

Metal carbonyls of Group VI

Chromium, molybdenum and tungsten form hexacarbonyl (M(CO)₆),

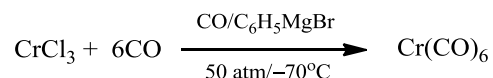
Hexacarbonylchromium, Cr(CO)₆

Chromium carbonyl, also known as **chromium hexacarbonyl**, is solid is stable to air, although it does have a high vapor pressure and sublimes readily. Cr(CO)₆ is zerovalent, meaning that Cr has an oxidation state of zero, and it is a homoleptic complex, which means that all the ligands are identical. The complex is octahedral with Cr–C and C–O distances of 1.91 and 1.14 Å, respectively.

Preparation

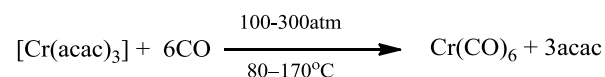
1. By Job's method from Chromium chloride

Carbon monoxide is passed through suspension of chromium chloride in ether at room temperature and 50 atm. The reaction mixture is then treated with phenyl magnesium bromide at –70°C.

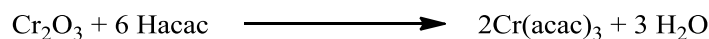


2. From Chromium chloride acetylacetonates

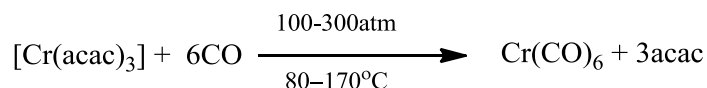
Chromium(III)acetylacetonate and chromous/chromic salts of organic acids dissolved in pyridine are treated with carbon monoxide at 100-300 atm and 80-130°C in the presence of finely powdered Zn or Mg to prepare Cr(CO)₆ in 85% yield.



Chromium(III)acetylacetonate is prepared by the reaction of **chromium(III) oxide** with **acetylacetone** (Hacac).



The chromic salt dissolved in ether is treated with CO in the presence of triethyl aluminium at high temperature and pressure to prepare Cr(CO)₆.



Structure and chemical reactivity

The structural geometry of Cr(CO)₆ is octahedral which is obtained by d²sp³ hybridization of Cr atom in zero oxidation state. As CO is strong field ligand it will pair up the electrons and inner

pair complex of octahedral geometry will be formed which is diamagnetic in nature. The nature of bond is shown in figure (a) and (b). The bond between Cr and C consists of single and double bond. Actual bond is the resonance hybrid of the structure (a) and (b) .



Hybridization scheme and formation of σ and π bond $\text{Cr}(\text{CO})_6$ is shown in fig. 1 and MO diagram is shown in fig.2

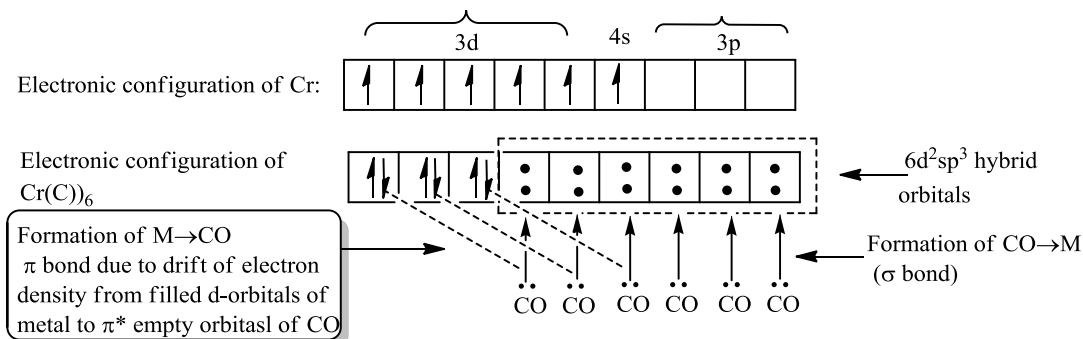


Fig.1: Hybridization scheme and formation of σ and π bond $\text{Cr}(\text{CO})_6$

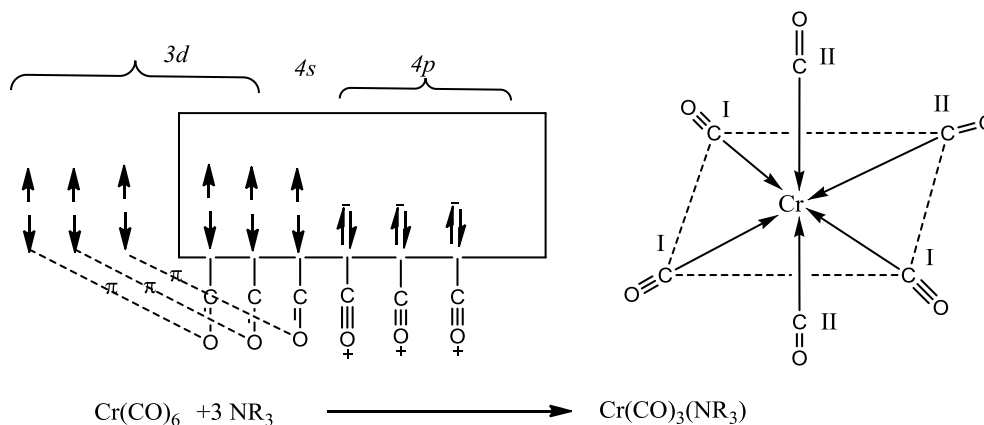
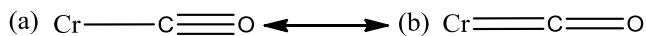


Fig.2: MO diagram $\text{Cr}(\text{CO})_6$

Six electrons are provided by Cr and 12 electrons are donated by 6CO groups. There are two types bonds between Cr and CO in $\text{Cr}(\text{CO})_6$: (a) three simple bonds $\text{Cr}-\text{CO}$ bonds and (b) double bonds $\text{Cr} = \text{CO}$. However the resultant bonds are identical due to resonance.

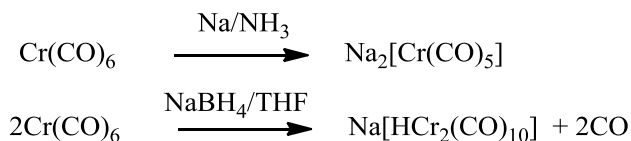


Three of the six CO groups in $\text{Cr}(\text{CO})_6$ are linked to Cr through π -bonds in addition to σ -bonds and this assumption is supported by the fact that only three CO groups in $\text{Cr}(\text{CO})_6$ (denoted as I in fig.2) are ionic and are substituted by amines as shown in fig.2.

Properties

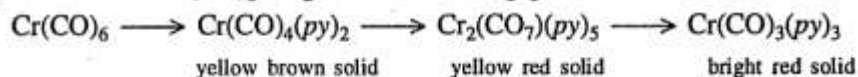
1. Chromium hexacarbonyl is white crystalline solid soluble in benzene, CCl₄ and ether. It is not attacked by cold aqueous solutions of acid and alkalis. However it reacts with conc. HNO₃
2. **Reduction of Cr(CO)₆ by alkali metals and NaBH₄**

Cr(CO)₆ is reduced by alkali metals and NaBH₄ to yield anions of chromium carbonyls.



3. It is decomposed by F₂ at - 75 C° to form [CrF₆]³⁻ or by conc.HNO₃

(vi) *Reaction with amines.* Cr(CO)₆ reacts with amines like *py*, *phen*, *en* to form the products in which CO groups in Cr(CO)₆ are replaced by molecules of the amine. For example above 140°C, *py* reacts with Cr(CO)₆ to give the following products in succession :



Molybdenum hexacarbonyl

Molybdenum hexacarbonyl (also called molybdenum carbonyl) is colorless solid, like its [chromium](#) and [tungsten](#) analogues.

Preparation

Mo(CO)₆ is prepared by the reduction of molybdenum chlorides or oxides under a pressure of carbon monoxide. The compound is somewhat air-stable and sparingly soluble in nonpolar organic solvents.

Mo(CO)₆ is a popular reagent in organometallic synthesis^[3] because one or more CO ligands can be displaced by other donor ligands.^[4] Mo(CO)₆, [Mo(CO)₃(MeCN)₃], and related derivatives are employed as catalysts in organic synthesis for example, alkyne metathesis and the Pauson–Khand reaction.

Mo(CO)₆ reacts with 2,2'-bipyridine to afford Mo(CO)₄(bipy). UV-photolysis of a THF solution of Mo(CO)₆ gives Mo(CO)₅(THF).

[Mo(CO)₄(piperidine)₂][edit]

The thermal reaction of Mo(CO)₆ with piperidine affords Mo(CO)₄(piperidine)₂. The two piperidine ligands in this yellow-colored compound are labile, which allows other ligands to be introduced under mild conditions. For instance, the reaction of [Mo(CO)₄(piperidine)₂] with triphenyl phosphine in boiling dichloromethane (b.p. ca. 40 °C) gives *cis*-[Mo(CO)₄(PPh₃)₂]. This *cis*- complex isomerizes in toluene to *trans*-[Mo(CO)₄(PPh₃)₂].^[5]

[Mo(CO)₃(MeCN)₃][edit]

Mo(CO)₆ also can be converted to its tris(acetonitrile) derivative. The compound serves as a source of "Mo(CO)₃". For instance treatment with allyl chloride gives [MoCl(allyl)(CO)₂(MeCN)₂], whereas treatment with KTp and sodium cyclopentadienide gives

$[\text{MoTp}(\text{CO})_3]^-$ and $[\text{MoCp}(\text{CO})_3]^-$ anions, respectively. These anions react with a variety of electrophiles.^[6] A related source of $\text{Mo}(\text{CO})_3$ is cycloheptatrienemolybdenum tricarbonyl.

Metal carbonyls of Group VII

Carbonyls of manganese and rhenium are well known. $\text{Mn}_2(\text{CO})_{10}$ and $\text{Re}_2(\text{CO})_{10}$ are crystalline solids.

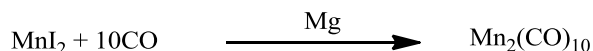
Decacarbonyldimanganese, $\text{Mn}_2(\text{CO})_{10}$

Decacarbonyldimanganese, $\text{Mn}_2(\text{CO})_{10}$ is golden yellow crystalline solid.

Preparation

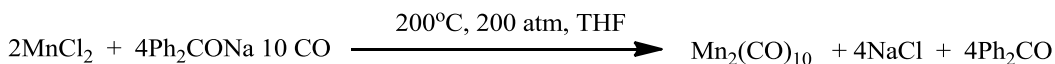
1. By reduction of MnI_2 with Mg

The compound was first prepared in low yield by the reduction of manganese iodide with magnesium under CO.



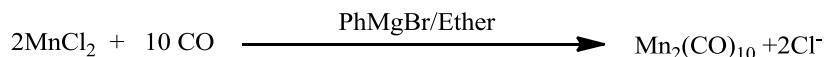
2. By reduction of MnCl_2 with Ph_2CONa

A more efficient preparation entails reduction of anhydrous MnCl_2 with sodium benzophenone under 200 atmospheres of CO. The availability of inexpensive methylcyclopentadienyl manganese tricarbonyl ("MMT") has led to a low pressure route to $\text{Mn}_2(\text{CO})_{10}$.



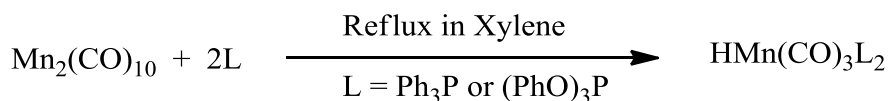
3. By reduction of MnCl_2 with PhMgBr

Reduction of MnCl_2 with PhMgBr is carried out in diethyl ether in presence of CO to get $\text{Mn}_2(\text{CO})_{10}$ in moderate yield.

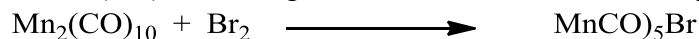


Reactivity

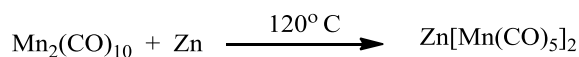
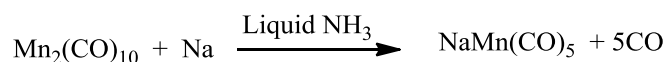
- 1) Carbonyl groups can be substituted with other ligands. The reactions can be carried under UV radiation or under reflux conditions.



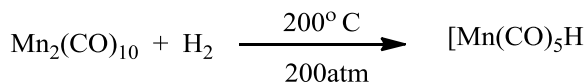
- 2) Halogens react with $\text{Mn}_2(\text{CO})_{10}$ in halogenated solvents to form carbonyl halides



- 3) $\text{Mn}_2(\text{CO})_{10}$ reacts with reducing metals such as Na, Zn, etc and it is reduced to an anion, $\text{Mn}(\text{CO})_5^-$.



- 4) Pyrrole reacts with $\text{Mn}_2(\text{CO})_{10}$ to substitute CO groups
 $\text{Mn}_2(\text{CO})_{10} + \text{C}_4\text{H}_5\text{N} \longrightarrow (\pi\text{-C}_4\text{H}_4\text{N})\text{Mn}(\text{CO})_3$
- 5) $\text{Mn}_2(\text{CO})_{10}$ reacts with hydrogen gas to give carbonylhydride in Mn is in -1 oxidation state.



Structure

The molecular structure of $\text{Mn}_2(\text{CO})_{10}$ in solution shows that it has dimeric structure. $\text{Mn}_2(\text{CO})_{10}$ has no bridging CO ligands: it can be described $(\text{CO})_5\text{Mn-Mn}(\text{CO})_5$. There are two kinds of CO ligands; one CO on each Mn is coaxial with the Mn-Mn bond (293 pm), and four on each manganese that are perpendicular to it (equatorial). In the stable rotamer, the two $\text{Mn}(\text{CO})_5$ subunits are *staggered*. The overall molecule thus belongs to the **point group** D_{4d} , which is an uncommon symmetry.

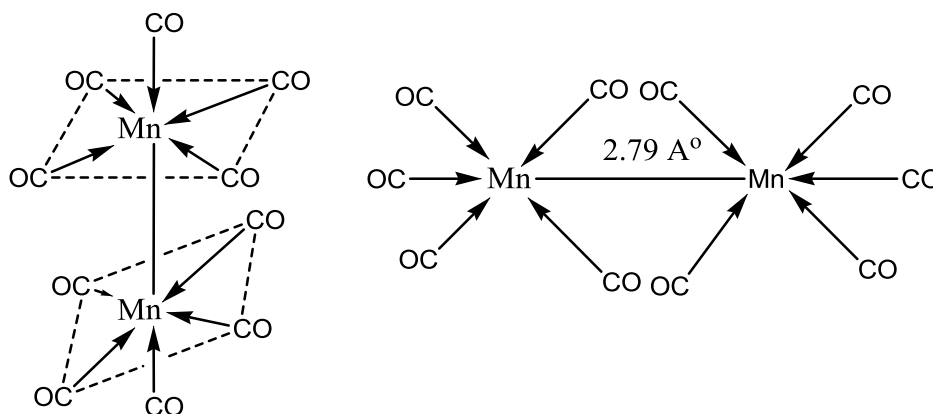


Figure: Molecular Structure

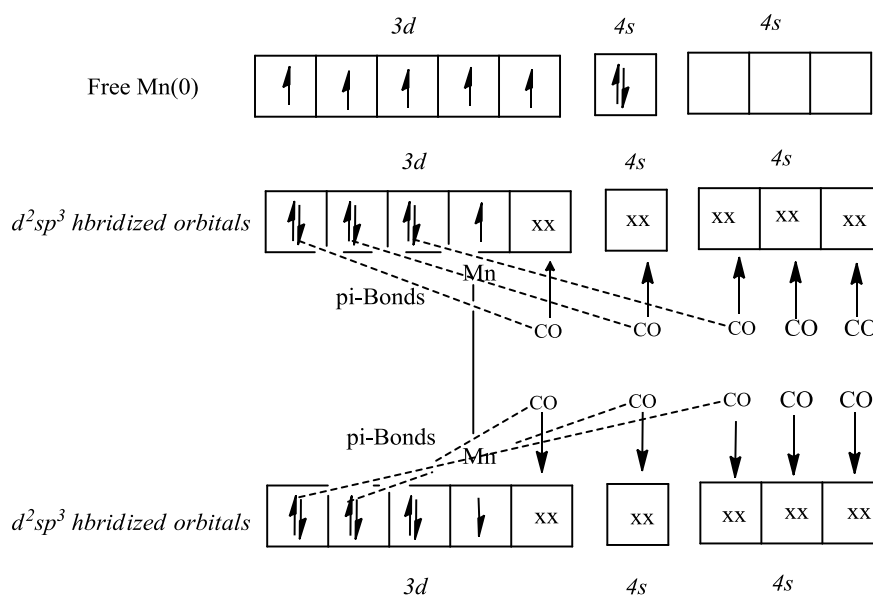


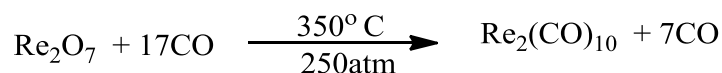
Figure: Electronic Structure of $\text{Mn}_2(\text{CO})_{10}$

Decarbonyldirhenium:

Dirhenium decacarbonyl is the [inorganic compound](#) with the chemical formula $\text{Re}_2(\text{CO})_{10}$. It is used as a starting point for the synthesis of many rhenium [carbonyl](#) complexes. It was first reported in 1941 by [Walter Hieber](#), who prepared it by reductive carbonylation of rhenium. The compound consists of a pair of [square pyramidal](#) $\text{Re}(\text{CO})_5$ units joined *via* a Re-Re bond, which produces a homoleptic carbonyl complex.

It is white crystalline solid and forms monoclinic crystals which sublimes under vacuum. It is soluble in organic solvents but less than decacarbonyldimanganese.

It is prepared by the reduction of rhenium heptoxide with CO at 250°C at 200 atm pressure.

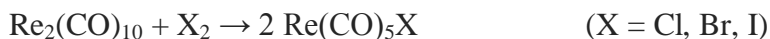


Reactivity

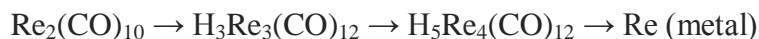
The carbonyl ligands may be displaced by other ligands such as [phosphines](#) and [phosphites](#) (denoted L).



This compound may also be "cracked" to mononuclear Re(I) carbonyl complexes by [halogenation](#):



When bromine is used, [bromopentacarbonylrhenium\(I\)](#) is formed, which is an intermediate for many more rhenium complexes. This compound may also be hydrogenated to form various polyrhenium complexes, eventually giving elemental rhenium.



In the presence of water, photolysis of $\text{Re}_2(\text{CO})_{10}$ yields a hydroxide complex:^[11]



This reaction includes the cleavage of Re-Re bond and the synthesis of $\text{HRe}(\text{CO})_5$, which can be used to prepare surface structures designed to incorporate isolated surface-bound Re carbonyl complexes.

Loss of a carbonyl ligand by photolysis generates a [coordinatively unsaturated](#) complex that undergoes [oxidative addition](#) of Si-H bonds, for example:

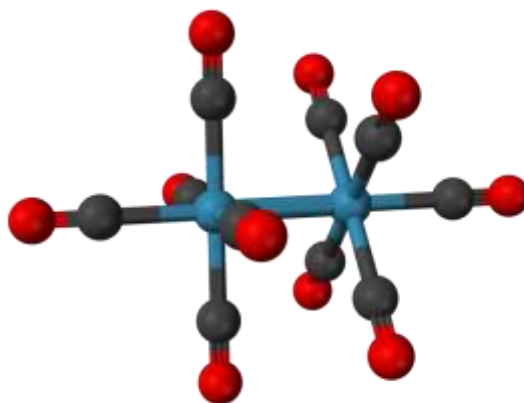


Structure

The crystal structure of $\text{Re}_2(\text{CO})_{10}$ is relatively well known. The compound consists of a pair of **square pyramidal** $\text{Re}(\text{CO})_5$ units linked by a Re-Re bond. There are two different conformations that can occur: staggered and eclipsed. The **eclipsed conformation** occurs about 30% of the time, producing a D_{4h} **point group**, but the staggered form, with point group D_{4d} , is more stable. The Re-Re bond length was experimentally found to be 3.04 Å.

The Re atom exists in a slightly distorted octahedral configuration with the C axial-Re-C equatorial angle equal to 88° . The mean Re-C bond length of 2.01 Å is the same for the **axial** and **equatorial** positions. The mean C-O distance is 1.16 Å.

This compound has a broad IR absorption band at 1800 cm^{-1} region can be assigned to two components centered at 1780 and 1830 cm^{-1} , resulting from CO adsorption. The remaining nine CO groups in $\text{Re}_2(\text{CO})_{10}$ give the complex IR absorption in the $1950\text{--}2150\text{ cm}^{-1}$ region.



Applications

Rhenium-based catalysis have been used in **metathesis**, reforming, **hydrogenation** and various hydrotreating processes such as **hydrodesulfurization**. $\text{Re}_2(\text{CO})_{10}$ can be used to promote the silylation of alcohols and prepare the **silyl ethers**, and its reaction.

