METAL CARBONYLS

1. Introduction

Carbon monoxide [630-08-0] (qv), CO, the most important π-acceptor ligand, forms a host of neutral, anionic, and cationic transition-metal complexes. There is at least one known type of carbonyl derivative for every transition metal, as well as evidence supporting the existence of the carbonyls of some lanthanides (qv) and actinides, although often in combination with other ligands (see ACTINIDES AND TRANSACTINIDES; COORDINATION COMPOUNDS) (1).

Carbonyls are involved in the preparation of high purity metals as in the Mond process for the extraction of nickel from its ores (see NICKEL AND NICKEL ALLOYS), in catalytic applications, and in the synthesis of organic compounds. Transition-metal carbonyls of the type $M_x(CO)_y$, where M is a metal and x and y are integers, are referred to as binary (or homoleptic) compounds. Metal carbonyls are often used as starting materials in the preparation of complexes where the carbon monoxide is replaced by other ligands such as phosphines, arsines, hydrides, halides, and many chelating ligands (see CHELATING AGENTS) and unsaturated organic ligands such as alkenes, alkynes and arenes. Substitution rates on some metal carbonyls such as those of Cr, Mo, W, and Mn can be easily measured (2). Detailed mechanistic studies on metal carbonyls have become increasingly important in understanding the factors influencing ligand substitution processes, especially as they apply to catalytic activity. Complexes containing several metal atoms held together mainly by metal–metal bonding are termed clusters and they have received increasing attention for the interest in the rules governing the stoichiometry and structure as well as for possibilities in homogeneous and heterogeneous catalysis (see CATALYSIS).

2. Bonding and Structure of Metal Carbonyls

2.1. Bonding. Coordination of carbon monoxide to a metal is through the carbon atom, and is made up of two parts (Fig. 1):

1. σ Donation of the lone pair of electrons on the carbon to an empty metal orbital.
2. π Back-donation from filled metal d orbitals to the empty π^* CO antibonding orbitals.

The σ and π components work cooperatively, with the back-donation of electron density into the CO π^* antibonding orbitals improving the ability of the CO to donate electron density to the metal. This type of bonding is termed *synergic*, and has profound effects on the M–C–O linkage. The M–C bond is strengthened due to the partial double-bond character, and bond lengths are generally 20–30 pm shorter than metal–carbon bonds where π bonding is not possible, such as in metal alkyl complexes. The C–O bond is weakened, and this is manifested most strongly in the CO stretching frequency observed using infrared (ir) spectroscopy. Just how much is dependent on the oxidation state of the metal and the nature of the other ligands.

	M−C, pm	C−O, pm	ν(CO), cm^{-1}
free CO		113	2143
$Ni(CO)_4$	182	113	2060
$[Co(CO)_4]^-$	177	115	1890
$[Fe(CO)_4]^{2-}$	175	117	1790

Note that the C−O distance is relatively insensitive to the changing C−O bond strength. However, the ν(CO) stretching frequency is very diagnostic of the extent of back-bonding. The data above show how increasing negative charge leads to expansion of the metal *d* orbitals with a concomitant increase in $M(d\pi) - CO(\pi^*)$ overlap, weakening the C−O bond.

A variety of different bonding modes is known for CO in clusters. In addition to the familiar terminal bonding mode, the CO ligand can bridge between two metal atoms, a binding mode described as μ_2-CO. The Greek letter μ (mu) indicates a bridging mode, and the *sub*scripted number refers to how many metals the ligand is bonding to (the "2" in μ_2 is often dropped for convenience, so by default, μ-CO means μ_2-CO). Therefore, the other common bonding mode, in which the CO bridges three metals, is called μ_3-CO (Fig. 2).

Rather more exotic bonding modes have also been observed, in which the CO ligand bonds in a "side-on" fashion and bonds through the oxygen atom as well. To indicate that more than one atom of the ligand is bonding to a metal, the usual nomenclature uses the Greek letter η(eta), and this time a *super*scripted number refers to how many atoms in the ligand are bonding to the metal(s). Therefore, a CO ligand that is bonding in side-on fashion to a face of three metal atoms is referred to as μ_3-η^2-CO. Some examples of side-on (η^2) bonding are shown below (Fig. 3).

The ir ν(CO) stretching frequencies of transition-metal carbonyl complexes can also be used to determine structure predicted by group theory (3). For clusters, this method has proved disappointing and the spherical harmonic model has been developed to improve the situation (4).

The 18-Electron Rule. The vast majority of the thermodynamically stable mononuclear metal carbonyls have a valence electron count of 18 and are therefore said to obey the 18-electron rule (sometimes called the "effective atomic number rule"). The 18-electron rule arises from the fact that transition metals have 9 valence atomic orbitals [$5 \times nd$, $(n+1)s$, and $3 \times (n+1)p$], which can be used either for metal–ligand bonding or for the accommodation of nonbonding electrons. Filling of these 9 orbitals allows the metal to gain the electronic configuration of the next highest noble gas.

The simplest way to count the electrons about a single metal uses the following rules:

1. Consider the metal and ligands to have an oxidation state of zero.
2. Add together the valence electrons of the metal and the electrons donated by the ligands (bridging ligands provide an equal share of their electrons to each metal they interact with).

3. Account for the overall charge on the complex by adding or subtracting the appropriate number of electrons.
4. Consider each metal–metal bond as providing one electron to each metal.

The rule can be extended to clusters by stating that the *average* number of electrons per metal atom will be 18 (provided electrons are calculated for each metal separately then averaged). Clusters that obey this rule are said to be *electron precise* (5), and the rule works well for clusters with up to 5 metal atoms (or for larger examples in which the metal framework is very open). Other electron counting methods are required for larger clusters (see below).

2.2. Structure.

Mononuclear Carbonyls. The stable, 18-electron neutral mononuclear complexes are represented by nickel tetracarbonyl (see NICKEL COMPOUNDS), iron pentacarbonyl (see IRON COMPOUNDS) and the Group 6 (VI B) hexacarbonyls (see CHROMIUM, MOLYBDENUM AND TUNGSTEN COMPOUNDS), which adopt tetrahedral, trigonal bipyramidal and octahedral structures, respectively (Fig. 4). Vanadium hexacarbonyl, $V(CO)_6$, is paramagnetic and is a 17-electron species, but does not dimerize to form a metal–metal bond due to steric reasons. It is, however, very easily reduced to the relatively stable 18-electron species $[V(CO)_6]^-$.

The carbonyl ligands in the tetrahedral and octahedral structures are all equivalent. However, the trigonal bipyramidal arrangement gives rise to two different environments, two axial and three equatorial. While the ir spectrum of $Fe(CO)_5$ is consistent with this structure, the ^{13}C nuclear magnetic resonance (nmr) spectrum displays just a single signal even at very low temperatures. This phenomenon is representative of stereochemical nonrigid behavior or *fluxionality* (6), and in this case it is thought to proceed by a process known as the Berry *pseudo*-rotation, in which the equatorial and axial sites are interchanged via a square pyramidal intermediate. The ruthenium and osmium pentacarbonyls are thermally unstable and rapidly form $M_3(CO)_{12}$ ($M = Ru$, Os) at room temperature.

Many thermally stable (though generally air-and moisture-sensitive) anionic 18-electron species are known. Typical examples are $[Co(CO)_4]^-$, $[Mn(CO)_5]^-$, and $[Fe(CO)_4]^{2-}$, and these species are widely used as precursors to derivatives of carbonyl complexes; $[Fe(CO)_4]^{2-}$, as the sodium salt, is known as “Collman's reagent” and has found application in organic synthesis (7). A variety of highly reduced metal carbonyls has also been characterized (8), including the trianionic species $[Nb(CO)_5]$ (3–9) and $[Ir(CO)_3]$ (3–10).

Similarly, a large number of metal carbonyls in positive oxidation states are also known, for example $[M(CO)_6]^+$ ($M = Mn$, Re). The more highly oxidised species, such as $[M(CO)_6]^{2+}$ ($M = Ru$, Os) (11) or $[Ir(CO)_6]^{3+}$ (12) are generally prepared in superacid media (see FRIEDEL-CRAFTS REACTIONS) (13).

Dinuclear Carbonyls. $Fe_2(CO)_9$ provided the first example of a structurally characterized dinuclear carbonyl, but because of the presence of three bridging CO ligands, there was much speculation as to whether or not an Fe–Fe bond was present in the molecule. However, electron counting, the observed diamagnetism and the short Fe–Fe distance of 2.56 Å all supported the presence of a bond. The CO ligands are arranged in the form of a tricapped trigonal prism.

The structure of $Co_2(CO)_8$ (see COBALT COMPOUNDS) is related to that of $Fe_2(CO)_9$, except the metal–metal bond is bridged by just two bridging ligands. The structure of $Mn_2(CO)_{10}$ (see MANGANESE COMPOUNDS), however, is quite different, with all 10 carbonyls in terminal positions. This was the first example of a structurally characterized unsupported metal–metal bond. The coordination geometry about each manganese atom is octahedral, and the configuration is staggered, such that the ligands describe a bicapped square antiprism (Fig. 5). Rhenium carbonyl has the same structure (see RHENIUM AND RHENIUM COMPOUNDS).

Tri-, Tetra-, and Pentanuclear Carbonyls. Iron, in addition to forming stable mono- and dinuclear carbonyl complexes, also forms a trimer, $Fe_3(CO)_{12}$. This compound has been the subject of extensive study, due to its unusual structure (14). The determination of the crystal structure of $Fe_3(CO)_{12}$ proved problematic due to disorder of the iron atoms. However, the eventual solution showed that the CO ligands are arranged such that two of the ligands bridge one of the Fe–Fe edges, with the remainder in terminal positions. Overall, the CO ligands describe an icosahedral shape. $Fe_3(CO)_{12}$ was found to be a highly fluxional molecule, and the mechanism by which this occurs has been the subject of intense debate (15). Possibilities include the concerted motion (libration) of the metal core inside the icosahedral array of ligands (16), or more localized migrations of the ligands in a "merry-go-round" fashion around the core (6).

The heavier congeners of Group 8 (VIII), ruthenium and osmium, also form trinuclear dodecacarbonyl species (see PLATINUM-GROUP METALS, COMPOUNDS), but as the Ru_3 and Os_3 triangular cores are larger, the surrounding carbonyls describe the larger anticuboctahedron. This results in all the CO ligands bonding in terminal fashion, with six in axial and six in equatorial positions (Fig. 6).

The homoleptic tetranuclear carbonyl complexes, $M_4(CO)_{12}$ (M = Co, Rh, Ir) all have tetrahedral cores, but again, the arrangement of CO ligands differs. For cobalt and rhodium, the metal core is surrounded by a shell of CO ligands that are arranged in an icosahedron, resulting in one unique metal atom that has only terminal CO ligands. The atoms share three bridging carbonyls, one on each edge of the triangular face. However, in $Ir_4(CO)_{12}$, the ligands are arranged in a cuboctahedron, such that all metal atoms and ligands are equivalent (Fig. 7).

Many mixed-metal tri- and tetranuclear clusters are known, and if clusters are included that have ligands other than just CO, the number of examples is vast. The majority of these clusters can be rationalized electronically in terms of localized two-center, two-electron bonds, and the various metal core geometries have characteristic electron counts. The most common shape for the metal atom core of trinuclear clusters is triangular (48 e), but linear and bent (50 e) clusters are also known; likewise, while tetrahedral (60 e) is the shape of most tetranuclear clusters, butterfly (62 e), rectangular and spiked triangular (64 e) examples are all well documented.

Pentanuclear carbonyl clusters are in general electron precise. A variety of shapes are known; examples include the trigonal bipyramidal $Os_5(CO)_{16}$ (72 e, 9 Os–Os bonds), the planar raft $Os_5(CO)_{18}$ (76 e, 7 Os–Os bonds) and the bowtie shaped cluster $Os_5(CO)_{19}$ (78 e, 6 Os–Os bonds) (Fig. 8).

3. High Nuclearity Carbonyl Clusters

Synthesis and characterization of high nuclearity clusters can be very difficult, though modern spectroscopic and mass spectrometric techniques are making the task somewhat easier (17). Typically, several different clusters are formed in any given synthetic procedure, and each component of the mixture must be extracted and identified. There is a strong reliance on X-ray crystallography as a means of fully characterizing cluster compounds.

The first high nuclearity cluster was synthesized in 1943 by the reaction of $RhCl_3$ with CO under pressure at 80̄C. The resulting black crystalline product was formulated, at that time, as $Rh_4(CO)_{11}$ (18), and it was not until 20 years later that the correct structure was determined to be $Rh_6(CO)_{16}$ (19). The rhodium atoms are arranged in at the corners of an octahedron, with two terminal CO ligands coordinated to each of the rhodium atoms. The four remaining ligands cap four of the eight faces of the octahedron ($_3$−CO) (Fig. 9).

The electron count for $Rh_6(CO)_{16}$ is 86, nine from each rhodium atom ($9 \times 6 = 54$) and two from each of the CO ligands ($16 \times 2 = 32$). An electron-precise cluster, in which each edge of the octahedron represented a localized two-center two-electron bond between adjacent metals, would only require a total of $6 \times 14 = 84$ valence electrons (each metal would obey the 18-electron rule, as the extra four electrons required for each metal would come from the four metal−metal bonds that each metal forms). $Rh_6(CO)_{16}$ thus represents the first member of a family of polyhedra in which the skeletal cluster bonding is delocalized and departs from the electron precise description. The polyhedral skeletal electron pair theory (PSEPT) (20) successfully explains the bonding in such clusters, by modifying Wade's rules for boranes (see BORANES) using isolobal analogies (21).

Despite the complexity of transition-metal clusters, their structures can often be broken down into basic units. A triangular network of metal atom faces occurs in most clusters sometimes leading to their description as deltahedra, Δ, for triangular (22). For example, the molecule $Os_6(CO)_{18}$ (23) has a bicapped tetrahedral geometry, and can be considered as three tetrahedra sharing two triangular faces. The large cluster $[Rh_{12}(CO)_{30}]^{2-}$ consists of two octahedral arrays of rhodium atoms joined by a rhodium−rhodium bond. Structures such as these, which consist of fused polyhedra, can be rationalized by use of the *condensation principle*, summarized by, "the total electron count in a condensed polyhedron is equal to the sum of the electron counts for the parent polyhedra minus the electron count characteristic of the atom, pair of atoms, or face of atoms common to both polyhedra" (24).

Very large clusters often take the form of fragments of a close-packed lattice of metal atoms. $[Os_{20}(CO)_{40}]^{2-}$, for example, consists of a cubic close packed array of osmium atoms, whose overall shape describes a giant tetrahedron (25). Similarly, the mixed-metal cluster $[Ni_{38}Pt_6(CO)_{48}]^{5-}$ (Fig. 10) consists of a close-packed array of metal atoms, whose overall shape describes a giant octahedron (26). The six platinum atoms are arranged octahedrally in the centre of the cluster, forming the "stone" of what is called a "cherry" cluster. In both clusters, just as in the bulk metal, all the interstitial cavities are octahedral or tetrahedral.

4. Physical Properties of Metal Carbonyls

Most metal carbonyls are volatile solids that sublime easily. The vapor pressures of many metal carbonyls have been tabulated elsewhere (27). The thermodynamic properties of simple metal carbonyls have been compiled (28). The volatility of metal carbonyls coupled with their toxicity is an important safety consideration. Nickel tetracarbonyl, a volatile liquid, is particularly dangerous due to its high volatility and extreme toxicity. It is potentially fatal if inhaled, causes respiratory tract burns, allergic reactions, and is carcinogenic (see NICKEL COMPOUNDS).

Some selected properties of metal carbonyls are listed in Table 1.

5. Preparation

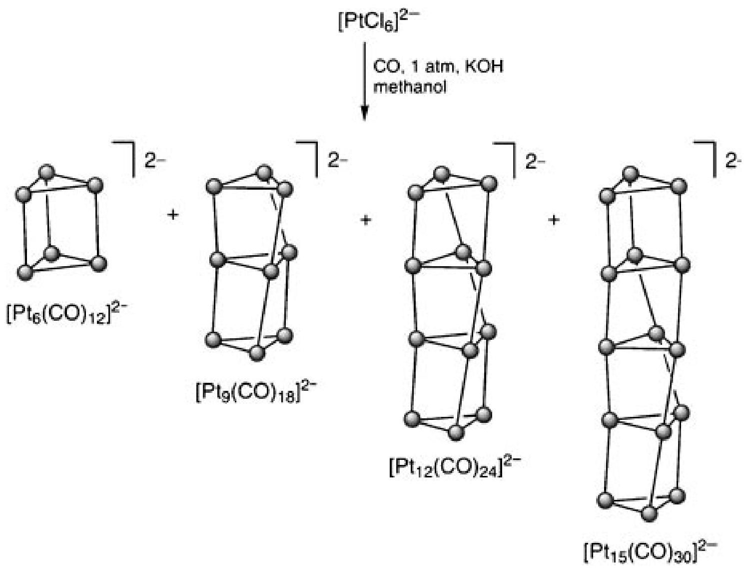
Since the discovery of nickel carbonyl in 1890 (29), carbonyls of many other metals have been prepared. Nickel and iron are the only metals that combine directly with CO at atmospheric pressure to produce carbonyls in reasonable yields. Because transition metals even in a finely divided state do not readily combine with CO, metal salts tend to be used as precursors to metal carbonyls. The metal in a salt is in a higher oxidation state than the resulting carbonyl complex and therefore, most metal carbonyls result from the reduction of the metal in the starting material, and such a process is called reductive carbonylation. In some cases, CO itself is the reducing agent. Rhenium (30) and technetium (31) carbonyls are conveniently prepared from the oxides. Reducing agents, such as silver or copper, can be used in the dry state to effect carbonylation. The presence of Cu metal is deemed to be beneficial in the synthesis of $Re_2(CO)_{10}$ by reaction of Re_2O_7 and CO for 16 h at 186 atm and 250°C (32).

More frequently, metal carbonyls are prepared in solvents. A few examples of syntheses of metal carbonyls in aqueous solution have been reported. For example, $Co_2(CO)_8$ may be prepared from $CoSO_4$ (66% yield) or $CoCl_2$ (56% yield) and CO at 95–110 atm in aqueous ammonia at 120°C for 16–18 h (33). Triiron dodecacarbonyl may also be prepared in aqueous solution. Quantitative yields of $Fe_3(CO)_{12}$ have been obtained by oxidizing alkaline solutions of carbonyl ferrates with manganese dioxide (34).

Metal carbonyls that are synthesized in nonaqueous media often use reactive metals, such as sodium (35), magnesium (36), zinc (37), and aluminium (38), as reducing agents. Again, in some cases CO itself is the reducing agent. Reagents, such as trialkylaluminiums (39) have been used to synthesize $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ in high yields and sodium benzophenone has also been found to be a useful as reducing agent (40).

The majority of metal carbonyls are synthesized under medium pressures of CO, eg, $Ru_3(CO)_{12}$ can be conveniently prepared from $RuCl_3{\cdot}nH_2O$ in methanol at 125°C for 8 h under 50 atm CO (41). In general, the most recent and simplest methods used to prepare metal carbonyls are described in the series *Inorganic Syntheses* (42).

Synthesis of High Nuclearity Metal Carbonyls from Salts. A few high nuclearity carbonyl clusters can be made directly from salts. For example, reaction of $RhCl_3$ under a high pressure of CO in methanol followed by addition of KOH affords $[Rh_6C(CO)_{15}]^{2-}$ (43). The stacked triangular clusters $[Pt_3(CO)_6]_n^{2-}$ ($n = 2 - 5$), are prepared from platinum(IV) chloride (44). The reaction of $[PtCl_6]^{2-}$ with potassium hydroxide under an atmosphere of carbon monoxide affords a number of compounds depending on the concentration of the potassium hydroxide used (see **Scheme 1**).



Scheme 1. Carbonyl ligands have been omitted for clarity.

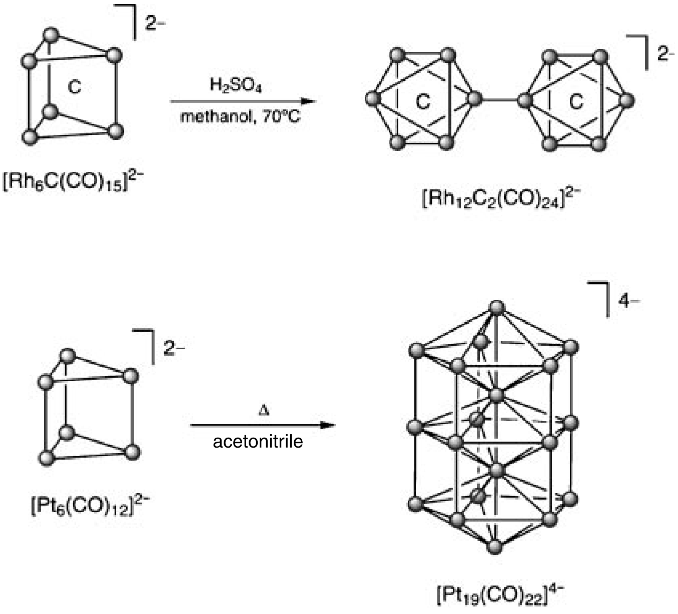
Synthesis of High Nuclearity Metal Carbonyls from Smaller Carbonyls. A considerable number of high nuclearity homoleptic carbonyl clusters, and those containing interstitial atoms or other ligands introduced during reaction are known. The presence of interstitial atoms and ligands such as hydrides, while not added deliberately, stems from the way in which many clusters are synthesized. For example, many high nuclearity clusters that are prepared in protic solvents contain hydride ligands. In addition, if the precursor cluster employed in the reaction contains hydride ligands then the product is also likely to contain hydrides.

The main methods used to prepare high nuclearity carbonyl clusters are thermolysis (heating in a solvent), pyrolysis (heating without a solvent present), and chemical reduction. For example, thermolysis of $Ru_3(CO)_{12}$ in ethanol affords the hexanuclear cluster $[HRu_6(CO)_{18}]^-$ in almost quantitative yield, extending the reaction time results in $[H_2Ru_{10}(CO)_{25}]^{2-}$ (45). In high boiling hydrocarbon solvents the thermolysis of $Ru_3(CO)_{12}$ affords carbide containing clusters, such as $Ru_6C(CO)_{17}$ and $[Ru_{10}C(CO)_{24}]^{2-}$, as well as a number of other products depending upon the actual solvent used (46). Pyrolysis of $Os_3(CO)_{12}$ results in the formation of a number of clusters including

$Os_5(CO)_{16}$, $Os_6(CO)_{18}$, $Os_7(CO)_{21}$, $Os_8(CO)_{23}$, $Os_5C(CO)_{15}$, $Os_5C(CO)_{16}$, $Os_8C(CO)_{22}$, and $[Os_{10}C(CO)_{24}]^{2-}$ (47). The precise range and distribution of products depends on the temperature and time of the pyrolysis. Reduction of $Rh_4(CO)_{12}$ with sodium hydroxide in propanol affords $[Rh_{17}(CO)_{30}]^{3-}$ in 20% yield (see Fig. 11) (48), whereas the reduction of $Rh_6(CO)_{16}$ with potassium hydroxide in methanol results in only a slight increase in nuclearity with the formation of $[Rh_7(CO)_{16}]^{3-}$ (49).

These methods are similar in that reactive fragments are generated that undergo condensation. However, mechanistic detail on cluster aggregation processes is poorly developed. Many high nuclearity cluster preparations result in the formation of a number of products that require separation by fractional crystallization or chromatographic methods.

There are a large number of compounds that can be prepared from the condensation of high nuclearity clusters, eg, oxidation of the octahedral cluster $[Rh_6C(CO)_{15}]^{2-}$ with sulfuric acid forms $[Rh_{12}C_2(CO)_{24}]^{2-}$ (50) and the thermolysis of $[Pt_6(CO)_{12}]^{2-}$ in acetonitrile affords $[Pt_{19}(CO)_{22}]^{4-}$ (51) (see **Scheme 2**).



Scheme 2. Carbonyl ligands have been omitted for clarity.

Synthesis of High Nuclearity Metal Carbonyls from Larger Carbonyls. Degradation (or decomposition) reactions can be used to prepare certain compounds that cannot be obtained in other ways. The best examples comprise the synthesis of the square pyramidal clusters from octahedral clusters. Treatment of $[Fe_6C(CO)_{16}]^{2-}$ with sulfuric acid gives $Fe_5C(CO)_{15}$ (52) and reaction of $Ru_6C(CO)_{17}$ under a high pressure of CO affords $Ru_5C(CO)_{15}$ (53) in what is termed a degradative carbonylation reaction.

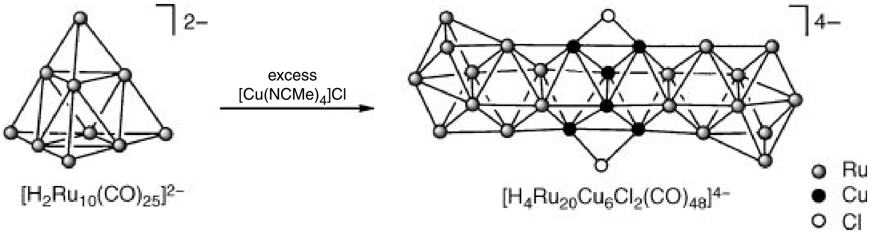
5.1. Synthesis of Heteronuclear Metal Carbonyls.

Heteronuclear metal carbonyls are prepared by a number of different ways. For example, in ligand displacement reactions metal complexes that contain a good leaving group will react with metal-containing nucleophiles to form new metal–metal bonds. A notable example is the reaction of $[Ni_6(CO)_{12}]^{2-}$ with $[PtCl_4]^{2-}$ in acetonitrile, which gives many products that are separated by fractional crystallization including $[Ni_9Pt_3(CO)_{21}]^{4-}$, $[HNi_9Pt_3(CO)_{21}]^{3-}$ $[Ni_{36}Pt_4(CO)_{45}]^{6-}$, $[Ni_{37}Pt_4(CO)_{46}]^{6-}$, $[Ni_{38}Pt_6(CO)_{48}]^{5-}$, and $[HNi_{38}Pt_6(CO)_{48}]^{4-}$ (54). The addition of mercury salts to anionic metal carbonyl complexes or clusters often results in the formation higher nuclearity compounds. Mercury usually forms the core of the resulting heteronuclear cluster, holding the metallic subunits together like a "glue" (55).

Redox condensation involves the reaction between complexes with metals in different formal oxidation states and has been widely used for the synthesis of mixed-metal carbonyl clusters. A simple example is provided by the reaction of the trinuclear clusters $M_3(CO)_{12}$ ($M = Fe$, Ru, Os) with $[M'(CO)_4]^-$ ($M' = Co$, Rh, Ir) to generate the tetrahedral clusters $[M_3M'(CO)_{13}]^-$ in good yield (56):

$$M_3(CO)_{12} + [M'(CO)_4]^- \longrightarrow [M_3M'(CO)_{13}]^- + 3CO$$

The reaction of anionic ruthenium clusters with the copper reagent $[Cu(NCMe)_4]Cl$ in CH_2Cl_2 leads to the formation of large ruthenium–copper clusters in good yield. The most impressive cluster obtained in this way was isolated from the reaction between $[H_2Ru_{10}(CO)_{25}]^{2-}$ and excess $[Cu(NCMe)_4]Cl$, which affords $[H_4Ru_{20}Cu_6Cl_2(CO)_{48}]^{4-}$ (see **Scheme 3**) (57).



Scheme 3. Carbonyl ligands have been omitted for clarity.

Introduction of main group metal atoms into clusters is also possible, eg, the mixed-metal cluster $BiCo_3(CO)_9$ has been prepared by reaction of $BiCl_3$ and $[Co(CO)_4]^-$ to form $Bi\{Co(CO)_4\}_3$ followed by thermal decarbonylation (58). Subsequent reduction with cobaltacene affords $[Bi_2Co_4(CO)_{11}]^-$ (59). Clusters with more than two different metal elements are also known (60).

6. Economic Aspects

The following homoleptic metal carbonyls are also commercial available from the major chemical suppliers: $Na[V(CO)_6]$, $M(CO)_6$ ($M = Cr$, Mo or W), $M_2(CO)_{10}$

(M = Mn or Re), $Fe(CO)_5$, $Fe_2(CO)_9$, $M_3(CO)_{12}$ (M = Fe, Ru, or Os), $Co_2(CO)_8$, $M_4(CO)_{12}$ (M = Co, Rh, or Ir), $Rh_6(CO)_{16}$, and $Ni(CO)_4$. Many other metal carbonyl derivatives are commercially available.

7. Health and Safety Aspects

Exposure to metal carbonyls can present a serious health threat. Nickel carbonyl is considered to be one of the most poisonous organometallic compounds known. However, the toxicological information available on metal carbonyls is restricted to the more common, commercially important compounds. Other metal carbonyls are considered potentially dangerous, especially in the gaseous state, by analogy. Data concerning toxicological studies on a few common metal carbonyls are listed in Table 2 (61). Additional toxicity data are Occupational Safety and Health Administration (OSHA) personal exposure limits (PEL): for $Fe(CO)_5$ this is 8 h at 0.1 ppm, whereas for the much more toxic $Ni(CO)_4$ it is 8 h at 0.001 ppm, with a toxic concentration TCL_0 low (of 7 mg/m^3) for human inhalation.

The toxic symptoms from inhalation of nickel carbonyl are believed to be caused by both nickel metal and carbon monoxide. In many acute cases, the symptoms are headache, dizziness, nausea, vomiting, fever, and difficulty in breathing. If exposure is continued, unconsciousness follows with subsequent damage to vital organs and death. Iron pentacarbonyl produces symptoms similar to nickel carbonyl but is considered less toxic than nickel carbonyl.

Hazard data for metal carbonyls is usually supplied when purchased.

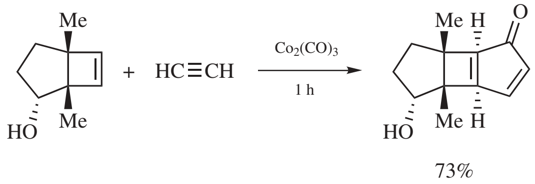
8. Uses

8.1. Metal Carbonyls in Stoichiometric Organic Synthesis.

The number of reactions involving transition metal carbonyls and organic molecules is seemingly inexhaustible. While many of these reactions are of essentially academic curiosity, some reactions are important in organic synthesis and allow certain organic molecules to be made much more simply than when the metal carbonyl is not present. For example, $Cr(CO)_6$ reacts with many arenes to afford complexes of formula $Cr(CO)_3(\eta^6\text{-arene})$ in which the reactivity of the arene is modified by coordination to the electron withdrawing chromium tricarbonyl fragment as shown in Figure 12 (62).

Similarly, many dienes reacts with $Fe(CO)_5$ to form complexes of formula $Fe(CO)_3(\eta^6\text{-diene})$ in which the subsequent reactivity of the diene has been significantly modified from the uncoordinated molecule.

$Co_2(CO)_8$ has also been widely used in organic synthesis (63), the most notable example being in the Pauson-Khand reaction shown in **Scheme 4** (64).



Scheme 4.

The use of metal carbonyls in organic synthesis has been thoroughly reviewed and many books are available on the subject (65).

8.2. Metal Carbonyls in Catalysis. Metal carbonyls have been extensively studied as homogeneous catalysts and have been shown to effectively catalyse a wide range of reactions from bulk chemical products to fine chemicals. Mechanistic understanding is well developed for mononuclear metal carbonyl catalysed reactions, but far less is known about the mechanisms of clusters. Only recently has direct evidence been given for catalysis by intact clusters rather than fragments generated during reaction (66).

Hydroformylation and Hydrogenation. Hydroformylation (or the OXO process) involves the addition of hydrogen and carbon monoxide to an unsaturated organic substrate (see **Scheme 5**) and it is effectively catalysed by a number of metal carbonyls, in particular $Co_2(CO)_8$ and its phosphine derivatives and various rhodium carbonyl complexes (67). In fact, hydroformylation only proceeds in the presence of metal carbonyl catalysts although some are generated *in situ* due to the high pressures of CO present. In the classical cobalt catalyzed process, many forms of cobalt may be used as the catalyst precursor, eg, $Co_2(CO)_8$, cobalt metal, Raney cobalt, and hydroxides, oxides, and carbonates. All are believed to be converted into common cobalt carbonyls and carbonylhydride complexes.

$$\mathrm{RCH{=}CH_2} + \mathrm{CO} + \mathrm{H_2} \xrightarrow{\text{catalyst}} \underset{n\text{-}}{\mathrm{RCH_2CH_2CHO}} + \underset{iso\text{-}}{\mathrm{RCH(CH_3)CHO}}$$

Scheme 5.

Although the majority of hydroformylation processes conducted by industry involve relatively simple olefin substrates, the reaction is also used to provide fine chemicals such as vitamin A (68).

Metal carbonyl complexes can function as hydrogenation catalysts (**Scheme 6**) for a wide range of substrates although it would appear that none are used in commercial processes. Supported compounds show considerable promise in this area (see below) (69).

$$\mathrm{RCH{=}CH_2} + \mathrm{H_2} \xrightarrow{\text{catalyst}} \mathrm{RCH_2CH_3}$$

Scheme 6.

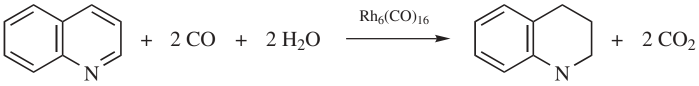
Water–Gas Shift Reaction. The conversion of carbon monoxide and water into carbon dioxide and H_2 is referred to as the water-gas shift reaction (**Scheme 7**).

$$H_2O + CO \xrightarrow{\text{catalyst}} H_2 + CO_2$$

Scheme 7.

It can be carried out using metal carbonyl catalysts to generate H_2. In the presence of alkenes, the hydrogen generated can be used to produce alkanes or aldehydes. Some of the most effective homogeneous catalysts for the water-gas shift reaction are anionic metal carbonyls. For example, $Ru_3(CO)_{12}$ forms $[HRu_3(CO)_{11}]^-$, and $[H_3Ru_4(CO)_{12}]^-$ in alkaline aqueous-alcoholic solutions under an atmospheric pressure of CO, which are highly active catalysts (70).

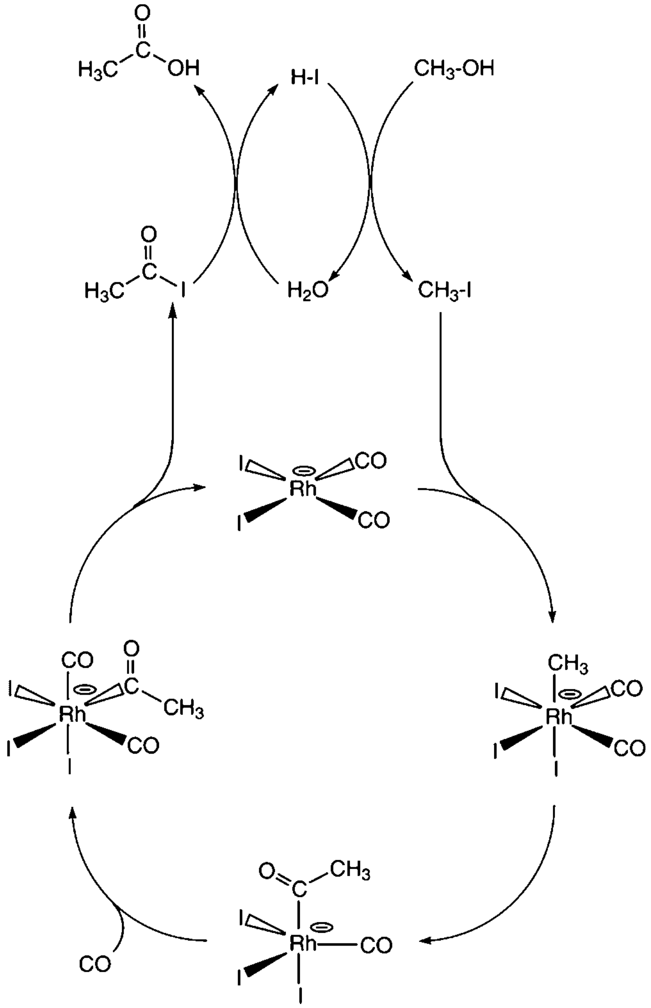
The ability to generate H_2 from water is an extremely useful process in itself, however, being able to make new organic compounds *in situ* is also highly desirable. An example of a hydrogenation reaction where this can be achieved comprises the selective hydrogenation of quinoline (see **Scheme 8**) (71). The nitrogen containing ring is hydrogenated using carbon monoxide and water in the presence of catalytic amounts of $Rh_6(CO)_{16}$.



Scheme 8.

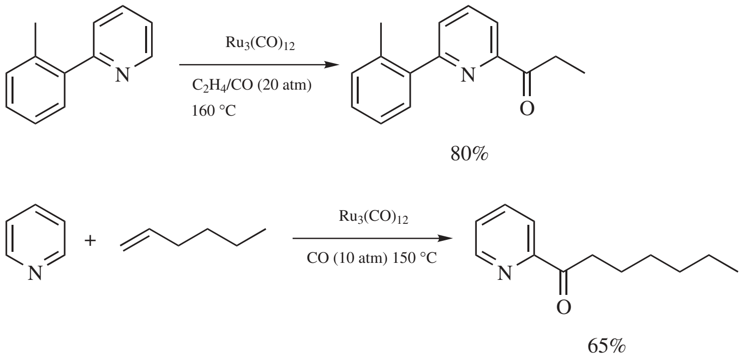
An example of hydroformylation using water as the source of H_2 employed on an industrial scale is the conversion of propene to butanol. The process is known as the Reppe synthesis. The reaction uses iron carbonyls as the catalysts and while species such as $[HFe_3(CO)_{11}]^-$ have been isolated from the reaction, the active catalysts is believed to be the mononuclear species $[HFe(CO)_4]^-$ (72).

The insertion of carbon monoxide into the C–O bond in methanol yields acetic acid. This process is catalyzed by rhodium (Monsanto process) and iridium (Cativa process) carbonyl complexes (73). The proposed catalytic cycle for the Monsanto process is shown in **Scheme 9**.



Scheme 9.

Other Reactions Catalyzed by Metal Carbonyls. Many other reactions can be catalyzed by metal carbonyl compounds. For example, $Ru_3(CO)_{12}$ is currently finding many new uses in highly regioselective catalyzed processes and the activity of $Ru_3(CO)_{12}$ in these reactions is unique. Two examples are displayed in **Scheme 10** (74).



Scheme 10.

Supported Metal Carbonyl Catalysts. Metal carbonyl catalysts may be attached to solid supports which, in principle, facilitates their separation from the reactions products, which can be a problem with homogeneously catalyzed reactions (75). In some instances, the molecular compounds are used as a source of metal nanoparticles and in general the smaller the nanoparticle the larger the fraction of metal atoms that are exposed at the surface and therefore able to participate in catalysis. It has been found that supports containing tiny groups of metal atoms can be prepared by depositing a metal carbonyl on the support and then convert it to a metal particle, usually by heating at a high temperature to drive off all the ligands (76). These naked metal particles are generally preferred to actual tethered molecular compounds as they are more robust and strongly bound to the support and can therefore be reused indefinitely.

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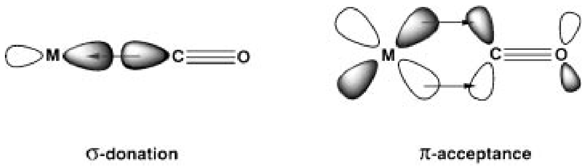


Fig. 1. The two components of the metal-carbonyl bond.

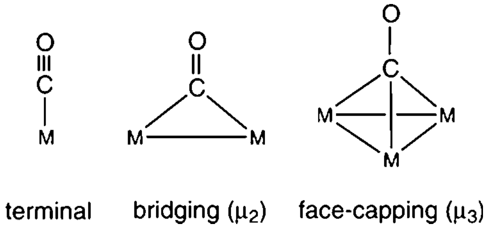


Fig. 2. Common bonding modes of the carbonyl ligand.

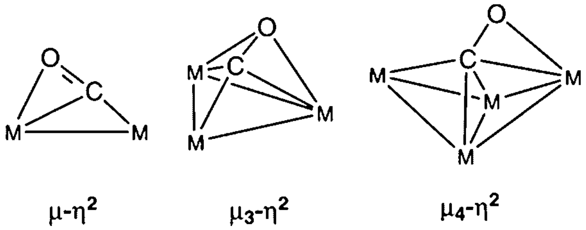


Fig. 3. Unusual bonding modes of the carbonyl ligand.

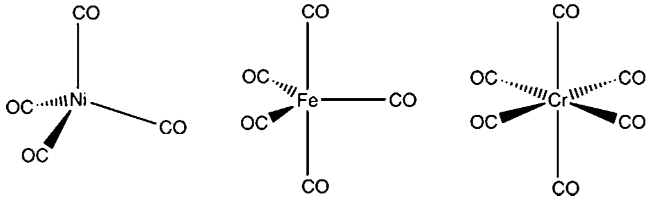


Fig. 4. The structures of nickel tetracarbonyl, iron pentacarbonyl and chromium hexacarbonyl.

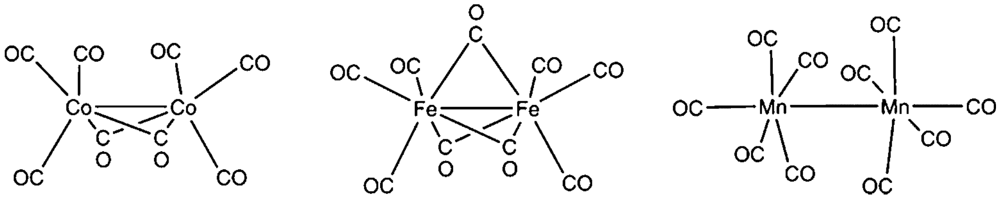
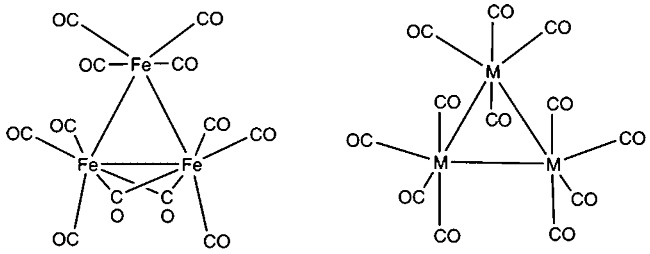
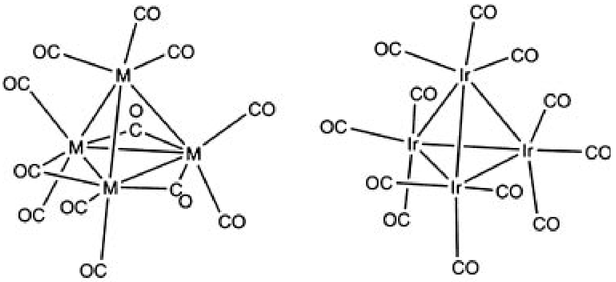


Fig. 5. The structures of dicobalt octacarbonyl, diiron nonacarbonyl and dimanganese decacarbonyl.



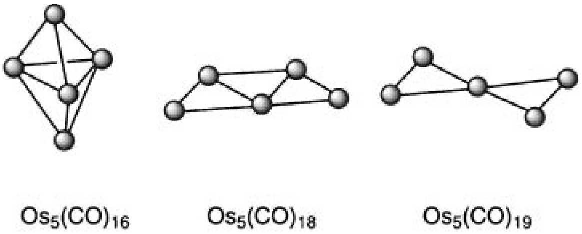
(M = Ru or Os)

Fig. 6. The structures of triiron dodecacarbonyl and triruthenium (and triosmium) dodecacarbonyl.



(M = Co or Rh)

Fig. 7. The structures of tetracobalt (or tetrarhodium) dodecacarbonyl and tetrairidium dodecacarbonyl.



$Os_5(CO)_{16}$ $Os_5(CO)_{18}$ $Os_5(CO)_{19}$

Fig. 8. The metal cores of some pentaosmium carbonyl clusters. Carbonyl ligands have been omitted for clarity.

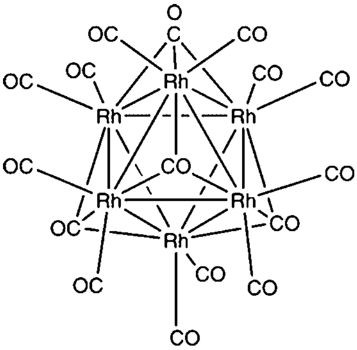


Fig. 9. The structure of hexarhodium hexadecacarbonyl.

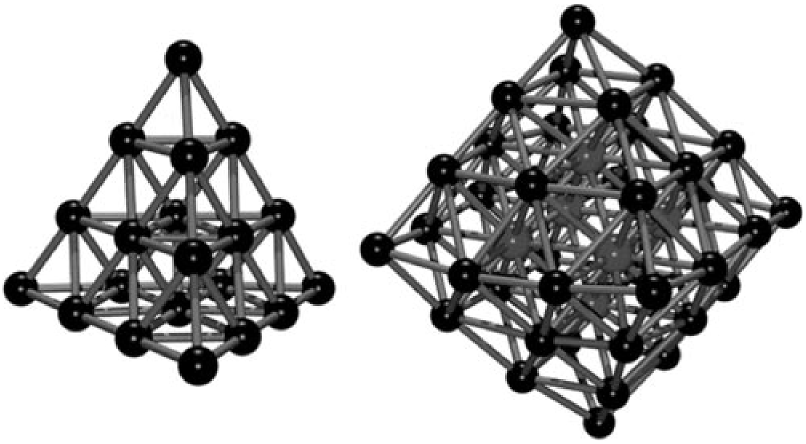
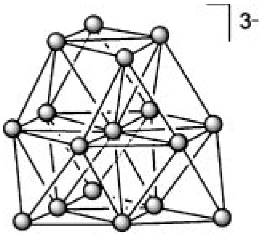


Fig. 10. The metal cores of $[Os_{20}(CO)_{40}]^{2-}$ and $[Ni_{38}Pt_6(CO)_{48}]^{5-}$. Carbonyl ligands have been omitted for clarity.



$[Rh_{17}(CO)_{30}]^{3-}$

Fig. 11. The metal core of $[Rh_{17}(CO)_{30}]^{3-}$. Carbonyl ligands have been omitted for clarity.

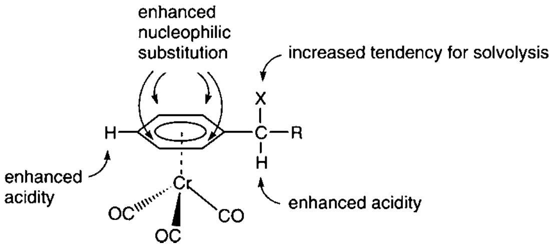


Fig. 12. Modification of arene reactivity due to coordination to chromium tricarbonyl.

Table 1. **Physical Properties of Metal Carbonyls**

Name	Molecular formula	CAS Registry Number	Color (solid)	Melting point, °C	Boiling point, °C^{a}	M–M distances, pm	References
vanadium hexacarbonyl	$V(CO)_6$	[14024-00-1]	blue-green	50 dec	$40–50^{2}$ sub		56
chromium hexacarbonyl	$Cr(CO)_6$	[13007-92-6]	white	149–155	$70–75^{2}$ sub		57
molybdenum hexacarbonyl	$Mo(CO)_6$	[13939-06-5]	white	150–151 dec			57
tungsten hexacarbonyl	$W(CO)_6$	[14040-11-0]	white	169–170	50 sub		57
dimanganese decacarbonyl	$Mn_2(CO)_{10}$	[10170-69-1]	yellow	151–155	$50^{0.001}$ sub	0.293	58
ditechnectium decacarbonyl	$Tc_2(CO)_{10}$	[14837-15-1]	white	159–160	$40^{0.001}$ sub	0.3036	59
dirhenium decacarbonyl	$Re_2(CO)_{10}$	[14285-68-8]	white	177	$60^{0.001}$ sub	0.302	58
iron pentacarbonyl	$Fe(CO)_5$	[13463-40-6]	white	−20	103		(60–62)
diiron nonacarbonyl	$Fe_2(CO)_9$	[15321-51-4]	yellow	100 dec		0.2523	63
triiron dodecacarbonyl	$Fe_3(CO)_{12}$	[12088-65-2]	green-black	140 dec	$60^{0.01}$ sub	0.263^{b}	(64,65)
triruthenium dodecacarbonyl	$Ru_3(CO)_{12}$	[15243-33-1]	orange	150 dec		0.2848	66
triosmium dodecacarbonyl	$Os_3(CO)_{12}$	[15696-40-9]	yellow	224		0.288	(67,68)
dicobalt octacarbonyl	$Co_2(CO)_8$	[10210-68-1]	orange	50–51	$45^{0.1}$ sub	0.2542	69
tetracobalt tri-μ-carbonylnonacarbonyl	$Co_4(CO)_{12}$	[17786-31-1]	black	60 dec		0.249	(70,71)
tetrarhodium tri-μ-carbonylnonacarbonyl	$Rh_4(CO)_{12}$	[19584-30-6]	red	dec		0.275^{b}	(71,72)
hexarhodium hexadecacarbonyl	$Rh_6(CO)_{16}$	[28407-51-4]	black	220 dec		0.2776	43
tetrairidium dodecacarbonyl	$Ir_4(CO)_{12}$	[11065-24-0]	yellow	210 dec		0.268	73
nickel tetracarbonyl	$Ni(CO)_4$	[13463-39-3]	white	−25	43		74

[a] Bp is at 101.3 kPa unless otherwise noted in superscript. To convert kPa to torr, multiply by 7.5.

[b] Value given is average value.

Table 2. **Metal Carbonyls by Inhalation, 30 min. LC_{50} Values for Rats**[a]

Metal carbonyl	Carbonyl, mg/m^3	Metal, mg/m^3	Toxicity relative to $Ni(CO)_4$	Reference
$Ni(CO)_4$	240	85	1	186
$HCo(CO)_4$	560	165	0.52	186
$Fe(CO)_5$	910	260	0.33	187
	2190	625 (mice)	0.14	187
$Co_2(CO)_8$	1400[b]	480[b]	0.17	188

[a] Ref. 61.

[b] A concentration that for 60 min resulted in no toxic signs.