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TRANSITION-METAL MOLECULAR CLUSTERS

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I. Introduction

The advances in the field of cluster chemistry in the past few years have been considerable; and, although some of the chemistry to be discussed in this review has been the subject of report elsewhere (*1–9*), many of the principles of structure and reactivity have not been discussed previously. In no way do we regard this article as a comprehensive account, but rather an assessment of the current views of cluster compounds.

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Muetterties (*9*) has drawn attention to the similarities between the chemistry of transition-metal surfaces and transition-metal clusters, and encourage the view that the study of transition-metal clusters would provide information about interactions occurring at the surface of heterogeneous catalysts. The clusters also possess intrinsic novel properties which suggest that these clusters might serve as potential catalysts for a range of processes. The report (*10*) that rhodium carbonyl clusters were effective catalysts in the production of ethylene glycol considerably enhanced this view, but there remains the considerable problem of whether the true catalyst in these reactions is a cluster rather than some mononuclear species. Work is now in hand at several centers to resolve this dilemma. In particular, the synthesis of optically active cluster compounds should go a long way in establishing whether or not the integrity of the cluster is maintained throughout the catalyzed reaction.

We take as our main themes in this review the structure, bonding, and reactivity of cluster systems, and will note any correlation between these aspects and work on heterogeneous systems.

II. Structure and Bonding in Transition-Metal Clusters

A. Some General Comments

In order to appreciate the bonding and geometries in clusters of metal atoms, it is first necessary to consider the principles governing the bonding of ligands to a single transition-metal ion. The isolated transition-metal ion has nine valence orbitals, one ns, three np, and five $(n-1)$d. According to Sidgwick (*11*), these nine orbitals are filled either by the donation of electron pairs from ligands or by nonbonding electrons. This forms the basis of the well-known effective atomic number (E.A.N.) or 18-electron rule, and the large majority of low-valent, diamagnetic complexes, particularly the binary metal carbonyls, obey this rule. Indeed, the rule has been outstandingly successful both in predicting and in rationalizing the structures of low-valent transition-metal organometallic complexes.

Exceptions to the E.A.N. rule do occur, particularly with d^8 metal ions, where many examples of square-planar, 16-electron complexes are known. In these complexes, the high-lying p_z orbital is nonbonding and remains empty. This deviation from the rule is often said to be due to the large s-to-p promotion energies found for the free atoms. As the atomic number increases across a given transition-metal series, the energies of the s and d orbitals drop more rapidly than that of the p orbital, thereby increasing the s(d)-to-p promotion energies. Exceptions to the 18-electron rule are also found for the Group IB metals. Here again, the p orbitals may not be fully utilized; for example, gold(I) forms primarily two-coordinate 14-electron metal complexes. In transition-metal clusters, the s(d)–p separation is also important and may govern the geometry adopted by metallic clusters. In general, the useful application of the 18-electron rule to cluster systems is restricted to the smaller clusters containing five or fewer metal atoms and makes a number of important assumptions: (*i*) M–M bonds correspond to polyhedral edge-bonds; (*ii*) all M–M bonds will be two-center/two-electron bonds; and (*iii*) ligands serve as a source of electrons only, leading to the view that the same M_m polyhedron will be derived irrespective of whether the electrons are present as charge or by donation from ligands. Although the E.A.N. rule is restricted in its application, it nevertheless provides a convenient method of classifying structural types and will be used as such throughout the following sections. A more detailed appraisal of the rule is given in Section II,D.

B. CLUSTER TYPES

We may classify cluster compounds of the transition metals into two extreme types:

1. "Naked Clusters." These are clusters which have no ligands associated with them and which sit in an inert matrix. In reality, this is not an easy situation to achieve, but the aggregation of metal atoms in an inert matrix has been observed by Ozin (*12*). Studies of this sort may be of importance not only as a method of producing highly active naked clusters but also as a means of establishing the growth of microcrystalline metal particles. For many years the view was held that in the formation of a metal there was a steady and systematic addition of metal atoms from one to infinity, and from the beginning the close-packed metallic geometry (hexagonal or cubic) was predetermined. These views have been questioned, particularly by Hoare and Pal (*13*), who have provided evidence for stable pentagonal symmetries.

Another subsidiary class of clusters is often referred to as "naked." This class, which includes ions such as Bi_5^{3+}, Sn_5^{3-}, Ge_9^{4-} and Sn_9^{4-}, is largely unexplored, but clearly its chemistry will be dominated by large ion–ion or ion–solvent interactions. Such clusters will not be considered in this account.

2. "Conventional Clusters." These may be represented as M_mL_n in

which the metallic cluster, M_m, is associated with *n* ligands L. These may be further subdivided into:

a. Low-valent clusters: In these, the metal ions are in the zero or a low oxidation state and are commonly found with π-acid ligands such as carbon monoxide, tertiary phosphines, or isocyanides. These are by far the most widely occurring and numerous of the cluster compounds. Even so, values of *m* are small. There are large numbers of cluster compounds for $m = 3$ or 4, but relatively few for $m \geq 5$. It is in this class that some of the most elegant structural studies have been made, notably by Chini (*14*), who has prepared carbonyl cluster anions of rhodium containing Rh_{13}, Rh_{14}, and Rh_{15} units which change progressively from hexagonal close-packed to face-centered cubic geometries.

b. High-valent clusters: In these, L is a ligand such as Cl^- or O^{2-}. The so-called naked clusters supported in oxide-containing matrices are almost certainly of this type. Apart from a number of instances, e.g., the work on some transition-metal halide clusters (*15*), these compounds have not been systematically examined. Of importance is the recent trend toward the study of alkyl clusters, e.g., $Re_3Me_6Cl_3$ (*16*), which also fall within this class.

We may anticipate a somewhat different chemistry for groups (a) and (b). In general, compounds of group (b) are found for the earlier transition metals—a region where strong metal–carbon, –nitrogen, or –oxygen multiple bonds are commonly observed—and those of group (a) are observed for the later members of the transition series. The organometallic chemistry of the earlier transition elements also tends to differ from those of the Group VIII metals, for example.

Recent $X\alpha$ calculations have led to the conclusion that even for relatively small clusters ($m = 6$) there is a remarkable similarity in the electronic structure of these and those of bulk metals. In essence, "band theory" may also apply to small aggregates of metal atoms. It is clear that clusters, microcrystallites, and macroscopic crystals may have a common arrangement of atoms in the faces, for example M_3-triangular, M_4-butterfly, or M_4-square, which they present to an incoming substrate. How the reactivity of these faces is modified as the number of atoms within the aggregate increases remains a subject for further study. It is conceivable that, by studying the mode of behavior of small molecules such as CO, H_2, alkenes, and alkynes with metal clusters having different arrangements of metal atoms, information leading to a better understanding of surface phenomena of metals will be made available about:

a. The preferential bonding modes adopted by these molecules with triangular, butterfly, or square metal-atom arrangements on the surface of a metal and their consequent chemistries.

b. The energies of interconversion of one bonding mode to another. For example, it is known that in metal carbonyl clusters the CO ligand may bond in at least six different ways (see Section III,B). These modes almost certainly parallel those considered in the interaction of carbon monoxide with metal surfaces, and clearly some idea of the energy necessary to convert one mode to another will be of importance.

c. Whether or not the cluster geometry is affected by the reacting species. For many years there was the implicit assumption that the geometry of the metal cluster unit was insensitive to reactions on its surface. This is not necessarily true, even for reactions with microcrystallites and macroscopic crystals.

d. The chemistry, catalytic and otherwise, of the metal clusters and the possible correlation with that occurring on metal surfaces.

C. CLUSTER GEOMETRIES M_m ($m = 3-6$)

Many cluster geometries have now been established. They range from the simple triangle to the more complicated 1:5:1:5:1:5:1 arrangement of metals $[Pt_{19}(CO)_{24}]^{4-}$ (*17*). Although at present most cluster geometries approximate to a close-packed metal arrangement, an increasing number do not. However, all contain triangulated or square faces, supporting the view that only three of the available nine metal orbitals are utilized in the formation of cluster bonds (see below). The use of only three orbitals severely limits the connectivity of metal atoms in cage polyhedra; the use of additional orbitals would allow a much wider range of cluster geometries.

Experimental bond enthalpy determinations (*18*) tend to support the view that M–M bond energies are comparatively small and that the stronger M–ligand interactions will be important in any consideration of cluster geometries. Ligand–ligand interactions, although making a much smaller contribution to the overall energy, have been shown to be of importance in determining the ligand geometry about the central metal polyhedron; and it is important to recognize that the sum of the M–CO bond enthalpies, for example, is not especially sensitive to the ligand arrangements (within reason) about the M_m cluster (see Section II,G).

The majority of clusters M_m represent fragments of a close-packed array of metal atoms: hcp or ccp. The triangle, tetrahedron, square-based pyramid, trigonal bipyramid, edge-bridged tetrahedron, and octahedron, all relatively common cluster geometries, are fragments of hcp. However, it is important to recognize, *first,* that these geometries are idealized arrangements and in reality distortions are commonly observed; and *second,* that these polyhedra are fragments of the body-centered cuboctahedron (smallest complete fragment of hcp), which is a consequence of geometry and not necessarily of chemical significance. The bicapped tetrahedron, which is not a fragment of hcp, is a close-packed arrangement of metal atoms. It is an octahedron with C_{2v} symmetry rather than the more commonly observed O_h symmetry. The trigonal prism, a geometry observed for both rhodium and platinum clusters, is neither close-packed nor a fragment of hcp.

1. *Three-Atom Clusters*

A large number of triangular clusters are known, many of which have been structurally characterized by single-crystal X-ray analysis. In most, the three metal atoms are arranged to form an equilateral triangle, but there are exceptions. Triiron dodecacarbonyl, $Fe_3(CO)_{12}$, with one Fe–Fe bond distance of 2.56 Å and two of 2.68 Å, is a well-known example (*19*). Analysis of the bonding in an M_3 cluster shows that, according to the E.A.N. (see Section II,D,1) rule, 48 valence electrons are required to form a stable triangular cluster. Most three-atom clusters have this number of electrons, leading to the view that they contain three M–M single bonds (two-electron/two-center). It also follows from the E.A.N. rule that all triangulated clusters which contain fewer than 48 electrons will have multiple bonds. The complex $H_2Os_3(CO)_{10}$, with only 46 electrons, has two Os–Os distances of 2.88 Å and a shorter Os–Os distance of 2.60 Å. This shorter distance is considered to correspond to an Os–Os double bond, thereby preserving the 18-electron rule. Evidence that this cluster is unsaturated is provided by its chemical reactivity. It readily combines with an additional electron-pair donor, such as CO, to produce the 48-electron system $H_2Os_3(CO)_{11}$ (*20*), and in this molecule all three Os–Os distances approach a "single-bond" value of 2.88 Å.

Other electron-poor clusters include the 44-electron $Pt_3(CO)_3(PPh_3)_4$ and the 42-electron species $Pd_3(CO)_3(PPh_3)_3$ and $[Re_3Cl_{12}]^{3-}$. For the 44-electron system, the 18-electron rule predicts two double bonds within the M_3 triangle and for the 42-electron complexes, three double bonds. The structures of the platinum and palladium complexes are unknown, but the Re–Re distances of 2.47–2.49 Å in the anion $[Re_3Cl_{12}]^{3-}$ are regarded (*20*) as short and consistent with a formal bond order of two.

Thus, as the electron count in M_3 clusters decreases from 48 to 42, an increase in the degree of unsaturation is anticipated. This effect may be illustrated as

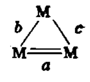
In the past, this tendency to produce stable M_3 clusters with fewer than 48 electrons has been associated with steric interactions between the bound ligands. Certainly the complexes $Pt_3(CO)_3(PPh_3)_4$, $Pd_3(CO)_3(PPh_3)_3$, and $Pd_3(CN\text{-}t\text{-}Bu)_6$ contain bulky ligands, but it is worth noting that the compound $Os_3(CO)_9(PPh_3)_3$, in which three osmium atoms are in association with nine CO and three PPh_3, is perfectly stable. Clearly, arguments based solely on steric interactions are not satisfactory. The inability of the palladium and platinum systems to achieve the 48-electron state is probably associated with the relatively high s(d) → p promotion energy expected for these metals (see Section II,A), and they do not obey the 18-electron rule.

Certainly, steric factors may control the interconversion

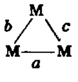
$$H_2Os_3(CO)_{10} \underset{-CO}{\overset{+CO}{\rightleftharpoons}} H_2Os_3(CO)_{11}$$

The arrangement of 12 ligands around the Os_3 unit in $H_2Os_3(CO)_{10}$ corresponds to the favorable icosahedron. The packing of 13 ligands around the same Os_3 unit necessarily imposes greater ligand–ligand interactions, leading to a less stable arrangement (see Section II,G).

In the structure of $H_2Os_3(CO)_{12}$, which contains 50 electrons, two Os–Os distances approximate to 2.8 Å, but the third distance is long (~3.0 Å) and said to correspond (*21*) to a nonbonding value. Thus, as electron pairs are added to or subtracted from the 48-electron system, bond opening or bond contraction occurs, and a progression from a linear to a highly unsaturated triangular arrangement is observed.



$H_2Os_3(CO)_{10}$
triangular
$b = c > a$



$H_2Os_3(CO)_{11}$
triangular
$a = b = c$

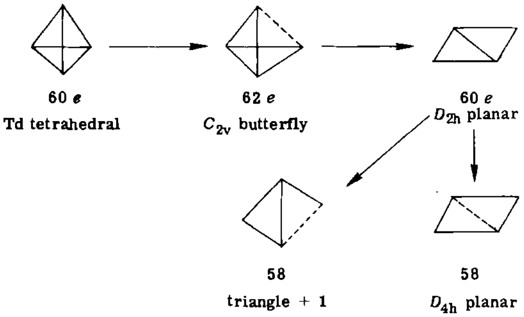
M—M—M

$H_2Os_3(CO)_{12}$
linear

2. *Four-Atom Clusters*

According to the E.A.N. rule, all clusters of four atoms possessing the tetrahedral geometry require a total of 60 valence electrons. A tetrahedron with *six* two-electron/two-center bonds corresponding to the six tetrahedral edges may then be constructed. A number of such cluster compounds are known, the best known examples being the binary carbonyls $M_4(CO)_{12}$ (M = Co, Rh or Ir). Again, it follows from the E.A.N. rule that M_4 clusters possessing fewer than 60 electrons will possess multiple bonds. Examples of both 58- and 56-electron species are known. The compound $H_4Re_4(CO)_{12}$, with 56 electrons, is known to possess a tetrahedral geometry. All Re–Re distances are equal, and, unlike $H_2Os_3(CO)_{10}$, double bonds may not be associated with any particular polyhedral edges. In order to explain this result, the concept of resonating structures has been invoked.

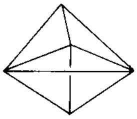
A better explanation is that the bonding in the complex corresponds to four face-centered bonds (see below). Compounds with more than 60 electrons are also found. The dianion, $[Re_4(CO)_{12}]^{2-}$, a 62-electron system, has the D_{2h} butterfly geometry. The carboxylato derivative, $Pt_4(OCCH_3)_8$, with a total of 64 electrons, is, as expected, square-planar. Thus, the following sequence of geometries is available.



There are a number of exceptions to the E.A.N. rule within this group. The 60-electron systems $Co_4(CO)_{10}C_2R_2$ and $Ru_4(CO)_{12}C_2R_2$ have the C_{2v} butterfly geometry, and $Pt_4(CO)_5(PPhMe_2)_4$ is an example of 58-electron cluster which also has the butterfly geometry, reflecting the limited number of valence orbitals available for cluster bonding. At present, unlike the triangular systems discussed above, there is no coherent series of compounds based on the same metal which exhibits the systematic change from T_d tetrahedral to D_{4h} square-planar.

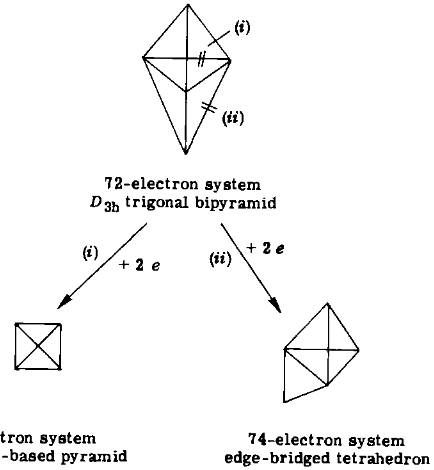
3. *Five-Atom Clusters*

For five-metal clusters, two "parent" polyhedra may be considered, viz., the trigonal bipyramid and square-based pyramid.



In monometal coordination chemistry, there is little energy difference between these two geometries and, as a consequence, they are usually highly fluxional. In cluster chemistry, according to the E.A.N. rule, there is a clear and precise difference. For a trigonal-bipyramidal core of metal atoms with nine edge bonds, a total of 72 electrons is required. The binary osmium carbonyl, $Os_5(CO)_{16}$, which is a 72-electron system, has such an arrangement. On the other hand, the C_{4v} square-pyramidal geometry, which has eight polyhedral edges, requires 74 electrons. There is no binary system which has this structure. However, the carbido clusters $Fe_5(CO)_{15}C$, $Ru_5(CO)_{15}C$, and $Os_5(CO)_{15}C$ do have a square-pyramidal arrangement of metals with the carbon atom, which provides four electrons, sitting just beneath the equatorial square plane.

Other geometries are possible. One, the edge-bridge tetrahedron, is found for the dihydride $H_2Os_5(CO)_{16}$ (also a 74-electron system), and another based on two fused, orthogonal triangles is observed with $Pt_5(CO)_6(PPh_3)_4$, a 70-electron complex, which cannot be rationalized by the E.A.N. rule. The effect of adding or removing electron pairs to these systems may be seen from the following scheme.



It is important to note that in none of the geometric forms are the five metal atoms equivalent. It follows that M–M distances will vary within a given cluster and may reflect geometric or symmetry constraints as well as simple electronic effects.

4. *Six-Atom Clusters*

The O_h octahedron is commonly observed for six-metal clusters, but many octahedral clusters have 86 valence electrons rather than the expected (E.A.N. rule) 84. However, not all 86-electron systems possess the O_h octahedral geometry. The dihydride $H_2Os_6(CO)_{18}$ has a monocapped square-pyramidal arrangement, and the platinum anion $[Pt_6(CO)_{12}]^{2-}$ has a trigonal-prismatic arrangement of metal atoms. The hexanuclear osmium cluster, $Os_6(CO)_{18}$ (*21b*), which does contain 84 electrons, adopts a monocapped trigonal-bipyramidal shape. Clearly, it is within this group that the first major breakdown of the E.A.N. rule occurs, and it is here, therefore, that we should more carefully examine this rule and its application and the other methods available for the rationalization of cluster bonding and geometries.

D. BONDING THEORIES

Theories of bonding within metal cluster compounds remain primitive. Attempts to rationalize the bonding interactions within discrete groups of transition-metal ions are necessarily of a qualitative nature because of the complexity of the problem. A number of empirical rules have been applied with varying degrees of success. One of the more successful treatments has been the skeletal electron pair theory developed independently by Wade (*22*) and Mingos (*23*). A limited number of semiempirical LCAO–MO treatments have also been applied to specific systems by Mingos (*24*) and Fenske (*25*). Bonding interactions in bare metal clusters have also been examined, since these may serve as models for surface and bulk metal phenomena. Within this group of studies are numerous LCAO–MO calculations (26–28) and the more sophisticated Xα treatment (*29*).

Here we compare the applications and the usefulness of the two simpler approaches (E.A.N. rule and S.E.C.)

1. *The Effective Atomic Number Rule*

A large proportion of mononuclear transition-metal complexes involving π-acceptor ligands can be considered to possess the 18 electrons of an inert-gas shell configuration. Justification for this can readily be seen in the energy-level diagrams obtained for the Group VI octahedral metal hexacarbonyls. The nine metal valence orbitals form nine metal–ligand bonding orbitals which house the 18 electrons of an inert-gas configuration. It is also apparent that carbonyls of other geometries, e.g., tetrahedral, will also be stable with an inert-gas shell configuration. As applied to metal carbonyl clusters, the electron counts are considered to be the sum of the metal valence electrons, those from the ligands and any ionic charge, and the remainder is provided by two-center/two-electron metal–metal bonds. Although this rule can be applied to the individual atoms in a cluster, it is more satisfactory to consider the cluster as a whole. For two and three metal atoms, the rule gives valuable information about the number of single bonds and shortened, formally multiple, bonds within the metal framework (see Section II,C). For four and five metal atoms, the fit is only moderately good. Three types of complex, at least, form exceptions to the rule: $Co_4(CO)_{10}RCCR$, $H_4Re_4(CO)_{12}$, and $[Ni_5(CO)_{12}]^{2-}$. Two others, $Fe_5(CO)_{15}C$ and $H_2Os_5(CO)_{16}$, both fit, each having the required number of eight nearest-neighbor links, but possess different structures. There is little correspondence between the predicted number of nearest-neighbor links and the number found in clusters of six metal atoms or more.

This breakdown is not surprising. Translating this scheme back into bonding terms shows that stringent adherence to an arbitrarily determined number of occupied orbitals is required. In any cluster of N metal atoms, there are $9N$ metal valence orbitals for bonding to both ligands and metals. If the total number of edges of the metal polyhedron is E, then this rule requires that $2E$ metal valence orbitals have combined to give E bonding and E antibonding metal–metal orbitals. The total number of occupied orbitals in the cluster is thus $(9N - E)$. Of this number, E are metal–metal bonding and $(9N - 2E)$ are metal–ligand bonding. Three examples illustrate the consequences of this breakdown.

a. $Os_3(CO)_{12}$: $N = 3$, $E = 3$. Total number of metal orbitals, $9N = 27$. Total number of occupied orbitals, $9N - E = 24$. $E = 3$ is the number of M–M bonding orbitals; number of M–L bonding orbitals, $9N - 2E = 21$. The three metals are the same, and of the nine metal orbitals, seven are formally used for bonding to the ligands and two to the other metals.

b. $Ir_4(CO)_{12}$: $N = 4, E = 6$. Total number of metal orbitals, 36. Total number of occupied orbitals, 30. Six are M–M bonding and 24 are M–L bonding. Thus, for each metal, six orbitals are used for bonding to the ligands and three to the other metals.

c. $[Os_6(CO)_{18}]^{n-}$ ($n = 0$ or 2): For each, the total number of metal orbitals is 54. Total number of occupied orbitals would be $9N - E = 42$; 12 of these would be M–M bonding and 30 M–L bonding. So, for each metal, five orbitals are metal–ligand bonding and four metal–metal bonding.

It can be seen that application of the 18-electron rule to clusters necessitates this arbitrary assignment of the number of orbitals of a particular predominant character. The number of orbitals per metal used for cluster skeletal bonding is a consequence of N and E. It varies from two for the $M(CO)_4$ unit in $Os_3(CO)_{12}$ to three for an $M(CO)_3$ unit in $Ir_4(CO)_{12}$. Since these two metal moieties differ, this variation seems reasonable. However, the distribution for an $M(CO)_3$ unit varies with cluster shape as in $Ir_4(CO)_{12}$ and $[Os_6(CO)_{18}]^{n-}$.

2. *Skeletal Electron Counting* (22, 23)

Such distributions of orbitals are kept fixed within this counting scheme. In a transition-metal cluster, the nine orbitals of the $M(CO)_n$ fragments are arbitrarily assigned as six low-lying, primarily metal–ligand bonding orbitals and three higher lying orbitals suitable for metal–metal bonding. It is apparent that this distribution coincides with that obtained for the $M(CO)_3$ group in $Ir_4(CO)_{12}$ above. These three higher lying orbitals of the fragment are then allowed to mix and form skeletal molecular orbitals. The number of occupied orbitals is obtained by a comparison with the appropriate borane polyhedron. In this scheme, the structure is determined by N, the number of skeletal atoms, and S, the total number of skeletal electron pairs. Closo structures are predicted when $S = 1$. For other relationships of S and N, it is still S which determines the basic skeletal polyhedron. As recently extended, the structure types for various S and N values are:

$S = N + 4$	hypho structure (closed polyhedron – three vertices)
$S = N + 3$	arachno structure (closed polyhedron – two vertices)
$S = N + 2$	nido structure (closed polyhedron – one vertex)
$S = N + 1$	closo structure (closed polyhedron)
$S = N$	closed polyhedron with one face capped
$S = N - 1$	closed polyhedron with two faces capped

Agreement is poor for small clusters, but this does not present a fair test—the smallest structure type considered is that derived from a trigonal bipyramid having an S value of 6. However, the predictive power for clusters of four to six atoms, for which the rules perform best, is only moderate. Even in that region, correspondence with the actual structures found is only as good as that for the E.A.N. rule, which was then considered to be breaking down. Evidently, a more informative approach would be advantageous.

3. *Metal Carbonyl Fragments within Clusters*

Elian and Hoffmann (*30*) have recently carried out extended Hückel calculations on metal carbonyl fragments, which allow one to determine the bonding properties of these moieties in the frontier region. As already noted, in terms of the number, type, and occupancy of the frontier orbitals, $M(CO)_n$ moieties are exactly analogous to the more familiar BH_m and CH_m species. So, as a first approximation, it is more appropriate to consider these orbital properties of the various fragments rather than arbitrarily to assign a number of orbitals for cluster bonding, as in the skeletal electron counting approach.

It is also apparent that, rather than merely assign a two-center/two-electron bond to each edge in the skeleton of a cluster, one should, again as a first approximation, allow these fragment frontier orbitals to mix and form skeletal molecular orbitals. In the most simple example, two $Mn(CO)_5$ units each provide one singly occupied σ-type fragment orbital. These interact in the dimer, the bonding orbital, of course, being occupied.

Since $M(CO)_3$ and BH units are isolobal, each with three fragment orbitals, it is obvious that the skeletal electron counting scheme is most likely to apply to structures solely involving $M(CO)_3$ units. Indeed, this is so: $Ir_4(CO)_{12}$ (nido trigonal bipyramid), $Os_5(CO)_{15}^{2-}$ (trigonal bipyramid), $Os_6(CO)_{18}$ (capped trigonal bipyramid), $Os_6(CO)_{18}^{2-}$ (octahedron), and $Os_7(CO)_{21}$ (capped octahedron) all comply. Similarly, the effective atomic number rule is also likely to apply when the orbital assignments it imposes correspond to those of the particular fragment and cluster skeleton. This occurs for $Os_3(CO)_{12}$ (each metal using two orbitals for skeletal bonding, and the number of skeletal bonding orbitals equals the number of edges) and $Ir_4(CO)_{12}$. Other agreements, such as for $Os_6(CO)_{18}$, which call for differing assignments can be regarded as fortuitous.

4. *Idealized Polyhedral Structures*

Wade's electron-counting procedures (*22*) start from a closed polyhedron and require that neither removing a vertex from this polyhedron nor capping a face will alter the number of skeletal bonding orbitals. This capping principle has been demonstrated to be general (*31*). For many polyhedra, up to seven or eight vertices, this can be traced to the molecular-orbital properties of the basic *polygon* within a structure. Other structures are derived by sequentially capping the faces of the original polygon and also the faces derived in earlier capping processes. It is also general that this procedure also maintains the number of accessible bonding and nonbonding skeletal orbitals. For example, a triangular B_3H_3 arrangement generates three in-plane skeletal bonding orbitals (a'_1 and e'), an out-of-plane π-bonding orbital (a''_2), and two low-lying out-of-plane π^* (e'') orbitals, giving a total of six accessible orbitals. Occupation of the whole six would still give a net M–M bond order of 1. The other three skeletal orbitals—in-plane and antibonding in character (e' and a'_2)—are so high in energy that they must be unoccupied in any stable complex. Interaction of these orbitals with the three of a face-capping BH group serves only to lower the energy of these six occupiable orbitals, but not to create any new bonding ones. One can follow similar arguments for the square and pentagon. So there are families of structures which possess the same number of skeletal bonding orbitals as is defined by the basic polygon. In addition, for $(B_6H_6)^{n-}$ units at least, the structure which is most stable out of six studied is that derived by this approach. Thus, for S values of 6, 7, and 8, the most stable calculated form was the capped trigonal bipyramid, octahedron, and pentagonal pyramid, respectively. When S equaled 9, the trigonal prism was preferred. For larger borane units, the picture was less defined.

Comparatively few clusters are idealized polyhedra. Whenever the number of ligands is not a multiple of the number of vertices, symmetry must be reduced. Addition of extra ligands does not create extra bonding orbitals. Instead, bonding to additional hydrogen atoms is accommodated in B_5 and B_6 structures by the skeletal orbitals of the pure polyhedron. So these extra atoms do not affect the count of skeletal bonding orbitals. However, the addition of these atoms may alter the stability balance between polyhedra, particularly in both B_5 and B_6 systems, and extra bridging hydride ligands show a marked preference for edge-bridging positions on a square, rather than a triangular face. For example, octahedral $(B_6H_6)^{2-}$ was calculated to be 2 eV more stable than the capped square-pyramidal form (both these structures are derived from the square: the first by capping two square faces, and the second by capping one square and one triangular one). However, this gap is narrowed to less than 0.4 eV in B_6H_8 structures having two edge-bridges. So it is apparent that the presence of extra ligands could have an influence on the preferred polyhedron of a cluster compound.

5. *Application to Carbonyl Clusters*

Evidently one can obtain an approximate idea of the bonding within a carbonyl cluster skeleton by comparison to an appropriate isolobal analog. Some species involving bridging carbonyl groups and other bridging ligands, e.g., acetylenes, cannot satisfactorily be treated in this way. In those cases there seems inevitably to be considerable mixing between ligand–metal and metal–metal orbitals, so the factorization between these two types employed will not be applicable. Many structures can be accommodated, and one can obtain some more detailed rationalizations about the relative bond lengths within clusters. The short metal–metal bonds in $H_2Re_2(CO)_8$ and $H_2Os_3(CO)_{10}$ can easily be explained. As another example, the distortions within the $Os_5(CO)_{16}$ structure which involve relatively long bonds to the $M(CO)_4$ unit can be related to that unit having two as opposed to three skeletal fragment orbitals, giving rise to one less bonding orbital between it and the other two groups in the central plane.

6. *Deviations of Carbonyl Clusters from Main-Group Analogs*

Even though qualitative bonding descriptions of metal atom clusters up to six or seven atoms can be derived and in some cases correlated with structural detail, it is clear that most structures observed for higher clusters cannot be treated thus. Nor do the structures observed correlate with those observed for borane derivatives with the same number of vertices. Much of borane chemistry is dominated by the tendency to form structures derived from the icosahedron found in elemental boron. However, elemental transition metals possess either a close-packed or body-centered cubic arrangement. In this connection, one can find the vast majority of metal polyhedra in carbonyl cluster compounds within close-packed geometries, particularly hexagonal close-packing.

There are some exceptions to this observation. Many of these are carbides and this is only to be expected. In both carbonyl cluster carbides and transition-metal carbides, trigonal-prismatic geometries around carbon atoms are found. For example, this arrangement is found in cementite, Fe_3C, in which the metal atoms have a distorted hcp arrangement, some being 12- and some 11-coordinate. The other exceptions are the capped trigonal-bipyramidal structure of $Os_6(CO)_{18}$ and trigonal-prismatic arrangements seen within the $[Pt_3(CO)_6]_n^{2-}$ ($n = 2$–6) ions. Adherence to a close-packed build-up of metal atoms is not in line with prediction (see above). Using various theoretical models for the clustering of atoms, Hoare and Pal (*13*) constructed Lennard-Jones potential-energy surfaces for metal clusters of up to 60 atoms. Their striking result was the stability of the non-close-packed pentagonal and polytetrahedral growth patterns. For three to nine atoms the favored structures were the triangle, tetrahedron, trigonal bipyramid, octahedron, pentagonal bipyramid, capped pentagonal bipyramid, and adjacently bicapped pentagonal bipyramid. Molecular-orbital calculations on Ti, Cr, Fe, and Ni clusters of up to six metal atoms have been used to give optimized structures (*21*). Again, non-close-packed forms were sometimes predicted, but giving more open structures than found either in boranes, metal–carbonyl clusters or predicted for the Lennard-Jones potential. For example, the pentagon was found to be the stable form for both Cr_5 and Ni_5, the trigonal prism for Cr_6 and Fe_6, and the hexagon for Ni_6. Apparently, metal–carbonyl clusters may be more bulk metal-like than small assemblies of metal atoms.

The adherence to close-packed structural arrangements lends support to the idea that these compounds can be used as models for metal surface chemistry—with respect to chemisorbed species and their mobility and reactions of substrates on these surfaces. It also indicates a marked deviation from the behavior of boranes and their derivatives. Structures based upon some polyhedra favored by boron, such as the pentagonal bipyramid, triangulated dodecahedron, and especially the icosahedron, are absent so far in metal–carbonyl cluster chemistry. In this connection, it has been mentioned that $[M(CO)_3]_m^{n-}$ compounds should be the closest analogs to $[BH]_m^{n-}$. On skeletal electron counting and isolobal grounds, the cluster $Os_7(CO)_{21}$ is expected to possess the pentagonal bipyramidal structure of $(B_7H_7)^{2-}$ (*24*). Instead, it adopts the capped octahedral fragment of a close-packed structure. With larger clusters, this driving force toward bulk metal structures becomes more obvious, with $[H_3Rh_{13}(CO)_{24}]^{2-}$ adopting the basic 13-atom unit of an hcp arrangement.

What may well be behind this deviation from borane structure classes is the breakdown of the frontier approximation used to obtain the fragment orbitals. There is a higher density of eigenvalues in the frontier region of a metal–carbonyl moiety than for the corresponding borane fragment, a situation which could give rise to a deviation of the total number of bonding orbitals of the cluster from that of the first row analog. It is also apparent that the stability of various alternative polyhedral arrangements for a cluster will depend on quantitative factors, not merely qualitative ones, which will be unique to any particular metal. Calculated energy differences between alternative structures for $[B_nH_n]^{2-}$ anions are quite small and it will, in all probability, be likely that a change to a transition metal could alter this balance. The structural differences between the ruthenium and osmium clusters of formulas $[M_6(CO)_{18}]^{2-}$, $[HM_6(CO)_{18}]^{-}$, and $H_2M_6(CO)_{18}$, and between the nickel and platinum $[M_6(CO)_{12}]^{2-}$ and $[M_9(CO)_{18}]^{2-}$ (*17*) systems are likely to require rigorous quantitative treatments and probably demonstrate that a failsafe qualitative systemization of metal cluster might be unattainable. Nevertheless, a satisfactory qualitative scheme would be of some benefit.

Such a scheme would also have to take into account the important structural implications of having transition metals entirely surrounded by carbonyl ligands which seem to have a considerable bonding interaction between them. Any consideration of molecular structure must consider not only the maximization of metal–ligand and metal–metal interactions but also ligand–ligand interactions. The structures of the two anions $[Fe_4(CO)_{13}]^{2-}$ and $[HFe_4(CO)_{13}]^{-}$ (see Section III,G) demonstrate the importance of these interactions. In the latter anion, the addition of the extra ligand—a hydrogen at that—causes the metal polyhedron to open from a tetrahedron to a butterfly.

In conclusion, we would stress that for any method of accounting for the polyhedron adopted by polymetal units, metal–metal, metal–ligand, and ligand–ligand interactions must be considered. The E.A.N. rule and Wade's rules are concerned only with metal–metal and metal–ligand interactions. An overall treatment must combine the following factors: (*i*) a satisfactory skeletal bonding treatment, and (*ii*) a provision for a good, "nonrattling" fit of the M polyhedron within the L polyhedron (Section II,G).

E. METAL–METAL BOND DISTANCES AND BOND ORDERS

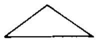
Here, as in other branches of inorganic chemistry, interatomic distances show a considerable variation; and, although some correlation with bond order is possible, attempts to do so should be regarded with caution.For metals with close-packed structures, the coordination number of any atom is 12 for cubic or hexagonal structures, and 14 (8 plus 6 more neighbors at about 15% further away) for body-centered cubic structures. In general, this number exceeds the number of electrons per atom available for metal–metal bond formation and precludes the formation of localized, two-electron bonds between metal atoms. Bond orders of less than 1 are therefore commonly recorded. For metal clusters, it is necessary to consider the variety of ways in which valence electrons may be utilized in chemical bonding within the M_m

cluster units in order to more fully appreciate the problems encountered with the concept of bond order when applied to these systems (Section II,D). Clusters are known, e.g., the triangle and the tetrahedron, in which there are sufficient electrons to allow polyhedral edge-bonds with a supposed bond order of 1, a situation different from that within the bulk metal. Bond orders of 1 and 2 are also recorded (Section II,C).

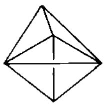
Information about internuclear distances in organic compounds has led to the view that the *effective* radius of an atom varies directly with bond order. This is understandable for elements like carbon, with a limited range of hybridized states, but less so for metallic (cluster) systems. The problem is threefold:

1. It is not possible to establish directly the value of the M–M distance corresponding to bond order of 1. Methods so easily applied to organic systems cannot be so readily applied here. First, the metallic radius for 12-coordinate metal is an average value, and second, as mentioned, the M–M distance (average) established for close-packed metals generally corresponds to a bond-order value of less than 1. At best only, the distance taken to correspond to a bond order of 1 is a crude approximation. Clearly, such arguments are enforced in any attempt to establish which correspond to bond orders of 2 or more.

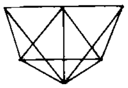
2. Cluster fragments, e.g., $M(CO)_3$, can display a variety of bonding capabilities even within the same molecule. This is the case in the structures of the binary carbonyls of osmium. The simplest cluster, illustrated in (a), is $Os_3(CO)_{12}$. This consists of an equilateral triangle formed by three $Os(CO)_4$ units. In (b) is shown $Os_5(CO)_{16}$, which has a distorted trigonal-bipyramidal structure with four $Os(CO)_8$ units and one $Os(CO)_4$ unit. Of the four $Os(CO)_3$ units, two have a connectivity of 4 and two a connectivity of 3. The bicapped tetrahedron depicted in (c) is found for $Os_6(CO)_{18}$. Six $Os(CO)_3$ units are arranged so that two $Os(CO)_3$ units have a connectivity of 3, two others a connectivity of 4, and the remaining two a connectivity of 5. Thus the carbonyls $Os_3(CO)_{12}$, $Os_5(CO)_{16}$, and $Os_6(CO)_{18}$ may be regarded as being built up from the following units:



(a)

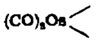


(b)

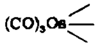


(c)

(A)



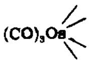
"5-coordinate"



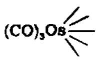
"6-coordinate"

(B)

(C)



"7-coordinate"



"8-coordinate"

(D)

In a formal (E.A.N. rule) sense, the Os–Os bond order in each of the three clusters corresponds to 1, and yet it is clear that a variety of different Os–Os bond types exist since each of the different metal centers (A) → (D) will utilize a different basis set of hybrid (or frontier) orbitals.

3. The ligand type and ligand-field symmetry impose constraints on M–M distances. Strongly electronegative ligands such as F^- or Cl^- will lead to metal-orbital contraction and consequently shorter M–M bonds. Softer ligands such as CO or PR_3 will have the opposite effect, leading to orbital expansion and longer M–M distances. Metal–metal distances will also be affected by ligand–ligand interactions (repulsive and attractive). The so-called "long" Mn–Mn distance in $Mn_2(CO)_{10}$ may be regarded as the consequence of CO–CO interactions (see Section II,G), just as the "normal" Co–Co distance of 2.5 Å is a consequence of the less demanding arrangement of the eight CO ligands in $Co_2(CO)_8$ (see Sections II,D and II,F).

The effect of ligand-field symmetries is less easily understood. In $Fe_3(CO)_{12}$, two Fe–Fe distances of 2.56 Å and 2.68 Å are observed. It may be argued that these distances reflect the packing of a triangle within the icosahedron, each polyhedron undergoing distortion until a common C_{2v} symmetry is reached.

In summary, (1) metal–metal distances in metal carbonyl clusters $\geq$ in bulk metal; and (2) metal–metal distances in metal halide clusters $\leq$ in bulk metal. Possible explanations of these effects are: (*i*) Electronegative ligands, such as halide ion, cause metal-orbital contraction and hence shorter bonds. (*ii*) "Soft" ligands, such as CO, increase the electron density on metal ions and hence bring about metal-orbital expansion and consequently longer bonds. (*iii*) Steric constraints are imposed by ligand–ligand interactions. The decrease in metal–metal distance in passing from $Mn_2(CO)_{10}$ (2.98 Å) to $Co_2(CO)_8$ (2.52 Å) reflects the diminishing CO–CO constraints in going from a ten- to an eight-CO-polyhedron. In general, the metal–metal distances in the binary carbonyls decrease on passing from the left- to the right-hand side of the transition series, corresponding to a decrease in the

CO/metal ratio as the number of available metal valence orbitals decreases.

The concept of bond order may have little real value; metal–metal distances supposedly corresponding to a bond order of 1 vary and bear little relation to those observed in the bulk metal.

F. THE STOICHIOMETRY OF BINARY CARBONYL CLUSTERS $M_m(CO)_n$

From the preceding discussions, it is clear that the stoichiometry of the binary carbonyl cluster is primarily determined by valence considerations. This aspect has been considered in some detail by Lauher (*32*) who, on the basis of an MO treatment, has shown convincingly that the value of n for a given value of m is dependent on the polyhedral arrangement of the m metal atoms. However, a secondary consideration must be the steric constraints imposed by the packing of CO ligands about the given M_m polyhedra. According to any theoretical treatment, it follows that since the number of nonbonding electrons for the metal ion M increases as we progress from the left-hand side to the right-hand side of the transition block, the number of orbital vacancies will show a corresponding decrease and the ratio $n:m$ will decrease. As this takes place, there will be a corresponding decrease in ligand–ligand nonbonding interactions. These ligand–ligand nonbonding interactions will also be sensitive to the size (or volume) of M_m and, for a given transition-metal triad, are expected to decrease on going from the first to the second to the third transition series. Such arguments lead to the following conclusions.

1. For a given value of m, the stability of binary carbonyl clusters will decrease in passing from the bottom right (Pt) to the upper left (V) of the transition block.
2. Since a CO ligand may be replaced by a dinegative charge, larger clusters to the left of the transition series (Mn, Tc, Re, Cr, Mo, W) will tend to be anionic.
3. Substitution of CO by larger ligands such as tertiary phosphines will tend to give either coordinatively unsaturated clusters or cluster fragmentation.

G. LIGAND–LIGAND INTERACTIONS

It has been noticed by a number of workers that the ligands L in cluster molecules M_mL_n occupy positions which define (to a fair approximation) the vertices of regular and semiregular polyhedra. In

$[Mo_6Cl_8]^{4+}$, the eight Cl^- ions define a cube, and in $[Nb_6Cl_{12}]^{n+}$ a cuboctahedron. In 1975 it was proposed (*33*) that the important factor governing the structures of the binary cluster molecules $M_m(CO)_n$ is the interaction between carbonyl groups. The *n* carbonyls form a polyhedron which represents the most favorable way of packing them in space, and the M_m unit then orients itself within this polyhedron (interstitial site) so as to maintain close contact between the metal atoms, M, and the surrounding CO ligands. This orientation may be deduced from a consideration of the sites available within the CO polyhedron.

Thus, in $Fe_3(CO)_{12}$ the carbonyls define an icosahedron—the *best* way of arranging 12 ligands in space—and the C_{2v}-bridged structure arises as a simple consequence of packing a triangle of iron atoms within this icosahedron. The carbonyl ligand was assigned an effective radius of 3.02 Å, and calculations were made on the basis of the close-packing of spheres to give the maximum size of a metal cluster that could be accommodated within a range of 12-vertex polyhedra. Thus, although the icosahedron is the most favorable way of packing 12 carbonyls, there is insufficient space inside it to accommodate the larger Ru_3 and Os_3 triangles. Hence, the molecules $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ possess the slightly less favorable anticuboctahedral packing of ligands. It follows that these two molecules have the all-terminal D_{3h} structure. A number of molecular structures may be explained by this method (Table I).

H. THE REACTIVITY OF METAL CLUSTERS

1. *Cluster Expansion*

The way in which cluster expansion occurs is not understood. One suggestion is that radical species such as $Fe(CO)_4$ (*triplet*) or $Co(CO)_4$ are produced and that attack of these radicals on substrates leads to polyhedral expansion:

$$\mathrm{Fe(CO)_5 \rightleftarrows \ddot{F}e(CO)_4 + CO}$$

$$\mathrm{Fe(CO)_5 + \ddot{F}e(CO)_4 \rightarrow Fe_2(CO)_9}$$

This mechanism bears a close relationship to the polymerization of polyhedral boranes. Certainly there is clear evidence for the formation of $\ddot{F}e(CO)_4$ from $Fe(CO)_5$. The production of $Fe_2(CO)_9$ from $Fe(CO)_5$ is catalyzed by light, but further polymerization of $Fe_2(CO)_9$ to $Fe_3CO)_{12}$ is not observed under these conditions. For the related osmium systems, there is some evidence for the formation of $Os_2(CO)_9$ from $Os(CO)_5$, but irradiation of $Os_3(CO)_{12}$ does not produce higher clusters although in the presence of molecules such as CO or C_2H_4(L) the compounds

TABLE I

POLYHEDRAL ARRANGEMENTS OF CO GROUPS FOR BINARY CARBONYLS $M_m(CO)_n$

	Carbonyl $M_m(CO)_n$	CO Polyhedron	Föppl notation
$m = 2, n = 8$	$Co_2(CO)_8$	Bicapped trigonal prism	3:2:3
$n = 9$	$Fe_2(CO)_9$	Tricapped trigonal prism	3:(3):3
$n = 10$	$Mn_2(CO)_{10}$	Bicapped square antiprism	1:4:(4):1
$m = 3, n = 12$	$Fe_3(CO)_{12}$	Icosahedron	1:5:(5):1
	$Ru_3(CO)_{12}$	Anticuboctahedron	3:6:3
	$Os_3(CO)_{12}$		
$m = 4$	$Co_4(CO)_{12}$	Icosahedron	1:5:(5):1
	$Rh_4(CO)_{12}$		
	$Ir_4(CO)_{12}$	Cuboctahedron	3:6:(3)
$m = 5$	$[Ni_5(CO)_{12}]^{2-}$	Cuboctahedron	3:6:(3)
$m = 6$	$[Ni_6(CO)_{12}]^{2-}$	Hexagonal antiprism	6:(6)
	$[Pt_6(CO)_{12}]^{2-}$	Hexagonal prism	6:6
$m = 4, n = 13$	$[Fe_4(CO)_{13}]^{2-}$	Capped icosahedron	1:3:(3):3:(3)
$n = 14$	$[Co_6(CO)_{14}]^{4-}$	Hexacapped cube	1:4:(4):4:1
$n = 15$	$[Co_6(CO)_{15}]^{2-}$		3:(3):3:(3):3
$n = 16$	$Os_5(CO)_{16}$	Tetracapped truncated tetrahedron	1:6:3:(3):3
	$Rh_6(CO)_{16}$		
	$Fe_6C(CO)_{16}^{2-}$		

$Os(CO)_4L$ are produced, indicating the formation of $Os(CO)_4$ as an intermediate. The suggestion, therefore, that cluster expansion is brought about by radical attack does not receive support from experimental observation, at least as far as the higher clusters ($m > 2$) are concerned.

As an alternative, it may be argued that, apart from the initial polymerization of monometal species to dimers, which almost certainly progresses according to the above scheme, aggregation occurs first by *cluster breakdown.*

An initial degradation step takes place via the ejection of a saturated metal fragment (18-electron), e.g., $M(CO)_5$ ($M =$ Fe, Ru, or Os) or $M(CO)_4$ ($M =$ Co, Rh, or Ir). Thus, $Fe_3(CO)_{12}$ is considered to undergo the *reversible* fragmentation

$$Fe_3(CO)_{12} \rightleftarrows \text{“}Fe_2(CO)_7\text{”} + Fe(CO)_5$$

and $Rh_4(CO)_{12}$

$$Rh_4(CO)_{12} \rightleftarrows \text{“}Rh_3(CO)_8\text{”} + Rh(CO)_4$$

Evidence for this proposal is difficult to obtain. However, $Fe_3(CO)_{12}$ is almost invariably contaminated with $Fe(CO)_5$, and there is mass-spectroscopic evidence to suggest that, in the gas phase at least, $Fe_3(CO)_{12}$ undergoes decomposition to produce $Fe(CO)_5$ and $Fe_2(CO)_7$.

On the assumption that this suggestion is correct, cluster formation may then be considered to occur by combination of the unsaturated fragments such as $Fe_2(CO)_7$ or $Os_2(CO)_7$. Thus, the polymerization of $Os_3(CO)_{12}$ to $Os_6(CO)_{18}$ may be viewed as follows:

$$Os_3(CO)_{12} \rightleftarrows \text{“}Os_2(CO)_7\text{”} + Os(CO)_5 \tag{1}$$

$$2\text{“}Os_2(CO)_7\text{”} \rightleftarrows Os_4(CO)_{14} \tag{2}$$

$$Os_4(CO)_{14} \rightleftarrows \text{“}Os_3(CO)_9\text{”} + Os(CO)_5 \tag{3}$$

$$2\text{“}Os_3(CO)_9\text{”} \rightarrow Os_6(CO)_{18} \tag{4}$$

$$\text{“}Os_2(CO)_7\text{”} + \text{“}Os_3(CO)_9\text{”} \rightarrow Os_5(CO)_{16} \tag{5}$$

and of $Rh_4(CO)_{12}$ to $Rh_6(CO)_{16}$ as

$$Rh_4(CO)_{12} \rightleftarrows \text{“}Rh_3(CO)_8\text{”} + Rh(CO)_4$$

$$2\text{“}Rh_3(CO)_8\text{”} \rightarrow Rh_6(CO)_{16}$$

These ideas are not restricted simply to binary carbonyls and may apply equally to all conventional cluster fragments. On hydrogenation, $Os_3(CO)_{12}$ reacts first to produce $H_2Os_3(CO)_{10}$ and then (at slightly higher temperatures) $H_4Os_4(CO)_{12}$. In this case, the polymerization step $H_2Os_3(CO)_{10} \rightarrow H_4Os_4(CO)_{12}$ may be viewed as

$$H_2Os_3(CO)_{10} \xrightarrow{H_2} H_4Os_3(CO)_{10} \rightarrow \text{“}H_2Os_2(CO)_6\text{”} + H_2Os(CO)_4$$

46*e* unsaturated system → 48*e* saturated system

$$\text{“}2H_2Os_2(CO)_6\text{”} \rightarrow H_4Os_4(CO)_{12}$$

In this case, the eliminated fragment is $H_2Os(CO)_4$.

Support for these proposals comes from several sources: *first,* the disproportionation reactions of mixed metal clusters such as $Rh_2Co_2(CO)_{12}$ or $Fe_2Ru(CO)_{12}$:

$$3Fe_2Ru(CO)_{12} \rightleftarrows 2Fe_3(CO)_{12} + Ru_3(CO)_{12}\ [+\text{ some }FeRu_2(CO)_{12}]$$

$$2Rh_2Co_2(CO)_{12} \rightleftarrows Co_4(CO)_{12} + Rh_4(CO)_{12}$$

A simple explanation of these observations may be made on the basis of the above proposal:

$$Fe_2Ru(CO)_{12} \rightleftarrows Fe_2(CO)_7 + Ru(CO)_5$$

$$Fe_2Ru(CO)_{12} \rightleftarrows FeRu(CO)_7 + Fe(CO)_5$$

$$Fe_2(CO)_7 + Fe(CO)_5 \rightleftarrows Fe_3(CO)_{12}$$

$$FeRu(CO)_7 + Ru(CO)_5 \rightleftarrows FeRu_2(CO)_{12}$$

$$FeRu_2(CO)_{12} \rightleftarrows Ru_2(CO)_7 + Fe(CO)_5$$

$$Ru_2(CO)_7 + Ru(CO)_5 \rightleftarrows Ru_3(CO)_{12}$$

and

$$\mathrm{Rh_2Co_2(CO)_{12} \rightleftarrows Rh_2Co(CO)_8 + Co(CO)_4}$$

$$\mathrm{Rh_2Co_2(CO)_{12} \rightleftarrows RhCo_2(CO)_8 + Rh(CO)_4}$$

$$\mathrm{Rh_2Co(CO)_8 + Rh(CO)_4 \rightleftarrows Rh_3Co(CO)_{12}}$$

$$\mathrm{RhCo_2(CO)_8 + Co(CO)_4 \rightleftarrows RhCo_3(CO)_{12}}$$

$$\mathrm{Rh_3Co(CO)_{12} \rightleftarrows Rh_3(CO)_8 + Co(CO)_4}$$

$$\mathrm{Rh_3(CO)_8 + Rh(CO)_4 \rightleftarrows Rh_4(CO)_{12}}$$

$$\mathrm{RhCo_3(CO)_{12} \rightleftarrows Co_3(CO)_8 + Rh(CO)_4}$$

$$\mathrm{Co_3(CO)_8 + Co(CO)_4 \rightleftarrows Co_4(CO)_{12}}$$

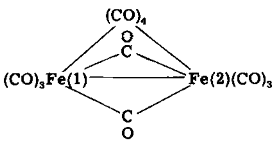
Second, the idea of the ejection of a saturated fragment is compatible with the established view of the bond enthalpies for metal–carbon monoxide > metal–metal. Thus the formation of M–CO bonds at the expense of M–M bonds is to be anticipated.

The formation of the saturated monometal fragments will depend upon the ratio of CO:M in the cluster and also, to a lesser extent, upon the arrangement of the carbonyl ligands about the central M_m cluster unit. Clearly, the higher the CO:M ratio, the greater the probability of ejecting the appropriate $M(CO)_n$ saturated unit. Consider the osmium series Os_m (m = 1–8):

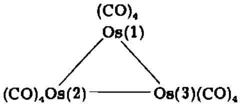
m	n	n/m	Compound
1	5	5	$Os(CO)_5$
2	9	4.5	$Os_2(CO)_9$
3	12	4	$Os_3(CO)_{12}$
4	14	4.5	$Os_4(CO)_{14}$
5	16	3.2	$Os_5(CO)_{16}$
6	18	3	$Os_6(CO)_{18}$
7	21	3	$Os_7(CO)_{21}$
8	23	2.875	$Os_8(CO)_{23}$

Since the ratio CO:Os falls from 4.5 to 2.88 on going from $Os_2(CO)_9$ to $Os_8(CO)_{23}$, we might anticipate a rise in *kinetic* stability across the same series, because the probability of finding five carbonyl ligands in association with an individual osmium atom decreases.

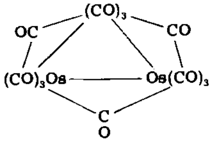
If we pursue this theme further, we can demonstrate that to some degree the tendency to eject $Os(CO)_5$ will depend upon the arrangement of CO ligands about the cluster Os_m. If for the moment we return to $Fe_3(CO)_{12}$, then from the structural analysis we can see that in the ground-state configuration we already have an arrangement of carbonyl groups such that Fe atoms 1 and 2 are each in association with five CO ligands (three terminal and two bridges):



This is not the case for $Os_3(CO)_{12}$, which contains only $Os(CO)_4$ fragments:



On the assumption that the bond enthalpies E_{M-M} and E_{M-CO} increase systematically down the triad Fe, Ru, and Os, it may be taken that the tendency to form $M(CO)_5$ remains *more or less* constant. Part of the ***kinetic stability*** will then be due to the availability of a bridged form of $Os_3(CO)_{12}$. This does not necessarily mean that the bridged form has to be of the same structure as $Fe_3(CO)_{12}$, but merely one in which there are five carbonyl groups in association with the osmium atom. Thus, an alternative might be

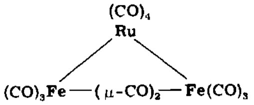


The energies of interconversion nonbridged ⇌ bridged normally fall within the range 20–80 kJ mol^{-1}, but for $Os_6(CO)_{18}$, for example, the migration of CO from osmium atom to osmium atom requires an energy in excess of 80 kJ mol^{-1}. In $Fe_3(CO)_{12}$, it has been estimated that the energy of such a process is <20 kJ mol^{-1}.

For cluster breakdown to occur, therefore, we must consider two stages. (*i*) The formation of an excited state geometry which contains CO bridges and must satisfy the criteria laid out above, i.e., there must be sufficient CO groups per metal atom within the cluster to produce a saturated unit. This will require an energy E_1. (*ii*) The ejection of the saturated unit, which will require an additional energy E_2.

Clearly, the term E_2 will dominate, but if we assume that this does not vary significantly from metal to metal (see above), then the important term will be E_1. Experimentally, it is observed that it is those carbonyl clusters that exhibit low values of E_1 which more readily undergo decomposition, disproportionation, or polymerization reactions. Thus, $Fe_3(CO)_{12}$ readily decomposes to produce, among other products, $Fe(CO)_5$.

Similarly, $Rh_4(CO)_{12}$ easily converts to $Rh_6(CO)_{16}$. Again, E_1 is effectively zero since the C_{3v} arrangement has been established in both the solid and solution. The mixed system $Fe_2Ru(CO)_{12}$, which contains CO bridges, undergoes disproportionation more readily than $Ru_2Fe(CO)_{12}$, which does not.



In the osmium series, clearly $Os_3(CO)_{12}$ with an Os:CO ratio of 1:4 is more able to produce $Os(CO)_5$ than is $Os_6(CO)_{18}$.

The effect of external CO pressure is also of importance. Any tendency for the carbonyl to undergo CO dissociation will decrease the ability to eject a saturated unit.

$$Os_3(CO)_{12} \rightleftarrows Os_3(CO)_{11} + CO$$

Carbonyl dissociation will diminish in the presence of external CO. Carbon monoxide will also tend to trap out the unsaturated low-cluster fragments and therefore prevent cluster formation. The formation of Os_5, Os_6, Os_7, and Os_8 clusters from $Os_3(CO)_{12}$ is [CO]-dependent, the relative yields of the lower or higher clusters depending on the CO pressure.

2. *The Activation of Carbonyl Cluster Compounds*

A major problem encountered in studies of the cluster carbonyls is the comparatively drastic conditions required to bring about chemical reaction with substrates such as acetylene or ethylene. The difficulty lies in the reluctance of these systems to undergo ligand exchange either via (*a*) a CO dissociation step,

$$\begin{array}{ccc} M_m(CO)_n & \rightleftharpoons & M_m(CO)_{n-1} + CO \\ \text{coordinatively} & & \text{coordinatively} \\ \text{saturated} & & \text{unsaturated} \end{array}$$

or (*b*) a M–M cleavage (associative) step. Carbonyls such as $Ni(CO)_4$ readily undergo ^{13}CO exchange under moderate conditions and in short periods of time, whereas exchange with $Os_3(CO)_{12}$, for example, takes several days at 80°C, and under the same conditions exchange with $Os_6(CO)_{18}$ is negligible. There is some debate as to the mechanism of exchange or substitution in these clusters, but there is growing evidence to suggest that both exchange and substitution occur via an associative metal–metal bond-break mechanism. Reaction with a substrate such as ethylene is understandably slow under moderate conditions of pressure and temperature. Other, more amenable methods of activation have therefore been sought.

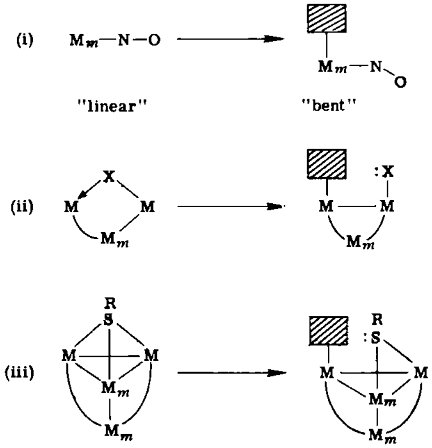
a. CO Displacement. We illustrate two methods by which a coordinatively unsaturated species such as "$Os_3(CO)_{11}$" may be generated.

$$M_m\text{—CO} \xrightarrow[mh\nu]{\Delta} M_m\text{—}▨ + \text{CO} \qquad \text{(i)}$$

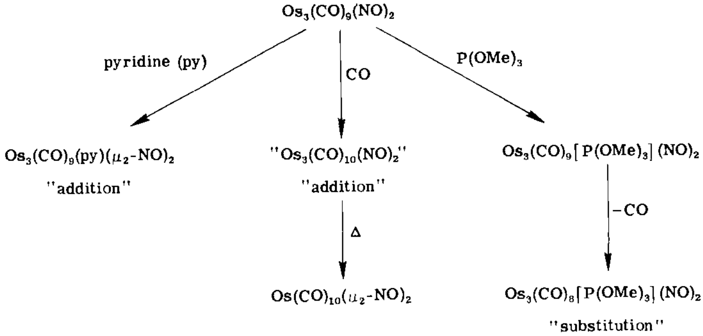
$$M_m\text{—CO} \xrightarrow{Me_3NO} M_m\text{—}▨ + CO_2\uparrow + Me_3N\uparrow \qquad \text{(ii)}$$

Method (i), the thermal or photolytic ejection of CO, is known to be unfavorable (see above). Method (ii), the removal of CO as CO_2 by oxidation with Me_3NO, is an easily carried-out procedure and has led to the synthesis of many hitherto inaccessible compounds. By this route the ethylene cluster $Os_3(CO)_{11}C_2H_4$ has been synthesized.

b. Ligand–Metal Redox Systems. Three of many possible examples are



Method (i) is a route commonly utilized in monometal nitrosyl complexes. The nitrosyl ligand may function as (*formally*) a three-electron donor (NO^+) with a linear bonding mode, or as (*formally*) a one-electron donor (NO^-) with a bent (~120°) M–N–O arrangement. Conversion of the M–$\overset{+}{N}$O system to a M–$\overset{-}{N}$O system has two effects. First, it increases the metal oxidation state by two; second, it generates a vacant coordination site. The dinitrosyl cluster $Os_3(CO)_9(NO)_2$, which has been shown (*34*) to possess the *quasi*-$Os_3(CO)_{12}$ structure, undergoes both substitution and addition reactions by this route.

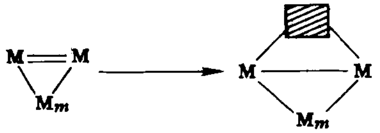


In method (ii), the group X (e.g., a halogen) may function as a three-electron donor when present as a bridging group, but as a one-electron donor when combined to one metal center. The simple act of bridge-opening creates a vacant coordination site on one metal atom. Behavior of this sort is invoked to explain the stereospecific incorporation of ^{13}CO in the complex $Os_3(CO)_{10}Cl_2$.

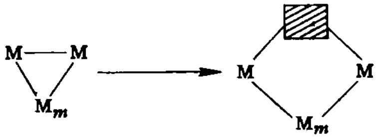
Related to method (ii) is method (iii). This is considered to occur when a ligand, instead of spanning two metal atoms as a three-electron donor or ligand (e.g., the SR group), spans three (or more) metal atoms. Again, as in (ii), a vacant coordination site is created by the ligand moving away from the capped system (three-center bridge) to an edge-bridge system, thereby creating a vacant site on one metal atom. The complex $HOs_3(CO)_9SR$ containing an SR group spanning three Os atoms undergoes reaction with ethylene to produce the adduct $HOs_3(CO)_9(\mu_2\text{-}SR)(C_2H_4)$, in which the SR grouping is folded back to permit coordination of the ethylene molecule (*35*).

c. Metal–Metal Bond Cleavage. Finally, two alternatives are illustrated below:

(i)



(ii)



These are based on the idea that vacant coordination sites may be generated by cleavage of metal bonds. Case (i) illustrates a double-bond → single-bond conversion. The reaction of a coordinatively unsaturated species such as $H_2Os_3(CO)_{10}$ (46 electrons as opposed to a 48-electron species) readily undergoes reaction with an electron-pair donor ligand to produce an adduct $H_2Os_3(CO)_{10}L$. Such reactions may be viewed as saturating a double bond. Thus, a metal–ligand bond is formed at the expense of one metal–metal bond.

In example (ii), a metal–ligand bond is formed at the expense of a single metal–metal bond leading to cluster rearrangement or fragmentation.

III. Polynuclear Complexes of Ruthenium and Osmium

A. INTRODUCTION

This section is devoted to the structure and chemical behavior of the carbonyl clusters of ruthenium and osmium. The first parts will be principally devoted to the trinuclear complexes, $M_3(CO)_{12}$ (M = Ru and Os), since the triangulated structure of these molecules forms the basic unit of the higher polyhedra. The later parts will be concerned with the higher cluster compounds. One of the major points of interest in a study of polynuclear compounds is the comparison between the bonding modes adopted by ligands in a cluster and in mononuclear compounds. Even for the simplest example, viz. the trinuclear complexes, it has been shown that major variations in bonding type occur, the ligands normally bonding to two or more metal centers whenever possible. With the higher cluster units, significant additional variations occur, often involving bond fission within the ligand molecule, and the bonding of organo fragments to more than one face of the metal polyhedron.

We shall first summarize the bonding modes that have been identified for carbon monoxide, hydrogen and hydrocarbon groups—alkene and alkyne—and follow this by a general discussion of the chemistry of the $M_m(CO)_n$ clusters with special emphasis on the $M_3(CO)_{12}$ molecules.

B. BONDING TO CARBON MONOXIDE

In Table II are listed the neutral homonuclear carbonyls of the Group VIII metals that have been identified to date. Although palladium and platinum do not have any stable neutral carbonyls, a large

TABLE II

NEUTRAL BINARY CARBONYLS OF GROUP VIII ELEMENTS

Fe, Ru, Os	Co, Rh, Ir	Ni
$Fe(CO)_5$	$Co_2(CO)_8$	$Ni(CO)_4$
$Fe_2(CO)_9$	$Co_2(CO)_{12}$	
$Fe_3(CO)_{12}$	$Co_6(CO)_{16}$	
$Ru(CO)_5$	$Rh_2(CO)_8$	
$Ru_3(CO)_{12}$	$Rh_4(CO)_{12}$	—
	$Rh_6(CO)_{16}$	
$Os(CO)_5$	$Ir_4(CO)_{12}$	
$Os_2(CO)_9$	$Ir_6(CO)_{16}$	
$Os_3(CO)_{12}$		
$Os_5(CO)_{16}$		—
$Os_6(CO)_{18}$		
$Os_7(CO)_{21}$		
$Os_8(CO)_{23}$		

range of anionic carbonyl species has been isolated for these and other Group VIII elements (*7*).

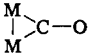
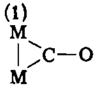
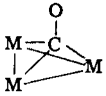
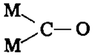
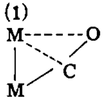
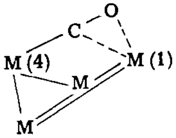
Table III shows the bonding modes that have been established for carbon monoxide in these polynuclear aggregates. In addition to the terminally bonded group (μ_1) observed for the mononuclear complexes, a variety of bridging carbonyl species have also been identified, involving two-electron and four-electron donation from the carbonyl group to the cluster unit.

1. Edge-Bridging Carbonyl

The carbonyl bridge in $Fe_2(CO)_9$ was one of the first established by X-ray analysis (*36*). The $\widehat{MCM}$ bond angle in these complexes is ~80°, and the nature of this bridge bond has provided a point of discussion for a number of years. Either a three-centered delocalized bonding scheme or a two-centered bent-bond approach is now generally accepted to be satisfactory in explaining the nature of this bridging form (*37*). Recently, Cotton (*38*) has drawn attention to the number of metal–CO bonding interactions ranging from a linear combination to a symmetric bridge arrangement. Such interactions have been considered as a means of alleviating asymmetric charge distributions within the molecule, but this is not a complete explanation since bridges occur in molecules in which no charge disparity exists. An illustration of this is pro-

TABLE III

BONDING MODES FOR CARBON MONOXIDE

No. of Electrons	Bonding type	Compound	M–C Distances (Å)	Angle M–$\widehat{C}$–O (deg)	Infrared frequency (ν, cm^{-1})
2	M—C—O	$Fe_2(CO)_9$	Fe–C = 1.838	177.1	2080 2034
2		$Fe_2(CO)_9$	Fe–C = 2.016	141.2	1829
2		$[Fe_4(CO)_{13}^{2-}]$	M–C = 1.85 M(1)–C = 2.33	155	Terminal
2		$[Fe_4(CO)_{13}]^{2-}$	M–C = 2.00	151	1600
2		$[Pd(Ph_2As)_2CH_2)Cl]_2CO$	M–C = 1.84	120	1720
4		$Mn_2(CO)_5[(Ph_2P)_2CH_2]_2$	M–C = 1.93 M(1)–C = 2.01 M(1)–O = 2.29	173	1645
4		$[HFe_4(CO)_{13}]^-$	M(4)–C = 1.81 M(1)–C = 2.17 M(1)–O = 2.00	—	—

vided by the ion $[Fe_4(CO)_{13}]^{2-}$ (Fig. 1), in which the asymmetrically edge-bridged CO groups occur between the metal atoms in the basal plane and are related to the marked deviation of the Fe–C–O group from the linearity of the terminally bonded species (*39*).

Recently, a new form of carbonyl bridge has been recognized in the complex $[Pd[(Ph_2As)_2CH_2]X]_2CO$ (X = Cl, Br) (*40*). In this complex, the CO group bonds between two metal centers; the Pd–C–Pd bond angle is large (119°), and the Pd–Pd distance of 3.27 Å is considered to be too long for a direct metal–metal bond. This complex is the first example of a "metal-unsupported" carbonyl bridge. A related platinum complex $[Pt[(Ph_2P)_2CH_2]Cl]_2CO$ is also known, and in solution an equilibrium between a terminal and a bridging carbonyl species is believed to exist (*41*). A surprising feature of these molecules is the bridging of metals by the carbonyl rather than the halide group, and the large metal–carbon–metal angle may reflect the severe steric requirements of the diphosphine and diarsine ligands.

2. *Face-Bridging Carbonyl*

A face-centered metal bonded carbonyl group has also been detected in a number of cluster molecules. The $[Fe_4(CO)_{13}]^{2-}$ (*39*) ion (Fig. 1a) also provides an example of this bonding mode. As anticipated, the progression of terminal, asymmetric, symmetric edge-bridging, and face-centered carbonyl groups is associated with a decrease in the carbonyl stretching frequency from the region of 2100 cm^{-1} to 1650 cm^{-1}, consistent with a drift of negative charge to the oxygen and decreasing

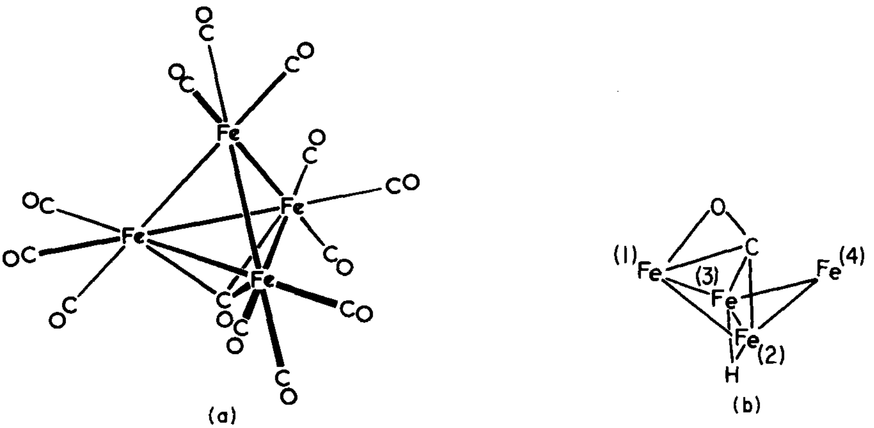


FIG. 1. (a) Molecular structure of $[Fe_4(CO)_{13}]^{2-}$ anion; (b) molecular structure of $[HFe_4(CO)_{13}]^-$ anion.

bond order of the C–O bond. The infrared spectra of compounds have often been used as indications of the bonding mode within a cluster carbonyl compound. For the three-centered carbonyl group, these absorptions are often very weak.

3. "Four-Electron" Carbonyl Donation

In all the above examples, the carbonyl group donates two electrons to the metal cluster unit. Four-electron donation by the carbonyl group has recently been observed; although this appears to be a much less frequent mode of bonding in cluster systems, it has often been invoked to explain the properties of absorbed carbon monoxide on a metal surface.

The structures of two complexes in which four-electron donation by the carbonyl group has been suggested are shown in Figs. 1b and 2. On the basis of a normal electron count for CO and phosphine groups in the manganese complex (Fig. 2), the metal Mn(1) appears to be two electrons short of the inert-gas configuration (*42, 43*). This deficiency is considered to be satisfied by an extra two-electron bond from the π-bond of the CO group, bonding to Mn(2). The Mn(1)–O and Mn(1)–C distances are certainly consistent with a bonding interaction of this type.

The structure of the iron complex $[HFe_4(CO)_{13}]^-$ (Fig. 1b) provides an interesting comparison with that of the related dianion $[Fe_4(CO)_{13}]^{2-}$ (Fig. 1a). A major rearrangement of the carbonyl polyhedron has occurred on the addition of a proton to the dianion (*44*). Electronically, the two ions are equivalent, but, as is discussed in Section III,C, hydrogen incorporation into clusters often involves significant structural changes, especially as the hydrogen appears to take up a spatial requirement approximately equivalent to a carbonyl group. For the ion $[Fe_4(CO)_{13}]^{2-}$, Dahl (*39*) has pointed out that the structure is determined to a significant amount by the close-packing of the carbonyl group, and Dahl commented on the difficulties of formulating a regular $[Fe_4(CO)_{14}]$ cluster unit. In agreement with this, the interjection of the hydrogen causes significant distortion of the metal tetrahedron with lengthening of the Fe(1)—Fe(4) edge to such an extent that bonding no

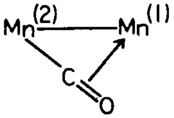


FIG. 2. CO Bonding mode in $Mn_2(CO)_7[Ph_2P(CH_2)_2PPh_2]$.

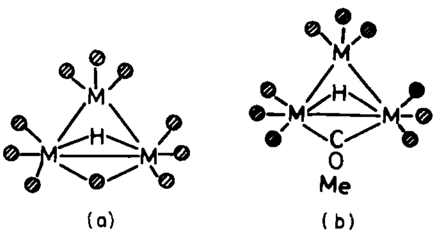
longer occurs between the metals. The bonding of an oxygen to the metal Fe(1) is then suggested to maintain the inert-gas configuration at the metal center Fe(1). The interaction in this case is more appropriately considered as involving a more direct bond from the oxygen of a carbonyl group than in the manganese adduct, with a pattern Fe(1)–O–C–Fe(4).

Four-electron donor bonds of the type proposed for $Mn_2(Ph_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PPh_2)_2(CO)_7$ have also been suggested for a series of complexes in which multiple bonding occurs between the metal centers. In the molecules $[(\pi\text{-}C_5H_5)_2M_2(CO)_4]$, where M = Cr or Mo, either a triple bond is envisaged between the metal centers or a single bond with a further two-electron donation from the π-electron of a carbonyl group on the other metal (*45*). The bond distances between the metals are significantly shorter than has been reported for "single-bond" distances, but it cannot be unequivocally assigned a bond order of 3. At this stage it is not possible to differentiate between these two alternatives, emphasizing the difficulty of bond-length/bond-order relationships in multiple-bonded metal systems of this type (see Section II,F).

A number of molecules in which there is donation from the oxygen of a metal–carbonyl group to a Lewis acid have been identified. As may be anticipated, the bridging carbonyl group forms bonds of this type more readily than a terminal carbonyl, since this involves a larger charge drift to the oxygen. In fact, it has been possible to use this effect to stabilize a bridging carbonyl bond. Thus it has been suggested that $Ru_3(CO)_{12}$ may be stabilized in a carbonyl bridging modification in the adduct $Ru_3(CO)_{12}{\cdot}AlBr_3$ (*21b*). For systems with more than one bridging carbonyl group, it is possible to form a series of addition complexes corresponding to addition at more than one center. In the tetramer $[(\pi\text{-}C_5H_5)Fe(CO)]_4$, 1:1, 1:2, 1:3, and 1:4 adducts with $AlBr_3$ have been prepared corresponding to interaction with each oxygen center of the four bridging carbonyl groups. It must be recognized, however, that in carbonyl complexes of this type there is the potential of interaction of Lewis acid with the metal center rather than the oxygen of the carbonyl. For the ion $[(\pi\text{-}C_5H_5)W(CO)_3]^-$, complex formation with Ph_3Al occurs at oxygen, while for Ph_3In, attack occurs at the metal center with the production of a W–In bond (*21b*).

This ambivalence in behavior of electrophiles toward both the metal and oxygen centers may be extended to other systems. Thus protonation of metal carbonyl species normally occurs at the metal center, although recently it has been suggested, on the basis of NMR evidence, that, below −30°C, protonation of the anion $[HFe_3(CO)_{11}]^-$ occurs at the bridging carbonyl oxygen to give $H_2Fe_3(CO)_{11}$ (*46*), whereas the related reaction with the carbonium ion CH_3^+, generated via $[(CH_3)_3O]^+$ or CH_3SO_3F, often leads to attack at the carbonyl oxygen, in a manner analogous to that considered for aluminum derivatives above. The structure of the anions $[HM_3(CO)_{11}]^-$ (M = Fe, Ru, Os), which may be generated by borohydride reduction of the carbonyls $M_3(CO)_{12}$ (M = Ru, Os), or by base attack for $Fe_3(CO)_{12}$, is shown in Fig. 3a. Methylation of the bridging carbonyl group can be readily accomplished with the above reagents, and the X-ray structures of the series $[HM(CO)_{10}(COCH_3)]$ [M = Fe (*46*), Ru (*47*), Os (*48*)] have been determined (Fig. 3b).

The bonding of the $COCH_3$ group in these complexes is of interest, and provides an example of one of the major problems of nomenclature that can arise in transcribing terms from mononuclear to polynuclear systems. In the complex $HFe_3(CO)_{10}(COCH_3)$, the group was described as a "triple metal semibridge unit" and a weak interaction was assumed to occur between the bridging carbon atom and the unique iron atom. For the related osmium complex, the $COCH_3$ ligand was regarded as an "O-alkylated carbonyl group." For the ruthenium complex $HRu_3(CO)_{10}(COCH_3)$, we prefer to view this as a μ_2-carbyne group. This is consistent with the low C–O stretching vibration in the infrared spectrum at 1450 cm^{-1} and the CO bond length of 1.299 Å, which is intermediate between a double and single bond. The partial π-character of the CO bond is apparent from the hindered rotation of the CH_3 group, as indicated by the variable-temperature ^{13}C-NMR measurements. The partial multiple-bond character in the metal–carbon framework is also related to the metal–metal distance, which is shorter than in the anion $[HRu_3(CO)_{11}]^-$, and to the significant reduction (0.093 Å) of the Ru–C (carbyne) bond length. A similar problem exists for the complex $HRu_3(CO)_{10}(CNMe_2)$, the structure of which has recently been determined (*49*). In polynuclear species of this type, the possibility of establishing bonding modes directly from structural data

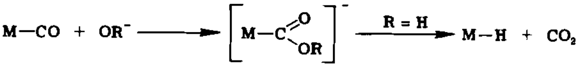


(a) (b)

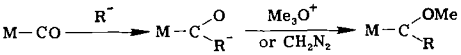
FIG. 3. (a) Molecular structure of $[HM_3(CO)_{11}]^-$ anion; (b) molecular structure of $HM_3(CO)_{10}COMe$.

can be fraught with difficulties, as the comparisons used for this assessment in mononuclear complexes have not been documented in sufficient detail for polynuclear compounds. If this is coupled with incipient bonding interactions, which are often considered and which may reflect only steric requirements within the molecule, the problem is seen to be compounded. The main difficulty is that the use of a specific nomenclature may influence or prejudice the approach to the chemistry of the complex under consideration.

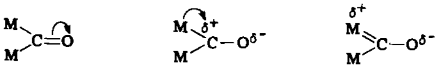
A somewhat related problem is the nature of the bridged carbonyl group between two metal centers. Obvious correlations with organic ketonic behavior in general provide difficulties. In general nucleophilic attack by OR^- (R = H or Me) does appear to occur at the carbon center. For R = Me, stable $M-CO_2R$ complexes may often be isolated, but for R = H, transfer of hydrogen to the metal with elimination of CO_2 occurs readily, to yield the hydridocarbonyl.



Also, the initial step of the Fischer carbene synthesis is considered to occur via nucleophilic attack at the carbon center (*50, 51*).



However, these reactions are associated with terminal rather than bridging carbonyl groups. In metal "ketonic" compounds, the center for attack is normally the metal. This may be rationalized in terms of additional delocalization of the positive charge from the carbon to the metal center and implies a "carbyne" contribution to the carbonyl bridge, of the form discussed above for the methylated products, again emphasizing the possibility that in systems of this type reaction may occur at either the metal or ligand center



C. Bonding to Hydrogen

Hydrogen forms an extensive series of compounds with the metal carbonyls, and the nature of the H bonding within these complexes has been a point of debate for a considerable period. Both the chemistry and structure of metal carbonyl hydride compounds have been extensively reviewed by Humphries and Kaesz (*52*) and by Bau (*53*). For an understanding of the chemistry of polynuclear complexes, it is important to consider certain chemical and structural aspects. We shall therefore briefly review this field, but would refer the reader to the above reviews for a more detailed discussion of this area. In Table IV are indicated the various bonding modes that have been observed for hydrogen in metal cluster systems, and in Table V are listed the hydridocarbonyls that have been identified for ruthenium and osmium

Two main techniques are normally employed in establishing the presence of a bond between hydrogen and metal, namely infrared and ^{1}H-NMR spectroscopy. Historically, infrared spectroscopy was first utilized to detect M–H bonds, and was normally employed in conjunction with deuteration studies. For terminally bonded hydrogen, the M–H stretching frequency falls in the range 2000–1850 cm^{-1}. However, for bridging hydrogen, both the position and intensity of the vibration are changed. As indicated in Table IV, a large reduction in the frequency of the vibration occurs on forming bonds to more than one metal center. Perhaps the most important feature of this bonding, however, is the major decrease in the intensity of the vibration from what are often strong absorption bands for the terminal bonded species to weak absorptions in multicentered bonding modes. The intensities of the vibra-

TABLE IV

HYDROGEN BONDING MODES IN CLUSTER COMPOUNDS

Bonding mode	Compound	$\nu_{(M-H)}$, cm^{-1}
M–H terminal	—	~2000–1850
$\genfrac{}{}{0pt}{}{M}{M}\!>\!H$ edge-bridge	$[HW_2(CO)_{10}]^-$	H: 1680, 714 D: 1220
	$H_4Ru_4(CO)_{12}$	H: 1605, 1272 D: 1095, 895
	$H_2Os_3(CO)_{10}$	H: 1245, 732 D: 905, 710
	$H_2Os_3(CO)_{11}$	H: 1922, 818[a] D: 1515, 777[b]
$\genfrac{}{}{0pt}{}{M}{M}\!>\!H{-}M$ face-bridge	$[HOs_6(CO)_{18}]^-$	H: 1250 D: 890
	$H_4Re_4(CO)_{12}$	H: 1023[c]
$[M_6H]$ interstitial	$[HRu_6(CO)_{18}]^-$	H: 800

[a] Terminal.

[b] Bridging.

[c] Band intensity temperature-dependent.

TABLE V

HYDRIDOCARBONYLS OF RUTHENIUM AND OSMIUM

Ru	$H_2Ru(CO)_4$	—	$H_2Ru_3(CO)_{12}$	$H_4Ru_4(CO)_{12}$ $H_2Ru_4(CO)_{13}$	—	$H_2Ru_6(CO)_{18}$ $H_2Ru_6C(CO)_{16}$	—
Os	$H_2Os(CO)_4$	$H_2Os_2(CO)_8$	$H_2Os_3(CO)_{12}$ $H_2Os_3(CO)_{11}$ $H_2Os_3(CO)_{10}$	$H_4Os_4(CO)_{12}$ $H_2Os_4(CO)_{13}$	$H_2Os_5(CO)_{15}$ $H_2Os_5(CO)_{16}$	$H_2Os_6(CO)_{18}$	$H_2Os_7(CO)_{20}$ $H_2Os_7(CO)_{19}C$

tions are, however, very sensitive to temperature and increase markedly on reduction to liquid-nitrogen temperatures (*54*).

The lack of appreciation of this variation in both frequency and intensity on bonding to more than one metal center has provided difficulties in the infrared studies of absorbed organic molecules on a metal surface. Until recently, few direct structural techniques were available for determining the nature of absorbed species on a metal surface. Infrared spectroscopy, with the detailed knowledge of the vibrational frequencies associated with various functional groups, has provided such a technique. However, in a number of instances, the presence of a metal–hydrogen vibration, which was anticipated from the nature of the other fragments of those organic species that could be identified, was not observed. This arose because the primary area considered was the terminally bonded region, and examination of the lower region gave no indication of M–H bonding due to the lower intensity of absorption bands.

Perhaps the most powerful method of detecting the presence of metal–hydrogen linkages is the ^{1}H-NMR spectrum. In M–H systems, the proton chemical shift occurs in the region of 20–40 τ. Although no absolute range has been defined, in general, the chemical shift of terminal hydrides tends to occur in lower regions, $\sim 20\ \tau$. Anomalous shifts have been detected for hydrogen which is bonded within a metal polyhedron, for example $[HRu_6(CO)_{18}]^-$ (*54*) and $HCo_6(CO)_{15}^-$ (*56*), in which τM–H occurs at $\sim 6.4\ \tau$ and $13.2\ \tau$, respectively.

Considerable activity has recently occurred in determining the structural details of hydrogen–metal bonds by neutron diffraction techniques. Table VI (*21a, 57–69*) gives the details of those complexes for which the X-ray/neutron diffraction studies have been carried out. Prior to the utilization of neutron studies, the main criterion employed in determining hydrogen positions in coordination polyhedra was from X-ray data, using arguments based on (*a*) the lengthening of metal–metal bonds on bonding a hydrogen between two metal centers; (*b*) the distortion of the carbonyl groupings around a metal to accommodate the hydrogen; and (*c*) overall symmetry considerations of the molecules that could place a hydrogen by relation to major symmetry within the structure (see Section II,C). As may be anticipated, these methods often lead either to ambiguities in interpretation or incorrect assignment. Thus, for the complex $[HW_2(CO)_{10}]^-$, the X-ray data were taken to indicate a high degree of symmetry for the molecule. The W–W distance showed a significant increase consistent with a W–H–W bridging arrangement, and the hydrogen was reasonably assigned to a bridging situation midway between the W–W atoms and lying along the W–W

TABLE VI

X-RAY/NEUTRON DIFFRACTION DATA FOR HYDRIDO-BRIDGED COMPLEXES

Compound	M–H (Å)	Comment	Ref.
Hydrogen bridging two metal centers			
$HRu_3(CO)_9(C{\equiv}C\text{-}t\text{-}Bu)$	1.789(5) 1.796(5)		*57*
$H_2Os_3(CO)_{10}$	1.850(5) 1.854(5)	Bonds across short Os–Os bond	*21a*
$HOs_3(CO)_{10}(C_2H_3)$	1.813(4) 1.857(4)	Vinyl complex; shorter Os–H bond to the σ-bonded metal	*58*
$H_2Os_3(CO)_{10}CH_2$	1.7(1) 2.0(1)	Only X-ray data reported, but Os–H distances determined from neutron data	*59*
$H_2Os_3(CO)_9S$	1.825(3) 1.804(3) 1.837(3)		*60*
$[Et_4N][HCr_2(CO)_{10}]$	1.737(19) 1.707(21)	A bent Cr–H–Cr bond Cr–H–Cr = 1589	*61*
$[(Ph_3P)_2N][HCr_2(CO)_{10}]$	1.675	Linear Cr–H–Cr	*62*
$HMo_2(\pi\text{-}C_5H_5)_2(CO)_4(PMe_2)$	1.851(4) 1.869(4)		*63*
$[Et_4N][HW_2(CO)_{10}]$	1.718(12) 2.070(12)	Asymmetric bonding to metals off the metal–metal bond	*64*
$HW_2(CO)_9NO$	1.875(4)	W–H–W angle is 125°	*65*
$HW_2(CO)_8(NO)[P(OMe)_3]$	1.859(6) 1.894(6)	W–H–W angle is 129.4° W–H does not reflect asymmetry of metal centers	*66*
$H_8Re_2(PEt_2Ph)_4$	1.878(7)	Terminal Re–H bond is 1.669 Å	*67*
Hydrogen bridging three metal centers			
$HFeCo_3(CO)_9(P(OMe)_3)_3$	1.734(4)	0.978 Å out of cobalt plane	*68*
$H_3Ni_4(\pi\text{-}C_5H_5)_4$	1.691(8)	0.90 Å out of nickel plane	*61*
Hydride in octahedron of metals			
$[(Ph_3P)_2N]_2[H_2Ni_{12}(CO)_{21}]$	1.84 2.00	Displaced toward one of metal faces	*69*
$[(Ph_3P)_2N]_3[HNi_{12}(CO)_{21}]$	1.72	Displaced toward one of metal faces	*69*
$[HCo_6(CO)_{15}]^-$	1.82(1)	At center of metal octahedron	*56*

vector. A neutron-diffraction study has established that the hydrogen is indeed between the two tungsten atoms (*64*), but the high symmetry of the system is apparent rather than real and arises from disorder within the structure. The hydrogen is found to lie 0.71 Å off the W–W axis, and at distances of 1.718 Å from one tungsten atom and 2.070 Å from the other metal atom.

Neutron-diffraction studies have now established hydrogen positions in a number of molecules. The "interstitial" incorporation of hydrogen at the center of metal octahedra has been illustrated by this technique for hexanuclear nickel and cobalt complexes. The symmetry of hydrogen between two metal centers has been found in certain instances to be relatively insensitive to difference in substitution at the metal centers—e.g., $[HW_2(CO)_9(NO)]$ and $[HW_2(CO)_8NO(P(OMe)_3)]$—while other systems reflect this asymmetry, e.g., $HOs_3(CO)_{10}(CH{=}CH_2)$. Sheldrick and his co-workers have shown from neutron diffraction studies that for the molecule $H_2Os_3(CO)_{10}$ both hydrogens bridge the shortest metal–metal edge in the osmium triangle.

A novel method used for the determination of hydrogen positions is nematic-phase NMR, which has been applied to the complexes $H_3M_3(CO)_9C{\cdot}CH_3$ (M = Ru, Os). The structure established by this method and X-ray analysis is shown in Fig. 4. The three hydrogens lie below the plane of the metal triangle on the opposite side to the "capping" $C{\cdot}CH_3$ group, each hydrogen bridging between two metal atoms (*70*).

Structural work has established that hydrogen has a significant stereochemical "size" in transition-metal–hydride complexes. This is contrary to the initial suggestion that the size of hydrogen was negligible, and that the hydrido ligand was "buried" in the electron cloud of the metal. For mononuclear complexes, a recent electron-diffraction study of the series of hydrido carbonyls $HMn(CO)_5$, $H_2Fe(CO)_4$, and $HCo(CO)_4$ (Fig. 5) has shown that the hydrogen ligand occupies a "nor-

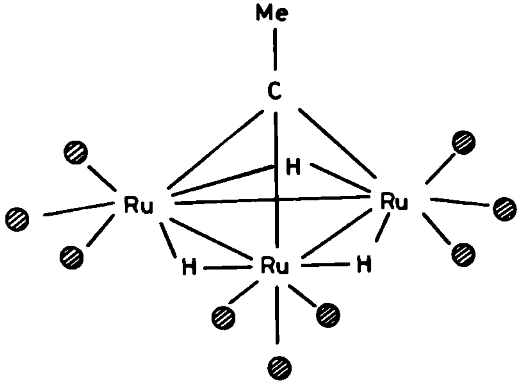


FIG. 4. Molecular structure of $H_3Ru_3(CO)_9Me$.

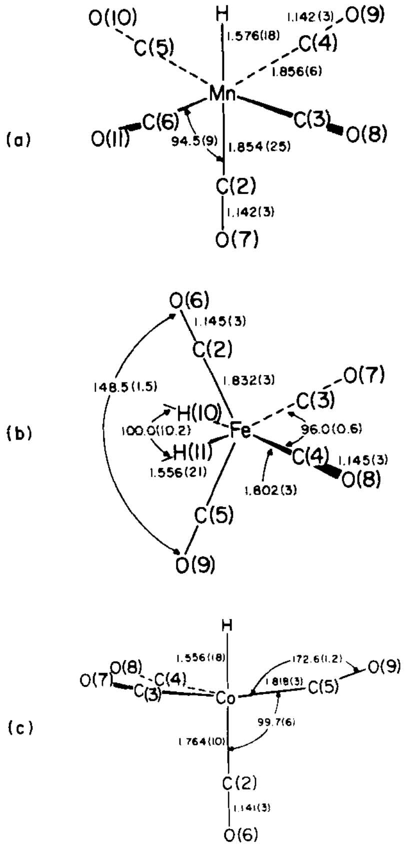


FIG. 5. Molecular structure of (a) $HMn(CO)_5$, (b) $H_2Fe(CO)_4$, and (c) $HCo(CO)_4$.

mal" stereochemical position in the ligand polyhedron (*71*). These combined X-ray and neutron-diffraction studies also indicate an overall radius slightly less than that of the carbon in the carbonyl group. This, of course, agrees with the criterion, put forward by Churchill, for determining hydrogen positions in carbonyl–hydrido complexes from X-ray structures by examining the stereochemical demands on the carbonyl distribution within the molecule.

A general review of the structures of polynuclear metal hydrides shows that the most common bonding modes for hydrogen in the cluster are those in which it combines with more than one metal center, with both edge- and face-bridging bonding occurring. The assignment between these alternative bridging sites can often be difficult to establish, but Bau (*53*) has illustrated how the carbonyl distributions relative to the metal framework within a molecule can be used to differentiate between these alternatives. In the molecules $H_4Ru_4(CO)_{12}$ and $H_4Re_4(CO)_{12}$, each metal has three carbonyl groups coordinated; the carbonyl distribution at a given metal differs with respect to the other metal centers in the two molecules. For the ruthenium (*72*) compound, the three CO groups on a given metal are staggered relative to the three edges of the metal tetrahedron, while for the rhenium (*73*) compound, the three CO groups eclipse the three edges of the tetrahedron. This is consistent with four edge-bridging hydrides for the ruthenium complex and four face-bridging hydrogens for the rhenium complex, as this would minimize the steric interaction between the hydrogen and the carbonyl groups in each case. With these systems there is the possibility of more than one isomer; e.g., for $H_4Ru_4(CO)_{12}$, there are four hydrogens to six edges of the metal tetrahedron. Such isomers have been detected for the ion $[H_3Ru_4(CO)_{12}]^-$ (see Section II,C) (*74*).

Although terminal hydrido groups are rare, they do occur, but generally in molecules where steric constraints impose a terminal rather than a bridging hydride position. In the molecules $H_2Os_3(CO)_{10}L$ (L = CO, PR_3, CNR, py), both bridging and terminal hydrogens occur, and in these molecules there is considerable steric interaction between the ligand groups (*75*). For the compound $H_4Os_3S(CO)_8$, three of the hydrides form bridges beneath the edges of the metal triangle, with the sulfur atom capping the face of the metal triangle on the opposite side to the hydrogens, in the manner described for $H_3Os_3(CO)_9C{\cdot}CH_3$ (*76*). The steric demands of placing the remaining hydrogens along an edge that is already bridged by hydrogen and sulfur are obviously too great, and the hydrogen occupies a terminal position. However, steric factors are not the only factors involved in this problem, as the structure of the complex ion $[H_2Ir_4(CO)_{10}]^{2-}$ has recently shown that the two hydrogens occupy terminal positions with carbonyl groups bridging between metal centers (*77*). The osmium complexes $H_2[Os(CO)_4]_n$ (n = 1–4) involve linear chains of osmium atoms, with terminal hydrogen bonds (*78*). The series $H_2Os_4(CO)_{12}$, $H_2Os_3(CO)_{11}$, and $H_2Os_3(CO)_{10}$ provides an interesting progression. Loss of CO, which occurs on heating, is accompanied by metal–metal bond formation and the introduction of one and then two bridging hydrogen atoms.

There is a marked difference in chemical reactivity between bridging and terminal hydrogens. Terminally bonded hydrogens readily react in a similar manner to that observed for mononuclear hydrides. Thus reactions with chlorinated hydrocarbons such as carbon tetrachloride yield the chloro cluster complexes and chloroform. In contrast, bridging hydrides are stable and may be studied in chlorinated solvents. This inert character has led, in certain instances, to difficulties in removing the hydrogen in bridging environments, and resort to powerful chemical reagents, such as KH or Na/Hg, has been necessary.

Many of the methods used for the preparation of mononuclear hydrides may be applied to the polynuclear systems. Base attack on metal carbonyls, which furnished one of the first methods for the production of carbonyl hydride species, is applicable to a wide range of carbonyls. Borohydride reduction leads to a variety of products, depending upon the reaction conditions, $Os_3(CO)_{12}$ reacting with $NaBH_4$ in dioxane under reflux to give, after 4 hours, a mixture of the anions $[H_3Os_4(CO)_{12}]^-$ and $[H_2Os_4(CO)_{12}]^{2-}$ (*79*). The related reaction in tetrahydrofuran for 1 hour yields the anion $[HOs_3(CO)_{11}]^-$ as the main product with minor amounts of the two tetranuclear anions.

Many polynuclear complexes dissolve in strong acids or solutions of acids in hydrocarbon solvents, to yield hydrido complexes by protonation of the metal cluster. For $Os_3(CO)_{12}$ in 98% H_2SO_4, the ion $[HOs_3(CO)_{12}]^+$ has been detected (*80*). In the majority of cases, protonation occurs at the metal; however, in the complex $H_4Os_3S(CO)_8$, discussed above, the steric crowding in this molecule forces protonation to the sulfur rather than the metal. For the related complex $H_2Ru_3S(CO)_9$, protonation occurs at the metal to give bridging hydrogens along each edge of the formation of the ion $[H_3Ru_3S(CO)_9]^+$ (*81*). The majority of reactions of this kind have been followed by ^1H-NMR measurements.

Perhaps the most important development in polynuclear carbonyl hydride complexes was the observation by Kaesz *et al.* that good yields of hydridocarbonyls could be obtained by direct reaction of hydrogen with polynuclear carbonyls (*82*). This has been applied to a number of systems. Thus, the anion $[Rh_{12}(CO)_{30}]^{2-}$ yields the cluster anion $[Rh_{13}(CO)_{24}H_{5-n}]^{n-}$ ($n = 2$ or 3) (*83*), while $Re_2(CO)_{10}$ yields $H_3Re_3(CO)_{12}$ and $H_4Re_4(CO)_{12}$. For the ruthenium and osmium carbonyls, ready reaction occurs to give the tetranuclear hydride $H_4Ru_4(CO)_{12}$ for ruthenium, and initially the trinuclear hydride $H_2Os_3(CO)_{10}$ for osmium, consistent with the greater stability of the metal–metal bonds in osmium. Further reaction does occur to yield the tetranuclear species $H_4Os_4(CO)_{12}$:

$$Os_3(CO)_{12} \underset{CO}{\overset{H_2}{\rightleftharpoons}} H_2Os_3(CO)_{10} \underset{CO}{\overset{H_2}{\rightleftharpoons}} H_4Os_4(CO)_{12}$$

In many instances these reactions are reversible.

The facility for hydrogen incorporation into metal carbonyls appears to be general, and a wide range of H–X bonds oxidatively add to the ruthenium and osmium carbonyl systems. For H_2X, the complexes $H_2M_3(CO)_9X$ ($X = S, Se$; $M = Ru, Os$) are readily formed by direct reaction (*84*), and the ruthenium derivatives have been obtained from the reaction of $Ru_3(CO)_{12}$ with the anions XO_3^{2-} ($X = S, Se, Te$) (*85*). The structure of these complexes is shown in Fig. 6. There is a wide range of ligands which undergo C–H bond fission, and this provides one of the major topics of interest in the following sections (III,D and III,E)—the chemistry of alkenes and alkynes, which is dominated by this effect.

The interaction of water with the metal carbonyls of osmium and ruthenium has proved to be a very facile route to the metal carbonyl hydrides (*86*). The corresponding oxygen derivative, $H_2Os_3(CO)_9O$, has not been identified in these reactions. There is a wide range of products, summarized in the following chemical equations:

$$Ru_3(CO)_{12} + H_2O \xrightarrow{130-150^\circ C} H_2Ru_4(CO)_{13} + H_4Ru_4(CO)_{12}$$

$$\begin{aligned}Os_3(CO)_{12} + H_2O \xrightarrow{230^\circ C} HOs_3(CO)_{10}(OH) &+ H_2Os_4(CO)_{13} + H_4Os_4(CO)_{12} + H_2Os_5(CO)_{15}\\ &+ H_2Os_5(CO)_{16} + H_2Os_6(CO)_{18} + H_2Os_7(CO)_{19}C\end{aligned}$$

For osmium, many of the higher polynuclear hydrides arise from the reaction of the higher polynuclear carbonyls with water, and their presence in the above reaction possibly occurs via their intermediate formation, although pyrolysis of $H_4Os_4(CO)_{12}$ at 230°C also leads to production of the higher cluster compounds. These reactions with water do, however, emphasize the potential intermediacy of carbonyl hydrides in many reactions reported in the literature. The small scale under which many reactions of osmium carbonyl are carried out, coupled with the high molarity of water in many organic solvents, can lead to the production of relatively large concentrations of hydridocarbonyls in these reactions, and in many reactions reported hydrido derivatives are isolated from systems in which no hydrogen appears to be present. The overall chemical reaction that occurs appears to be re-

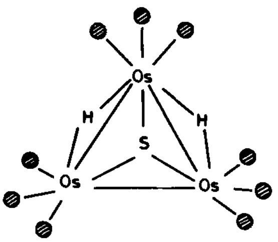


FIG. 6. Molecular structure of $H_2Os_3(CO)_9S$.

lated to the water–gas shift reaction, and it is interesting to note that carbon dioxide was detected in the above reactions.

$$CO + H_2O \rightleftharpoons H_2 + CO_2$$

It has been shown that $Ru_3(CO)_{12}$ in basic solution acts as an effective catalyst for the water–gas shift reaction, the active species being considered to be $[H_3Ru_4(CO)_{12}]^-$ and $[HRu_4(CO)_{13}]^-$. Interestingly, the mixed hydridocarbonyl $H_2FeRu_3(CO)_3$ is the most effective catalyst for this process (*87*).

D. Bonding to Alkenes

1. *Monoolefins*

The various modes of bonding that have been observed for alkenes to the trinuclear osmium clusters are shown in Fig. 7 [see (*88*)]. The simple π-bonded structure (a) is relatively unstable and readily converts to (c); the vinyl intermediate (b) is obtained by interaction of alkene with $H_2Os_3(CO)_{10}$ and also readily converts to (c) on warming. Direct reaction of ethylene with $Os_3(CO)_{12}$ produces (c), which is considered to be formed via the sequence (a) → (b) → (c) and (d). Both isomers (c) and (d) are observed and involve metal–hydrogen and metal–carbon bond formation at the expense of carbon–hydrogen bonds. In the reaction of $Os_3(CO)_{12}$ with C_2H_4, the complex $H_2Os_3(CO)_9C_2H_2$, (c), is formed in preference to (d). Acyclic internal olefins also react with the carbonyl, with isomerization, to yield a structure related to (c). Structure (c) is

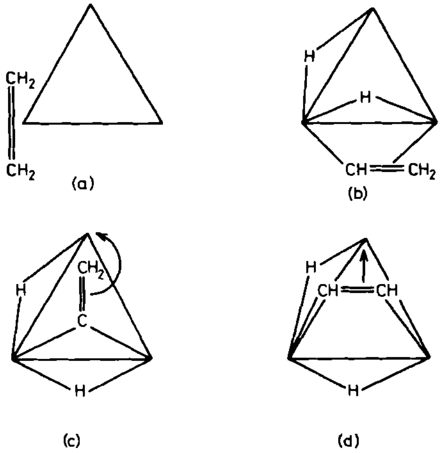
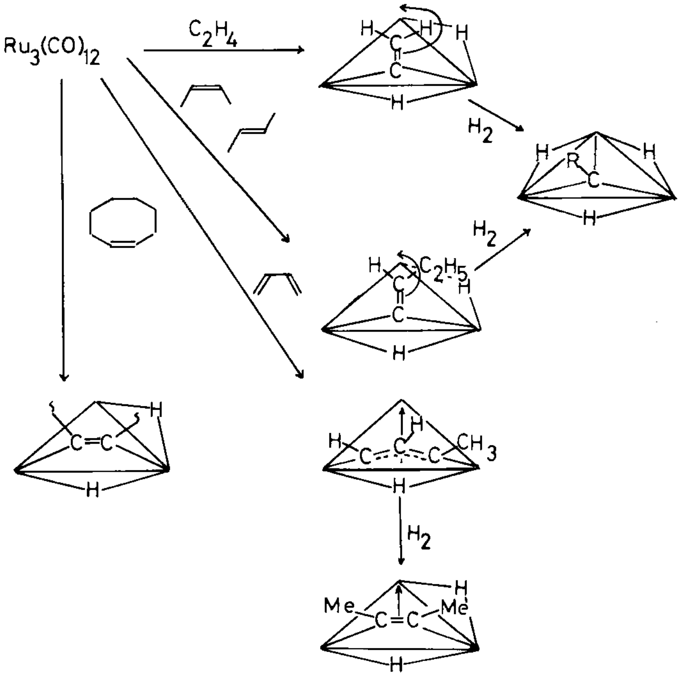


FIG. 7. Bonding modes observed for C_2 units bonded to Os_3 triangle.

termed a 1:1 complex and (d) a 1:2 complex, denoting the carbon atoms involved in σ-bonding to the metal system. The class (d) type of bonding can be obtained for acyclic complexes via the π-allyl complex, obtained from diene interaction with the carbonyl, followed by hydrogenation. In cyclic monoene systems, this is the only bonding isomer found, since formation of a 1:1 bonding mode could only occur via C–C bond rupture. Scheme 1 summarizes some of the important reactions of olefins with $Ru_3(CO)_{12}$ (*89, 90*).

The chemistry of the 1:1 and 1:2 complexes differs with respect to hydrogenation (*84, 89*). The 1:2 derivatives are inert to hydrogenation, while the 1:1 compounds are smoothly transformed into an ethylidene complex (see Scheme 1). This difference in behavior may well reflect the cause of differences in behavior of olefins on metal surfaces toward hydrogenation. The ethylidene complex may be converted back to the olefin adduct by reaction with trityl ion. The ethylidene adduct was first obtained for ruthenium by interaction of ethylene with $H_4Ru_4(CO)_{12}$ (89), and is structurally related to the corresponding cobalt derivatives, $Co_3(CO)_9RC$. As discussed above, the structure has been established in detail and involves a capping of the metal triangle



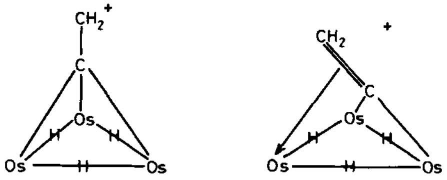
SCHEME 1. Some reactions of $Ru_3(CO)_{12}$ with alkenes.

by the RC group, with the hydrogen atoms on the other side of the metal plane.

The structural-chemical variations that can appear in systems of this kind may be important in explaining the differences that can occur in catalytic processes, between different metals, or even different crystallographic faces of a given metal surface. It has been found that in cluster complexes the bonding of the organic group to a cluster may vary with variation in metal or cluster composition. As indicated above, ethylene reacts with $Os_3(CO)_{12}$ to yield a 1:1 derivative, but with $H_4Os_4(CO)_{12}$ yields a tetranuclear cluster with a 1:2 alkene bonding mode (*91*). A 1:2 isomer has been isolated with $Os_3(CO)_{12}$, but appears to be by far the less stable of the two isomeric forms. The difference in the relative stability of these two forms may be a reflection of the difference toward hydrogenation: the 1:1 isomer appears to hydrogenate readily, while the 1:2 isomer is inert.

A more subtle variation in structure arises in comparing, the "carbonium ions" of cobalt and ruthenium or osmium clusters, derived from the compounds $Co_3(CO)_9(CR)$ and $H_3M_3(CO)_9(CR)$ (M = Ru or Os). Recently, Seyferth (*92*) prepared the primary carbonium ion $[Co_3(CO)_9{-}C{=}CH_2]^+$ for which he proposed the structure shown in Fig. 8a. The related osmium complex may be obtained by protonation of the osmium-ethylene adduct $[H_2Os_3(CO)_9(C{=}CH_2)]$ (*93*). This reaction occurs in a variety of acids, and the same product may be obtained by hydride ion abstraction with the Ph_3C^+ ion in liquid sulfur dioxide. The ^1H-NMR spectrum of the osmium ion has two high-field hydride signals, with an intensity ratio of 1:2 indicative of nonequivalence in the hydrogen positions around the metal triangle. This has been taken to indicate a structure of the form Fig. 8b.

Both the 1:1 and the 1:2 bonded alkenes should show structural isomers, with, for the ethylene adduct, nonequivalence of the two protons bonded to the carbon. For substituted olefins, it is often possible to detect the presence of both isomeric forms, especially with the osmium derivatives. However, all these molecules are fluxional and the flux-



(a) (b)

FIG. 8. Possible molecular structures of $[H_3Os_3(CO)_9CCH_2]^+$ cation.

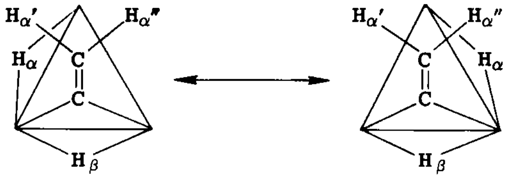
ional nature of these alkene complexes has been studied in detail by both ^1H- and ^{13}C-NMR spectroscopy. Some of the relevant data are given in Table VII. In summary, for the 1:1 complexes the initial process observed is the equilibration of proton positions α' and α''. This may occur by other migration of the H(α) proton to the unprotonated metal–metal bond or by a rotation of the olefin group on the metal triangle. Evidence in favor of the first alternative is provided by using an olefin in which a chiral center is induced on coordination to the metal cluster (*21a*). The two isomers of the olefin complex $H_2Os_3(CO)_9C(1){:}C(2)(CH_3)(CH_2CH(CH_3)_2)$ were prepared and their NMR spectra recorded in deuterochloroform. The olefin carbon (2) is a chiral center produced on coordination to the metal framework. On equilibration of the methyl resonances of the group directly bonded to this carbon (2) (i.e., isomerization), the diastereotopic splitting observed for the isopropyl methyl group remains, implying that the equilibration process does not involve the breaking of the metal–olefin bond and hence transposition of the H(α) proton between the sides of the metal triangle. The final process observed is the equilibration of the protons H(α), and H(β).

For the 1:2 complexes, a full ^1H- and ^{13}C-NMR study has been carried out and has been interpreted on the basis of a similar process initially involving the movement of the H(α) atom between the two metal edges and finally the equilibration of the H(α)/H(β) systems (*90*). The

TABLE VII

ACTIVATION PARAMETERS FOR LIGAND MOBILITIES IN $H_2M_3(CO)_9C_2H_2$ COMPOUNDS (M = Ru OR Os)

		M–H		C–H	
Olefin	Metal	T (°C)	ΔG (kcal mol^{-1})	T (°C)	ΔG (kcal mol^{-1})
Cyclooctene	Ru	−9	11.8	—	—
Cyclooctene	Os	97	16.9	—	—
Ethylene 1:1	Ru	>100	>17.0	−4	13.4
Ethylene 1:1	Os	>115	>17.0	72	20.3
Ethylene 1:2	Ru	−5	12.0	−20	12.1
Ethylene 1:2	Os	−100	8.0	—	—



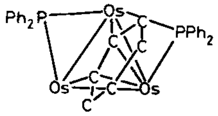


FIG. 9. Molecular structure of $H_2Os_3(CO)_7C_6H_4(PPh_2)_2$.

^{13}C NMR of the carbonyl groups also is consistent with this latter step, but may equally be interpreted as involving a rotation of the olefin about the metal triangle, a process not envisaged to occur with the 1:1 adducts (*96*). A recent study of the ^1H-NMR spectra, particularly of the methylene protons of the 1:2 adduct formed by indene and $Os_3(CO)_{12}$, also indicates a rotation of the olefin fragment about the metal triangle (*97*).

A related bonding pattern to the 1:2 alkene systems has been observed on coordination of benzene (*98*). The compounds were first identified in the form of their phosphine-substituted derivatives (see Section III,D), but Deeming was able to show that benzene reacts slowly with $Os_3(CO)_{12}$ to yield the parent compound $H_2Os_3(CO)_9(C_6H_4)$. From an X-ray determination (*99*) of the structure of the phosphine adducts, the "benzene" was shown to cap the Os_3 metal triangle with an edge-bridging structure, similar to that proposed for a 1:2 olefin interaction (see Fig. 9). From a study of the related complexes $Os_3(CO)_7(EMe_2)_2(C_6H_4)$ (E = As, P), Deeming has been able to show, in an elegant study of the temperature-dependent NMR spectra of these compounds, that the organic ring, bonded by carbon atoms ortho to the Os_3 triangle and inclined at an angle of 70°, undergoes stepwise rotation as illustrated in Fig. 10.

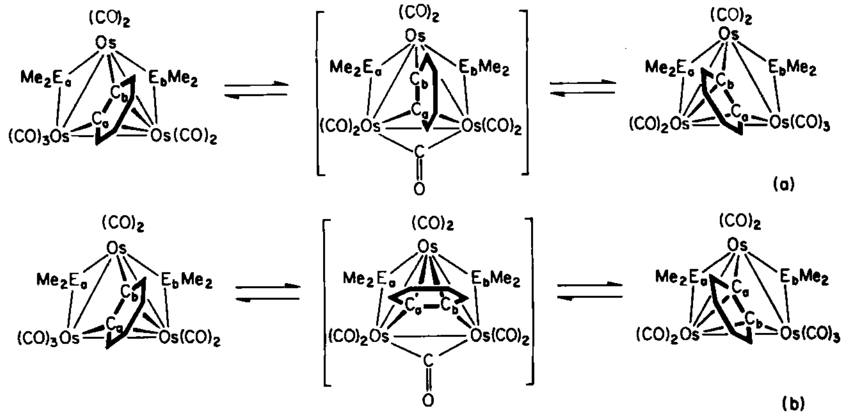


FIG. 10. Mechanism of C_6H_4 mobility in $H_2Os_3(CO)_7C_6H_4(PPh_2)_2$.

2. *Oligoolefins*

Initial studies in this area were concerned with the nonconjugated diene 1,5-cyclooctadiene. With $H_4Ru_4(CO)_{12}$, a variety of products were observed and illustrated a range of bonding potentials within these systems (*90*). Thus, a tetranuclear complex $Ru_4(CO)_{11}(C_8H_{10})$ involves a "butterfly" bonding pattern (*100*) similar to that observed from acetylene reactions with cobalt carbonyls, plus a π-olefin interaction of the remaining olefin group with one metal center (see Fig. 11). A number of trinuclear adducts were also isolated, a major component being the monohydride $HRu_3(CO)_9C_8H_{11}$, in which the organic group is bonded by a π-allyl grouping to the metal triangle. This complex reacts smoothly with hydrogen to give the cyclooctadiene derivative $H_2Ru_3(CO)_9(C_8H_{12})$, which may also be obtained by the direct interaction of cyclooctadiene with $Ru_3(CO)_{12}$ (*90*).

In contrast to the behavior with the hydridocarbonyl $H_4Ru_4(CO)_{12}$, 1,5-cyclooctadiene reacts with $Ru_3(CO)_{12}$ to yield, as the main product, the mononuclear compound $Ru(CO)_3(C_8H_{12})$ (*101*). This complex provides a starting point for the preparation of a range of tricarbonylruthenium–diene systems by a simple displacement reaction. This is useful since, in general, reaction of dienes with $Ru_3(CO)_{12}$ leads to metal trinuclear complexes. The reaction of 1,3-cyclooctadiene with $Ru_3(CO)_{12}$ gives a mixture of products, the main component of which is the π-allylic complex $HRu_3(CO)_9(C_8H_{11})$ (*90*) obtained with the 1,5 isomer. A dihydrido derivative, $H_2Ru_3(CO)_9C_8H_{10}$, in which only one olefinic double bond is coordinated (as a 1:2 adduct), is also produced.

Other conjugated diene systems readily react with either H_4Ru_4-$(CO)_{12}$ or $Ru_3(CO)_{12}$, to yield π-allyl complexes. Thus, butadiene yields the crotyl derivative $HRu_3(CO)_9C_4H_5$. The X-ray structure of the related adduct formed from *cis–trans-* or *trans–trans-*2,4-diene is shown in Fig. 12. The hydride is considered to bond to the Ru(1)–Ru(2) edge, as this is the longest metal–metal bond in the structure; and in the

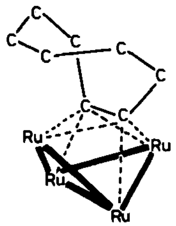


FIG. 11. Molecular structure of $Ru_4(CO)_{11}C_8H_{10}$.

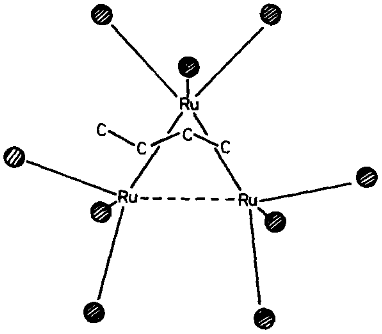


FIG. 12. Molecular structure of $HRu_3(CO)_9C_4H_7$.

^{13}C-NMR spectrum, only the Ru(3) carbonyl groups are not affected by proton decoupling (*102*). An intermediate isomeric form of the complex $HRu_3(CO)_9(C_6H_9)$ has also been isolated, and the X-ray structure (Fig. 13) establishes the coordination of a π-allene group (*103*). This isomer converts to the π-allyl derivative on warming. π-Allyl derivatives may

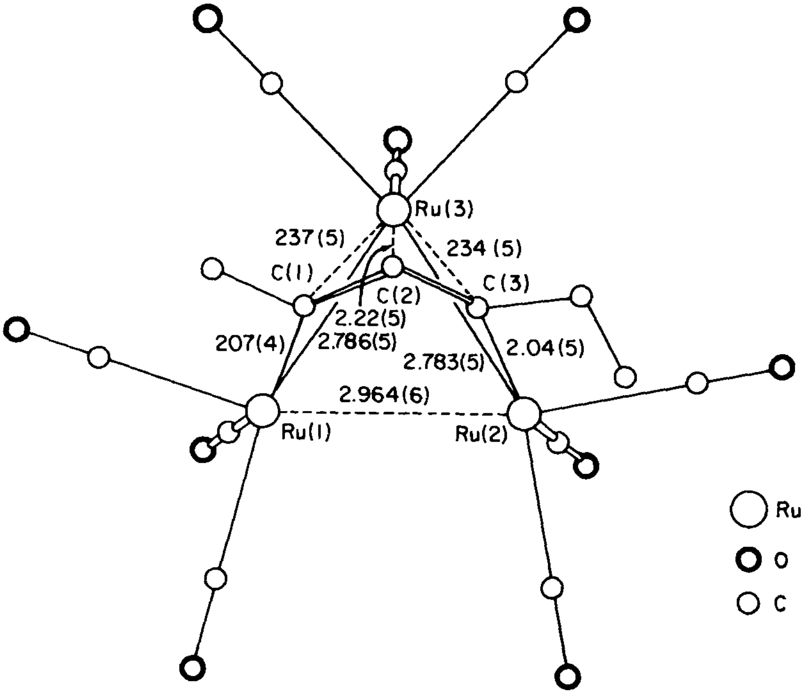
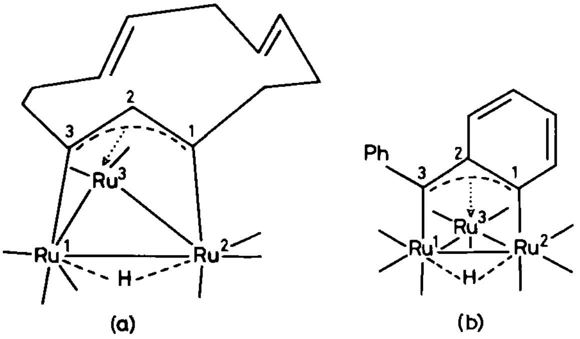


FIG. 13. Molecular structure of $HRu_3(CO)_9C_6H_9$.

also be formed by hydrogen abstraction from monoolefins. Thus, 1-butene reacts with $Ru_3(CO)_{12}$ to yield, among other products, the π-crotyl derivative, $HRu_3(CO)_9(CH{\cdot}CH{\cdot}CHMe)$, which, on hydrogenation, yields the 2-butene cluster $H_2Ru_3(CO)_9(CH_3C{=}CCH_3)$ (*94*) (see Scheme 1).

π-Allyl compounds are also readily formed via the interaction of more complex polymeric systems. Thus, the cyclic polyene cyclododeca-1,5,9-triene (*104*) with $Ru_3(CO)_{12}$ gives a good yield (70%) of the π-allyl species shown in Fig. 14a. This structure is closely related to a complex obtained by Fischer *et al.* (*105*) by reaction of phenyllithium with $Ru_3(CO)_{12}$ (Fig. 14b).

Another structural type has been observed by utilizing seven-membered ring systems. With cycloheptatriene, $Ru_3(CO)_{12}$ yields a trinuclear species involving two cycloheptatriene moieties $Ru_3(CO)_6(C_7H_7)(C_7H_9)$ (*106*), in which one ring bonds via a dienyl group (C_7H_9) to one ruthenium center, and the other via a delocalized bond to the two remaining ruthenium atoms (see Fig. 15). Dienyl complexes of the six-membered ring (C_6H_7) have also been prepared for osmium clusters (see Section III,D). Two types have been identified, with the dienyl group coordinated to one metal center, $[C_6H_7Os_3(CO)_{10}]^+$, and also to all three metal centers in $[HOs_3(CO)_9(C_6H_7)]$ (*107*). This latter complex reacts with the trityl ion to yield an ion $[HOs_3(CO)_9(C_6H_6)]^+$ in which there is



(a) (b)

	(a)	(b)
Ru^1-Ru^2	2·921	2·914 Å
Ru^1-Ru^3	2·773	2·773
Ru^2-Ru^3	2·779	2·776
Ru^1-C^3	2·04	2·08
Ru^2-C^1	2·04	2·10
Ru^3-C^2	2·15	2·36

FIG. 14. Molecular structure of (a) $HRu_3(CO)_8C_{12}H_{15}$ and (b) $HRu_3(CO)_9C_{13}H_{10}$.

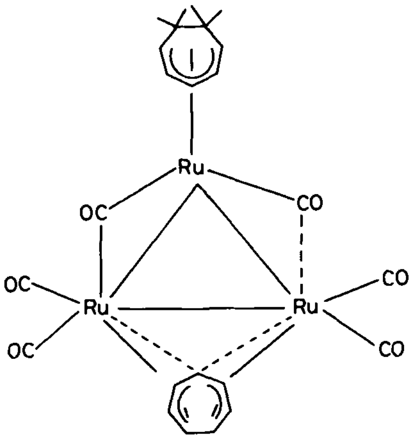


FIG. 15. Molecular structure of $Ru_3(CO)_6(C_7H_7)(C_7H_9)$.

only one NMR singlet for the hydrogens of the benzene ring. The benzene is coordinated to all three metal centers as a six-electron donor to yield a symmetrically bound complex.

It is perhaps important to emphasize that, in the above reactions, often a range of products is formed, and the compounds identified by X-ray structure analysis are not necessarily the major products of the reactions.

E. BONDING TO ALKYNES

As may be anticipated from the chemistry of the related iron complex, which has been extensively reviewed (*108*), the interaction of alkynes with both $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ leads to a range of complexes involving addition of one or more acetylenic units to the cluster.

For iron, dinuclear, trinuclear, and tetranuclear metal species have been identified. Thus, the reactions of $Fe_3(CO)_{12}$ with a range of acetylenes, RC_2R^1, and HC_2R, ($R = R^1 =$ H, Me, Et, *n*-Pr, *t*-Bu, and Ph) have been studied. Binuclear complexes involving cyclization of three acetylene groups, $Fe_2(CO)_6(RC_2R^1)_3$ (*109*), and cyclic molecules produced by CO insertion into acetylenic fragments have been identified, e.g., $[Fe_2(CO)_5(RC_2R^1)_3CO]$ (*110, 111*), and $[Fe_2(CO)_6(RC_2R^1)_2CO]$ (*112*). Ferracyclopentadiene rings have been established in the complexes $Fe_3(CO)_8(RC_2R^1)_2$ (*113*) and $Fe_2(CO)_8(RC_2R^1)_2$ (*114*), and a planar ferracyclohexadiene ring has been identified in the compound $Fe_3(CO)_8(HC_2Me)_3$ (*115*). Methylacetylene reacts with $Fe_3(CO)_{12}$ to give in a low yield the two complexes $Fe_3(CEt)(C_5H_2Me)_2(CH{=}CH_2)(CO)_8$ and $Fe_3(CO)_8(HC_2Me)_4$ (*116*).

Another complex involving the formation of a cyclopentadienyl unit is obtained from the interaction of ethyl or propyl acetylene with $Fe_3(CO)_{12}$ *(117)*. The products contain the complexes $Fe_3(CO)_7(HC_2R)_4$ (R = Et, *n*-Pr), and the crystal structure of the ethyl derivative indicates the presence of the substituted 1,2,3-triethylcyclopentadienyl group bonded to one iron center with an ethylallyl group σ- and π-bonded to the three metal centers. The formation of adducts of this type must involve the fission of the C≡C bond of the acetylene.

More recently, tetranuclear complexes, related to those previously obtained for both ruthenium and osmium, have been obtained for iron, and their structures have been established by X-ray analysis *(118)*. The reported adducts are $[Fe_4(CO)_{11}(RC_2R^1)_2]$ ($R = H$, $R^1 =$ Me, Et, *n*-Pr; $R = R^1 =$ Me), and are obtained in very low yield (<1%). For $R = H$, $R^1 = C_2H_5$, the structure is shown in Fig. 16. This involves a distorted tetrahedral metal system with the two alkyne groups bonding in a manner similar to that observed for the "butterfly" molecule $[Co_4(CO)_{10}(EtC_2Et)]$ *(119)*.

The variety of these products and the complexity of the structural forms observed emphasize the difficulties in elucidating the structures of these compounds by methods other than X-ray analysis. The bonding of the alkyne fragment in these complexes involves major changes in the carbon–carbon distance, as well as deviation of the molecule from linearity. Table VIII *(57, 100, 113, 118–128)* includes some of the C–C distances for various modes of bonding.

Two basic structural modifications of acetylene bonding to all three

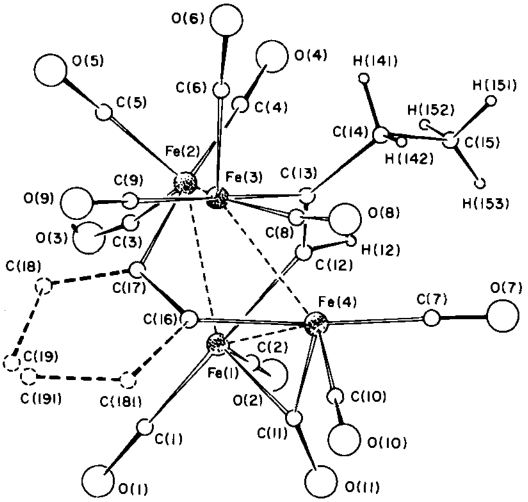


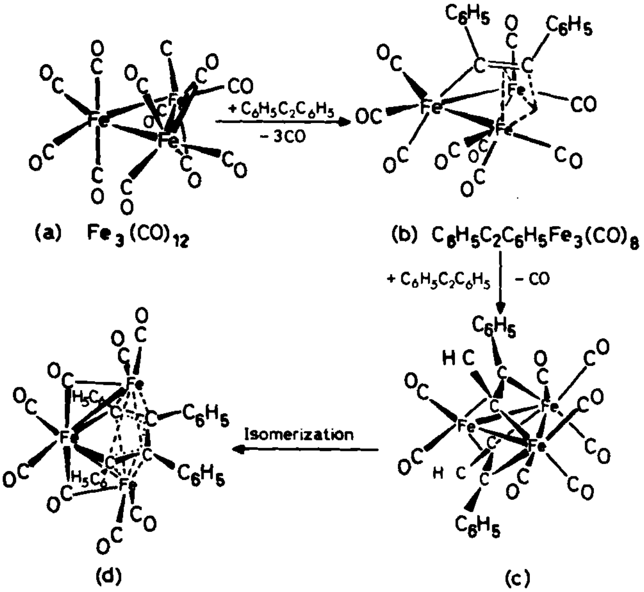
FIG. 16. Molecular structure of $Fe_4(CO)_{11}(HC_2Et)_2$.

TABLE VIII

C–C DISTANCES IN SOME ALKYNE CLUSTER COMPOUNDS

Compound	Coordination mode	C–C Distance (Å)	Ref.
$Fe_3(CO)_8(PhC_2Ph)_2$	μ_3–η^1	1.395 1.375	*113*
$Ni_4(CN\text{-}t\text{-}Bu)_4(PhC_2Ph)_3$	μ_3–η^2	1.344	*120*
$Ru_3(CO)_9(C_2\text{-}t\text{-}Bu)H$	μ_3–η^2	1.315	*57*
$Fe_3(CO)_7(C_2Ph)(\eta\text{-}C_5H_5)$	μ_3–η^2	1.299	*121*
$Fe_3(CO)_9(PhC_2Ph)$	μ_3–η^2	1.409	*122*
$Os_3(CO)_9(PhC_2Ph)_3$		1.33	*123*
$Co_4(CO)_{10}(EtC_2Et)$	μ_4–η^2	1.44	*119*
$Ru_4(CO)_{11}(C_8H_{10})$	μ_4–η^2	1.43	*100*
$Fe_4(CO)_{11}(HC_2Et)_2$	μ_4–η^2	1.374 1.394	*118*

metals in triangular metal units have been identified, which may be typified by the iron complex found from interaction of diphenylacetylene with $Fe_3(CO)_{12}$. The initial product of the reaction, $Fe_3(CO)_9(PhCCPh)$, has a structure shown in Fig. 17b, in which the acetylene fragment lies symmetrically across a triangular edge with one carbon lying outside the metal triangle and the other carbon lying



(a) $Fe_3(CO)_{12}$ (b) $C_6H_5C_2C_6H_5Fe_3(CO)_8$

(d) (c)

FIG. 17. Products of the reaction of $Fe_3(CO)_{12}$ with Ph_2C_2.

above its center (*122*). The acetylene group must contribute six electrons to the metal cluster of the compound to maintain the same electronic structure as the parent carbonyl. This complex is transformed by excess of diphenylacetylene into a violet isomer, $(Ph_2C_2)_2Fe_2(CO)_8$, which has a structure shown in Fig. 17c. In this instance, the two acetylene groups are bonded as four-electron donors, involving the formation of two σ-bonds to two metal centers and two electron π-interactions with the remaining metal. In this instance, the C–C bond of the acetylene group lies parallel to one edge of the metal triangle, and both carbon atoms lie "within" the metal triangle. The violet isomer, on warming, is converted to a black isomer, in which the presence of a ferracyclopentadiene ring is observed (Fig. 17d). Thus the formation of these five-membered metallocyclic systems appears to occur on the metal triangular cluster by the addition of two units of the acetylenic groups.

This observation may well explain the considerable difference between metal–olefin and metal–acetylene chemistry observed for the trinuclear metal carbonyl compounds of this group. As with iron, ruthenium and osmium have an extensive and rich chemistry, with acetylenic complexes involving in many instances polymerization reactions, and, as noted above for both ruthenium and osmium trinuclear carbonyl derivatives, olefin addition normally occurs with interaction at one olefin center. The main metal–ligand framework is often the same for both acetylene and olefin adducts, and differs in that, for the olefin complexes, two metal–hydrogen bonds are formed by transfer of hydrogen from the olefin. The steric requirements of these two edge-bridging hydrogen atoms appear to be considerable and may reduce the tendency for the addition of the second olefin molecule to the metal cluster unit and hence restrict the equivalent chemistry to that observed for the acetylene derivatives.

If this is so, then in higher clusters, where more than one face is available, a more extensive olefin chemistry may be anticipated (see below). Certainly, in complexes of this nature, the presence of bridging hydrogen atoms has been found to impose severe restrictions on the reactivity of molecules, and this may, in part, be associated with these steric requirements.

It is convenient to discuss the interaction of alkynes with ruthenium and osmium decacarbonyls separately.

1. Ruthenium

The chemistry of the reaction of ruthenium decacarbonyl and alkynes has been less extensively studied. Two classes of reaction appear to occur, depending on the presence or absence of a hydrogen in the alkyne. We will first discuss the chemistry of monosubstituted alkynes and then that of disubstituted alkynes. The structure of the reaction product of 3,3-dimethyl-1-butyne with $Ru_3(CO)_{12}$ has been of central importance to the structural chemistry of the monosubstituted alkynes (*57*). A combined X-ray and neutron diffraction study of the product, $HRu_3(CO)_9C_2C(Me)_3$, has not only established the basic molecular framework but also the position of the hydrogen (Fig. 18). The reaction has brought about the transfer of the acetylenic hydrogen to the metal triangle. The alkyne residue is oriented along the median of the metal triangle with one of the carbon atoms outside the metal triangle, involving the alkyne in a $\mu_3-\eta_2$ bonding scheme. The relationship between alkyne and alkene bonding in these structures is emphasized by the reactivity of this complex. Reaction of this complex with hydrogen or acid leads to addition reactions (*124*). Hydrogen reacts to yield the dihydride $H_2Ru_3(CO)_9(HC_2CMe_3)$, which is related to the alkene adducts prepared as above. Alternatively, protonation of the complex leads to the dication $[H_2Ru_3(CO)_9HC_2CMe_3]^{2+}$, in which protonation of both the metal triangle and the organic ligand has occurred.

Complex condensation products are obtained by reaction of the alkyne complex with excess of 3,3-dimethyl-1-butyne, which yields two isomeric products of formulas $Ru_3(CO)_6[HC_2C(Me)_3\text{-}COCH_2CMe_3][HC_2CMe_3]_2$ (*125*). The X-ray structure of one of those adducts (Fig. 19) shows that both dimerization of two alkyne molecules and the insertion of carbon monoxide into the alkyne metal bonds have occurred. The Ru–Ru distances of 2.820, 2.828, and 2.686 Å in the ring are of interest. The value of 2.686 Å is one of the shortest found in a

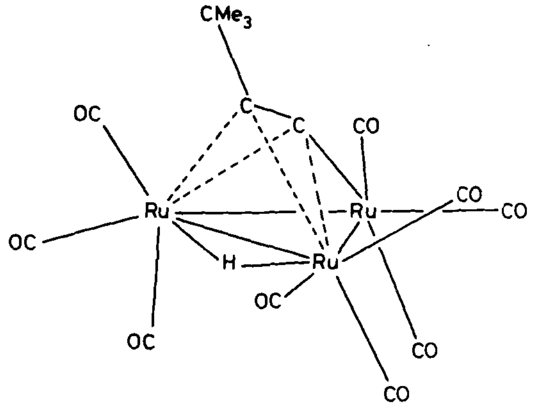


FIG. 18. Molecular structure of $HRu_3(CO)_9C{\cdot}CMe_3$.

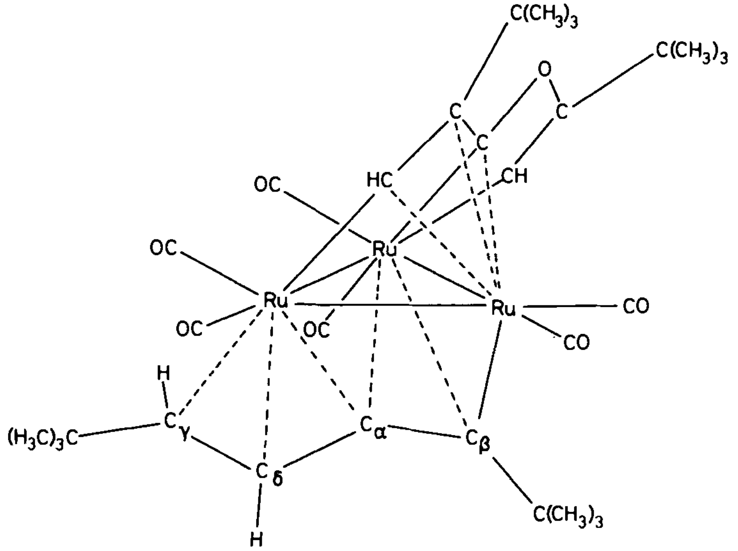


FIG. 19. Molecular structure of $Ru_3(CO)_6[HC_2CMe_3{\cdot}CO{\cdot}CH_2{\cdot}CMe_3]$.

ruthenium complex. The structure of the second isomer has not been determined. A complex carbonyl substitution, rather than ligand reaction, is obtained in the reaction of $HRu_3(CO)_9C_2C(CH_3)_3$ with either 2-*cis,* 4-*trans*-hexadiene or 1,5-hexadiene (*126*). The same product, $HRu_3(CO)_7(C_6H_9)(C_6H_{10})$, is obtained in each case (Fig. 20).

A carbonyl substitution reaction accompanied by a ligand hydrogenation has been observed in the reaction of $HRu_3(CO)_9C_2$-*t*-Bu with cyclopentadiene, to yield, among other products, the complex (π-C_5H_5)$Ru_3(CO)_8(CCH_2CMe_3)$, in which the ruthenium metal triangle is capped by the $C{\cdot}CH_2CMe_3$ group (*127*).

The structure and chemistry of disubstituted alkyne complexes may be illustrated by considering diphenylacetylene. Its reaction with $Ru_3(CO)_{12}$ provides a number of compounds which are similar to those obtained for iron and osmium. The ruthenium derivatives, however, have not been studied in the same detail. The reaction between Ph_2C_2 and $Ru_3(CO)_{12}$ leads to a complex mixture of products (*128*). Two isomers, $Ru_3(CO)_8(C_2Ph_2)_2$, were isolated and shown to correspond to the violet and black isomers observed in the corresponding iron chemistry (Fig. 17). An interesting feature of these isomers is the presence of bridging carbonyl groups. Trinuclear adducts of a similar composition to those observed for osmium have also been isolated, but their structures have not been established with certainty, i.e., $Ru_3(CO)_9(Ph_2C_2)$,

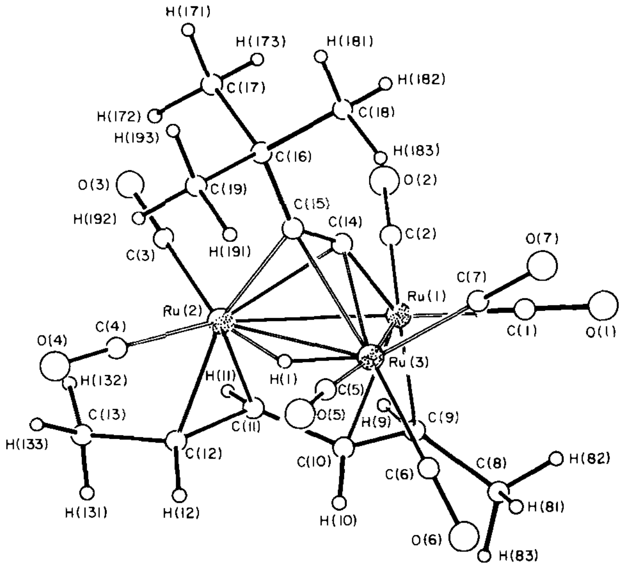


FIG. 20. Molecular structure of $HRu_3(CO)_7(C_6H_9)(C_6H_{10})$.

$Ru_3(CO)_{10}(Ph_2C_2)_2$, and $Ru_3(CO)_9(C_2(Ph)_2)_3$ *(128)*. The dinuclear complex $Ru_2(CO)_6(C_2Ph_2)_2$, containing a metallocyclopentadiene ring similar to that observed for both iron and osmium, is a further product in the reaction; this does imply very similar structures for the trinuclear adducts to those observed for iron and osmium. The carbonyl reacts with tetracyclone to yield the complex $Ru_3(CO)_{10}(C_2Ph_2)_2$, which may be related to the osmium compounds discussed later. Phosphine substitution of the carbonyls in some of these compounds has been established.

The formation of tetranuclear cluster compounds occurs readily with ruthenium. Direct reaction of alkyne with $Ru_3(CO)_{12}$ in refluxing cyclohexane gives the adducts $Ru_4(CO)_{12}(RC_2R^1)$ (where $R = R^1 =$ Ph, CH_3OCH_2; R = Ph, R^1 = Me; R = Ph, R^1 = Et) *(129)*. The X-ray structure of the $Ru_4(CO)_{13}(PhC_2Ph)$ adduct has established a *closo*-Ru_4C_2 unit with the alkyne capping a butterfly arrangement of the four ruthenium atoms *(130)*. These complexes are structurally related to the products obtained from cyclic alkenes with $H_4Ru_4(CO)_{12}$ (see Section III,D).

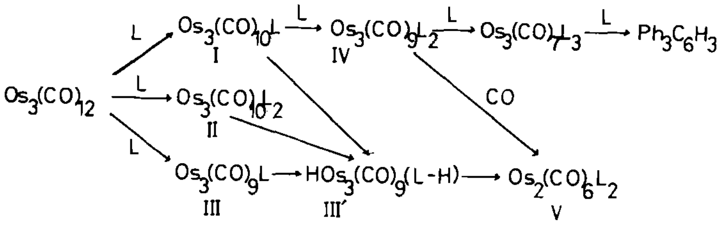
Further reaction occurs with excess alkyne to yield products which may be formally considered as disubstituted adducts, $Ru_4(CO)_{11}(RC_2R^1)(PhC_2R^2)$ (where R = R = Ph; R^2 = Me; R = R = Ph, R^2 = Et; R = Ph, R = R^1 = Me). The structures of these products have not been elucidated in detail; they appear to involve a variety of condensation products of a type similar to those observed for iron.

2. *Osmium*

Reaction of acetylenic complexes with triosmium dodecacarbonyl leads to a variety of products involving one, two, or three acetylenic units. As with ruthenium, for the monosubstituted alkynes, hydrogen transfer can occur to the metal cluster. Thus, $Os_3(CO)_{12}$ and phenylacetylene (L) yield, in refluxing benzene, the derivatives $Os_3(CO)_{10}L$, $Os_3(CO)_{10}L_2$, $Os_3(CO)_9L$, and $HOs_3(CO)_9(L-H)$. The general chemistry is summarized in Scheme 2 (*131*).

The ^{1}H-NMR and infrared spectra of the complex **I** are consistent with the acetylenic group acting as a four-electron donor to the osmium triangle, with a CO group bridging two osmium centers. The two isomers **III** and **III′** are considered to have structures related to $Fe_3(CO)_9C_2(C_6H_5)_2$ and $HRu_3(CO)_9C_2(t\text{-}C_4H_9)$, respectively (see above) and to involve the migration in **III′** of the hydrogen to the metal triangle. Complex **II** is viewed as a single replacement of two carbonyl groups within the metal cluster by two-electron, π-donor, acetylenic groups.

Treatment of these complexes with excess phenylacetylene leads ultimately to the symmetrical triphenyl benzene as the main product, but the intermediate adduct **IV**, $Os_3(CO)_9L_2$, exists in three isomeric forms which are considered to be related to the osmacyclopentadiene complex $Os_3(CO)_9[C_2(C_6H_5)_2]_2$, obtained from reaction of diphenylacetylene with the $Os_3(CO)_{12}$. The structure of this complex has been established by X-ray crystallography (*132*) to be that shown in Fig. 21, with R = R^1 = R^2 = R^3 = Ph. The three isomeric derivatives in the case of the phenylacetylene adduct arise from the various permutations of the phenyl and hydrogen groups around the osmacyclopentadiene ring.



SCHEME 2. Some reactions of $Os_3(CO)_{12}$ with HC_2Ph.

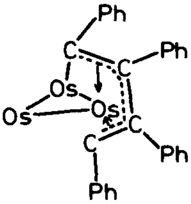
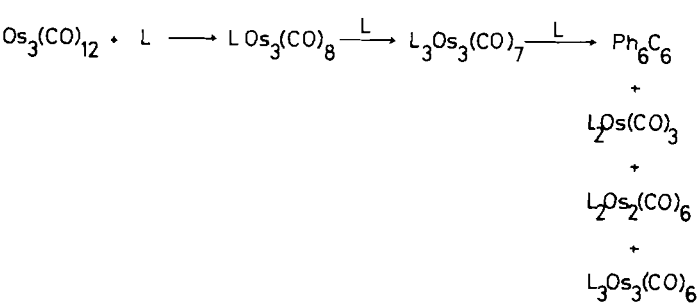


FIG. 21. Molecular structure of $Os_3(CO)_9Ph_4C_4$ (CO groups omitted for clarity).

Reaction of the isomers **IV** with phenylacetylene yields a range of complexes, of which $Os_3(CO)_7L_3$ is one. This is related to the complex $Os_3(CO)_7[C_2(C_6H_5)_2]_3$, obtained in the corresponding diphenylacetylene reaction and shown to be an intermediate in the cyclotrimerization of diphenylacetylene to hexaphenylbenzene (*124*). The structure of this complex is discussed in Section III,F.

Complexes related to those discussed above have been obtained with monosubstituted acetylenes, CH_3C_2H and $C_2H_5C_2H$. With the methylphenylacetylene, a variety of other derivatives are formed in which *meta*-carbon bonding occurs via a methylene group which is formed by hydrogen transfer from the methyl group to the metal. This gives the bonding structure $Os—CH_2—C{\equiv}C—C_6H_5$, with a σ-Os—C bond and π donation from the $C{\equiv}C$ group (*131*).

Reaction of $Os_3(CO)_{12}$ with diphenylacetylene yields as the initial product $[(C_6H_5)_2C_2]_2Os_3(CO)_8$ (Scheme 3) (*133*), which has an osmacyclopentadiene ring formed from fusion of two ligand molecules with a metal center and orthometallation of one of the phenyl groups with an osmium center (see Section III,E). Excess ligand yields the complex $[(C_6H_5)_2C_2]_3Os_3(CO)_7$, which is related to the phenylacetylene adduct above (*124*). The X-ray structure of this complex has been determined (Fig. 22), and involves an osmacyclopentadiene ring with the third



SCHEME 3. Some reactions of $Os_3(CO)_{12}$ with Ph_2C_2.

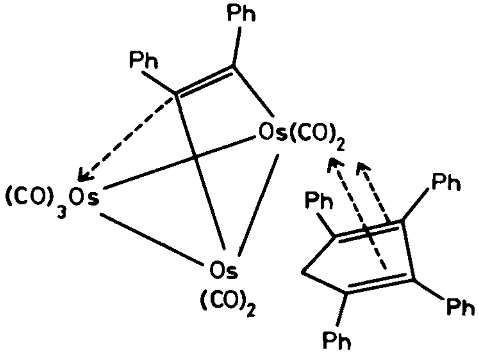


FIG. 22. Molecular structure of $Os_3(CO)_7(Ph_2C_2)_3$.

acetylenic group bonding as a $2\sigma + \pi$ ligand to the Os_3 triangle (*133*). Further reaction yields hexaphenylbenzene and a series of mononuclear, binuclear, and trinuclear adducts. The mononuclear species is considered to be tetraphenylcyclobutadiene tricarbonylosmium, similar to $[(C_6H_5)_4C_4]Fe(CO)_3$, while the binuclear adduct is an osmacyclopentadiene derivative. The structure of the trimeric derivative, $[(C_6H_5)_2C_2]_3Os_3(CO)_6$, has not been determined, but it is believed to involve the linkage of all three ligand molecules, as it readily yields hexaphenylbenzene on heating. The complexes $L'_3Os_3(CO)_7$ have also been identified in the reaction of excess ligand with the complexes $L'_2Os_3(CO)_8$ formed initially by interaction of the free ligand with the parent carbonyl for $L' = (p\text{-}ClC_6H_9)_2C_2$ and $(p\text{-}CH_3C_6H_4)_2C_2$ (*124*).

Extensive studies on the use of $H_2Os_3(CO)_{10}$ rather than the parent carbonyl as a source of the triangular osmium unit have been carried out. In general, the reaction conditions are milder and it is possible to isolate a series of intermediate complexes, and, using this reagent, the diphenylacetylene adduct $(C_6H_5)_2C_2Os_3(CO)_{10}$ has been isolated. The initial product in these reactions is the vinyl derivative $HOs_3(CR^1{=}CHR^2)(CO)_{10}$ ($R^1 = R^2 = H$ or Ph; $R^1 = H$, $R^2 = Me$, Et, Ph, *t*-Bu; $R^1 = Ph$, $R^2 = Me$, Et) as well as the alkenylene derivatives $Os_3(CR^1{=}CR^2)(CO)_{10}$, where $R^1 = R^2 = H$ or Me; $R^1 = H$, $R^2 = Me$. On heating, hydrogen transfer to the metal ring with loss of CO occurs to give complexes of the type $H_2Os_3(C_2R_2)(CO)_9$ and $[HOs_3(C_2R)(CO)_9]$, in which the organic group is bonded to three metal centers (*134–136*).

On the basis of the infrared spectra, the alkenyl complexes are considered to have a structure of the type shown in Fig. 23a, with a bridging CO group. This structure is related to those of the rhodium cyclopentadienyl adducts $Rh_3(C_5H_5)_3(alkyne)(CO)$ (*137*). In the rhodium

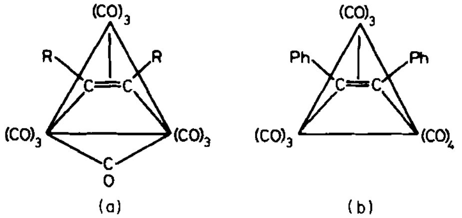


FIG. 23. Molecular structures of (a) $Os_3(CO)_{10}(RC{=}CR)$ and (b) $Os_3(CO)_{10}(PhC{=}CPh)$.

complexes, when the alkyne is hexafluorobut-2-yne, a double-bridge CO group has been established, while when the alkyne is diphenylacetylene, an asymmetric face-bridge CO occurs. The X-ray structure of the diphenylacetylene adduct $[(C_6H_5)_2C_2]Os_3(CO)_{10}$, however, established a nonbridging carbonyl structure, as implied by the infrared spectrum. The structure is shown in Fig. 23b and exhibits an asymmetry of the bonding of the diphenylacetylene group to the cluster, in particular the C=C bond not being parallel to the Os(1)–Os(3) bond (*138*).

This structure emphasizes some of the novel bonding features in this class of compound. Diphenylacetylene may be considered to be a two-electron π-bonded donor to Os(2), and σ-bonded to Os(1) and Os(2), yielding one electron to each metal center. Considering the CO groups to bond in terminal manner, this yields an asymmetry in the electron balance within the molecule which may be compensated by considering the electron-rich Os(1) center donating two electrons to the electron-deficient Os(3) center via a donor bond, a bonding pattern first invoked to explain the structure of the metallacyclopentadiene complex, $Fe_2(CO)_6C_4(CH_3)_2(CH)_2$, shown in Fig. 25 (*139*). This iron complex was one of the first metallacarbocyclic compounds to be prepared via acetylene and iron carbonyl reactions, and has presumably the same structure as the binuclear osmium derivative cited above, $Os_2(CO)_6$-$[(C_6H_5)_2C_2]$. A related structure of a ferrocarbocyclic complex $(C_{12}H_{16})Fe_2(CO)_6$ has also been recently reported and involves a similar bonding pattern (*140*). Cotton (*38*) has pointed out that this electronic imbalance will tend to an asymmetric charge build-up within the metal system, and he associates the semibridging nature of one of the carbonyl groups of the donor metal atom as a method of alleviating this problem. In both structures, the iron–iron distance falls within the range expected for a metal–metal bond (2.49 and 2.46 Å for Fig. 25a and b, respectively), and the presence of a metallocyclic group may lead to bonds in the shorter end of the range for metal–metal systems

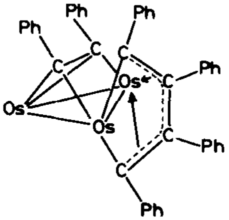


FIG. 24. Molecular structure of $Os_3(CO)_7(Ph_2C_2)(Ph_4C_4)$ (carbonyl groups omitted for clarity).

[cf. distance of 2.61 Å in Fe_2(dipyridyl)$(CO)_7$ (*141*)]. Consistent with the above, two of the carbonyls on the electron-rich metal Os(1) are considered to semibridge to the other metal atoms. However, the metal–metal bond lengths do not reflect this asymmetric charge distribution, the Os(1)–Os(2) and Os(2)–Os(3) bond distances being similar with values of 2.844 and 2.883 Å, respectively. There is, however, a significant shortening of the remaining metal–metal bond, for Os(2)–Os(3), to 2.711 Å. For the related osmacyclopentadiene molecule $Os_3(Ph_4C_4)(CO)_7(Ph_2C_2)$ in Fig. 24, in which two of the carbonyl groups of the Os(1) center have been replaced by four-electron donation from the diene system, the donor metal–metal bond, Os(1)–Os(3), is significantly shorter, at 2.680 Å, than the other metal–metal bonds of 2.814 and 2.744 Å (*133*). This is very close to the value of 2.670 Å reported for the "double-bonded" structure in $H_2Os_3(CO)_{10}$, and emphasizes the effect of these carbocyclic compounds on the metal–metal distance and perhaps the failure of any correlation of bond length with the electronic nature of the metal–metal bond, which seems in this instance to be more directly related to the nature of the ligand polyhedral environment.

When excess of acetylene is used in reaction with $H_2Os_3(CO)_{10}$, a larger range of products is produced; the trinuclear derivatives are

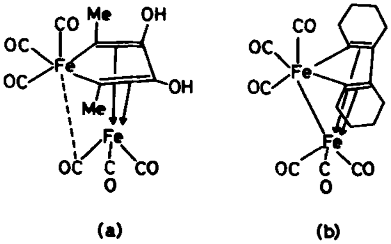


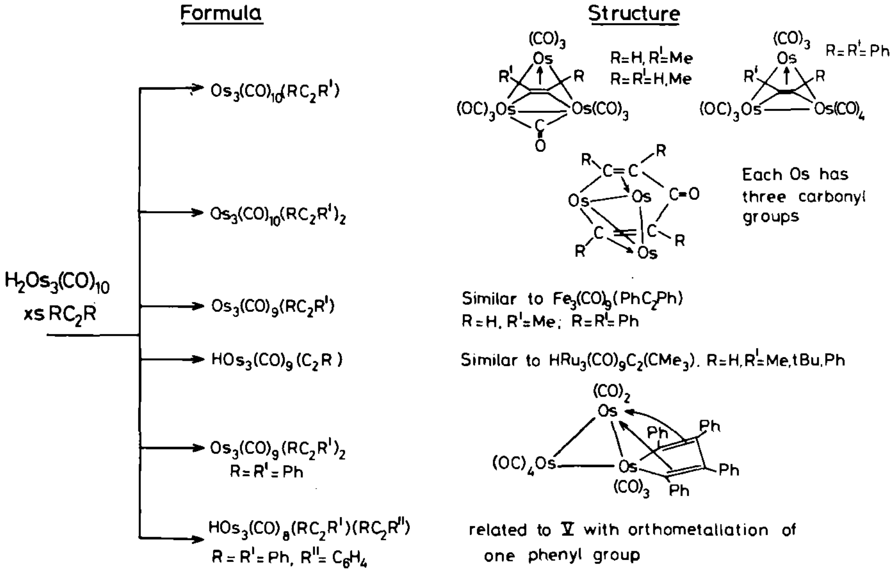
FIG. 25. Molecular structure of (a) $Fe_2(CO)_6[C_4Me_2(OH)_2]$ and (b) $(C_{12}H_{16})Fe_2(CO)_6$.

summarized in Scheme 4, with their proposed structures (*135, 136*). Complexes (V) and (VI) are similar to those previously reported and can be interconverted by a reversible orthometallation reaction of one of the phenyl groups in the substituted osmacarbocyclic ring.

$$Os_3(CO)_9(PhC_2Ph)_2 \underset{CO,\ 20^\circ}{\overset{heat}{\rightleftharpoons}} HOs_3(CO)_8(Ph_2CPh)(Ph_2C_2(C_6H_4))$$

Thus the compound which is formally equivalent to the iron violet and black salts, $Fe_3(CO)_8(Ph_2C_2)_2$, has a totally different structure. Compound (II) is considered to involve a six-membered osmacyclic structure, with one of the CO groups incorporated as a ketonic group. For the monoacetylenes, RC≡CH (R = Me, Et, *t*-Bu, Ph), the reaction occurs with high yields (~20–50%) while disubstituted acetylenes, $RC{\equiv}CR^1$ (R = Ph, R^1 = Me, Et) give low yields (≤3%). As may be expected for unsymmetrically substituted acetylenes, three isomers of the osmacyclic ring are possible, and these are normally observed in approximately equal concentrations (*136*).

A novel bonding pattern has been established from the reaction of phenylacetylene with $H_2Os_3(CO)_{10}$, which gives, in addition to the vinyl derivative $HOs_3(CH{=}CHPh)(CO)_{10}$, a phenyl acetylide adduct



SCHEME 4. Some reactions of the compounds $H_2Os_3(R_2PCX)(CO)_9$ and $H_2Os_3(R_2PCX)(CO)PR_2$ (where X = H or Me).

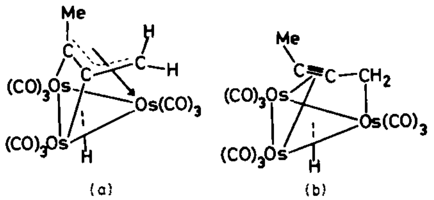


FIG. 26. Possible molecular structures of $HOs_3(CO)_9C_4H_5$ isomer A.

$HOs_3(C{\equiv}CPh)(CO)_{10}$, in which the acetylene behaves as a σ-donor to one osmium center and a two-electron π-donor to another (*134*).

As noted above, hydrogen abstraction onto the metal cage readily occurs for the monosubstituted alkynes; it has also been observed for some alkyl disubstituted derivatives. Thus $Os_3(CO)_{10}(Me_2C_2)$, on warming in heptane, loses carbon monoxide to yield two isomeric forms of a monohydrido species, $HOs_3(CO)_9(C_4H_5)$. The initial isomer formed (A) is transformed in toluene to isomer B. Isomer B is analogous to the ruthenium complex $[HRu_3(CO)_9(C_4H_5)]$, the π-allyl complex formed by interaction of butadiene and $Ru_3(CO)_{12}$ (see Section III,D) (*134*). In the formation of these complexes, two hydrogens have been transferred from a methyl group. Isomer A, which is initially formed, may be an intermediate in this transformation, and two possible structures have been suggested (Fig. 26a and b). The first involves a 1,2 rather than a 1,3 bonding of the π-allyl group, while the second is similar to that already postulated for the bonding of $MeC{\equiv}CPh$ to the osmium cluster.

F. TRINUCLEAR CLUSTERS

The most extensive studies of the chemistry of cluster complexes have been associated with the trinuclear cluster unit, as may be anticipated. A wide range of substitution reactions has been demonstrated for both $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$, with the full range of ligands normally employed in the study of metal carbonyl chemistry. In general, the trinuclear osmium cluster is more readily maintained, ruthenium often giving rise to cluster breakdown, yielding mononuclear and binuclear adducts. This reflects the increased bond energy of the metal–metal bond on descending the triad (see Table X later in this section).

It has been shown that the mechanistic pathway for these reactions can be complex. Thus, for ruthenium, the oxidation of $Ru_3(CO)_{12}$ with halogens, X_2 (X = Cl, Br, I), gives a mixture of the monomeric *cis*-

$Ru(CO)_4X_2$, the dimeric $Ru_2(CO)_4X_4$, the trimeric species $Ru_3(CO)_{12}X_6$, and the polymeric $[Ru(CO)_2X_2]_n$. The relative proportions differ with variation in the reaction conditions. However, the *initial* product in all these reactions is *cis*-$Ru(CO)_4X_2$, which subsequently polymerizes to yield the other derivatives (*142*).

The main preparative method utilized until recently in the preparation of carbonyl-substituted derivatives was either thermal or photochemical (UV irradiation) activation of the cluster. As may be anticipated with many reagents, these techniques lead to a mixture of products, which are normally separated by chromatographic techniques. Thus, with heavier Group V donor ligands (phosphorus, arsenic, or antimony), this leads to mixtures of $M_3(CO)_{12-x}L_x$ ($x = 1-4$) for monodentate groups, and $M_3(CO)_{12-2x}(L-L)_x$ ($x = 1, 2, 3$) for bidentate species (*143*). Substitution normally occurs progressively on different metal centers. The structure of $Os_3(CO)_9L_3$ involves the replacement of an equatorial carbonyl group on each metal center to give a structure of the type shown in Fig. 27 (*144, 145*). This stereochemical arrangement minimizes the steric interaction between the phosphine ligands. In complexes of the type $Ru_3(CO)_{10}(PhPCH_2CH_2PPh)$, and $Ru_3(CO)_8(As-As)_2$ [where As–As = 1,2-bis(dimethylarsino)-3,3,4,4,-tetrafluorocyclobutene], the ligand acts as a bridging group between two metal centers. The structure of the second compound, which has been determined by X-ray analysis is shown in Fig. 28 (*145*). Using the tridentate ligand, $MeSi(PBu_2)_3{=}L$, Masters *et al.* (*146*) have been able to prepare the capped species $[Ru_3(CO)_9L]$ with phosphorus-donor centers. The sensitivity of these reactions to the reaction conditions is greater, and many of the compounds may react further to yield mixed derivatives, or undergo fragmentation of the ligand group while maintaining the cluster identity. The osmium phosphine clusters provided the first example of the wide range of derivatives, with remarkable structural changes that can occur on thermolysis of these types of adducts.

Nyholm *et al.* reported (*147*) that in the reaction of Ph_3P with

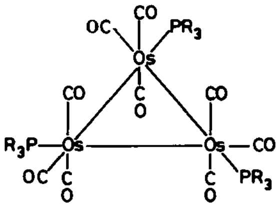


FIG. 27. Molecular structure of $Os_3(CO)_9(PR_3)_3$.

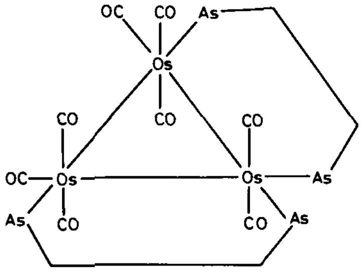


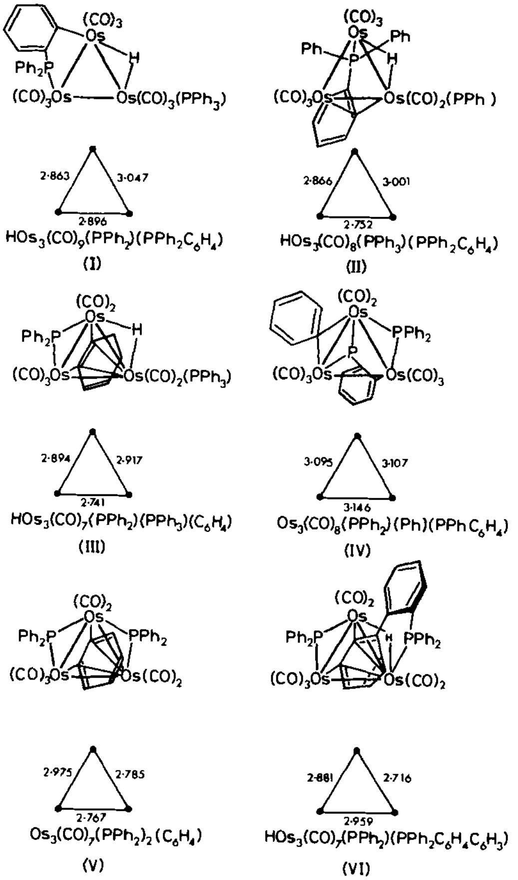
FIG. 28. Molecular structure of $Os_3(CO)_8(diars)_2$.

$Os_3(CO)_{12}$, nine products were obtained. Three of these were identified as the substituted adducts $Os_3(CO)_{12}(Ph_3P)_{12-x}$ ($x = 1, 2$, or 3), but for others, the fission of C–H and C–P bonds had occurred to yield a variety of compounds in which there were radical variations in the structure and mode of bonding of the triphenylphosphine group. Figure 29 shows details of the structures of six of these complexes. As indicated above, significant ligand rearrangements have taken place.

The benzene molecule is attached as a phenyl group, between two metal centers (structure **I**), and as a "benzene" four-electron donor, three-center coordinating group in structures **II**, **VI**, and **X**. The C–C distance in all these molecules is 1.42 Å, and the dihedral angle between the planes containing the osmium atoms and the mean plane of the benzyne in the three complexes is remarkably constant at 69 ± 3°.

A similar range of reactions has also been reported for the ruthenium carbonyl–triphenylphosphine systems (*148*). In these systems, a high percentage of the products were dinuclear, reflecting the weaker bonding in the ruthenium system, and as for some of the osmium complexes discussed above, some contain orthometallated phenylphosphine groups (see Fig. 29, structures **I**, **IV**, **X**).

The chemistry of related complexes has been developed by Deeming *et al.* (*149*), who studied the controlled pyrolysis of the complexes $[Os_3(CO)_{12-x}(EMe_2Ph)_x]$ (E = P, As; $x = 1, 2$). These yield the "benzyne" (C_6H_4) bridge adducts $[HOs_3(C_6H_4)(EMe_2)(CO)_9]$, $[HOs_3(C_6H_4)(PMe_2)(PME_2Ph)(CO)_8]$, $[Os_3(C_6H_4)(EMe_2)_2(CO)_7]$, and $[HOs_3(Me_2PC_6H_4C_6H_3)(PMe_2)(CO)_8]$, as well as some dimeric complexes containing C_6H_4 bridges. On occasion, the alkylphenylphosphine derivatives differ in stoichiometry from the triphenylphosphine adducts by one carbonyl group, i.e., $[HOs_3(C_6H_4)(EMe_2)(CO)_9]$ and $[HOs_3(C_6H_4)(PMe_2)(CO)_8(PMe_2Ph)]$ as compared with $[HOs_3(C_6H_4)(PPh_2)(CO)_7(PPh_3)]$ and the coupled arene systems $[HOs_3[R_2PC_6H_4C_6H_3](PR_2)(CO)_x]$ ($x = 8$ when R = Me, $x = 7$ when R = Ph).



$HOs_3(CO)_9(PPh_2)(PPh_2C_6H_4)$
(I)

$HOs_3(CO)_8(PPh_3)(PPh_2C_6H_4)$
(II)

$HOs_3(CO)_7(PPh_2)(PPh_3)(C_6H_4)$
(III)

$Os_3(CO)_8(PPh_2)(Ph)(PPhC_6H_4)$
(IV)

$Os_3(CO)_7(PPh_2)_2(C_6H_4)$
(V)

$HOs_3(CO)_7(PPh_2)(PPh_2C_6H_4C_6H_3)$
(VI)

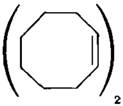
FIG. 29. Some products of the reaction of $Os_3(CO)_{12}$ with PR_3 (R = Ph).

These differences have been attributed to the "benzyne" group behaving as a four- or two-electron donor system. The fluxionality in these molecules has been investigated by NMR studies over a temperature range. These have established that the benzyne ring rotates about the osmium triangle (see Section III,D).

The great tendency for osmium to sever carbon–hydrogen bonds with concomitant formation of metal–hydrogen and metal–carbon bonds is emphasized by the extension of the above class of compounds to alkylphosphine derivatives (*150*). Pyrolysis of the compounds $Os_3(CO)_{12-x}(PR_3)_x$ (R = Me, Et; $x = 1, 2$) gave the hydrido derivatives $H_2Os_3(R_2PCX)(CO)_9$ or $H_2Os_3(R_2PCX)(CO)_8(PR_3)$, where X = H or Me. These complexes involve the ligand R_2PCX, bridging between the three metal centers, as indicated in Scheme 4, for the nonacarbonyl

TABLE IX

PREPARATION OF SUBSTITUTED OSMIUM CARBONYL DERIVATIVES

Method	Comments
1. Thermal photochemical	Leads to a variety of products; distribution dependent on solvent and temperature
2. Displacement reactions	
a.  $Os_3(CO)_{10}$	Both olefin groups coordinated to same metal center
b.  $Os_3(CO)_{10}$	Olefin groups coordinated to different metal centers
c. $(CH_3CN)_2Os_3(CO)_{10}$ $(CH_3CN)Os_3(CO)_{11}$	Groups coordinated to different metal centers; may be replaced sequentially used for production of monosubstitutes
d. $HOs_3(CO)_9SR$	Adds a ligand to one metal center with retention of sulfur coordinated group
3. Addition reactions $H_2Os_3(CO)_{10}$	Useful for preparation of organic unsaturated compounds

species. The derivative obtained from the triethylphosphine was found to undergo dehydrogenation by a series of hydride ion abstraction reactions followed by deprotonation (*151*). This dehydrogenation process was found to be reversible, the compound absorbing hydrogen to give the starting material (see Scheme 4), in a manner reminiscent of the behavior of the ethylidine complexes $[H_3Os_3(CO)_9CMe]$ (see Section III,D). Thermolysis of the deprotonated product leads to C–P bond fission with the production of a 1:2 olefin adduct.

It is apparent that the chemistry of such systems is rich, but the preparation by either thermal or photochemical substitution normally leads to complex mixtures of compounds. Recently, substituted products, which can be prepared in high yield, have been utilized as precursors. Two classes of reactions (Table IX) may be employed for the preparation of cluster derivatives: those involving displacement in systems typified by complexes (a), (b), (c), and (d), or addition reactions to the nominally "unsaturated" species $H_2Os_3(CO)_{10}$ (see also Section II,I,2).

1. Displacement Reactions

The two olefin adducts (a) and (b) differ structurally in that, for the cyclohexadiene, substitution occurs at one metal center, while for the cyclooctene derivative, two metal centers are involved. This allows, in principle, for the production of two isomeric compounds, as has been observed for the two forms of the butadiene-substituted complexes $(C_4H_6)Os_3(CO)_{10}$; one corresponds to coordination of both olefin groups in a cisoid form to one metal center, while the other has a transoid conformation (*152*). In all other cases examined, only one isomer appears to have been isolated.

The cyclohexadiene complex $(C_6H_8)Os_3(CO)_{10}$ is prepared in good yield from reaction of 1,3- or 1,4-cyclohexadiene with $H_2Os_3(CO)_{10}$ (*153*). The complex is stable and readily reacts with a whole range of other ligands to yield the disubstituted compounds. If excess diene is used or the reaction temperature is higher, the complex $HOs_3(CO)_9$-(C_6H_7) is formed. This involves a dienyl ligand coordinated above the osmium triangle to all three osmium centers (*154*), as in Fig. 30. The hydrogen is considered to bond along the Os(1)–Os(3) edge. This complex reacts with trityl ion to give the ion $[HOs_3(CO)_9C_6H_6]^+$ in which the benzene is considered to be symmetrically bonded to the three metals (*154*).

A related dienyl species may be obtained by reaction of the diene complex with trityl ion, when hydride ion abstraction occurs from the diene to yield a dienyl group coordinated to one metal center, $[(C_6H_7)Os_3(CO)_{10}]^+$ (*153*).

Scheme 5 summarizes the types of displacement reactions that have been reported, and it is evident that these provide facile routes to a whole range of adducts, often in high-yield reactions. This is in contrast to the reactions of $Os_3(CO)_{12}$, when some of the intermediate products cannot be isolated. Thus in the reaction of H_2S and $Os_3(CO)_{12}$, the only product identified is the sulfur-capped species, $H_2Os_3(CO)_9S$; the potential intermediate $[HOs_3(CO)_{10}HS]$ is readily formed in the cyclohexadiene reaction and smoothly converts to the capped species on heating.

The majority of the reactions given in Scheme 5 involve the forma-

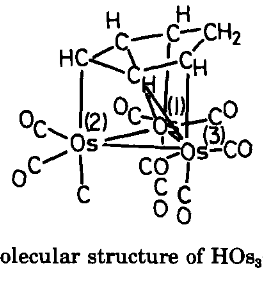
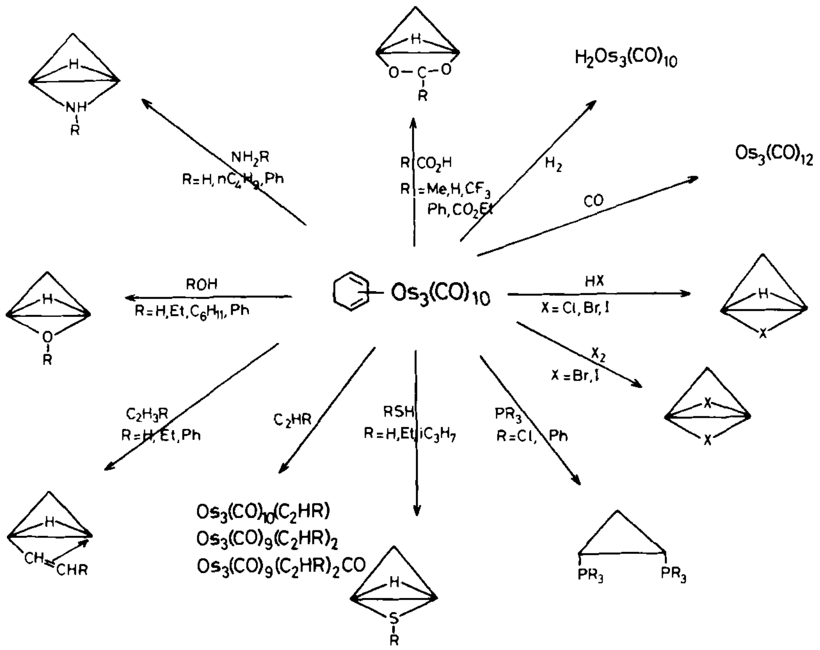


FIG. 30. Molecular structure of $HOs_3(CO)_9C_6H_7$.



SCHEME 5. Reactions of cyclohexadiene triosmium decacarbonyl.

tion of hydrido species. In the reaction with CF_3CO_2H, it has been shown that the initial step is attack at the diene to produce a π-allylic intermediate which is then converted to the substituted hydrido species. Reaction with alkene and alkynes often leads to the same products as with $Os_3(CO)_{12}$ *(155)*. However, for alkenes, the intermediate vinyl derivatives may be isolated, and for the alkynes the reaction products which have been summarized in the previous section are produced in good yields but with a different distribution of compounds.

The diene may be displaced by hydrogen to revert to the hydridocarbonyl, $H_2Os_3(CO)_{10}$, and this forms the basis for a cyclic catalytic reaction for the hydrogenation of the diene to the monoene:

$$H_2Os_3(CO)_{10} \underset{H_2}{\overset{\bigcirc}{\rightleftharpoons}} Os_3(CO)_{10}(C_6H_8) + C_6H_{10}$$

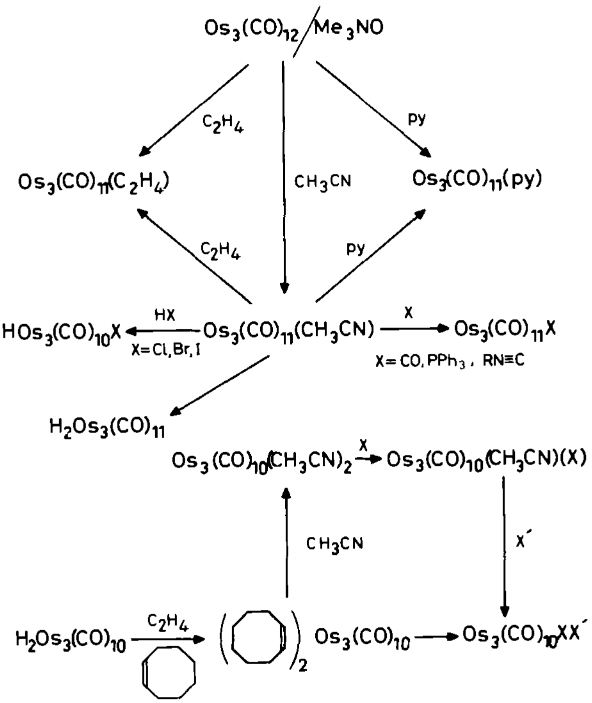
The cyclooctene complex was first isolated and adapted to cluster synthesis by Shapley and co-workers *(156)*. The complex is formed by reaction of ethylene with $H_2Os_3(CO)_{10}$ in cyclooctene, when only a trace of the vinyl adduct $HOs_3(CO)_{10}{\cdot}CH{=}CH_2$ is formed. The ^{13}C-NMR spectrum indicates that substitution by the olefin of equatorial carbonyl groups on two different metal centers has occurred. The complex readily reacts with a range of adducts to give high yields of the complexes $Os_3(CO)_{10}L_2$ or $Os_3(CO)_{10}(L-L)$ (where L is phosphine, isonitrile, L–L is diphosphine or diene). In particular, the reaction yields compounds that appear to be inaccessible by other routes, e.g., $Os_3(CO)_{10}$(diene) (diene = norbornadiene or 1,5-cyclooctadiene). Reaction also occurs with a large range of hydrogen-containing molecules, to yield the hydrido species $HOs_3(CO)_{10}X$ (X = OR, SR, NHR, or halogen). With organic molecules, it appears that a prerequisite for reaction to form a metal–carbon bond is the presence of an additional donor center in the molecule; and this has led to the production of a whole range of novel compounds. Thus, with formyl compounds the adducts $HOs_3(CO)_{10}(COX)$ (X = Me, OMe, NMe_2) are produced, while with acetophenone, $HOs_3(CO)_{10}(CH_2COPh)$ and $HOs_3(CO)_{10}(C_6H_4COMe)$ are the products. Reaction of the cyclooctene complex with acetronitrile yields the disubstituted adduct $Os_3(CO)_{10}(CH_3CN)_2$; the same complex was prepared directly from $Os_3(CO)_{12}$ and trimethylamine oxide dihydrate in acetonitrile. The use of one equivalent of trimethylamine oxide dihydrate yielded the mono-substituted complex $Os_3(CO)_{11}(CH_3CN)$ (*157*).

The disubstituted acetonitrile complex has been found to undergo all the reactions cited above for the cyclooctene complex. A particular advantage of these compounds is that it is possible sequentially to replace the ligands to produce the intermediate compound $[Os_3(CO)_{10}(CN_3CN)X]$, which may then be further reacted to give a mixed complex $[Os_3(CO)_{10}XX']$.

The monosubstituted adduct offers the ready synthesis of a whole range of monosubstituted adducts (see Scheme 6); it is often possible to isolate in these reactions intermediates that are not readily obtained by alternative methods. Thus, in the reaction with halogen acids to yield the bridged hydrido complexes $HOs_3(CO)_{10}X$, it is possible to identify the intermediate $HOs_3(CO)_{11}X$ complex in which the halogen functions as a one-electron donor bonding to only one metal center (*158*).

In many instances it is not necessary to isolate the acetonitrile complex or to carry out the reaction in acetonitrile. The use of amine oxide as a means of displacing carbonyl groups in metal carbonyls is well documented, and reaction proceeds smoothly with the carbonyl in the presence of a variety of ligands—e.g., ethylene or pyridine—to yield the monosubstituted derivatives. The advantage of the acetonitrile adducts is the stability of the compounds and the reactivity of the amine oxide toward acidic ligands.

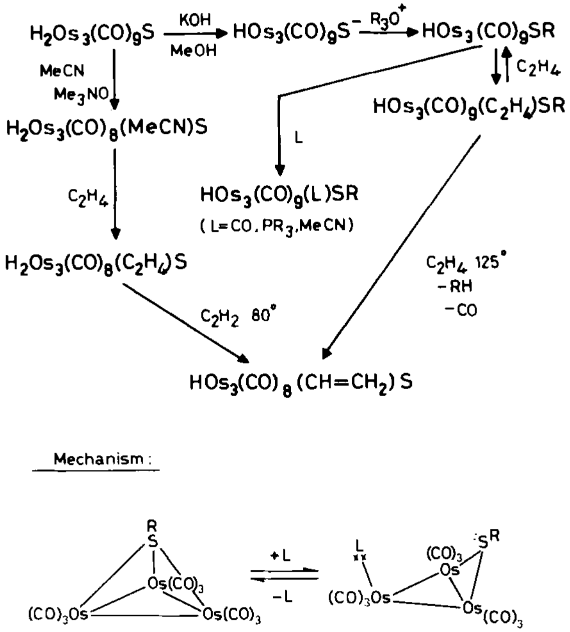
Shapley has recently adapted the acetonitrile adducts to produce



SCHEME 6. Some reactions of $Os_3(CO)_{11}MeCN$.

heternuclear metal clusters via reaction with $HRe(CO)_5$. These reactions yield the mono- and disubstituted $HOs_3(CO)_{11}[Re(CO)_5]$ and $H_2Os_3(CO)_{10}[Re(CO)_5]_2$. The structure and chemistry of these are discussed below, but this certainly provides an exciting entry into a designed synthetic pathway to heteronuclear cluster systems (*159*). It is of interest that little work has been carried out in the development of related ruthenium trinuclear cluster systems.

An alternative form of displacement reaction that has proved to be of limited preparative use, but does represent a potentially large field of chemistry, occurs for groups that are bonding to more than one metal center. The possibility arises of the group generating a coordination vacancy in the metal cluster by a bridge-opening mechanism. This is summarized for di- and tribridged species in Scheme 7. A variation on this is the possibility of a mononuclear species, in which there is ambivalence in the electron-donor capacity, giving the same result by an internal metal–ligand redox reaction (*158*). This is also illustrated for the NO ligand in Section II,I.



SCHEME 7. Preparation and reactivity of $HOs_3(CO)_9SEt$.

For the dibridged species, such as the halogen derivatives $HOs_2(CO)_{10}X$ (X = Cl, Br), we have used this type of behavior to explain the stereospecific incorporation of ^{13}CO into the molecules (*160*). The halogen group varies from a three-electron donor in bridged molecules to a one-electron donor in the terminally bonded species.

We have been able to extend this type of behavior to sulfur donor ligands which can behave as one- (terminal), three- (bridged), or five- (capped) electron donor systems. We have been able to prepare the thiol bridged species $HOs_3(CO)_9SR$ via the reaction outlined in Section II,I. For iron and ruthenium, the corresponding thiol derivatives may be prepared directly by reaction of the parent carbonyl with a thiol; for iron, the primary product is $HFe_3(CO)_9SR$; while for ruthenium, the intermediate $HRu_3(CO)_{10}SR$ may be isolated. Controlled thermolysis of this, in benzene, gives carbon monoxide evolution and the formation of the product $HRu_3(CO)_9SR$. The corresponding reaction with the carbonylthiols of osmium, $HOs_3(CO)_{10}SR$, leads to olefin elimination and the formation of the sulfur-capped species, $H_2Os_3(CO)_9S$ (*161*).

The osmium complexes undergo ready reaction with a variety of donor ligands; for the ethylene adduct, the X-ray structure has been obtained and clearly indicates the folding back of the SR ligand and the coordination of the ethylene to the empty metal site (see Fig. 31) (*161*). The complex is relatively unstable, and the back reaction, the elimination of ethylene, readily occurs to regenerate the initial compound $HOs_3(CO)_9SR$. However, if the complex is heated in the presence of ethylene, the vinyl derivative $HOs_3(CO)_8(CH{=}CH_2)S$ is formed (*158*). The same complex may be formed from the complex $H_2Os_3(CO)_9S$ via the amine oxide–acetonitrile reaction (see Scheme 7). The facility with which substitution reactions of this type occur is obviously related to the electron-withdrawing capacity of the group R in the thiol. For the sulfur-capped species, $H_2Os_3(CO)_9S$, there is no tendency for substitution reactions of this nature. As may be anticipated, the addition of an electron-withdrawing group to the sulfur center reduces the potential donation to the cluster unit and enhances the possibility of substitution reactions by the above mechanism. The greater inertness of the sulfur species to nucleophilic attack has been utilized in the synthesis of a novel carbene derivative. Attack by MeO^- ion on the cluster followed by the oxonium ion, R_3O^+ (R = Me, Et), leads to the carbene complex $H_2Os_3(CO)_8(C(OR)Me)S$ (*58*).

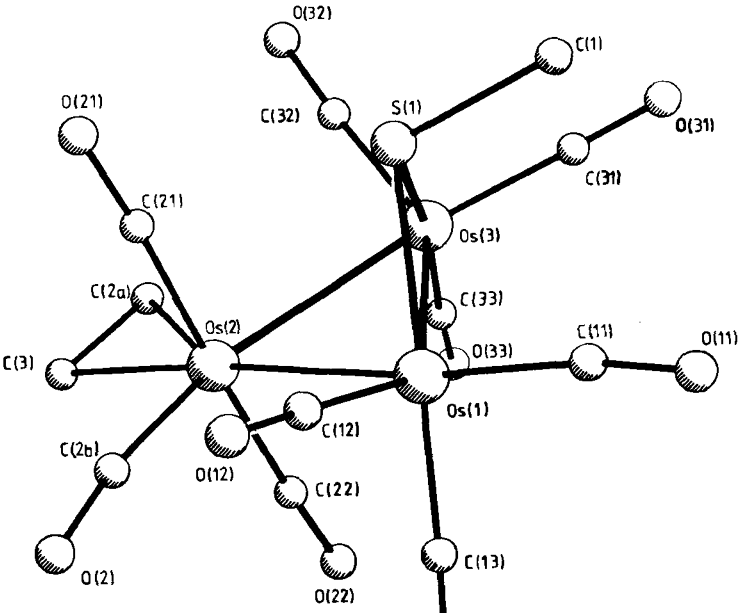


FIG. 31. Molecular structure of $HOs_3(CO)_9SMe(C_2H_4)$.

The method illustrated above for the preparation of thiol derivatives is limited by the availability of the corresponding oxonium salt. Recently, it has been shown that it is possible to obtain the capped species $H_2Os_3(CO)_9SR$ from the bridged complex $H_2Os_3(CO)_{10}SR$ by the amine oxide reagent R_3NO, although yields are only moderate (*162*).

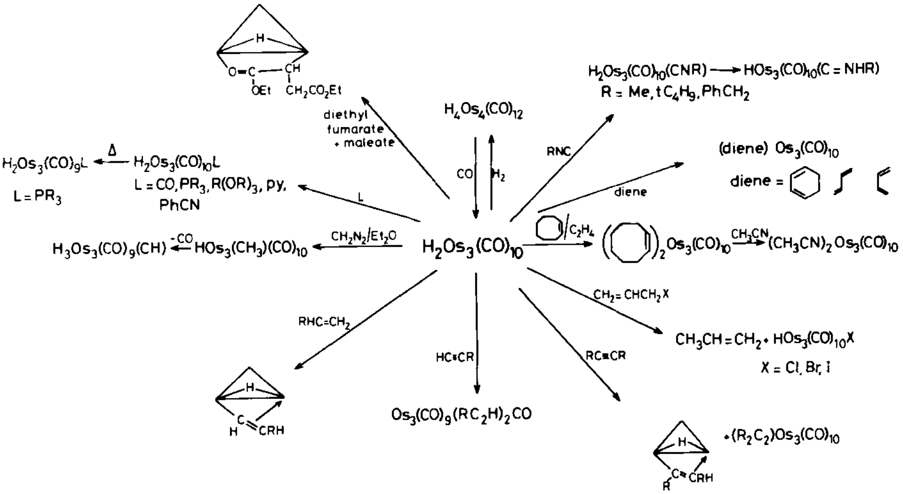
2. *Addition Reactions*

The structure of the compound $H_2Os_3(CO)_{10}$ has provided an example of an "unsaturated" metal cluster system. The molecule is a 46-electron system, $Os_3(CO)_{12}$ being a 48-electron molecule. The structures of the molecules $H_2Os_3(CO)_{10}$, $H(SEt)Os_3(CO)_{10}$, and $Os_3(CO)_{10}(OMe)_2$ provide an interesting comparative series, corresponding to 46-, 48-, and 50-electron systems (see Section II,C) (*163*). The length of the bridged osmium–osmium bond progressively increases with increased electron addition from 2.670 Å in the dihydride $H_2Os_3(CO)_{10}$ to 2.863 Å in the complex $HOs_3(CO)_{10}(SEt)$ and 3.078 Å in the dimethoxy derivative $Os_3(CO)_{10}(OMe)_2$. This is to be compared with the osmium–osmium distance of 2.88 Å in the parent carbonyl. The electronically equivalent molecule $HOs_3(CO)_{10}(SEt)$ having a similar metal–metal distance is considered to have a single bond between the metal centers, while the dimethoxy complex is considered to have no bond between the metals. The dihydride is then considered to have a double bond between the two osmium atoms which are being bridged, and the decrease in the distance is consistent with this. However, it may equally reflect the potentially smaller size of the hydrogen-bridged species, which would also lead to a smaller metal–metal distance. However, the complex behaves as an unsaturated molecule, readily adding donor molecules to attain the 48-electron configuration. This property has been of considerable utility in the development of the synthetic chemistry of the triosmium cluster unit.

The compound was initially prepared, in a low yield, from the reaction of $Os_3(CO)_{12}$ with base or sodium amalgam (*164*), but it was subsequently obtained in high yield from the reaction of hydrogen gas with $Os_3(CO)_{12}$ (*82*).

Scheme 8 summarizes some of the reactions that have been observed for $H_2Os_3(CO)_{10}$ (*135, 136, 165*). A wide range of products may be obtained, but some of the reactions are complicated by hydrogenation of the products, a situation that does not occur in the displacement reactions considered above. This reagent was the first used to prepare vinyl adducts from alkenes and alkynes.

The addition products $H_2Os_3(CO)_{10}L$ (L = CO, PR_3, C_5H_5N, CNR) in-



SCHEME 8. Some reactions of $H_2Os_3(CO)_{10}$.

volve a bridging and terminal hydride. This has been established by X-ray analysis for the complexes $H_2Os_3(CO)_{11}$ and $H_2Os_3(CO)_{10}PPh_3$ (*166*). Phosphorus ligands are shown from NMR studies to take up equatorial positions, while pyridine and isonitrile bond to axial sites. For axial substitution, two isomers occur, depending on the orientation relative to the bridging hydrogen atom. The phosphine complexes lose CO on heating to yield the "unsaturated" complexes $H_2Os_3(CO)_9L$ (*167*).

The isonitrile complex undergoes a prototropic rearrangement to yield the complex $HOs_3(CO)_{10}(C{=}NHR)$. The hydrogen of the imine group may react with methyl iodide to yield derivatives of the form $HOs_3(CO)_{10}(C{=}NMeR)$. The structure of these is considered to be similar to that obtained by Churchill and deBoer for the related ruthenium complex $HRu_3(CO)_{10}(C{=}NMe_2)$, prepared by reaction of $Ru_3(CO)_{12}$ with $Me_3SnCH_2NMe_2$ (see Fig. 32) (*168*). The iron complex $HFe_3(CO)_{10}$-$(CNMe_2)$ has also been reported (*169*). The complexes formed involve unsaturated groups produced via the elimination of alkane or hydrogen from the ligand, and fall into two classes: $HOs_3(RC{=}NMe)(CO)_{10}$ (R = H, Ph) and $HOs_3(C{=}NMeR)(CO)_{10}$ (R = Me or $PhCH_2$). The first of these complexes involves a bridging structure with bonding across a metal–metal bond by a "C=N" fragment and is isomeric with the derivatives discussed above. The X-ray structure of the complex $HOs_3(CO)_{10}(Ph\text{"}C{=}N\text{"}{-}CH_3)$ has recently been reported (*170*). This bonding situation is reminiscent of the two modes observed for alkene

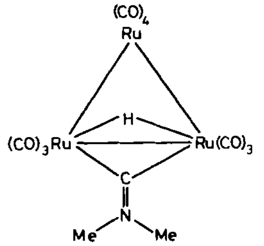


FIG. 32. Molecular structure of $HRu_3(CO)_{10}CNMe_2$.

groups with the trimetallic cluster. Reaction of phenyl isocyanide with $H_2Os_3(CO)_{10}$ yields $H_2Os_3(CO)_{10}(CNPh)$, which on warming decarbonylates to $HOs_3(CO)_9(CH{=}N{-}Ph)$; the *N*-phenylformimidoyl ligand bonds to three osmium centers, and represents a prototropic shift to the carbon rather than the nitrogen.

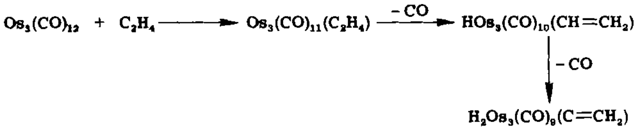
Complexes of this nature may also be prepared by direct reaction. $Os_3(CO)_{12}$ reacts with *N*-benzylidenemethylamine $PhCH{=}NMe$ to give $HOs_3(CO)_{10}(PhC{=}NMe)$ (*171*). Deeming has prepared a similar series of compounds, in a low yield, by the reaction of $Os_3(CO)_{12}$ with the tertiary amines Me_3N or $Me_2(PhCH_2)N$, while Shapley *et al.* have obtained the iminium $\overset{-}{C}H{-}CH{=}\overset{+}{N}Et_2$ complex via reaction of Et_3N with $Os_3(CO)_{10}(CH_3CN)_2$, X-ray analysis being used to confirm the structure $HOs_3(\overset{-}{C}O)_{10}(CH{-}CH{=}\overset{+}{N}Et_2)$ (*172*). A related 1,3-dipolar ligand has been also isolated in the reaction of a phosphine with the vinyl complex $HOs_3(CO)_{10}(CH{=}CH_2)$ to yield the compound $HOs_3(CO)_{10}(\overset{-}{C}H{-}CH_2{-}\overset{+}{P}Me_2Ph)$ (*173*). The structure of this adduct shows a $\overset{-}{C}H{-}R$ bridge between two osmium metal atoms of the metal triangle, with the hydride also bridging between the two same metal centers. Interestingly, this reaction also reflects on the relative effects of replacing a hydrogen in the ethylene group by a metal, which would be expected to enhance the nucleophilicity of the double bond, and donation of the olefin π electron to a low-valent metal ion, which would be expected to increase the electrophilic character. Electrophilic reactions do not appear to occur readily at coordinated centers, while nucleophilic coordinated reactions appear to occur more readily than with the uncoordinated molecule. This would indicate that the σ-substitution dominates over the π-electron effects in these systems.

Although the corresponding chemistry for ruthenium has not been investigated, Bruce *et al.* recently reported an interesting hydrogenation reaction which produces complexes of this type. Reaction of hydrogen with $Ru_3(CO)_{11}(CN\text{-}t\text{-}Bu)$ has been found to yield the nonacarbonyl $HRu_3(CO)_9(HCN\text{-}t\text{-}Bu)$, in which the ligand is postulated to be a four-electron donor. (*174*).

One of the most elusive types of compounds in the cluster chemistry of this group is complexes with an alkyl group bonded to one metal center. The dimethyl adduct $(CH_3)_2Os_3(CO)_{12}$ is the rare example of a polynuclear complex containing a terminally bonded alkyl group (*175*). Application of the methods normally employed for alkyl formation to the triangulated metal clusters generally leads to decomposition, or to carbon-capped species. Shapley has shown recently that diazomethane reacts with $H_2Os_3(CO)_{10}$ to give an alkyl derivative $HOs_3(CO)_{10}CH_3$ (*59, 176*); this complex does, however, show unusual properties, and it is suggested that the C–H bond in the methyl is interacting with another osmium center than that to which the carbon is bonded. The methyl compound is in equilibrium, in solution, with a methylene-bridged isomer, $H_2Os_3(CO)_{10}CH_2$, the solid which has been isolated from these solutions being the methylene isomer. Warming leads to the facile removal of CO and the production of the carbon-capped species $H_3Os_3(CO)_9CH$. The bonding in the methylene compound has been confirmed by an X-ray/neutron diffraction study (*59*).

Substitutions of hydrogen in the alkyl group, particularly with donor groups which may also interact with a metal center, have been found to stabilize the metal–carbon bonding mode. Thus the interaction of diethyl fumarate and maleate with $H_2Os_3(CO)_{10}$ leads to saturation of the double bond and coordination of the group $OC(OR)CHCH_2CO_2R$ via carbon and oxygen centers (see Scheme 8) (*177*). Similarly, reaction of $H_2Os_3(CO)_{10}$ with ethyldiazoacetate gives the compound $HOs_3(CO)_{10}(CH_2CO_2Et)$, which appears to be stabilized by coordination of the ester oxygen.

Replacement of a carbonyl group in the $Os_3(CO)_{12}$ molecule leads to the complexes $Os_3(CO)_{11}L$, which vary considerably in their thermal stability. For monodentate ligands such as phosphines, the complexes are in general stable (but see Section III,E for reactions involving C–H fission); when the group L has the potential of providing extra electrons to the cluster, the complexes often decompose readily to yield the deca- or nonacarbonyl, depending upon the availability of an extra two or four electrons from the ligand group. In contrast to the initial CO substitution, these internal reactions often occur very readily, and in many instances it is extremely difficult to isolate the initial product, $Os_3(CO)_{11}L$, as the conditions required to activate the parent carbonyl are thermally so severe that the decacarbonylation reaction occurs before isolation of the products. The reagent $Os_3(CO)_{11}(CH_3CN)$ has been useful in establishing the existence and nature of these primary $Os_3(CO)_{11}L$ species. As discussed above for the reaction of ethylene with $Os_3(CO)_{12}$, the following reaction scheme has been proposed:



$$\begin{tikzcd} Os_3(CO)_{12} + C_2H_4 \arrow[r] & Os_3(CO)_{11}(C_2H_4) \arrow[r, "-CO"] & HOs_3(CO)_{10}(CH{=}CH_2) \arrow[d, "-CO"] \\ & & H_2Os_3(CO)_9(C{=}CH_2) \end{tikzcd}$$

The only compound isolated was the final product $H_2Os_3(CO)_9$-$(C{=}CH_2)$. However, the intermediate ethylene adduct $(C_2H_4)Os_3(CO)_{11}$ was prepared via the reaction with $Os_3(CO)_{11}(CH_3CN)$ (Scheme 6), and the vinyl adduct by reactions involving $H_2Os_3(CO)_{10}$ (Scheme 8). In agreement with the above scheme, both convert smoothly to the nonacarbonyl adduct on warming.

The facility of these decarbonylation reactions is obviously related to the donor capacity of the ligand groups. The halogens follow the variation that may be anticipated for this series. The reactions of $Os_3(CO)_{11}L$ with the halogen acids HX (X = Cl, Br, I) involve sequential evolution of carbon monoxide, but their facility increases with the donor capacity of the halogen, Cl < Br < I *(157, 162)*.

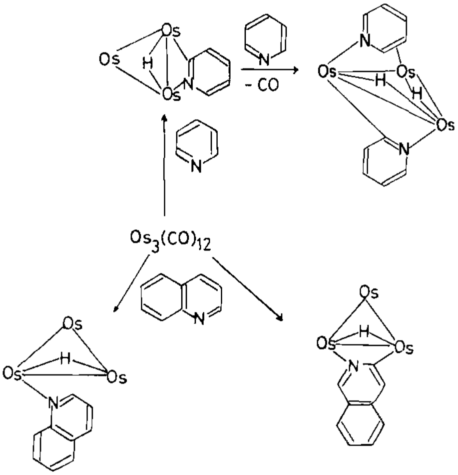
$$Os_3(CO)_{11}(CH_3CN) \xrightarrow{HX} HOs_3(CO)_{11}X \longrightarrow HOs_3(CO)_{10}X \longrightarrow HOs_3(CO)_9X$$

The initial complex $HOs_3(CO)_{11}X$ cannot be isolated for X = I, is readily transformed to the decacarbonyl for X = Br, but is more stable if X = Cl. The iodide initially gives the decacarbonyl and on warming yields the nonacarbonyl, $HOs_3(CO)_9I$, in which the iodine becomes a capping atom to the three metal centers. The corresponding "capped" bromide and chloride complexes are not formed.

Deeming has utilized this type of reaction to produce some very interesting donor molecules. Two classes of reaction have been observed corresponding to all the electrons being donated from one center, to yield progressively terminal, bridging, and capping systems, or from two donor centers within a molecule to yield bridging ligand–metal systems. Normally, in this latter case, carbon provides the extra center of coordination of the ligand via fission of a C–H bond and formation of a metal–carbon and often a metal–hydrogen linkage. The tendency for this class of reaction to occur appears to increase with atomic number of the element Os > Ru > Fe, the order of increasing stability of both metal–hydrogen and metal–carbon bonds. The compounds formed involve the formation of a metallocyclic system, with two metal centers in the ring. The formation of four- rather than five-membered rings normally observed in mononuclear species, i.e., orthometallation reactions with phosphine ligands, occurs in these systems. This possibility reflects the smaller angular strain in the four-membered cluster–ring systems because of the longer metal–metal bond which provided one side of the ring structure. However, larger ring systems are observed in these systems.

Pyridine reacts with $Os_3(CO)_{12}$ at 180°C to give a series of 2-pyridyl bridging complexes, as indicated in Scheme 9, in which the pyridine replaces two carbonyl groups (*178*). The intermediate complex $Os_3(CO)_{11}(py)$ has been prepared via $Os_3(CO)_{11}(CH_3CN)$ (*157*) (see Section II,H), and on heating converts to the bridged complex. Isoquinoline behaves in a similar manner to give two products corresponding to the metallation of the two alternative sites ortho to the nitrogen (metallation is favored at the 1-position). Quinoline gives the isomer shown involving α-CH bond cleavage with no indication of the alternative complex formed by a β-CH fission, as occurs for mononuclear species, even when this is sterically possible. Further reaction is possible with pyridine to give the substituted product with two ligands bonded via the nitrogen and the α-carbon atoms (Scheme 9).

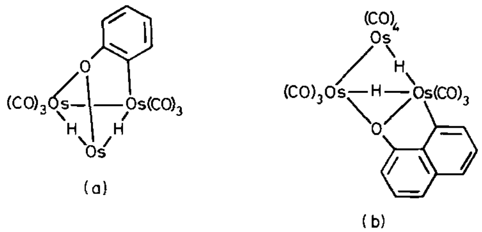
Aniline reacts with $Os_3(CO)_{12}$ to give the adduct $Os_3(CO)_8(PhNH_2)_2$



SCHEME 9. Reactions of $Os_3(CO)_{12}$ with some N-donor ligands.

(*179*). One of the aniline molecules is terminally bonded to one metal atom and is readily displaced by reacting with the CO gas to give the orthometallated product $H_2Os_3(CO)_9(HNC_6H_4)$. This complex reacts with excess of carbon monoxide to give the bridged aniline species $[HOs_3(CO)_{10}(NHPh)]$. This reverse orthometallation involves the reformation of the C–H bond on addition of CO to the cluster. Heating of the decacarbonyl leads to quantitative conversion of the orthometallated nonacarbonyl, $[H_2Os_3(CO)_9(NHC_6H_4)]$. However, protracted heating of the nonacarbonyl species leads to isomerization to the nitrogen-capped species $[H_2Os_3(CO)_9(NPh)]$, which appears to be the thermodynamically stable isomer. The related ruthenium complex $[H_2Ru_3(CO)_9(NPh)]$ has recently been prepared by hydrogenation of $Ru_3(CO)_{10}(NPh)$, which is obtained from the reaction of nitrobenzene with $Ru_3(CO)_{12}$. This system shows an interesting interplay of kinetic and thermodynamic factors in the formation of the orthometallated carbon-bonded species via C–H bond breakage and the nitrogen-capped moiety via N–H bond rupture.

The extension of this work to the oxygen complexes, ROH, shows a parallel chemistry for the initial steps, with the formation of the decacarbonyl oxygen-bridged species $HOs_3(CO)_{10}OR$ for a large range of alcohols with R = Ph, 2-naphthyl, —$CHMe_2$, —CH_2Ph, —CHMePh, and —CMe_2Ph (*180*). However, on conversion to the nonacarbonyl on heating, the phenol and 2-naphthyl derivatives give adducts in which orthometallation has occurred and which was considered, by analogy with aniline, to occur from the 1-position, to give complexes of the structure of Fig. 33a. With 1-naphthol, no intermediate decacarbonyl is observed, the reaction proceeding to the nonacarbonyl adducts. Two isomers have been isolated, one corresponding to that observed for phenol, with bonding to the β-carbon atom, while the second isomer is considered to have a structure as in Fig. 33b, bonding occurring to the γ-carbon atom with formation of a five-membered metallocyclic with



(a) (b)

FIG. 33. Molecular structures of (a) $H_2Os_3(CO)_9(OC_6H_4)$ and (b) $H_2Os_3(CO)_9(OC_{10}H_6)$.

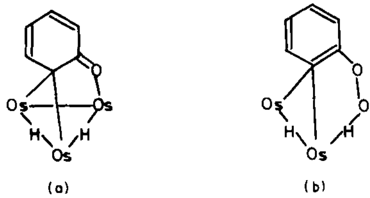


FIG. 34. Molecular structures of $H_2Os_3(CO)_9(OC_6H_4)$.

only one metal atom. A compound related to the γ-isomer has been obtained from the alcohol $PhMe_2COH$.

A recent X-ray determination of the structure of the 2-benzyl phenol derivative $[H_2Os_3(CO)_9(OC_6H_3CH_2Ph)]$ indicates a different bonding mode from that in Fig. 33a, with a switch in the nature of the bonding groups between bridging and terminal roles (*181*). Detailed analysis of the X-ray data favors the structure form in Fig. 34a, although attempts to identify chemically the diene character were not successful. This structure does throw some doubt on the nature of the related aniline complex.

This work has also led to a reconsideration of the formulation of some of the products of reaction of aldehydes with $Os_3(CO)_{12}$ (*182*). Reaction with a range of aldehydes RHCO (R = Ph, $PhCH_2$, n-C_6H_{11}, n-C_6H_{13}, or i-Pr) gives the bridging acyl adducts $[HOs_3(RC{=}O)(CO)_{10}]$ (Fig. 35a). Some of these acyl complexes may be prepared from the complex $[HOs_3(OCH{=}CR_2)(CO)_{10}]$, formed from the ketene $O{=}C{=}CR_2$ and $H_2Os_3(CO)_{10}$ on warming. For R = Me, the complex is completely isomerized to the acyl complex (R = i-Pr) at 150°C in toluene. However, for the complex $[HOs_3(OCH{=}CH_2)(CO)_{10}]$, only traces of the acyl isomer, $[HOs_3(OCCH_3)(CO)_{10}]$ are obtained, the main products being the carbon-capped species, $[H_3Os_3(CH)(CO)_9]$, presumably formed by decarbonylation to yield the methyl derivative, which, as observed above, readily isomerizes to bridged or capped species. In addition, the bridged species $H_2Os_3(OCH{=}CH)(CO)_9$ was also isolated.

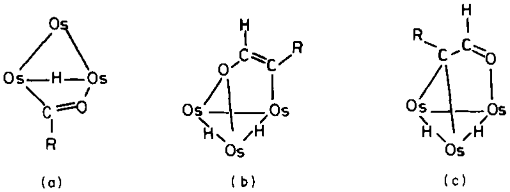


FIG. 35. Molecular structures of (a) $H(RC{=}O)Os_3(CO)_{10}$ and (b) and (c) $H_2Os_3(OCHCH)(CO)_9$.

This was initially formulated as in Fig. 35b, but on the basis of the structure of the phenol derivatives and reassessment of the spectroscopic data, the alternative formulation Fig. 35c is now preferred, with a switch in the oxygen bonding mode such as occurs in the phenol complex.

For benzyl alcohol, Deeming has established an interesting reaction with $Os_3(CO)_{12}$ to yield benzene (*183*). This involves the initial formation of an oxygen-bridged species, $HOs_3(CO)_{10}(OCH_2Ph)$, which evolves carbon monoxide on heating to give the orthometallated species $[H_2Os_3(CO)_9OCH_2C_6H_4]$. This complex decarbonylates to the benzyne complex $[H_2Os_3(CO)_9C_6H_4]$, which with carbon monoxide yields benzene and osmium carbonyl.

A reaction of the above type indicates the chemical flexibility of these systems, involving major structural arrangements within the ligand groups and the facility of the ligand to bond to a number of metal centers within the trinuclear species, with novel bonding modes. The development of these reactions to higher cluster units, when more flexible arrangements of metal–ligand bonding mode are possible, emphasizes the extensive chemistry that may be anticipated in these systems. It is important to stress that for the range of ligands studied to date, the majority appear to favor bonding to more than one metal center, so that analogies drawn between the reactivity of polynuclear systems and mononuclear complexes may be misleading.

These reactions highlight the great tendency for the formation of metal–hydrogen bonds within this series. The energy of the metal–hydrogen bond has not been determined, but we may get an insight into its magnitude by considering the orthometallation reaction of the pyridine–$Os_3(CO)_{12}$ system:

$$Os_3(CO)_{11}(py) \xrightarrow{\Delta H} H{\cdot}Os_3(CO)_{10}(NC_5H_4)$$

The energy change, ΔH, is $[\Delta H_{M-CO} + \Delta H_{C-H(py)} - \Delta H_{M-C(py)} - \Delta H_{M-H}]$ where M = Os. Very few data are available for metal–carbon bonds, but Table X (*184, 185*) summarizes those that are. For the manganese/rhenium couple, the increase in bond energy of the metal–carbon bond of the carbonyl is paralleled by an increase in the metal–carbon bond energy of the methyl derivatives. Assuming a comparable behavior for the iron–osmium group, the energy changes for decarbonylation and orthometallation would approximately compensate each other. As Deeming (*179*) has shown, the above orthometallation reaction is reversible; we may deduce therefore that ΔH is not large. With the above assumptions, this would imply that the metal–hydrogen bond strength is of the order of the C–H bond strength in pyridine, with a value of the

TABLE X

BOND ENTHALPY (kcal mol^{-1}) IN METAL CARBONYLS[a]

	Cr	Mn	Fe	Co	Ni
Metal	—	16	19.2	22	—
Carbonyl	25.7	23.7	28.1	32.5	35.1
Methyl	—	27.9	—	—	—
	Mo	**Tc**	**Ru**	**Rh**	
Metal	—	—	28	26.8	
Carbonyl	36.3	—	41.2	39.4	
Methyl	35.8[b]				
	W	**Re**	**Os**	**Ir**	
Metal	—	30.5	31.1	31	
Carbonyl	42.6	44.8	45.8	45.3	
Methyl	47.5[b] 38.0[c]	53.2	—	—	

[a] From Connor (*184*) and Calado *et al.* (*185*).

[b] Obtained from data on [π-Cp_2MR_2].

[c] Obtained from data on WMe_6.

order of 80–90 kcal mol^{-1}. This is in considerable excess of that observed for other bond energies determined to date.

There is, however, supplementary evidence in favor of a high bond energy for the M–H bonds in these systems. Muetterties *et al.* (*186*) have noted the close comparison between metal–ligand bond energies and the energy of ligand absorption to the metal surface. On this basis, the energy of a metal–hydrogen bond would be expected to be greater than that of a metal–carbonyl bond, as the absorption energy is greater for hydrogen. An increase in bond energy on descending the triad is also consistent with the limited data available on the bond dissociation energies of diatomic hydrides, where for nickel and platinum the values are 60 and 83 kcal mol^{-1}, respectively, and for copper and gold are 66 and 74 kcal mol^{-1}, respectively.

G. TETRANUCLEAR CLUSTERS

The parent carbonyls, $M_4(CO)_{14}$ (M = Ru, Os), have not been isolated, but the related hydrides $H_2M_4(CO)_{13}$ and $H_4M_4(CO)_{12}$ have been prepared for both ruthenium and osmium by direct reaction of the trinuclear carbonyl with hydrogen or water (see Section III,C) (*82*, *86*).

An interesting linear species, $H_2Os_4(CO)_{16}$, has been reported as being formed together with the trinuclear species $H_2Os_3(CO)_{12}$ in the high-pressure carbonylation of OsO_4 (*78*). The main studies of these hydrides have centered on the $H_4M_4(CO)_{12}$ complexes, and it will be convenient to discuss first the structure of these hydrides and then their reactivity.

1. *Preparation and Structure*

The anions $[H_3M_4(CO)_{12}]^-$ (M = Ru, Os) and $[H_2M_4(CO)_{12}]^{2-}$ have been prepared by the use of either ethanolic/KOH or potassium hydride in tetrahydrofuran (*187, 188*). The related reaction using potassium hydride with $H_2Ru_4(CO)_{13}$ leads to CO displacement and the production of the salt $K_2[H_2Ru_4(CO)_{12}]$.

The infrared spectra of these complexes establish that the neutral compound and monoanion have no bridging carbonyl groups, in contrast to the dianion $[H_2Ru_4(CO)_{12}]^{2-}$ which has bridging carbonyl groups (*188*). This trend is consistent with the increase in negative charge on the dianion, favoring bridging-carbonyl bridge formation. The ^{13}C-NMR spectrum of the dianion shows the presence of three bridge carbonyl groups, and the temperature variation of the spectra has been interpreted in terms of the normal carbonyl terminal–bridged exchange process observed in the fluxional processes occurring within carbonyl–metal systems.

The position of the hydride groups in these species has been established by a combination of ^{1}H chemical shifts in the NMR spectra and X-ray crystallographic analysis. The position of the hydrogen is determined by a combination of the lengthening of the metal–metal bond, and the bending of the carbonyl groups to accommodate the hydride group. In all the higher polynuclear complexes, hydrogen is found either to bridge to an edge between two metal atoms or to a face bonding three metal atoms. For the tetranuclear hydrides of ruthenium and osmium, all the complexes studied to date involve edge-bridging hydrogen. In the series of tetrahydrides, $H_4Ru_4(CO)_{12}$, $H_4Ru_4(CO)_{11}P(OMe)_3$, and $H_4Ru_4(CO)_{10}(PPh_3)_2$, the hydrides take up a D_{2d} configuration relative to the metal atoms (Fig. 36a), while for the complex

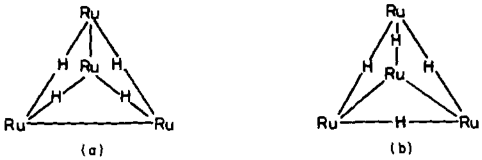
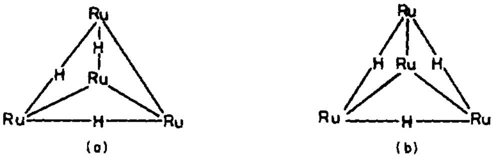


FIG. 36. Isomers of $H_4Ru_4(CO)_{10}(PR_3)_2$.



(a) (b)

FIG. 37. Isomers of the anion $[H_3Ru_4(CO)_{12}]^-$.

$H_4Ru_4(CO)_{10}$(diphos), the C_s conformation (Fig. 36b) is observed (*72, 186*).

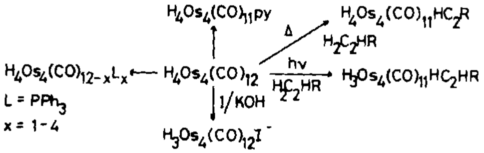
The anion $[H_3Ru_4(CO)_{12}]^-$ exists in two isomeric forms. The initial evidence for this was from infrared and ^{1}H-NMR studies (*182*). Recently, the X-ray structure of two modifications has been determined (*184*). The two isomeric structures are shown in Fig. 37a and b, and this has established, for the first time, that the polynuclear hydridocarbonyls may exist in more than one isomeric form.

The dihydride, $H_2Ru_4(CO)_{13}$, involves two edge-bridging hydrogen atoms, and two of the carbonyl groups appear to be semibridging, with marked deviation of the metal–carbon–oxygen structure from linearity (150°) and metal–carbon distances of 1.94 and 2.40 Å (*185*). This structure bears comparison with the related iron complexes $[HFe_4(CO)_{13}]^-$ and $[Fe_4(CO)_{13}]^{2-}$ (see Section III,C).

The structure of the related osmium hydridocarbonyls has not been investigated in such extensive detail. However, the X-ray structures of the anions $[H_3Os_4(CO)_{12}]^-$ and $[H_2Os_4(CO)_{12}]^{2-}$ are being determined (*191*).

2. *Reactivity of $H_4Os_4(CO)_{12}$ and $H_4Ru_4(CO)_{12}$*

A general summary of the chemistry of $H_4Os_4(CO)_{12}$ is given in Scheme 10 (*159, 166*). Substitution reactions with phosphine, phosphites, or pyridine have been observed. An addition reaction occurs with I_2 to yield the anionic species $[H_3Os_4(CO)_{12}I]^-$. The X-ray structure of this anion has established that the iodide is bridging between two metal centers, to yield an Os_4 "butterfly" configuration in which one of the metal–metal bonds of the initial Os_4 tetrahedron has been broken (Os–Os = 3.817 Å) (Fig. 38). Interestingly, if the two Os–I



SCHEME 10. Some reactions of $H_4Os_4(CO)_{12}$.

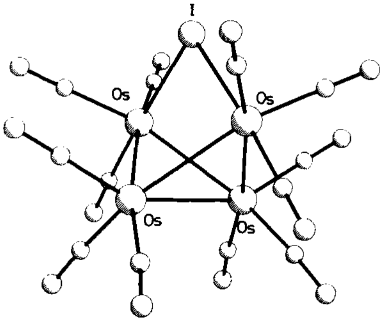


FIG. 38. Molecular structure of $H_3Os_4(CO)_{12}I$.

bonds replace a hydrido bridge in the parent carbonyl compound, then the hydride, $H_4Os_4(CO)_{12}$, would have the D_{2d} symmetry observed for $H_4Ru_4(CO)_{12}$ (*160*).

The interaction of the hydrido species with alkynes and alkenes has been investigated (*184, 194, 195*). Low yields of a vinyl-substituted product, similar to that observed from the interaction of alkenes with $H_2Os_3(CO)_{10}$ (see Section III,F), were observed for the thermal reaction. The structure of the cyclohexane adduct is given in Fig. 39 (*195*). This complex, on heating, was transformed to a 1:2 olefin adduct. This behavior contrasts markedly with the behavior of ethylene with the triosmium derivatives, which yield the 1:1 olefin complex. The vinyl adduct may be prepared in higher yields photochemically. The complex has been found to insert alkenes and alkynes in the metal–carbon σ-bond to give a variety of linear polymers, the length of the polymer chain being markedly affected by the degree of substitution on the alkyne. The chain length of the polymer is reduced on substitution in the alkyne, indicating that steric effects may play an important role in these reactions.

The main reactions that have been reported for $H_4Ru_4(CO)_{12}$ are concerned with alkene or alkyne derivatives. Thus the reaction of $H_4Ru_4(CO)_{12}$ with olefins yields a variety of products. With ethylene, the ethylidene complex $H_2Ru_3(CO)_9C{\cdot}CH_3$ is produced (with a high yield of $H_2Ru_4(CO)_{13}$). Cyclooctene and cycloheptene react to give the 1:2 olefin adducts $H_2Ru_3(CO)_9(C_8H_{12})$ and $H_2Ru_3(CO)_9C_7H_{10}$, respectively (*196*). The same compounds are obtained from the reaction of these olefins with $Ru_3(CO)_{12}$. With cyclic dienes, complex mixtures of compounds are often produced, some in low yields. Thus, with cyclo-1,5-octadiene or the 1,3-diene, the trinuclear adducts $H_2Ru_3(CO)_9(C_8H_{12})$ and $HRu_3(CO)_9C_8H_{11}$ are formed. The first of these is identical with the

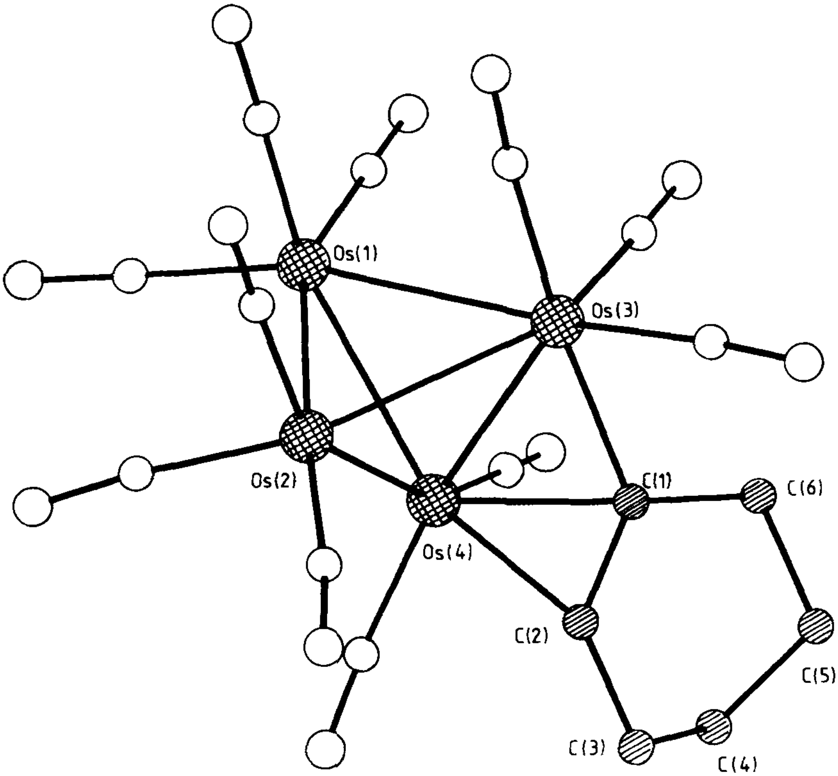


FIG. 39. Molecular structure of $H_3Os_4(CO)_{11}(C_8H_9)$.

product obtained from cyclooctene and $H_4Ru_4(CO)_{12}$, while the second appears to involve π-allyl bonding of the organic moiety to the cluster.

In addition to these, a variety of tetranuclear adducts are also formed (*196*). These are all based on a *closo*-Ru_4C_2 unit, and the structure of the complex $Ru_4(CO)_{11}(C_8H_{10})$ (*197*) illustrates the equivalence of this structure to the Co_4C_2 skeleton first established for the complex $Co_4(CO)_{10}C_2Et_2$. The structures of the two main tetranuclear adducts produced, $Ru_4(CO)_{12}(C_8H_{10})$ and $Ru_4(CO)_{12}(C_8H_{12})$, are also considered to be based on the Ru_4C_2 unit, with the complex $Ru_4(CO)_{12}C_8H_{10}$ having a free uncoordinated double bond. Attempts to hydrogenate this double bond to yield the second adduct. $Ru_4(CO)_{12}C_8H_{12}$, lead to cluster breakdown and the production of the 1:2 olefin adduct $H_2Ru_3(CO)_9(C_8H_{12})$. Reaction of 1,3-cyclohexadiene with triruthenium dodecacarbonyl has been shown to yield a novel tetranuclear species, $Ru_4(CO)_9(C_6H_6)(C_6H_8)$ (Fig. 40) (*198*).

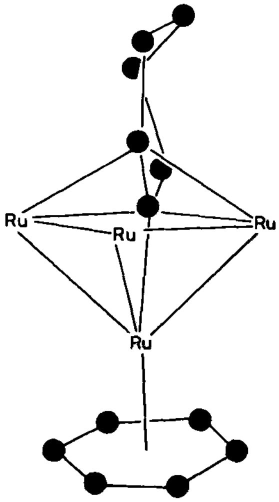


FIG. 40. Molecular structure of $Ru_4(CO)_9(C_6H_6)(C_6H_8)$.

As discussed above, tetranuclear complexes can be produced, in high yields, from the reaction of an alkyne with $Ru_3(CO)_{12}$ (*199*).

$$Ru_3(CO)_{12} + RC{\equiv}CR' \xrightarrow{n\text{-hexane}} Ru_4(CO)_{12}(RC_2R')$$
$$(R = Ph, R' = Ph; R = Ph, R' = Me; R = Ph, R' = Et; R = R' = CH_3OCH_2)$$

The behavior of $Ru_3(CO)_{12}$ contrasts with that of $Fe_3(CO)_{12}$ and $Os_3(CO)_{12}$, which on reaction with acetylenes gives predominantly trinuclear species.

An interesting oxycarbonyl cluster has been isolated in the reaction of OsO_4 with CO under pressure. This was an intermediate in the preparation of the $Os_3(CO)_{12}$. The X-ray analysis has established this as a cubane structure, with an oxygen bridging the four faces of the osmium tetrahedron. The Os–Os distance is ~3.20 Å and implies no bonding between the osmium centers. This molecule is of obvious interest as a potential model in the studies of carbon monoxide interaction with metal oxides and also metal surfaces, when the formation of metal oxides occurs (*200*).

H. PENTANUCLEAR CLUSTERS

1. Carbonyl and Carbonylhydrides

Five-metal-atom clusters have been obtained only with osmium. The binary carbonyl $Os_5(CO)_{16}$ was initially formed in low yield (~10%) by the thermolysis of $Os_3(CO)_{12}$ (*201*). The yield of the compound may be slightly increased by varying the temperature of the reaction and solvent employed. The X-ray structure (Fig. 41) has established a distorted bipyramidal stereochemistry of the metal atoms, with one metal atom being associated with four carbonyl groups and each of the remainder coordinating to three carbonyl moieties (*202*). The arrangement of CO groups around the five osmium atoms may reflect the preferred interstitial packing of the five atoms within the close-packed arrangements of the CO groups. An alternative local bonding scheme consistent with each metal center maintaining the E.A.N. rule would require three different electronic environments for the metal atoms, the unique four-carbonyl-bonded osmium providing two electron-donor bonds to the two axial metal atoms, with the two remaining metal atoms forming conventional metal–metal bonds to each of four metal centers. Implicit in this would be a significant polarity within the metal–metal bonding framework. The distortions exhibited by the carbonyl groups from the linear Os–C–O angle anticipated for a terminal group are consistent with this, although the deviations are not great. The variation in bond length within the metal polyhedron also reflects the unique bonding nature of the Os(CO)$_4$ fragment (see Section II).

The major entry into Os$_5$ cluster chemistry comes from the reaction of base with Os$_6$(CO)$_{18}$ (*203*). This gives the [Os$_5$(CO)$_{15}$]$^{2-}$ anion in high yield (~80%). The general chemistry of these species is summarized in

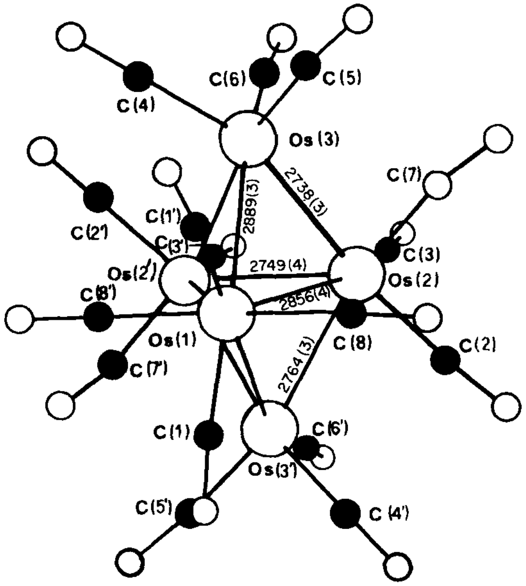
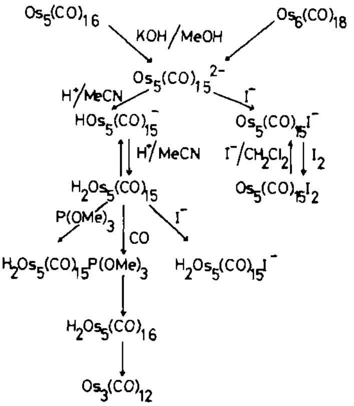


FIG. 41. The structure of [Os$_5$(CO)$_{16}$].



SCHEME 11. Some reactions of $Os_5(CO)_{16}$.

Scheme 11. Acidification of the anion yields progressively the anion $[HOs_5(CO)_{15}]^-$ and the neutral hydride $H_2Os_5(CO)_{15}$. The X-ray structure of the anion has been determined and shows a trigonal-bipyramidal arrangement of metal atoms with three carbonyl groups coordinated to each metal (*204*). The hydrogen is considered to lie along the equatorial edge Os(1)–Os(3) (see Fig. 42). The ^{13}C-NMR spectrum at −40°C is consistent with this assignment, but the high-temperature spectrum at + 55°C indicates only two regions of CO absorption in the ratio 3:2, similar to that observed for the anion $[Os_5(CO)_{15}]^{2-}$. This is interpreted in terms of H migration around all three edges of the trigonal plane Os(1)–Os(2)–Os(3), equilibrating all the metal centers,

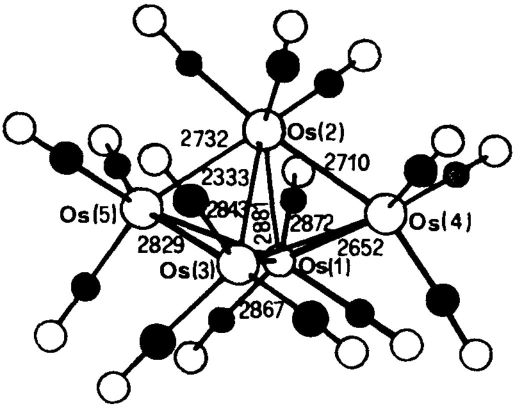


FIG. 42. Molecular structure of the $[HOs_5(CO)_{15}]^-$ anion.

and a trigonal-bipyramidal structure for the ion $[Os_5(CO)_{15}]^{2-}$ similar to that of the ion $[HOs_5(CO)_{15}]^-$.

As indicated in Scheme 11, there are basically two classes of chemistry that have been observed for $[Os_5(CO)_{15}]^{2-}$. One involves expansion of the ligand coordination sphere, without changing the stereochemistry of the metal cluster, and is electronically related to the parent carbonyl $Os_5(CO)_{16}$, while the second involves redox reactions, with addition of two electrons to the metal cluster and concomitant structural changes in the metal polyhedra (*204*).

The reaction of iodine with the ion $[Os_5(CO)_{15}]^{2-}$ falls into the first group. The X-ray structure (*206*) shows that the iodine has replaced one of the carbonyls of the $Os(CO)_4$ group in the $Os_5(CO)_{16}$ molecule, to give the ion $[Os_5(CO)_{15}I]^-$ (see Fig. 43). This reacts further with iodine to give the diiodide $Os_5(CO)_{15}I_2$. This complex reacts reversibly with iodide to generate the monoiodide. Reaction with triphenylphosphine occurs to yield a compound in which orthometallation of one phenyl ring in the triphenylphosphine has occurred for each of the three triphenylphosphine ligands, producing in the process the trihydrido complex $H_3Os_5(CO)_{10}(PPh_2C_6H_4)_3$.

In the second class of reaction, two extra electrons are added to the metal system, with the resultant breaking of a metal–metal bond.

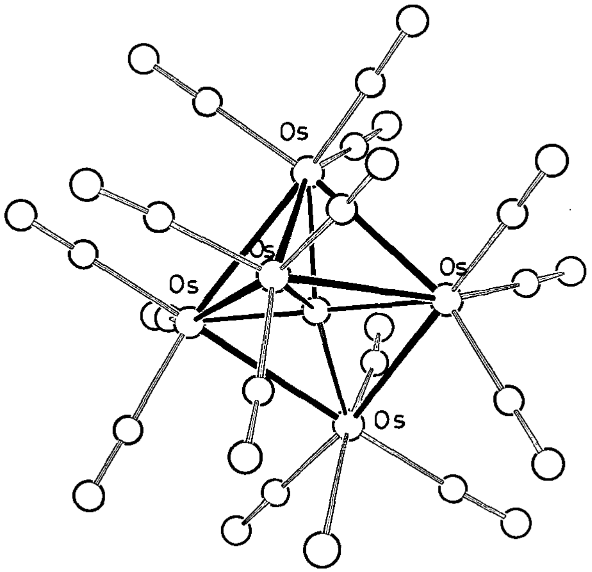


FIG. 43. Molecular structure of the $[Os_5(CO)_{15}I]^-$ anion.

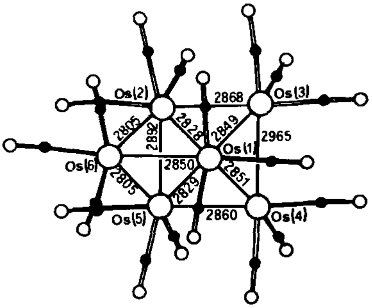


FIG. 44. Molecular structure of $H_2Os_5(CO)_{16}$ (H-ligands omitted—see text).

Reaction of the hydride $H_2Os_5(CO)_{15}$ with carbon monoxide gives $H_2Os_5(CO)_{16}$ in good yields (~ 50%). This hydride was initially obtained in low yield from the pyrolysis of $Os_3(CO)_{12}$ with water (*207*). The structure of this compound is shown in Fig. 44, and reflects a major change in the structure of the metal polyhedron on addition of the extra two electrons and the breaking of one edge of the trigonal bipyramid of metal atoms in the $Os_5(CO)_{16}$ structure (*208*). A stereochemically equivalent transformation may be accomplished by addition of iodide to the $H_2Os_5(CO)_{15}$, to give the anion $[H_2Os_5(CO)_{15}I]^-$. The iodide replaces one of the axial carbonyl groups in the $Os(CO)_4$ fragment of the $H_2Os_5(CO)_{16}$ molecule (*204*). A similar substitution reaction occurs with $P(OMe)_3$, when the phosphite is found to occupy an equatorial rather than an axial site. This difference in stereochemistry possibly reflects the greater steric requirements of the phosphite ligand relative to iodine (Fig. 45). The position of the two hydrogen atoms in the molecules $H_2Os_5(CO)_{16}$, $[H_2Os_5(CO)_{15}]^-$, and $H_2Os_5(CO)_{15}[P(OMe)_3]$ is of some interest. Bond length arguments coupled with symmetry considerations of $H_2Os_5(CO)_{16}$ would indicate that the hydrogens lie along the Os(1)–Os(4) and the Os(2)–Os(4) edges. Consistent with this, the parent hydride, $H_2Os_5(CO)_{16}$, shows only one high-field proton signal in the NMR spectrum, while two signals for $H_2Os_5(CO)_{15}[P(OMe)_3]$ are not inconsistent with the structure observed. However, the two signals observed in $[H_2Os_5(CO)_{15}I]^-$ are more difficult to understand. In terms of a simple bonding pattern, this structure also imposes an "electron deficiency" on the Os(3) $(CO)_3$ group, which could be accommodated by invoking a delocalized donor bond within the Os(1)–Os(2)–Os(3) system.

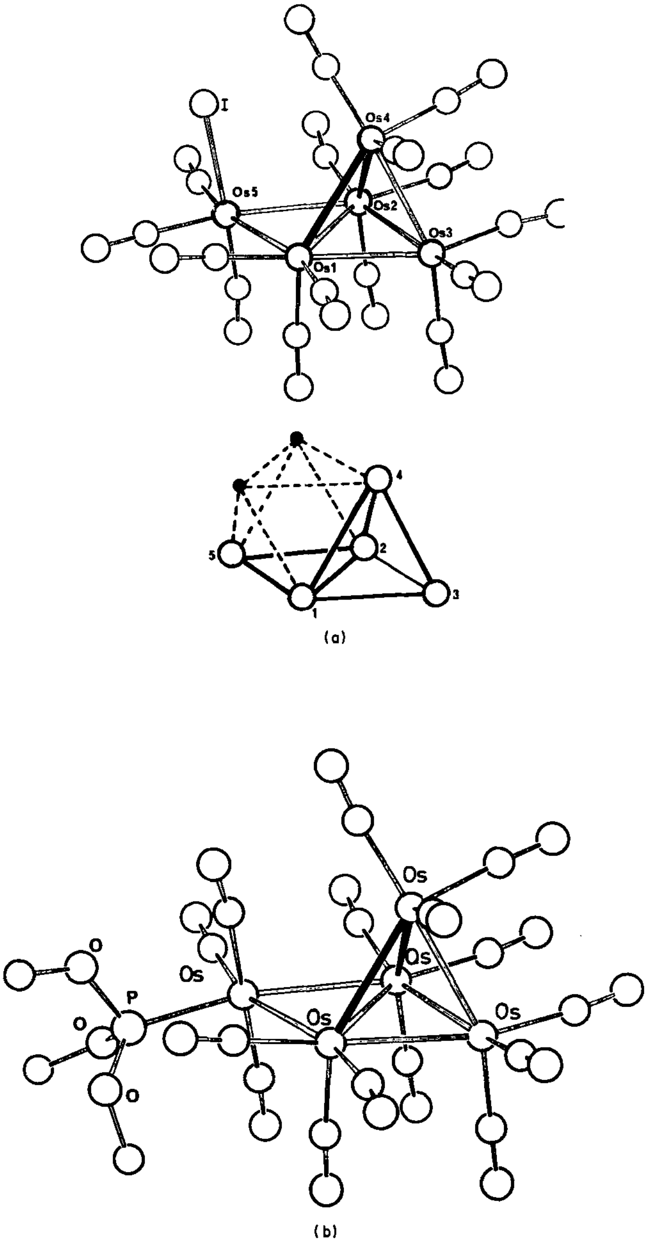


FIG. 45. (a) Molecular structure of $H_2Os_5(CO)_{15}I^-$; (b) molecular structure of $H_2Os_5(CO)_{15}P(OMe)_3$.

2. *Carbido Clusters*

The pentanuclear carbido species $M_5(CO)_{15}C$ (M = Fe, Ru, Os) have been prepared. The iron compound has been known for some considerable time (*209*), but the ruthenium and osmium complexes were prepared recently by pyrolysis reactions (*210*). The ruthenium adduct was only isolated in low yield (~1%), while the osmium complex was obtained in higher yield (~40%). The infrared spectrum and mass spectral breakdown pattern indicate a common structure to these compounds. The molecular structure of the iron complex is shown in Fig. 46.

The formation of carbido–carbonyl cluster compounds with ruthenium and osmium appears to be common in pyrolysis reactions; the basic reaction may be viewed as the transformation of the coordinated carbon monoxide to carbide and carbon dioxide. Small variations in

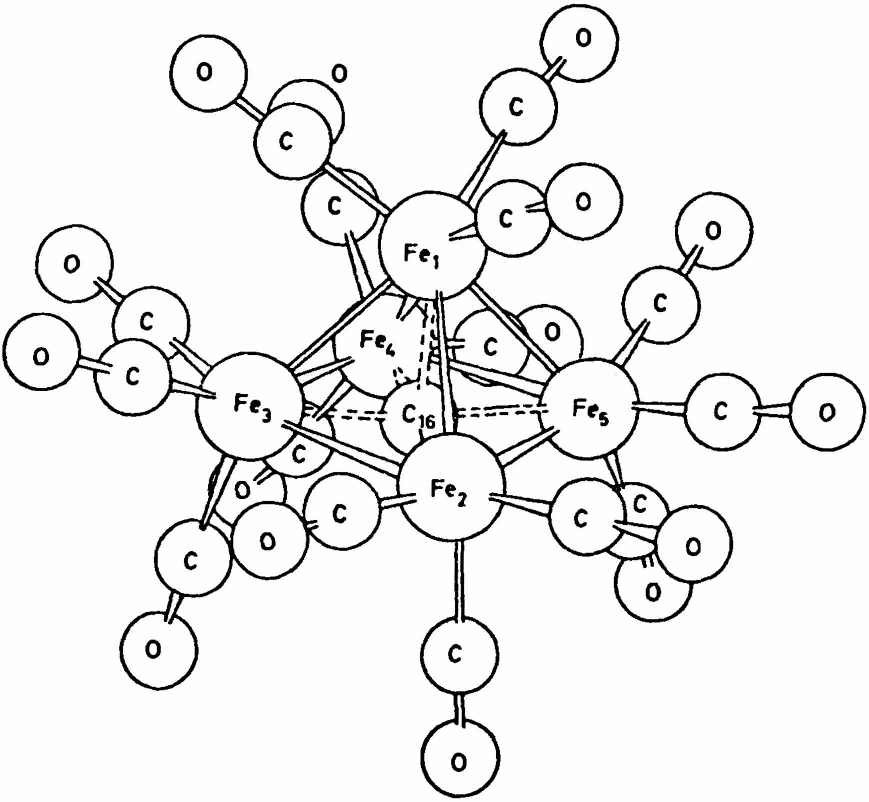


FIG. 46. Molecular structure of $Fe_5(CO)_{15}C$.

temperature, solvent, or substituent appears to markedly influence the nature of the product, and major differences occur between ruthenium and osmium complexes of the same stoichiometry.

Thus, in contrast to $Ru_3(CO)_{12}$ (*211, 212*), which readily yields the hexanuclear cluster $Ru_6C(CO)_{17}$ (*vide infra*), osmium yields $Os_5(CO)_{15}C$ and $Os_8(CO)_{21}C$ on pyrolysis. Substitution of a carbonyl also may lead to a radical change in product distribution. Thermolysis of $Os_3(CO)_{11}$-$[P(OMe)_3]$ yields a series of pentanuclear carbonyl–carbido–phosphite derivatives (*213*). The overall yields of these products are not great, but the conversion is high. The X-ray structures of three of the complexes isolated which appear to provide progressive steps in a series of reactions are shown in Figs. 47–49 (*213, 214*). The characteristic unit is the Os_5C cage, which is given in Fig. 48 and indicates the carbido group bonding to all five metal centers which are in a different stereochemical arrangement to that observed in $Os_5(CO)_{15}C$ (*215*). The facility that carbon has to bond to a variety of different stereochemical arrangements of metals must reflect in the chemistry of the carbido group. The chemistry of this class of compounds has been virtually untouched, and a comparative study between these carbido complexes and carbide transition on metal surfaces is of obvious importance.

I. Hexanuclear Clusters

The first hexanuclear cluster obtained was for ruthenium, as the carbonyl–carbido $Ru_6C(CO)_{17}$. This was prepared by heating $Ru_3(CO)_{12}$ in

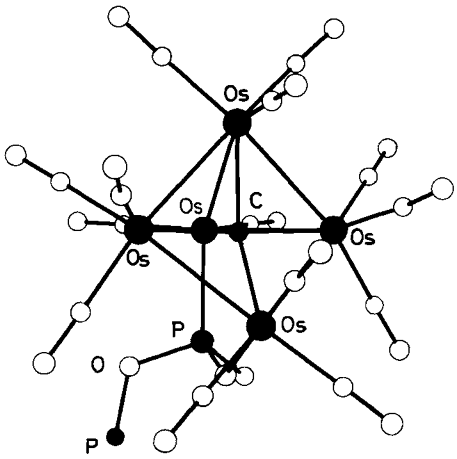


Fig. 47. Molecular structure of $H_2Os_5(CO)_{14}C[P(OMe)_2]$.

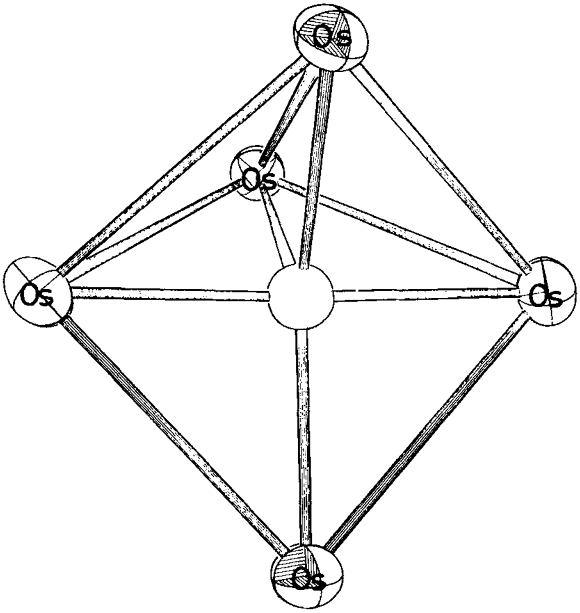
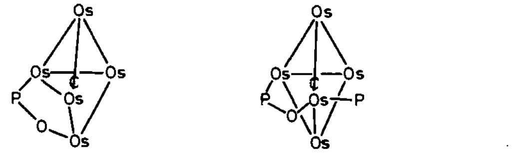
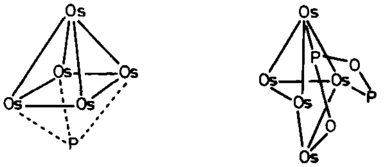


FIG. 48. Os_5C cage in $HOs_5(CO)_{14}[OP(OMe)_2]C$.



$HOs_5(CO)_{14}[OP(OMe)_2]C$ $HOs_5(CO)_{13}[OP(OMe)_2][P(OMe)_3]C$



$Os_5(CO)_{15}POMe$ $HOs_5(CO)_{13}[OP(OMe)OP(OMe)_2]C$

FIG. 49. Molecular structure of some Os_5C derivatives.

an inert solvent such as paraffin, or by heating the solid carbonyl (*201, 211, 212*). This latter experiment proves that the carbido group arises from the carbonyl group (*201*), in contrast to the observation in rhodium–carbonyl–carbide complexes where the carbido group arises from the solvent (*216*). If the reaction is carried out in aromatic solvents, it is possible to isolate the arene-substituted derivative, (arene)$Ru_6(CO)_{14}C$, in which the arene complexes as a six-electron π-system displacing three carbonyl groups (arene = benzene, toluene, mesitylene) (*217*). The corresponding osmium compound, $Os_6C(CO)_{17}$, has been obtained in very small yield. These compounds were the first examples in which it was established that the carbon was bonded to six metal atoms, at the center of the metal octahedron. For the mesitylene complex $Ru_6(CO)_{14}C(C_6H_3Me_3)$ (*218*), the arene is bonded to one metal center, with terminal and bridging carbonyl groups around the rest of the metal cluster unit (see Fig. 50).

The chemistry of these compounds has not been investigated in detail. Scheme 12 summarizes some of the chemistry that has been established for the ruthenium complex $Ru_6C(CO)_{17}$ (*192*). In general, the octahedral metal–carbido skeleton is maintained, substitution reactions occurring with phosphine, phosphites, and arsine ligands. Base attack leads to the production of the anion $[Ru_6C(CO)_{16}]^{2-}$, which is

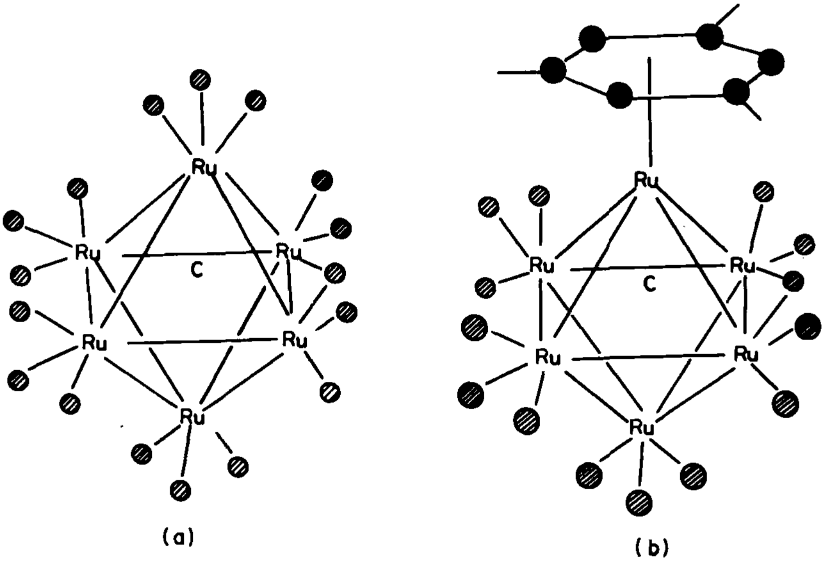
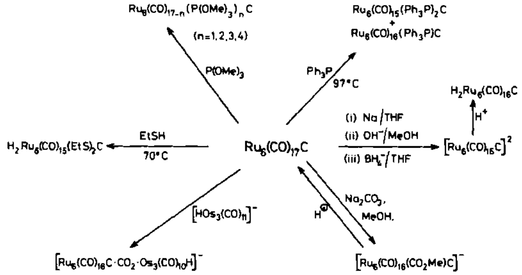


FIG. 50. Molecular structures of (a) $Ru_6C(CO)_{17}$ and (b) $Ru_6C(CO)_{14}(C_6H_3Me_3)$.



SCHEME 12. Some reactions of $Ru_6C(CO)_{17}$.

isoelectronic with $Ru_6(CO)_{16}$, but which, from the infrared spectrum, appears to have a different structure. This ion is presumably formed via attack at the carbonyl center by hydroxide ion; the related reaction with MeO^- yields the carbomethoxy derivative. Acidification of the anion $[Ru_6C(CO)_{16}]^{2-}$ yields the unstable hydride $H_2Ru_6C(CO)_{16}$.

Reaction with sulfur ligands leads to rupture of the metal framework, and the structure of one of the compounds isolated is shown in Fig. 51. The reaction of the parent carbonyl with the ion $[HOs_3(CO)_{11}]^-$

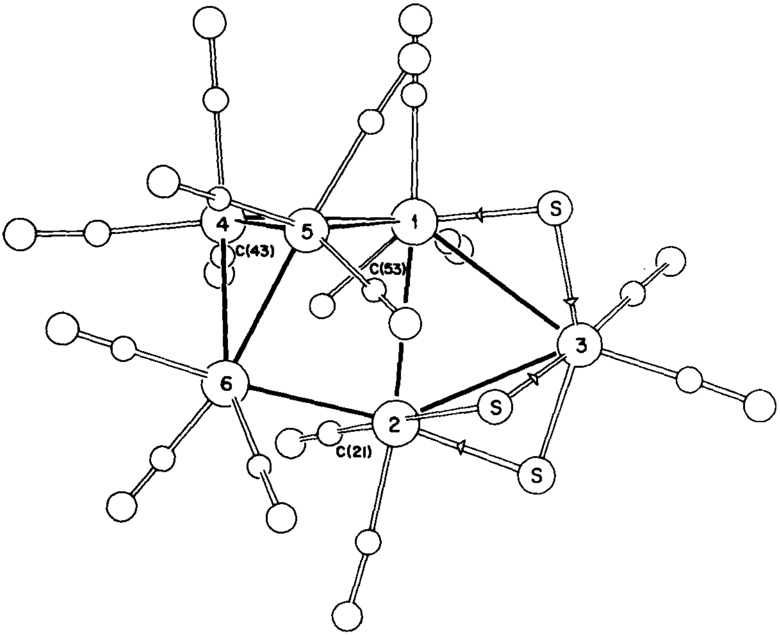


FIG. 51. Molecular structure of $Ru_6C(CO)_{15}(SEt)_3C$.

leads to the formation of the Ru–CO_2–Os bridged species, $[Ru_6C(CO)_{16}CO_2Os_3(CO)_{10}H]^-$, similar to those obtained for polynuclear osmium carbonyls (see Section III,J) (*192*).

The thermolysis of triosmium carbonyl, $Os_3(CO)_{12}$, leads to a mixture of higher carbonyls with a high conversion; $Os_6(CO)_{18}$ is the major product (80%) (*201*). As anticipated from the Wade–Mingos theory, the compound was found to have an octahedral structure of C_{2v} symmetry, involving a bicapped (or a monocapped trigonal-bipyramidal) arrangement of osmium atoms (Fig. 52) (*219*). The structure involves three different metal environments, and requires a metal donor–metal bonding scheme for two of the metal–metal bonds if the conventional E.A.N. rule is applied to each metal center. The chemistry of the molecule does correspond to an electron-deficient system, readily accepting electrons, to yield the anion $[Os_6(CO)_{18}]^{2-}$ in which the hexaosmium octahedron assumes O_h symmetry (*220*). This general sensitivity of the polynuclear framework to the addition of electrons reflects the high metal orbital involvement in the LUMO in these systems. This redox reaction can be accomplished by a variety of reducing agents such as zinc metal, Fe^{2+}, $[\pi\text{-}Cp_2Co]$, and I^- (*221*). In the case of the iodide/iodine couple, the reaction is reversible:

$$Os_6(CO)_{18} \underset{I_2}{\overset{I^-}{\rightleftharpoons}} Os_6(CO)_{18}^{2-}$$

Acidification of the anion leads progressively to $[HOs_6(CO)_{18}]^-$ and $H_2Os_6(CO)_{18}$. These two compounds may be compared with the related ruthenium complexes. The dihydride, $H_2Ru_6(CO)_{18}$, was initially prepared by interaction of $[Mn(CO)_5]^-$ with $Ru_3(CO)_{12}$ (*222*). However, a

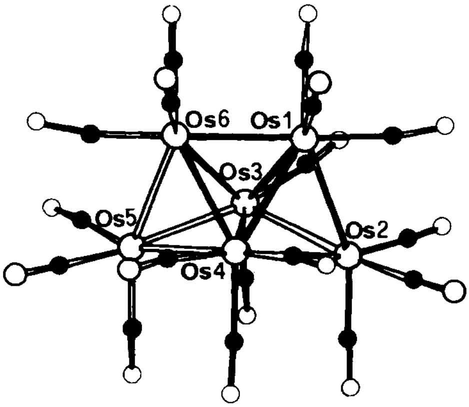
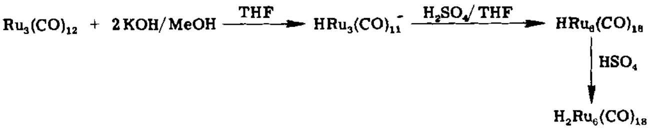


FIG. 52. Molecular structure of $Os_6(CO)_{18}$.

direct and more efficient reaction involves the use of base, as indicated in the following scheme (*223*):

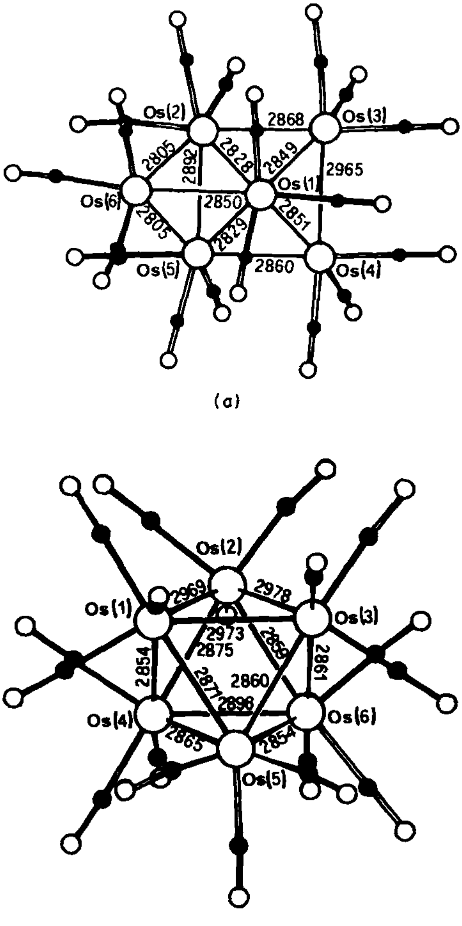


$$Ru_3(CO)_{12} + 2KOH/MeOH \xrightarrow{THF} HRu_3(CO)_{11}^- \xrightarrow{H_2SO_4/THF} HRu_6(CO)_{18} \xrightarrow{HSO_4} H_2Ru_6(CO)_{18}$$

When a large excess of base is used, the anion $Ru_6(CO)_{18}^{2-}$ may be isolated in good yields by the use of large cations. Acidification of the anion yields the dihydride $H_2Ru_6(CO)_{18}$.

The X-ray structures of the five compounds $H_2Os_6(CO)_{18}$, $H_2Ru_6(CO)_{18}$, $[HRu_6(CO)_{18}]^-$, $[HOs_6(CO)_{18}]^-$, and $Os_6(CO)_{18}]^{2-}$ have been obtained. The complex $H_2Ru_6(CO)_{18}$ is considered to involve bonding of the two hydrogens in opposite faces of a Ru_6 octahedron, as implied by the larger metal–metal bonds within these faces, consistent with the lengthening normally observed in bonding of hydrogen between two metal centers (*224*). In contrast to this, in $H_2Os_6(CO)_{18}$ (Fig. 53), the metal atoms form a capped tetragonal-pyramidal structure (*220*). If the same criterion of metal–metal bond distance is used to assign the hydrogen positions, then the hydrogens are placed along two edges of the square face.

The anion $[HOs_6(CO)_{18}]^-$ is structurally related to $H_2Ru_6(CO)_{18}$, and on the basis of bond lengths within the metal polyhedron, the hydrogen is considered to occupy one of the triangular faces of the osmium octahedron, Os(1)–Os(2)–Os(3) (Fig. 53) (*200*). In contrast to this, for the ruthenium analog $[HRu_6(CO)_{18}]^-$, the hydrogen is viewed as being at the center of the ruthenium octahedron, in a manner similar to the carbon in the carbido species mentioned above. Three separate X-ray structures of the anion $[HRu_6(CO)_{18}]^-$ have been undertaken, which all yield a metal structure similar to that observed for the dianion $[Os_6(CO)_{18}]^{2-}$; however, in all cases some crystallographic disorder problems exist (*225*). Consistent with an unusual bonding pattern for the hydrogen, the chemical shift for the hydrogen in the NMR spectrum occurs at $-6.41\ \tau$, well outside the range normally anticipated for metal–hydrogen systems. In contrast to the parent acid $H_2Ru_6(CO)_{18}$, which reacts with base to give the anion $[Ru_6(CO)_{18}]^{2-}$, the anion $[HRu_6(CO)_{18}]^{2-}$ appears to be stable in the presence of excess base (*223*). This may be expected if deprotonation occurs by attack at hydrogen on the inside of the metal octahedron. The presence of a hydrogen in the middle of an octahedron of metals was initially suggested for the ion $[HRu_6(CO)_{18}]^-$; it has now become firmly established with



(a)

(b)

FIG. 53. Molecular structures of (a) $H_2Os_6(CO)_{18}$ and (b) $[HOs_6(CO)_{18}]^-$ anion.

various nickel and cobalt octahedral systems by means of neutron diffraction measurements (see Section III,C).

The anion $[Os_6(CO)_{18}]^{2-}$ has an octahedral arrangement of metal atoms of approximately O_h symmetry, and is crystallographically very similar to the $[HRu_6(CO)_{18}]^-$ ion. This collection of structural data on electron-equivalent systems emphasizes some of the dangers in trying to predict the structure of complexes solely on the basis of electron counting procedures (*220*).

The substitution chemistry of the $Os_6(CO)_{18}$ unit has not been extensively investigated. Amine oxide oxidation reactions carried out in the presence of acetonitrile yielded the mono- and disubstituted derivatives $Os_6(CO)_{17}(CH_3CN)$ and $Os_6(CO)_{16}(CH_3CN)_2$. The stereochemistry of the substitution products is not known, but displacement with pyridine occurs from both to yield the same adduct, $Os_6(CO)_{16}(py)$, which appears to be an orthometallated species similar to those observed in the trinuclear cluster system (*226*).

Reaction with *p*-tolylisocyanide leads to an addition complex $Os_6(CO)_{18}(CNC_6H_4CH_3)_2$ (*227*). The X-ray structure indicates two types of isocyanide bonding; as anticipated from the stoichiometry, a major change has occurred in the structure of the metal polyhedron, with three of the Os–Os bonds of the parent carbonyl $Os_6(CO)_{18}$ being ruptured (Fig. 54a). The six electrons required to accomplish this are provided by the two isocyanide groups. The terminal isocyanide donates two electrons, while the bridging isocyanide group contributes four electrons to the cluster unit (see Fig. 54). These are formally related to the complexes $HOs_3(CO)_{10}(C{=}NMeR)$, discussed above, with R being an osmium atom within the cluster. An alternative structure for an isocyanide, involving substitution rather than addition, is shown in Fig. 54b. The complex $Os_6(CO)_{16}(CNCMe_3)_2$ was obtained by pyrolysis of the triosmium cluster $Os_3(CO)_{11}(CNCMe_3)$. The substitution of the two carbonyl groups of the $Os_6(CO)_{18}$ slightly lengthens the metal–metal bond lengths involving those metal atoms bonded to the isocyanide groups, but the metal polyhedron is in general insensitive to this substructure (*195*).

The interaction of the $Os_6(CO)_{18}$ unit with olefins has been studied in a preliminary way. A large range of products occurs, and the structures of two of them obtained in the reaction with ethylene, $Os_6(CO)_{16}(C_4H_6)$ and $Os_6(CO)_{16}(C_5H_6)$, have been determined (Fig. 55a and b) (*228*). They show a major modification in the basic metal arrangement, the first compound having a triangular face and a square face capped by a $C{-}CH_3$ grouping. The second of the two compounds involves the coupling of these two units to yield a "butterfly" arrangement of metals with the insertion of a $CH_3C{\cdot}CCH_3$ group and a carbido group bonded to the square face of the polyhedron (*229*). The same complexes may also be prepared from acetylene via $H_2Os_6(CO)_{18}$ (163°C, decane) or $Os_3(CO)_{12}$ (at 200°C). A complex related to $Os_6(CO)_{16}C_4H_6$, in which the two capping $C{\cdot}CH_3$ groups are replaced by the C–Ph unit, is obtained from reaction of $Os_6(CO)_{18}$ with $PhC{\equiv}CH$ (*197*). The ability of ethylene to lead to polymerization reactions of a similar type of alkynes in the trinuclear system is consistent with the postulate that the restriction for polymerization in alkene/$Os_3(CO)_{12}$ chemistry is associated with steric effects, the availability of more than one triangular

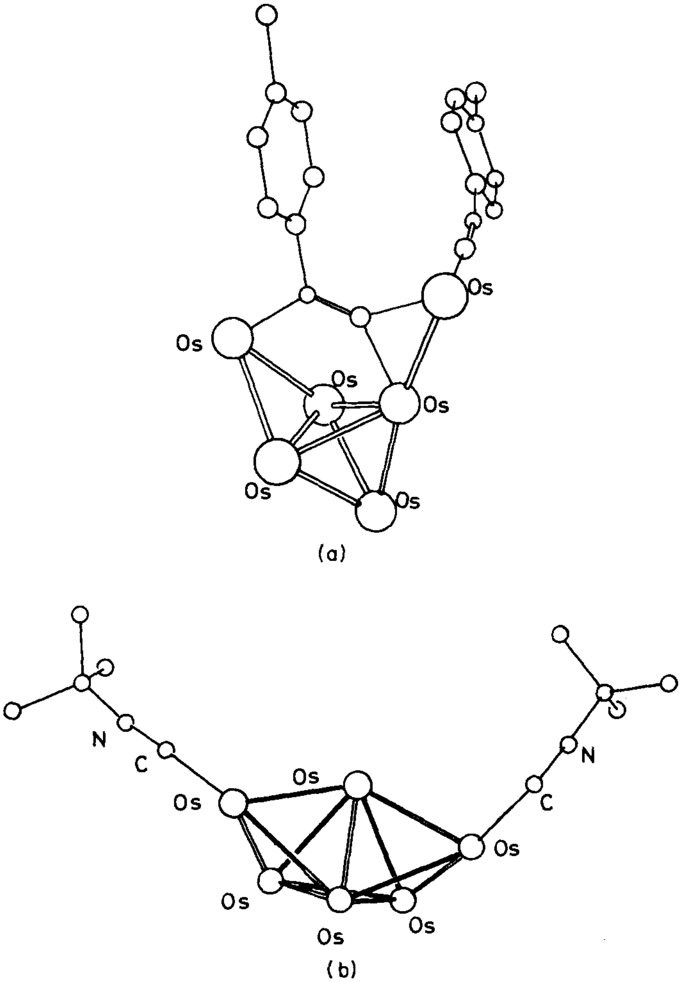
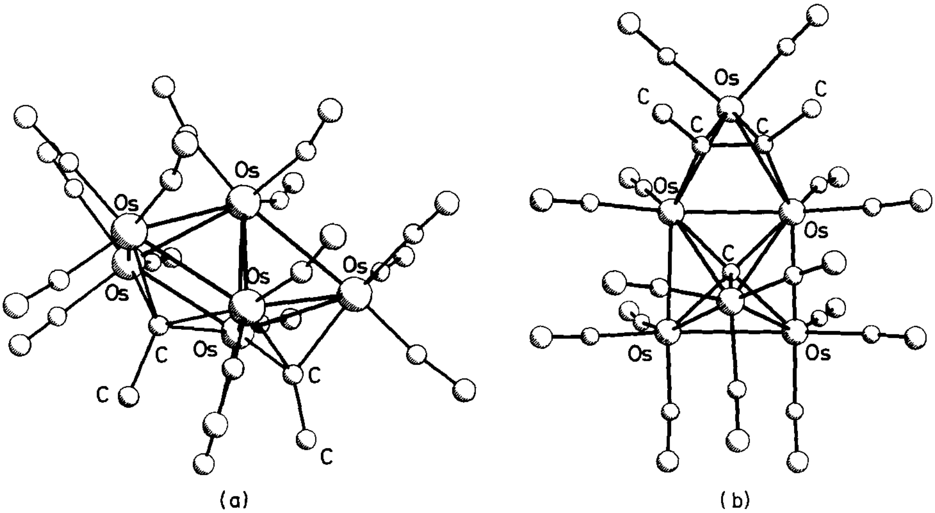


FIG. 54. (a) Molecular structure of $Os_6(CO)_{18}(CNC_6H_4Me)_2$; (b) molecular structure of $Os_6(CO)_{16}(CNCMe_3)_2$.

metal face to the polyhedra allowing the coordination of the second alkene group.

J. HIGHER POLYNUCLEAR CLUSTERS

From the pyrolysis of $Os_3(CO)_{12}$, it was possible to isolate the carbonyls $Os_7(CO)_{21}$ and $Os_8(CO)_{23}$ in small yields (*201*). A study of the chemistry of these species has been restricted because of the small



(a) (b)

FIG. 55. (a) Molecular structure of $Os_6(CO)_{16}(CMe)_2$; (b) molecular structure of $Os_6(CO)_{16}(C_4H_6)C$.

amount of materials available. Pyrolysis of $Os_3(CO)_{12}$ at higher temperatures provides carbido species, as mentioned above, and one such species is $Os_8(CO)_{21}C$; the complex $H_2Os_7C(CO)_{19}$ (*230*) was also prepared in small yields in the reaction of $Os_3(CO)_{12}$ with water. As with the whole development of the higher polynuclear clusters, the identification of these species was very dependent on the use of mass spectrometric methods, with a careful analysis of fragmentation patterns which, for instance, give characteristic spectra for carbido–metal species. The hydrides were identified by a combination of infrared–deuteration studies and the characteristic high-field metal–hydrogen signal in the ^1H-NMR spectra of the compounds

The structure of the heptaosmium carbonyl $Os_7(CO)_{21}$ has been determined by X-ray studies, and the ^{13}C-NMR is consistent with the same structure in solution (*231*). The stereochemistry of the metal polyhedron follows Wade theory and is a monocapped octahedron (see Fig. 56). As anticipated for this structure, the ^{13}C-NMR spectrum of an isotopically enriched sample ($^{13}CO \sim 40\%$) shows three different chemical shifts, with an intensity ratio of 3:5:1. This spectrum is related to that of $[HOs_6(CO)_{18}]^-$, which also has an idealized C_{3v} symmetry, and may be viewed as $[Os_7(CO)_{21}]$ with the $Os(CO)_3$ cap replaced by the hydrido group. The NMR spectrum of $Os_7(CO)_{21}$ only begins to show evidence of structure to the three bonds at $-120°$, but the resolution of the 2:1 component for each group, expected on the basis of the X-ray struc-

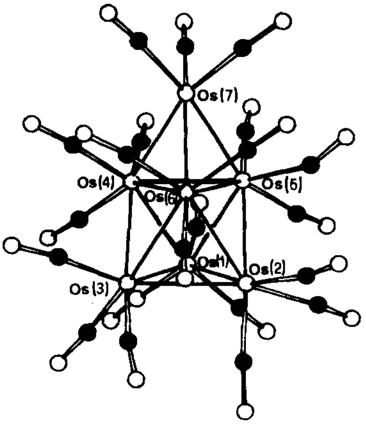


FIG. 56. Molecular structure of $Os_7(CO)_{21}$. The bond lengths within the metal polyhedron are: Os(1)–Os(2), 2.880; Os(1)–Os(3), 2.935; Os(1)–Os(4), 2.849; Os(1)–Os(5), 2.849; Os(2)–Os(3), 2.892; Os(2)–Os(5), 2.876; Os(2)–Os(6), 2.876; Os(3)—Os(4), 2.854; Os(3)–Os(6), 2.839; Os(4)–Os(5), 2.834; Os(4)–Os(6), 2.824; Os(4)–Os(7), 2.806; Os(5)–Os(6), 2.848; Os(5)–Os(7), 2.830; Os(6)–Os(7), 2.821; average e.s.d., 0.006 Å.

ture, is not complete at this temperature. It is noteworthy that $[HOs_6(CO)_{18}]^-$ exhibits a similar low barrier to fluxionality.

The structure of $Os_8(CO)_{23}$ has not been determined; from Wade's theory, this would be expected to be a bicapped octahedron, or obtained from the $Os_7(CO)_{21}$ stereochemistry by capping another trigonal face. Obviously there are a number of ways in which this may be accomplished. An interesting chemical consequence, for structures that involve capping of metal polyhedra, appears to be the facile reaction of such systems with base to remove the capping group and decrease the metal nuclearity by one. In the hexa-, hepta-, and octanuclear osmium species, the following reactions with base (OH^-) have been observed to occur with high yields:

$$Os_6(CO)_{18} \rightarrow [Os_5(CO)_{15}]^{2-}$$

$$Os_7(CO)_{21} \rightarrow [Os_6(CO)_{18}]^{2-}$$

$$Os_8(CO)_{23} \rightarrow [Os_7(CO)_{21}]^{2-}$$

In the case of the octaosmium carbonyl, it is not clear whether the heptaosmium carbonyl anion has 20 or 21 carbonyl groups in the ion. If the latter is the case, then the ion corresponds to the "electron"-precise system according to or the Wade theory, and arises from an "electron-deficient" neutral carbonyl species. These reactions are of considerable preparative utility for the Os_6/Os_5 system, and, as has been amplified in the discussion of the pentaosmium carbonyl series, form a natural

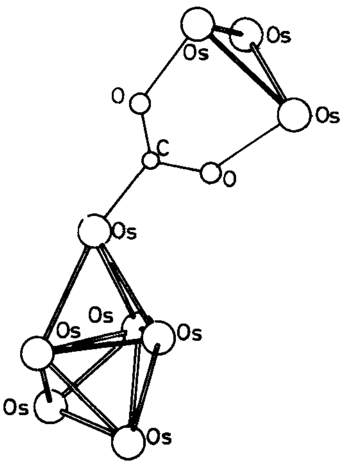


FIG. 57. Molecular structure of the $[HOs_3(CO)_{10}O_2C{\cdot}OS_6(CO)_{17}]^-$ anion.

entry to this chemistry from the readily prepared $Os_6(CO)_{18}$ species. $Os_6(CO)_{18}$ was found to undergo an interesting reaction with the anion $[HOs_3(CO)_{11}]^-$, to yield a complex in which the two cluster units are linked via a CO_2 bridge (see Fig. 57). This appears to be a general reaction: the cluster $Os_5(CO)_{16}$ giving $[HOs_3(CO)_{10}O_2C{\cdot}Os_5(CO)_{15}]^-$ and $Os_7(CO)_{21}$ the corresponding complex $[HOs_3(CO)_{10}O_2C{\cdot}Os_7(CO)_{20}]^-$ (*232*). As indicated above, a similar complex was isolated with the ruthenium carbido cluster $Ru_6C(CO)_{17}$. This reaction appears to be specific to the $[HOs_3(CO)_{11}]^-$ ion and did not occur with $[HRu_3(CO)_{11}]^-$. The obvious potential intermediate in this reaction is $[HOs_3(CO)_{10}(OH)]$, which may be viewed as attacking a group of three other metal clusters, by the coordinated OH, in a manner reminiscent of the methoxide or hydroxide ion discussed above. However, the hydroxy derivative was found not to react with these complexes.

The detailed bonding in the CO_2 bridged unit is of interest. From the X-ray details of the Os_9 species, it may be considered as either bonding as a carbene to the Os(4) or a carboxylato group to the $[HOs_3(CO)_{10}]$ fragment. The bond lengths fall in an intermediate range for these two alternatives. The presence of the —CO_2 bridging group is readily identified in the infrared by strong absorption in the region ~1250 cm^{-1}.

K. HETERONUCLEAR CLUSTERS OF IRON, RUTHENIUM, AND OSMIUM

We have restricted the discussion in the section primarily to mixed carbonyl, carbonyl–hydride, or phosphine-substituted cluster compounds. On the basis of electronegativity, there should be an enhance-

TABLE XI

ELECTRONEGATIVITIES OF LATER TRANSITION ELEMENTS

Cr	Mn	Fe	Co	Ni	Cu
1.66	1.55	1.83	1.88	1.91	1.90
Mo	Tc	Ru	Rh	Pd	Ag
2.16	1.9	2.2	2.28	2.20	1.93
W	Re	Os	Ir	Pt	Au
2.36	1.9	2.2	2.20	2.28	2.54

ment to the metal–metal bond energy by combining metals within different rows and groups of the periodic table, as there are significant differences in the electronegativity of the metals. Table XI summarizes the Pauling values of the electronegativities for this triad of elements and their immediate neighbors in the periodic table. In particular, bonding with this group and the later members of the transition elements, Au and Pt, should be very favorable. A broad range of heteronuclear clusters has recently been isolated and the compounds are given in Tables XII and XIII. A wide range of stabilities has been observed. In some instances there is a tendency toward disproportionation to the component homonuclear species. The polarity of the metal–metal bond in these heteronuclear compounds is often reflected in a greater kinetic lability within the systems.

In the majority of cases, the chemistry of these complexes has not been investigated in any detail, and in many instances the compounds have not been isolated in the pure state but have been identified as a component in a complex mixture of derivatives. In such cases, the

TABLE XII

TRINUCLEAR CARBONYLS AND SUBSTITUTED CARBONYLS FOR HETERONUCLEAR CLUSTERS

$[Fe_2Mn(CO)_{12}]^-$ $[Fe_2Tc(CO)_{12}]^-$ $[Fe_2Re(CO)_{23}]^-$	$FeRu_2(CO)_{12}$ $FeOs_2(CO)_{12}$ $Fe_2Ru(CO)_{12}$ $Fe_2Os(CO)_{12}$	$FeCo_2(\pi\text{-}C_5H_5)_2(CO)_6$ $FeRh_2(\pi\text{-}C_5H_5)_2(CO)_6$ $Fe_2Co(\pi\text{-}C_5H_5)(CO)_9$ $Fe_2Rh(\pi\text{-}C_5H_5)(CO)_9$	$FePt_2(CO)_8(PR_3)_3$ $Fe_2Pt(CO)_9(PR_3)$ $Fe_2Pt(CO)_8(PR_3)_2$
$RuRe_2H_2(CO)_{12}$	$RuOs_2(CO)_{12}$		$RuPt_2(CO)_4(PR)_3)_4$
$[Os_2Mn(CO)_{12}]^-$ $Os_2MnH(CO)_{12}$ $[Os_2Re(CO)_{12}]^-$ $Os_2ReH(CO)_{12}$		$OsCo_2(CO)_{11}$	

TABLE XIII

Heteronuclear Carbonyls and Substituted Carbonyls

$[Fe_2Mo(\pi C_5H_5)_2(CO)_{10}]^{2-}$ $[Fe_2W_2(\pi C_5H_5)_2(CO)_{10}]^{2-}$	—	$FeRu_3H_4(CO)_{12}$ $FeRu_3H_2(CO)_{12}$ $FeOs_3H_2(CO)_{13}$ $FeRuOs_3H_3(CO)_{13}$ $FeRu_2OsH_2(CO)_{13}$ $FeRu_2H_2(CO)_{13}$	$[FeCo_3(CO)_{12}]^-$ $FeCo_3H(CO)_{12}$ $FeCo_3H(CO)_9L_3$ $FeCo_3H(CO)_{10}L_2$ $FeCo_3H(CO)_{11}L$ $[Fe_2Co(CO_{13}]^-$ $Fe_2Rh_2(CO)_8(\pi\text{-}C_5H_5)$ $Fe_3Rh(CO)_{11}(\pi\text{-}C_5H_5)$	$[Fe_3Ni(CO)_{12}]^-$ $Fe_3NiH(CO)_{12}$	—
—	$Ru_2Re_2H_2(CO)_{16}$ $[Ru_3Re(CO)_{16}]^-$	$RuOs_3H_4(CO)_{12}$ $Ru_2Os_2H_4(CO)_{12}$ $Ru_3OsH_4(CO)_{12}$	$RuCo_3H(CO)_{12}$	—	—
—	$Os_3MnH_3(CO)_{13}$ $Os_3ReH_3(CO)_{13}$ $Os_3MnH(CO)_{16}$ $Os_3ReH(CO)_{15}$ $Os_3ReH(CO)_{16}$ $Os_3Re_2H_2(CO)_{19}$ $Os_3Re_2H_2(CO)_{20}$	—	$OsCo_3H(CO)_{12}$ $Os_2Co_2H_2(CO)_{12}$ $Os_3CoH_3(CO)_{12}$	$Os_2Pt_2H_2(CO)_8[(C_6H_5)_3P]_2$ $Os_3NiH_2(CO)_{10}[(C_6H_5)_3P]_2$ $Os_3PtH_2(CO)_{10}(C_5H_5)_3P$ $Os_3PtH_2(CO)_{10}[(C_6H_5)_3P]_2$	$Os_2AuCl(CO)_{12}$ $Os_3AuH(CO)_{10}(C_6H_5)_3P$

structure has been established by mass, NMR, and infrared spectroscopic analysis of the mixtures. Recently, the separation of some of these mixtures by more refined techniques such as high-pressure liquid-phase chromatography (HPLC), has proved possible, and this certainly is seen as a potential development in the field. In the field of mass spectrometry, it is important to have the facility for C.I. as well as E.I. spectroscopy, as this simplifies the identification of the components of the mixed products. In general, the stability of these compounds increases with increase in the atomic weight of the metal components, reflecting the increase in the bond strength of metal–metal bonds on descending a triad, and also the increase in the electronegativity on descending a group (see Table X). It will be of obvious interest to study the variation in the reactivity of these heteronuclear clusters on varying the polarity of the metal–metal bond.

This field has developed at a rapid pace since 1968, and a wide range of heteronuclear complexes of the tri- and tetranuclear variety has been established. It will be convenient to discuss the compounds in the first instance on the basis of nuclearity and, for the tetranuclear species, to subdivide the discussion on the basis of the carbonyl stoichiometry and cluster electron count. We have excluded from the discussion the interaction with nontransition elements, such as Hg, Tl, and Cd, which form a wide range of compounds.

1. *Trinuclear Compounds*

All the various mixed metal carbonyls containing two of the metals in the triad, Fe, Ru and Os, in the form $M^1M^2_2(CO)_{12}$ have been prepared. The ruthenium and osmium combination was the initial group to be obtained and resulted from refluxing the two carbonyls together in xylene, when a statistical distribution of $Ru_3(CO)_{12}$, $Ru_2Os(CO)_{12}$, $RuOs_2(CO)_{12}$ and $Os_3(CO)_{12}$ occurs (*233*). The related iron complexes have been prepared by a number of reactions, the first two representing an "equilibration" reaction while the last utilizes the "redox-condensation" reaction, used with so much effect by Chini (*234*). It must be recognized, however, that the mechanistic courses of such reactions are often difficult to establish, as the carbonyls of this group react readily with any protonic medium, especially water, to give hydrido derivatives which may be intermediates in reactions of the first type and often appear as additional products in the reaction.

$$Fe(CO)_5 + Ru_3(CO)_{12} \longrightarrow Fe_2Ru(CO)_{12} + FeRu_2(CO)_{12} + H_2FeRu_3(CO)_{13}$$

$$Ru_3(CO)_{12} + Fe(CO)_5 \xrightarrow{UV} Fe_2Ru(CO)_{12}$$

$$Fe(CO)_5 + [Ru(CO)_3Cl_2]_2 \longrightarrow H_2FeRu_3(CO)_{13} + FeRu_2(CO)_{12} + Fe_2Ru(CO)_{12}$$

The structures of the derivatives have been inferred from their infrared spectra; the carbonyls $Fe_2M(CO)_{12}$ (M = Ru, Os) are similar to $Fe_3(CO)_{12}$ with bridging carbonyl groups between the iron centers, while the carbonyls $FeM_2(CO)_{12}$ have the $Ru_3(CO)_{12}$ structure (*235–237*).

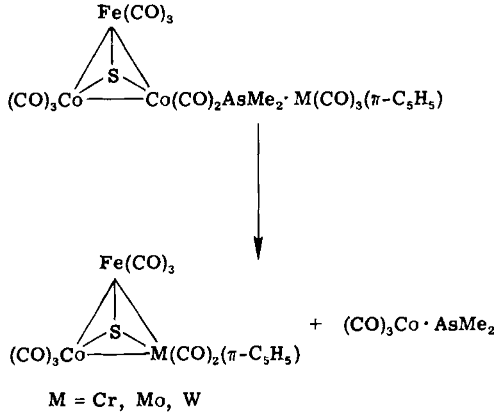
Related rhenium and manganese derivatives have been obtained by the reduction of $Os_3(CO)_{12}$ with $Mn(CO)_5^-$ or $Re(CO_5^-$, to yield the anions $[MnOs_2(CO)_{12}]^-$ and $[ReOs_2(CO)_{12}]^-$; acidification yields the corresponding hydrides (*238*). The infrared spectra for both the ionic species and the hydrides indicate the absence of bridging carbonyl groups and presumably structures based on that of the parent compound $Os_3(CO)_{12}$. The related iron anions $[MFe_2(CO)_{12}]^-$ (M = Mn, Tc, Re) have also been reported (*239*). The corresponding reaction with ruthenium carbonyl, $Ru_3(CO)_{12}$, yielded heteronuclear compounds only for rhenium; the trinuclear component was $H_2Re_2Ru(CO)_{12}$, while the tetranuclear adducts $H_2Re_2Ru_2(CO)_{16}$ and $[Re_3Ru(CO)_{16}]^-$ were also formed (*238*).

Complexes of composition $(\pi\text{-}C_5H_5)MFe_2(CO)_9$ and $(\pi\text{-}C_5H_5)_2M_2\text{-}Fe(CO)_6$ (M = Co, Rh) have been isolated. These may be considered to be based on the $Fe_3(CO)_{12}$ molecule with the (π-CpM) group equivalent to an $[Fe(CO)_3]$ moiety. The ^{13}C-NMR of the dirhodium complex $(\pi\text{-}C_5H_5)_2Rh_2Fe(CO)_6$ indicates two bridging carbonyl groups between the rhodium atoms with no carbonyl bridging to the iron atom (*240*).

Reaction of the manganese and rhenium carbonyls, $M_2(CO)_{10}$, with $Ru_3(CO)_{12}$ or $Os_3(CO)_{12}$ in a 3:1 ratio yields the products $[M(CO)_5]_2M'(CO)_4$, with M = Re or Mn, M' = Ru or Os. These are considered to be linear trinuclear metal systems. The only other trinuclear carbonyl derivative isolated is $OsCo_2(CO)_{11}$, obtained as one of a number of compounds from the reaction of $Co_2(CO)_8$ with $H_2Os(CO)_4$. No structural data are available for this compound (*241*).

A range of trinuclear iron, ruthenium, and osmium–platinum phosphine–carbonyl complexes has been obtained by reaction of the metal carbonyls $M_3(CO)_{12}$ (M = Fe, Ru) or the hydride $H_2Os(CO)_4$ with the platinum phosphine complexes $Pt(PR_3)_4$ or $Pt(PR_3)_2$(olefin) (*242*). A wide range of phosphine, phosphite, and arsine derivatives have been prepared by these methods and form two series for iron, namely $Fe_2Pt(CO)_9L$ and $Fe_2Pt(CO)_8L_2$ (*243*). A basic triangulated metal structure has been established and, with triphenylphosphite, the derivative $FePt_2(CO)_8L_3$ has also been isolated. For ruthenium, the compounds $RuPt_2(CO)_5L_3$, $Ru_2Pt(CO)_7L_3$, and $RuPt_2(CO)_4L_4$ were obtained with a variety of phosphines and phosphites (*244*). The structure of the compound $[(MePh_2)P]_3RuPt_2(CO)_5$ has been determined (*245*). With osmium, the compounds formed were more limited and of the types $OsPt_2(CO)_5L_3$ and $Os_2Pt(CO)_7L_3$. These are of interest as they involve phosphine and carbon monoxide transfer between metal centers, as is illustrated in the structure of the compound $Ph_3P(CO)PtFe_2(CO)_8$ (*243*). In these compounds, as discussed below for the tetranuclear derivatives, the platinum configuration often does not correspond to the E.A.N. rule (see Section II).

Although not within the general coverage of this review, it is of interest to note the preparation of a series of trinuclear metal compounds which are chiral. Vahrenkamp, using an elimination reaction, has been able to prepare a series of tetrahedral molecules containing three different metal centers:



Related phosphine-substituted derivatives were also obtained, and the chirality of the clusters demonstrated by the NMR spectra of the compounds (*246*). Molecules of this type have obvious utility in establishing the potential intermediacy of the polynuclear adduct in a catalytic reaction by the formation of optically active products.

2. *Tetranuclear Compounds*

The tetranuclear derivatives are classified as derivatives of the three principal carbonyl cluster units observed, $H_4M_4(CO)_{12}$, $H_2M_4(CO)_{13}$, and $M_4(CO)_{16}$, with a final group involving bonding to platinum or gold.

a. $H_4M_4(CO)_{12}$ Derivatives. The iron complex $H_4FeRu_3(CO)_{12}$ (*235, 236*) is readily prepared by the action of hydrogen on the complex

$H_2FeRu_3(CO)_{13}$ (*247*). This relates to the corresponding reaction observed for homonuclear species, $H_2 + H_2Ru_4(CO)_{13} \rightarrow H_4Ru_4(CO)_{12} + CO$. The reaction of the corresponding osmium compound, $H_2FeOs_3(CO)_{13}$, described below, has not been investigated. The full range of mixed ruthenium osmium complexes $H_4M_{(4-n)}M^1_n(CO)_{12}$ (M = Ru, M^1 = Os, $n = 1-4$) was obtained as a mixture, which could not be separated, from the reaction of $Os(CO)_4^{2-}$ or $Ru(CO)_4^{2-}$ with $Ru_3(CO)_{12}$ or $Os_3(CO)_{12}$, respectively. The composition of the mixture was readily established by C.I. mass spectroscopy, in contrast to the E.I. mass spectrum, which was too complex to allow identification of the species. The infrared spectrum of the mixture was similar to that of the two parent species $H_4M(CO)_{12}$ (M = Ru, Os), and the structure is taken to be similar (*247*).

For mixed carbonyl adducts, from other groups, redox condensation reactions have been employed to considerable effect. Thus for osmium–cobalt, a range of derivatives has been prepared (*241, 248, 249*) by reactions of the types:

$$Co_2(CO)_8 + H_2Os(CO)_4 \longrightarrow OsCo_2(CO)_{11} + H_2Os_2Co_2(CO)_{12}$$

$$Na_2OsCl_6 + CO + Co_2(CO)_8 \xrightarrow{H^+} HOsCo_3(CO)_{12}$$

$$H_2Os_3(CO)_{10} + Co_4(CO)_{12} \longrightarrow H_3CoOs_3(CO)_{12}$$

The complexes appear to be based on a tetrahedral distribution of metal atoms, with the di- and triosmium derivatives containing no bridging carbonyl group. A detailed X-ray structure of the complex $H_3CoOs_3(CO)_{12}$ has been carried out (*249*).

Related complexes for ruthenium and iron, namely $HRuCo_3(CO)_{12}$ (*250*), $HFeCo_3(CO)_{12}$, and the anion $FeCo_3(CO)_{12}^-$ have been prepared (*251*). The substitution reactions of the derivative with phosphine and phosphites have been fully investigated (*252*). The hydride is a strong acid and, for a cobalt-containing cluster, shows a remarkable stability. The structure of these compounds involves a basal triangular plane of cobalt atoms, with three carbonyl bridges between the metal centers, capped by a $Fe(CO)_3$ group. The position of the hydrogen in the present compound was considered to be at the center of the tetrahedron; a recent X-ray/neutron diffraction study structure of the trimethylphosphite derivative $HFeCo_3(CO)_9[P(OMe)_3]_3$ has shown that for this compound the hydrogen bridges the cobalt triangular face, lying on the opposite side of the plane to the iron atom (*253, 254*). The Mössbauer spectra indicate that this is the case for all the following derivatives studied: $HFeCo_3(CO)_{12-n}L_n$ [$n = 1, 2$, L = PEt_3, $PMePh_2PPh_3$, $P(OMe)_3$, $P(OPr)_3$, $P(OPh)_3$; $n = 3$, L = $PMePh_2$, $P(OMe)_3$].

The anion $[Fe_3Co(CO)_{12}]^-$ has recently been reported to be prepared by Chini from the redox reaction of $Fe_3(CO)_{12}$ with $Co(CO)_4^-$, but no details of its chemistry have been given *(234)*. Similarly, the complex $[NiFe_3(CO)_{12}]^{2-}$ has been observed in the reaction of $Ni(CO)_4$ with $Fe_3(CO)_{11}^{2-}$. The hydrido anion $[HFe_3Ni(CO)_{12}]^-$ has been identified, and the infrared spectra indicate a $Co_4(CO)_{12}$ structure with nickel in the basal plane *(234)*.

b. $H_2M_4(CO)_{13}$ Derivatives. As indicated above, the stability of polynuclear species increases on descending the triad. In keeping with this, the adducts $H_2FeM_3(CO)_{13}$ (M = Ru, Os) are markedly more stable than the iron adduct $H_2Fe_4(CO)_{13}$ *(247)*. The ruthenium complex has been prepared in high yield (~50%) by the reaction of $Fe(CO)_4^{2-}$ with $Ru_3(CO)_{12}$; the corresponding osmium complex, however, is only produced in low yield (~10%) from the related reaction between $Fe(CO)_4^{2-}$ and $Os_3(CO)_{12}$. The structure of the iron–ruthenium complex has been shown to be equivalent to the structure of $H_2Ru_4(CO)_{13}$ *(190)*, with the iron in the basal plane, involving semibridging carbonyl groups between the metal centers *(247)*.

The complex $H_2Fe_2Ru_2(CO)_{13}$ was prepared by the reaction of $Fe(CO)_4^{2-}$ with $FeRu_2(CO)_{12}$. It was produced with a number of other tetranuclear derivatives and could be separated from all other compounds but $H_2FeRu_3(CO)_{13}$. The infrared spectrum has been interpreted as indicating a structure similar to $H_2FeRu_3(CO)_{13}$. Attempts to prepare the final member of the series, $H_2Fe_3Ru(CO)_{13}$, were not successful. The related Fe/Os derivatives have not been isolated *(247)*.

Clusters containing all three metals of this group have recently been isolated. These were prepared by an extension of the preparative procedure used for the mixed Fe/Ru clusters. The reaction of $Fe(CO)_4^{2-}$ with the trimers $Ru_2Os(CO)_{12}$ and $RuOs_2(CO)_{12}$, obtained as a mixture by pyrolysis of $Os_3(CO)_{12}/Ru_3(CO)_{12}$ (*vide supra*), gave a mixture of products, from which by HPLC techniques it was possible to isolate the complexes $H_2FeRu_2Os(CO)_{13}$ and $H_2FeRuOs_2(CO)_{13}$ in good yields (36 and 74%, respectively) *(215)*.

The infrared, NMR, and electronic absorption spectra of the two complexes $H_2FeRu_2Os(CO)_{13}$ and $H_2FeRuOs_2(CO)_{13}$ have been taken to indicate a structure for these compounds similar to $H_2FeRu_3(CO)_{13}$. However, the infrared and low-temperature proton NMR spectra of both compounds indicate that they exist as a mixture of isomers; the two projected isomers for $H_2FeRu_2Os(CO)_{13}$ are shown in Fig. 58 *(247)*. The mixed manganese and rhenium–osmium complexes, $H_3MOs_3(CO)_{13}$, have been prepared by acidification of the reaction mix-

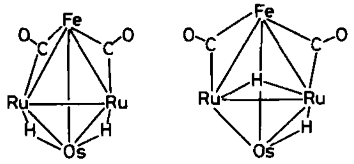


FIG. 58. Isomers of $H_2FeRu_2Os(CO)_{13}$.

ture of $Os_3(CO)_{12}$ with the corresponding anion $[M(CO)_5]^-$ (M = Mn, Re) (*238*). They were identified by mass spectroscopy and are air-stable. The infrared spectra indicate the presence of both terminal and bridging carbonyl groups. The reactions of the anions $[M(CO)_5]^-$ (M = Mn, Re) with $Ru_3(CO)_{12}$ do not yield the related ruthenium derivatives, but give other polynuclear carbonyl adducts (*206*).

Chini has recently reported the redox condensation between $Fe_3(CO)_{12}$ and the anion $[Co(CO)_4]^-$ to yield the anion $[Fe_3Co(CO)_{13}]^-$, but no details of the structure or stability of the complex are cited (*234*).

c. $M_4(CO)_{16}$ Derivatives. Although the polynuclear carbonyls have been isolated for $n = 3, 5, 6, 7$, and 8, the tetranuclear carbonyl derivative, $M_4(CO)_{14}$, has not been prepared. A number of tetranuclear derivatives have recently been prepared as hydrido or anionic species, which suggests that, at least for the metals of higher atomic number, it may be possible to isolate a neutral carbonyl, but that the structure may not be based on one closed tetrahedral arrangement of metal atoms. Thus the structure of the anion $[Fe_4(CO)_{13}]^{2-}$ has emphasized that for the tetrahedral iron complex the steric crowding of the carbonyl groups may be a significant factor in determining the stability and structure, and it certainly would be of interest to determine the structure of the related ruthenium and osmium derivatives. A series of complexes has been prepared based on the $M_4(CO)_{16}$ rather than the $M_4(CO)_{14}$ unit. The structures that have been determined to date for these $M_4(CO)_{16}$ compounds, as would be anticipated on electron counting (see below), have not involved a tetrahedral arrangement of metal atoms.

The mixed-metal tetranuclear derivatives that have been prepared are $H_2Re_2Ru_2(CO)_{16}$, $[ReRu_3(CO)_{16}]^-$, $HMnOs_3(CO)_{16}$, and $HReOs_3(CO)_{16}$ (*238*). All the complexes result from the reaction of the carbonyl, $M_3(CO)_{12}$, with the related anion, $[Mn(CO)_5]^-$ or $[Re(CO)_5]^-$. The ruthenium anion $[ReRu_3(CO)_{16}]^-$ was isolated as its tetramethylammonium salt. The infrared spectrum was complex, but consistent with

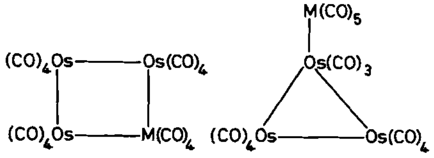


FIG. 59. Possible structures of $[Os_3M(CO)_{16}]^-$ species.

structures of the type shown in Fig. 59. Acidification of this anion yields a mixture of products, from which, using TLC techniques, it was possible to isolate the hydride $H_2Re_2Ru_2(CO)_{16}$. This illustrates the caution that must be employed in trying to characterize the anions present in solution from the hydrides isolated on acidification (*238*).

For the osmium complexes $HMOs_3(CO)_{16}$ (M = Mn, Re), the infrared spectra indicate that there are no bridging carbonyl groups, and two potential structures were postulated; see Fig. 59a and b. Recently Shapley has prepared a related rhenium derivative, by reaction of $Os_3(CO)_{10}(C_8H_{14})_2$, the cyclooctene complex, with excess of $HRe(CO)_5$ to produce the complex $H_2Os_3Re_2(CO)_{20}$ (*255*). On the basis of infrared, NMR, and X-ray crystallography, this complex has been shown to have the structure shown in Fig. 60, with two of the equatorial carbonyl groups in $Os_3(CO)_{12}$ replaced by $Re(CO)_5$ groups, in a manner observed for phosphine substitution [cf. $Os_3(CO)_{10}(PEt_3)_2$ (*256*)].

The hydrogen positions were assigned, on the basis of bond length arguments, to the Os(1)–Os(2) (3.058 Å) and Os(3)–Os(2) (3.083 Å) pairs, the Os(1)–Os(3) bond length being 2.876 Å.

The product $HReOs_3(CO)_{15}$ was obtained by reaction of $HReOs_3(CO)_{16}$ with $Me_3NO \cdot 2H_2O$/NCMe, and the corresponding disubstituted rhenium derivative $H_2Re_2Os_3(CO)_{20}$ gave $H_2Re_2Os_3(CO)_{19}$ with the same reactants (*255*).

The structure of an adduct $HReOs_3(CO)_{15}$ has recently been determined by Churchill (*257*); this was isolated as a product of the reaction of $Re(CO)_5^-$ with $Os_3(CO)_{12}$ by Mays and Knight (*238*). The structure is based on a rhomboid distribution of metal atoms (see Fig. 61). The hy-

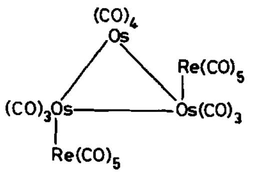


FIG. 60. Molecular structure of $H_2Os_3(Re)_2(CO)_{20}$.

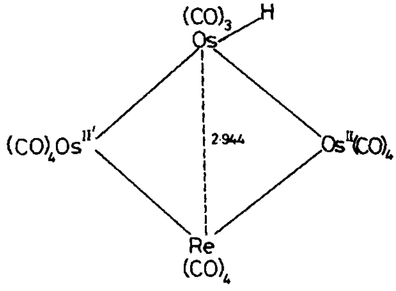


FIG. 61. Molecular structure of $HReOs_3(CO)_{15}$.

drogen is considered to bond in a terminal rather than a bridging position to the unique osmium(1) atom, on the basis of bond lengths and carbonyl group dispositions within the molecule. A direct bond can now be anticipated on the E.A.N. rule between the rhenium and osmium(1) atoms (2.944 Å), and this accounts for the rhomboid distribution of metal atoms. This structure is obviously derived from the alternative structure Fig. 59 proposed by Mays for the complex $HRe^1Os(CO)_{16}$. Shapley (*255*) comments that the product obtained by the $Me_3NO/NCCH_3$ reaction may not be the same as that isolated by Mays via the $Re(CO)_5^-/Os_3(CO)_{12}$ reaction, as there are differences in the reported solubility and infrared spectra of the two samples. The structure of the hydride is similar to that of the equivalent 62-electron system $[Re_4(CO)_{16}]^{2-}$ reported previously (*258*).

On the basis of the 18-electron rule, a 64-electron tetranuclear cluster would require four metal–metal bonds; a 62-electron system, five metal–metal bonds; and a 60-electron system, six metal–metal bonds. The 60-electron system would therefore require a tetrahedral distribution of bonds, or a planar array with multiple bonding; a 62-electron system would require one bond of the tetrahedron to be severed, to yield the rhomboid arrangement; and a 60-electron system may be considered as breaking one of the remaining bonds of the rhomboid to give a square or the substituted triangular form exhibited by $HReOs_3(CO)_{16}$ and also the complex $[H_4Re_4(CO)_{15}]^{2-}$; in the case of the latter compound, the $Re(CO)_4$ group replaces an axial rather than equatorial carbonyl of the metal triangle (Fig. 62) (*259*). Thus the problem considered at the beginning of this section on the stability of the $M_4(CO)_{14}$ cluster for M = Fe, Ru, and Os, being related to steric crowding of carbonyl groups, does suggest that the variation in stereochemistry of the higher electron clusters makes the neutral tetranuclear carbonyl of the type $M_4(CO)_{16}$ possible. Consistent with the lower steric require-

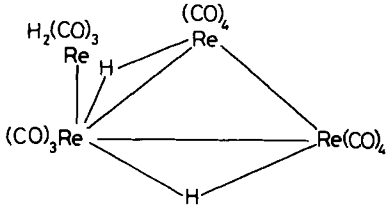


FIG. 62. Structure of the anion $[H_4Re_4(CO)_{15}]^{2-}$.

ments of the cyclopentadiene ion, which electronically is equivalent to three carbonyl ligands, cyclopentadiene–carbonyl complexes, derived from the $M_4(CO)_{16}$ unit, have been prepared by interaction of $Fe_2(CO)_9$ with the cyclopentadienyl carbonyl anions $[M(CO)_3\pi\text{-}C_5H_5)]^-$ (M = Mo, W), yielding the anion $[(\pi\text{-}C_5H_5)_2M_2Fe_2(CO)_{10}]^{2-}$, (M = Mo and W). As 60-electron systems, these ions are postulated to have a tetrahedral structure (*260*).

3. *Electron-Deficient Clusters*

The separation of the s and p orbitals of a metal ion increases on descending a triad, and on moving to the right-hand side of the transition block. This leads to the possibility of producing polynuclear metal clusters in which the E.A.N. rule is not maintained at each metal center. This applies particularly to the clusters of the elements platinum and gold. Using $H_2Os_3(CO)_{10}$ or $H_2Os(CO)_4$ as an osmium source, mixed complexes with the elements to the right side of the periodic table have been prepared, some of which involve a 58-valence-electron distribution. Thus 58-electron systems occur in the complexes $H_2Os_3Pt(CO)_{10}L$ $L = (C_6H_{11})_3P$ $(Ph_3P)]$, $H_2Os_2Pt_2(CO)_8(PPh_3)_2$, $HOs_3Au(CO)_{10}(Ph_3P)$, $H_2Os_3Rh(acac)(CO)_{10}$, and 60-electron systems in the compounds $H_2Os_3Pt(CO)_{10}(Ph_3P)L$ (L = Ph_3P, Ph_3As, CO) and $H_2Os_3Ni(CO)_{10}$ $(Ph_3P)_2$ (*261*). The complex $H_2Os_3Pt(CO)_{10}(Ph_3P)$ behaves as an electron-deficient system, readily adding ligands to produce the 60-electron systems $H_2Os_3Pt(CO)_{10}(Ph_3P)L$ cited above. The X-ray structures of two of the complexes, $H_2Os_3Pt(CO)_{10}P(C_6H_{11})_3$ and $H_2Os_2Pt_2$ $(CO)_8(PPh_3)_2$, have been determined and are shown in Fig. 63 (*261*). In both molecules, migration of a CO group has occurred from an osmium to platinum. The position of the hydrides has been assessed from a combination of X-ray data and the ^{195}Pt–H coupling constants in the NMR spectra of the complexes.

The electron distribution in these molecules is best considered in terms of a delocalized model, but it is also convenient to consider the

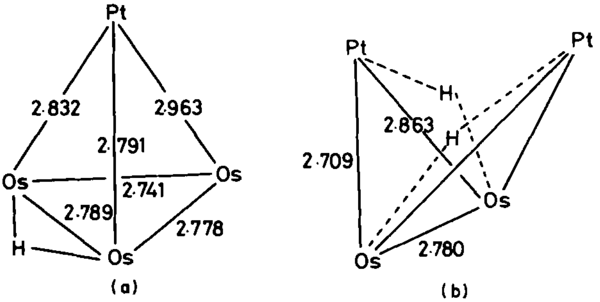


FIG. 63. (a) Molecular structure of $\{Os_3Pt(\mu\text{-}H)_2(CO)_{10}[(C_6H_{11})_3P]\}$; Pt–Os distances are given in the text: Os(1) – Os(2), 2.778(2); Os(2)–Os(3), 2.798(2); Os(1)–Os(3), 2.741(2); and Pt–P, 2.373(4) Å. (b) Molecular structure of $[Os_2Pt_2(\mu\text{-}H)_2(CO)_8(Ph_3P)_2]$; metal–metal distances are given in the text: Pt–P, 2.319(2) Å.

distribution at each metal center. As with $Os_6(CO)_{18}$, in order to attain the inert-gas configuration at each osmium center, it is necessary to invoke a two-electron donor bond between certain metal atoms. Thus in the complex $H_2Os_3Pt(CO)_{10}(C_6H_{11})_3P$ (see Fig. 63a), if osmium(1) and osmium(2) are formally considered as attaining the E.A.N., a two-electron donor bond is required from the platinum center to the Os(3) to maintain the E.A.N. at this site. The platinum atom then has two electrons short of that required for a complete outer 18-electron configuration. In the complex $H_2Os_2Pt_2(CO)_8(PPh_3)_2$, the inert-gas configuration of both osmium atoms may be attained without the necessity of a donor metal bond from platinum, but both platinum atoms are two electrons short of the inert-gas configuration, behaving as 16-electron systems. It is of interest that the first of these two molecules readily adds a further ligand, L, which is bonded to the osmium(3) center and may reflect the presence of this two-electron donor bond from platinum to the Os(3) center. The structures of the other complexes have not been elucidated.

A series of gold-containing complexes, $Os_3(CO)_{10}(AuPPh_3)X$ (X = Cl, Br, I, SCN), have been obtained from the interaction of Ph_3PAuX with $Os_3(CO)_{12}$. The complexes have been shown to have a triangular structure of osmium atoms, with one edge-bridged by the Ph_3PAu group and the halide (*262*). Surprisingly, the bond distance within the osmium metal triangle appears to be very slightly greater for the edge bridged by the gold and halogen groups.

Studies of the compounds involving elements of the triad with platinum and gold are important both from the point of view of the structure of the compounds formed and their potential use as catalysts. The strength of the metal–metal bond formed between these elements should be high, as platinum and gold exhibit the highest electronegativities of the transition elements. In addition, both these metals are electronically unsaturated in these compounds and hence provide a potential site for donor addition, a normal prerequisite in catalytically active systems. As indicated above, there is a facility for transfer of ligand groups between the metal centers, and the novel chemistry exhibited by simple unsaturated organic and the homonuclear species makes a comparative study very attractive.

REFERENCES

1. B. R. Penfold, *Perspect. Struct. Chem.* **2,** 71 (1968).
2. E. W. Abel and F. G. A. Stone, *Q. Rev., Chem. Soc.* **23,** 325 (1969).
3. R. D. Johnston, *Adv. Inorg. Chem. Radiochem.* **13,** 471 (1970).
4. R. B. King, *Prog. Inorg. Chem.* **15,** 287 (1972).
5. D. L. Kepert and K. Vrieze, *Compr. Inorg. Chem.* **4,** 199 (1973).
6. K. Wade, *Adv. Inorg. Chem. Radiochem.* **18,** 1 (1976).
7. P. Chini, G. Longoni, and V. G. Albano, *Adv. Organomet. Chem.* **14,** 285 (1976).
8. P. Chini and B. T. Heaton, *Top. Curr. Chem.* **71,** 1 (1977).
9. E. L. Muetterties, T. N. Rodin, E. Band, C. F. Bruncker, and W. R. Pretzer, *Chem. Rev.* **79,** 91 (1979).
10. See, for example, R. Whyman, *in* "Transition Metal Clusters" (B. F. G. Johnson, ed.), p. 545. Wiley, New York, 1980.
11. N. V. Sidgwick and R. W. Bailey, *Proc. Soc. London, Ser. A* **144,** 521 (1934).
12. G. Ozin, *Adv. Inorg. Radiochem.* **21,** (1980).
13. M. R. Hoare and P. Pal, *Adv. Phys.,* **20,** 161 (1971); *J. Cryst. Growth* **17,** 77 (1972).
14. See, e.g., ref. *7.*
15. See, for example, J. H. Canterford and R. Colton, "Halides of the Second and Third Row Transition Metals." Wiley, New York, 1968.
16. See, e.g., M. B. Hursthouse and K. M. A. Malik, *J. Chem. Soc., Dalton, Trans.* p. 1334 (1978).
17. P. Chini, *Spring Meet. Am. Chem. Soc. 1978* (1978).
18. J. A. Connor, *in* "Transition Metal Clusters" (B. F. G. Johnson, ed.), p. 345. Wiley, New York, 1980.
19. F. A. Cotton and J. M. Troup. *J. Am. Chem. Soc.* **96,** 4155 (1974).
20. J. A. Bertrand, F. A. Cotton, and W. A. Doliase, *J. Am. Chem. Soc.* **85,** 1349 (1963). *Inorg. Chem.* **2,** 1166 (1963).
21. For a discussion of this structure, see Section 3 and also ref. *21a.*
21a. A. G. Orpen, A. V. Rivera, E. G. Bryan, D. Pippart, G. M. Shedlrick, and K. D. Rouse, *Chem. Commun.* p. 723 (1978).
21b. J. S. Kristoff and D.F. Shriver, *Inorg. Chem.* **13,** 499 (1974); J. M. Burlitch and R. B Petersen, *J. Organomet. Chem.* **24,** C69 (1970); H. A. Hodali, D. F. Shriver, and C. A. Ammlung, *J. Am. Chem. Soc.* **100,** 5239 (1978).
22. K. Wade, *Adv. Inorg. Chem. Radiochem.* **18,** 67 (1976).
23. D. M. P. Mingos, *Nature (London), Phys. Sci.* **236,** 99 (1972).

24. D. M. P. Mingos, *J. Chem. Soc., Dalton Trans.* p. 133 (1974).
25. B. K. Teo, M. B. Hall, R. F. Fenske, and L. F. Dahl, *J. Organomet. Chem.* **70,** 413 (1974).
26. R. C. Baetzold and R. E. Mack, *J. Chem. Phys.* **62,** 1513 (1975).
27. A. B. Anderson and R. Hoffmann, *J. Chem. Phys.* **61,** 4545 (1974).
28. L. W. Anders, R. S. Manson, and L. S. Bartell, *J. Chem. Phys.* **62,** 1641 (1975).
29. R. P. Mesmer, S. K. Knudson, K. H. Johnson, J. B. Diammel, and C. Y. Yang, *Phys. Chem. Rev. B* **13,** 1396 (1976).
30. M. Elian and R. Hoffmann, *Inorg. Chem.* **14,** 1058 (1975).
31. D. M. P. Mingos and M. I. Forsyth, *J. Chem. Soc., Dalton Trans.* p. 610 (1977).
32. J. W. Lauher, *J. Am. Chem. Soc.* **100,** 5305 (1978).
33. B. F. G. Johnson, *J. Chem. Soc., Chem. Commun.* p. 703 (1975).
34. A. V. Rivera and G. M. Sheldrick, *Acta Crystallogr., Sect. B* **34,** 3372 (1978), and references therein.
35. B. F. G. Johnson, J. Lewis, and D. Pippard. *Eur. Coor. Chem. Meet., 3rd 1978,* unpublished.
36. J. Dewar and H. O. Jones, *Proc. R. Soc. London, Ser. A* **76,** 558 (1905); F. A. Cotton and J. M. Troup, *J. Chem. Soc., Dalton Trans.* p. 800 (1974).
37. P. S. Braterman, *Struct. Bonding (Berlin)* **10,** 1 (1972).
38. F. A. Cotton, *Prog. Inorg. Chem.* **21,** 1 (1976).
39. R. J. Doedens and L. F. Dahl, *J. Am. Chem. Soc.* **88,** 4850 (1966).
40. R. Colton, M. J. McCormick, and C. D. Pannan, *Aust. J. Chem.* **31,** 1425 (1978).
41. See also Section 3 for a further discussion of this bonding mode.
42. R. Colton and C. J. Commons, *Aust. J. Chem.* **28,** 1673 (1975).
43. C. J. Commons and R. F. Hoskins, *Aust. J. Chem.* **28,** 1663 (1975).
44. M. Manassero, M. Sansoni, and G. Longoni, *Chem. Commun.* p. 919 (1976).
45. R. J. Klinger, W. M. Butler, and M. D. Curtis, *J. Am. Chem. Soc.* **100,** 5034 (1978).
46. D. F. Shriver, D. Lehman, and D. Strope, *J. Am. Chem. Soc.* **97,** 1594 (1975).
47. B. F. G. Johnson, J. Lewis, A. G. Orpen, P. R. Raithby, and G. Suss, *J. Chem. Soc., Dalton Trans.* (in press).
48. P. D. Gavens and M. J. Mays, *J. Organomet. Chem.* **137,** B33 (1977).
49. M. R. Churchill, B. G. de Boer, and F. J. Rotella, *Inorg. Chem.* **15,** 1843 (1976).
50. E. O. Fischer and A. Massbol, *Chem. Ber.* **100,** 2445 (1967).
51. E. O. Fischer and H. J. Kellmeier, *Angew. Chem., Int. Ed. Engl.* **9,** 309 (1970).
52. See, e.g., Refs. *53* and *61*.
53. R. Bau, R. G. Teller, S. W. Kirtley, and T. F. Koetzle, *Acc. Chem. Res.* **12,** 176 (1979).
54. D. C. Harris and H. B. Gray, *J. Am. Chem. Soc.* **97,** 3073 (1975).
55. C. R. Eady, B. F. G. Johnson, J. Lewis, M. C. Malatesta, P. Machin, and M. McPartlin, *Chem. Commun.* p. 271 (1976).
56. D. W. Hart, R. G. Teller, C. Y. Wei, R. Bau, G. Longoni, S. Campanella, P. Chini, and T. F. Koetzle, *Angew. Chem., Int. Ed. Engl.* **18,** 80 (1979).
57. M. Catti, G. Gerrasio, and S. A. Mason, *J. Chem. Soc., Dalton Trans.* p. 2260 (1977).
58. A. G. Orpen, D. Pippard, G. M. Sheldrick, and K. D. Rouse, *Acta Crystalllogr., Sect. B* **34,** 2766 (1978).
59. R. B. Calvert, J. R. Shapley, A. J. Schultz, J. M. Williams, S. S. Suib, and G. D. Stucky, *J. Am. Chem. Soc.* **100,** 6240 (1978).
60. B. F. G. Johnson, J. Lewis, D. Pippard, P. R. Raithby, G. M. Sheldrick, and K. D. Rouse, *J. Chem. Soc., Dalton Trans.* (in press).
61. R. Bau, W. E. Carroll, D. W. Hart, R. G. Teller, and T. F. Koetzle. *Pure Appl. Chem.* **50,** 55 (1978).

62. J. Roziere, J. M. Williams, R. P. Stewart, Jr., J. L. Petersen, and L. F. Dahl, *J. Am. Chem. Soc.* **99,** 4497 (1977).
63. J. L. Petersen, L. F. Dahl, and J. M. Williams, *J. Am. Chem. Soc.* **96,** 6610 (1974).
64. R. Bau, S. A. Graham and R. D. Wilson, *J. Organomet. Chem.* **91,** C49 (1975).
65. J. P. Olsen, T. F. Koetzle, S. W. Kirtley, M. A. Andrews, D. L. Tipton, and R. Bau, *J. Am. Chem. Soc.* **96,** 6621 (1974).
66. R. A. Love, H. B. Chin, T. F. Koetzle, S. W. Kirtley, B. R. Whittlesey, and R. Bau, *J. Am. Chem. Soc.* **98,** 4491 (1976).
67. R. Bau, W. E. Carroll, R. G. Teller, and T. F. Koetzle, *J. Am. Chem. Soc.* **99,** 3872 (1977).
68. R. G. Teller, R. D. Wilson, R. K. McMillan, T. F. Koetzle, and R. Bau, *J. Am. Chem. Soc.* **100,** 3871 (1978).
69. L. F. Dahl, R. W. Braach, J. M. Williams, G. Longoni, and P. Chini, *Jt. Conf. C.I.C. A.C.S., 2nd, 1977,* unpublished.
70. G. M. Sheldrick and J. P. Yesinowski, *J. Chem. Soc., Dalton Trans.* p. 873 (1975).
71. E. A. McNeill and F. R. Scholer, *J. Am. Chem. Soc.* **99,** 6243 (1977).
72. R. D. Wilson, S. M. Wu, R. A. Love, and R. Bau, *Inorg. Chem.* **17,** 1271 (1978).
73. R. D. Wilson and R. Bau, *J. Am. Chem. Soc.* **98,** 4689 (1976).
74. P. F. Jackson, B. F. G. Johnson, J. Lewis, M. McPartlin, and W. J. H. Nelson, *Chem. Commun.* p. 920 (1978).
75. A. J. Deeming and S. Hasso, *J. Organomet. Chem.* **88,** C21 (1975); J. R. Shapley, J. B. Keister, M. R. Churchill, and B. G. DeBoer, *J. Am. Chem. Soc.* **97,** 4145 (1975); J. B. Keister and J. R. Shapley, *ibid.* **98,** 1056 (1976).
76. B. F. G. Johnson, J. Lewis, and D. Pippard, *J. Organomet. Chem.* **160,** 263 (1978).
77. G. Ciani, M. Manassero, V. G. Albano, F. Canziani, G. Giordano, S. Martinengo, and P. Chini, *J. Organomet. Chem.* **156,** C17 (1978).
78. J. R. Moss and W. A. G. Graham, *Inorg. Chem.* **16,** 75 (1977).
79. B. F. G. Johnson, J. Lewis, P. R. Raithby, G. M. Sheldrick, and G. Suss, *J. Organomet. Chem.* **162,** 179 (1978).
80. J. Knight and M. J. Mays, *J. Chem. Soc. A* p. 711 (1970).
81. A. J. Deeming, R. Ettorre, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc. A* p. 1797 (1971); E. G. Bryan, W. G. Jackson, B. F. G. Johnson, J. W. Kelland, J. Lewis, and K. T. Schorpp, *J. Organomet. Chem.* **108,** 385 (1976).
82. H. D. Kaesz, S. A. R. Knox, J. W. Koepke, and R. B. Saillant, *Chem. Commun.* p. 477 (1971).
83. V. G. Albano, A. Ceriotti, P. Chini, G. Ciani, S. Martinengo, and W. M. Anker, *Chem. Commun.* p. 859 (1975).
84. A. J. Deeming and M. Underhill, *Chem. Commun.* p. 277 (1973).
85. E. Sappa, O. Gambino, L. Milone, and G. Cetini, *J. Organomet. Chem.* **35,** 375 (1972).
86. C. R. Eady, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc., Dalton Trans.* p. 838 (1977).
87. P. C. Ford, R. G. Rinker, C. Ungermann, R. M. Laine, V. Landis, and S. A. Moya, *J. Am. Chem. Soc.* **190,** 4595 (1978).
88. J. Lewis and B. F. G. Johnson, *Pure Appl. Chem.* **44,** 43 (1975).
89. A. J. Canty, B. F. G. Johnson, J. Lewis, and J. R. Norton, *Chem. Commun.* p. 1331 (1972).
90. A. J. Canty, A. J. P. Domingos, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc., Dalton Trans.* p. 2056 (1973).
91. B. F. G. Johnson, J. W. Kelland, J. Lewis, and S. K. Rehani, *J. Organomet. Chem.* **113,** C42 (1976).

92. D. Seyferth, G. H. Williams, and D. D. Traficante, *J. Am. Chem. Soc.* **96,** 604 (1974).

93. A. J. Deeming, S. Husso, M. Underhill, A. J. Cantrv, B. F. G. Johnson, W. G. Jackson, J. Lewis, and T. W. Matheson, *Chem. Commun.* p. 807 (1974); W. G. Jackson, B. F. G. Johnson, and J. Lewis, *J. Organomet. Chem.* **90,** C13 (1975).

94. A. J. Canty, B. F. G. Johnson, and J. Lewis, unpublished results.

95. A. J. Deeming, S. Hasso, and M. Underhill, *J. Chem. Soc.* p. 1614 (1975).

96. J. Evans, B. F. G. Johnson, J. Lewis, and T. W. Matheson, *J. Organomet. Chem.* **97,** C10 (1975).

97. A. J. Deeming, *J. Organomet. Chem.* **150,** 123 (1978).

98. A. J. Deeming, R. E. Kimber, and M. Underhill, *J. Chem. Soc.* p. 2589 (1973).

99. C. W. Bradford, R. S. Nyholm, G. J. Gainsford, J. M. Guss, P. R. Ireland, and R. Mason, *Chem. Commun.* p. 87 (1972).

100. R. Mason and K. M. Thomas, *J. Organomet. Chem.* **43,** C39 (1972).

101. A. J. P. Domingos, B. F. G. Johnson, and J. Lewis, *J. Organomet. Chem.* **49,** C33 (1973).

102. M. Evans, M. Hursthouse, E. W. Randall, E. Rosenberg, L. Milone, and M. Valle, *Chem. Commun.* p. 545 (1972).

103. G. Gervasio, D. Osella, and M. Valle, *Inorg. Chem.* **15,** 1221 (1976).

104. M. I. Bruce, M. A. Cairns, and M. Green, *J. Chem. Soc., Dalton Trans.* p. 1293 (1972); M. I. Bruce, M. A. Cairns, A. Cox, M. Green, M. D. H. Smith, and P. Woodward, *Chem. Commun.* p. 735 (1970).

105. A. W. Parkins, E. O. Fischer, G. Huttner, and D. Regler, *Angew. Chem., Int. Ed. Engl.* **9,** 633 (1970).

106. R. Bau, J. C. Burt, S. A. R. Knox, R. M. Laine, R. P. Phillips, and F. G. A. Stone, *Chem. Commun.* p. 726 (1973).

107. E. G. Bryan, B. F. G. Johnson, J. W. Kelland, J. Lewis, and M. McPartlin, *Chem. Commun.* p. 254 (1976).

108. W. Hubel, *in* "Organic Syntheses via Metal Carbonyls" (I. Wender and P. Pino, eds.), p. 273. Wiley (Interscience), New York, 1968.

109. J. Mennier-Piret, P. Piret, and M. Van Meerssche, *Acta Crystallogr.* **19,** 85 (1965).

110. G. S. D. King, *Acta Crystallogr.* **15,** 243 (1962).

111. E. Sappa, L. Milone, and G. D. Andreetti, *Inorg. Chim. Acta* **13,** 67 (1975).

112. F. A. Cotton, D. L. Hunter, and J. M. Troup, *Inorg. Chem.* **15,** 63 (1976).

113. R. P. Dodge and V. Shomaker, *J. Organomet. Chem.* **3,** 274 (1965).

114. A. A. Hode and O. S. Mills, *Acta Crystallogr.* **14,** 139 (1961).

115. E. Sappa, L. Milone, and A. Tiripicchio, *J. Chem. Soc., Dalton Trans.* p. 1843 (1976).

116. S. Aime, L. Milone, E. Sappa, and A. Tiripicchio, *J. Chem. Soc., Dalton Trans.* p. 227 (1977).

117. E. Sappa, A. Tiripicchio, and A. M. M. Lanfredi, *J. Chem. Soc., Dalton Trans.* p. 552 (1978).

118. E. Sappa, A. Tiripicchio, and M. Tiripicchio Camellini, *J. Chem. Soc., Dalton Trans.* p. 419 (1978).

119. L. F. Dahl and D. L. Smith, *J. Am. Chem. Soc.* **84,** 2450 (1962).

120. M. G. Thomas, E. L. Muetterties, R. O. Day, and V. W. Day, *J. Am. Chem. Soc.* **98,** 4645 (1976).

121. K. Yasufuku, K. Aoki, and H. Yamazaki, *Bull. Chem. Soc. Jpn.* **48,** 1616 (1975).

122. J. F. Blount, L. F. Dahl. C. Hoogzand, and W. Hubel, *J. Am. Chem. Soc.* **88,** 292 (1966).

123. G. Ferraris and G. Gervasio, *J. Chem. Soc., Dalton Trans.* p. 1933 (1973).

124. G. A. Voglio, O. Cambino, R. P. Ferrari, and G. Cetini, *Inorg. Chim. Acta* **7,** 193 (1973).

125. S. Aime, G. Gervasio, L. Milone, E. Sappa, and M. Franchini-Angela, *Inorg. Chim. Acta* **26,** 223 (1978).

126. S. Aime, L. Milone, E. Sappa, A. Tiripicchio, and M. Tiripicchio Camellini, *Inorg. Chim. Acta* **32,** 163 (1979).

127. V. Raverdino, S. Aime, L. Milone, and E. Sappa, *Inorg. Chim. Acta* **30,** 9 (1978).

128. O. Gambino, E. Sappa, and C. Cetini, *J. Organomet. Chem.* **44,** 18 (1972).

129. B. F. G. Johnson, J. Lewis, and K. T. Schorpp, *J. Organomet. Chem.* **91,** C13 (1975).

130. B. F. G. Johnson, J. Lewis, B. E. Reichert, K. T. Schorpp, and G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.* p. 1417 (1977).

131. O. Gambino, R. P. Ferrari, M. Chinone, and G. A. Vaglio, *Inorg. Chim. Acta* **12,** 155 (1975).

132. G. Ferraris and G. Gervasio, *J. Chem. Soc., Dalton Trans.* p. 1813 (1974).

133. G. Ferraris and G. Gervasio, *J. Chem. Soc., Dalton Trans.* p. 1933 (1973).

134. O. Gambino, G. A. Vaglio, R. P. Ferrari, and G. Cetini, *J. Organomet. Chem.* **30,** 381 (1971).

135. A. J. Deeming, S. Husso, and M. Underhill, *J. Chem. Soc., Dalton Trans.* p. 1614 (1975).

136. W. G. Jackson, B. F. G. Johnson, J. W. Kelland, J. Lewis, and K. T. Schorpp, *J. Organomet. Chem.* **87,** C27 (1975).

137. S. A. Gardner, P. S. Andrews, and M. D. Rausch, *Inorg. Chem.* **12,** 2396 (1973); T. Yamamoto, A. R. Garber, G. M. Bodner, L. T. Todd, M. D. Rausch, and S. A. Gardner, *J. Organomet. Chem.* **56,** C23 (1973).

138. C. G. Pierpont, *Inorg. Chem.* **16,** 636 (1977).

139. A. A. Hock and O. S. Mills, *Acta Crystallogr.* **14,** 139 (1961).

140. H. B. Chin and R. Bau, *J. Am. Chem. Soc.* **95,** 5068 (1973).

141. F. A. Cotton and J. M. Troup, *J. Am. Chem. Soc.* **96,** 1233 (1974).

142. B. F. G. Johnson, R. D. Johnson, and J. Lewis, *J. Chem. Soc. A* p. 792 (1969).

143. W. R. Cullen and J. P. Crow, *Inorg. Chem.* **10,** 1529 (1971); M. J. Bruce, G. Shaw, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.* p. 2094 (1972); A. J. Deeming, B. F. G. Johnson, and J. Lewis, *J. Organomet. Chem.* **17,** 40 (1969); A. J. Deeming, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc. A* p. 897 (1970).

144. W. R. Cullen and O. A. Harbourne, *Inorg. Chem.* **9,** 1839 (1970); R. J. Roberts and J. Trotter, *J. Chem. Soc. A* p. 1479 (1971).

145. R. J. Roberts and J. Trotter, *J. Chem. Soc. A* p. 3246 (1970).

146. J. J. De Boer, J. A. van Doorn, and C. Masters, *Chem. Commun.* p. 1005 (1978).

147. C. W. Bradford, R. S. Nyholm, G. J. Gainsford, J. M. Guss, P. R. Ireland, and R. Mason, *Chem. Commun.* p. 87 (1972); G. J. Gainsford, R. S. Nyholm, J. M. Guss, P. R. Ireland, R. Mason, and C. W. Bradford, *J. Organomet. Chem.* C70 (1972).

148. M. J. Bruce, G. Shaw, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.* p. 2094 (1972).

149. A. J. Deeming, R. E. Kimber, and M. Underhill, *J. Chem. Soc., Dalton Trans.* p. 2589 (1973).

150. A. J. Deeming and M. Underhill, *J. Chem. Soc., Dalton Trans.* p. 2727 (1973).

151. A. J. Deeming, *J. Organomet. Chem.* **128,** 63 (1977).

152. C. G. Pierpont, *Inorg. Chem.* **17,** 1976 (1978).

153. E. G. Bryan, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc., Dalton Trans.* p. 1328 (1977).

154. E. G. Bryan, B. F. G. Johnson, J. W. Kelland, J. Lewis, and M. McPartlin, *Chem. Commun.* p. 254 (1976).

155. E. G. Bryan, B. F. G. Johnson, and J. Lewis, unpublished results.

156. M. Tachikawa and J. R. Shapley, *J. Organomet. Chem.* **124,** C19 (1977).

157. B. F. G. Johnson, J. Lewis, and D. Pippard, *J. Organomet. Chem.,* **145,** C4 (1978).

158. B. F. G. Johnson, J. Lewis, and D. Pippard, *J. Organomet. Chem.* **160,** 263 (1978).

159. J. R. Shapley, G. A. Pearson, M. Tockikawa, G. E. Schmidt, M. R. Churchill, and F. J. Hollander, *J. Am. Chem. Soc.* **99,** 8064 (1977).

160. R. G. Bryan, B. F. G. Johnson, and J. Lewis, *Chem. Commun.* p. 329 (1977).

161. B. F. G. Johnson, J. Lewis, D. Pippard, and P. R. Raithby, *Chem. Commun.* p. 551 (1978).

162. B. F. G. Johnson, J. Lewis, and D. Pippard, unpublished results.

163. R. Mason and D. M. P. Mingos, *J. Organomet. Chem.* **50,** 53 (1973).

164. B. F. G. Johnson, J. Lewis, and P. A. Kitty, *Chem. Commun.* p. 130 (1963).

165. J. B. Keister and J. P. Shapley, *J. Organomet. Chem.* **85,** C27 (1975).

166. M. R. Churchill, B. G. de Boer, J. R. Shapley, and J. B. Keister, *J. Am. Chem. Soc.* **97,** 4145 (1975).

167. A. J. Deeming and S. Hasso, *J. Organomet. Chem.* **114,** 313 (1976).

168. M. R. Churchill, B. G. de Boer, and F. J. Rotella, *Inorg. Chem.* **15,** 1843 (1976); M. R. Churchill, B. G. de Boer, F. J. Rotella, E. W. Abel, and R. J. Rowley, *J. Am. Chem. Soc.* **97,** 7158 (1975).

169. R. Greatrex, N. N. Greenwood, I. Rhee, M. Ryang, and S. Tsutsumi, *Chem. Commun.* p. 1193 (1970).

170. R. D. Adams and N. M. Golembeski, *Inorg. Chem.* **17,** 1969 (1978).

171. C. Choo Yin and A. J. Deeming, *J. Organomet. Chem.* **133,** 123 (1977).

172. B. F. G. Johnson, J. Lewis, and B. E. Hanson, unpublished observations.

173. M. R. Churchill and B. G. de Boer, *Inorg. Chem.* **16,** 1141 (1977).

174. M. Catti, G. Gervasio, and S. A. Mason, *J. Chem. Soc., Dalton Trans.* p. 2260 (1977).

175. J. Norton, J. Evans, S. J. Okrasinski, and A. J. Pribula, *J. Am. Chem. Soc.* **98,** 4000 (1976).

176. R. B. Calvert and J. R. Shapley, *J. Am. Chem. Soc.* **99,** 5225 (1977).

177. J. B. Keister and J. R. Shapley, *J. Am. Chem. Soc.* **98,** 1056 (1976).

178. C. Choo Yin and A. J. Deeming, *J. Chem. Soc., Dalton Trans.* p. 2091 (1975).

179. A. J. Deeming and C. Choo Yin, *J. Chem. Soc., Dalton Trans.* p. 1013 (1974).

180. K. A. Azam, A. J. Deeming, R. E. Kimber, and P. R. Shukla, *J. Chem. Soc., Dalton Trans.* p. 1853 (1976).

181. K. A. Azam, A. J. Deeming, I. P. Rothwell, M. B. Hursthouse, and L. New, *Chem. Commun.* (1979).

182. K. A. Azam and A. J. Deeming, *Chem. Commun.* p. 472 (1977).

183. K. A. Azam and A. J. Deeming, *Chem. Commun.* p. 852 (1976).

184. J. A. Connor *Top. Curr. Chem.* **71,** 77 (1977).

185. J. C. G. Calado, A. R. Dias, and J. A. Martinho Simoes, *Chem. Commun.* p. 737 (1978).

186. E. L. Muetterties, T. N. Rhodin, E. Band, C. F. Brucker, and W. R. Pretzer, *Chem. Rev.* **79,** 91 (1979).

187. J. W. Koepke, J. R. Johnson, S. A. R. Knox, and H. D. Kaesz, *J. Am. Chem. Soc.* **97,** 3947 (1975).

188. K. E. Inkrott and S. G. Shore, *J. Am. Chem. Soc.* **100,** 3954 (1978).

189. J. R. Shapley, S. I. Richter, M. R. Churchill, and A. Lashewycz, *J. Am. Chem. Soc.,* **99,** 7384 (1977).

190. P. F. Jackson, B. F. G. Johnson, J. Lewis, M. McPartlin, and W. J. H. Nelson, *Chem. Commun.* p. 920 (1978); D. B. W. Yawney and R. J. Doedens, *Inorg. Chem.* **11,** 838 (1972).

191. P. R. Raithby, private communication.

192. B. F. G. Johnson, J. Lewis, and K. Wong, unpublished results.

193. B. F. G. Johnson, J. Lewis, P. R. Raithby, G. M. Sheldrick, K. Wong, and M. McPartlin, *J. Chem. Soc., Dalton Trans.* p. 673 (1978).

194. B. F. G. Johnson, J. W. Kelland, J. Lewis, and S. K. Rehani, *J. Organomet. Chem.* **113,** C42 (1976).

195. S. Bhaduri, B. F. G. Johnson, J. W. Kelland, J. Lewis, P. R. Raithby, S. K. Rehani, G. M. Sheldrick, K. Wong, and M. McPartlin, *J. Chem. Soc., Dalton Trans.* p. 562 (1979).

196. A. J. Canty, A. J. P. Domingos, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc. A* p. 2056 (1973).

197. R. Mason and K. M. Thomas, *J. Organomet. Chem.* **43,** C39 (1972).

198. B. F. G. Johnson, J. Lewis, and A. J. Canty, unpublished observations.

199. B. F. G. Johnson, J. Lewis, and K. T. Schropp, *J. Organomet. Chem.* **91,** C13 (1975); B. F. G. Johnson, J. Lewis, B. E. Reichert, K. T. Schropp, and G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.* p. 1417 (1977).

200. D. Bright, *Chem. Commun.* p. 1169 (1970).

201. C. R. Eady, B. F. G. Johnson, and J. Lewis, *J. Organomet. Chem.* **37,** C39 (1972); C. R. Eady, B. F. G. Johnson, and J. Lewis *J. Chem. Soc., Dalton Trans.* p. 2606 (1975).

202. C. R. Eady, B. F. G. Johnson, J. Lewis, B. E. Reichert, and G. M. Sheldrick, *J. Chem. Soc.; Chem. Commun.* p. 271 (1976).

203. G. R. John, B. F. G. Johnson, and J. Lewis, *J. Organomet. Chem.*

204. G. R. John, B. F. G. Johnson, and J. Lewis, *J. Organomet. Chem.* **169,** C9 (1979); G. R. John, B. F. G. Johnson, J. Lewis, W. J. Nelson, and M. McPartlin, *ibid.* **171,** C14.

205. C. R. Eady, J. J. Guy, B. F. G. Johnson, J. Lewis, M. C. Malatesta, and G. M. Sheldrick, *J. Chem. Soc., Chem. Commun.* p. 807 (1976).

206. C. R. Eady, J. J. Guy, B. F. G. Johnson, J. Lewis, M. C. Malatesta, and G. M. Sheldrick, *J. Chem. Soc., Chem. Commun.* p. 807 (1976).

207. C. R. Eady, B. F. G. Johnson, and J. Lewis, *J. Organomet. Chem.* **57,** C84 (1973).

208. J. J. Guy and G. M. Sheldrick, *Acta Crystallogr. Sect. B* **34,** 1725 (1978).

209. E. H. Braye, L. F. Dahl, W. Hubel, and D. L. Nampler, *J. Am. Chem. Soc.* **84,** 4633 (1962).

210. C. R. Eady, B. F. G. Johnson, J. Lewis, and T. Matheson, *J. Organomet. Chem.* **57,** C82 (1973).

211. B. F. G. Johnson, J. Lewis, and I. G. Williams, *J. Chem. Soc. A* p. 901 (1970).

212. A. Singer, M. Bianchi, and E. Benedetti, *Chem. Commun.* p. 596 (1969).

213. J. M. Fernandez, B. F. G. Johnson, J. Lewis, P. R. Raithby, and G. M. Sheldrick, *Acta Crystallogr., Sect. B* **34,** 1997 (1978).

214. A. G. Orpen and G. M. Sheldrick, *Acta Crystallogr. Sect. B* **33,** 173 (1977).

215. B. F. G. Johnson, J. Lewis, and P. Jackson, to be published.

216. V. G. Albano, M. Sansoni, P. Chini, and S. Martinengo, *J. Chem. Soc., Dalton Trans.* p. 651 (1973).

217. B. F. G. Johnson, R. D. Johnston, and J. Lewis, *J. Chem. Soc. A* p. 2865 (1968).

218. R. Mason and W. R. Robinson, *Chem. Commun.* p. 468 (1968).

219. R. Mason, K. M. Thomas, and D. M. P. Mingos, *J. Am. Chem. Soc* **95,** 3802 (1973).

220. M. McPartlin, C. R. Eady, B. F. G. Johnson, and J. Lewis, *Chem. Commun.* p. 883 (1976).

221. C. R. Eady, B. F. G. Johnson, and J. Lewis, *Chem. Commun.* p. 302

222. M. R. Churchill, J. Wormald, J. Knight, and M. J. Mays, *Chem. Commun.* p. 458 (1970).

223. P. Jackson, B. F. G. Johnson, and J. Lewis, unpublished results.
224. M. R. Churchill and J. Wormald, *J. Am. Chem. Soc.*, **93**, 5671 (1971).
225. C. R. Eady, B. F. G. Johnson, J. Lewis, M. C. Malatesta, P. Machin, and M. McPartlin, *Chem. Commun.* p. 945 (1976).
226. P. Jackson, B. F. G. Johnson, J. Lewis, and M. Suss, unpublished results.
227. C. R. Eady, P. D. Gavens, B. F. G. Johnson, J. Lewis, M. C. Malatesta, M. J. Mays, A. G. Orpen, A. V. Rivera, and G. M. Sheldrick, *J. Organomet. Chem.* 1978, **149** C43 (1978).
228. C. R. Eady, J. M. Fernandez, B. F. G. Johnson, J. Lewis, P. R. Raithby, and G. M. Sheldrick, *Chem. Commun.* p. 421 (1978).
229. J. M. Fernandez, B. F. G. Johnson, J. Lewis, and P. R. Raithby, *Acta Crystallogr. Sect. B* **34**, 3086 (1978).
230. C. R. Eady, B. F. G. Johnson, and J. Lewis, *J. Organomet. Chem.* **57**, C84 (1973); *J. Chem. Soc., Dalton Trans.* p. 838 (1977).
231. C. R. Eady, B. F. G. Johnson, J. Lewis, R. Mason, P. B. Hitchcock, and K. M. Thomas, *Chem. Commun.* p. 385 (1977).
232. G. R. John, B. F. G. Johnson, J. Lewis, and K. Wong, *J. Organomet. Chem.* **169**, C23 (1979).
233. B. F. G. Johnson, R. D. Johnston, J. Lewis, I. G. Williams, and P. A. Kilty, *Chem. Commun.* p. 861 (1963).
234. P. Chini and B. T. Heaton, *Top. Curr. Chem.* **71**, (1979).
235. J. Knight and M. J. Mays, *Chem. Ind. (London).* **34**, 1159 (1968).
236. D. B. W. Yawney and F. G. A. Stone, *J. Chem. Soc. A* p. 502 (1969).
237. J. Knight and M. J. Mays, *Chem. Commun.* p. 1006 (1979).
238. J. Knight and M. J. Mays, *J. Chem. Soc., Dalton Trans.* p. 1022 (1972).
239. U. Anders and W. A. G. Graham, *Chem. Commun.* p. 291 (1966).
240. J. Knight and M. J. Mays, *J. Chem. Soc. A* p. 654 (1970); J. A. S. Howell, T. W. Matheson, and M. J. Mays, *J. Organomet. Chem.* **88**, 363 (1975).
241. J. R. Moss and W. A. G. Graham, *J. Organomet. Chem.* **23**, C23 (1970).
242. M. I. Bruce, G. Shaw, and F. G. A. Stone, *Chem. Commun.* p. 1288 (1971).
243. R. Mason, J. Zubieta, A. T. T. Hsieh, J. Knight, and M. J. Mays, *Chem. Commun.* p. 200 (1972).
244. M. I. Bruce, G. Shaw, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.* p. 1781 (1972).
245. A. Modinas and P. Woodward, *J. Chem. Soc., Dalton Trans.* p. 1534 (1975).
246. F. Richter and H. Vahrenkamp, *Angew. Chem. Int. Ed. Engl.* **17**, 864 (978).
247. G. L. Geoffroy and W. L. Gladfelter, *J. Am. Chem. Soc.* **99**, 7565 (1977).
248. J. Knight and M. J. Mays, *J. Chem. Soc. A* p. 711 (1970).
249. S. Bhaduri, B. F. G. Johnson, J. Lewis, P. R. Raithby, and D. J. Watson, *Chem. Commun.* p. 343 (1978).
250. M. J. Mays and R. N. F. Simpson, *J. Chem. Soc. A* p. 1444 (1968).
251. P. Chini, L. Colli, and M. Pavaldo, *Gazz. Chim. Ital.* **90**, 1005 (1960).
252. C. G. Cooke and M. J. Mays, *J. Chem. Soc., Dalton Trans.* p. 455 (1975).
253. B. T. Huie, C. B. Knobler, and H. D. Kaesz, *Chem. Commun.* p. 684 (1975); *J. Am. Chem. Soc.* **100**, 3059 (1978).
254. R. G. Teller, R. D. Wilson, R. K. McMullan, T. F. Koetzle, and R. Bau, *J. Am. Chem. Soc.* **100**, 3071 (1978).
255. J. R. Shapley, G. A. Pearson, M. Tachikawa, G. E. Schmidt, M. R. Churchill, and F. J. Hollander, *J. Am. Chem. Soc.* **99**, 8064 (1977).
256. M. R. Churchill and F. J. Hollander, *Inorg. Chem.* **17**, 3546 (1978).

257. M. R. Churchill and F. J. Hollander, *Inorg. Chem.* **16,** 2493 (1977).

258. R. Bau, B. Fontal, H. D. Kaesz, and M. R. Churchill, *J. Am. Chem. Soc.* **89,** 6374 (1967).

259. V. G. Albano, G. Ciani, M. Freni, and P. Romiti, *J. Organomet. Chem.* **96,** 259 (1975).

260. A. T. T. Hsieh and M. J. Mays, *J. Organomet. Chem.* **39,** 157 (1972).

261. L. T. Farrugia, J. A. K. Howard, P. Mitrprachachon, J. L. Spencer, F. G. A. Stone, and P. Woodward, *Chem. Commun.* p. 260 (1978).

262. C. W. Bradford, W. von Bronswijk, R. J. H. Clark, and R. S. Nyholm, *J. Chem. Soc. A* p. 2889 (1970).