30(3)	
Fe: 2.314(2)	Fe–Rh: 2.762(1)		91.56(4)	
2.322(2)	2.700(1)		90.70(4)	
2.317(2)				
2.347(2)				
2.284(2)				
2.289(2)				
2.579(1)(P···P)				
$Rh_4(COD)_2(\mu_4\text{-}PPh)_2$				
2.423(2)	2.836(1)		90.0	150
2.409(2)	2.850(1)		90.0	
2.415(2)			90.0	
2.414(2)				
2.679(4)(P···P)				
$Co_4(CO)_8(\mu\text{-}CO)_2(\mu_4\text{-}S)_2$				
2.244(11)	2.598(10)(no CO bridge)	66.8(4)	89.4(2)	145, 151
2.256(10)	2.480(9)(CO bridged)	66.5(4)	90.6(2)	
2.262(11)		70.3(4)		
2.269(10)		70.2(4)		
2.74(2)(S···S)				
$Fe_2Co_2(CO)_{11}S_2$				
Fe: 2.27(ave)	Fe–Fe: 2.604(2)			148
Co: 2.31(ave)	Co–Co: 2.495(2)			
	Co–Fe: 2.58(ave)			
$Ru_4(CO)_9(PMe_2Ph)_2(\mu_4\text{-}S)_2$				
2.459(1)	2.7807(7)	103.67(5)	91.74(2)	152
2.470(1)	2.8147(8)	70.12(4)	92.38(2)	
2.443(1)	2.7330(7)	65.83(4)	86.67(2)	
2.466(1)	2.7516(8)	69.12(4)	89.16(2)	
2.532(1)		69.52(4)		
2.584(1)		104.29(5)		
2.441(1)		68.57(4)		
2.479(1)		101.88(5)		
		66.41(4)		
		69.31(4)		
		105.50(5)		
		66.09(4)		
$Ru_8(CO)_{17}(tolyl)(\mu_4\text{-}S)_2$				
2.401(4)	2.739(2)			153
2.348(4)	2.862(2)			
2.395(3)	2.739(2)			
2.451(4)	2.855(2)			
2.470(4)	2.873(2)			
2.391(4)	2.867(2)			
2.403(4)	2.769(2)			
2.398(4)	2.791(2)			

TABLE VII (*cont.*)

Compound M–E	M–M	<M–E–M	<M–M–M	References
	2.689(2)			
	2.735(2)			
	2.791(2)			
	2.750(2)			
	2.752(2)			
	2.749(2)			
	2.808(2)			
	2.843(2)			
$Os_5(CO)_{15}(\mu_4\text{-}S)$				
2.418(9)	2.882(2)	71.7(2)	90.19(5)	78
2.502(10)	2.840(2)	70.6(2)	88.49(5)	
2.432(10)	2.853(2)	70.6(3)	91.16(5)	
2.496(9)	2.822(2)	69.9(3)	89.92(5)	
		111.2(3)		
		108.4(3)		
$Os_6(CO)_{17}(\mu_4\text{-}S)$				
2.398(5)	2.756(1)	69.08(15)	91.44(4)	154
2.642(6)	2.855(1)	71.22(14)	90.04(4)	
2.544(5)	2.860(1)	69.67(15)	89.84(3)	
2.503(6)	2.830(1)	68.20(15)	88.68(3)	
		106.99(20)		
		108.03(20)		
$Os_7(CO)_{19}(\mu_4\text{-}S)$				
2.439(7)	2.772(2)	69.52(19)	90.96(4)	77
2.423(7)	2.788(2)	69.56(19)	91.11(5)	
2.449(7)	2.802(1)	69.84(20)	89.31(4)	
2.471(7)	2.874(2)	71.47(21)	88.60(4)	
		108.28(28)		
		108.93(29)		
$Os_6(CO)_{16}(\mu_4\text{-}S)(\mu_3\text{-}S)$				
2.432(4)	2.884(1)	73.05(12)	88.54(3)	82, 83
2.414(4)	2.781(1)	69.62(12)	87.42(3)	
2.440(4)	2.863(1)	71.65(11)	93.15(3)	
2.476(4)	2.686(1)	66.24(11)	90.86(3)	
		108.03(15)		
		109.14(16)		
$Os_6(CO)_{17}(\mu_4\text{-}S)_2$				
2.489(7)	2.945(2)	73.2(2)	97.66(5)	83
2.449(7)	2.920(2)	72.8(2)	75.01(4)	
2.430(7)	2.898(2)	74.2(2)	74.03(4)	
2.522(8)	2.988(2)	71.3(2)	97.70(5)	
		90.5(2)		
		130.6(3)		
2.475(8)	2.945(2)	73.6(2)	97.66(5)	
2.439(7)	2.940(2)	73.8(2)	75.01(4)	
2.420(7)	2.898(2)	71.9(2)	74.21(4)	
2.496(7)	2.957(2)	73.9(2)	98.33(5)	
		91.4(2)		
		131.4(3)		
$PtOs_4(CO)_{13}(PPh_3)(\mu_4\text{-}S)$				
Pt: 2.326(3)	Os–Os: 2.770(1)	74.19(9)	89.84(2)	155

TABLE VII (*cont.*)

Compound M–E	M–M	<M–E–M	<M–M–M	References
Os: 2.499(4)	2.799(1)	69.30(9)	87.43(2)	
2.445(4)	Os–Pt: 2.900(1)	68.14(10)	94.12(2)	
2.477(3)	2.875(1)	73.03(10)	88.46(2)	
$PtOs_5(CO)_{15}(PPh_3)(\mu_4\text{-}S)$				
2.454(4)	2.847(1)	70.6(1)	91.00(3)	155
2.471(4)	2.804(1)	68.8(1)	86.17(2)	
2.509(4)	2.914(1)	66.16(9)	91.62(3)	
2.442(4)	2.703(1)	72.8(1)	91.20(5)	
		108.0(1)		
		107.0(1)		
$PtOs_5(CO)_{15}(PPh_3)_2(\mu_4\text{-}S)$				
Pt: 2.333(4)	3.030(1)		90.78(3)	155, 156
Os: 2.521(5)	2.818(1)		88.18(3)	
2.550(5)	2.791(1)		98.24(3)	
2.443(4)	2.719(1)		57.78(3)	
$Co_4(CO)_8(\mu\text{-}CO)_2(\mu_4\text{-}Te)_2$				
2.54(1)	2.88(2)(ave, non-CO bridged)	61.0(3)(ave)		144
3.30(1)(Te···Te)	2.58(2)(ave, CO bridged)			

TABLE VIII

Structural data summary of average M–E and M–M bonds for clusters containing M_6E octahedral and trigonal prismatic units. For high nuclearity clusters, the average distances given include only those parameters that are part of the M_6E unit. Distances in Å.

Compound	M–E	M–M	References
octahedral:			
$[Ph_3PMe]_2[(\mu_3\text{-}H)_2Re_6(CO)_{18}C]$			
	2.136(1)	3.020	157
$[PPh_4]_3[Re_7(CO)_{21}C]$			
	2.13	3.007	158
$[Et_4N]_2[Re_8(CO)_{24}C]$			
	2.116	2.992	159
$[(n\text{-}Bu)_4N]_5[\{AgRe_7(CO)_{21}C\}_2Br]$			
	2.13	3.007	160
$[Me_4N]_2[Fe_6(CO)_{16}C]$			
	1.89	2.671	161
$[PPN][Fe_6(CO)_{15}(NO)C]$			
	1.89	2.673	162
$Fe_6(CO)_{11}(NO)_4C$			
	1.90	2.684	162
$[Et_4N]_2[MoFe_5(CO)_{17}C]$			
	2.117(6)(Mo)	2.915(ave, Mo–Fe)	127
	1.947(6)(Fe_{ap})	2.643(ave, Fe_{ap}–Fe_{eq})	
	1.894(ave, Fe_{eq})	2.673(ave, Fe_{eq}–Fe_{eq})	
$Fe_4CoRh(CO)_{16}C$			
	1.919	2.714	126
$(\mu\text{-}AuPPh_3)Fe_5\{AuPPh_3\}(CO)_{12}C$			
	2.117(Au)	2.685(Fe–Fe)	163
	1.918(Fe)	2.936(Fe–Au)	

TABLE VIII (*cont.*)

Compound	M–E	M–M	References
$Ru_6(CO)_{17}C$	2.05	2.902	164
$[Et_4N]_2[Ru_6(CO)_{16}C]$	2.045	2.864	165
$[AsPh_4]_2[Ru_6(CO)_{16}C]$	2.05	2.89	166
$Ru_6(CO)_{16}(CuNCMe)_2C$	2.05	2.89	167
$Ru_6(CO)_{15}(NO)(\mu\text{-}AuPPh_3)C$	2.07	2.92	168
$Ru_6(CO)_{14}(NO)_2C$	2.04	2.88	169
$Ru_6(CO)_{16}(PPh_2Et)C$	2.060	2.912	169
$Ru_6(CO)_{14}$(bitropyl)C	2.06	2.907	170
$Ru_6(CO)_{15}(C_6H_{10})C$	2.06	2.899	171
$Ru_6(CO)_{14}(C_6H_3Me_3)C$	2.04	2.882	172
$Ru_6(CO)_{11}(\mu_3\text{-}\eta^2:\eta^2\text{-}C_6H_6)(\eta^6\text{-}C_6H_6)C$	2.043	2.889	173
$Ru_6(CO)_{15}(\mu\text{-}CO)(CN\text{-}t\text{-}Bu)C$	2.060	2.909	174
$Ru_6(CO)_{16}(AuPMePh_2)_2C$	2.062	2.870	175
$Ru_5W(CO)_{17}(AuPEt_3)_2C$	W: 2.05(4) Ru: 2.09(ave)	W–Ru: 2.964(ave) Ru–Ru: 2.930(ave)	175
$[Ph_3PC_2H_4PPh_3][Ru_{10}(CO)_{24}C_2]$	2.070	2.928 (range 2.803–3.098)	176
$[PPN]_2[Os_{10}(CO)_{24}C]$	2.04	2.882	177, 122
$[Ph_3PMe][HOs_{10}(CO)_{24}C]$	2.04	2.887	178
$[Ph_4As][HOs_{10}(CO)_{24}C]$	2.04	2.881	178
$[Ph_3PMe][Os_{10}(CO)_{24}\{Au(PPh_3)\}C]$	2.04	2.884	179, 180
$[Ph_3PMe][Os_{10}(CO)_{24}\{Cu(MeCN)\}C]$	2.05	2.890	179, 180
$[PPN][Os_{10}(CO)_{24}\{AuBr\}C]$		2.901	181
$[PPN][Os_{10}(CO)_{24}(\mu\text{-}NO)C]$	2.06	2.911	182
$[PPN][Os_{10}(CO)_{23}(NO)\}C]\cdot CH_2Cl_2$	2.04	2.883	182
$[PPN][Os_{10}(CO)_{24}(\mu\text{-}I)C]$	2.05	2.901	183

TABLE VIII (*cont.*)

Compound	M–E	M–M	References
$Os_{10}(CO)_{24}(\mu\text{-}I)_2C$			
	2.07	2.911	183
$[Et_4N]_2[Co_6(CO)_{13}C]$			
	1.87	2.638	184
$[Me_4N][Co_6(CO)_{14}C]$			
	1.90	2.66	185
$[H_3O][Rh_{15}(CO)_{28}C_2]$			
	2.04	2.898	186

trigonal prismatic:

M–E	M–M (within the triangular faces)	M–M (between triangular faces)	References
$[Ph_3PMe][Os_{11}(CO)_{27}\{Cu(NCMe)\}C]$			
2.17	2.840	2.835	187
$[PhCH_2NMe_3]_2[Co_6(CO)_{15}C]$			
1.95	2.537	2.575	188
$[PPN][Co_6(CO)_6(\mu\text{-}CO)_9N]$			
1.938	2.517	2.564	189
$Co_6(CO)_{12}(\mu_3\text{-}S)_2C$			
1.94	2.437	2.669	87
$[PhCH_2NMe_3]_2[Rh_6(CO)_{15}C]$			
2.134	2.776	2.817	190
$[PPN][Rh_6(CO)_{15}N]$			
1.863	2.758	2.828	191
$[PPh_4]_2[Rh_7(CO)_{15}N]$			
2.14	2.824	2.706	192
$Rh_6(CO)_{15}(\mu_3\text{-}CuNCMe)_2C$			
2.127	2.765	2.810	193
$Rh_8(CO)_{19}C$			
2.127	2.81		186, 194
$[PhCH_2NMe_3]_3[Co_{13}(CO)_{24}C_2]$			
1.97	cavity 1: 2.580	2.573	195
	cavity 2: 2.571	2.576	
$[PhCH_2NMe_3]_4[Co_{13}(CO)_{24}C_2]\cdot Me_2CO$			
1.98	cavity 1: 2.569	2.579	196
	cavity 2: 2.574	2.592	
$[Et_4N]_2[Co_6Ni_2(CO)_{16}C_2]$			
1.998	2.649	2.555	197
$[PPN]_2[Rh_{12}(CO)_{24}C_2]$			
2.12	2.782	2.769	198
$[Pr_4N]_3[Rh_{12}(CO)_{23}C_2]$			
2.125	cavity 1: 2.848	2.740	199
	cavity 2: 2.818	2.805	
$[Pr_4N]_4[Rh_{12}(CO)_{23}C_2]$			
2.13	cavity 1: 2.821	2.736	200
	cavity 2: 2.817	2.736	
$[PPh_4]_3[Ag\{Rh_6(CO)_{15}C\}_2]$			
2.136	2.780	2.826	201
$[Rh(CO)_2(NCMe)_2]_2[Rh_{14}(CO)_{33}C_2]$			
2.14	2.779 2.742	2.825	202

TABLE IX
Structural comparisons for clusters containing an E_2M_2 core. Distances are in Å and angles in degrees.

Compound								
E–E	E–M	M–M	$E\text{–}M_{external}$	<M–E–M	<E–E–M	<M–M–E	<E–M–E	References
$Mn_2(CO)_8\{\mu\text{-}GaMn(CO)_5\}_2$								
{3.846(1)}	2.440(1)	3.052(1)	2.446(1)	76.86(2)			103.46(2)	203
	2.460(1)						102.82(2)	
$Re_2(CO)_8\{\mu\text{-}GaMn(CO)_5\}_2$								
(4.25)		3.05		71			109	204
$Mn_2(CO)_8\{\mu\text{-}InMn(CO)_5\}_2$								
{4.103(1)}	2.610(1)	3.227(1)	2.596(1)	76.36(2)			103.64(2)	203, 205
	2.610(1)						103.64(2)	
$Re_2(CO)_8\{\mu\text{-}InRe(CO)_5\}_2$								
(4.525)	2.754(1)	3.232(1)	2.738(1)	71.07(3)			108.93(4)	204
$Fe_2(CO)_8\{\mu\text{-}InMn(CO)_5\}_2$								
{3.250(1)}	2.662(1)	{4.218(1)}	2.635(1)	104.8(0)			75.2(0)	206
	2.663(1)						75.2(0)	
$[Et_4N]_2[Fe_2(CO)_8\{\mu\text{-}TlFe(CO)_4\}_2]$								
	2.632(5)	(4.352)	2.553(5)	100.1(1)	45.11	36.55	80.0	207
	3.038(4)							
$Mn_2(CO)_8\{\mu\text{-}Ge(Br)Mn(CO)_5\}_2$								
	2.480(2)	2.923(2)	2.502(2)	72.20(5)			107.80(6)	208
	2.482(2)							
$Mn_2(CO)_8\{\mu\text{-}Sn(Cl)Mn(CO)_5\}_2$								
	2.620(1)	3.091(1)	2.626(1)	72.17(2)			107.83(2)	9
$Mn_2(CO)_8\{\mu\text{-}Sn(Br)Mn(CO)_5\}_2$								
	2.625(1)	3.086(1)	2.634(1)	71.91(2)			108.09(3)	209
	2.630(1)							
$Fe_2(CO)_6(NMe)_2$								
1.366(8)	1.873(4)	2.496(3)		83.1(2)	68.3(2)	48.2(1)	42.7(2)	210
	1.882(4)			83.6(2)	69.0(3)	48.4(1)		
$Fe_2(CO)_6(P^tBu)_2$								
2.059(3)	2.212–	2.740(1)						211
	2.232(2)							
$Fe_2(CO)_6(\mu\text{-}CO)\{PCr(CO)_5\}_2$								
2.087(6)	2.294(5)	2.605(3)	2.305(5)					28
	2.282(4)		2.308(6)					
	2.280(5)							
	2.283(5)							
$Co_2(CO)_5(PPh_3)P_2$								
2.019(9)	2.270(5)	2.574(3)		69.6(2)	64.1(2)	54.7(1)	52.6(2)	212
	2.286(5)			69.1(2)	63.2(2)	55.7(1)	53.4(2)	
	2.243(5)				63.6(2)	54.9(1)		
	2.255(5)				63.0(2)	56.0(1)		
$Co_2(CO)_6\{PCr(CO)_5\}\{PW(CO)_5\}$								
2.061(3)	2.258(2)	2.573(1)	2.365(2)*	69.7(1)	62.6(1)	55.0(1)	54.5(1)	213
	2.245(2)		2.357(2)*	69.8(1)	63.1(1)	55.4(1)	54.5(1)	
	2.246(2)				62.9(1)	55.2(1)		
	2.252(2)				62.4(1)	54.9(1)		
*Cr and W disordered, 50 : 50								
$Fe_2(CO)_6(\mu\text{-}S_2P\{Fe(CO)_4\}\{C_6H_4OMe\text{-}p\})$								
(2.878)	2.293(3)	2.486(2)		65.8(1)		56.9(1)	77.8(1)	214
	2.289(3)			65.9(1)		56.9(1)	78.2(1)	

TABLE IX (*cont.*)

Compound E-E	E-M	M-M	E-$M_{external}$	<M-E-M	<E-E-M	<M-M-E	<E-M-E	References
	2.283(3)					57.3(1)		
	2.282(3)					57.2(1)		
$Co_2(CO)_5(PPh_3)As_2$								
2.273(3)	2.354	2.594		65.6			57.4	215, 216
	2.376			66.1			56.4	
	2.404							
	2.410							
$Co_2(CO)_4(PPh_3)_2As_2$								
2.281(3)	2.406(2)	2.576(3)		64.98	61.20	57.18	56.81	216
	2.389(2)				61.98	57.84		
$Co_2(CO)_4[P(OMe)_3]_2\{AsW(CO)_5\}_2$								
2.28(1)	2.36(2)	2.59(2)	2.60(1)	66.8(1)	60.6(1)	56.3(1)	58.1(1)	217
	2.35(1)				61.3(1)	56.9(1)		
$Cp_2Mo_2\{AsCr(CO)_5\}_2$								
2.310(3)	2.531(3)	3.064(3)	2.471(3)	66.1(1)	55.5(1)		53.0(1)	218
	2.645(3)							
$W_2(CO)_7(I)(\mu\text{-}I)As_2$								
2.305(10)	2.704(9)	3.069(7)		70.3(2)			50.6(2)	218
	2.687(10)			70.7(2)			52.2(2)	
	2.625(10)							
	2.619(8)							
$As_2\{(C_5Me_5)Mn(CO)_2\}_2$								
2.225(1)	2.544(3)			104.5(1)	65.0(1)		51.5(1)	219, 220
	2.545(3)			103.2(1)	64.4(1)		51.7(1)	
	2.575(2)							
	2.558(3)							
$\{\mu\text{-}Bi(Me)W(CO)_5\}W_2(CO)_8Bi_2$								
2.796(1)	2.987(1)	3.142(3)		63.34(2)	62.28(2)		55.57(2)	18
	3.001(1)			63.33(2)	72.16(2)		55.78(2)	
	2.990(1)				62.15(2)			
	2.997(1)				62.06(2)			
$[Et_4N][Fe_2(CO)_6Bi_2\{\mu\text{-}Co(CO)_4\}]$								
3.092(2)	2.682(5)	2.682(7)	2.894(5)	60.03(15)		60.02(15)	70.60(13)	221
	2.680(6)		2.868(5)	60.02(15)		59.55(15)	70.27(13)	
	2.669(5)					59.95(15)		
	2.693(5)					60.43(15)		
$Fe_2(CO)_6S_2$								
A.								
2.007(5)	2.223(4)	2.552(2)		70.08(11)	62.88(15)		53.48(14)	222
	2.222(3)			69.67(12)	63.64(16)		53.58(14)	
	2.238(4)				63.42(15)			
	2.230(4)				63.01(15)			
B.								
2.07	2.21	2.55		70			55	223
	2.22						56	
$Fe_2(CO)_6(SEt)_2$								
	2.266(13)	2.537(10)		67.78(36)			81.62(47)	224
	2.221(14)			68.88(37)			80.30(38)	
	2.284(12)							
	2.264(11)							
$\{Fe_2(CO)_6(\mu\text{-}SMe)\}_2S$								
{2.812(9)}	2.268(7)	2.543(6)		68.2(2)		55.8(2)	77.0(3)	31

TABLE IX (*cont.*)

Compound								
E-E	E-M	M-M	E-$M_{external}$	<M-E-M	<E-E-M	<M-M-E	<E-M-E	References
{2.822(9)}	2.265(8)	2.536(7)		67.5(2)		55.9(2)	77.0(2)	
	2.280(8)			68.8(2)*		56.3(2)	77.0(2)	
	2.284(7)			68.7(2)*		56.2(2)	77.2(2)	
	2.247(7)*					55.7(2)*		
	2.253(7)*					55.5(2)*		
	2.254(7)*					55.4(2)*		
	2.239(7)*					55.9(2)*		
*μ_4-S parameter								
$Fe_2(CO)_6\{\mu\text{-}SC_5H_4N\}\{\mu\text{-}SFe_2(CO)_6C_5H_4N\}$								
	2.247(2)	2.532(1)	2.236(2)	68.32(6)		56.48(6)	76.63(8)	32
	2.263(2)		2.248(2)	67.44(9)		56.14(5)	76.10(7)	
	2.276(2)					56.08(6)		
	2.286(2)					55.54(6)		
$C_2S_4\{Fe_2(CO)_6\}_2$								
	2.296(2)	2.486(2)		65.6(1)		57.1(1)	73.5(1)	225
	2.288(2)			65.7(1)		57.3(1)	73.4(1)	
	2.292(2)					57.3(1)		
	2.295(2)							
$\{Fe_2(CO)_6\}[SC(Ph){=}C(Ph)S]$								
A. (2.861)	2.242(6)	2.511(4)		68.0		56.1	78.7	226
	2.268(6)			67.5		56.0	78.9	
	2.248(6)					55.9		
	2.253(6)					56.5		
B. (2.871)	2.264(6)	2.504(4)		67.0		56.7	78.7	
	2.266(6)			67.2		56.3	78.6	
	2.273(6)					56.3		
	2.259(6)					56.5		
$Fe_2(CO)_6\{S_2CH_2\}$								
2.673(2)	2.262(1)	2.485(1)		66.64(4)			72.45(4)	227
$Fe_2(CO)_5(CC_6H_6Me_4)(S_2CC_6H_6Me_4)$								
		2.521(2)						228
$Os_6(CO)_{18}(\mu_4\text{-}S)_2(\mu\text{-}HC{=}NPh)_2$								
	2.424(4)	2.752(1)	2.411(4)	69.2(1)		55.5(1)		33
	2.411(5)		2.413(5)	69.4(1)		55.1(1)		
	2.420(4)		2.421(4)			55.3(1)		
	2.426(5)		2.433(5)			55.6(1)		
$Fe_2(CO)_6Se_2$								
2.293(2)	2.354(2)	2.575(2)		66.3(1)	61.5(1)	56.8(1)	58.0(1)	229
	2.378(2)			65.8(1)	60.5(1)	57.3(1)	58.1(1)	
	2.355(2)				60.7(1)	56.9(1)		
	2.366(2)				61.2(1)	56.9(1)		
$Cp_2Cr_2(CO)_4Se_2$								
2.277	2.208–							
	2.011			100.2(1)	63.6(1)		53.1(1)	230
				100.3(1)	63.1(2)		53.1(2)	
					63.3(1)			
					63.7(1)			
$[FeW(CO)_8Se_2][PF_6]_2$								
2.281(3)	W: 2.601(2)	2.857(3)						231
	2.606(2)							

TABLE IX (*cont.*)

Compound E-E	E-M	M-M	E-M$_{external}$	<M-E-M	<E-E-M	<M-M-E	<E-M-E	References
$\{(triphos)Ni\}_2Te_2$								
2.802(1)	2.576(1) 2.596(1)			114.5 56.9(1)	57.6(1)		65.61(1)	232
$CpMoFe(CO)_5(Te_2Br)$								
2.807(1)	Mo: 2.717(1) 2.776(1) Fe: 2.510(1) 2.573(1)	2.876			60.3(0) 57.6(0)			233
$CpMoFe(CO)_5\{Te_2(S_2CNEt_2)\}$								
2.954(1)	Mo: 2.740(1) 2.792(1) Fe: 2.517(1) 2.575(1)	2.894(1)			58.6 55.5(0)			233
$Fe_2(CO)_6Te_2\{\mu\text{-}Fe(CO)_3(PPh_3)\}$								
3.138(1)	2.577(1) 2.565(1) 2.575(1) 2.567(1)	2.585(1)	2.657(1) 2.668(1)	60.35(2) 60.36(2)		60.06(2) 59.67(2) 59.59(2) 59.97(2)	75.25(2) 75.17(2)	234
$CpMoFe(CO)_5Te_2(\mu\text{-}CpMo(CO)_2)$*								
3.146(1)	Mo: 2.781(1) 2.780(1) Fe: 2.584(1) 2.582(1)	2.850(1)	2.822(1) 2.816(1)	64.1(0) 64.1(0)		54.6(0) 54.6(0)	Fe: 75.0(0) Mo: 68.9(0)	92

*only data for one molecule presented

TABLE X

Structural comparisons of molecules containing an E_2M_3 moiety.

Compound E–M	M–M	<M–E–M	<M–M–M	References
trigonal bipyramidal:				
$Fe_3(CO)_9\{\mu_3\text{-}SnFe(CO)_2Cp\}_2$				
2.537(4)(ave) 2.471(ave, terminal Fe)	2.792(6)(ave)	64.5(ave)		235
$(C_8H_{12})_3Pt_3(\mu_3\text{-}SnCl_3)_2$				
2.80(1)(ave)	2.58(1)(ave)	54.9(ave)	60.0(ave)	236
$Fe_3(CO)_9\{\mu_3\text{-}PMn(CO)_2Cp\}_2$				
Fe: 2.241(9)–2.297(8) Mn: 2.145(9) 2.142(9)	2.608(6)–2.671(6)		59.9(2)–61.3(2)	28

TABLE X (*cont.*)

Compound E–M	M–M	<M–E–M	<M–M–M	References
$Fe_3(CO)_9\{\mu_3\text{-}PMn(CO)_2Cp\}\{\mu_3\text{-}PFe(CO)_4\}$				
Fe: 2.219(8)–2.297(8)	2.668(5)–2.6781(5)		58.9(1)–60.8(1)	28
2.191(8)*				
Mn: 2.165(8)				
*external Fe				
$Fe_3(CO)_9\{\mu_3\text{-}PCrCO)_5\}\{\mu_3\text{-}PFe(CO)_4\}$				
Fe: 2.224(3)–2.279(3)	2.603(2)–2.662(4)		59.0(1)–61.1(1)	28
2.163(4)*				
Cr: 2.301(4)				
*external Fe				
$Fe_3(CO)_6\{P(O\text{-}{}^iPr)_3\}_3\{\mu_3\text{-}PMn(CO)_2Cp)\}\{\mu_3\text{-}P\}$				
Fe: 2.204(3)–2.239(2)	2.600(2)–2.625(2)		59.6(1)	28
Mn: 2.166(3)				
$Fe_3(CO)_9\{\mu_3\text{-}PMn(CO)_2Cp\}\{\mu_3\text{-}PFe_2(CO)_8\}$				
Fe: 2.206(4)–2.263(4)	2.606(3)–2.781(3)		58.6(1)–61.1(1)	28
2.452(3)*				
Mn: 2.155(2)				
*external Fe				
$Fe_3(CO)_9(\mu_3\text{-}As)_2$				
2.331(3)	2.626(6)	68.4(1)	59.6(1)	237
2.338(3)	2.612(7)	67.4(1)	60.1(1)	
2.376(3)	2.630(7)	67.8(1)	60.3(1)	
$Fe_3(CO)_9(\mu_3\text{-}Bi)_2$				
2.623(2)	2.742(4)	63.11(8)	59.64(10)	238
2.617(2)	2.757(5)	63.14(8)	60.45(10)	
2.643(2)	2.735(5)	62.65(9)	59.91(10)	
square pyramidal:				
$Fe_3(CO)_9(\mu_3\text{-}NMe)_2$				
1.89(2)	2.436(7)	78.6(7)	76.4(2)	239
1.96(2)	2.488(7)	104.7(8)		
1.95(2)	3.044(8)	79.1(7)		
1.94(2)		78.0(7)		
1.92(2)		104.7(8)		
1.90(2)		81.2(7)		
$Fe_3(CO)_9(\mu_3\text{-}PPh)_2$				
A. 2.216(5)	2.718(3)	106.8(2)	81.7(1)	240
2.216(5)	2.717(3)	107.0(2)		
2.222(4)	3.54(1)			
2.214(4)				
2.211(5)				
2.207(5)				
2.587(5)(P–P)				
B. 2.202(4)	2.714(3)	106.3(2)	81.2(1)	
2.199(5)	2.717(3)	106.9(2)		
2.225(5)				
2.231(5)				
2.214(5)				
2.199(4)				

TABLE X (*cont.*)

Compound E–M	M–M	<M–E–M	<M–M–M	References
$Fe_3(CO)_6\{P(OMe)_3\}_3(\mu_3\text{-}PPh)_2$				
2.234(1)	2.681(1)	108.31(4)	83.93(2)	241
2.222(1)	2.736(1)	109.52(4)		
2.242(1)	3.622(1)			
2.252(1)				
2.234(1)				
2.213(1)				
2.566(1)(P–P)				
$CrCo_2(CO)_{10}\{\mu_3\text{-}AsCr(CO)_5\}_2$				
Cr: 2.417(2)	2.804(3)	98.8(1)	80.0(1)	58
2.421(2)	2.782(3)			
2.428(2)*	3.592(2)(Co–Co)			
2.435(2)*				
Co: 2.368(2)				
2.362(2)				
2.355(2)				
2.372(2)				
*external Cr				
$Fe_3(CO)_9(\mu_3\text{-}AsPh)_2$				
A. 2.323(3)	2.792(4)	105.7(1)	83.9(1)	242
2.323(4)	2.738(6)	105.3(1)		
2.317(4)	3.699(5)	73.5(1)		
2.330(4)		73.8(1)		
2.344(4)		71.9(1)		
2.327(4)		72.0(1)		
B. 2.346(2)	2.752(2)	73.58(6)	83.82(5)	243
2.330(2)	2.796(2)	73.20(6)		
2.324(2)	3.705(2)	72.30(6)		
2.335(2)		105.26(6)		
2.322(2)		73.78(6)		
2.328(2)		105.78(6)		
2.7981(2)(As–As)				
$[Et_4N]_2[Fe_3(CO)_9(\mu_3\text{-}Bi)\{\mu_3\text{-}BiFe(CO)_4\}]$				
2.645(2)	2.808(2)	135.40(6)	91.96(7)	221
2.687(2)	2.796(2)	128.63(5)		
2.678(2)	4.03	122.48(6)		
2.683(2)		101.91(5)		
2.597(2)		64.78(5)		
2.592(2)		97.38(5)		
3.398(1)(Bi···B)		62.87(5)		
		64.52(5)		
		63.06(5)		
$Fe_3(CO)_9(\mu_3\text{-}S)_2$				
A. 2.223(1)	2.598(1)	71.26(3)	81.01(2)	244
2.242(1)	2.589(1)	98.28(3)		
2.237(1)		70.83(2)		
2.257(1)		70.54(2)		
2.231(1)		97.53(3)		
2.238(1)		70.34(2)		
B. 2.228(9)	2.582(9)	98.4(4)	81.0(3)	223
2.225(9)	{3.371(10)}	71.6(3)		
2.233(9)		70.7(3)		

TABLE X (*cont*)

Compound E–M	M–M	<M–E–M	<M–M–M	References
$Fe_3(CO)_9(\mu_3\text{-PPh})(\mu_3\text{-S})$				
S. 2.244(5)	2.664(5)		82.8(1)	245
2.270(6)	2.646(5)			
2.260(5)	3.511(6)			
P. 2.259(5)				
2.189(5)				
2.199(6)				
2.713(5)(P···S)				
$Fe_3(CO)_9(\mu_3\text{-AsPh})(\mu_3\text{-S})$				
S. 2.217(4)	2.679(3)		83.2(1)	245
2.273(3)	2.667(3)			
2.271(3)	3.550(3)			
As. 2.359(2)				
2.275(2)				
2.276(3)				
2.816(3)(As···S)				
$Fe_3(CO)_9(\mu_3\text{-S})(\mu_3\text{-SO})$				
2.140(1)	2.623(1)			246
2.222(1)	2.647(1)			
2.139(1)				
2.269(1)				
2.230(1)				
2.263(1)				
2.72(S···S)				
$Os_3(CO)_9S_2$				
2.454(2)	2.814(1)	70.63(7)	81.21(1)	247
2.434(2)	2.812(1)	70.77(7)		
2.415(2)	{3.662(1)}	98.97(8)		
2.392(2)		71.35(6)		
2.402(2)		71.31(7)		
2.390(2)		99.95(9)		
$Os_3(CO)_8(PMe_2Ph)S_2$				
2.452(3)	2.770(1)	69.19(7)	82.57(2)	247
2.446(2)	2.856(1)	71.89(7)		
2.426(2)	{3.713(1)}	100.19(9)		
2.405(2)		69.62(7)		
2.413(2)		72.39(7)		
2.389(2)		101.49(9)		
$Os_3(CO)_8(CS)S_2$				
2.380(9)	2.830(2)	71.9(2)	81.0(1)	248
2.440(9)	2.780(2)	99.3(3)		
2.400(9)	{3.642(3)}	70.1(3)		
2.365(10)		72.7(3)		
2.408(11)		100.3(4)		
2.381(9)		71.0(3)		
3.030(12)(S···S)				
$H_2Os_3(CO)_7(CS)S_2$				
2.435(14)	2.813(1)		82.8(1)	244
2.373(12)	2.808(1)			
2.431(12)	{3.70}			
2.427(17)				
2.464(18)				
2.401(18)				
3.077(S···S)				

TABLE X (*cont*)

Compound E–M	M–M	<M–E–M	<M–M–M	References
A. 2.407(8)	2.804(2)	72.0(2)	82.21(5)	250
2.459(9)	2.815(2)	72.4(2)		
2.364(8)		103.0(3)		
2.426(8)		70.1(2)		
2.357(8)		71.0(2)		
2.384(8)		100.3(2)		
W: 2.522(8)				
B. 2.419(7)	2.818(2)	71.1(2)	82.44(5)	
2.467(8)	2.784(2)	72.4(2)		
2.354(8)		102.8(3)		
2.396(8)		70.8(2)		
2.370(8)		69.5(2)		
2.414(9)		100.3(3)		
W: 2.550(8)				
$\{Os_3(CO)_8S_2\}_2$				
	2.957(1)			251
	2.792(1)			
	2.941(1)			
	2.789(1)			
$H_2Os_3(CO)_8S_2$				
2.428(4)	2.802(1)		82.84(3)	251
2.414(4)	{3.707(1)}			
2.425(4)				
$Fe_3(CO)_9(\mu_3\text{-}Se)_2$				
2.34(1.7)	2.64(1.7)	96.6(ave)		252
2.35(1.7)	2.66(1.7)	68(ave)		
2.35(1.7)	3.51(1.7)			
2.36(1.7)				
2.34(1.7)				
2.37(1.7)				
3.10(1.6)(Se· · ·Se)				

TABLE XI

Structural comparisons for complexes of the type $E_2\{\mu\text{-}M(CO)_5\}_3$. Distances in Å and angles in degrees.

Compound	E–E	E–M	References
$As_2\{\mu\text{-}W(CO)_5\}_3$	2.279(4)	2.803(2)–2.855(2)	253
$Sb_2\{\mu\text{-}W(CO)_5\}_3$	2.663		254
$Bi_2\{\mu\text{-}W(CO)_5\}_3$	2.818(3)	3.083(3)–3.134(3)	255

TABLE XII

Structural data for $E_3(\mu_3\text{-}ML_n)$ and $E_3(\mu_3\text{-}ML_n)_2$ complexes. Distances are in Å and angles in degrees.

Compound E–E	M–E	<E–E–E	<E–M–E	<M–E–E	References
$P_3\{Co(1,1,1\text{-tris(diphenylphosphinomethyl)ethane})\}$					
2.13–2.16	2.301		55.5(1)		256

TABLE XII (*cont.*)

Compound E–E	M–E	<E–E–E	<E–M–E	<M–E–E	References
P_3Co(triphos)					
2.141(2)	2.301(1)	60.0	55.43(5)	62.3(4)	257
P_3Co{tris(2-diphenylphosphinoethyl)amine}					
2.137(6)	2.311(6)		55.1(2)		258
2.128(7)	2.310(5)		54.6(2)		
2.139(7)	2.325(4)		55.0(2)		
[(triphos)PdP_3]BF_4·EtOH					
2.108(11)	2.414(8)	60.3(4)	51.9(3)	63.8(3)	259
2.121(11)	2.403(8)	60.1(4)	52.1(3)	64.1(3)	
2.116(10)	2.419(8)	59.7(4)	52.0(3)	64.3(3)	
				63.6(3)	
				64.4(3)	
				63.8(3)	
[(triphos)CoP_3]$_2$$Cu_6Br_6$					
2.03(1)(ave)	Cu: 2.54(5)(ave)				260
	Co: 2.20(1)(ave)				
P_3{Cr(CO)$_5$}$_2$}Co(triphos)					
2.145(6)	2.340(4)	59.2(2)	55.0(1)	61.6(1)	261
2.154(6)	2.303(4)	60.2(2)	55.7(1)	60.5(1)	
2.124(4)	2.270(4)	60.6(2)	55.3(1)	63.3(1)	
				61.5(1)	
				63.8(2)	
				63.1(1)	
$As_3Co(CO)_3$					
2.372(5)	2.439(5)	60.0(-)	58.2(1)	60.9(1)	262
As_3{MoCp(CO)$_2$}					
2.372(1)	2.706(2)	60.2(1)			263
2.377(2)	2.639(1)	59.9(0)			
[P_3{Ni(1,1,1-tris(diphenylphosphinomethyl)ethane)}$_2$][BF_4]$_2$					
2.13–2.16	2.35		53–55		256
	2.36				
	2.37				
	2.33				
	2.33				
	2.35				
[P_3{Ni(triphos)}$_2$][BPh_4]$_2$·2.5$(CH_3)_2CO$					
2.169(6)	2.363(7)		54.8(2)		263
2.151(8)	2.352(5)		53.9(2)		
2.171(8)	2.386(5)		54.5(2)		
	2.340(4)		55.4(2)		
	2.328(6)		54.5(2)		
	2.355(7)		55.2(2)		
[P_3{Ni(triphos)}{Co(triphos)}][BPh_4]$_2$·2$(CH_3)_2CO$					
2.169(9)	2.327(10)		55.5(3)		263
2.150(14)	2.337(8)		54.9(3)		
2.173(11)	2.328(7)		55.5(3)		
	2.322(8)		55.5(3)		
	2.334(10)		55.1(3)		
	2.325(11)		55.6(3)		
[{(triphos)Pd}$_2$$P_3$]$BPh_4$					
2.143(9)	2.495(4)	59.3(4)	50.8(2)	64.7(3)	259
2.120(3)	2.500(7)	60.3(4)	51.0(2)	64.1(3)	

TABLE XII (*cont.*)

Compound E-E	M-E	<E-E-E	<E-M-E	<M-E-E	References
				64.5(2)	
				64.3(2)	
				64.9(2)	
				65.3(2)	
$[As_3\{Co(triphos)\}_2][BPh_4]_2 \cdot 2(CH_3)CO$					
2.45(1)	2.40(2)		61.2(6)		263, 264
2.42(2)	2.42(2)		60.6(6)		
2.45(2)	2.40(2)		61.2(6)		
	2.41(1)		61.4(4)		
	2.40(2)		59.8(5)		
	2.44(2)		60.8(6)		

TABLE XIII
Summary of the C-C distances in the known dicarbide clusters.

Cluster	C–C distance (Å)	Reference
$Rh_{12}(CO)_{25}C_2$	1.48	357
$[Co_{11}(CO)_{22}C_2]^{2-}$	1.62	355
$[Ni_{10}(CO)_{16}C_2]^{2-}$	1.40	360
$[Co_3Ni_7(CO)_{16}C_2]^{2-}$	1.41	362
$[Co_3Ni_7(CO)_{15}C_2]^{2-}$	1.48	362
$[Co_6Ni_2(CO)_{16}C_2]^{2-}$	1.49	363

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