

## Lecture 6. Polymeric compounds of elements of groups III and IV of the periodic system.

### *d- and f-block organometallic compounds*

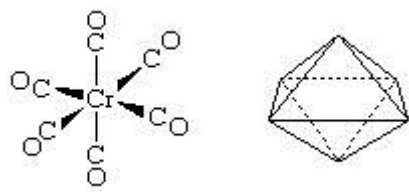
The nomenclature for organometallic compounds of the *d*-block elements, also known as transition metals, follows rules similar to those described for the main-group organometallics. Groups attached to the metal (ligands) are named first, followed by the metal. When a ligand is attached to the metal by more than one carbon atom, the number of sites of attachment is indicated by *n* in  $\eta n$ .

### **Metal carbonyls**

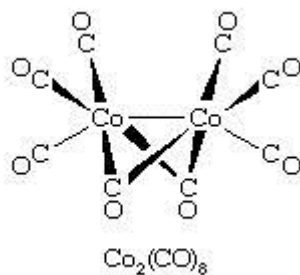
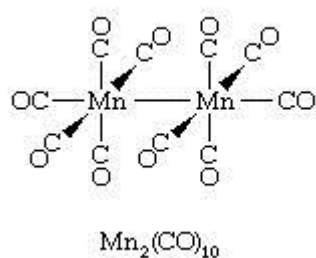
Many of the early discoveries in *d*-block organometallic chemistry involved the metal carbonyls—i.e., compounds consisting of a metal atom bonded to one or more carbon monoxide (CO) ligands. Mond's discovery of the first simple metal carbonyl, tetracarbonylnickel,  $\text{Ni}(\text{CO})_4$ , at the end of the 19th century was quickly followed by a series of discoveries in his laboratory and elsewhere showing that most of the *d*-block metals form neutral homoleptic carbonyls. (The term *homoleptic* refers to identical groups attached to a central atom.) The remarkable volatility of tetracarbonylnickel, whose boiling point is  $43\text{ }^\circ\text{C}$ , prompted one of Mond's contemporaries to state that "Mond put wings on metals." The ease of formation of tetracarbonylnickel (from metallic nickel and carbon monoxide) and its high volatility led Mond to develop an efficient industrial process for separating nickel and cobalt, which often occur together in their ores. This process requires diligent safety measures because tetracarbonylnickel is extremely toxic.

### **THE STRUCTURE OF METAL CARBONYLS**

The carbonyl ligands in the tetracarbonylnickel molecule project toward the vertices of a tetrahedron, and thus the structure is referred to as tetrahedral. Similarly, the six carbonyl ligands in hexacarbonylchromium project toward the vertices of an octahedron.



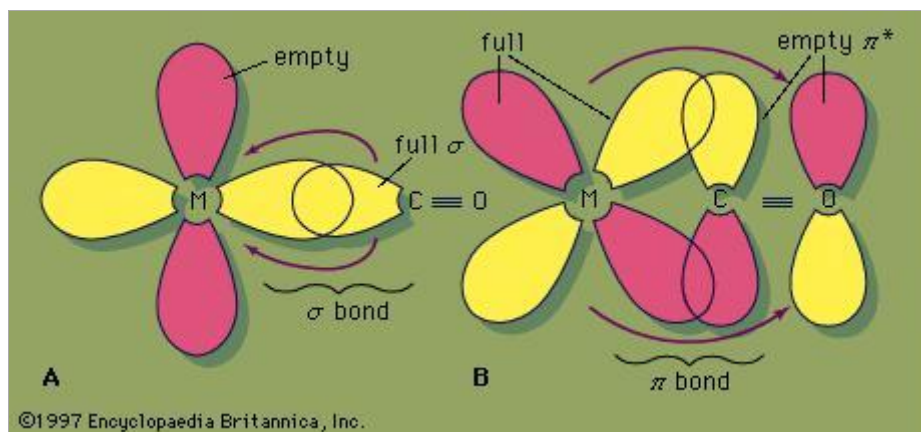
Many other metal carbonyls contain two or more metal atoms, such as decacarbonyldimanganese and octacarbonyldicobalt, shown here.



In all these structures carbon monoxide is connected to the metal through its carbon atom. When more than one metal atom is present, as in octacarbonyldicobalt, the carbon of the carbonyl ligand may bridge between metal atoms.

The formulas of most homoleptic metal carbonyl compounds conform to the rule that each metal atom in the metal carbonyl molecule must have 18 valence electrons. The valence electrons represent the outer electrons on the metal plus those from the ligand. For example, the electron count for  $\text{Fe}(\text{CO})_5$  includes eight from the iron atom (it is in group 8 and hence has eight valence electrons) and two from each carbonyl ligand, giving a total of 18 electrons. This 18-electron rule applies to many organometallic compounds of the *d*-block metals other than carbonyls, but there are exceptions in the organometallic chemistry of the *d*-block metals. The most notable exceptions are metals on the far left of the *d* block (e.g.,  $\text{V}(\text{CO})_6$  contains 17 electrons) and on the right of the *d* block where the platinum metals—rhodium (Rh), iridium (Ir), palladium (Pd), and platinum (Pt)—often exhibit a 16-electron count in their organometallic compounds.

### ZERO-OXIDATION-STATE METAL CARBONYLS

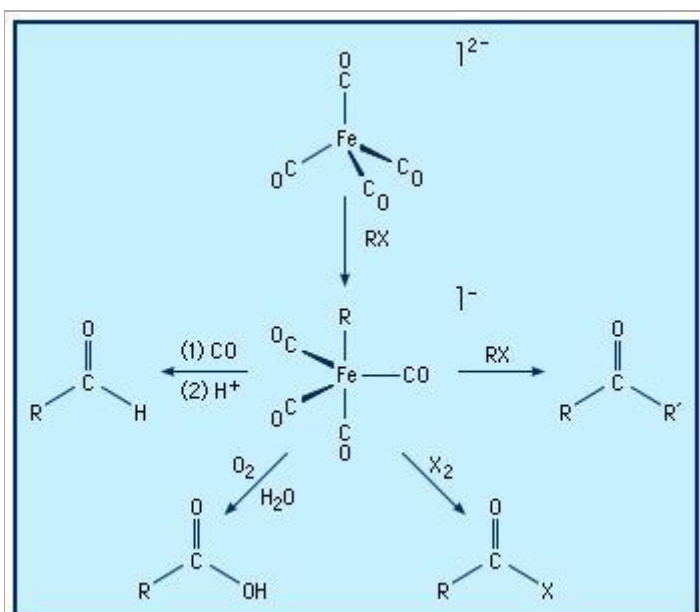


The central metal in a neutral metal carbonyl, such as those described above, is assigned an oxidation state of zero, quite unlike the case in simple inorganic compounds in which positive oxidation states are the norm, as, for example,  $\text{Fe}^{3+}$  in  $\text{FeCl}_3$  or  $\text{Ni}^{2+}$  in  $\text{NiBr}_2$ . Unlike the free metals, which also have a zero oxidation state, many carbonyls are soluble in a variety of simple organic solvents and are highly reactive. Because of these chemical and physical properties, the metal carbonyls are convenient starting materials for the synthesis of compounds with the metal atom in a zero or low oxidation state. One simple reaction is the substitution of other ligands such as

triethylphosphine,  $P(Et)_3$ , for CO (Et is a common abbreviation for the ethyl group,  $-C_2H_5$ ).  $Cr(CO)_6 + P(Et)_3 \rightarrow Cr(CO)_5P(Et)_3 + CO$  Because most other ligands are far bulkier than carbon monoxide and also because of differences in bonding properties, it is often not possible to replace all the carbonyl ligands by groups such as triethylphosphine, and a mixture of products with varying degrees of substitution can result.

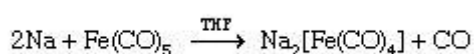
The remarkable ability of the carbonyl ligand to stabilize compounds with metals in the zero oxidation state has led to detailed studies of M–CO bonds. A minor part of the M–CO bonding can be attributed to the tendency of the carbonyl ligand to donate a pair of electrons to the metal, which is the principal mode of interaction for most ligands with metal cations in classical coordination compounds such as  $[Co(NH_3)_6]^{3+}$ . The second mode of interaction with the metal is the simultaneous back-donation of electron density from the metal to the carbonyl ligand, which is called back  $\pi$  bonding.

### METAL CARBONYL ANIONS



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More remarkable than the formation of zero-oxidation-state metal carbonyls is the reduction of many of these carbonyl compounds to metal carbonyl anions, in which the metal has a negative oxidation state. The following example demonstrates that the two-electron reduction by sodium metal is accompanied by the loss of the two-electron donor carbonyl ligand, and so the 18-electron count on iron is preserved; the solvent is tetrahydrofuran (THF).



The stabilization of very electron-rich complexes, such as  $[Fe(CO)_4]^{2-}$ , is attributed to the back  $\pi$  bonding that shifts electron density from the metal to the carbonyl ligands, and this view is substantiated by C–O bond distances and other physical data. The metal atom in these carbonyl

anions is assigned a negative oxidation state (−2 in the above example). This formalism does not acknowledge the delocalization of electron density from the metal to the ligand, but the chemical properties of the carbonyl anions do suggest that some of the negative charge resides on the metal. For example, a metal carbonyl anion can be protonated with the  $\text{H}^+$  ion, which generally attaches to the central metal and not a carbonyl ligand, as in the following example.  $[\text{Fe}(\text{CO})_4]^{2-} + \text{HCl} \rightarrow [\text{HFe}(\text{CO})_4]^- + \text{Cl}^-$

Owing to their high reactivity, carbonyl anions are useful starting materials for the synthesis of other organometallic compounds, and this accounts for their applications in organic synthesis. For example,  $[\text{Fe}(\text{CO})_4]^{2-}$  is used to extend a carbon chain by transfer of the carbonyl substituent, producing aldehydes, ketones, or carboxylic acids.

**Reference:**

<http://www.britannica.com/science/organometallic-compound#toc277970>