TRANSITION METAL CLUSTERS WITH Π-ACID LIGANDS

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I. Introduction

Current interest in metal cluster compounds has arisen from the demonstration that metal–metal bonds play a key role in determining the chemistry of large classes of compounds, in particular, those with heavy metal atoms in low valent states. The occurrence of metal–metal bonding in transition metal complexes has been surveyed (*21*, *26*, *59*, *271*, *275*), and the criteria for metal–metal bonding and the factors contributing to the stability of such bonds have been discussed. Schäfer and Schnering (*344*) and more recently Keppert and Vrieze (*229*) have reviewed the lower halide, oxide, and oxyhalide clusters of the heavier transition metals. Cotton (*102*) has considered the transition metal clusters in terms of structural types, and a similar approach has been adopted in a review of molecular polyhedra of high coordination number (*309*).

The definition of a metal cluster proposed by Cotton (*101, 102*) requires only the presence of direct covalent bonds between metal atoms. As this includes the whole class of compounds containing metal–metal bonds, it has been considered desirable in this review to restrict the term cluster to those compounds containing at least three metal atoms linked directly by covalent bonds. Hence on the basis of geometry, clusters fall into two groups: "closed" clusters, in which every metal atom is bonded directly to at least two others, and "open" clusters, in which some metal atoms are not bonded to two other metal atoms (*222*).

In view of the definition of a cluster, it is relevant to consider briefly the experimental criteria for the existence of covalent bonds directly between metals. In general, the geometrical data available from X-ray diffraction studies provide the most reliable and direct method for detecting the presence of a metal–metal bond. There is no precise and accurate standard, however, for a metal–metal single bond distance, and for large metal–metal separations the bond distance does not provide a valid means for detection of the presence of a covalent bond between the metal atoms. For compounds in which the metals have an odd number of electrons in their valence shell, a study of the magnetic properties may reveal the electron pairing inherent in the formation of a metal–metal bond. In certain cases, polarized absorption spectra (*20, 330, 383*) have been used to detect metal–metal interaction. The observation of bands in the infrared and Raman spectra which can be assigned to metal–metal vibrations are criteria which are being increasingly used (Section III, A). Indirect evidence for metal–metal bonding can often be obtained by a detailed study of the fragmentation pattern of a compound in the mass spectrometer. Each of these physical methods has certain limitations and hence caution must be exercised in their use as evidence for the existence of metal–metal bonding.

Closed transition metal clusters, in which the ligands are capable of acting as good π acceptors, form the subject of this review. Clusters involving posttransition metals will not be included. Compounds containing metal–metal bonds between transition metals and the metallic elements of Group IV are numerous and have been reviewed by Young (*385*). Compounds with bonds between transition metals and Group II and Group III metals are also known, but are less numerous (*188*). A wide variety of polynuclear compounds which fall under the definition of open clusters have been prepared and they display geometries varying from linear as in $Mn_2Fe(CO)_{14}$ (*9*), to bent as in $Fe_3(CO)_9S_2$ (*369*), and pyramidal as in Roussin's Black Salt $Fe_4S_3(NO)_7^-$ (*207*) (Fig. 1).

An excellent review by Penfold (*323*) of the stereochemistry of metal cluster compounds has recently appeared, in which the X-ray crystallographic data and structural description of the metal clusters have been comprehensively presented. With this in mind, references only to structural studies will be included, except where the properties of the clusters in solution do not correlate with the structures determined in the solid state. This is intended to be a comprehensive review of the literature up to and including September, 1969. While this work was in preparation, an article entitled "The Closed Metal Carbonyl Clusters" appeared (*82*).

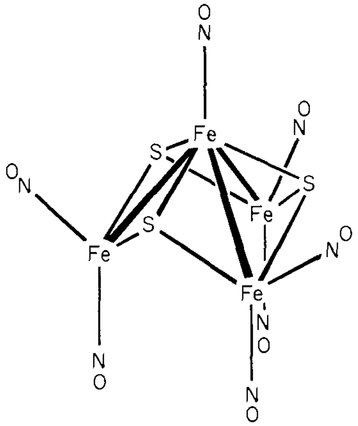


FIG. 1. Molecular structure of $Fe_4S_3(NO)_7^-$.

Common abbreviations such as M for metal, L for ligand, X for halogen, Me for methyl, Et for ethyl, Bu for butyl, and Ph for phenyl have been used. Unless otherwise specified, organic radicals will refer to the straight chain isomers. Other abbreviations are noted when they occur.

II. Survey of Transition Metal Cluster Compounds

A. INTRODUCTION

Transition metal clusters in which the metals are coordinated to each other and to π-acid ligands are known for all the metals of Groups VI, VII, and VIII. Clusters of the formally zero-valent Group IB metals (electron configuration $d^{10}s^1$) will be included in this survey because of the similarity of their properties to those of the transition metal clusters. Clusters have been prepared in which all the ligands are carbon monoxide groups, and where a number of CO groups have been substituted by

Lewis bases or organic ligands containing multiple carbon–carbon bonds. Other derivatives of the "simple" carbonyl clusters are the carbonyl anion and carbonyl hydride clusters. Other clusters have been prepared in which the principal π-acceptor ligands are π-cyclopentadienyl, nitrosyl, or phosphine groups.

A useful classification of clusters is based on the number of metal atoms directly bonded to each other in the cluster. In order to be able to refer readily to this number, the term "nuclearity" is proposed (*222*). In Table I a portion of the periodic table is presented with an indication of the metals forming homonuclear clusters with π-acid ligands and the known range of the nuclearity of these clusters.

TABLE I

PERIODIC DISTRIBUTION OF CLOSED CLUSTERS SHOWING NUCLEARITY

Cr 3, 4	Mn 3, 4	Fe 3, 4, 5	Co 3, 4, 6, 8	Ni 3, 4, 5	Cu 8
Mo 3	Tc 3	Ru 3, 4, 6	Rh 3, 4, 6, 7, 12	Pd 3, 4	Ag —
W 3, 4	Re 3, 4	Os 3, 4	Ir 3, 4, 8	Pt 3, 4	Au 3

B. UNSUBSTITUTED NEUTRAL CARBONYL CLUSTERS

Early investigations in this field led to the identification of homonuclear clusters with nuclearities of 3, 4, and 6. Recent efforts have been directed to extending the series by preparation of the related heteronuclear clusters.

The general feature of syntheses of carbonyl clusters in most cases would appear to involve a condensation reaction of labile intermediates which have a lower nuclearity than that of the final product. One approach is via the production of coordinatively unsaturated species under conditions in which they can stabilize themselves only by condensation reactions. Coordinatively unsaturated species have been produced in a variety of ways, involving simple metal salts or carbonyl compounds as starting materials.

1. Reaction of Carbon Monoxide with a Metal at High Pressure and Temperature

The metal carbonyls were accidently discovered by this reaction. In 1910 Mond *et al.* (*306*) observed the formation of orange crystals, subsequently identified as $Ru_3(CO)_{12}$, by the action of CO on ruthenium metal at 300°C and 350–450 atm.

2. *Reaction of Carbon Monoxide with a Metal Salt in the Presence of a Reducing Agent*

Because of the limitations of the first method, attempts were made to use the commonly available compounds of the metals as starting materials. This method requires the effective reduction of the metal to the zero-valent state.

a. Dry Methods. Commonly used before the surge of interest in clusters was the reaction of a metal halide with CO at high temperatures and pressures in the presence of a finely divided halogen acceptor such as Cu, Ag, Cd, or Zn. The halide acceptor, which was necessary to avoid contamination with intermediate halocarbonyl compounds, acted by driving the reaction toward the formation of the carbonyl. In this way $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$ (*185*) were first prepared by the action of CO at 200 atm on $RhCl_3$, the former at 50°–80°C and the latter at 80°–230°C.

$$4\,RhCl_3 + 12\,CO + 12\,Cu \rightarrow Rh_4(CO)_{12} + 12\,CuCl \tag{1}$$

$$6\,RhCl_3 + 16\,CO + 18\,Cu \rightarrow Rh_6(CO)_{16} + 18\,CuCl \tag{2}$$

$Ir_4(CO)_{12}$ was first prepared by the reaction of IrX_3 or M_2IrX_6 ($X = Cl$, Br, I; $M = NH_4$, Na, K) with CO at 150°C and 350 atm in the presence of copper (*184, 186*).

Related syntheses of $Ru_3(CO)_{12}$ from RuI_3 (*284*) and RuS_2, (*178*) and $Os_3(CO)_{12}$ from $OsCl_3$ and Os_2Br_9 (*194*) have been reported. $Os_3(CO)_{12}$ is better prepared by dry reduction of OsO_4 by CO itself (*194*).

$$3\,OsO_4 + 24\,CO \rightarrow Os_3(CO)_{12} + 12\,CO_2 \tag{3}$$

b. Reduction in Solution. A more general method involves reaction of a metal salt with CO in the presence of a suitable solvent. Under these homogeneous conditions reducing agents such as H_2 and CO are sufficiently powerful to enable the syntheses to be carried out at considerably lower pressures and temperatures. Thus, under heterogeneous conditions 200 atm of CO are necessary for the efficient preparation of $Ir_4(CO)_{12}$ (*184, 186*), whereas in methanol solution high yields can be obtained under 40 atm of CO (*79*).

Ercoli and co-workers (*132*) have reported the preparation of $Co_4(CO)_{12}$ from reaction of cobalt(II) 2-ethylhexanoate or cobalt(II) and cobalt (III) acetylacetonates with hydrogen at 30–50 atm and with $Co_2(CO)_8$ as follows:

$$2\,(RCOO)_2Co + 3\,Co_2(CO)_8 + 2\,H_2 \rightarrow 2\,Co_4(CO)_{12} + 4\,RCOOH \tag{4}$$

$Ru_3(CO)_{12}$ has been prepared by the action of CO and H_2 on ruthenium(III) acetylacetonate (*44, 329*) and stearate (*301*) in methanol or benzene.

c. *Reduction with Another Metal Carbonyl.* An elegant variation on the above method involves the use of an excess of another metal carbonyl both as the reducing agent and the source of CO. $Rh_6(CO)_{16}$ can be prepared under ambient conditions by the reaction of $Fe(CO)_5$ with $RhCl_3$ (*39*).

$$6\ RhCl_3 + 9\ Fe(CO)_5 \rightarrow Rh_6(CO)_{16} + 9\ FeCl_2 + 29\ CO \qquad (5)$$

3. *Halogen Abstraction from Halocarbonyl Compounds*

This preparative method would appear to be a special set of the previous class of reactions (Section II,B,2), as there is considerable evidence that halocarbonyl compounds are intermediates in the formation of carbonyl clusters from metal halides. In the reaction of $RhCl_3$ with CO in a methanol solution, the chlorocarbonyl dimer $[Rh(CO)_2Cl]_2$ has been isolated as an intermediate in the formation of $Rh_4(CO)_{12}$ (*79*).

a. *Heterogeneous Reduction.* As for the metal halides, reaction of the halocarbonyls with CO in the presence of a halogen acceptor can lead to reduction and cluster formation (*79*). An interesting variation in which

$$2\ [Rh(CO)_2Cl]_2 + 4\ CO + 2\ Zn \rightarrow Rh_4(CO)_{12} + 2\ ZnCl_2 \qquad (6)$$

the halogen acceptor is the cation of an anionic carbonyl species has been used to prepare heteronuclear carbonyl clusters (*91*).

$$Zn[Co(CO)_4]_2 + [Rh(CO)_2Cl]_2 \rightarrow Co_2Rh_2(CO)_{12} + ZnCl_2 \qquad (7)$$

b. *Homogeneous Reduction.* As for the metal halides (Section II,B,2,b) more efficient reduction can be achieved by reagents such as CO or K_2CO_3 in solution. $Ru_3(CO)_{12}$ has been prepared by the action of K_2CO_3 on $[Ru(CO)_3Cl_2]_2$ (*58*).

c. *Metal Carbonyls.* These have been used both as a reducing agent and as a source of CO in the absence of free CO. The trinuclear cluster

$$3\ [Ru(CO)_3Cl_2]_2 + 6\ Fe(CO)_5 \rightarrow 2\ Ru_3(CO)_{12} + 6\ FeCl_2 + 24\ CO \qquad (8)$$

of ruthenium has been obtained by the action of $Fe(CO)_5$ on $[Ru(CO)_3Cl_2]_2$ (*384*). This type of reaction has been used particularly to synthesize heteronuclear clusters. The reaction of $Fe(CO)_5$ with $[Ru(CO)_3Cl_2]_2$ also yields $Fe_2Ru(CO)_{12}$ and $FeRu_2(CO)_{12}$ (*384*).

$$3\ [Ru(CO)_3Cl_2]_2 + 12\ Fe(CO)_5 \rightarrow 2\ Fe_2Ru(CO)_{12} + 6\ FeCl_2 + 30\ CO + 2\ FeRu_2(CO)_{12} \qquad (9)$$

4. *Pyrolysis of Metal Carbonyl Compounds*

This reaction was used to obtain the first carbonyl cluster, $Fe_3(CO)_{12}$ (*124*). Pyrolysis apparently produces an $Fe(CO)_4$ species which can condense either with other similar molecules or with an $Fe_2(CO)_8$ intermediate. $Co_4(CO)_{12}$ was similarly prepared first by pyrolysis of solid $Co_2(CO)_8$) (*306*). The yield was improved considerably by the use of hydrocarbons as solvents (*149, 313*). $Ru_3(CO)_{12}$ has been shown to originate from the decomposition of $Ru(CO)_5$ formed by the reduction of Ru(III) compounds in the presence of CO (*64*).

$$3\,Fe_2(CO)_9 \xrightarrow{\Delta} 2\,Fe_3(CO)_{12} + 3\,CO \qquad (10)$$

$$2\,Co_2(CO)_8 \xrightarrow{\Delta} Co_4(CO)_{12} + 4\,CO \qquad (11)$$

5. *Condensation of Carbonyl Anions and/or Carbonyl Compounds*

Condensation reactions can also occur between compounds which are not coordinatively unsaturated. The condensation of metal carbonyls and carbonyl anions provide an example of this reaction. Such a reaction is that of iron carbonyl with the trinuclear carbonyl anion (*192*). Synthesis of carbonyl clusters often involves a predisproportionation step to produce an anionic intermediate. Thus, $Co_2(CO)_8$ reacts with ethers and sterically hindered alcohols to form $Co_4(CO)_{12}$. Chini and Albano (*83*) have postulated the formation of the $Co(CO)_4^-$ anion which undergoes condensation with unreacted $Co_2(CO)_8$. The dimer cluster $[ReFe_2(CO)_{12}]_2$ has recently been obtained by the simple one-electron oxidation of $ReFe_2(CO)_{12}^-$ by the tropylium ion (*147*). This would appear to offer a general method for the synthesis of many more clusters of considerably increased nuclearity.

$$Fe(CO)_5 + Fe_3(CO)_{11}^{2-} \rightarrow Fe_4(CO)_{13}^{2-} + 3\,CO \qquad (12)$$

$$2\,[CoB_6][Co(CO)_4]_2 + Co_2(CO)_8 \rightarrow 2\,Co_4(CO)_{12} + 12\,B^1 \qquad (13)$$

The formulas of the known unsubstituted neutral carbonyl clusters, their methods of preparation, and references to mass spectral studies and structural data based on crystallographic studies are collected in Table II. Of the compounds listed more than half were unknown prior to 1965, and hence it can be expected that the obvious missing members of the series will be obtained in the near future.

[1] B = Lewis base.

TABLE II

UNSUBSTITUTED NEUTRAL CARBONYL CLUSTERS

Cluster	Preparation (section number)	Refs.	Mass spectral refs.	Structural data refs.
$[Re(CO)_4]_n$	II, B, 2, a	*316*		
$[ReFe_2(CO)_{12}]_2$	II, B, 5	*147*		
$Fe_3(CO)_{12}$	II, B, 4; 5	*124, 165, 243*	*19, 244, 274*	*116, 375*
$Fe_2Ru(CO)_{12}$	II, B, 4; 3, c	*259, 384*	*259, 384*	
$FeRu_2(CO)_{12}$	II, B, 4; 3, c	*259, 384*	*259, 384*	
$Ru_3(CO)_{12}$	II, B, 1; 2, a, b; 3, b, c; 4	*44, 57, 58, 64, 178, 284, 301, 306, 329, 384*	*244, 274*	*97, 295*
$Ru_2Os(CO)_{12}$	II, B, 4	*215, 216*	*215*	
$RuOs_2(CO)_{12}$	II, B, 4	*215, 216*	*215*	
$Os_3(CO)_{12}$	II, B, 2, a, b	*46, 194, 217*	*220*	*97*
$Co_4(CO)_{12}$	II, B, 4; 5	*83, 132, 149, 306, 313, 379*	*220, 244*	*99, 370*
$Co_6(CO)_{16}$	II, B, 4;5	*81*		*15*
$Co_2Rh_2(CO)_{12}$	II, B, 3, a	*91*		
$Co_2Rh_4(CO)_{16}$	II, B, 3, c	*355*		
$Rh_4(CO)_{12}$	II, B, 2, a; 3, a, b	*39, 79, 88, 185*	*220*	*377*
$Rh_6(CO)_{16}$	II, B, 2, a, b, c; 3, a, c; 4	*39, 79, 88, 185*		*98*
$Ir_4(CO)_{12}$	II, B, 2, a, b	*79, 184, 186*	*218*	*377*
$[Pt(CO)_2]_n$	II, B, 2, b; 3, b	*41*		

C. CARBONYL ANION AND HYDRIDE CLUSTERS

Hieber and his school have carried out a systematic investigation of the transition metal carbonyl anions and derivative hydrides (*169*), and have synthesized many carbonyl anion and hydride clusters, particularly of the first row transition metals. The preparations of these clusters were all based on the reduction of a carbonyl compound. More recently a number of heteronuclear carbonyl anion and hydride clusters have been produced by condensation reactions.

1. *Reduction of a Metal Carbonyl Compound*

There are three types of reactions in which anions may be obtained by reduction of a carbonyl compound. The corresponding carbonyl hydride compounds are usually prepared by acid hydrolysis of the anions. In a number of reactions, the hydride has originated from the solvent, either by solvent breakdown or from traces of H_2O present in the solvent.

a. Reduction with Sodium Borohydride in Liquid Ammonia or Tetrahydrofuran. In the formation of the carbonyl hydride clusters by this method, the borohydride often acts both as the reducing agent and as the source of the hydride ion. Many of the simple carbonyl anions, such as the series $M_3(CO)_{14}^{2-}$ (M = Cr, Mo, or W) (*28*, *29*), have been prepared by the reduction of the mononuclear carbonyl by $NaBH_4$.

In the reduction of $Mn_2(CO)_{10}$ with $NaBH_4$ to form $H_3Mn_3(CO)_{12}$, Kaesz *et al.* (*224*) have also isolated the polynuclear compound $Mn_3(CO)_{10}(BH_3)_2H$, the structure of which is shown in Fig. 2. This structure suggests the means whereby the borohydride acts to unite mononuclear carbonyl species into clusters.

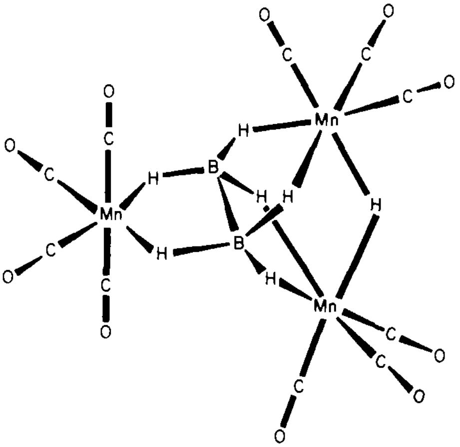


FIG. 2. Molecular structure of $Mn_3(CO)_{10}(BH_3)_2H$. Reproduced by permission.

b. Reduction by an Alkali Metal. This reaction has been used to prepare a number of anionic carbonyl clusters, though, in general, this reaction will lead to a mononuclear carbonyl metallate (*27*) as in the reaction of $Fe_3(CO)_{12}$ with sodium (*32*). However, $Ni(CO)_4$ in tetrahydrofuran is reduced by lithium amalgam to the trinuclear carbonyl anion (*176*). This may be related to the obvious difference in stability expected for the $Fe(CO)_4^{2-}$ and $Ni(CO)_3^{2-}$ ions. In the same medium K, Na, and Mg amalgam, presumably because of their smaller oxidation–reduction potentials, can reduce $Ni(CO)_4$ only to the tetranuclear anion (*176*).

$$Fe_3(CO)_{12} + 6\,Na \rightarrow 3\,Na_2[Fe(CO)_4] \qquad (14)$$

$$3\,Ni(CO)_4 + 2\,Li \rightarrow Li_2[Ni_3(CO)_8] + 4\,CO \qquad (15)$$

$$4\,Ni(CO)_4 + 2\,M \rightarrow M_2[Ni_4(CO)_9] + 7\,CO \qquad (16)$$

c. Reaction with a Base. Strong alkali reacts by reduction of the metal accompanied by a corresponding oxidation of coordinated CO to CO_3^{2-}. In this way $Fe_3(CO)_{11}^{2-}$ can be prepared by the action of alcoholic alkali on the parent carbonyl (*172*).

$$Fe_3(CO)_{12} + 4\ OH^- \rightarrow Fe_3(CO)_{11}^{2-} + CO_3^{2-} + 2\ H_2O \qquad (17)$$

Amines usually cause disproportionation of the carbonyl, and liberation of the excess CO, as in the reaction of $Fe(CO)_5$ with pyridine (*195*).

$$5\ Fe(CO)_5 + 6\ C_5H_5N \rightarrow [Fe(NC_5H_5)_6][Fe_4(CO)_{13}] + 12\ CO \qquad (18)$$

2. *Condensation of a Carbonyl Metallate and/or a Metal Carbonyl Compound*

In many of the reactions classified as reduction of a metal carbonyl compound (Section II,C,1) it is implicit that a condensation reaction occurs, although the condensation may be followed by disproportionation. There are a number of syntheses of carbonyl metallate clusters in which this condensation is explicit. $Fe(CO)_5$ reacts with $Fe_3(CO)_{11}^{2-}$ to form $Fe_4(CO)_{13}^{2-}$ as in Eq. (12) (*186*). This reaction has been used in particular to synthesize a number of heteronuclear clusters.

$$Mn(CO)_5^- + 2\ Fe(CO)_5 \rightarrow MnFe_2(CO)_{12}^- + 3\ CO \quad (\mathit{17}) \qquad (19)$$

$$2\ [NiB_6][Co(CO)_4]_2 + 2\ Co(CO)_4^- \rightarrow Ni_2Co_4(CO)_{14}^{2-} + Co_2(CO)_8 + 2\ CO + 12\ B \quad (\mathit{91}) \qquad (20)$$

3. *High Pressure Reactions*

There have been a limited number of syntheses based on reaction of a carbonyl compound with hydrogen or a hydrogen-containing compound, and of carbonyl hydride compounds with free CO, at high pressures. $H_4Ru_3(CO)_{10}$ has been prepared by the reaction of $Ru_3(CO)_{12}$ with hydrogen at 150 atm and 120°C (*328*).

$$Ru_3(CO)_{12} + 2\ H_2 \rightarrow H_4Ru_3(CO)_{10} + 2\ CO \qquad (21)$$

Data for the known carbonyl anion and carbonyl hydride clusters are collected in Table III, along with their methods of preparation and references to mass spectral and structural studies. Although many of the compounds listed have not been shown conclusively to be clusters, on the basis of comparative evidence and application of the noble gas rule, it is considered that all the compounds have a closed cluster structure.

D. SUBSTITUTED CARBONYL CLUSTERS

There are a large number of clusters which contain groups or atoms other than the metal atoms and carbonyl molecules. In many of these compounds a number of carbonyl groups are substituted by an equal number of molecules of a Lewis base. In particular, bases in which the donor atom is a Group V atom, excepting nitrogen, can substitute a number of CO groups without rupture of the cluster. The reaction of $Ni(CO)_4$ with the tertiary phosphine $P(CH_2CH_2CN)_3$ to form the cluster $Ni_4(CO)_6L_4$ (*35*) is one of the few reported syntheses of a cluster by reaction of a mononuclear carbonyl compound with a Group V ligand. Compounds with Group IV and Group VI donor atoms, however, play an important part in the syntheses of many clusters, in that they can bond to two or more metal atoms.

The substituted carbonyl clusters will be surveyed in terms of the donor atom of the substituent ligand.

1. Group IV

There are two interesting clusters which contain a lone carbon atom bonded directly to metal atoms. The first of these to be reported was $Fe_5(CO)_{15}C$, which was prepared in 0.5% yield by the reaction of $Fe_3(CO)_{12}$ with a variety of alkynes, in particular, methylphenylacetylene and 1-pentyne (*199*, *200*). An X-ray study showed the carbon atom to lie in the basal plane of a tetragonal pyramid of Fe atoms and to be bonded to all five metal atoms (*50*).

This compound was shown not to be a complete novelty by the preparation of $Ru_6(CO)_{17}C$ (*94*, *211*, *324*) and the arene-substituted derivatives $Ru_6(CO)_{14}(\text{arene})C$ (*211*). The latter were obtained by refluxing $Ru_3(CO)_{12}$ in the appropriate arene (mesitylene, *m*-xylene, or toluene) or by reaction of the arene with the hexanuclear cluster. $Ru_6(CO)_{17}C$ was obtained by refluxing $Ru_3(CO)_{12}$ in a variety of high-boiling "inert" solvents such as octane and nonane. Structural studies revealed the position of the carbon atom, in this case at the center of the regular octahedron or ruthenium atoms and equidistant from all six of them (*296*, *349*) (Fig. 3).

The high coordination number of the carbon atom in these compounds has aroused some interest, but six-coordinate carbon is well known in metal carbides such as Fe_3C, in which the carbon atoms lie in the interstices of almost regular trigonal pyramidal prisms of iron atoms (*382*).

A large number of clusters with the general formula $Co_3(CO)_9CY$, where Y is a great variety of substituents, have been prepared. The first compound of this type was prepared by the action of acid on 1-alkyne derivatives of $Co_2(CO)_8$ (*289*). A more general synthetic route to the

$$Co_2(CO)_6(HC{\equiv}CH) + H^+ \rightarrow Co_3(CO)_9C_2H_3 \qquad (22)$$

TABLE III

CARBONYL ANION AND HYDRIDE CLUSTERS

Cluster	Preparations (section number)	Refs.	Mass spectral refs.	Structural data refs.
$Cr_3(CO)_{14}^{2-}$	II, C, 1, a	*28*		
$Mo_3(CO)_{14}^{2-}$	II, C, 1, a	*28*		
$W_3(CO)_{14}^{2-}$	II, C, 1, a	*29*		
$HW_3(CO)_9(OH)_2(H_2O)^{3-}$ [a, c]	II, C, 3	*177*		
$HW_3(CO)_9(OH)(OMe)(MeOH)^{3-}$ [a, b, c]	II, C, 3	*177*		
$H_4W_4(CO)_{12}(H_2O)_4$	II, C, 2	*177*		
$H_3Mn_3(CO)_{12}$ [d]	II, C, 1, a, c	*138, 213, 351*	*213, 351*	
$H_3Tc_3(CO)_{12}$	II, C, 1, b	*226*		
$H_3Re_3(CO)_{12}$ [b, c, d]	II, C, 1, a, c	*93, 201*	*213, 351*	*95*
$Re_4(CO)_{16}^{2-}$	II, C, 1, a	*25*		*25, 92*
$H_6Re_4(CO)_{12}^{2-}$ [d]	II, C, 1, a	*225*		*225*
$MnFe_2(CO)_{12}^{-}$	II, C, 2	*17, 276, 342*		
$TcFe_2(CO)_{12}^{-}$	II, C, 2	*276*		
$ReFe_2(CO)_{12}^{-}$	II, C, 2	*135*		
$Fe_3(CO)_{11}^{2-}$ [a, b]	II, C, 1, a, c; 2	*61, 71, 171, 172, 173, 187, 191*		*115, 303*
$Fe_4(CO)_{13}^{2-}$ [a, b]	II, C, 1, c	*179, 181, 187, 195*		*127*
$HFe_3(CO)_{11}(NMe_2)$	[e]	*337*		
$H_2FeRu_3(CO)_{12}$ [f]	II, C, 2	*259, 384*	*384*	
$H_4Ru_3(CO)_{10}$ [b]	II, C, 3; 1, c	*328*		
$H_2Ru_3(CO)_{11}$	II, C, 3	*328*		
$H_4Ru_4(CO)_{12}$ [d, g]	II, C, 1, a–c; 3	*204, 213, 214*	*204, 213, 214*	
$H_2Ru_4(CO)_{13}$ [d]	II, C, 1, a–c; 2[f]	*211, 213, 214, 384*	*213, 214*	
$HRu_3(CO)_{10}(SR)$	[h]	*110, 215*	*110*	
$HRu_3(CO)_{12}^{+}$	[i]	*120, 260*		
$H_2Os_3(CO)_{10}$	II, C, 1, b, c	*217*	*217*	*216*
$H_2Os_4(CO)_{13}$	II, C, 1, b, c	*217*	*217*	

$H_4Os_4(CO)_{12}$	II, C, 1, b, c	*213, 217*	*213, 217*	
$HOs_3(CO)_{10}(OMe)$	II, C, 1, b, c; 3	*217*	*217*	
$HOs_3(CO)_{10}(OH)$	II, C, 3	*217*	*217*	
$HOs_3(CO)_{10}(SR)$	[h]	*110*	*110*	*294*
$HOs_3(CO)_{12}^{+}$	[i]	*120, 260*		
$HOs_3(CO)_{10}X$[j]	II, C, 1, a	*120*	*120*	
$FeCo_3(CO)_{12}^{-}$[a]	II, C, 2	*83, 86, 298*	*298, 299*	
$HRuCo_3(CO)_{12}$[f]	II, C, 2	*298, 299, 384*	*298*	
$HOsCo_3(CO)_{12}$[f]	II, C, 2	*297*		
$Co_6(CO)_{15}^{2-}$[b]	II, C, 1, b, c	*80, 83*		*15*
$Co_6(CO)_{14}^{4-}$	II, C, 1, c	*81, 85*		*13, 15*
$Co_8(CO)_{22}^{2-}$	[k]	*85*		
$Rh_7(CO)_{17}^{3-}$	II, C, 1, c	*12*		*12*
$Rh_{12}(CO)_{30}^{2-}$	II, C, 1, c	*84, 89*		*12*
$Rh_{12}(CO)_{34}^{2-}$	II, C, 3	*89*		
$Ir_8(CO)_{20}^{2-}$	II, C, 1, c	*280*		
$H_2Ir_4(CO)_{11}$[b, f]	II, C, 1, c	*280*		
$Co_4Ni_2(CO)_{14}^{2-}$	II, C, 2	*92*		
$Ni_3(CO)_8^{2-}$[a]	II, C, 1, b, c	*176, 352*		
$Ni_4(CO)_9^{2-}$[a,b]	II, C, 1, b, c	*175, 176, 182*		
$Ni_5(CO)_9^{2-}$[b]	II, C, 1, c	*175*		

---

[a] The corresponding neutral hydrido compound has been reported.

[b] Derivatives of the corresponding hydrido monoanion have been reported.

[c] Derivatives of the corresponding hydrido dianion have been reported.

[d] Deutero analog also obtained.

[e] Prepared by reaction of $Fe_3(CO)_{12}$ with $C_6H_5CH_2COCl$ in HCO_2NMe_2.

[f] Proton abstracted from the solvent.

[g] Two isomers isolated.

[h] R = Et, Bu, or Ph; prepared by the reaction of $M_3(CO)_{12}$ with RSH.

[i] Prepared by the reaction of $M_3(CO)_{12}$ with H^+; trisubstituted derivatives $HM_3(CO)_9L_3^+$ (L = PEt_3, PEt_2Ph) also reported.

[j] X = Cl, Br, or I.

[k] $Co_4(CO)_{12}$ + π-Cp_2Co.

enneacarbonyltricobalt alkane clusters was developed by Dent *et al.* (*121*) and a large number of derivatives were prepared by varying Y.

$$\begin{matrix} Co_2(CO)_8 \\ Co_4(CO)_{12} \end{matrix} + X_3CY \rightarrow Co_3(CO)_9CY \qquad (23)$$

Similar compounds can also be prepared by treatment of solutions of the $Co(CO)_4^-$ anion with halogenated compounds. The skeletal structure of this class of compound was elucidated by chemical techniques (*266*) and shown to consist of a triangular cluster of cobalt atoms, each of which was bonded to the apical carbon atom of an alkane. The Y substituent completed the fourth valence of carbon. An X-ray examination of $Co_3(CO)_9CMe$ (*357*) has confirmed this structure.

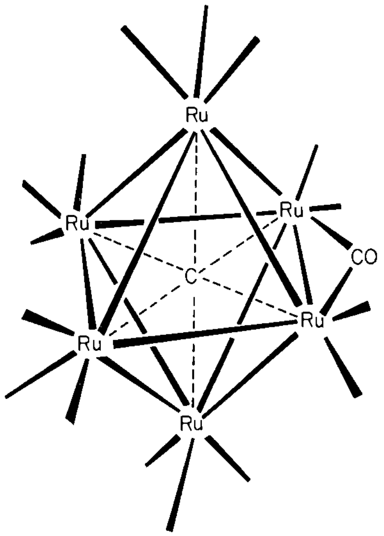


FIG. 3. Molecular structure of $Ru_6(CO)_{17}C$.

The clusters of the type $Co_3(CO)_9CY$ are listed in Table IV along with references to their preparation, mass spectral studies, and structural data.

The esters $Co_3(CO)_9(COOR)$ (R = Me, Et) were prepared by the alcoholysis of $Co_3(CO)_9CBr$ (*133*). The dimer related to $Co_3(CO)_9CY$ has been prepared by the action of CCl_4 on $Co(CO)_4^-$ (*42*) and by heating $Co_3(CO)_9CBr$ (*16*). In this dimer a carbon–carbon single bond links the two clusters. Another product of the action of heat on $Co_3(CO)_9CBr$ was

$$5\ Co_2(CO)_8 + 2\ CCl_4 \rightarrow [Co_3(CO)_9C]_2 + 4\ CoCl_2 + 22\ CO \qquad (24)$$

TABLE IV

ENNEACARBONYLTRICOBALT ALKANE CLUSTERS AND DERIVATIVES

Cluster	Preparative refs.	Mass spectral refs.	Structural data refs.
$Co_3(CO)_9CH$	*42, 133*	*299, 340*	
$Co_3(CO)_9CMe$	*121, 133, 289*	*244, 299, 340*	*357*
$Co_3(CO)_9CBu$	*289*		
$Co_3(CO)_9CPh$	*42, 121*	*299, 340*	
$Co_3(CO)_9CCH_2Ph$	*266*		
$Co_3(CO)_9CCH{=}CHCOOH$	*11*		
$Co_3(CO)_9CCH_2CH_2COOH$	*11*		
$Co_3(CO)_9CCH(COOMe)_2$	*121*		
$Co_3(CO)_9CCOOH$	*121*		
$Co_3(CO)_9CCOOMe$	*42, 133*		
$Co_3(CO)_9CCOOEt$	*121, 133*		
$Co_3(CO)_9CCF_3$	*36, 40, 121*	*299*	
$Co_3(CO)_9CCH_2CF_3$	*55*	*55*	
$Co_3(CO)_9CF$	*121, 133*	*299, 340*	
$Co_3(CO)_9CCl$	*42, 121, 133*	*244, 299, 340*	
$Co_3(CO)_9CBr$	*133*	*299, 340*	
$Co_3(CO)_9CI$	*133*		
$Co_3(CO)_9COBH_2NEt$	*254*		*254*
$[Co_3(CO)_9C]_2$	*16, 42*	*299*	
$[Co_3(CO)_9C]_2CO$	*16*		
$[Co_3(CO)_9C_2]_2$	*338, 339*		*338*
$Co_3(CO)_9C\cdot C_2HCo_2(CO)_6$	*338, 339*	*339*	*338*
$Co_3(CO)_9C_2\cdot C_2[Co_2(CO)_6]C_2Co_3(CO)_9$	*338, 339*		*338*
$Co_3(CO)_8LCMe$[a]	*341*		
$Co_3(CO)_7L_2CMe$[b]	*341*		
$Co_3(CO)_6(C_6H_3Me_3)CMe$	*339*	*339*	

[a] L = PPh_3, $AsPh_3$, PBu_3, $AsBu_3$, or $P(C_6H_{11})_3$.

[b] L = PPh_3 or $AsBu_3$.

the acyl dimer $[Co_3(CO)_9C]_2CO$, which may be regarded as a derivative of acetone (*16*).

The analogous silicon compounds $Co_3(CO)_9SiCH{=}CH_2$ and $[Co_3(CO)_9Si]_2$ have been reported as the products of the reaction of $Co_2(CO)_8$ with tetravinylsilane (*232*), but in more recent reports (*254*) workers have been able to isolate only the chloroderivative under the same conditions. $Co_3(CO)_9SnBu$ has been reported as the product of the reaction of $BuSnCl_3$ with $Co_2(CO)_8$ (*202*), but other workers have shown the product to have the formulation $BuSn[Co(CO)_4]_3$ (*321*) which is not a cluster.

Robinson and co-workers have examined the reactivity of the $Co_3(CO)_9CY$ clusters. When Y = Me or Cl, substitution by tertiary alkyl phosphines and arsines can occur to yield $Co_3(CO)_8LCY$ and $Co_3(CO)_7L_2CY$ (*341*). When Y is an alkyl or aryl group, $Co_3(CO)_9CY$ reacts with arenes to form the substituted clusters $Co_3(CO)_6(arene)CY$ and also compounds with stoichiometry $Co_5(CO)_{15}C_3H$, $Co_6(CO)_{18}C_4$, and $Co_8(CO)_{24}C_6$ (*338*, *339*). The pentanuclear compound appears to involve the $Co_3(CO)_9C$ cluster linked to an ethylene C_2H group, to which is bonded a $Co_2(CO)_6$ dimer in which all the CO groups are terminal (*338*). $Co_6(CO)_{18}C_4$ is composed of two $Co_3(CO)_9C$ clusters linked by an acetylene moiety. The third compound has a structure which combines the features of the first and second (*338*).

2. *Group V*

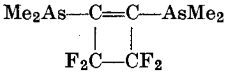
The majority of carbonyl clusters which have been substituted by ligands with Group V donor atoms have been prepared by allowing the parent carbonyl to react with the ligand in solution.

a. Under the Influence of Heat. Nearly all the substituted carbonyl compounds can be prepared in this way. $Co_4(CO)_{12}$ reacts with triphenylphosphine, -arsine, and -stibine to form the monosubstituted cluster (*75*).

$$Co_4(CO)_{12} + L \rightarrow Co_4(CO)_{11}L + CO \tag{25}$$

The action of heat is indiscriminate, however, and may often lead to cleavage of more bonds than desired. A more controlled method of providing the energy necessary for bond cleavage is provided by irradiation.

b. Irradiation. This technique is being increasingly used, as by adjustment of the wavelength of irradiation the possibility is presented of breaking bonds of a specific energy. Triiron dodecacarbonyl is substituted by the chelating arsine-substituted olefin ligand $Me_2AsC[C(AsMe_2)C_2F_4]$ (**1**) under ultraviolet irradiation (*111*).



(**1**)

$$Fe_3(CO)_{12} + L\text{–}L^2 \xrightarrow{h\nu} Fe_3(CO)_{10}(L\text{–}L) + 2\,CO \tag{26}$$

c. Other Substituents. A small number of substituted clusters have been prepared in which the starting materials were not the parent carbonyls. These reactions would appear to involve production of a labile intermediate followed by a condensation reaction. In this way

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[2] L–L is the generic symbol for a bidentate ligand.

$Ni_4(CO)_6[P(CH_2CH_2CN)_3]_4$ is obtained by the reaction of $Ni(CO)_4$ with the phosphine ligand (*35*).

$$4\ Ni(CO)_4 + 4\ P(CH_2CH_2CN)_3 \rightarrow Ni_4(CO)_6[P(CH_2CH_2CN)_3]_4 + 10\ CO \qquad (27)$$

The carbonyl clusters substituted by ligands with Group V donor atoms are listed in Table V along with their preparations and references to structural studies.

TABLE V

GROUP V SUBSTITUTED CARBONYL CLUSTERS

Cluster	Preparation (section number)	Refs.	Structural data refs.
$Mo_3(CO)_3(PPh_2)_3(\pi\text{-}Cp)_3$	II, D, 2, c	*161*	
$Mn_3(CO)_6(Et_2NCH_2CN)_3$	II, D, 2, c	*203*	
$Mn_3(CO)_9(PPh_2)_3$	II, D, 2, c	*8*	
$Re_3(CO)_9(PPh_2)_3$	II, D, 2, c	*8*	
$Fe_3(CO)_{11}(PPh_3)$	II, D, 2, a	*18*	*118*
$Fe_3(CO)_{11}P(OMe)_3$[a]	II, D, 2, a	*331*	
$Fe_3(CO)_{10}[Me_2AsC(C(AsMe_2)C_2F_4)]$	II, D, 2, b	*111*	
$Fe_3(CO)_9(PMe_2Ph)_3$	II, D, 2, a	*307*	
$Ru_3(CO)_9L_3$[b,c]	II, D, 2, a, b	*54, 66, 67, 210, 222, 326, 327*	
$Ru_3(CO)_{10}(AsPh_3)_2$	II, D, 2, a	*54*	
$Ru_3(CO)_6(diars)_3$[d]	II, D, 2, a	*222*	
$Ru_3(CO)_6(diphos)_3$[e]	II, D, 2, a	*222*	
$Os_3(CO)_9(PMePh_2)_3$	II, D, 2, a	*53*	
$Os_3(CO)_{11}L$[a,f]	II, D, 2, a	*46, 120*	
$Os_3(CO)_6(diars)_3$[d]	II, D, 2, a	*46*	
$Co_4(CO)_{11}L$[g]	II, D, 2, a	*75*	
$Co_3(CO)_7(PMe_2)_2$	II, D, 2, c	*163*	
$Co_3(CO)_6L_3$[h]	II, D, 2, c	*333*	
$Rh_4(CO)_{10}(PPh_3)_2$	II, D, 2, a	*88*	
$Ir_4(CO)_{10}(PPh_3)_2$	II, D, 2, a	*73, 280*	*14*
$Ir_4(CO)_9(PPh_3)_3$	II, D, 2, a	*73, 280*	*14*
$Ni_4(CO)_6[P(CH_2CH_2CN)_3]_4$	II, D, 2, c	*35*	*35*
$Pt_3(CO)_3L_4$[i]	II, D, 2, c	*41*	

[a] Corresponding di- and trisubstituted cluster also isolated.

[b] L = PPh_3, PBu_3, $P(OPh)_3$, PEt_3, PPh_2Et, $PPhEt_2$, PPh_2Me, or $PPhMe_2$.

[c] A number of isomers reported.

[d] diars = *o*-phenylenebisdimethylarsine, $C_6H_4(AsMe_2)_2$.

[e] diphos = bisdiphenylphosphinoethane, $C_2H_4(PPh_2)_2$.

[f] L = PEt_3, PEt_2Ph (*120*), or PPh_3 (*46*).

[g] L = PPh_3, $AsPh_3$, or $SbPh_3$.

[h] L = PBu_3, PPh_2Bu, or PPh_3.

[i] L = PPh_3 or PEt_3.

It is of note that many of the clusters which were prepared by the method above (Section II,D,2,c) involve the reaction of a carbonyl compound with a ligand which can bridge between two metal atoms and, hence, assist in cluster formation. The diphosphines have been particularly effective in this way, and remain bridging in the final product.

$$3\ Mn(CO)_5Br + 3\ Me_3SiPPh_2 \rightarrow Mn_3(CO)_9(PPh_2)_3 + 3\ Me_3SiBr + 6\ CO \quad (\textit{8}) \qquad (28)$$

$$3\ Co_2(CO)_8 + 2\ Me_4P_2 \rightarrow 2\ Co_3(CO)_7(PMe_2)_2 + 10\ CO \quad (\textit{163}) \qquad (29)$$

3. *Group VI*

A large number of carbonyl compounds substituted with ligands having Group VI donor atoms and, in particular, sulfur, have been reported. Elemental sulfur or sulfur atoms in thio compounds can assist in cluster formation by their capability of bridging between two or more metal atoms.

The structure of the compounds $[Mn(CO)_3SR]_n$ and $[Re(CO)_3SR]_n$ and the analogous selenol-substituted compounds have been a matter of controversy for some time. The sulfur compounds were first prepared by the reaction of the halopentacarbonyl with $Me_2Sn(SMe)_2$ (*1*, *3*), and

$$Mn(CO)_5Br + Me_2Sn(SMe)_2 \rightarrow [Mn(CO)_3SMe]_n + Me_2Sn(SMe)Br + 2\ CO \qquad (30)$$

reaction of the hydridopentacarbonyl with a thiol (*317*). The selenol

$$Re(CO)_5 + PhSH \rightarrow [Re(CO)_3SPh]_n + 2\ CO + H_2 \qquad (31)$$

compounds were similarly prepared (*4*). These compounds were postulated to be trinuclear clusters. Osmometric and mass spectral data (*10*, *221*), however, indicated that the compounds were tetrameric. Analyses of the infrared spectra in the ν(M–M) region (*5*) and the ν(C–O) overtone region (*49*) finally showed that there is no significant metal–metal bonding in this series of polynuclear compounds, the metal atoms being distributed at the apices of a regular tetrahedron and linked only by face-bridging thio groups.

Bor, Markó, and their co-workers have made a detailed investigation of the reactions of various cobalt carbonyl compounds with elemental sulfur and organosulfur compounds, and isolated a large number of cobalt–sulfur clusters. More recently Dahl has examined the structure of a number of these compounds and has attempted to place the stoichiometry, structure, and bonding of these clusters on a rational basis. The clusters have been prepared by a variety of methods.

a. Reaction of a Carbonyl Compound with Elemental Sulfur. This method has found only limited applications. $Co_3(CO)_9S$ can be prepared by reacting $Co_2(CO)_8$ with elemental sulfur in an atmosphere of carbon

$$12\ Co_2(CO)_8 + S_8 \rightarrow 8\ Co_3(CO)_9S + 24\ CO \qquad (32)$$

monoxide (*291*). Further reaction with elemental sulfur leads to $[Co_3(CO)_7S]_2S_2$ (*293*).

$$8\ Co_3(CO)_9S + S_8 \rightarrow 4\ [Co_3(CO)_7S]_2S_2 + 16\ CO \qquad (33)$$

b. Reaction of a Carbonyl Compound with CS_2. There is now considerable evidence that CS_2 can act as a bidentate ligand, bonding via one sulfur and the carbon atom (*151*). As with reactions of carbonyls with other sulfur-containing compounds, reactions with CS_2 lead to a number of products. When $Co_2(CO)_8$ is treated with CS_2, the products include $Co_4(CO)_{10}S_2$, $Co_3(CO)_9S$, $[Co_3(CO)_9C]_2$, and $Co_3(CO)_6(S)CS$, besides a number of unidentified products (*257*).

c. Reaction of a Carbonyl Compound with a Thiol or Thio ether. This method is the most commonly used for preparation of a carbonyl compound substituted with a sulfur ligand. The reaction of $Co_2(CO)_8$ with ethanethiol produces a mixture of compounds which have been identified as $Co_3(CO)_9S$, $Co_3(CO)_6S(SEt)$, $Co_4(CO)_{10}S_2$, $Co_4(CO)_5(SEt)_7$, and $Co_4(CO)_7(SEt)_3$ (*258*). Analogous compounds have been obtained by reaction of $Co_2(CO)_8$ with diphenyl disulfide (*256*).

d. Reaction of a Metal Salt with a Thiol in Alkaline Medium in the Presence of CO. Under these reducing conditions tetranuclear thiocarbonyl clusters have been prepared from $CoCl_2$ (*290*).

$$8\ CoCl_2 + 15\ EtSH + 15\ OH^- + 17\ CO \rightarrow Co_4(CO)_4(SEt)_8 + Co_4(CO)_5(SEt)_7 + 8\ COCl_2 + 15\ H_2O \qquad (34)$$

Data on the Group VI substituted carbonyl clusters are listed in Table VI.

The preparative reactions of metal thiocarbonyl compounds are not specific, and a variety of compounds is formed in each reaction. As a result, separation techniques, such as chromatography, are of vital importance in isolating pure compounds.

As can be seen from Table VI, a few of the compounds are prepared in ways different from the general methods of preparation (Section II,D,3a–d). Of interest are the extraction of sulfur from $PhCH_2CNS$ by $Fe_3(CO)_{12}$ to form $Fe_3(CO)_9S(SCH_2Ph)_2$ and $Fe_4(CO)_{12}S_2$ (*128*), and the reduction of $Co(CO)_4^-$ by Na_2SO_3 to form $[Co_3(CO)_7S]_2S_2$ (*293*).

The compound $Os_4(CO)_{12}O_4$ has been isolated from the reaction of OsO_4 with CO under pressure to produce $Os_3(CO)_{12}$ (*46, 219*). In this compound an OsO_4 molecule has added to the triangular cluster and is thought to be bonding via the Os atom to the three metal atoms of the cluster. Attempts to add OsO_4 to other triangular carbonyl clusters have not been successful (*223*).

TABLE VI

GROUP VI SUBSTITUTED CARBONYL CLUSTERS

Cluster	Preparation (section number)	Refs.	Structural data refs.
$Fe_3(CO)_9S(SCH_2Ph)_2$	[a]	*128*	
$Fe_4(CO)_{12}S_2$	[a]	*128*	
$Fe_3(NO)_4S[S_2C_2(CF_3)_2]$	[b]	*240*	
$Os_3(CO)_{10}(OMe)_2$	[c]	*217*	*216*
$Os_4(CO)_{12}O_4$	[c]	*46, 219*	
$FeCo_2(CO)_9S$[d]	[e]	*234, 235*	*354*
$FeCo_2(CO)_9Se$	—	*113*	*113*
$FeCo_2(CO)_9Te$	—	*113*	*113*
$Co_3(CO)_9S$	II, D, 3, a–c[f]	*256, 258, 291*	*371*
$Co_3(CO)_9Se$	—	*113*	*113*
$Co_3(CO)_9Te$	—	*113*	*113*
$[Co_3(CO)_7S]_2S_2$[g]	II, D, 3, a[h]	*293*	*353*
$Co_3(CO)_6S(CS)$	II, D, 3, b	*257*	
$Co_3(CO)_4(SR)_5$[i,j]	II, D, 3, c, d	*258, 290*	*372*
$Co_3(CO)_6S(SR)$[i]	II, D, 3, c	*258*	
$Co_3(CO)_9(SR)$[k]	II, D, 3, c	*256*	
$Co_3(CO)_5(SEt)_4 \cdot Co_2(CO)_5(SEt)$	II, D, 3, c	*373*	*373*
$Co_3(CO)_5(SEt)_4 \cdot Co_3(CO)_6S$[l]	II, D, 3, c	*258*	*374*
$Co_3(CO)_4(SPh)_5 \cdot Co_3(CO)_6S$	II, D, 3, c	*256*	
$Co_4(CO)_{10}S_2$	—	*293*	*376*
$Co_4(CO)_{10}Te_2$	—		*114*
$Co_4(CO)_{10}S(CS)$[m]	II, D, 3, b	*292*	
$Co_4(CO)_4(SEt)_8$	II, D, 3, d	*290*	
$Co_3(CO)_3[S_2C_2(CF_3)_2]_3$	[n]	*239, 250*	

[a] $Fe_3(CO)_{12} + PhCH_2CNS$.

[b] $Hg[Fe(CO)_3NO]_2 + C_2S_2(CF_3)_2$.

[c] $OsO_4 + CO + MeOH$ at high pressures and temperatures.

[d] Mono- and disubstituted derivatives obtained with PPh_3 (*60*).

[e] $Co_2(CO)_8 + Fe(CO)_5 + EtS \cdot SEt$, EtSH, or S.

[f] $Co_2(CO)_8 + H_2S + CO$(100 atm).

[g] Identified as $Co_3(CO)_7S_2$ prior to X-ray study.

[h] $Co(CO)_4^- + Na_2SO_3$.

[i] R = Et or Ph.

[j] Identified as $Co_4(CO)_5(SEt)_7$ before X-ray study.

[k] R = Ph or $PhCH_2$.

[l] Identified as $Co_4(CO)_7(SEt)_3$ before X-ray study.

[m] Now thought to have a stoichiometry $Co_6(CO)_{16}C_2S_3$ (*112*).

[n] $Co_2(CO)_8 + C_2S_2(CF_3)_2$.

4. *Group VII*

A small number of compounds thought to be clusters have been prepared by the action of a halogen on a carbonyl cluster. Bromine reacts with $Fe_3(CO)_{12}$ to produce a compound postulated by Hieber (*167*) to be $Fe_3(CO)_9Br_6$.

$$2\ Fe_3(CO)_{12} + 6\ Br_2 \rightarrow 3\ Fe(CO)_4Br_2 + Fe_3(CO)_9Br_6 \qquad (35)$$

The compounds $Ru_3(CO)_{12}X_6$ (X = Cl, Br, or I) have been obtained by the action of halogens on $Ru_3(CO)_{12}$ (*210, 215*). They appear to be formed by the condensation of three *cis*-$Ru(CO)_4X_2$ molecules (*212*). A closed halocarbonyl cluster of osmium has been prepared by the action of heat on the linear $Os_3(CO)_{12}X_2$ (X = Cl, Br, or I) (*120*).

$$Os_3(CO)_{12}X_2 \xrightarrow{\Delta} Os_3(CO)_{10}X_2 + 2\ CO \qquad (36)$$

$Rh_4(CO)_{12}$ is reported to react with tetramethylammonium iodide to produce $Rh_6(CO)_{15}I^-$ (*88*).

5. *Carbonyl Clusters Substituted by Ligands with an Organic π System*

Organometallic derivatives of metal carbonyls have been shown to be intermediates in the polymerization and cyclization of acetylenes in the presence of metal carbonyls, and many acetylene derivatives of metal carbonyl compounds have been isolated (*43, 198*). Acetylene-substituted carbonyl clusters have, in general, been prepared by one of two methods.

a. Reaction of Acetylene with a Cluster Carbonyl in Solution under the Action of Heat or Ultraviolet Irradiation. Substitution of carbonyls with acetylenes usually does not occur in a 1:1 replacement fashion and, hence, quite marked changes can occur in the structure of the sub-

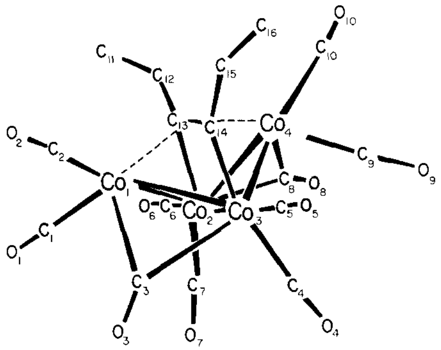


FIG. 4. Molecular structure of $Co_4(CO)_{10}(C_2Et_2)$. Reproduced by permission.

stituted compound compared with that of the parent carbonyl. In $Co_4(CO)_{10}(C_2Et_2)$, prepared by the action of the acetylene on the parent carbonyl, the cluster has a "butterfly" form, and there are only five Co–Co bonds compared with the six of the parent carbonyl (Fig. 4) (*117*). In the case of the similarly prepared $Ru_3(CO)_9(C_2Ph_2)_3$ and $Ru_3(CO)_{10}(C_2Ph_2)_2$, however, the acetylene molecule appears to have

TABLE VII

CARBONYL CLUSTERS SUBSTITUTED BY LIGANDS WITH ORGANIC π SYSTEMS

Cluster	Preparation (section number)	Refs.	Structural data refs.
$Fe_3(CO)_9(C_2Ph_2)$	II, D, 5, b	*200*	*38*
$Fe_3(CO)_8(C_2Ph_2)_2$[a]	II, D, 5, a	*199*	*126*
$Fe_4(CO)_{10}(C_8H_8)_2C_2H_4Cl_2$	II, D, 5, a	*62*	*93*
$Ru_3(CO)_9(C_2Ph_2)_3$	II, D, 5, a	*78*, *346*	
$Ru_3(CO)_9[C_2(C_6H_4Cl)_2]_3$	II, D, 5, a	*346*	
$Ru_3(CO)_{10}(C_2Ph_2)_2$	II, D, 5, a	*78*	
$Ru_3(CO)_9(C_2Ph_2)$	II, D, 5, a	*78*	
$Ru_3(CO)_8(C_2Ph_2)_2$[a]	II, D, 5, a	*78*	
$Ru_3(CO)_{10}(C_8H_{12})$[b]	II, D, 5, a	*67*	
$Ru_3(CO)_4(C_8H_8)_2$[c]	II, D, 5, a	*104*	*34*
$Ru_4(CO)_9(C_{10}H_5Me_3)$[d]	II, D, 5, b	*94*	*94*
$Ru_6(CO)_{14}(arene)C$[e]	II, D, 5, b	*211*	*296*
$Co_3(CO)_2(arene)_3{}^+$	[f]	*87*, *139*	*197*
$Co_3(CO)_6(C_6H_3Me_3)CMe$	II, D, 5, a	*339*	
$Co_4(CO)_{10}(C_2RR')$[g]	II, D, 5, a	*267*	*117*
$Co_4Hg_2(CO)_{12}(C_2HR)_2$[h]	II, D, 5, b	*267*	
$Co_6Hg_3(CO)_{16}(C_2HPh)_4$	II, D, 5, b	*267*	
$FeNi_2(CO)_3(\pi\text{-}Cp)_2(C_2RR')$[i]	[j]	*359*	
$FeNi_2(CO)_3(\pi\text{-}Cp)_2(C_2HPh)_2$	[j]	*359*	
$Fe_2Ni_2(CO)_6(\pi\text{-}Cp)_2(C_2RR')$[i]	[j]	*359*	
$Ni_4(CO)_3[C_2(CF_3)_2]_3$	II, D, 5, b	*249*	

[a] Violet isomer.

[b] C_8H_{12} = COD = 1,5-cyclooctadiene.

[c] C_8H_8 = COT = 1,3,5,7-cyclooctatetraene.

[d] $C_{10}H_5Me_3$ = 4,6,8-trimethylazulene.

[e] arene = toluene, *p*-xylene, or mesitylene.

[f] $Hg[Co(CO)_4]_2 + C_6H_6 + AlCl_3$ (*139*); $Co_2(CO)_8$ + arene + $AlBr_3$ (arene = C_6H_6, C_6H_5Me) (*87*).

[g] $C_2RR' = C_2Ph_2$, C_2Et_2, C_2H_2, $C_2(Ph)CO_2Me$, or $C_2(H)SiMe_3$.

[h] R = Me_3C or Ph.

[i] $C_2RR' = C_2Ph_2$, C_2HPh, or $C_2(CPh)_2$.

[j] $Fe(CO)_5 + Cp_2Ni_2(C_2RR')$; $Fe(CO)_5 + Cp_2Ni + C_2RR'$; no conclusive proof of stoichiometry or structure.

simply substituted a carbonyl group and be acting as a monodentate ligand, without causing rearrangement of the cluster (*78*, *346*).

b. Reaction of an Alkyne with a Noncluster Carbonyl Compound. This reaction in a small number of cases has led to an acetylene carbonyl cluster. An example of this is the reaction of perfluorodimethylacetylene with nickel carbonyl (*249*).

$$4\,Ni(CO)_4 + 3\,C_2(CF_3)_2 \rightarrow Ni_4(CO)_3[C_2(CF_3)_2]_3 + 13\,CO \qquad (37)$$

Acetylenes are not the only compounds with organic π systems which can substitute in metal carbonyls, and the same general synthetic methods can be used for other ligands. Reaction of carbonyl clusters with polyolefin systems, such as 1,5-cycloocatadiene and 1,3,5,7-cyclooctatetraene, have produced substituted carbonyl systems, but only with $Ru_3(CO)_{12}$ have clusters been isolated. Arene-substituted carbonyl clusters have also been obtained, as has been described in Section II.D.1.

The carbonyl clusters substituted by acetylenes, olefins, and arenes are listed in Table VII, together with their methods of preparation and references to structural studies.

Compounds with the formulation $Pt_3(COD)_3(SnCl_3)_2$ (*277*) and $Pd_3(COD)_3(SnCl_3)_2$ (*24*) have been obtained by the reaction of $PtCl_2$ with $SnCl_2$ and 1,5-cyclooctadiene, and $(COD)PdCl_2$ with $SnCl_2$ respectively. The platinum complex has been shown to contain a triangle of platinum atoms bonded to each other and to the two $SnCl_3$ groups (*156*).

E. π-CYCLOPENTADIENYL CLUSTERS

Many carbonyl compounds have been prepared in which terminal CO groups are replaced by π-bonded cyclopentadienyl groups (*37*, *381*). The relationship between cyclopentadienyl and carbonyl ligands has been discussed by King (*245*), who points out that an isoelectronic compound is obtained when either two or three CO groups are replaced by one cyclopentadienyl radical and the atomic number of the metal changes by −1 or +1, respectively. In general, in response to electronic factors three CO groups are substituted by a π-cyclopentadienyl group.

a. π-Cyclopentadienylcarbonyl Clusters. The π-cyclopentadienylcarbonyl clusters are prepared almost exclusively by the action of heat or ultraviolet irradiation on a corresponding π-cyclopentadienyl metal carbonyl compound with a lower nuclearity. The trinuclear cluster $Co_3(\pi\text{-}Cp)_3(CO)_3$[3] has been prepared by irradiating a solution containing

$$3\,Co(\pi\text{-}Cp)(CO)_2 \rightarrow Co_3(\pi\text{-}Cp)_3(CO)_3 + 3\,CO \qquad (38)$$

---

[3] π-Cp = π-Cyclopentadienyl.

the mononuclear compound $Co(\pi\text{-}Cp)(CO)_2$ (*245*). The action of heat on

$$4\ Co_3(\pi\text{-}Cp)_3(CO)_3 \rightarrow 3\ Co_4(\pi\text{-}Cp)_4(CO)_2 + 6\ CO \qquad (39)$$

the trinuclear cluster produces another π-cyclopentadienylcarbonyl cluster with a nuclearity of four (*245*).

b. Ligands not π Acceptors. There are a number of cyclopentadienyl metal clusters in which the other ligands bonded to the metal atoms are not π-acceptor ligands. These compounds are usually prepared by reaction of the ligand with a cyclopentadienyl compound, such as a cyclopentadienylcarbonyl or a metallocene compound. The cluster $Cr_4(\pi\text{-}Cp)_4O_4$ has been prepared by the action of oxygen on biscyclopentadienylchromium (*144*).

The π-cyclopentadienyl clusters, their preparation, and references to mass spectral and structural data are listed in Table VIII. The structures

TABLE VIII

π-CYCLOPENTADIENYL CLUSTERS

Cluster	Preparation (section number)	Refs.	Mass spectral refs.	Structural data refs.
$Cr_4(\pi\text{-}Cp)_4O_4$	II, E, 1, b	*144*		*378*
$Cr_4(\pi\text{-}Cp)_4S_4$	—	*137*		*378*
$Mn_3(\pi\text{-}Cp)_3(NO)_4$	II, E, 1, a	*247*	*130*	*130*
$Fe_4(\pi\text{-}Cp)_4(CO)_4$	II, E, 1, a	*245*	*246*	*315*
$Fe_4(\pi\text{-}Cp)_4(CO)_4^+$	[a]	*245, 307*		
$Ru_4(\pi\text{-}Cp)_4(CO)_4$	II, E, 1, a	*355*		
$Co_3(\pi\text{-}Cp)_3(CO)_3$[b]	II, E, 1, a	*245*	*245*	
$Co_4(\pi\text{-}Cp)_4(CO)_2$	II, E, 1, a	*245*	*245*	
$Co_3(\pi\text{-}Cp)_3S_2$	II, E, 1, b	*320*	*320*	
$Co_3(\pi\text{-}Cp)_3(CO)S$	II, E, 1, b	*320*	*320*	
$Co_3(\pi\text{-}Cp)_3(CO)O$	II, E, 1, a	*362*		*362*
$Rh_3(\pi\text{-}Cp)_3(CO)_3$[b]	II, E, 1, a	*140, 322*	*304, 322*	*304, 322*
$Rh_4(\pi\text{-}Cp)_4(CO)_2$[c]	II, E, 1, a	*304, 322*	*304, 322*	
$Rh_3(\pi\text{-}Cp)_4H$	[d]	*142, 145*	*142*	*142, 305*
$CoNi_2(\pi\text{-}Cp)_3(CO)_2$	—	*361*		*361*
$CoNi_2(\pi\text{-}Cp)_3(CO)S$	—	*113*		*113*
$Ni_3(\pi\text{-}Cp)_3(CO)_2$	II, E, 1, a	*143*	*345*	*197*
$Ni_3(\pi\text{-}Cp)_3(CO)S$	—	*113*		*113*
$Ni_3(\pi\text{-}Cp)_3S_2$	II, E, 1, b	*365*		*365*
$Ni_3(\pi\text{-}Cp)_3NBu$	II, E, 1, b	*319, 320*	*319*	*320*

[a] $Fe_4(\pi\text{-}Cp)_4(CO)_4 + Br_2$ (*245*); $Fe_4(\pi\text{-}Cp)_4(CO)_4 + X_2$ (X = Cl, Br) (*307*).

[b] Two isomers isolated.

[c] Prepared and identified in a mass spectrometer.

[d] $RhCl_3 + CpMgBr$.

of metal π-cyclopentadienyl compounds have recently been reviewed by Wheatley (*380*).

F. CLUSTERS WITH OTHER π-ACID LIGANDS

Although a large number of transition metal nitrosyl compounds have been prepared (*208*), $Mn_3(\pi\text{-}Cp)_3(NO)_4$ described in Section II, D is the only characterized nitrosyl cluster (*130*). King has isolated a compound for which he postulated the formula $Fe_2(NO)_2[S_2C_2(CF_3)_2]_2$, but the mass spectra indicated the formulation $Fe_3(NO)_4S[S_2C_2(CF_3)_2]_2$ (*240*).

TABLE IX

PHOSPHINE CLUSTERS

Cluster	Method of preparation	Refs.
$Ru_4(PPh_3)_5(NH_3)_3$	$(Ph_3P)_3Ru(N_2)H_2 + (Ph_3P)_3Ru(NH_3)H_2$	*261*
$Ru_3(CO)_8(PH_3)_4$	$Ru(CO)_2Cl_2 + PH_3$	*255*
$Rh_6(CO)_8(PH_3)_8$	$[Rh(CO)_2Cl]_2 + PH_3$	*255*
$Pd_4(PH_3)(PPh_3)_4Cl_4$	$(Ph_3P)_2PdCl_2 + PH_3$	*255*
$Pd_3(PPh_3)_3(PPh_2)_2Cl_2$	$(Ph_3P)_4Pd + PdCl_2$	*109*
$Pt_3(PH_3)_3(PPh_3)_3I_2$	$(Ph_3P)_2PtI_2 + PH_3$	*255*
$Pt_4(PPh_3)_4$	$(Ph_3)_4Pt + O_2$	*152*
	$[(Ph_3P)_2PtI]_2 + KOH$	*268*
$Pt_3(PPh_3)_6$	$(Ph_3P)_2Pt + \Delta$	*152*
$Pt_3(PPh_3)_5 \cdot C_6H_6$	$(Ph_3P)_nPt + O_2$, $n = 4, 3$	*364*
$Pt_3(PPh_3)_4 \cdot C_6H_6$	$(Ph_3P)_2PtCl_2 + KOH$	*364*
$Pt_3(PPh_3)_9CO$	$(Ph_3P)_2Pt(CO)_2 + N_2$	*363*
$Pt_3L_4(CO)_3$[a]	$(Ph_3P)_2Pt(CO)_2 + N_2$	*363*
	$Na_2PtCl_4 + CO + L + N_2H_4$	*41*
$Pt_3L_3(CO)_3$[a]	$Na_2PtCl_4 + CO + L + N_2H_4$	*41*
$Pt_4(CO)_5(PPhMe_2)_4$	$Na_2PtCl_4 + CO + L + N_2H_4$	*41, 359*
$[Au_3(PEtPh_2)_2Cl]_4$	$Ph_2EtPAuCl + NaBH_4$	*70*
$[Au_3(PEtPh_2)_2X]_4$	$[Au_3L_2Cl]_4 + X^-$[a]	*70*
	$Au_5L_4Cl + X^-$[b]	*282, 283*
$[Au_6(PEtPh_2)_4Cl]X$[c]	$[Au_3L_2Cl]_4 + X^-$	*70*
$Au_6(diphos)_2Cl_2 \cdot 2EtOH$	$(diphos)(AuCl)_2 + NaBH_4$	*312*
$Au_6(diphos)_2X_2 \cdot 2H_2O$[d]	$Au_6(diphos)_2Cl_2 \cdot 2EtOH + X^-$	*312*
$[Au_6(diphos)_2Cl]X$[e]	$Au_6(diphos)_2Cl_2 \cdot 2EtOH + X^-$	*312*

[a] L = PPh_3, $PPhMe_2$, PPh_2Me, or PPh_2CH_2Ph.

[b] X = Br, I, or SNC.

[c] X = I, SnI_3, or CN.

[d] X = ClO_4, PF_6, or BPh_4.

[e] X = Br or I.

A large number of clusters of Group VIII and Group IB metals have been prepared in which a variety of phosphines are the principal ligands. These clusters are listed in Table IX. The phosphine clusters have been prepared by a wide variety of methods as can be seen from Table IX, and no general methods of preparation can be designated for these compounds. Most of them involve either the reaction of a zero-valent phosphine metal compound, or reduction of a higher valent compound. The phosphine clusters listed in Table IX have all been reported since 1966, and the structure of only one of these compounds has been determined. Hence the postulated stoichiometry of some of these compounds may be incorrect. Experience with the carbonyl clusters has shown that formulations based only on analytical data do not have any high degree of reliability. Moreover, for these compounds the noble gas rule does not appear to be valid, so predictions cannot be made on this basis.

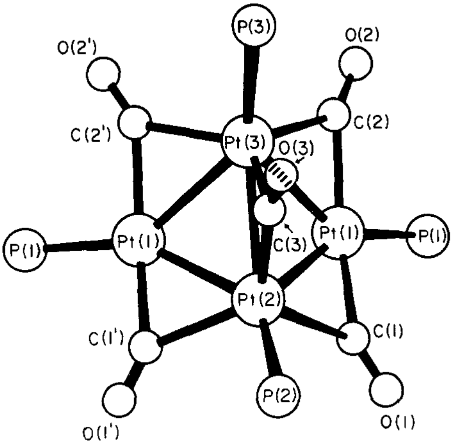


FIG. 5. Molecular structure of $Pt_4(CO)_5(PPhMe_2)_4$.

A series of compounds formulated as $Pt_3(CO)_3L_4$, $Pt_3(CO)_3L_3$, and $Pt_3(CO)_4L_3$ ($L = PPh_3$, PMe_2Ph, or PPh_2CH_2Ph) have been prepared by the reduction of $PtCl_4^{2-}$ with hydrazine in the presence of the phosphine and alcoholic KOH (*41*). A recent X-ray crystal structure of the supposed $Pt_3(CO)_4(PPhMe_2)_3$ showed it to have the formula $Pt_4(CO)_5(PPhMe_2)_4$ (*366*) and it may be that all the clusters are tetranuclear (Fig. 5).

The structure of the compound described as $Au_6(PPh_3)_4(SCN)_2$ (*312*) has been determined by X-ray studies and the correct formulation shown to be $Au_{11}(PPh_3)_7(SCN)_3$. The structure is described as apical sharing of a pentagonal bipyramid and a square pyramid with gold atoms at all the vertices. The outer ten gold atoms bond to the central Au at the apex, but not to each other (*302*). This compound is not a cluster and further structural investigations of the other phosphine gold clusters in Table IX may show more complex formulations for them also. Unfortunately, studies of a number of phosphine clusters in the mass spectrometer showed no skeletal ions; the only ions observed corresponded to free phosphine (*209*).

The cluster $Cu_4(PPh_3)_4$ has been reported (*269*), but later work showed the formulation to be incorrect (*270*).

The primary phosphine ligand PH_3 appears to be very effective in causing the aggregation of mononuclear units into clusters, if the preliminary reports of the compounds it forms prove to be accurate (*255*).

An octanuclear cluster of copper has recently been prepared by the reaction of copper(II) bromide with the dianion of 1,1-dicyanoethylene-2,2-dithiol (*136*). An X-ray determination of the structure has shown the cluster to have the formula $[Cu_8(i\text{-MNT})_6]^{4-}$ with the copper atoms arranged at the vertices of a slightly distorted cube (*300*).

III. Physical Properties of Clusters

Owing in part to the relatively recent development of cluster chemistry, there is an almost complete lack of thermodynamic data for cluster compounds. The measurement of appearance potentials of positively charged ions by mass spectrometry has offered a technique for ready measurement of this parameter, but the high values obtained for ionization potentials and heats of formation of ions by this method cast some doubt on its accuracy (*358*). It would appear that ions are generated in excited states (*22*). It may be expected that there will be a considerable increase in the thermodynamic investigations of clusters in the near future, so as to provide quantitative data on which to base theoretical considerations.

Apart from X-ray diffraction studies, the only physical properties of clusters which have been studied are the spectroscopic properties—the infrared and Raman, electronic, nuclear magnetic resonance, electron spin resonance, Mössbauer, and mass spectra.

A. Infrared and Raman Spectra

Symmetry theory is in common use for the prediction of the number of fundamental vibrations active in the infrared and Raman spectra for a particular molecule (*100*). This has found particular application to the metal carbonyls, where the C–O-stretching vibration produces a very intense absorption band. From the number of bands observed in solution, predictions of structure have been made. In molecules of low symmetry, however, it is unusual for all the permitted vibrations to be observed. Also, correlation of properties in solution with the structure in the solid state has been shown to be a potential source of error by the uncertainty over the structures of $Fe_3(CO)_{12}$ and $Co_4(CO)_{12}$. These structures were for a long time a subject of controversy because of the lack of agreement between properties measured in solution and those expected from the structures determined by X-ray diffraction studies of the clusters in the solid state. In particular, the number of ν(C–O) vibrations observed in solution are significantly less than predicted, indicating a structure of higher symmetry than observed in the solid state. Evidence is now mounting that both $Co_4(CO)_{12}$ (*103*, *157*, *279*, *350*) and $Fe_3(CO)_{12}$ (*18*, *375*) exist in solution in tautomeric forms with higher symmetry (Fig. 6). In view of these restrictions and the limitations of resolution, structural predictions based on this kind of spectroscopic data should be treated with caution. Overtones of the ν(C–O) bands have been used to obtain more information about the fundamental vibrations and, hence, assist in prediction of structure (*5*, *49*, *273*). As for mononuclear carbonyls, the frequencies of C–O stretching bands and force constants calculated from these by simplified force fields have been used as a relative measure of metal–carbon and carbon–oxygen bond strengths.

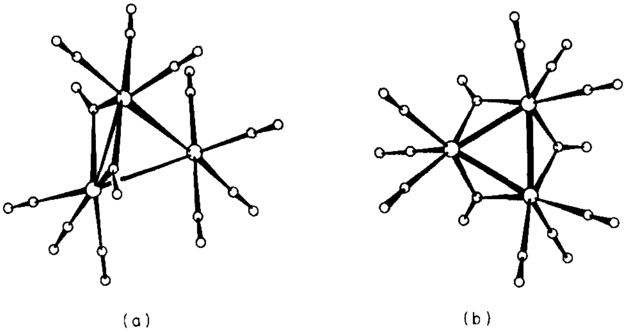


FIG. 6. Molecular structure of $Fe_3(CO)_{12}$. (a) In the solid state; (b) proposed in solution. Reproduced by permission.

The metal–metal vibrations of clusters are expected to produce absorptions in the region 250–100 cm^{-1} as a result of the heavy atomic weights of the atoms and also because of the low force constants expected for these bonds (*150*). Until recently, no equipment was available which could detect energy absorptions in this region. New far-infrared spectrophotometers and Raman spectrophotometers using laser sources, however, have enabled these absorptions to be measured. The Raman spectra are of considerable value in the detection of metal–metal bonds, as sharp strongly polarized lines are observed (*150*), whereas in the infrared the bands are at best observed at very low intensities (*69*).

Quicksall and Spiro (*334*) have assigned bands at 208, 164, and 105 cm^{-1} in the Raman spectrum of $Ir_4(CO)_{12}$ to a_1, t_2, and e iridium–iridium modes. This assignment is based on an idealized *Td* symmetry of the cluster and would suggest that the solid state structure (*377*) persists in solution. An infrared and Raman study by Abel *et al.* (*5*) has confirmed this assignment.

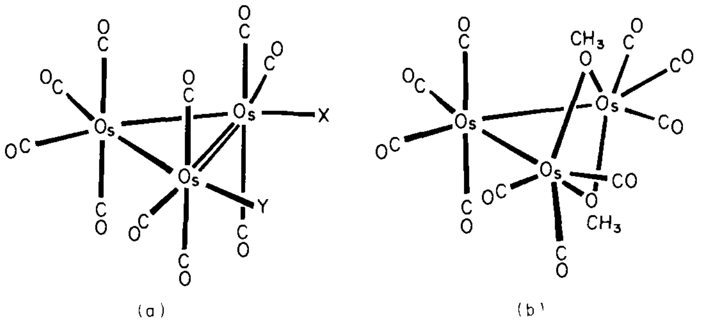


FIG. 7. Molecular structure of $Os_3(CO)_{10}(OMe)_2$. (a) Proposed; (b) determined.

Quicksall and Spiro (*335*) have also measured the Raman and infrared spectra of $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ in the low energy region and have assigned bands at 185 and 149 cm^{-1} and 158 and 117 cm^{-1}, respectively to the a_1 and e' cluster vibrations expected for a triangular model. Metal–metal stretching force constants were calculated on the basis of an approximate normal coordinate analysis, and found to be 0.82 mdyne/Å for $Ru_3(CO)_{12}$ and 0.91 mdyne/Å for $Os_3(CO)_{12}$. Ware and co-workers (*159*) have confirmed the assignment of the bands, but have obtained metal–metal stretching force constants of 1.7 and 1.6 mdyne/Å for $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$, respectively. These values are a factor of two larger than those obtained by Spiro and, moreover, place the Ru–Ru and Os–Os force constants in the opposite order. The calculations of Ware were based on a simple triatomic triangular system, and it would appear that force constants based on such a simple model may not be reliable.

Ware (*159*) also examined the infrared and Raman spectra of $Os_3(CO)_{10}(OMe)_2$ and assigned absorptions at 172, 136, and 119 cm^{-1} to a_1, a_1, and b_2 modes, respectively. This assignment and derivative force constants led to the postulation of a structure based on the arrangement of the Os atoms at the vertices of an isosceles triangle with terminal OMe groups and a double bond between the two Os atoms bonded to the methoxy ligands (Fig. 7a). A subsequent X-ray study (*216*) confirmed the isosceles arrangement of the metal atoms, but showed the methoxy ligands to be bridging the short Os–Os bond (Fig. 7b).

The far-infrared spectrum of $Rh_4(CO)_{12}$ has been measured (*7*) and the four bands observed have been assigned as 225 cm^{-1}, e; 200 cm^{-1}, e; 176 cm^{-1}, a_1; and 128 cm^{-1}, a_1. These bands are not markedly different from those observed for $Ir_4(CO)_{12}$ (*334*) despite their significantly different crystal structures (*377*). The single force constant, however, obtained from calculations based on a pseudotetrahedral structure could not satisfactorily predict the band positions. Using an M_3M' model, values of 0.95 mdyne/Å were obtained for the M_3 basal stretching force constant and 1.35 mdyne/Å for the M–M' force constant.

Griffith and Wickham (*155*) have reported absorptions at 221, 173, and 134 cm^{-1} in the Raman spectrum of $Rh_4(CO)_{12}$ and 199 and 172 cm^{-1} in that of $Rh_6(CO)_{16}$, but have not attempted assignments.

B. ELECTRONIC SPECTRA

Very few investigations of the electronic spectra of clusters have been made, probably because satisfactory assignment of the spectra of simple binuclear metal–metal-bonded carbonyls has yet to be made. Gray and co-workers (*72*) have had some success in measuring and assigning polarized electron absorption bands of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ by orienting the molecules in a nematic liquid crystal, but this technique would not appear to be capable of application to clusters.

It is a readily observable fact that the color of carbonyl clusters becomes darker with increasing nuclearity of the cluster. Thus, $Rh_2(CO)_8$ is orange, $Rh_4(CO)_{12}$ is brick red, and $Rh_6(CO)_{16}$ is black. In a study of the electronic spectra of a series of clusters, Abel and McLean (*6*) have found that the lowest energy band can, in general, be assigned to a transition from the highest skeletal bonding molecular orbital to the lowest antibonding orbital. The gradation of color would indicate that with increasing nuclearity the separation between the highest bonding and lowest antibonding skeletal orbital decreases.

C. NUCLEAR MAGNETIC RESONANCE SPECTRA

Proton NMR measurements have been used in the usual way for structural assignment of organosubstituted clusters and for the detection of hydrogen bonded to metal atoms. In many of the carbonyl hydride clusters, the chemical shift of the hydride is to higher field than normally found—in the range 15–35 τ. It has been suggested that this high field signal is indicative of the presence of a bridging hydride ligand (*214*, *222*).

Broad-line ^{59}Co NMR has been used to study the structure of $Co_4(CO)_{12}$ in solution (*157*). Noack and co-workers (*279*) have also measured the ^{59}Co NMR spectra of a number of cobalt clusters.

D. ELECTRON SPIN RESONANCE SPECTRA AND MAGNETISM

The majority of clusters known are diamagnetic and so there has been little study of magnetic properties. The only paramagnetic clusters are $Co_3(CO)_9S$, (*258*) $Co_3(CO)_9Se$ (*113*), $Ni_3(\pi\text{-}Cp)_3(CO)_2$ (*143*), $Ni_3(\pi\text{-}Cp)_3(CO)S$ (*113*), and $Ni_3(\pi\text{-}Cp)_3NBu$ (*319*), and room temperature magnetic susceptibilities have been measured for a number of them.

Longuet-Higgins and Stone (*278*) have measured the ESR spectrum of single crystals of $Ni_3(\pi\text{-}Cp)_3(CO)_2$ and proposed that the $g_{\parallel}$ and $g_{\perp}$ values of 2.11 and 2.02 are consistent with the unpaired electron being in an a_2'' orbital consisting of a bonding combination of $3d$ orbitals on the nickel atoms. Strouse and Dahl (*356*) have measured the ESR of $Co_3(CO)_9S$ in solution and in a diluted single crystal and have found $g_{\parallel} = 2.04$ and $g_{\perp} = 2.02$. This study leads to the conclusion that the molecular orbital containing the unpaired electron is an antibonding a_2 orbital which consists primarily of cobalt d_{xz} atomic orbitals localized in the tricobalt plane. Application of this kind of treatment to $Ni_3(\pi\text{-}Cp)_3(CO)_2$ indicates that the unpaired electron is in an antibonding orbital of the same type d character as that containing the unpaired electron in $Co_3(CO)_9S$, in contrast to the findings of Longuet-Higgins (*278*). This result is supported by the dramatically reduced metal–metal bond length in the diamagnetic $CoNi_2(\pi\text{-}Cp)_3(CO)_2$ (2.358 Å) compared with $Ni_3(\pi\text{-}Cp)_3(CO)_2$ (2.389 Å).

E. MÖSSBAUER SPECTRA

The first studies of the Mössbauer spectra of carbonyl clusters were made on $Fe_3(CO)_{12}$ and as two of the Fe atoms were markedly different from the third, a symmetric linear model was proposed (*148*, *164*, *227*). A later study which demonstrated the Mössbauer equivalence of $Fe_3(CO)_{12}$ and $Fe_3(CO)_{11}H^-$, the structure of which was known (*303*), led to the postulation of the correct unsymmetrical triangular model (*134*).

Greatrex and Greenwood (*154*) have measured the Mössbauer spectra of a series of iron carbonyl compounds, including the clusters $Fe_3(CO)_{11}^{2-}$, $Fe_3(CO)_{11}H^-$, $Fe_4(CO)_{13}^{2-}$, $Fe_4(CO)_{13}H^-$, $Fe_3(CO)_9(PMe_2Ph)_3$, and $Fe_4(\pi\text{-}Cp)_4(CO)_4$ and its monocation derivative. The spectra of the anions were interpreted to confirm the X-ray results (*115*, *303*, *127*). The spectrum of the phosphine-substituted cluster is very similar to that of $Fe_3(CO)_{12}$, indicating that the unsymmetrical triangular structure is retained by substitution of one CO group at each Fe atom. The spectra of $Fe_4(\pi\text{-}Cp)_4(CO)_4$ and $Fe_4(\pi\text{-}Cp)_4(CO)_4{}^+$ consist of simple quadrupole split doublets with essentially the same chemical isomer shift. This has been interpreted to indicate that oxidation involves a molecular orbital affecting all four iron atoms equally.

Recently Bor and co-workers (*60*) used the Mössbauer spectra of the series of clusters $Co_2FeS(CO)_9$, $Co_2FeS(CO)_8(PPh_3)$, and $Co_2FeS(CO)_7(PPh_3)_2$ to show that substitution occurs at the two cobalt atoms of the cluster.

F. MASS SPECTRA

The application of mass spectrometry to organometallic compounds in the last few years has provided a very powerful analytical tool, as highlighted in two recent reviews (*52*, *272*). With regard to carbonyl clusters, it has proved of major importance, as it provides the only means short of a full structure determination whereby reliable formulations of clusters can be made.

Mass spectra have been used principally for the determination of molecular weights and deduction of the detailed composition of the molecule from the isotopic patterns of the various ions. Structural information can also be obtained from a detailed analysis of the fragmentation pattern. The clusters which have been studied by mass spectrometric methods have largely been carbonyl, π-cyclopentadienyl, and carbonyl hydride clusters, and references to these studies have been included in Tables II, VIII, and III, respectively.

1. Carbonyl Clusters

The mass spectra of these compounds (*215*, *244*, *272*, *274*, *384*) have shown that under electron impact the metal carbonyls are first singly ionized and then progressively lose CO from the parent ion. No carbonyl cluster has been studied in which the parent ion was not observed. The cleavage of the metal cluster is dependent on the metal, and this tendency decreases rapidly in the order first row $<$ second row $\ll$ third row metal. Ions of the type $[M(CO)_xC]^+$ are fairly common for the heavier transition metals, but only after some CO groups have been lost. Doubly charged ions are also more common for the heavier metals. These properties are illustrated in Fig. 8 which shows the mass spectra of $Fe_3(CO)_{12}$, $Ru_3(CO)_{12}$, and $Os_3(CO)_{12}$. In the spectrum of $Fe_3(CO)_{12}$, all possible nuclear ions $Fe_3(CO)_n{}^+$ ($n = 0$–12) were observed along with binuclear and mononuclear ions. The appearance of the $Fe(CO)_5{}^+$ ion in high abundance may be readily correlated with the structure of the parent carbonyl, as there is little evidence for CO migration under electron impact. The spectra of $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ are much simpler (Fig. 8) and consist primarily of the $M_3(CO)_n{}^+$ ($n = 0$–12) series. The increased strength of metal–metal bonds down a triad is shown by the

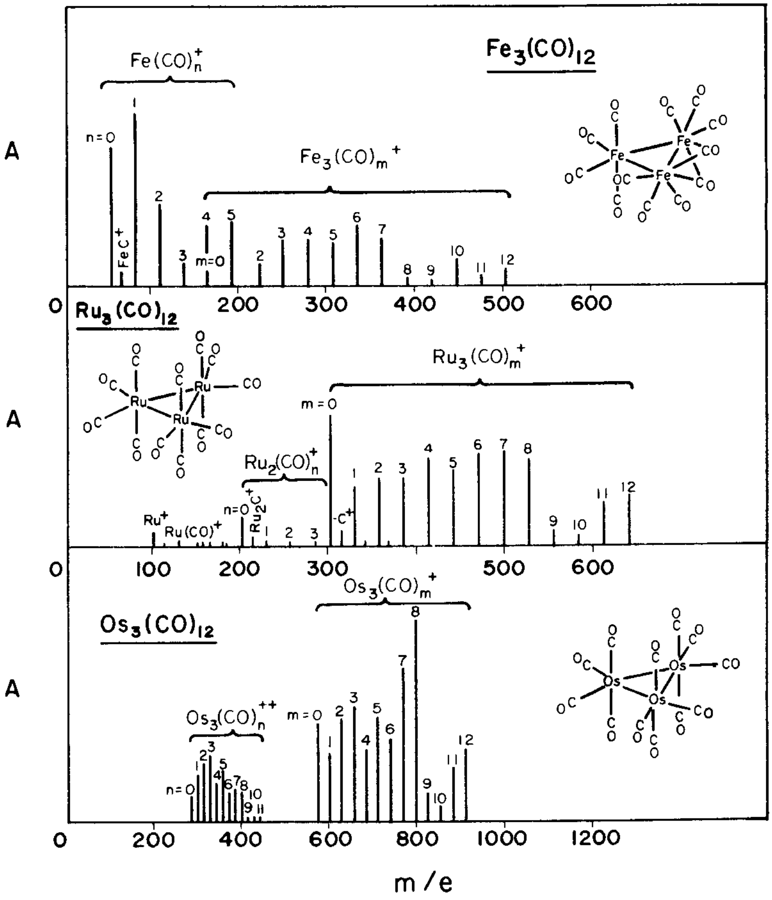


FIG. 8. Mass spectra of $Fe_3(CO)_{12}$, $Ru_3(CO)_{12}$, and $Os_3(CO)_{12}$. Reproduced by permission.

fact that 36% of the ions contained the trinuclear cluster in the spectrum of $Fe_3(CO)_{12}$, whereas for $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ the corresponding figures were 92 and 100%, respectively. The appearance of $Os_3(CO)_n^{2+}$ ($n = 0$–12) and Ru_3^{2+} may also be correlated with the stability of heavy metal clusters toward increased oxidation.

Similar features were observed in the mass spectra of the other carbonyls listed in Table I.

2. *π-Cyclopentadienyl Clusters*

The general feature of the mass spectra of π-cyclopentadienyl clusters after ionization is the successive loss of CO groups, followed by a complicated fragmentation of the cluster and the cyclopentadienyl groups.

The mass spectra of $Fe_4(\pi\text{-}Cp)_4(CO)_4$ (*246*) shows the loss of two CO groups before fragmentation of the cluster commences. It is of note that the $Fe_4(\pi\text{-}Cp)_4(CO)_nC^+$ ions are as abundant as $Fe_4(\pi\text{-}Cp)_4(CO)_n{}^+$ ions. King (*246*) has interpreted this as evidence for a relatively strong Fe–C and weak C–O bond, which correlates with the observed ν(C–O) at 1620 cm^{-1}.

The mass spectra of $Co_3(\pi\text{-}Cp)_3(CO)_3$ (*245*) and $Rh_3(\pi\text{-}Cp)_3(CO)_3$ (*304, 322*) show the loss of three CO groups followed by a complicated fragmentation of the π-Cp groups. It was in the mass spectrometer that $Rh_4(\pi\text{-}Cp)_4(CO)_2$ was first detected, resulting from thermal decomposition on the probe (*304, 322*).

Mass spectra were important in the identification of the π-cyclopentadienyl clusters $Ni_3(\pi\text{-}Cp)_3NBu$, (*319*) $Co_3(\pi\text{-}Cp)_3S_2$ and $Co_3(\pi\text{-}Cp)_3(CO)S$ (*320*), and $Rh_3(\pi\text{-}Cp)_4H$ (*142*). Other spectrometric studies of π-cyclopentadienyl clusters are listed in Table IV.

3. *Carbonyl Hydride Clusters*

Mass spectrometry has been of fundamental importance in the study of carbonyl hydride clusters as from an accurate molecular weight determination the number of protons in a compound can readily be determined. No other technique enables this to be done with any degree of accuracy. Fragmentation patterns for the hydrides generally involve loss of both CO and H.

In the mass spectra of $H_3M_3(CO)_{12}$ (M = Mn, Re) the parent ion is observed, providing the first clear evidence for their formulation as trinuclear hydrides (*213, 351*). With the manganese compound the parent ion is observed only in low abundance (~2%), but the related ions $H_3Mn_3(CO)_4{}^+$ and $H_3Mn_3(CO)^+$ occur in appreciable amounts (18 and

90%, respectively). In contrast with $H_3Re_3(CO)_{12}$, the parent ion occurs in 82% abundance. In the mass spectra of both $H_3Mn_3(CO)_{12}$, and $H_3Re_3(CO)_{12}$, no competitive loss of H radicals is observed until several CO groups have been ejected. On the basis of studies of terminal bridging halide ligands in carbonyl halide compounds (*129*, *274*), this has been interpreted to indicate that the hydride ligands are bridging between two metal atoms (*213*, *222*).

A similar competitive loss of H and CO only after loss of a number of CO groups has been observed in the fragmentation pattern of $H_2Ru_4(CO)_{13}$ (*213*, *214*), $H_2Os_4(CO)_{13}$ (*217*), $H_4Os_4(CO)_{12}$ and $H_2Os_3(CO)_{10}$ (*217*), and $H_2FeRu_3(CO)_{13}$ (*384*). In the mass spectra of $HMCo_3(CO)_{12}$ (M = Ru, Fe) no H loss is detected until six CO groups have been removed and it does not become significant until all the CO groups are lost and the MCo_3 cluster fragments. This has been interpreted to indicate that the hydride ligand is inside the MCo_3 cage (*298*, *299*).

In the mass spectra of the α and β isomers of $H_4Ru_4(CO)_{12}$, the highest peak corresponds to $H_2Ru_4(CO)_{12}$ (*204*, *213*, *214*), but a detailed examination of the remainder of the spectrum reveals ions which could only have originated from a parent $H_4Ru_4(CO)_{12}$.

The clusters $HM_3(CO)_{10}SR$ (M = Ru, Os; R = Et, Bu, Ph) were identified by their mass spectra, the principal feature of which are the ions $HM_3(CO)_nSR^+$ ($n = 0$–10) again indicating that the hydrogen is bridging (*110*). This has been confirmed by the structural determination of $HOs_3(CO)_{10}(SEt)$ (*294*).

The mass spectra of a number of other miscellaneous clusters have been measured. A number of compounds of the type $Co_3(CO)_9CY$ have been studied by various workers (Table IV). Parent peaks were observed for all the derivatives followed by stepwise loss of the nine CO groups. The Co_3CY cluster was observed to fragment as follows:

$$Co_3CY^+ \rightarrow Co_2CY^+ \rightarrow Co_2C^+ \rightarrow CoC^+ \rightarrow Co^+ \qquad (40)$$

The recently reported carbide clusters of ruthenium, $Ru_6(CO)_{17}C$ and $Ru_6(CO)_{14}(arene)C$ (*211*), provided a good example of the power of mass spectrometry as an analytical tool. The appearance of the ions $Ru_6(CO)_nC^+$ ($n = 0$–17) provided a clear differentiation between $Ru_6(CO)_{17}C$ and another proposed formula $Ru_6(CO)_{18}$ (*324*). The first carbonyl oxide cluster $Os_3(CO)_{12}\cdot OsO_4$ was characterized by its mass spectrum. The ions $Os_4O_4(CO)_n{}^+$ ($n = 0$–12) occur in high abundance and the tetranuclear cluster does not rupture until all CO groups are lost (*219*, *220*). Other clusters which have been characterized by mass spectrometry include $Os_3(CO)_{10}(OMe)_2$ (*217*), $Ru_3(CO)_{12}X_6$ (X = Cl, Br, I) (*212*),

$Ru_3(CO)_9(C_2Ph_2)_3$ (*346*), $Fe_3(NO)_4S[S_2C_2(CF_3)_2]_2$ (*240*), $Co_3(CO)_3[S_2C_2(CF_3)_2]_3$ (*239*), and $Ni_4(CO)_3[C_2(CF_3)_2]_3$ (*249*).

IV. Reactivity of Clusters

As a consequence of the recency of the development of cluster chemistry, most research in this field has been directed toward preparation of clusters and subsequent determination of their structure by X-ray studies. Sufficient preliminary studies of the reactivity of clusters, however, have been made to show that in a number of classes of reactions the closed cluster structure considerably affects the course of the reaction. The majority of reactivity studies have been made on the simple carbonyl clusters. A few reactions of carbonyl anion, carbonyl hydride, and substituted carbonyl clusters have also been reported. The intermediates and products of many reactions of clusters are air-sensitive and special techniques must be used to carry out reactions (*347*).

The reactions of clusters can be divided into two general classes: (1) reactions involving change of the oxidation number of one or more of the metal atoms in the cluster and (2) substitution reactions. The only type of reaction to lie outside the scope of these two classes is the addition reactions of electrophilic reagents. The most common and trivial example of this type of reaction is the protonation of carbonyl metallates (Section II,C,1). Acids also react with $M_3(CO)_{12}$ ($M = Ru$, Os) and $Os_3(CO)_9L_3$ ($L = PEt_3$, PEt_2Ph) to form the protonated clusters $HM_3(CO)_{12}^+$ and $HOs_3(CO)_9L_3^+$ (*120, 260*). The formation of an addition compound between $Co_4(CO)_{12}$ and the Lewis acid $AlBr_3$ has also been reported (*87*). $Fe_4(\pi\text{-}Cp)_4(CO)_4$ reacts with Al_2Et_6 to form a compound $Fe_4(\pi\text{-}Cp)_4(CO)_4(AlEt_3)_4$, but there is evidence that the aluminum alkyls are bonded to the oxygen of the bridging CO groups (*314*).

A. REACTIONS INVOLVING CHANGE IN OXIDATION NUMBER

Reactions of this type, in general, occur by cleavage of metal–metal bonds and produce compounds with a decreased nuclearity. In this class we will consider all the reactions which cause oxidation or reduction of the metal atoms.

1. Oxidation Reactions

a. Air Stability. The first-row carbonyl clusters are quite air-sensitive, whereas clusters of the second and third rows are reasonably stable to air. Thus, $Fe_3(CO)_{12}$ and $Co_4(CO)_{12}$ are oxidized in air, apparently via formation of a carbonate, whereas the carbonyl clusters of Ru, Os, Rh, and Ir are quite stable in air. A similar gradation is apparent for the carbonyl anion and hydride clusters, as $H_2Fe_4(CO)_{13}$ is pyrophoric and $H_2Fe_3(CO)_{11}$ decomposes at room temperature in air to form a complex mixture of $Fe_3(CO)_{12}$, $Fe(CO)_5$, H_2, and Fe^{2+} (*153*), whereas $H_2Ru_4(CO)_{13}$ (*214*) and $H_2Ru_3(CO)_{11}$ (*328*) are quite stable. Substitution of a CO group by a Lewis base which can act as a π acceptor appears to have little effect on the air stability of clusters (*222*). It must be realized that the decomposition of some cluster compounds in air may be due not only to the action of oxygen but also that of water.

b. Acids. Apart from the addition reactions described above, the action of oxidizing acids such as HNO_3 and H_2SO_4 leads to degradation of the cluster and formation of the metal salt. In certain cases the formation of the salt can be accompanied by the formation of a cluster (*252*). Oxidation can also be caused by normally nonoxidizing acids such as carboxylic acids. In this case, the oxidation can be regarded as a direct electron transfer from the metal carbonyl to the proton of the acid.

$$12\ HFe_3(CO)_{11}^{-} + 18\ H^+ \rightarrow 11\ Fe_3(CO)_{12} + 15\ H_2 + 3\ Fe^{2+} \qquad (41)$$

$$M_x(CO)_y + zH^+ \rightarrow M_x^{z+} + z/2\ H_2 + yCO \qquad (42)$$

Normally the metal will coordinate to the carboxylate ion. $Ru_3(CO)_{12}$ reacts with carboxylic acids to form polymeric compounds $[Ru(CO)_2(OOCR)]_n$ (R = Me, Et) (*222*). These compounds have also been prepared by the novel CO insertion reaction of a CO group from $Ru_3(CO)_{12}$ into ethers (*222*).

c. Weak Oxidizing Agents. The carbonyl anion cluster $Co_6(CO)_{15}^{2-}$ has been shown to react with $FeCl_3$ in water to produce $Co_6(CO)_{16}$ (*81*).

$$Co_6(CO)_{15}^{3-} + CO + 2\ FeCl_3 \rightarrow Co_6(CO)_{16} + 2\ FeCl_2 + 2\ Cl^- \qquad (43)$$

2. *Reduction Reactions*

a. Electrolytic Reduction. Dessy and co-workers have examined the electrochemical reduction of a large number of carbonyl compounds, including $Fe_3(CO)_{12}$, $Co_3(\pi\text{-}Cp)_3(CO)_3$, $Ni_3(\pi\text{-}Cp)_3(CO)_2$, $Mn_3(\pi\text{-}Cp)_3(NO)_4$ (*122*), and $Fe_4(\pi\text{-}Cp)_4(CO)_4$ (*123*).

b. Alkali Metals. These reducing agents are presumed to act by electron transfer from the alkali metal to the cluster; the extent of reduction is dependent on both the alkali metal and the solvent. The first-row carbonyl clusters are reduced to the mononuclear anions in liquid ammonia (*32*, *252*). However, if $Co_4(CO)_{12}$ is reduced in tetra-

$$Fe_3(CO)_{12} + 6\ Na \rightarrow 3\ Na_2[Fe(CO)_4] \qquad (44)$$

$$Co_4(CO)_{12} + 3\ Na \rightarrow 3\ Na[Co(CO)_4] + Co \qquad (45)$$

hydrofuran (THF) by Li, Na, or K, the product is the hexanuclear ion $Co_6(CO)_{15}^{2-}$, which is further reduced to $Co_6(CO)_{14}^{4-}$ (*85*). With cobaltocene, $Co_8(CO)_{22}^{2-}$ is the product (*85*). Similarly the action of sodium in liquid ammonia on $Ru_3(CO)_{12}$ apparently produces the mononuclear anion $Ru(CO)_4^{2-}$ (*107*), whereas in tetrahydrofuran the reaction produces an unidentified anion, which on acidification leads to a mixture of tetranuclear carbonyl hydride clusters (*213*, *214*). A similar reaction of $Os_3(CO)_{12}$ produces a mixture of trinuclear and tetranuclear hydride carbonyl clusters (*217*). The reactions of Na in THF with $Rh_4(CO)_{12}$ (*90*) and $Ir_4(CO)_{12}$ (*281*) have been reported to yield only mononuclear carbonyl anions. No reductions of substituted carbonyl clusters have been reported.

$$9\,Co_4(CO)_{12} + 20\,Na \rightarrow 4\,Na_2[Co_6(CO)_{15}] + 12\,Na[Co(CO)_4] \qquad (46)$$

$$2\,Co_4(CO)_{12} + 2\,\pi\text{-}Cp_2Co \rightarrow [\pi\text{-}Cp_2Co]_2[Co_8(CO)_{22}] + 2\,CO \qquad (47)$$

c. Sodium Borohydride. This reducing agent has been reacted with $Fe_3(CO)_{12}$, $Ru_3(CO)_{12}$, and $Os_3(CO)_{12}$ and the products are $Fe_3(CO)_{11}H^-$ (*61*), $H_2Ru_4(CO)_{13}$ and $H_4Ru_4(CO)_{12}$ (*213*, *214*), and $H_2Os_4(CO)_{13}$, $H_4Os_4(CO)_{12}$, and $H_2Os_3(CO)_{10}$ (*217*), respectively.

d. Solution of Alkali Hydroxides. The reaction of a metal carbonyl cluster with this reagent causes reduction to the carbonyl metallate with simultaneous formation of carbonate ion, but the mechanism of the reaction is uncertain. The mechanism for the reaction of $Fe(CO)_5$ with base has been envisaged (*63*) as:

$$Fe(CO)_5 + OH^- \rightarrow Fe(CO)_4OH^- + CO \rightarrow Fe(CO)_4^{2-} + CO_2 + H^+ \qquad (48)$$

Another postulated reaction mechanism is based on hydroxyl ion attack at the central metal atom followed by migration to an adjacent CO group (*259*). There is now considerable evidence for direct attack of hard nucleophiles at the carbon of a CO group.

$$Fe(CO)_5 + OH^- \rightarrow [(OC)_4Fe\text{–}C(O)OH]^- \rightarrow Fe(CO)_4^{2-} + H^+ + CO_2 \qquad (49)$$

The action of alcoholic alkali on $Fe_3(CO)_{12}$ produces an anion with the same nuclearity as the parent carbonyl (*173*). The $Fe_3(CO)_{11}^{2-}$ decomposes slowly at room temperature to form $Fe(CO)_4^{2-}$. The reactions of base with $M_3(CO)_{12}$ (M = Ru, Os) produce unidentified anions which on acidification yield a mixture of $H_2Ru_4(CO)_{13}$ and $H_4Ru_4(CO)_{12}$ (*213*, *214*), and $H_2Os_4(CO)_{13}$, $H_4Os_4(CO)_{12}$ and $H_2Os_3(CO)_{10}$ (*217*) (Section II,C,1,c).

$$Fe_3(CO)_{12} + 4\,OH^- \rightarrow Fe_3(CO)_{11}^{2-} + CO_3^{2-} + 2\,H_2O \qquad (50)$$

$Co_4(CO)_{12}$ is reduced to the mononuclear anion by the action of alkali (*153*), whereas $Ir_4(CO)_{12}$ forms the isonuclear monoanion with alcoholic K_2CO_3, and $Ir_8(CO)_{20}^{2-}$ with alcoholic KOH (*280*). The reduction

$$2\,Ir_4(CO)_{12} + 16\,OH^- \rightarrow Ir_8(CO)_{20}^{2-} + 4\,CO_3^{2-} + 8\,H_2O \tag{51}$$

of $Rh_4(CO)_{12}$ is similarly sensitive to the nucleophile and the solvent; with KOH, $Rh_6(CO)_{16}$ is the product (*82*), whereas with sodium or potassium acetate in alcohol/water the anion $Rh_{12}(CO)_{30}^{2-}$ is formed (*90*).

Many of these reduction reactions have been used in the preparation of carbonyl anion and hydride clusters (Section II, C).

3. *Disproportionation Reactions*

These reactions involve the formation of ionic compounds from neutral metal carbonyls in the presence of a Lewis base with a nitrogen or oxygen donor atom. The reaction of $Fe_3(CO)_{12}$ with pyridine typifies

$$5\,Fe_3(CO)_{12} + 18\,C_5H_5N \rightarrow 3\,[Fe(NC_5H_5)_6][Fe_4(CO)_{13}] + 21\,CO \tag{52}$$

these reactions (*195*). There is some evidence that the first step of this reaction involves a true disproportionation. Such an intermediate has been isolated from the reaction of $Co_2(CO)_8$ with aliphatic alcohols (*360*).

$$Co_2(CO)_8 + ROH \rightarrow [Co(CO)_4(ROH)]^+[Co(CO)_4]^- \tag{53}$$

Under various conditions $Fe_3(CO)_{12}$ reacts with a wide range of nitrogen and oxygen bases to form tetra-, tri-, di-, or mononuclear carbonyl anions (*153*). The tetranuclear cluster is formed in the reaction of $Fe_3(CO)_{12}$ with pyridine (*195*), pyridine *N*-oxide and dimethyl sulfoxide (*187*); $Fe_3(CO)_{11}^{2-}$ results from reaction with ethylenediamine

$$4\,Fe_3(CO)_{12} + 18\,NH_3 \rightarrow 3\,[Fe(NH_3)_6][Fe_3(CO)_{11}] + 15\,CO \tag{54}$$

(en) at 40°C (*191*), liquid NH_3 at −33°C (*196*), methanol (*173*), and ethanol (*169*). The binuclear $Fe_3(CO)_8^{2-}$ is formed by the reaction of

$$3\,Fe_3(CO)_{12} + 6\,ROH \rightarrow [Fe(ROH)_6][Fe_3(CO)_{11}] + 5\,Fe(CO)_5 \tag{55}$$

$Fe_3(CO)_{12}$ with en at 90°C (*191*), triphenylphosphine oxide, and triphenylarsine oxide (*187*). Liquid ammonia at room temperature forms

$$2\,Fe_3(CO)_{12} + 18\,NH_3 \rightarrow [Fe(NH_3)_6][Fe_2(CO)_8] + 3\,(NH_4)_2[Fe(CO)_4] \tag{56}$$

a mixture of compounds (*30*). The mononuclear carbonylferrate results from the reaction of $Fe_3(CO)_{12}$ with en at 145°C (*191*).

$$2\,Fe_3(CO)_{12} + 9\,en \rightarrow 3\,[Fe(en)_3][Fe(CO)_4] + 12\,CO \tag{57}$$

$Co_4(CO)_{12}$ forms the $Co(CO)_4^-$ ion on reaction with NH_3 (*31*), pyridine, (*190*), and methanol and ethanol (*83*). $Co_6(CO)_{16}$ reacts similarly with

$$3\,Co_4(CO)_{12} + 24\,B \rightarrow 4\,[CoB_6][Co(CO)_4]_2 + 4\,CO \tag{58}$$

pyridine, methanol, acetone, and wet diethylether, but with 2-propanol, dry ether, and also pyridine the product is $Co_4(CO)_{12}$ (*81*). $Co_3(arene)_3(CO)_2^+$ is also reduced by pyridine to $Co(CO)_4^-$ (*87*).

$$4\ Co_3(arene)_3(CO)_2 + 6\ py^{4} \rightarrow [Co(py)_6][Co(CO)_4]_2 + 7\ Co + 2\ Co^{2+} + 12\ arene \qquad (59)$$

4. *Oxidative Addition Reactions*

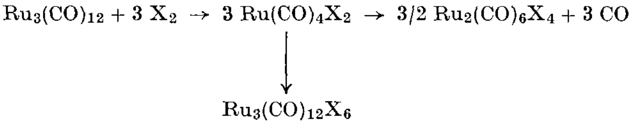
This decade has seen the thorough investigation of this class of reaction. With respect to clusters, reactions in which the attacking reagents replace the metal–metal bonds can be considered as oxidative addition reactions. These reactions have been observed in which only one metal–metal bond is replaced, the product thus being an open cluster,

$$M_3(CO)_{12} + X\text{–}Y \rightarrow X\text{–}M(CO)_4\text{–}M(CO)_4\text{–}M(CO)_4\text{–}Y \qquad (60)$$

and when all metal–metal bonds are broken.

$$M_3(CO)_{12} + 3\ X\text{–}Y \rightarrow 3\ M(CO)_4(X)(Y) \qquad (61)$$

Many oxidative addition reactions of carbonyl clusters occur with halogens and halo compounds. The first-row carbonyl clusters are, in general, quantitatively decomposed to the corresponding metal halide. Hieber *et al.* (*167*) have described a reaction of bromine with $Fe_3(CO)_{12}$ which yielded $Fe_3(CO)_9Br_6$ [Eq. (36)]. Second- and third-row clusters react to produce halogenocarbonyl compounds by breaking the metal–metal bonds rather than by CO substitution. $Ru_3(CO)_{12}$ reacts with halogens to form *cis*-$Ru(CO)_4X_2$. This monomeric carbonyl is unstable in solution and polymerizes to form two isomers of the halogen-bridged dimer $Ru_2(CO)_6X_4$ and the trinuclear $Ru_3(CO)_{12}X_6$, the structure of which is not known (*210, 212, 215*).



$$\begin{tikzcd}[column sep=small] Ru_3(CO)_{12} + 3\ X_2 \arrow[r] & 3\ Ru(CO)_4X_2 \arrow[r] \arrow[d] & 3/2\ Ru_2(CO)_6X_4 + 3\ CO \\ & Ru_3(CO)_{12}X_6 & \end{tikzcd} \qquad (62)$$

(X = Cl, Br, I)

The dimer has also been prepared by refluxing $Ru_3(CO)_{12}$ in halocarbons such as CCl_4, $CHCl_3$, and $CHBr_3$ (*45, 222, 343*). In these reactions the initial product has been shown to be an unidentified chlorocarbon derivative of a ruthenium carbonyl compound (*222*). The dimer is produced by decomposition of this compound in hot solvents.

$Ru_3(CO)_{12}$ (*332*) and $Os_3(CO)_{12}$ (*308*) react with $SnCl_4$ with the breaking of only one M–M bond. $Os_3(CO)_{12}$ reacts similarly with the

$$M_3(CO)_{12} + SnCl_4 \rightarrow Cl\text{–}M(CO)_4\text{–}M(CO)_4\text{–}M(CO)_4\text{–}SnCl_3 \qquad (63)$$

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[4] py = Pyridine.

halogens (*120, 215*) and with Ph_3PAuCl (*47*) to form the corresponding linear compounds. The kinetics of the reaction of $Os_3(CO)_{12}$ with halogens have been studied (*65*), and the reaction was found to be very rapid. The kinetics were interpreted on the basis of an initial fast preequilibrium step involving formation of a charge transfer or Lewis acid-base complex followed by cleavage of one osmium–osmium bond. Ruthenium and osmium carbonyl clusters react with the mercuric halides with complete cleavage of the cluster (*47, 48*). With $Os_3(CO)_{12}$ and $HgCl_2$ $Os(CO)_4$-

$$M_3(CO)_{12} + 6\,HgX_2 \rightarrow 3\,M(CO)_4(HgX)_2 + 6X^- \qquad (X = Cl, Br, I) \qquad (64)$$

(HgCl)Cl was also obtained.

Very few reactions of carbonyl hydride clusters have been reported. $[Tc(CO)_4Br]_2$ has been isolated from the reaction of bromine with $H_3Tc_3(CO)_{12}$ (*226*), and a mixture of $[Mn(CO)_4I]_2$ and $Mn(CO)_5I$ from the reaction of iodine with $H_3Mn_3(CO)_{12}$ (*222*).

Substituted carbonyl clusters react with halogens in much the same way as their parent carbonyls. The final products of the reaction of halogens with $Ru_3(CO)_9(PPh_3)_3$ are the dimers $[Ph_3PRu(CO)_2X_2]_2$, as detected by Piacenti and co-workers (*325, 326*), but the initial products are the mononuclear $Ph_3PRu(CO)_3X_2$ which dimerize with loss of CO just as the $Ru(CO)_4X_2$ compounds did (*212*). No trinuclear products were detected. The corresponding trisubstituted osmium carbonyl cluster

$$\begin{aligned} Ru_3(CO)_9(PPh_3)_3 + 3\,X_2 &\rightarrow 3\,Ph_3PRu(CO)_3X_2 \rightarrow \\ &3/2\,[Ph_3PRu(CO)_2X_2]_2 + 3\,CO \qquad (X = Cl, Br, I) \end{aligned} \qquad (65)$$

reacts with halogens to produce the monomer $LOs(CO)_3X_2$ ($L = PEt_3$, PEt_2Ph; $X = Cl, Br, I$), which shows no tendency to dimerize (*120*).

Other products of reaction of halogeno compounds with carbonyl clusters are $Os_2(CO)_6I_2$ and $Os_2(CO)_8I_2$ from the reaction of $Os_3(CO)_{12}$ with CF_3I, and $Os_2(CO)_6Cl_4$ from a similar reaction with HCl (*53*). $Ru_3(CO)_{12}$ reacts with allyl halides to form $Ru(CO)_3(C_3H_5)X$ ($X = Cl$, Br, I) (*45, 343*). $Rh_4(CO)_{12}$ is reported (*88*) to react with tetramethylammonium iodide to produce $Rh_6(CO)_{15}I^-$.

Triorganotin hydrides and triorganosilanes also react with $M_3(CO)_{12}$ ($M = Ru$, Os) to add oxidatively across metal–metal bonds. With $Ru_3(CO)_{12}$ and Me_3SnH, the product is $Ru(CO)_4(SnMe_3)_2$ (*108*), but with $Os_3(CO)_{12}$, $Os(CO)_4(SnMe_3)_2$ (*108*) and $HOs(CO)_4(SnMe_3)$ (*262*) have been isolated. With trimethylsilane, $Fe_3(CO)_{12}$ does not afford a stable iron–silicon complex, $Ru_3(CO)_{12}$ gives $Ru_2(CO)_8(SiMe_3)_2$ (*58*), and $Os_3(CO)_{12}$ yields $Os(CO)_4(SiMe_3)_2$ (*53*). With trichlorosilane, $Ru_3(CO)_{12}$ yields $Ru_2(CO)_8(SiCl_3)_2$ (*263*), whereas the product with $Fe_3(CO)_{12}$ is *cis*-$Fe(CO)_4(SiCl_3)_2$ and $Fe_2(CO)_8(SiCl_2)_2$ (*205*).

There is another class of reaction in which the reagent apparently does not replace a metal–metal bond, but substitutes CO groups and bridges a metal–metal bond in the product. An example of this is the reaction of $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ with thiols, the initial product of which is $HM_3(CO)_{10}SR$ (R = Et, Bu, Ph) (*110, 215, 344*). The structure of this compound is thought to be based on a triangular skeleton, with the SR and H bridging between two $M(CO)_3$ units. Further reaction of this compound with thiols yields $[M(CO)_3SR]_2$ (R = Me, Et, Bu, Ph) (*77, 110, 210, 215, 344*).

B. SUBSTITUTION REACTIONS

The great majority of these reactions occur without change in the nuclearity of the cluster, but there are reactions where the basicity of a soft nucleophile is sufficient to cause degradation of the cluster. The ligands which commonly lead to substitution are CO and NO, Lewis bases with Group V (excepting nitrogen) and Group VI donors, and ligands containing carbon–carbon unsaturated bonds.

1. Reactions with CO and NO

A special class of these substitution reactions is the isotopic carbon monoxide exchange reaction. There has been some study of these reactions and the rates of exchange in clusters have been found, in general, to be slower than in the corresponding mononuclear compounds. $Co_4(CO)_{12}$ exchanges all twelve CO groups at the same rate, but much more slowly than in $Co_2(CO)_8$ (*228*). The trinuclear carbonyls of Fe, Ru, and Os each exchange all twelve CO groups at the same rate, the rate decreasing in the order Fe > Ru > Os (*76*). In contrast, only three CO groups of $Co_3(CO)_9CY$ exchange (*74*). The kinetics of CO exchange in clusters have, in general, been interpreted in terms of dissociative mechanisms (*23*).

There are also a number of reactions of clusters with CO in which the CO replaces a metal–metal bond. The enthalpy of the reaction of $Co_4(CO)_{12}$ with CO has been determined as -33 kcal $mole^{-1}$ by measuring

$$Co_4(CO)_{12} + 4\,CO \rightleftharpoons 2\,Co_2(CO)_8 \qquad (66)$$

the equilibrium pressure at different temperatures (*131*).

Spectroscopic evidence has been obtained for the equilibrium (*91*).

$$Ru_3(CO)_{12} + 3\,CO \rightleftharpoons 3\,Ru(CO)_5 \qquad (67)$$

The substituted carbonyl cluster $Ru_3(CO)_9(PPh_3)_3$ reacts at 150°C and 150 atm CO pressure to form $Ru(CO)_4PPh_3$ exclusively, whereas the analogous osmium cluster produces $Os_3(CO)_{12}$ and free Ph_3P (*326, 327*).

It has been reported that all the octahedral clusters of cobalt react readily with CO under ambient conditions (*80, 81, 91*). The primary step of the reaction of $Co_6(CO)_{15}^{2-}$ in THF has been deduced as (*83*):

$$Co_6(CO)_{15}^{2-} + 9\ CO \rightarrow 2\ Co(CO)_4^- + 2\ Co_2(CO)_8 \qquad (68)$$

The iron carbonyl anion clusters $Fe_3(CO)_{11}^{2-}$ and $Fe_4(CO)_{13}^{2-}$ react with CO only under pressure at temperatures of 100°–200°C giving derivatives of the anion $Fe(CO)_4^{2-}$ (*170*).

$Cr_3(CO)_{14}^{2-}$ has been reported to react at 150°C under pressure with CO (*28*) according to Eq. (69):

$$Cr_3(CO)_{14}^{2-} + 3\ CO \rightarrow Cr(CO)_5^{2-} + 2\ Cr(CO)_6 \qquad (69)$$

NO apparently attacks metal–metal bonds as well as substituting CO ligands, as no substitution reactions of clusters with NO in which the cluster is not broken have been reported. $Fe_3(CO)_{12}$ gives $Fe(CO)_2(NO)_2$ (*51, 166*) and $Ru_3(CO)_{12}$ reacts with moist NO to yield the polymeric nitrite $[Ru(CO)_2(NO_2)_2]_n$ (*67*).

2. *Reactions with Ligands with Group V Donor Atoms*

The majority of substitution reactions have been carried out with these ligands. Many of these reactions substitute CO groups without breaking the cluster, and these have been listed in Table V (under Preparations, Sections II,D,2,a,b). Until recently only the second- and third-row carbonyl clusters reacted with phosphines and related ligands without cleavage of the cluster. Reaction of triphenylphosphine with $Fe_3(CO)_{12}$ yielded a mixture of $Fe(CO)_4PPh_3$ and $Fe(CO)_3(PPh_3)_2$ (*96*), and the product of the same reaction with $Co_4(CO)_{12}$ was $Co_2(CO)_6(PPh_3)_2$ (*174*).

Under similar conditions $Ru_3(CO)_{12}$ produces $Ru_3(CO)_9L_3$ ($L = PPh_3$, PBu_3, PEt_3, PPh_2Et, $PPhEt_2$, PPh_2Me, $PPhMe_2$, $P(OPh)_3$) (*54, 66, 67, 210, 222, 326, 327*) and $Ru_3(CO)_{10}(AsPh_3)_2$ (*54*), and $Os_3(CO)_{12}$ yields $Os_3(CO)_9L_3$, ($L = PEt_3$, PEt_2Ph, PPh_3, $PMePh_2$) (*46, 53, 120*), $Os_3(CO)_{10}L_2$, and $Os_3(CO)_{11}L$ ($L = PEt_3$, PEt_2Ph, PPh_3) (*46, 120*). $Ir_4(CO)_{12}$ reacts to form $Ir_4(CO)_9(PPh_3)_3$ and $Ir_4(CO)_{10}(PPh_3)_2$ (*73*).

More recently, however, a monosubstituted carbonyl cluster of iron, $Fe_3(CO)_{11}(PPh_3)$, has been isolated from the mixture of products of the reaction of $Fe_3(CO)_{12}$ with PPh_3, which consisted of 98% mononuclear compounds (*18*). The clusters $Co_4(CO)_{11}L$ ($L = PPh_3$, $AsPh_3$, $SbPh_3$) (*75*) were the products of reaction of L with $Co_4(CO)_{12}$ under mild conditions. By reaction with phosphite esters the clusters $Fe_3(CO)_{12-n}[P(OMe)_3]_n$ ($n = 1$–3) have also been obtained from $Fe_3(CO)_{12}$ (*331*). Apparently substitution without breakdown of the cluster is favored by the higher

π-acceptor and lower σ-donor ability of the phosphites compared with the phosphines. More CO groups can be replaced without breakdown of the cluster when the ligand is a chelate. Such substituted clusters include $Fe_3(CO)_{10}[Me_2AsC(C(AsMe_2)C_2F_4)]$ (*111*), $M_3(CO)_6(diars)_3$ (M = Ru, Os) (*46*, *222*), and $Ru_3(CO)_6(diphos)_3$ (*222*).

Under more severe conditions, mononuclear products can be obtained from the reaction of Group V ligands with second- and third-row metal carbonyl clusters. $Ru_3(CO)_{12}$ reacts with L at 140°C to produce $Ru(CO)_3L_2$ [L = PPh_3, PBu_3, $P(OPh)_3$] (*326*, *327*). Similar reactions occur with $Os_3(CO)_{12}$ (*46*), $Ru_3(CO)_9(PPh_3)_3$, and $Os_3(CO)_9(PPh_3)_3$ (*326*). $Ir_4(CO)_{12}$ produces $Ir_2(CO)_4L_6$ with trialkyl and triaryl phosphites (*386*). It is reported that $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$ react with Ph_3P to form $Rh_4(CO)_{10}(PPh_3)_2$, which subsequently decomposes to $Rh_2(CO)_4(PPh_3)_4$ (*88*).

Reaction between $Ru_3(CO)_{12}$ and the quadridentate ligands (o-$Ph_2PC_6H_4)_3P$ and (o-$Ph_2AsC_6H_4)_3As$ break down the cluster to produce compounds of the type Ru(CO)(L–L–L–L)[5] (*158*).

$Ir_4(CO)_{11}H^-$ reacts with triphenylphosphine to produce $Ir_4(CO)_{10}L_2$, and $Ir_8(CO)_{20}^{2-}$ undergoes a similar reaction to form $Ir_4(CO)_9L_3$ (*280*). $H_3Mn_3(CO)_{12}$ reacts with Ph_3P, Ph_3As, and Ph_3Sb by adding on three moles of the ligand, but the only products that could be isolated from the reaction mixture were $[Mn(CO)_4L]_2$ (*222*).

The kinetics of the reaction of $Ru_3(CO)_{12}$ with a variety of ligands [L = PPh_3, PPh_2Et. $PPhEt_2$, PEt_3, PBu_3, $AsPh_3$, $SbPh_3$, $P(OPh)_3$] have been examined (*68*) and were interpreted to indicate that the rate-determining step is a reversible dissociation of CO yielding $Ru_3(CO)_{11}$ as an intermediate; however, no evidence could be found for formation of $Ru_3(CO)_{11}L$.

$Co_3(CO)_9CMe$ reacts with phosphines and arsines with replacement of one or two CO groups. The compounds $Co_3(CO)_8LCMe$ [L = PPh_3, $AsPh_3$, $P(C_6H_{11})_3$] have only terminal CO groups in the solid state, but for L = Bu_3P and Bu_3As, ν(C–O) bands indicate both terminal and bridging CO groups. In solution all these compounds appear to be a mixture of the two isomers. The disubstituted $Co_3(CO)_7L_2CMe$ (L = PPh_3, $AsBu_3$) also have bridging groups (*341*).

A number of reactions of carbonyl clusters with diphosphines have also been reported. $Fe_3(CO)_{12}$ reacts with tetramethyldiphosphine at 80°C to produce $Fe_2(CO)_8(PMe_2)_2$ (*162*), whereas $Ru_3(CO)_{12}$ at 0°C yields $Ru_2(CO)_6(PMe_2)_2$ (*67*). Phenylthiodiphenylphosphine reacts with $Ru_3(CO)_{12}$ to produce the heterobridged $Ru_2(CO)_6(PPh_2)(SPh)$ (*206*).

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[5] L–L–L–L is the generic symbol for a quadridentate ligand.

3. *Reactions with Ligands with Group VI Donor Atoms*

Most of these reactions have only been examined with $Fe_3(CO)_{12}$, but recently studies of the reactions of $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ with thiols have been made. Many of these reactions lead to degradation of the cluster. Reactions between Group VI compounds and metal carbonyl compounds have been reviewed (*2*).

$Fe_3(CO)_{12}$ reacts with thiols (R = Et, *i*-Pr, Ph, C_6F_5, $C_{10}H_7$) (*189, 193, 233, 253*), dialkyl sulfides (R = Me, Et) (*189*), dialkyl disulfides (R = Me, Et, *t*-Bu, Ph) (*189, 237, 242, 248, 253*), or alkyl thiocyanates (R = Me, $PhCH_2$) (*128*) to form bridged dimers of the form $[Fe(CO)_3SR]_2$. A selenium analog has been prepared by the reaction of $Fe_3(CO)_{12}$ with Et_2Se_2 (*168*), and also a tellurium–iron compound using di-*p*-anisylditelluride (*183*). The sulfur-bridged compound has also been prepared by treating $Fe_3(CO)_{11}^{2-}$ with thiophenol (*189*).

Heterobridged analogs of these iron compounds have been obtained by the reaction of $Fe_3(CO)_{12}$ with *o*-aminothiophenol (*286*), vinylalkyl and divinylsulfides (*253*), and thianaphthene (*251, 253*).

The reaction of $Fe_3(CO)_{12}$ with 2-mercaptobenzothiazole or parathioformaldehyde was reported to give a compound formulated as $Fe_3(CO)_{10}(S_2CH_2)$ (*189*) in low yield, but it has recently been shown to to $Fe_3(CO)_9S_2$ (*160*). This noncluster polynuclear compound is also obtained by the reaction of dibenzyltetrasulfide with $Fe_3(CO)_{12}$ (*264*). With cyclohexene sulfide the product is a 1:1 mixture of $Fe_3(CO)_9S_2$ and $Fe_2(CO)_6S_2$ (*238, 369*). The compounds $Fe_4(CO)_{12}S_2$ and $Fe_3(CO)_9S(SCH_2Ph)_2$ are reported to be among the products of the reaction of $Fe_3(CO)_{12}$ with benzylthiocyanate (*128*).

Diphenyltelluride cleaves the $Fe_3(CO)_{12}$ cluster to give the mononuclear $Fe(CO)_4(TePh_2)$ (*183*).

4. *Reactions with Ligands Containing Carbon–Carbon Unsaturated Bonds*

There is a vast amount of literature on the reactions of iron dodecacarbonyl with olefins and acetylenes to form a large variety of organometallic compounds, and it is neither within the reviewer's aims, nor possible in this limited space, to review comprehensively this branch of cluster chemistry. In reactions such as these the cluster is functioning only as a source of a labile mononuclear species. There are a number of reviews which present an excellent survey of this area (*33, 43, 146, 198*).

a. Monoolefins. No simple substitution reactions of carbonyl clusters have yet been reported. $Fe_3(CO)_{12}$ reacts with perfluoroethylene to form $(C_2F_4)_2Fe(CO)_4$ (*367*), in which the C_2F_4 molecules are thought to have condensed and bond via Cσ bonds (*287*, *368*). $Ru_3(CO)_{12}$ is reported to react with alkenes to produce mixtures of products in low yields (*67*). $H_3Mn_3(CO)_{12}$ absorbs ethylene readily, but the only product isolated from the reaction was $Mn_2(CO)_{10}$ (*222*).

b. Diolefins. Iron dodecacarbonyl reacts with a wide variety of diolefins to produce complexes of the type (L–L)$Fe(CO)_3$ and (L–L)$Fe_2(CO)_6$. These compounds are formed with fulvenes, substituted cyclopentadienones, pentaphenylphospholes, cyclohexadienes, including anthracene which bonds in this fashion (*285*), cycloheptadienes, norbornadiene, cyclooctadiene, substituted butadienes, and pentadienes (*146*).

One product of the reaction of $Ru_3(CO)_{12}$ with 1,5-cyclooctadiene has been formulated as $(C_8H_{12})Ru_3(CO)_{10}$, in which the cluster is apparently retained (*67*). 1,3-Cyclohexadiene and its methoxy derivative, however, react with $Ru_3(CO)_{12}$ to give (L–L)$Ru(CO)_3$ (*210*), similar to $Fe_3(CO)_{12}$. Tetracyclone and $Ru_3(CO)_{12}$ yield a similar type of compound (*56*). A ligand exchange reaction occurs between $Ru_3(CO)_{12}$ and tetraphenylcyclobutadienepalladium(II) bromide to give $(Ph_4C_4)Ru(CO)_3$ (*346*).

The reaction product obtained from $Os_3(CO)_{12}$ and 2,3-dimethylbuta-1,3-diene is of the type (L–L)$Os_2(CO)_6$ (*141*), and X-ray studies (*125*) showed that one $Os(CO)_3$ group and the butadiene ligand form a planar five-membered ring by the loss of two hydrogen atoms, while the second $Os(CO)_3$ group is coordinated to the heterocycle.

c. Triolefins. $Fe_3(CO)_{12}$ reacts with cyclohepta-1,3,5-triene to give $C_7H_8Fe(CO)_3$, $C_7H_{10}Fe(CO)_3$, and a trinuclear complex of composition $(C_7H_8)_2Fe_3(CO)_9$ (*61*, *119*). With cyclooctatriene the products are $(C_8H_{10})Fe(CO)_3$, $(C_8H_{10})Fe_2(CO)_6$, and also, via a rearrangement reaction, bicyclo[4.2.0]octa-2,4-diene iron tricarbonyl (*241*). Azulene (az) occupies a special position as metal atoms may bond to the unsaturated seven-membered ring or to the five-membered ring, or to both. Azulene and substituted azulenes react with $Fe_3(CO)_{12}$ to form compounds of the type (az)$Fe_2(CO)_5$ and (az)$_2Fe_5(CO)_{13}$ (*62*).

$Ru_3(CO)_{12}$ reacts with 4,6,8-trimethylazulene to give $(C_{10}H_7Me_3)Ru_4(CO)_9$ (*94*), in which the bonding of the ligand is best visualized not to separate metal atoms, but to the cluster as a whole.

d. Tetraolefins. $Fe_3(CO)_{12}$ reacts with cyclooctatetraene to give a mononuclear complex $(C_8H_8)Fe(CO)_3$ and two binuclear complexes $(C_8H_8)Fe_2(CO)_6$ and $(C_8H_8)Fe_2(CO)_7$ (*288*, *310*, *336*). With 1,3,5,7-tetramethylcyclooctatetraene, the products are 1,3,5,7-tetramethylbicyclo[4.2.0]octa-2,4,7-trieneiron tricarbonyl and two isomers of composition $(C_8H_4Me_4)Fe_2(CO)_5$ (*106*). $Ru_3(CO)_{12}$ reacts with cyclooctatetraene to form $(C_8H_8)Ru(CO)_3$, $(C_8H_8)Ru_2(CO)_6$, $(C_8H_8)Ru_2(CO)_5$, and $(C_8H_8)_2$-$Ru_3(CO)_4$ (*104*). With $Os_3(CO)_{12}$ the products are two isomers of $(C_8H_8)Os(CO)_3$ (*53*). Many of these cyclooctatetraene complexes have aroused much interest because of their "fluxional" nature (*106*).

e. Acetylenes. Metal carbonyls generally react with alkynes in inert solvents to give a variety of stable organometallic compounds and cyclic organic products, the proportions of the various products being extremely sensitive to reaction conditions. $Fe_3(CO)_{12}$ reacts with diphenylacetylene in petroleum ether at 90°C to yield cyclopentadienone compounds $[(PhC_2Ph)_2CO]Fe(CO)_3$, $[(PhC_2Ph)_2CO]Fe_2(CO)_6$, Ph_4C_4CO, and $(PhC_2Ph)_2Fe_3(CO)_8$, which consists of a ferracyclopentadiene ring to which the two $Fe(CO)_2$ units are coordinated, $(Ph_4C_4)Fe(CO)_3$, which is a substituted cyclobutadiene complex, $(PhC_2Ph)_2Fe_2(CO)_6$, which involves a ferracyclopentadiene ring and one coordinated $Fe(CO)_3$, and (PhC_2Ph)-$Fe_2(CO)_3$, the structure of which is based on a substituted ferracyclopentadiene ring (*199*). With phenylacetylene the major product is a tropone complex $(PhC_2H)_3COFe_2(CO)_5$ (*199*), which consists of two fused five-membered rings having a carbon and iron atom in common, and a coordinated $Fe(CO)_2$ group (*236*).

With $Co_4(CO)_{12}$ two CO groups can be replaced without rupture of the cluster (*267*).

$$Co_4(CO)_{12} + RC{\equiv}CR' \rightarrow (RC_2R')Co_4(CO)_{10} + 2\,CO \qquad (70)$$

$$C_2RR' = C_2Ph_2,\ C_2Et_2,\ C_2H_2,\ C_2(Ph)CO_2Me,\ C_2(H)SiMe_3$$

A number of reactions of $Ru_3(CO)_{12}$ with alkynes have recently been reported. With diphenylacetylene, $(PhC_2Ph)_3Ru_3(CO)_9$ and $(Ph_4C_4)Ru_2$-$(CO)_6$ were obtained. With diethylacetylene, the product is (Et_4C_4CO)-$Ru(CO)_3$, and with 4,4′-dichlorophenylacetylene (L), the products are $L_3Ru_3(CO)_9$ and $L_2Ru_3(CO)_8$ (*346*). 3-Hexyne (*346*) and hexafluoro-2-butyne (*56*) yield cyclopentadienone complexes $(R_4C_4CO)Ru(CO)_3$. Other products from the reactions of acetylenes with $Ru_3(CO)_{12}$ are reported to be $[(PhC_2Ph)_2CO]Ru_3(CO)_9$, $(PhC_2Ph)Ru_3(CO)_9$, $(PhC_2Ph)_2$-$Ru_3(CO)_8$, $(PhC_2Ph)_2Ru_2(CO)_6$, $(PhC_2Ph)Ru_2(CO)_7$, $(PhC_2Ph)Ru_2(CO)_6$, and $(PhC_2Ph)Ru(CO)_4$ (*78*).

$Os_3(CO)_{12}$ is reported to react with dimethylacetylene to yield $(Me_4C_4CO)Os(CO)_3$ and $(MeC_2Me)_2Os_2(CO)_6$ (*53*).

f. Arenes. A small number of reactions in which three CO groups of a cluster are replaced by an arene have been reported, and have been discussed in Section II,D,1.

Reactions have also been reported between $Fe_3(CO)_{12}$ and allenes to form $(C_3H_4)Fe(CO)_3$ (*311*), and $Fe_3(CO)_{12}$ and *N*-methyldiphenylketenimine to form $(Ph_2C{=}C{=}NMe)Fe_2(CO)_6$ (*318*).

V. Bonding and Electronic Structure of Clusters

The empirical "inert gas rule" which was first proposed by Sidgwick (*348*) has been widely applied to metal carbonyl chemistry. This rule has a particular application to carbonyl clusters as, with a knowledge of the stoichiometry of a compound, a calculation of the number of electron pairings required to make up the noble gas configuration leads to a prediction of the nuclearity of the cluster and of the required number of metal–metal bonds and, hence, the type of structure.

There are a number of clusters which do not obey the noble gas rule. The only paramagnetic clusters are $Ni_3(\pi\text{-Cp})_3(CO)_2$ (*143*), $Ni_3(\pi\text{-Cp})_3NBu$ (*319*), $Co_3(CO)_9S$ (*256, 258, 291*), and $Co_3(CO)_9Se$ (*113*), which have one electron in excess of the noble gas configuration, and $Ni_3(\pi\text{-Cp})_3(CO)S$ (*113*), an electron count of which shows three electrons in excess of the noble gas configuration. Diamagnetic clusters which deviate from the noble gas rule are $Os_3(CO)_{10}(OMe)_2$ (*217*), $Co_3(CO)_4(SEt)_5$ (*372*), $Co_3(CO)_5(SEt)_4 \cdot Co_2(CO)_5(SEt)$ (*343*), and $Co_3(CO)_5(SEt)_4 \cdot Co_3(CO)_6S$ (*374*), in which the trinuclear clusters have an excess of two electrons. On the other hand, $Os_3(CO)_{10}H_2$ is two electrons short (*217*). The phosphine clusters (Table IX), in general, have at least two electrons short of the noble gas configuration for each metal. For these compounds it would appear that back-bonding is not necessarily at a maximum when all the low energy bonding molecular orbitals are filled.

A feature of the hexanuclear clusters is that they all have two electrons in excess of the total required for each metal to achieve the noble gas configuration and, moreover, they show no tendency to lose these two "extra" electrons. $Rh_{12}(CO)_{30}^{2-}$ also gives an excess electron count.

Thus, it is obvious that as an empirical rule, the noble gas formalism can be applied only with reservation. Moreover, it does not provide a realistic explanation of the bonding forces operating in a cluster.

The current view of the nature of metal–ligand bonds where the ligand can act as a π acceptor is that they consist of donation of an electron pair from the ligand to the metal in a sigma bond and back-donation of metal *d* electrons into vacant orbitals of suitable symmetry, forming a pi bond. The stability of carbonyl compounds may be related to the function of the metal in assisting transfer of electronic charge from σ to π^* orbitals on the CO itself, a transfer which is otherwise forbidden. This back-donation also assists in the stabilization of clusters by removal of excess charge from the metal. In carbonyl clusters the dissipation of excess charge by back-bonding to CO ligands appears to decrease in the order face bridging > edge bridging > terminal.

Metal–metal bonding is considered to be formed by the overlap of suitably oriented metal orbitals. There is evidence for multiple metal–metal bonding in the halide clusters (*102*), but to date there are no substantiated examples of this in clusters with π-acid ligands. Metal–metal bond overlap increases down a triad and it is therefore expected that clusters of the third-row transition metals will be the most stable.

It is of note that metal halide and oxide clusters may be prepared in general for metals of the Groups V, VI, and VII (*102*, *229*, *344*), whereas clusters with π-acid ligands are formed mainly by metals of Group VIII. If halide and oxide clusters were to be formed by Group VIII metals, there would be a surplus of electrons in antibonding orbitals, according to the Cotton–Haas model (*102*, *105*). As these antibonding orbitals cannot be stabilized by delocalization over the molecule through back-bonding, such compounds would be unstable. On the other hand, clusters of Group V, VI, and VII metals with π-acid ligands would not have sufficient electrons to fill all bonding orbitals.

A number of attempts have been made to account for the electronic structures of clusters by theoretical descriptions of their bonding. The valence-bond approach, based on localized two-center bonds formed by directed hybrid orbitals have been used by a number of workers. Sutton and Dahl (*357*) have rationalized the structures of a number of clusters in terms of "bent" metal–metal bonds. This concept is contrary, however, to the basic notion of the valence-bond approach, which is that orbitals should be directed to give maximum overlap. Moreover, the situation can arise in clusters where there is not an integral number of electron pairs per bond.

Qualitative LCAO–MO treatments have also been used and Dahl has provided a rationale for a number of clusters on the basis of delocalized bonding. The simple MO treatment reserves certain metal orbitals for localized metal–ligand σ bonding, π bonding being neglected. The remaining orbitals are then combined according to the operations of group theory to form molecular orbitals for the cluster. The ordering of these energy levels has been estimated usually by orbital overlap considerations.

The electronic structure of $Rh_6(CO)_{16}$ has been described in this way. The eight σ-bonding orbitals on each Rh atom are first filled. The rhodiumlike orbitals considered to be available for bonding with each other are the lowest-lying d_{z^2} and the next lowest degenerate ($d_{z^2-y^2}$, d_{xy}) orbitals. Under O_h symmetry the d_{z^2} orbitals of the six rhodium atoms will give a_{1g}, e_g, and t_{1u} levels, which will be filled with six electron pairs. Similarly, the six $d_{x^2-y^2}$ orbitals give rise to a_{2g}, e_g, and t_{2u} levels, and the d_{xy} yield a_{2u}, e_u, and t_{2g}. The remaining electron pair is then placed in the a_{2u} level as it is considered to be the lowest energy level from overlap considerations (*98*).

A related treatment of $Co_6(CO)_{16}$ (*15*) is based on each metal atom using sp^3 orbitals to bond to the two terminal and two bridging CO groups. This leaves the five d orbitals of the metal available for metal–metal bonding and for back-donation. With an orientation such that d_{xz} and d_{yz} are directed along the edges of the octahedron, the $d_{x^2-y^2}$ and d_{xy} orbitals will be essentially nonbonding, and will be involved in back-donation. Under O_h symmetry the d_{xz} and d_{yz} will give rise to four triply degenerate molecular orbitals (t_{1g}, t_{2g}, t_{1u}, and t_{2u}) and the d_{z^2} will give a_{1g}, e_g, and t_{1u}. The 86 valence electrons are considered to be distributed such that 48 are in the six sp^3 hybrids, 24 are located in the nonbonding orbitals, 12 electrons are in the t_{2g} and t_{1u}, and the last electron pair is located in the bonding a_{1g} orbital. Related treatments have been made of $Co_6(CO)_{15}^{2-}$ (*15*) and $Co_6(CO)_{14}^{4-}$ (*13*).

In $Ru_6(CO)_{17}C$ (*211*) the a_{1g} and t_{1u} orbitals derived from the six d_{z^2} metal orbitals pointing to the center of the octahedron are considered to be responsible for the bonding with the carbon atom.

A bonding scheme in terms of MO's has also been proposed for $Co_3(CO)_4(SEt)_5$ (*372*), $Co_3(CO)_5(SEt)_4 \cdot Co_2(CO)_5(SEt)$ (*373*), and $Co_3(CO)_5(SEt)_4Co_3(CO)_6S$ (*374*). Using the Cotton–Haas (*105*) model as applied to $Re_3Cl_{12}^{3-}$, $Co_3(CO)_5(SEt)_4$ was oriented such that the cobalt–ligand σ bonding involved the d_{xy}, s, $1/\sqrt{2}(p_x + p_y)$, $1/\sqrt{2}(p_x - p_y)$, and p_z orbitals of each Co atom. Then the twenty valence electrons for the tricobalt system would occupy not only all five of the metal-bonding orbitals, $d_2(a_1')^2$, $d_{xz}(e')^4$, $d_{yz}(a_1')^2$, $d_{x^2-y^2}(a')^2$, but also five antibonding orbitals, $d_{x^2-y^2}(e'^*)^4$, $d_{yz}(e'^*)^4$, and $d_{xz}(a_2'^*)^2$, which would account for the diamagnetism of the compound. For the $Co_3(CO)_6S(S_3)$ fragment a similar orbital ordering will lead to $d_{z^2}(a_1)^2$, $d_{yz}(a_1)^2$, $d_{xz}(e)^4$, $d_{xy}(e)^4$, $d_{yz}(e^*)^4$, and $d_{xy}(a_2{}^*)^2$.

Studies by Dahl on $Co_3(CO)_9S$ and related compounds by X-ray and ESR measurements (Section III, D) (*356*, *371*) have shown significant increases in metal–metal bond length associated with the presence of one excess electron and, hence, have substantiated the basis for assumptions of the delocalizability of metal–metal bonds.

Kettle has used a topological equivalent orbital treatment on $Co_4(CO)_{12}$, $Ir_4(CO)_{12}$, $Fe_3(CO)_{12}$, and $Os_3(CO)_{12}$ (*230*), and $Rh_6(CO)_{16}$ (*231*). This approach is based on a number of assumptions such as the fixed presence of metal–metal bonds in edge and face positions. While it does include the electrons formally involved in metal–CO π bonding, it appears that the questionable assumptions make the treatment unreliable at this stage (*222*). Kettle finds $Rh_6(CO)_{16}$ to be deficient of two electrons owing to the destabilization of an orbital of a_2 symmetry relative to an isolated metal orbital, but no experimental evidence has been obtained to support this view.

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