

METAL CARBONYLS

Carbon monoxide, 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 and actinides, although often in combination with other ligands.

Carbonyls are involved in the preparation of high purity metals as in the Mond process for the extraction of nickel from its ores, 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. 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.

BONDING AND STRUCTURE OF METAL CARBONYLS

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. The C–O bond is weakened, and this is manifested most strongly in the CO stretching frequency observed using infrared (ir) spectroscopy.

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

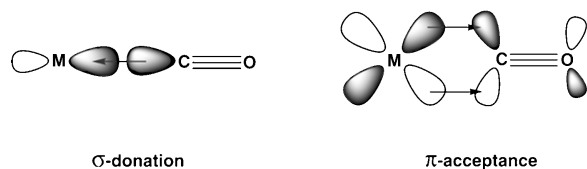


Figure 1. The two components of the metal-carbonyl bond.

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*, 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.

Structure

Mononuclear Carbonyls. 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*.

Many thermally stable (though generally air- and moisture-sensitive) anionic 18-electron species are known. A variety of highly reduced metal carbonyls has also been characterized. Similarly, a large number of metal carbonyls in positive oxidation states are also known. The more highly oxidised species are generally prepared in superacid media.

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. 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.

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 deltahehtra, Δ , for triangular. Very large clusters often take the form of fragments of a close-packed lattice of metal atoms.

PHYSICAL PROPERTIES OF METAL CARBONYLS

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

PREPARATION

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.

More frequently, metal carbonyls are prepared in solvents. Metal carbonyls that are synthesized in nonaqueous media often use reactive metals, such as sodium, magnesium, zinc, and aluminium, as reducing agents. Again, in some cases CO itself is the reducing agent. The majority of metal carbonyls are synthesized under medium pressures of CO. In general, the most recent and simplest methods used to prepare metal carbonyls are described in the series *Inorganic Syntheses*.

Synthesis of High Nuclearity Metal Carbonyls from Salts

A few high nuclearity carbonyl clusters can be made directly from salts.

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.

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.

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.

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. The addition of mercury salts to anionic metal carbonyl complexes or clusters often results in the formation higher nuclearity compounds. Mercury usually

Table 1. Physical Properties of Metal Carbonyls

| Name | Molecular formula | Color (solid) | Melting point, °C | Boiling point, °C ^a | M–M distances, pm |
|---|------------------------------------|---------------|-------------------|--------------------------------|--------------------|
| vanadium hexacarbonyl | V(CO) ₆ | blue-green | 50 dec | 40–50 ² sub | |
| chromium hexacarbonyl | Cr(CO) ₆ | white | 149–155 | 70–75 ² sub | |
| molybdenum hexacarbonyl | Mo(CO) ₆ | white | 150–151 dec | | |
| tungsten hexacarbonyl | W(CO) ₆ | white | 169–170 | 50 sub | |
| dimanganese decacarbonyl | Mn ₂ (CO) ₁₀ | yellow | 151–155 | 50 ^{0.001} sub | 0.293 |
| ditechnetium decacarbonyl | Tc ₂ (CO) ₁₀ | white | 159–160 | 40 ^{0.001} sub | 0.3036 |
| dirhenium decacarbonyl | Re ₂ (CO) ₁₀ | white | 177 | 60 ^{0.001} sub | 0.302 |
| iron pentacarbonyl | Fe(CO) ₅ | white | –20 | 103 | |
| diiron nonacarbonyl | Fe ₂ (CO) ₉ | yellow | 100 dec | | 0.2523 |
| triiron dodecacarbonyl | Fe ₃ (CO) ₁₂ | green-black | 140 dec | 60 ^{0.01} sub | 0.263 ^b |
| triruthenium dodecacarbonyl | Ru ₃ (CO) ₁₂ | orange | 150 dec | | 0.2848 |
| triosmium dodecacarbonyl | Os ₃ (CO) ₁₂ | yellow | 224 | | 0.288 |
| dicobalt octacarbonyl | Co ₂ (CO) ₈ | orange | 50–51 | 45 ^{0.1} sub | 0.2542 |
| tetracobalt tri- μ -carbonylnonacarbonyl | Co ₄ (CO) ₁₂ | black | 60 dec | | 0.249 |
| tetrarhodium tri- μ -carbonylnonacarbonyl | Rh ₄ (CO) ₁₂ | red | dec | | 0.275 ^b |
| hexarhodium hexadecacarbonyl | Rh ₆ (CO) ₁₆ | black | 220 dec | | 0.2776 |
| tetrairidium dodecacarbonyl | Ir ₄ (CO) ₁₂ | yellow | 210 dec | | 0.268 |
| nickel tetracarbonyl | Ni(CO) ₄ | white | –25 | 43 | |

^aBp is at 101.3 kPa unless otherwise noted in superscript. To convert kPa to torr, multiply by 7.5.

^bValue given is average value.

forms the core of the resulting heteronuclear cluster, holding the metallic subunits together like a "glue".

Introduction of main group metal atoms into clusters is also possible. Clusters with more than two different metal elements are also known.

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. The toxic symptoms from inhalation of nickel carbonyl are believed to be caused by both nickel metal and carbon monoxide.

USES

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

Metal Carbonyls in Catalysis

Metal carbonyls have been extensively studied as homogeneous catalysts and have been shown to effectively catalyze a wide range of reactions from bulk chemical products to fine chemicals. Mechanistic understanding is well developed for mononuclear metal carbonyl catalyzed 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.

Hydroformylation and Hydrogenation. Hydroformylation (or the OXO process) involves the addition of hydrogen and carbon monoxide to an unsaturated organic substrate and it is effectively catalysed by a number of metal carbonyls, in particular $\text{Co}_2(\text{CO})_8$ and its phosphine derivatives and various rhodium carbonyl complexes.

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. 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.

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.

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