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# Metal Carbonyls: Bonding, Syntheses and Reactions

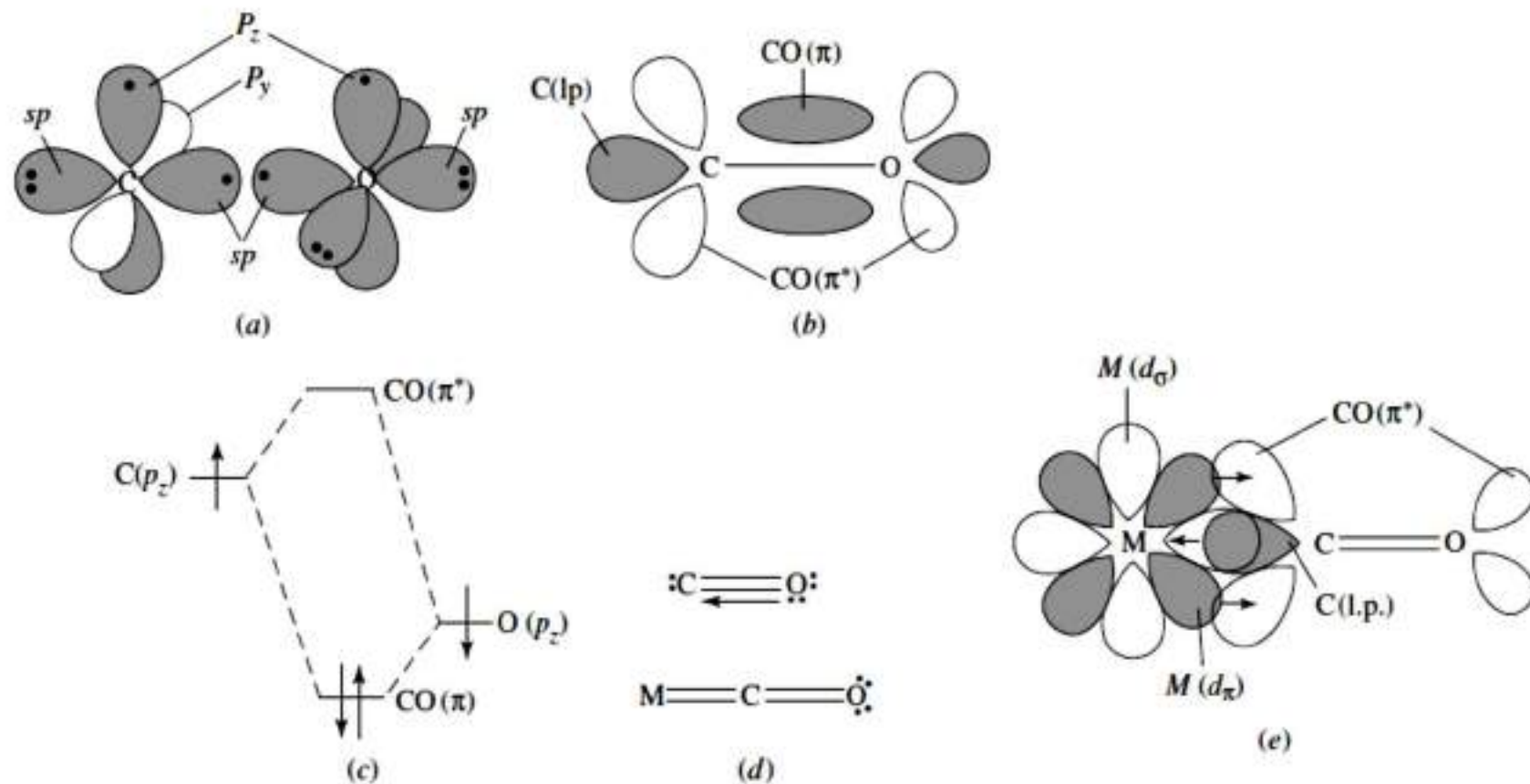
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# Historical Development

- In 1884, an experiment by Ludwig Mond led to an important advance in the nickel refining industry.
- Mond observed that his nickel valves were eaten away by CO.
- Then he deliberately heated Ni powder in a CO stream to form a volatile compound,  $\text{Ni}(\text{CO})_4$ . This was the first metal carbonyl.
- The Mond refining process was based on the fact that the carbonyl can be decomposed to give pure nickel by further heating.
- Lord Kelvin was so impressed by this result that he remarked that Mond “gave wings to nickel.”

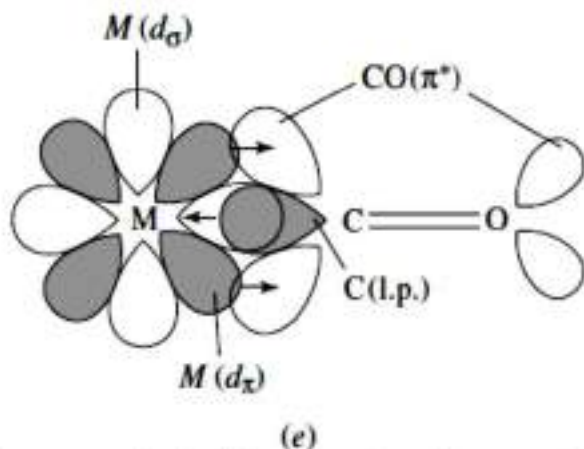
# Electronic feature

- CO is an unsaturated ligand because of the C–O multiple bond.
- such ligands are soft because they are capable of accepting metal  $d\pi$  electrons by back bonding. Hence, the CO can be regarded as the  $\pi$ -acceptor or  $\pi$ -acid ligands.
- CO can act as a spectator or an actor ligand.



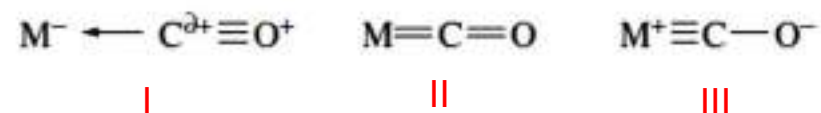
Electronic structure of CO and carbonyl complexes. Shading represents occupied orbitals (a) and (b) building up CO from C and O, each atom having two p orbitals and two  $sp$  hybrids. In (a), the dots represent the electrons occupying each orbital in the C and O atoms. In (b), only one of the two mutually perpendicular sets of  $\pi$  orbitals is shown. (c) An MO diagram showing a  $\pi$  bond of CO. (d) Valence bond representations of CO and the MCO fragment. (e)

- The electronic structure of free CO is presented in Figs. a and b.
- Both C and the O in CO are  $sp$  hybridized.
- The singly occupied  $sp$  and  $p_z$  orbitals on each atom form a  $\sigma$  and a  $\pi$  bond, respectively.
- This leaves the carbon  $p_y$  orbital empty, and the oxygen  $p_y$  orbital doubly occupied, and so the second  $\pi$  bond is formed only after we have formed a dative bond by transfer of the lone pair of O( $p_y$ ) electrons into the empty C( $p_y$ ) orbital.
- This transfer leads to a  $C^-O^+$  polarization of the molecule, which is almost exactly canceled out by a partial  $C^+O^-$  polarization of all three bonding orbitals because of the higher electronegativity of oxygen.
- The free CO molecule therefore has a net dipole moment very close to zero.
- In Fig. c the reason for the polarization of the  $\pi_z$  orbital is shown in MO terms. An orbital is always polarized so as to favor the AO that is closest in energy and so the C-O  $\pi$  MO has more O than C character.
- The valence bond picture of CO and one form of the MCO system is shown in Fig. d.



An MO picture of the MCO fragment. Again, only one of the two mutually perpendicular sets of  $\pi$  orbitals is shown.

- The metal binds to C, not O, because the ligand HOMO is the C, not the O lone pair; this is because O is more electronegative and so its orbitals have lower energy. In addition, the  $\text{CO}(\pi^*)$  LUMO is polarized toward C, and so M–CO  $\pi$  overlap will also be optimal at C not O.
- Figure e shows how the CO HOMO, the carbon lone pair, donates electrons to the metal LUMO, the empty  $\text{M}(d\sigma)$  orbital, and metal HOMO, the filled  $\text{M}(d\pi)$  orbital, back donates to the CO LUMO. While the former removes electron density from C, the latter increases electron density at both C and O because  $\text{CO}(\pi^*)$  has both C and O character.
- The result is that C becomes more positive on coordination, and O becomes more negative. This translates into a polarization of the CO on binding.

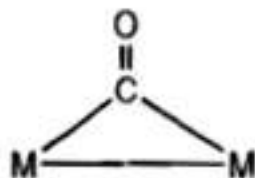


- This metal-induced polarization chemically activates the CO ligand and makes the carbon more sensitive to nucleophilic and the oxygen more sensitive towards electrophilic attack.
- It must be noted that the polarization will be modulated by the electronic effect of the other ligands on the metal as well as by the net charge on the complex.
- In  $L_nM(\text{CO})$ , the CO carbon becomes particularly  $\delta^+$  in character if the L groups are good  $\pi$  acids or if the complex is cationic (e.g.,  $\text{Mo}(\text{CO})_6$  or  $[\text{Mn}(\text{CO})_6]^+$ ), because the CO-to-metal  $\sigma$ -donor electron transfer will be enhanced at the expense of the metal to CO back donation. If the L groups are good donors or the complex is anionic (e.g.,  $\text{Cp}_2\text{W}(\text{CO})$  or  $[\text{W}(\text{CO})_5]^{2-}$ ), back donation will be encouraged, the CO carbon will lose its pronounced  $\delta^+$  charge, but the CO oxygen will become significantly  $\delta^-$ . The range can be represented in valence bond terms as I, the extreme in which CO acts as a pure  $\sigma$  donor, through II and III, the extreme in which both the  $\pi^*$  and  $\pi^*$  are both fully engaged in back bonding.
- Neither extreme is reached in practice, but each can be considered to contribute differently to the real structure in accordance to the circumstances.

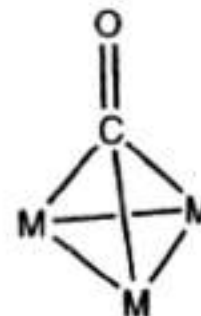
# Different Bonding Modes



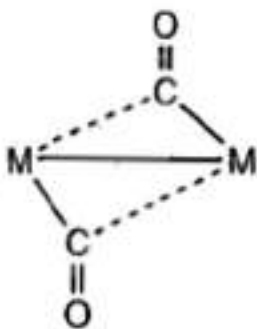
terminal  
 $\nu_{\text{CO}} 2120\text{--}1850 \text{ cm}^{-1}$



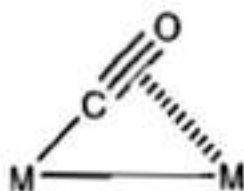
bridging  $\mu_2$   
 $1850\text{--}1700 \text{ cm}^{-1}$



bridging  $\mu_3$   
 $1730\text{--}1620 \text{ cm}^{-1}$



semibridging



$\sigma/\pi$  asymmetric bridge

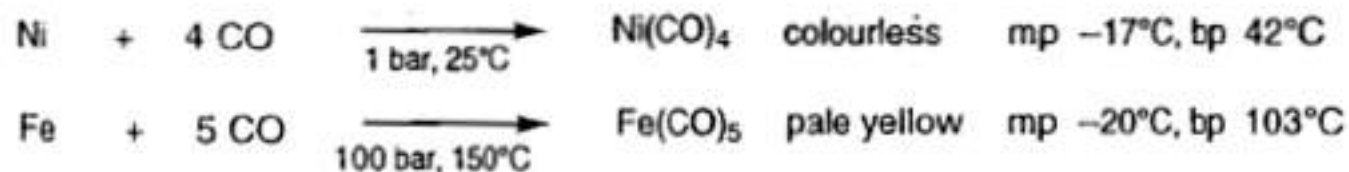


isocarbonyl coordination

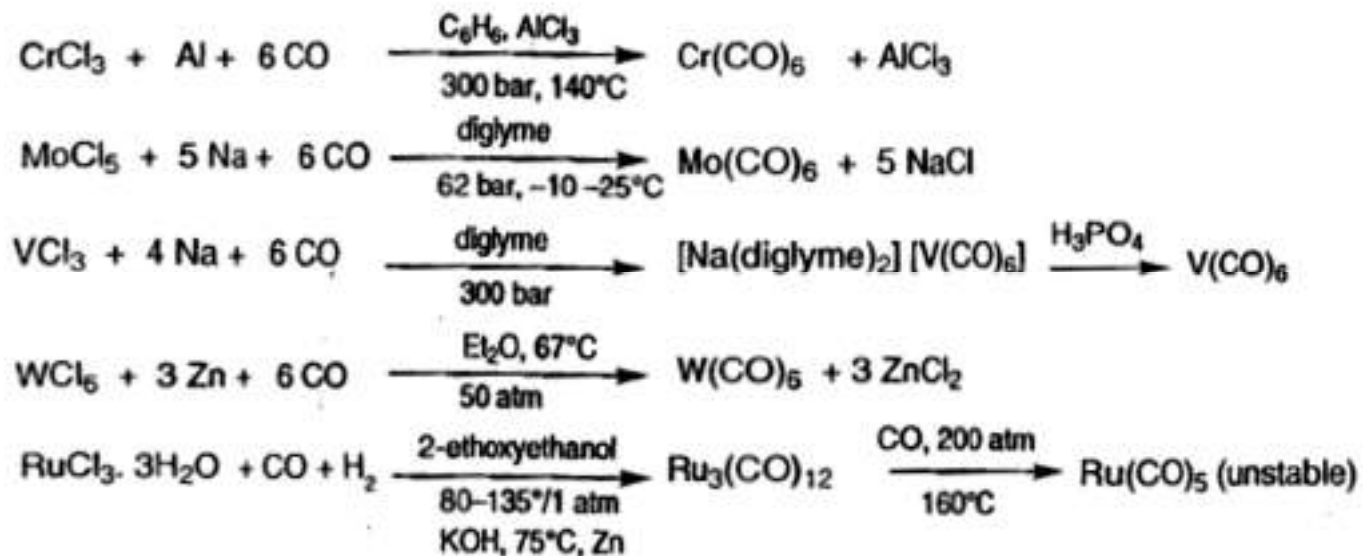


# Syntheses

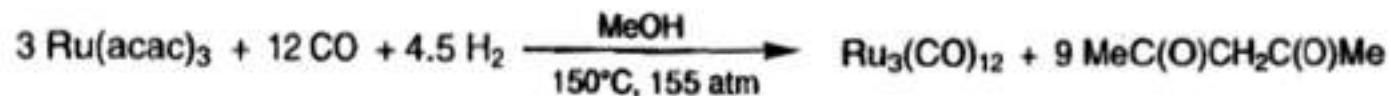
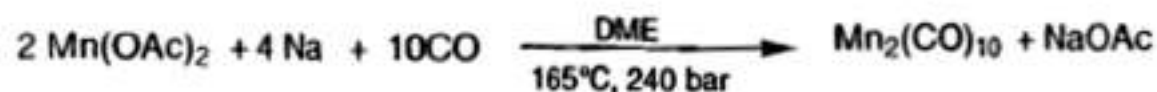
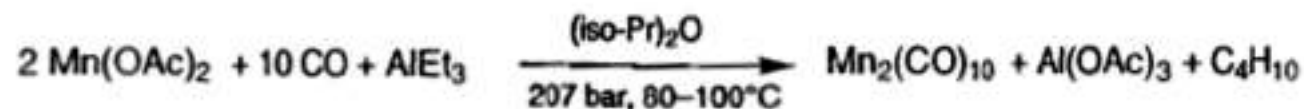
- Direct Carbonylation



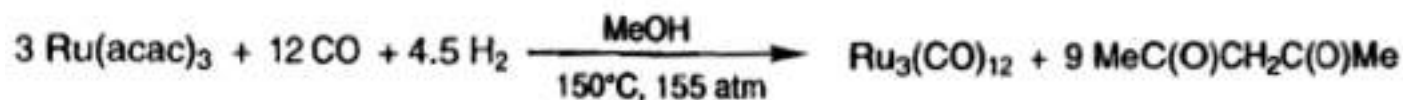
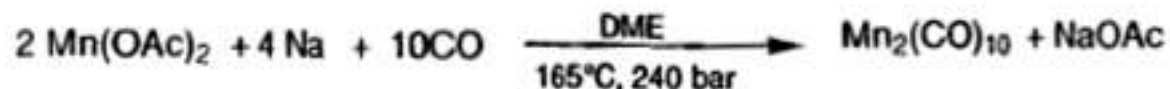
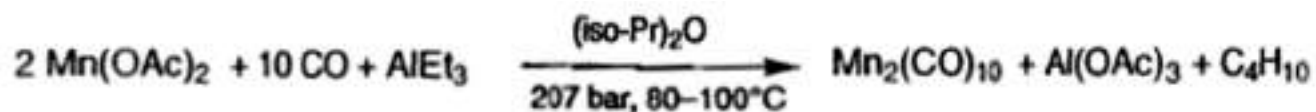
- Reductive Carbonylation



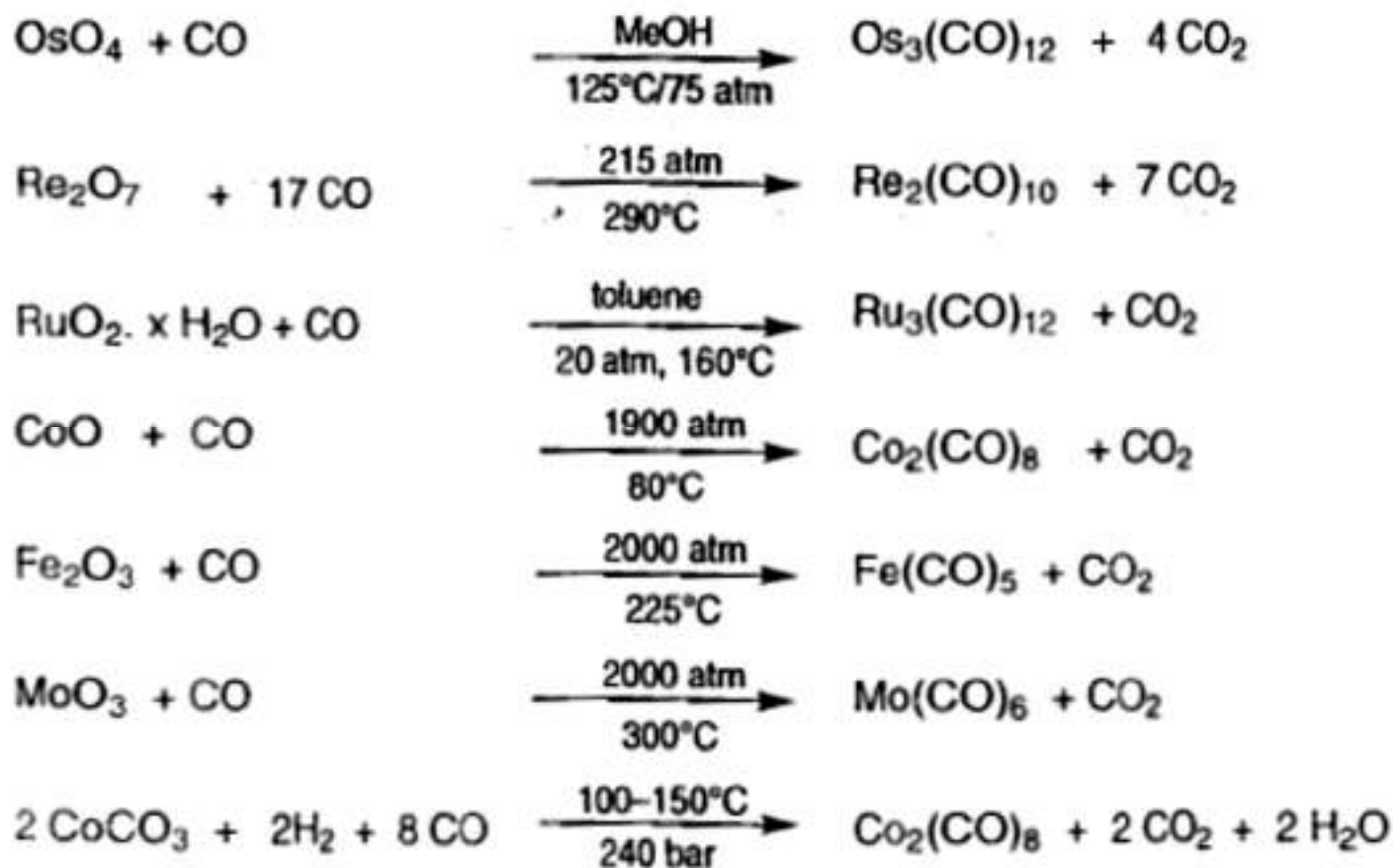
# Syntheses Continued



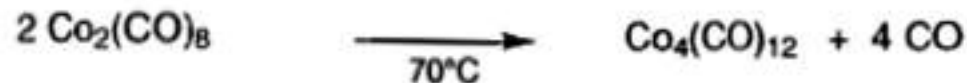
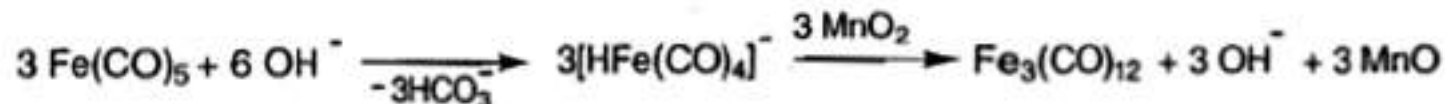
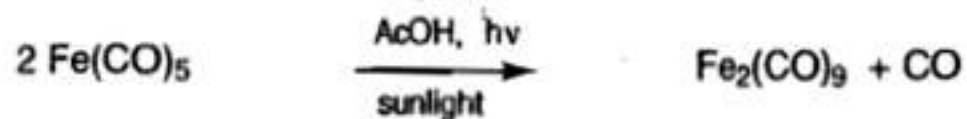
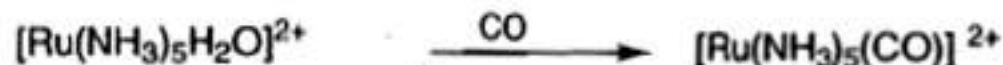
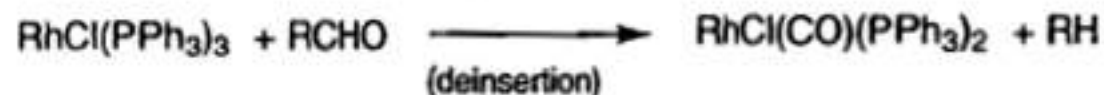
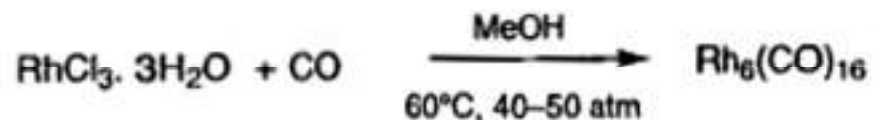
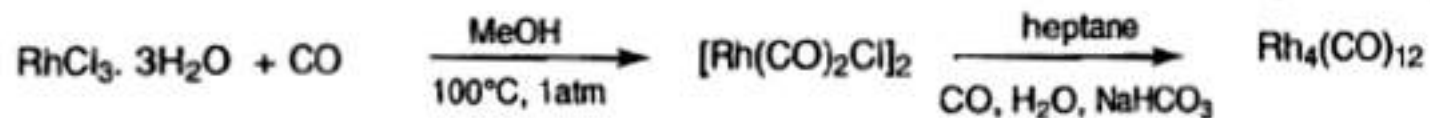
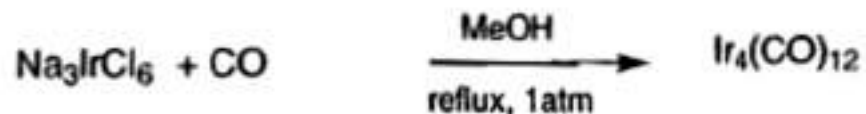
Reductive carbonylation is utilized for the syntheses of binary metal carbonyls. To execute these reactions with metal halides or acetates the reducing agents viz. Aluminium, sodium, zinc, trialkylaluminium and Grignard reagents are used alongwith CO at elevated temperature and pressure.



When instead of metal chlorides or acetates, metal oxides are used the CO ligand itself act as the reducing agents. But in these cases the reaction conditions are more drastic.



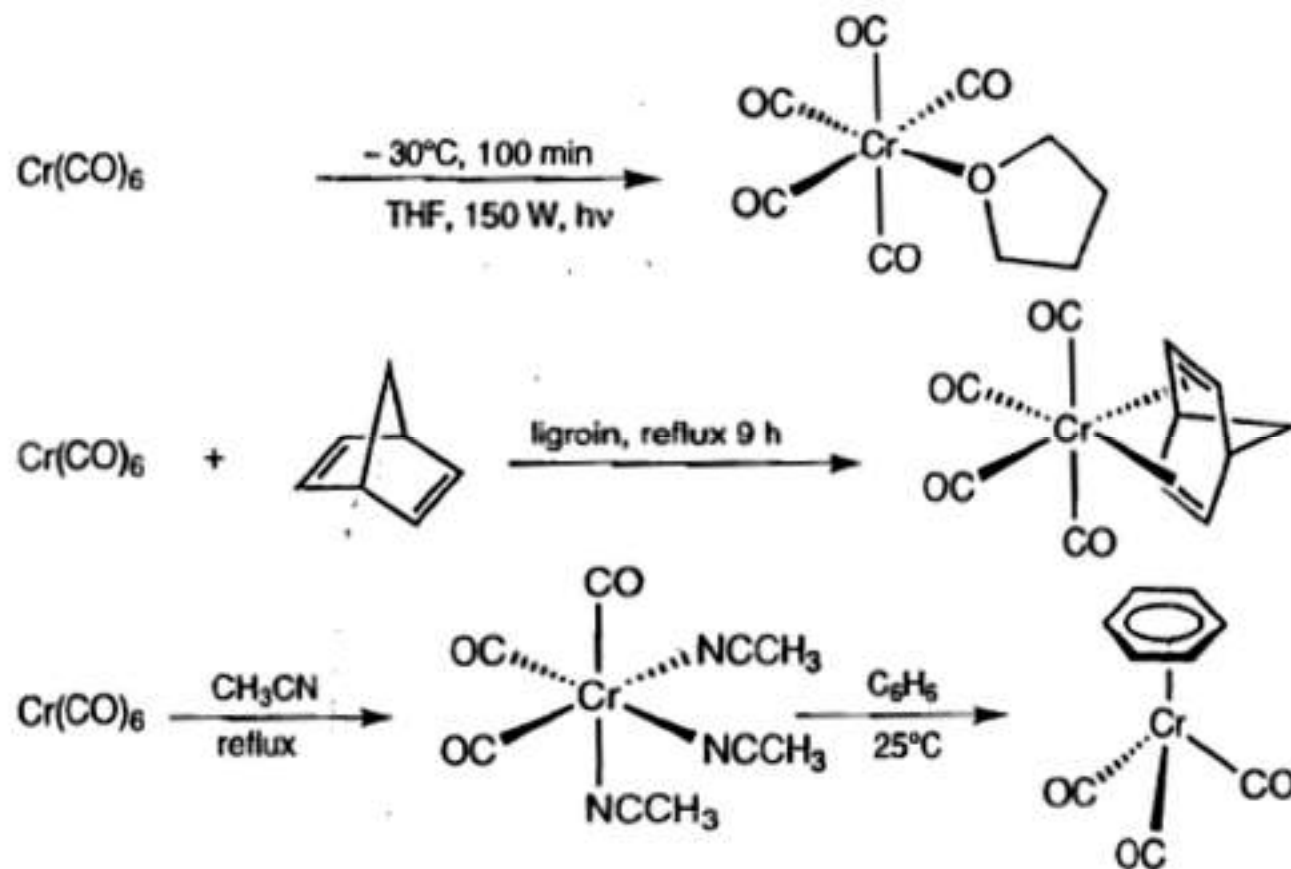
# Miscellaneous Reactions



# Reactions of Metal Carbonyls

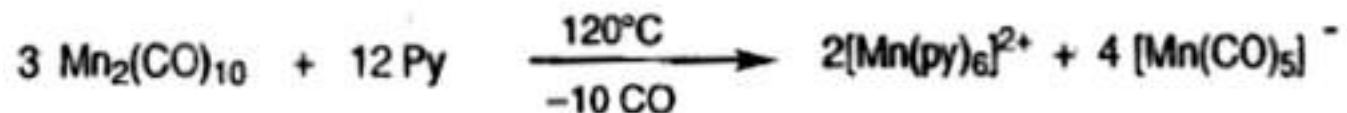
- The 16 or 17 electron containing metal carbonyl can react by an associative mechanism and these reactions are much faster than the reactions taking place in 18 electron metal carbonyls which proceeds by dissociative mechanism.
- The common reactions are
  - Substitution of carbonyl groups under thermal and photochemical conditions
  - Disproportionation
  - Oxidative decarbonylation
  - Reduction
  - Addition of nucleophiles on the CO

# Activation of Metal carbonyls

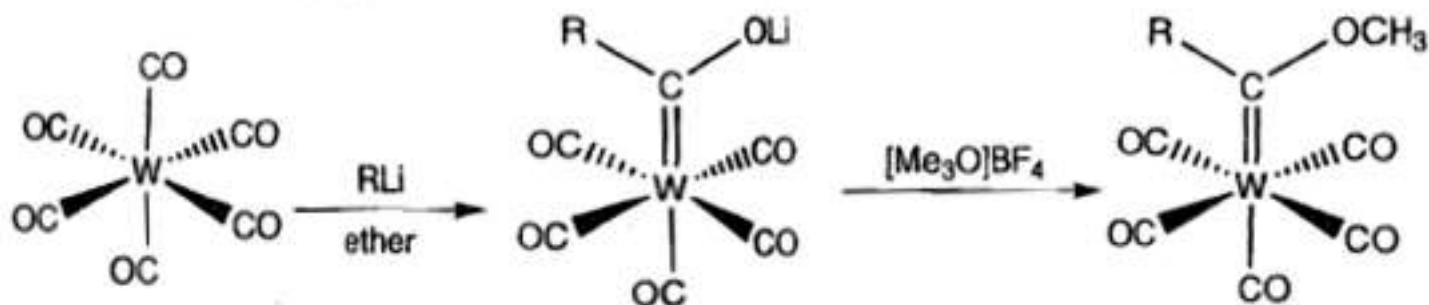


The complete substitution of all the CO groups is rarely achieved. Lewis bases, olefins, arenes are some ligands which can be substituted on metal carbonyls under thermal conditions.

- Disproportionation



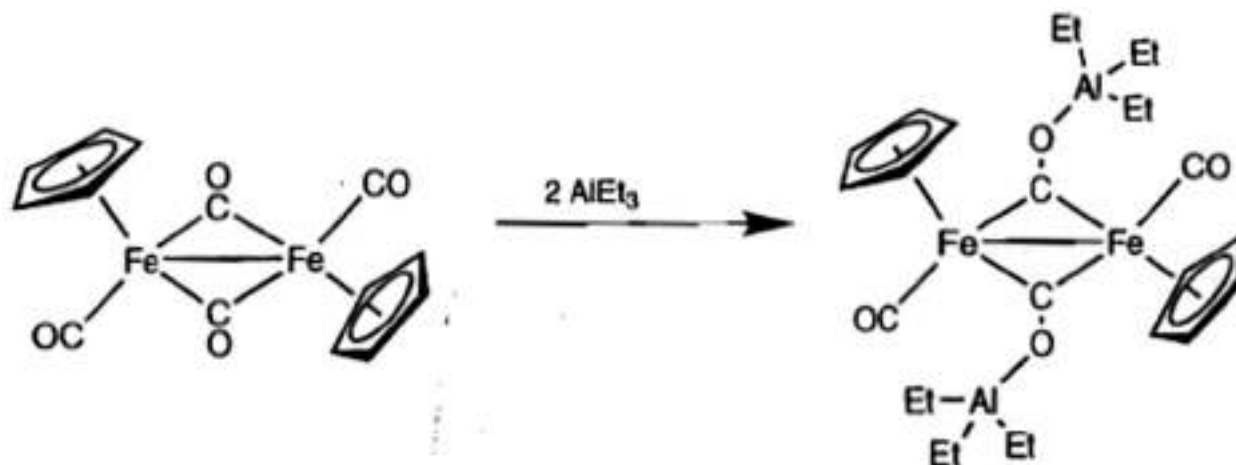
- Nucleophilic addition to carbonyls (Hieber Base Reaction)



**Fischer Carbene**

It leads to the formation of Fischer Carbene which can be prepared by the addition of alkyl lithium to the metal carbonyls with subsequent methylation.

- Electrophilic addition



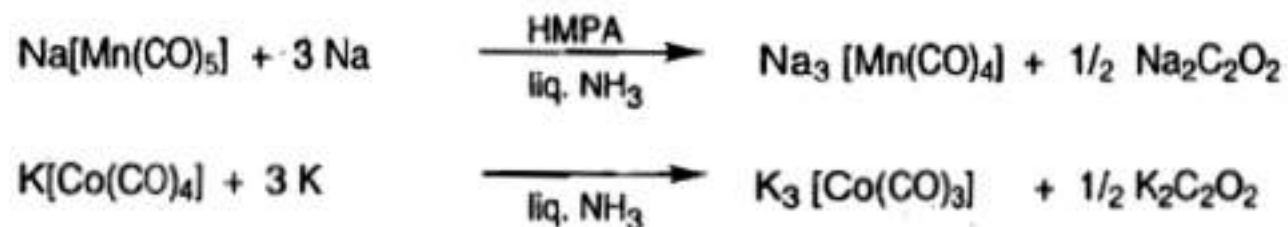
- Carbo While reduction with common reducing agents such as Na amalgam results in mono- or dianionic species, with strong reducing agents such as Na/liq. NH<sub>3</sub> or Na/HMPA, they can be further reduced with the formal oxidation states of the metal reaching even -4.



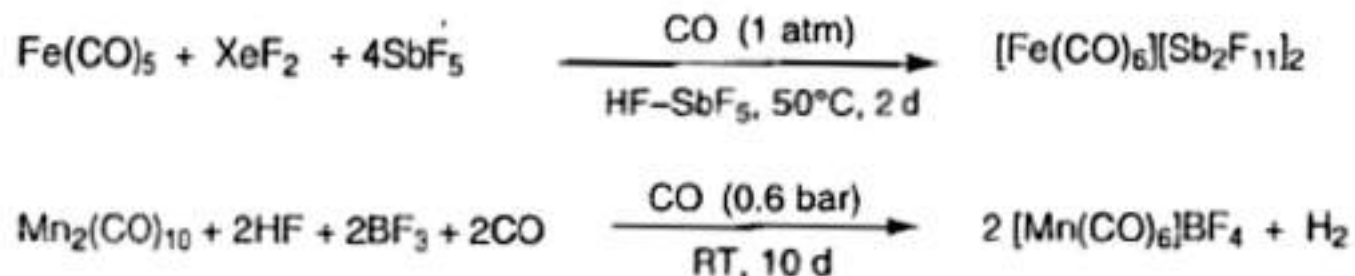
Reduction with common reducing agents viz. Na:Hg results in mono- or dianionic species



- Strong reducing agents like Na/liquid NH<sub>3</sub>, Na/HMPA the mono- and dianionic species can be further reduced having formal oxidation states on the metal reaching upto -4.



- Carbonyl cations are prepared through oxidative carbonylation. Lewis acids in HF (anhydrous) or superacids like HF-SbF<sub>5</sub> in addition to external oxidizing agents can yield metal carbonyl cations

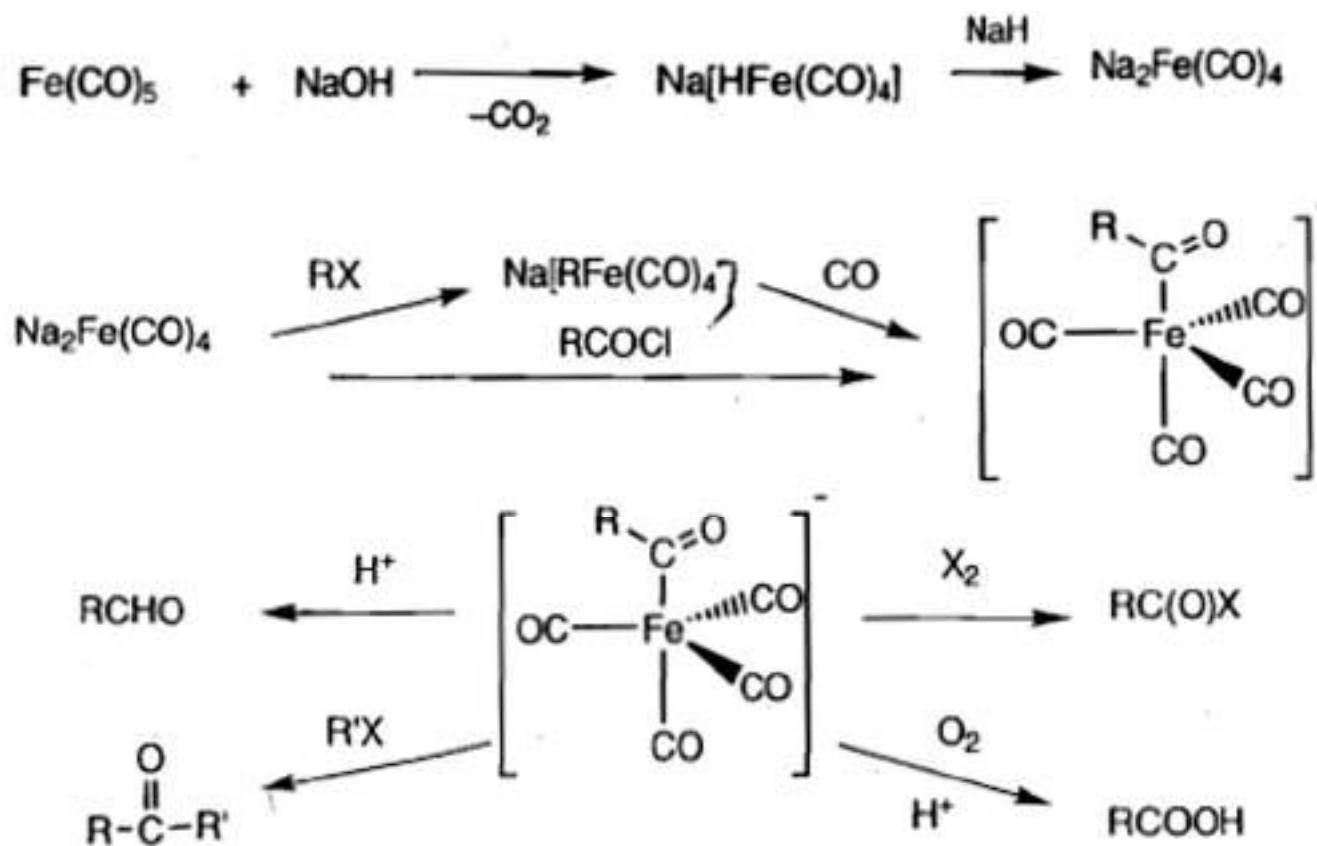


# Carbonyl Hydrides

Methods of synthesis		pKa	Comparable acidity	
$[\text{Co}(\text{CO})_4]^- + \text{H}^+$	$\longrightarrow$	$\text{HCo}(\text{CO})_4$	1	HCl
$\text{I}_2\text{Fe}(\text{CO})_4 + \text{NaBH}_4$	$\xrightarrow[150^\circ\text{C}]{200 \text{ bar}}$	$\text{H}_2\text{Fe}(\text{CO})_4$	4.7	$\text{CH}_3\text{COOH}$
$\text{Mn}_2(\text{CO})_{10} + \text{H}_2$	$\longrightarrow$	$2\text{HMn}(\text{CO})_5$	7	$\text{H}_2\text{S}$
$\text{Fe}(\text{CO})_5 + \text{OH}^-$	$\longrightarrow$	$[\text{HFe}(\text{CO})_4]^-$	14	$\text{H}_2\text{O}$

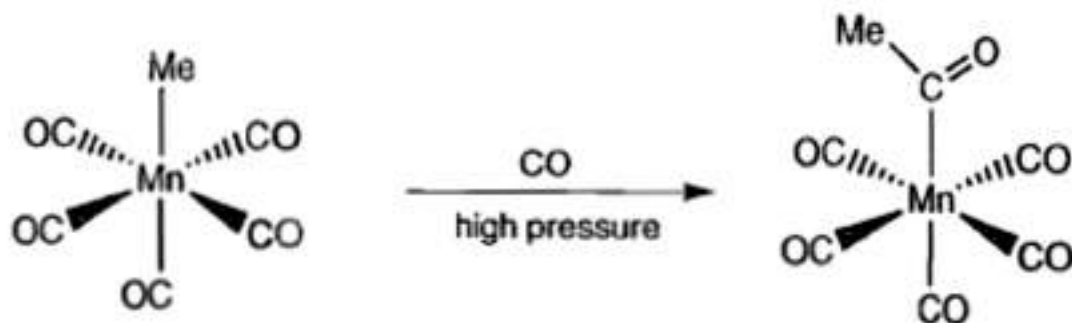
The carbonyl hydride can be synthesized from metal carbonyl anions, halides and dimeric metal carbonyls. The properties of these hydrides vary from hydridic to protic in nature. The above table is representing the  $\text{pK}_a$  values of the resulting hydrides and their comparable acidity.

# Collman's Reagent



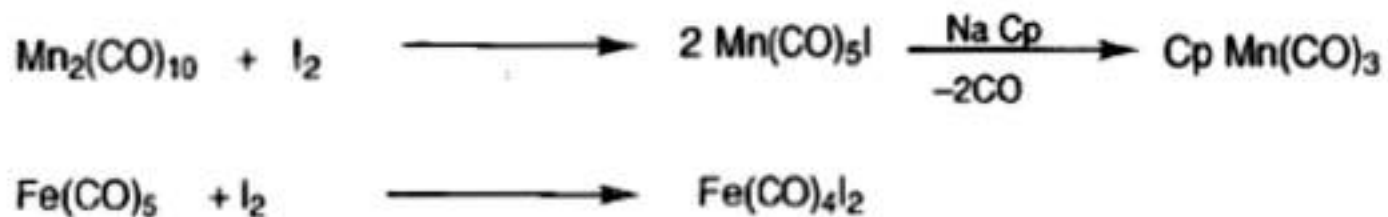
$\text{Na}_2[\text{Fe(CO)}_4]$  is regarded as the Collman's Reagent which is deployed in many organic transformations

- Migratory insertion



The migratory insertion has been used in organic synthesis for the preparation of acyl substituted metal carbonyls which are good precursors for a host of carbonyl containing organic compounds.

- Oxidative decarbonylation



# References

- **Basic Organometallic Chemistry: Concepts, Syntheses and Applications by B. D. Gupta and Anil J. Elias**
- **The Organometallic Chemistry of the Transition Metals by R. H. Crabtree**