Organometallic compounds-III Metal Carbonyls PG Semester I Gauhati University Lecture: 9, 10, 11

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Introduction

- Almost all transition metals can form M-CO bond
- \blacktriangleright Ni(CO)₄ is the first d-block carbonyl, synthesized by L. Mond, 1888
- ➤ It is almost colorless liquid with bp 34°C, decomposes on heating to CO and Ni
- \blacktriangleright Mond & Berthelot independently prepared Fe(CO)₅, from CO and finely divided Fe
- > The carbonyls of other metals can be prepared from metal salts and CO under reducing conditions.
- > Metal carbonyls are mostly volatile and toxic.
- Metal carbonyls can be homoleptic (one type of ligand) as well as heteroleptic (more than one different ligands)
- Metal carbonyls are useful synthetic precursors for other organometallic compounds and are used in organic syntheses and as industrial catalysts.

Group number	5	6	7	8	9	10
First row metals	V(CO) ₆ Dark blue solid; paramagnetic; dec. 343 K	Cr(CO) ₆ White solid; sublimes <i>in vacuo</i> ; dec. 403 K	Mn ₂ (CO) ₁₀ Yellow solid; mp 427 K	Fe(CO) ₅ Yellow liquid; mp 253 K; bp 376 K	Co ₂ (CO) ₈ Air-sensitive, orange-red solid; mp 324 K	Ni(CO) ₄ Colourless, volatile liquid; highly toxic vapour; bp 316K
				Fe ₂ (CO) ₉ Golden crystals; mp 373 K (dec.)	$Co_4(CO)_{12}$ Air-sensitive, black solid	
				Fe ₃ (CO) ₁₂ Dark green solid; dec. 413 K	Co ₆ (CO) ₁₆ Black solid; slowly dec. in air	
Second row metals		Mo(CO) ₆ White solid; sublimes <i>in vacuo</i>	Tc ₂ (CO) ₁₀ White solid; slowly dec. in air; mp 433 K	$\frac{\text{Ru}(\text{CO})_{5}}{\text{Colourless liquid;}}$ mp 251 K; dec. in air at 298 K to $\text{Ru}_{3}(\text{CO})_{12} + \text{CO}$	$\frac{\text{Rh}_4(\text{CO})_{12}}{\text{Red solid};} \\ >403 \text{ K dec. to} \\ \text{Rh}_6(\text{CO})_{16}$	
				Ru ₃ (CO) ₁₂ Orange solid; mp 427 K; sublimes <i>in vacuo</i>	Rh ₆ (CO) ₁₆ Black solid; dec. >573 K	
Third row metals		W(CO) ₆ White solid; sublimes <i>in vacuo</i>	Re ₂ (CO) ₁₀ White solid; mp 450 K	Os(CO) ₅ Yellow liquid; mp 275 K	Ir ₄ (CO) ₁₂ Slightly air- sensitive yellow solid; mp 443 K	
				Os ₃ (CO) ₁₂ Yellow solid; mp 497 K	Ir ₆ (CO) ₁₆ Red solid	

Neutral, low-nuclearity ($\leq M_6$) metal carbonyls of the *d*-block metals (dec. = decomposes).

18e⁻ rule and metal carbonyls

- A stable complex is obtained when the sum of the metal d-electrons, electrons donated from the ligands and of the overall charge of the complex equals 18.
- ➢ Formula & structure of metal carbonyls can be explained using 18e⁻ rule (99%).
- Binuclear carbonyls are formed by elements with odd number of valence electrons (odd-numbered groups) and therefore dimerize by forming M-M bonds
- Senerally, number of CO ligands decreases across a period. $V(CO)_6$ is an exception (17e⁻), sterically too crowded to dimerize and it is readily reduced to $18-e^-V(CO)_6^-$.
- Coordination number around the metal normally remains six or lesser
- Simple metal carbonyls follow VSEPR theory, CO ligands are at maximum distance.
- Counting the electrons helps to predict stability of metal carbonyls, cannot distinguish between bridging and terminal CO









Self-study exercises

- 1. Confirm that each Tc centre in $Tc_2(CO)_{10}$ obeys the 18electron rule.
- 2. Confirm that in *each* isomer of $Co_2(CO)_8$ shown in diagram 23.28, each Co centre obeys the 18-electron rule.
- 3. Does the 18-electron rule allow you to assign the structure shown in Figure 23.10c to Fe₂(CO)₉ in preference to a structure of the type (CO)₄Fe(μ-CO)Fe(CO)₄?

Structure of some mononuclear and dinuclear metal carbonyls







Co₂(CO)₈ (solid)



Structure of some polynuclear metal carbonyls































 $Rh = Rh(CO)_2$ $Rh_6(CO)_{16} = Rh_6(CO)_{12}(\mu_3 - CO)_4$

- > Other than $V(CO)_6$, each 3d-metal carbonyls obeys the 18e rule.
- > The 17e count in V(CO)₆ suggests the possibility of dimerization to $V_2(CO)_{12}$ with V-V bond (sterically unfavourable)
- \blacktriangleright Mn(CO)₅ will be a radical, undergoes dimerization: Mn₂(CO)₁₀, the lowest nuclearity neutral binary carbonyl of Mn
- A similar situation arises for cobalt: $Co(CO)_4$ is a 17e species and the lowest nuclearity binary carbonyl is $Co_2(CO)_8$.
- Solution Group 7 dimers $Mn_2(CO)_{10}$, $Tc_2(CO)_{10}$ and $Re_2(CO)_{10}$ are isostructural, have staggered arrangements with unbridged CO
- > In $Fe_2(CO)_9$, three CO ligands bridge between the Fe centres; each Fe atom obeys the 18e rule if an Fe-Fe bond is present and this is consistent with the observed diamagnetism of the complex.
- \blacktriangleright When solid Co₂(CO)₈ is dissolved in hexane one IR suggests the presence terminal CO only
- \succ The IR spectrum of solid Co₂(CO)₈ shows both terminal and bridging CO ligands
- Solid state ¹³C NMR spectroscopic data show that terminal-bridge CO exchange occurs even in solid $Co_2(CO)_8$.



- Group 8 metal (M = Fe, Ru, Os) forms a trinuclear binary carbonyl $M_3(CO)_{12}$ with a triangular M-M framework.
- > The arrangement of CO ligands in $Fe_3(CO)_{12}$ differs from that in $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$.
- In Fe₃(CO)₁₂ (solid state), Fe₃ triangular framework with one Fe-Fe edge (shortest) bridged by two CO ligands while for the rest four terminal CO per metal (Ru, Os).
- The solution ¹³C NMR spectrum of Fe₃(CO)₁₂ exhibits one resonance showing that the molecule is fluxional, can be described in terms of exchange of terminal and bridging CO ligands
- Shoup 9 carbonyls $Co_4(CO)_{12}$ and $Rh_4(CO)_{12}$ are isostructural; three μ -CO ligands are arranged around the edges of one face of the M₄ tetrahedron. In Ir₄(CO)₁₂, all ligands are terminal.
- Each group 9 metal forms a hexa-nuclear carbonyl, $M_6(CO)_{16}$, in which the metal atoms form an octahedral cluster.
- \blacktriangleright In Co₆(CO)₁₆, Rh₆(CO)₁₆ and the red isomer of Ir₆(CO)₁₆, each M atom has two terminal CO and there are four μ_3 -CO.
- > A black isomer of $Ir_6(CO)_{16}$ has been isolated and in the solid state has 12 terminal CO and four μ -CO.
- ➤ Other octahedral carbonyl clusters include $[Ru_6(CO)_{18}]^{2-}$ and $[Os_6(CO)_{18}]^{2-}$, but in contrast $Os_6(CO)_{18}$ has a bicapped tetrahedral structure

Synthesis of Metal Carbonyls

- Metal carbonyls can be made in a variety of ways.
- > For Ni and Fe, the homoleptic or binary metal carbonyls can be made by the direct interaction with the metal
- ▶ In other cases, a reduction of a metal precursor in the presence of CO (or using CO as the reductant) is used
- Carbon monoxide also reacts with various metal complexes, most typically filling a vacant coordination site or performing a ligand substitution reactions
- > Occasionally, CO ligands are derived from the reaction of a coordinated ligand through a de-insertion reaction

> **Direct carbonylation:** Directly heating CO with finely divided metals



Reductive carbonylation: Reduction of metal salts

$$VCl_{3} + 4 \text{ Na} \xrightarrow{CO (200 \text{ bar})}_{\text{diglyme, 150 °C}} \text{Na}[V(CO)_{6}]^{-} \xrightarrow{H_{3}PO_{4}}_{-H_{2}} V(CO)_{6}$$

$$18 \text{ VE} \qquad 17 \text{ VE}$$

$$CrCl_{3} + \text{Al} \xrightarrow{CO (300 \text{ bar})}_{\text{AlCl}_{3}, C_{6}H_{6}} Cr(CO)_{6} + \text{AlCl}_{3}$$

$$18 \text{ VE}$$

$$MoCl_{5} + 5 \text{ Na} + 6 \text{ CO} \xrightarrow{\text{diglyme}}_{62 \text{ bar, -10 - 25 °C}} Mo(CO)_{6} + 5 \text{ NaCl}$$

$$WCl_{6} + 3 \text{ Zn} + 6 \text{ CO} \xrightarrow{\text{Et}_{2}O, 67 °C}_{50 \text{ atm}} W(CO)_{6} + 3 \text{ ZnCl}_{2}$$

> Thermal or photochemical reaction of other binary carbonyls

2 Fe(CO)₅
$$\xrightarrow{h\nu}$$
 Fe₂(CO)₉ + CO
3 Fe(CO)₅ $\xrightarrow{\Delta}$ Fe₃(CO)₁₂ + 3 CO

Displacement Reactions: Certain metal carbonyls have been prepared by the reaction of metal compounds directly with CO owing to the fact that CO is a reducing agent.

$$2IrCl_3 + 11CO \rightarrow Ir_2(CO)_8 + 3COCl_2$$
$$Re_2O_7 + 17CO \rightarrow Re_2(CO)_{10} + 7CO_2$$

From reduction of metal oxides and carbonates



MO description of CO

- The C=O molecule shows the presence of a C-centered lone pair (HOMO), a σ -bond generated from the p_z orbitals of C and O, and two orthogonal π -bonds, which together give C-O triple bond
- > The HOMO is weakly C-O antibonding in character
- There are also two C-O antibonding π^* orbitals, which could accept electron density from sufficiently high lying orbitals such as the occupied 3d (or 4d,5d) levels of transition metals
- > The combination of σ , π , π^* orbitals is responsible for the reactivity of CO



MO diagram of CO

- Why CO binds a metal via less electronegative C-atom instead of more electronegative O-atom? What makes it a good π acceptor?
- > The HOMO of CO is weakly antibonding (compared with the O atomic orbitals) and is an MO which is carbon based.
- Secondly, the π^* antibonding orbital which is the LUMO is also of comparatively lower energy which makes it possible to interact with metal t_{2g} orbitals for π bonding.
- > There exists a strong back bonding of metal electrons to the π^* antibonding orbitals of CO



Bonding modes of CO

> CO can interact with a transition metal in three ways: as σ -donor, as π -donor and as π - acceptor.

 \succ Two are important: weak σ-bond (L → M) and strong π-back bonding (M → L).



- > Metal-CO complex is stable only with filled metal d orbitals, suitable for back donation to CO antibonding orbital.
- Synergic effect: Interplay of donation and back-donation of electronic charge between a metal and acceptor ligand.



 π -acceptor capacity of CO is responsible for its ability to bind to electron rich metal centers

Continued

- ➢ In a mononuclear complex, CO has only terminal mode of bonding
- ➤ In polynuclear complex, CO can be both terminal and bridging (symmetric and semi bridging)
- ➤ In symmetric bridging CO, CO ligand are unequally shared between the metal centers
- ➤ In semi bridging CO, the CO ligand are unequally shared between metal centers
- Semi bridging CO can be considered to be the intermediate between terminal and bridging ligation.
- ➢ Nature bonding or coordinating mode can be easily detected by IR spectroscopy.



Q. What stabilizes CO complexes is $M \rightarrow C \pi$ -bonding

Ans: The lower the formal charge on the metal ion the more willing it is to donate electrons to the π -orbitals of the CO.

Thus, metal ions with higher formal charges, *e.g.* Fe(II) form CO complexes with much greater difficulty than do zerovalent metal ions. For example Cr(0) and Ni(0), or negatively charged metal ions such as V(-I)

In general to get a feeling for stability examine the charges on the metals



Metal carbonyl bonding

- > MO description of CO shows the existence of C-centered lone pair (HOMO) and degenerate π^* levels (LUMO's)
- \blacktriangleright The C-lone pairs (σ) interacts with vacant d-orbital in donor fashion, important bonding contribution
- > The π^* orbital possesses the ideal symmetry for accepting electron density from an occupied metal d-orbital.
- > The powerful π -acceptor behavior stabilizes the M-CO bond significantly.
- > The process of electron delocalization over the ligand π^* system is known as back bonding
- > The back bonding lengthens the C-O bond and shortens the M-C bond
- > Another possible bonding contribution, the donation of CO π electrons into a vacant metal d-orbital, is relatively unimportant.



 $M(\sigma) \longleftarrow : C = 0$ σ -donor interaction (shading indicates the orbital phases)



 $M(\pi) \longleftarrow C = 0$ π -donor interaction



 $M(\pi) \longrightarrow C = O(\pi^*)$ π -acceptor interaction

M-CO bonding and MO diagram

- These interactions are responsible for strengthening of M-C bond.
- > Donation of σ -lone pair to the metal strengthens the C-

O bond while back donation from the metal into the

CO π^* orbital weakens the C-O bond.

> Overall, a M-CO interaction can be described by two resonance forms.

$$M \stackrel{\pi}{\underset{\sigma}{\longrightarrow}} C = O \longrightarrow IM \stackrel{\pi}{\underset{\sigma}{\longrightarrow}} C = O |^{+}$$





Infrared Spectroscopy of Metal Carbonyls

- > The most sensitive method of observing the bonding interactions in CO complexes is IR spectroscopy
- CO stretching vibrations involve substantial charges in dipole moment and therefore give rise to intense band in the IR spectrum
- > This gives diagnostic information about the electronic characteristics of a carbonyl complex
- Solution Gaseous CO has a stretching frequency $v_{CO} = 2143 \text{ cm}^{-1}$ and coordination to a metal it can reduce upto 1700 cm⁻¹ depending upon the degree of back bonding
- > Nature of CO also play some role in IR stretching frequency





- > The range in which the band appears decides bridging or terminal.
- > The number of bands is only related to the symmetry of the molecule



TABLE 13.2 Bridging Modes of CO



*Asymmetrically bridging µ2- and µ3-CO are also known.

	ν (CO)/cm ⁻¹		$v(CO)/cm^{-1}$		$\nu(CO)/cm^{-1}$
[Co(CO) ₆] ³⁺		[Rh(CO) ₆] ³⁺		[Ir(CO) ₆] ³⁺	2254
[Fe(CO) ₆] ²⁺	2204	[Ru(CO) ₆] ²⁺	2199	$[Os(CO)_6]^{2+}$	2190
[Mn(CO) ₆] ⁺	2100	$[\text{Tc}(\text{CO})_6]^+$	not reported	$[\text{Re}(\text{CO})_6]^+$	2085
Cr(CO) ₆	1986	Mo(CO) ₆	1986	W(CO) ₆	1977
[V(CO) ₆] ⁻	1847	[Nb(CO) ₆] ⁻	1850	[Ta(CO) ₆] ⁻	1850
[Ti(CO) ₆] ²⁻	1750	$[Zr(CO)_6]^{2-1}$	1757	[Hf(CO) ₆] ²⁻	1757

Factors which effecting v_{CO} stretching frequencies

> Charge on the metal: As the As the electron density on a metal centre increases, more π -back bonding to the CO ligand(s) takes place. This weakens the C=O reducing the bond order, the resonance structure M=C=O becomes more dominant

м—с≡о	\rightarrow M=	=c==o
v_{CO}	Higher	${\cal V}_{\rm CO\ Lower}$ More back bonding
Variation in v_{co} (cm ⁻	⁻¹) of the first row transition	n metal carbonyls
	free CO 2143	
Ni(CO) ₄ 2057		
Co(CO) ₄ ⁻ 1890		Co ₂ (CO) ₈ 2044(av, ter)
[Fe(CO) ₄] ²⁻ 1815		Fe(CO) ₅ 2030
[Mn(CO) ₄] ³⁻ 1600 &1790	Mn(CO) ₆ + 2098	Mn ₂ (CO) ₁₀ 2013 (av)
[Cr(CO)₄]⁴- 1462 &1657	Cr(CO) ₆ 2000	
	V(CO) ₆ [−] 1860	V(CO) ₆ 1976
	Ti(CO) ₆ ²⁻ 1747	

➤ Nature of other ligands

Other spectator ligands: Phosphines

PR ₃	v _{CO,} (cm⁻¹)	χ (cm ⁻¹) Δv_{co} wrt P(t-Bu) ₃	PR ₃	ν _{co} , (cm ⁻¹)	$\frac{\chi(\text{cm}^{-1})}{\Delta v_{\text{CO}} \text{ wrt } P(t-Bu)_3}$
P(t-Bu) ₃	2056.1	0.0	$PPh_2(C_6F_5)$	2074.8	18.7
PCy ₃	2056.4	0.3	P(OEt) ₃	2076.3	20.2
P(<i>i</i> -Pr) ₃	2059.2	3.1	P(<i>p</i> -C ₆ H ₄ -CF ₃) ₃	2076.6	20.5
PEt ₃	2061.7	5.6	P(OMe) ₃	2079.5	23.4
P(NMe ₂) ₃	2061.9	5.8	PH ₃	2083.2	27.1
PMe ₃	2064.1	8.0	P(OPh) ₃	2085.3	29.2
PBz ₃	2066.4	10.3	$P(C_6F_5)_3$	2090.9	34.8
P(o-Tol) ₃	2066.6	10.5	PCl ₃	2097.0	40.9
PPh ₃	2068.9	12.8	PF ₃	2110.8	54.7
PPh ₂ H	2073.3	17.2	P(CF ₃) ₃	2115.0	58.9



Effect of a ligands trans to CO

	Complex	ν _{CO} (cm ^{−1})	
	[Mo(PF ₃) ₃ (CO) ₃]	2055, 2090	
	[Mo(PCl ₃) ₃ (CO) ₃]	1991, 2040	More back bonding = More lowe
	[Mo{P(OMe) ₃ } ₃ (CO) ₃]	1888, 1977	of the C=O bond order = More lo
CO	[Mo(PPh ₃) ₃ (CO) ₃]	1835, 1934	is the v_{CO} stretching frequency
L	[Mo(NCMe) ₃ (CO) ₃]	1758, 1898	
	[Mo(Py) ₃ (CO) ₃]	1746, 1888	

 \blacktriangleright With each negative charge added to the metal center, the CO stretching frequency decreases by approximately 100 cm⁻¹.

> The better the σ donating capability of the other ligands on the metal, more electron density given to the metal, more back bonding (electrons in the antibonding orbital of CO) and lower the CO stretching frequency.

IR spectra and metal-carbon bonds

- > The v_{CO} stretching frequency of the coordinated CO is very informative
- > The stronger a bond gets, the higher its stretching frequency (from resonance M=C=O)
- \succ Lower v_{CO} stretching frequency as compared to the M-C=O structure (triple bond)



Summary

- 1. As the CO bridges more metal centers its stretching frequency drops same for all pi acceptor ligands More back donation
- 2. As the metal center becomes increasingly electron rich the stretching frequency drops

The influence of charge on CO str	f coordination and	Complexes	v _{CO} (f _{1u})/cm
Compound Frequency (cm ⁻¹)		[Hf(CO) ₆] ²⁻	1757
CO _(g)	2143	[Ta(CO) ₆] ⁻	1850
[Mn(CO) ₆] ⁺	2090	W(CO) ₆	1977
[Cr(CO) ₆]	2000	[Re(CO) ₆] ⁺	2085
[V(CO) ₆] ⁻	1860	[Os(CO) ₆] ²⁺	2190
[Ti(CO) ₆] ²⁻	1750	[lr(CO) ₆] ³⁺	2254

 Bridging CO groups can be regarded as having a double bond C=O group, as compared to a terminal C=O, which is more like a triple bond.

The C=O group in a bridging carbonyl is more like the C=O in a ketone, which typically has $v_{C=O} =$ 1750 cm⁻¹



Solid $Fe_2(CO)_9$





 $Os_3(CO)_{12}$ in solution



Terminal versus bridging carbonyls



		Bacl	<-bonding		
	V _{CO}		decreases		v _{co}
Ni(CO) ₄	2060		1	[Mn(CO) ₆]⁺	2098
[Co(CO) ₄] ⁻	1890			Cr(CO) ₆	2000
[Fe(CO) ₄] ^{2–}	1790			[V(CO) ₆] [−]	1860
		increases			

Ni(CO) ₄	2057 cm ⁻¹
Fe(CO) ₅	2034
Cr(CO) ₆	1981

CO	2143
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Complex	Ni(CO) ₄	$[Co(CO)_4]^-$	[Fe(CO) ₄] ²⁻
$\bar{\nu}_{\rm CO}/{\rm cm}^{-1}$	2060	1890	1790

Cr(CO) ₆	2100 cm ⁻¹
$Cr(CO)_3(NH_3)_3$	1900 cm ⁻¹

[Ti(CO) ₆] ²⁻	1748 cm ⁻¹
[V(CO) ₆] ⁻	1859
[Cr(CO) ₆]	1981
[Mn(CO) ₆]+	2090
[Fe(CO) ₆] ²⁺	2204

Detecting conformational isomers

➤ The number of bands in the CO stretching region for certain molecules can often be used to show that two conformational isomers are present

The molecule $[(\eta^5-C_5H_5Fe(CO)_2(\eta^1-C_5H_5)]$ is expected to show

only two bands due to sym. and asym. str. modes. But there are

four bands and which is due to the presence of two different conformations



Reaction mechanisms of metal carbonyls

- > Metal carbonyls display a number of key reaction pattern which are the basis of most catalytic cycles
- Ligand dissociation, ligand substitution, oxidative addition, reductive elimination, intra or intermolecular nucleophilic attack



Reactions of metal carbonyls

Substitution Reactions: Many substitution reactions occur between metal carbonyls and other potential ligands.
Substitution reactions of metal carbonyls frequently indicate differences in bonding characteristics of ligands.



substitutions by dienes



Metal with d6 configuration such as M⁰(M=Cr, Mo, W) and M¹ (M=Mn, Re) are kinetically inert and substitution requires more forcing conditions (THF, MeCN solvent coordination facilitates the process)





> Reactions with Halogens

1. Reactions of metal carbonyls with halogens lead to the formation of carbonyl halide complexes by substitution reactions or breaking metal-metal bonds. The reaction

 $[Mn(CO)_5]_2 + Br_2 \rightarrow 2 Mn(CO)_5Br$

involves the rupture of the Mn–Mn bond, and one Br is added to each Mn.

2. In the reaction

 $Fe(CO)_5 + I_2 \rightarrow Fe(CO)_4I_2 + CO$

one CO is replaced on the iron by two iodine atoms so that the coordination number of the iron is increased to 6. The formulas for these carbonyl halides obey the EAN rule.

3. The reaction of CO with some metal halides results in the formation of metal carbonyl halides directly, as illustrated in the following examples:

PtCl₂ + 2CO → Pt(CO)₂Cl₂ 2PdCl₂ + 2CO → [Pd(CO)Cl₂]₂ Substitution reactions of $Co_2(CO)_8$ are very facile (coordinatively unsaturated and dissociates readily to give 17e $Co(CO)_4$ • radical (similar to $V(CO)_6$ •

$$\dot{V}(CO)_6 + L \longrightarrow L - \dot{V}(CO)_6 \xrightarrow{fast} L - \dot{V}(CO)_5 + CO$$

17 VE 19 VE 17 VE

 \succ The addition of an alkyne to $Co_2(CO)_8$ results in the formation of a Co_2C_2 cluster

$$Co_2(CO)_8 + PhC \equiv CPh \longrightarrow Co_2(CO)_6(C_2Ph_2) + 2CO$$

> Reactions with NO

1. NO has one unpaired electron residing in an antibonding π^* MO. When that electron is removed, the bond order increases from 2.5 to 3, so in coordinating to metals, NO usually behaves as though it donates three electrons. The result is formally the same as if one electron were lost to the metal,

 $NO \rightarrow NO^{\scriptscriptstyle +} + e$

followed by coordination of NO⁺, which is isoelectronic with CO and CN.

2. Because NO⁺ is the nitrosyl ion, the products containing nitric oxide and carbon monoxide are called *carbonyl nitrosyls*.

The following reactions are typical of those producing this type of compound:

 $Co_{2}(CO)_{8} + 2NO \rightarrow 2Co(CO)_{3}NO + 2CO$ $Fe_{2}(CO)_{9} + 4NO \rightarrow 2Fe(CO)_{2}(NO)_{2} + 5CO$ $[Mn(CO)_{5}]_{2} + 2NO \rightarrow 2Mn(CO)_{4}NO + 2CO$

It is interesting to note that the products of these reactions obey the 18-electron rule

> Disproportionation

A number of metal carbonyls undergo disproportionation reactions in the presence of other coordinating ligands.

1. In the presence of amines, $Fe(CO)_5$ reacts as follows:

 $2\text{Fe}(\text{CO})_5 + 6\text{Amine} \rightarrow [\text{Fe}(\text{Amine})_6]^{2+}[\text{Fe}(\text{CO})_4]^{2-} + 6\text{CO}$

This reaction takes place because of the ease of formation of the carbonylate ions and the favorable coordination of the Fe²⁺ produced.

2. The reaction of $\text{Co}_2(\text{CO})_8$ with NH₃ is similar.

 $\operatorname{Co}_2(\operatorname{CO})_8 + 6 \operatorname{NH}_3 \rightarrow [\operatorname{Co}(\operatorname{NH}_3)_6][\operatorname{Co}(\operatorname{CO})_4]_2$

Formally, in each of these cases the disproportionation produces a positive metal ion and a metal ion in a negative oxidation

state. The carbonyl ligands will be bound to the softer metal species, the anion; the nitrogen donor ligands (hard Lewis bases)

will be bound to the harder metal species, the cation.

3. These disproportionation reactions are quite useful in the preparation of a variety of carbonylate complexes.

For example, the $[Ni_2(CO)_6]_2$ ion can be prepared by the reaction

 $3Ni(CO)_4 + 3phen \rightarrow [Ni(phen)_3][Ni_2(CO)_6] + 6CO$

4. The range of coordinating agents that will cause disproportionation is rather wide and includes compounds such as isocyanides, RNC:

 $\operatorname{Co}_2(\operatorname{CO})_8 + 5\operatorname{RNC} \rightarrow [\operatorname{Co}(\operatorname{CNR})_5][\operatorname{Co}(\operatorname{CO})_4] + 4\operatorname{CO}$

Q. Give a scheme for the synthesis of $Mn(CO)_4(PPh_3)[C(O)CH_3]$ starting from Manganese acetate, $Mn(OAc)_2$.;

$$2 \operatorname{Mn}(\operatorname{OAc})_{2} + 4 \operatorname{Na} + 10 \operatorname{CO} \xrightarrow{\text{high temp}} \operatorname{Mn}_{2}(\operatorname{CO})_{10} + 4 \operatorname{NaOAc}$$

$$\operatorname{Mn}_{2}(\operatorname{CO})_{10} + 2 \operatorname{Na} \longrightarrow 2 \operatorname{NaMn}(\operatorname{CO})_{5}$$

$$\operatorname{NaMn}(\operatorname{CO})_{5} + \operatorname{CH}_{3} \operatorname{I} \longrightarrow \operatorname{CH}_{3} \operatorname{Mn}(\operatorname{CO})_{5}$$

$$\operatorname{CH}_{3} \operatorname{Mn}(\operatorname{CO})_{5} + \operatorname{CO} \longrightarrow \operatorname{CH}_{3} \operatorname{C}(\operatorname{O}) \operatorname{Mn}(\operatorname{CO})_{5} \text{ (migratory insertion)}$$

$$\operatorname{CH}_{3} \operatorname{C}(\operatorname{O}) \operatorname{Mn}(\operatorname{CO})_{5} + \operatorname{PPh}_{3} \xrightarrow{h\nu} \operatorname{CH}_{3} \operatorname{C}(\operatorname{O}) \operatorname{Mn}(\operatorname{CO})_{4} \operatorname{PPh}_{3}$$

$$\operatorname{Or at step 3 direct reaction with acyl chloride instead of MeI. Step 1 other reducing agents e.g. AlEt_{3} can also be used.$$

➤ Reactions of alkenes with metal carbonyl clusters may give simple substitution products such as Os₃(CO)₁₁(η2-C₂H₄) or may involve oxidative addition of one or more CH bonds. Reaction of Ru₃(CO)₁₂ with RHC=CH₂ (R = alkyl) to give isomers of H₂Ru₃(CO)₉(RCCH) in which the organic ligand acts as a 4-electron donor (one -σ and two π-interactions).



> The reactions between alkynes and multinuclear metal carbonyls give various product types, with alkyne coupling and alkyne–CO coupling often being observed, the organic ligand in the shown product is a 6- electron donor (two $-\sigma$ and two π -interactions).



Allyl and related complexes can be prepared by formation of allyl ligands go via -bonded intermediateswhich eliminate CO or by protonation of coordinated buta-1,3-diene

 $Na[Mn(CO)_{5}] + H_{2}C = CHCH_{2}Cl$ $\longrightarrow Mn(\eta^{3}-C_{3}H_{5})(CO)_{4} + CO + NaCl$



Carbenes can also be made by nucleophilic attack on a carbonyl C-atom followed by alkylation (Fischer Carbene)

W(CO)₆
$$\xrightarrow{\text{MeLi}}$$
 (OC)₅W = C $\xrightarrow{O^-}$ $(R_3O)^+$ (OC)₅W = C \xrightarrow{OR}
Me Me, Et Me

The dimer $(\eta 5-Cp)_2Fe_2(CO)_4$ is a valuable starting material in organometallic chemistry. Reactions with Na or halogens cleave the Fe-Fe bond giving useful organometallic reagents, reactions of which are exemplified below

 $(\eta^{5}-Cp)_{2}Fe_{2}(CO)_{4} + 2Na \longrightarrow 2Na[(\eta^{5}-Cp)Fe(CO)_{2}]$

 $(\eta^{5}-Cp)_{2}Fe_{2}(CO)_{4} + X_{2} \rightarrow 2(\eta^{5}-Cp)Fe(CO)_{2}X$ X = Cl, Br, I



The reaction of $Cr(CO)_6$ or $Cr(CO)_3(NCMe)_3$ with benzene gives the half-sandwich complex ($\eta 6-C_6H_6$)Cr(CO)_3. The $Cr(CO)_3$ unit in $(\eta 6-C_6H_6)Cr(CO)_3$ complexes withdraws electrons from the arene ligand making it less susceptible to electrophilic attack than the free arene, but more susceptible to attack by nucleophiles



 $(\eta^6 - C_6 H_5 Cl) Cr(CO)_3 + NaOMe$ \rightarrow (η^6 -C₆H₅OMe)Cr(CO)₃ + NaCl

 $(\eta^6 - C_6 H_6) Cr(CO)_3$

 $(\eta^6-C_6H_6)Cr(CO)_3$ can be lithiated and then derivatized. The reactivity of half sandwich complexes is not confined to sites within the - bonded ligand, substitution of a CO ligand for PPh₃



 \leftarrow (η° -C₆H₅Li)Cr(CO)₃

- > Cycloheptatriene (23.62) can act as a 6-electron donor, and in its reaction with $Mo(CO)_6$, it forms $(\eta^6-C_7H_8)Mo(CO)_3$.
- > The abstraction of H- from coordinated η^6 -C₇H₈ to give the planar [η^7 -C₇H₇]+ ion, which has an aromatic -system and

retains the ability of cycloheptatriene to act as a 6-electron donor.

Metal carbonyl anions

- Reduction of metal salts with powerful reducing agent such as an alkali metal under CO pressure gives anionic carbonyl, provided this reduction results is an 18e complex
- > Pre-formed metal carbonyl complexes can also be reduced to give anionic product
- > Addition of two electrons is accompanied by the loss of one CO ligand
- Metal carbonyl hydrides may be deprotonated to give anionic compounds

By disproportionation:

$$3 \text{ Mn}_2(\text{CO})_{10} \xrightarrow{\text{pyridine}} 2 [\text{Mn}(\text{py})_6]^{2+} [\text{Mn}(\text{CO})_5^-]_2$$

By nucleophilic attack on CO:

$$Fe(CO)_{5} + Na^{+}OH^{-} \longrightarrow Na^{+} \begin{bmatrix} 0 & H \\ 0 & 0 \end{bmatrix} \xrightarrow{\bigcirc} \\ -CO_{2} & Na^{+}[HFe(CO)_{4}]^{-} \xrightarrow{Na} \\ -H_{2} & Na_{2}[Fe(CO)_{4}] \end{bmatrix}$$

By reduction:



reductive M-M bond cleavage:

 $Mn_{2}(CO)_{10} + 2 Na \xrightarrow{THF} Na[Mn(CO)_{5}] \xrightarrow{CO} \\ [\odot]{} CO_{2}(CO)_{8} + 2 Na \xrightarrow{THF} Na[Co(CO)_{4}] \xrightarrow{OC \xrightarrow{VV}CO} CO$

- Several carbonylate anions such as $Co(CO)_4^-$, $Mn(CO)_5^-$, $V(CO)_6^-$, and $[Fe(CO)_4]^{2-}$ obey the EAN rule.
- One type of synthesis of these ions is that of reacting the metal carbonyl with a reagent that loses electrons readily, a strong reducing agent. Active metals are strong reducing agents, so the reactions of metal carbonyls with alkali metals should produce carbonylate ions.
- > The reaction of $Co_2(CO)_8$ with Na carried out in liquid ammonia at 75°C is one such reaction.

 $Co_2(CO)_8 + 2 \text{ Na} \rightarrow 2 \text{ Na}[Co(CO)_4]$ Mn₂(CO)₁₀ + 2 Li $\rightarrow 2 \text{ Li}[Mn(CO)_5]$

> Although $Co(CO)_4$ and $Mn(CO)_5$ do not obey the 18-electron rule, the anions $Co(CO)_4^-$ and $Mn(CO)_5^-$ do

Carbonylate anions can be prepared by the reaction of metal carbonyls with strong bases.

 $Fe(CO)_{5} + 3NaOH \rightarrow Na[HFe(CO)_{4}] + Na_{2}CO_{3} + H_{2}O$ $Cr(CO)_{6} + 3KOH \rightarrow K[HCr(CO)_{5}] + K_{2}CO_{3} + H_{2}O$

With $Fe_2(CO)_9$, the reaction is

 $\operatorname{Fe}_2(\operatorname{CO})_9 + 4\operatorname{OH}^- \to \operatorname{Fe}_2(\operatorname{CO})_8{}^{2-} + \operatorname{CO}_3{}^{2-} + 2\operatorname{H}_2\operatorname{O}$

Reactions of metal carbonyl anions:

- Carbonyl metallate anions oxidatively add alkyl and acyl halides to generate M-alkyl bonds, due to the negative charge of the complexes, possess Grignard like reactivity
- > The iron carbonyl salt $Na_2Fe(CO)_4$ (Collman's reagent) has synthetic applications



Reduction of metal carbonyl with common reducing agent such as sodium amalgam in THF stops at the stage of mono or dianions, more forcing conditions (Na in liq NH3 or Na in hexamethylphosphoramide) generate highly reduced carbonyl metallates with formal oxidation state of metal centers may be as low as –IV (Super reduced metal carbonyl anion)

$$Na[V(CO)_{6}] + 3 Na \xrightarrow{NH_{3} liq.} Na_{3}[V(CO)_{5}] + 0.5 Na_{2}C_{2}O_{2}$$

$$Na[Mn(CO)_{5}] + 3 Na \xrightarrow{HMPA} Na_{3}[Mn(CO)_{4}] + 0.5 Na_{2}C_{2}O_{2}$$

$$K[Co(CO)_{4}] + 3 K \xrightarrow{NH_{3} liq.} K_{3}[Co(CO)_{3}] + 0.5 K_{2}C_{2}O_{2}$$

- > Carbonyl anions are extremely strong bases and metal centers is very electron rich
- \succ Consequently these compounds show extensive back bonding and show exceptionally low v_{CO}

Carbonyl anion	v _{CO} [cm ⁻¹]	Super-reduced anion	v _{CO} [cm ⁻¹]	
[V(CO) ₆] ⁻	1860	[V(CO) ₅] ³⁻	1807(w), 1630(s), 1580(s)	
[Cr(CO) ₅] ²⁻	1750	[Cr(CO) ₄] ^{4–}	1462(s)	
[Mn(CO) ₅] ⁻	1893, 1860	[Mn(CO) ₄] ^{3–}	1790(w), 1600(s)	
$[Fe(CO)_4]^{2-}$	1790			
[Co(CO) ₄] ⁻	1890 (AsPh4+)	[Co(CO) ₃] ^{3–}	1740, 1610(vs)	

IR frequencies of metal carbonyl anions.

Metal carbonyl cations

- > Placing a positive charge on the metal center contracts the d-shell and reduces the tendency towards back bonding.
- This weakens the M-CO bond and facilitates the displacement of CO by more nucleophilic ligands such as halide or water
- > Cationic metal carbonyl complexes are therefore formed only of p[aired with anions of low nucleophilicity

By halide abstraction with Lewis acids:

$$Mn(CO)_{5}Cl + AlCl_{3} \xrightarrow{100 \circ C} [Mn(CO)_{6}]^{+}AlCl_{4}^{-}$$
By oxidation:

$$Mn_{2}(CO)_{10} + 2 HF + 2 BF_{3} \xrightarrow{0.6 \text{ bar CO}} 2 [Mn(CO)_{6}]^{+}BF_{4}^{-} + H_{2}$$

$$Co_{2}(CO)_{8} + 2 (CF_{3})_{3}B-CO + 2 HF \xrightarrow{CO} HF_{anhydr.} 2 [Co(CO_{5}]^{+}[FB(CF_{3})_{3}]^{-} + H_{2}$$

> A particular successful strategy are reactions in super acidic media HF/SbF5, which generate the extremely non nucleophilic anions SbF_6^- and $Sb_2F_{11}^-$

$$Fe(CO)_{5} + XeF_{2} + CO + 4SbF_{5} \xrightarrow{50 \text{ °C}, 1 \text{ bar}}_{HF/SbF_{5}, 2d} [Fe(CO)_{6}]^{2+}[Sb_{2}F_{11}^{-}]_{2} + Xe$$

$$2 IrF_{6} + 15 CO + 12 SbF_{5} \xrightarrow{1 \text{ bar } CO}_{SbF_{5}, 50 \text{ °C}} 2 [Ir(CO)_{6}][Sb_{2}F_{11}]_{3} + 3 COF_{2}$$

> Under these conditions highly electrophilic carbonyl complexes of metals in oxidation states +II and +III can be isolated

> These are so called non classical metal carbonyls. Back bonding is nearly absent, very long M-C bonds

IR frequencies of homoleptic metal carbonyl cations.

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d ⁶	v _{co} [cm ⁻¹]	d ⁸	v _{CO} [cm ⁻¹]	d ¹⁰	v _{CO} [cm ⁻¹]
[Fe(CO) ₆] ²⁺	2215	[Pd(CO) ₄] ²⁺	2259	$[Au(CO)_2]^+$	2235
[Ru(CO) ₆] ²⁺	2214	[Pt(CO) ₄] ²⁺	2261	[Hg(CO) ₂] ²⁺	2280
[Os(CO) ₆] ²⁺	2209				
[lr(CO) ₆] ³⁺	2268				

Carbonyl Hydrides

Generally, carbonyl hydrides are obtained by acidifying solutions containing the corresponding carbonylate anion or by the reactions of metal carbonyls with hydrogen.

 $Co(CO)_{4}^{-} + H^{+}(aq) \rightarrow HCo(CO)_{4}$ $[Mn(CO)_{5}]_{2} + H_{2} \rightarrow 2HMn(CO)_{5}$ $Na[HFe(CO)_{4}] + 2H^{+}(aq) \rightarrow H_{2}Fe(CO)_{4} + Na^{+}(aq)$

- Monomeric hydrides of first row transition metal carbonyls are volatile liquids which are stable under an atmosphere of CO at low temperature, In presence CO they liberate H₂
- > The hydrides of the heavier metals within a triad are much more stable.
- > $HCo(CO)_4$ was the first metal hydride to be discovered (olefin hydroformylation)
- > Strong acids are required for the protonation of neutral metal carbonyl complexes
- > A general route to hydrides is by reduction of metal carbonyl halides and H- addition to carbonyls
- The anions [M₂(µ-H)(CO)₁₀]⁻ (M = Cr, Mo, W) are examples of bent M-H_M bridged systems without the support of M-M bonds or bridging CO



The action of alkali on $Fe(CO)_5$ gives [HFe(CO)_4]-; nucleophilic attack by [OH]- on a CO ligand is followed by Fe-H bond formation and elimination of CO₂. The [HFe(CO)_4]- ion has a variety of synthetic uses.

$$Fe(CO)_5 + 3NaOH \xrightarrow{H_2O} Na[HFe(CO)_4] + Na_2CO_3 + H_2O_4$$



> Hydrido ligands can be introduced by various routes including protonation, reaction with H_2 and action of $[BH_4]^-$ ion

$$Na[Mn(CO)_{5}] \xrightarrow{H_{3}PO_{4}, \text{ in THF}} HMn(CO)_{5}$$

$$Mn_{2}(CO)_{10} + H_{2} \xrightarrow{200 \text{ bar}, 470 \text{ K}} 2HMn(CO)_{5}$$

$$Ru_{3}(CO)_{12} + H_{2} \xrightarrow{\text{ in boiling octane}} (\mu-H)_{4}Ru_{4}(CO)_{12}$$

$$Cr(CO)_{6} \xrightarrow{\text{Na[BH_4]}} [(OC)_{5}Cr(\mu-H)Cr(CO)_{5}]^{-}$$

$$Ru_{3}(CO)_{12} \xrightarrow{\text{Na[BH_4] in THF}} [HRu_{3}(CO)_{11}]^{-}$$

> Metal hydrides play an important role in organometallic chemistry, ligand transformations involving M-H bonds



Mononuclear hydrido carbonyl anions include [HFe(CO)₄]⁻ and [HCr(CO)₅]⁻, both of which can be made by the action of hydroxide on the parent metal carbonyl



Selected reactions of $[HCr(CO)_5]^-$.

Carbonyl Halides

- > The reaction of metal carbonyl complexes with halogens leads to oxidative addition and formation of M-X bonds
- > This is an easy way to functionalize carbonyl complexes



Noble metal carbonyl halides can be prepared from metal halides Methods of forming carbonyl halides include starting from binary metal carbonyls or metal halides.



- The 16-electron halide complexes cis-[Rh(CO)₂I₂]- and trans-[Ir(CO)Cl(PPh₃)₂] (Vaska's compound) undergo many oxidative addition reactions and have important catalytic applications. [Ru(CO)ClH(PPh₃)₃] is a catalyst precursor for alkene hydrogenation
- \succ Vaska's compound readily takes up O₂ to give the peroxo complex



trans-Ir(CO)Cl(PPh₃)₂ + C₆₀ \rightarrow Ir(CO)Cl(η^2 -C₆₀)(PPh₃)₂

