SYNTHESIS, STRUCTURE AND BONDING IN METAL CARBONYLS.

[Ref: Emeleus & Sharpe, Chapter 20]

Complexes of transition metals with carbon monoxide are known as metal carbonyls. All metal carbonyls except $V(CO)_6$ appear to follow the E. A. N. Rule. This rule may help in determining the possible presence of metal-metal bonds. *Compounds containing only carbonyl groups and metal atoms (no other ligands present) are called* ***binary*** *metal carbonyls. If the carbonyls contain only one metal atom, it is called a* ***mononuclear*** *metal carbonyl. If there are more metal atoms, they are called* ***polynuclear*** *carbonyls. If the metal atoms in a polynuclear metal carbonyl are of different kinds, then it is called a* ***heteronuclear*** *carbonyl.*

E.g., $V(CO)_6$, $Fe(CO)_5$, $Mn_2(CO)_{10}$ and $Co_6(CO)_{16}$ are all ***binary*** metal carbonyls.

$Fe(CO)_5$ and $Ni(CO)_4$ are ***mononuclear*** metal carbonyls.

$Mn_2(CO)_{10}$, $Co_6(CO)_{16}$ and $Mn(CO)_5$-$Re(CO)_5$ are ***polynuclear*** metal carbonyls.

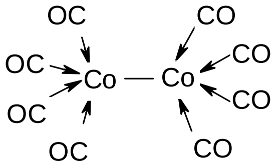
$Mn_2(CO)_{10}$ is a *binuclear* carbonyl, and $Co_6(CO)_{16}$ is a *hexanuclear* carbonyl.
But both are ***homonuclear*** metal carbonyls.

$Mn(CO)_5$-$Re(CO)_5$ and $Mn(CO)_5$-$Co(CO)_4$ are ***heteronuclear*** carbonyls.

A list of the common binary metal carbonyls, their formulae and physical appearance are listed in the following table:

Electrons needed to attain noble gas config. →	13	12	11	10	9	8
First transition series	$V(CO)_6$ Blue solid	$Cr(CO)_6$ White solid	$Mn_2(CO)_{10}$ Yellow solid	$Fe(CO)_5$ Yellow liquid $Fe_2(CO)_9$ Orange solid $Fe_3(CO)_{12}$ Black solid	$Co_2(CO)_8$ Orange solid $Co_4(CO)_{12}$ Black solid $Co_6(CO)_{16}$ Black solid	$Ni(CO)_4$ Colourless liquid
Second transition series		$Mo(CO)_6$ White solid	$Tc_2(CO)_{10}$ White solid	$Ru(CO)_5$ Colourless liquid	$Rh_4(CO)_{12}$ Orange solid	
Third transition series		$W(CO)_6$ White solid	$Re_2(CO)_{10}$ White solid	$Os(CO)_5$ Colourless liquid	$Ir_4(CO)_{12}$ Yellow solid	

Structure of metal carbonyls: Although the E.A.N. rule acts as a guide to the probable structure, it cannot predict the correct structure because there may be more than one structure agreeing with the E.A.N. rule. E.g., $Co_2(CO)_8$ can have any of the following structures, all of them conforming to the E.A.N. rule.



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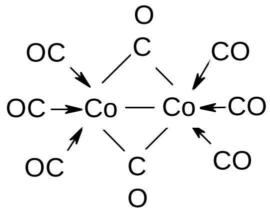

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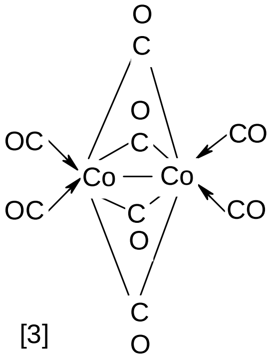
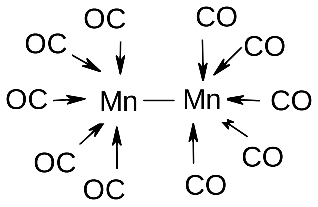


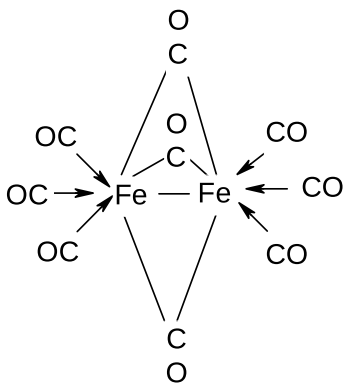
[3]

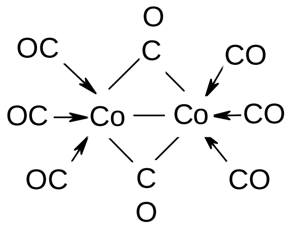
CO groups donating to only one metal atom are called **terminal** carbonyl groups. They donate a pair of electrons to that metal atom. CO groups which bond to two metal atoms at the same time are called **bridging** carbonyl groups. They contribute one electron to each of the two metal atoms to form covalent bonds. The presence of the two types of CO groups can be distinguished using IR spectroscopy. The terminal CO groups show absorption bands close to that of carbon monoxide [C-O stretching frequency of carbon monoxide = 2143 cm^{-1}, terminal CO = 2125 to 2000 cm^{-1}], while the bridging CO groups show absorption bands close to that of a keto group [1900 to 1800 cm^{-1}]. But the possible existence of π-bonds of different strengths make quantitative interpretation impossible.

Other methods of structure determination adopted in metal carbonyls are X-ray and electron diffraction studies, and measurement of magnetic susceptibilities. Such studies show that nickel carbonyl has a tetrahedral structure. All the mononuclear hexacarbonyls have octahedral structures. Iron pentacarbonyl has a trigonal bipyramidal structure in which the Fe-C apical bond length is slightly shorter than the equatorial ones (180.6 and 183.3 pm respectively).

Binuclear metal carbonyls $Mn_2(CO)_{10}$, $Fe_2(CO)_9$ and $Co_2(CO)_8$ have the following structures:

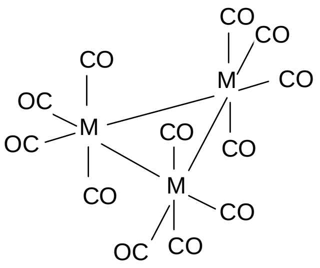






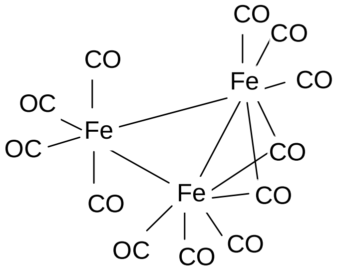
The structure of $Mn_2(CO)_{10}$ may be described as two octahedral sharing one corner. $Fe_2(CO)_9$ consists of two octahedra sharing a face. This compound is diamagnetic and the Fe-Fe bond distance is very short like in metallic iron (246 pm). These measurements indicate the existence of a metal-metal bond. This is also true for $Co_2(CO)_8$. Recent studies indicate that in $Co_2(CO)_8$, both bridged and non-bridged structures are present in equal amounts as their energy difference is small. The Mn-Mn bond length in $Mn_2(CO)_{10}$ is larger, probably because of the absence of bridging carbonyls.

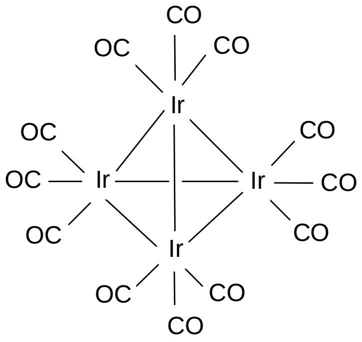
Structures of some polynuclear metal carbonyls are discussed below:



Non-bridged structure of crystalline
$Os_3(CO)_{12}$ and $Ru_3(CO)_{12}$ [M = Os or Ru]

Bridged structure of $Fe_3(CO)_{12}$ with two bridging carbonyls





Non-bridged structure of $Ir_4(CO)_{12}$ in which the four Ir atoms are arranged tetrahedrally using metal-metal bonds.

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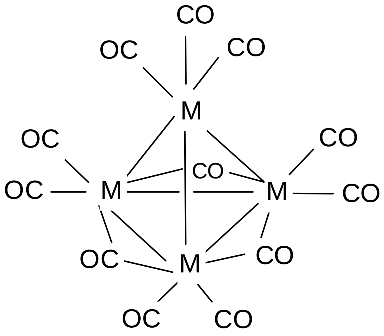
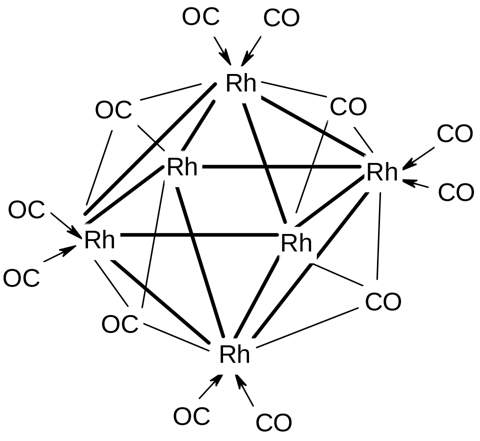
Bridged structure of $Co_4(CO)_{12}$ and $Rh_4(CO)_{12}$. Three bridging CO groups along the base edges. [M = Co or Rh]

→





The only hexanuclear carbonyl whose structure has been determined is $Rh_6(CO)_{16}$ shown on the left. The six Rh metal atoms are at the corners of an octahedron. Four bridging carbonyl groups are present, each sharing a pair of electrons with **three** Rh atoms on a face. (Multicenter bond, $^2/_3$ electrons shared with each Rh atom!). Two more terminal CO groups are present on each Rh atom (those on two Rh atoms in the picture are omitted for clarity). Thus the number of electrons around each Rh appears to be [1×4(Rh) + 2×$^2/_3$(bridge) + 2×2(terminal) = 9$^1/_3$] whereas each Rh requires only 9 electrons for inert gas configuration. Thus there are a total of 6×$^1/_3$ = 2 electrons extra in the molecule, and it appears that the E.A.N. rule is not followed unless the formula is $[Rh_6(CO)_{16}]^{2+}$.

Metallic carbonyls containing large numbers of CO groups (many of which were described above) are also known as **carbonyl clusters**. Those carbonyl clusters containing a small number of metal atoms in them, such as $Ni(CO)_4$, $Mn_2(CO)_{10}$ etc. are called ***low-nuclear carbonyl clusters*** (**LNCC**s) and those containing large numbers of metal atoms, such as $Rh_6(CO)_{16}$, are called ***high-nuclear carbonyl clusters*** (**HNCC**s).

Synthesis of metal carbonyls:

(1) **Direct synthesis**: Simple metal carbonyls can some times be made by the direct combination of carbon monoxide with the finely powdered metal, especially if the surface is very clean and free fro the oxide. E.g., nickel reacts with carbon monoxide at atmospheric pressure and 310 K to give nickel carbonyl. $Fe(CO)_5$ and $Co_2(CO)_8$ can be produced at 473 K and 20 atm pressure.

(2) **Reductive carbonylation**: Many metal carbonyls can be prepared form carbon monoxide and a compound of the metal such as oxide, sulfide or halide in presence of a reducing agent. The reducing agent may be hydrogen, sodium, magnesium, aluminium, lithium aluminium hydride or sometimes even excess carbon monoxide. E.g.,

$$OsO_4 + CO \xrightarrow{\text{523 K, 350 atm.}} Os(CO)_5 + Os_3(CO)_{12} + CO_2$$

$$RuI_3 + CO + Ag \xrightarrow{\text{450 K, 250 atm.}} Ru(CO)_5 + AgI$$

$$CoS + CO + Cu \xrightarrow{\text{473 K, 200 atm.}} Co_2(CO)_8 + Cu_2S$$

$$CrCl_3 + CO + LiAlH_4 \xrightarrow[\text{Ether}]{\text{388 K, 70 atm.}} Cr(CO)_6 + LiCl + AlCl_3$$

$$Cr(acac)_3 + CO + Mg \xrightarrow[\text{Pyridine}]{\text{433 K at 300 atm.}} Cr(CO)_6$$

$$CoCO_3 + CO + H_2 \xrightarrow[\text{Petroleum ether}]{\text{423 K, 300 atm.}} Co_2(CO)_8$$

$$VCl_3 + Na + CO \xrightarrow[\text{Diglyme}]{\text{373 K, 150 atm.}} [V(CO)_6]^- \xrightarrow{\text{acid}} V(CO)_6$$

$$WCl_6 + 3\,Fe(CO)_5 \xrightarrow{\text{373 K}} W(CO)_6 + 3\,FeCl_3 + 9\,CO$$

(3) **From mononuclear or binuclear carbonyls**: Some carbonyls may be prepared from other carbonyls of the same metal. E.g.,

$$2\,Fe(CO)_5 \xrightarrow[\text{acetic acid soln.}]{\text{low temp., UV}} Fe_2(CO)_9 + CO$$

$$Fe_2(CO)_9 \xrightarrow{\text{323 K}} Fe(CO)_5 + Fe(CO)_4; \qquad 3\,Fe(CO)_4 \longrightarrow Fe_3(CO)_{12}$$

$$3\,Ru(CO)_5 \longrightarrow Ru_3(CO)_{12} + 3\,CO$$

$$3\,Os(CO)_5 \longrightarrow Os_3(CO)_{12} + 3\,CO$$

$$2\,Co_2(CO)_8 \xrightarrow{\text{343 K}} Co_4(CO)_{12} + 4\,CO$$

(4) **From complex cyanides**:

Although of no preparative importance, the formation of $Ni(CO)_4$ by the disproportionation of a Ni(I) complex is of scientific interest. Reduction of a solution of the well-known potassium tetracyanonickelate complex with potassium amalgam gives a red solution containing tetracyano dinickelate ion. This ion absorbs carbon monoxide and disproportionates in water to $Ni(CO)_4$.

$$2\ K_2[Ni(CN)_4] + 2\ K \longrightarrow \underset{\text{red solution}}{K_4[Ni_2(CN)_6]} + 2\ KCN$$

$$[Ni_2(CN)_6]^{4-} + 2\ CO \longrightarrow [Ni_2(CN)_6(CO)_2]^{4-}$$

$$2\ [Ni_2(CN)_6(CO)_2]^{4-} + 2\ H^+ \longrightarrow 3\ [Ni(CN)_4]^{2-} + Ni(CO)_4 + H_2$$

Properties of metal carbonyls:

Physical: The metal carbonyls are all crystalline solids, except for $Fe(CO)_5$, $Ru(CO)_5$, $Os(CO)_5$, and $Ni(CO)_4$ which are liquids. On heating, they decompose at low temperatures, or sometimes change into polynuclear carbonyls. In any case, they finally decompose into the metal and carbon monoxide at higher temperatures. They are insoluble in water and are often decomposed by it. Except for $Fe_2(CO)_9$, all are soluble in organic solvents.

Chemical: Most of the carbonyls are oxidized by air. $Ni(CO)_4$ and $Co_2(CO)_8$ undergo exchange of CO with ^{14}C-labelled carbon monoxide. In such exchange reactions, all eight CO groups in $Co_2(CO)_8$ are equivalent, indicating that there is an equilibrium between bridged and non-bridged structures in this compound. In the case of $Ni(CO)_4$, kinetics of the exchange reaction is first order with respect to the metal carbonyl, indicating that its dissociation is the rate-determining step.

$$Ni(CO)_4 \xrightarrow{\text{slow}} Ni(CO)_3 + CO$$

$$Ni(CO)_3 + {}^{14}CO \xrightarrow{\text{fast}} Ni(CO)_3\ ({}^{14}CO)$$

All neutral metal carbonyls can be converted into anions by the action of sodium hydroxide solution, with the loss of one CO group. E.g.,

$$Fe(CO)_5 + 2\ OH^- \longrightarrow [Fe(CO)_4]^{2-} + H_2O + CO_2$$

The anions may pick up protons to yield $[HFe(CO)_4]^-$ and then $H_2Fe(CO)_4$.

The metal carbonyls may also be attacked by strong acids to produce complex cations. E.g.,

$$Fe(CO)_5 + H^+ \longrightarrow [HFe(CO)_5]^+$$

The action of halogens on some metal carbonyls yield carbonyl halides. E.g.,

$$2\ Mo(CO)_6 + 2\ Cl_2 \longrightarrow [Mo(CO)_4Cl_2]_2 + 4\ CO$$

$$Mn_2(CO)_{10} + Br_2 \longrightarrow 2\ Mn(CO)_5Br$$

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

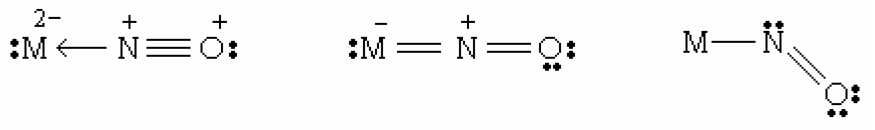
Nitrosyl Complexes: [Ref: Douglas B., McDaniel D. and Alexander J., Concepts and Models of Inorganic Chemistry, 3rd edn., John Wiley, (2001), p.573.]

Complexes containing NO as ligand nearly always contain them as NO^+ (see pages 6,7 under π-acceptor ligands). In such compounds, the 18 electron rule is obeyed with the same consistency as in the metal carbonyls. Nitric oxide is a paramagnetic molecule with one electron in an antibonding orbital. This electron is easily lost to form NO^+, resulting in an increase in the N—O stretching frequency from 1878

$\mathrm{cm^{-1}}$ (in NO) to 2200-2400 $\mathrm{cm^{-1}}$ (in nitrosonium salts). Most complexes of nitric oxide and transition metals are best considered to be those of NO^+, three electrons being donated to the metal atom. M→N back π-bonding then takes place exactly as in CO. Only the following mononuclear metal nitrosyls or nitrosyl carbonyls are known:

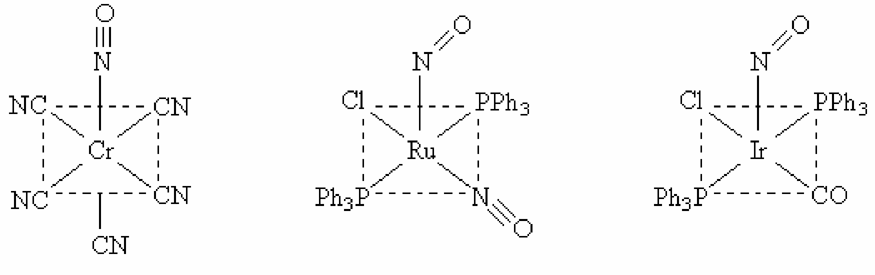
$[Co(NO)(CO)_3]$ $[Fe(NO)_2(CO)_2]$ $[Mn(NO)_3(CO)]$ $[Co(NO)_3]$	All isoelectronic with $[Ni(CO)_4]$
$[Mn(NO)(CO)_4]$	Isoelectronic with $Fe(CO)_5$
$[V(NO)(CO)_5]$	Isoelectronic with $Cr(CO)_6$
$Mn_2(NO)_2(CO)_7$ (binuclear)	Isoelectronic with $Fe_2(CO)_9$

NO contains one more electron than CO in a π^* orbital, and therefore acts as a three-electron donor. In electron-counting terms, 3CO = 2NO. Thus $[Fe(NO)_2(CO)_2]$ is isoelectronic with $[Fe(CO)_5]$, and $[Cr(NO)_4]$ and $[V(CO)_5NO]$ are isoelectronic with $[Cr(CO)_6]$. Three valence bond structures can be written for nitrosyl complexes:



(a) (b) (c)

In structure (a), NO places its a π^* electron in a singly occupied π metal orbital producing a non-bonding pair on the metal atom and donates two electrons to form a sigma bond with the metal atom. This is called the **NO^+ coordination mode**. The formal charges in (a) are larger than the ones in the analogous isocyanide structure. In structure (b), the nonbonding pair is back-donated into the π^* orbital of NO, thereby lowering the NO bond order. In (c), an electron pair is localized on the N in an sp^2 orbital, leading to a bent structure. In a formal sense, one lone pair electron must have come from the metal, giving the so-called **NO^- coordination mode**. Nitrosyl complexes are known with both linear and bent NO. Complexes of the first-row transition metals with a relatively small number of electrons on the metal atom tend to give linear nitrosyl complexes, while complexes of the third-row transition metals having a large number of electrons on the metal atom tend to give bent nitrosyl complexes.



(a) (b) (c)

For example, $[Cr(CN)_5NO]^{3-}$ has an octahedral structure with a linear NO (structure *a*). Likewise, $[Co(diars)_2(NO)]^{2+}$ {diars = *o*-$(Me_2As)_2C_6H_4$} has a trigonal bipyramidal structure with a linear equatorial NO. But when an additional electron pair is introduced into the coordination sphere as in $[Co(NCS)(diars)_2(NO)]^+$, it has an octahedral structure with a bent NO. The complex (Ru belongs to the second transition series) $[RuCl(PPh_3)_2(NO)_2]^+$ has one linear equatorial and one bent apical NO groups (structure *b*). On the other hand, the isoelectronic complex of Ir (Ir belongs to the third transition series) $[Ir(CO)(PPh_3)_2(NO)_2]^+$ has a square-pyramidal structure with a bent apical NO (structure *c*). It may be considered as a compound of Ir(III) in which two electrons from Ir(I) have converted NO^+ to NO^- with a bent geometry. The energy factors involved in bending are influenced by other factors also, so that it is not always possible to correctly predict the mode of coordination observed.

Preparation: Nitrosyl complexes can be prepared by the direct displacement of CO groups with NO, or by treatment with acidified nitrites. E.g.,

$$V(CO)_6 + NO \longrightarrow V(NO)(CO)_5 + CO\uparrow$$

$$(Ph_3P)_2Mn_2(CO)_8 + 2\,NO \longrightarrow 2\,Mn(NO)(CO)_4 + 2\,Ph_3P$$

$$Mn(NO)(CO)_4 + 2\,NO \longrightarrow Mn(NO)_3(CO) + 3\,CO\uparrow$$

$$Fe_2(CO)_9 + 4\,NO \longrightarrow 2\,Fe(NO)_2(CO)_2 + 5\,CO\uparrow$$

$$Co_2(CO)_8 + 2\,NO \longrightarrow 2\,Co(NO)(CO)_3 + 2\,CO\uparrow$$

$$Co(NO)(CO)_3 + 2\,NO \longrightarrow Co(NO)_3 + 3\,CO\uparrow$$

$$Fe(CO)_5 + 2\,NO \rightarrow Fe(CO)_2(NO)_2 + 3\,CO$$

$$[Co(CO)_4]^- + H^+ + HNO_2 \rightarrow [Co(CO)_3(NO)] + H_2O + CO$$

Properties: All these compounds are low-melting solids, thermally unstable, oxidized by air and decomposed by water.

Structures:

$Fe(NO)_2(CO)_2$ = tetrahedral

$Co(NO)(CO)_3$ = tetrahedral

$Mn(NO)(CO)_4$ = trigonal bipyramid with NO in the equatorial plane

$(Ph_3P)_2Mn(NO)(CO)_2$ = trigonal bipyramid with Ph_3P at the apices

Two other nitrosyl complexes of iron need special mention because they are important in analytical chemistry. The brown ring formed in the test for nitrate is due to the formation of the brown-coloured complex $[Fe(H_2O)_5NO]^{2+}$.

$$2\,KNO_3 + H_2SO_4 \longrightarrow K_2SO_4 + 2\,HNO_3$$

$$2\,HNO_3 + 6\,FeSO_4 + 3\,H_2SO_4 \longrightarrow 3\,Fe_2(SO_4)_3 + 4\,H_2O + 2\,NO$$

$$Fe^{2+} + 6\,H_2O \longrightarrow [Fe(H_2O)_6]^{2+}$$

$$[Fe(H_2O)_6]^{2+} + NO \longleftrightarrow [Fe(H_2O)_5NO]^{2+} + H_2O$$

The equilibrium in the last step is reversible, and the brown complex can be destroyed by blowing nitrogen through the solution to remove nitric oxide. The magnetic moment of the complex is 3.9 BM corresponding to the presence of three unpaired electrons. This indicates that, formally, the ion is a high-spin d^7 complex of Fe(I) and NO^+. But the N—O stretching frequency of 1745 cm^{-1} indicates very strong π-bonding and the intense brown colour suggests $Fe^1 \rightarrow NO^+$ charge transfer.

Another important nitrosyl complex compound of iron is sodium nitroprusside, $Na_2[Fe(CN)_5NO]$ i.e., sodium nitroso pentacyano ferrate(II). {Prussic acid = old name for HCN}. A solution of the compound is colourless, but turns purple in presence of sulfide ions.
It is prepared by the action of nitric acid on hexacyanoferrate(II).

$$[Fe(CN)_6]^{4-} + 4\,H^+ + NO_3^- \longrightarrow [Fe(CN)_5NO]^{2-} + CO_2 + NH_4^+$$

The formulation of the complex anion as NO^+ derivative of Fe(II) is supported by its diamagnetism, N—O stretching frequency of 1939 cm^{-1} and N—O bond distance of 113 pm. The purple colour developed with sulphide ions is due to the formation of $[Fe(CN)_5NOS]^{4-}$.

$$[Fe(CN)_5NO]^{2-} + S^{2-} \longrightarrow [Fe(CN)_5NOS]^{4-}$$

Complexes of NO^- are also known. For example, a black compound is formed by the action of nitric oxide on an ammoniacal solution of Co(II) salts. It contains a monomeric cation $[Co(NH_3)_5NO]^{2+}$. The very low N—O stretching frequency of 1170 cm^{-1} and a long N—O bond distance (variously reported as 126 and 141 pm) suggest the presence of NO^-.

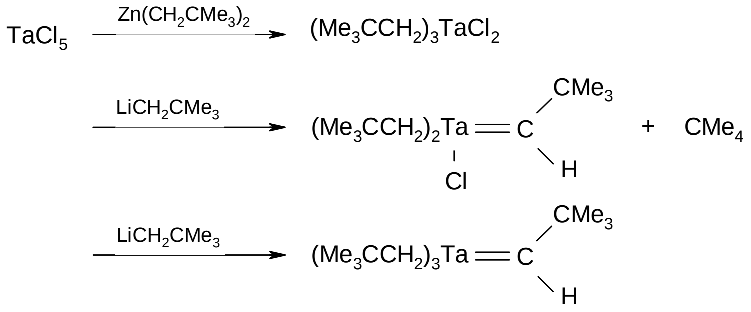
Metal cyanides:

Since the orbital structures of CO and CN^- are very similar, there are remarkable structural similarities in the complexes of CO and CN^- (see pages 6,7 under π-acceptor ligands). Since it is a negatively charged ion, it shows a lesser back-bonding ability compared to CO. The range of C≡N stretching frequencies observed in complex cyanides is quite small (2000-2170 cm^{-1}, compared with 2080 cm^{-1} in KCN). Because of the structural similarities, CO in metal complexes can often be replaced by CN^-. A few examples are $[Mo(CO)_3(CN)_3]^{3-}$, $[W(CO)_3(CN)_3]^{3-}$, $[Fe(CO)(CN)_5]^{3-}$, $[Ni_2(CO)_2(CN)_6]^{4-}$ and $[Ni(CO)_2(CN)_2]^{2-}$.

Carbene (alkylidine) and carbyne (alkylidyne) complexes:
(Ref: Alan G. Sharpe, Inorganic Chemistry International Student Edition, 3rd edn, Addisson-Wesley, 1999, p 558-9)

These are organometallic complexes which have been prepared very recently. The carbene or alkylidine complexes have a metal-carbon double bond (M=C) in them. The carbyne or alkylidyne complexes have a metal-carbon triple bond (M≡C). They can be prepared by the α-deprotonation of suitable alkyl compounds. E.g.,

For the last compound, only one structure is possible and the Ta—C(Me) bond (225 pm) is substantially longer than the Ta=C (carbene) bond (205 pm). We can think of the bond in two ways:

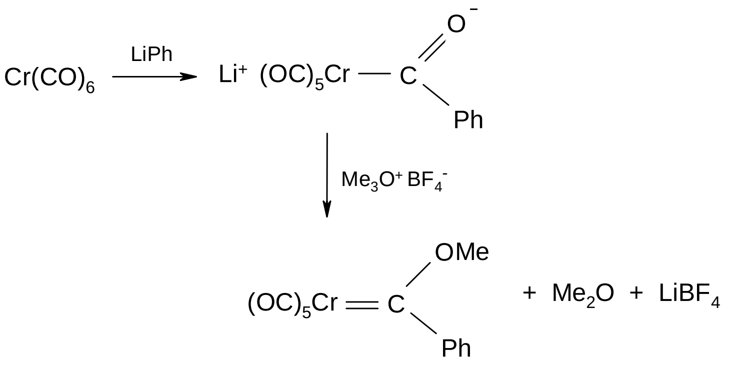


(1) the CH_2 as a neutral molecule forming a σ-bond to the metal using its lone pair of sp^2 electrons, and in turn receiving a pair of electrons from Ta^{3+} ion into its empty *p*-orbital.

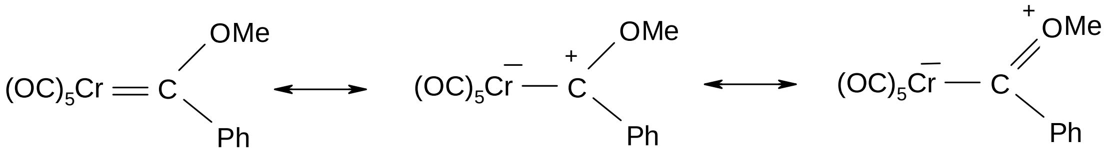
(2) as a CH_2^{2-} ion (CH_4 minus 2 H^+) donating four electrons to a Ta^{5+} ion.

The all-alkyl compound with the above structure has 10 electrons in its valence shell. The cycopentadienyl methyl carbene complex $[(\eta^5\text{-}C_5H_5)_2(Me)Ta{=}CH_2]$ has 18 electrons (the Ta is considered to be in the +5 oxidation state with each methyl group donating a pair of electrons). The tungsten atom in $[(OC)_5W{=}CPh_2]$ also has 18 electrons.

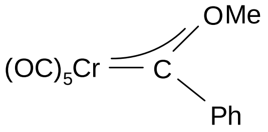
When the carbine contains substituents capable of donating electrons (like the OMe group), the structure becomes more complicted. One such compound is synthesized as follows:



The Cr—CO distance in the carbene complex is almost the same as in $Cr(CO)_6$ (188 pm and 199 pm respectively), but the Cr=C distance is longer (204 pm) indicating a weaker bond with very little metal-carbon π-bonding. Further, the C—OMe bond distance is 133 pm, which is intermediate between that of a C—O single bond (143 pm) and a C=O double bond (123 pm). These data suggest that the molecule is a resonance hybrid which is represented as:



which is equivalent to



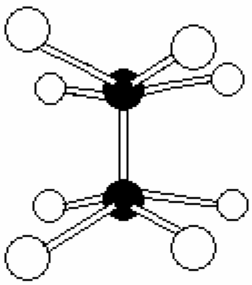
Carbynes or alkylidynes contain the M≡C triple bond and a typical preparation is given below.

$$WCl_6 + LiCH_2CMe_3 \longrightarrow Me_3C\text{-}C{\equiv}W(CH_2CMe_3)_3 + CMe_4 + LiCl$$

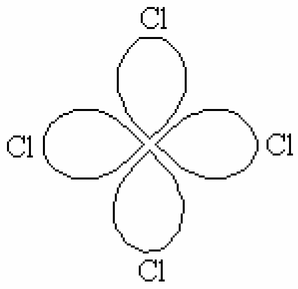
Very short C—M bond lengths confirm the presence of a triply bonded structure.

Metal-metal triple and quadruple bonds – $[Re_2Cl_8]^{2-}$. [Ref: Douglas B., McDaniel D. and Alexander J., Concepts and Models of Inorganic Chemistry, 3rd edn., John Wiley, (2001), p.752.]

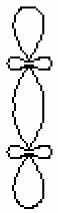
Cotton and co-workers found that compounds such as $CsReCl_4$ contains a dimmer, $[Re_2Cl_8]^{2-}$ and a trimer $[Re_3Cl_{12}]^{3-}$. The dimmer has a surprising structure containing two **eclipsed** planar $[ReCl_4]^-$ units joined only by an Re–Re bond. The eclipsed configuration is unexpected because of strong repulsion between adjacent Cl^- ions. This distortion is evident from the deviation from planarity of the $ReCl_4$ units, with Cl–Cl distances between the units much longer than the Re–Re distance. The unusually short Re–Re distance (224 pm, compared with 275 pm in the metal) and the eclipsed configuration led Cotton and co-workers to propose a quadruple bond between the Re atoms. The nearly planar $ReCl_4$ units are assumed to use the $d_{x^2-y^2}\,sp^2$ hybrid orbitals of Re for Re–Cl bonding. A σ Re–Re can be formed using the d_{z^2} orbitals. Two equivalent π bonds are formed using d_{xz} and d_{yz} orbitals on each Re. The d_{xy} orbitals of the two Re atoms are parallel, forming a δ bond. This bond requires the eclipsed configuration for the proper alignment of the *d* orbitals.



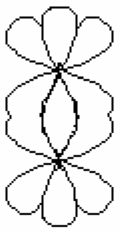
Eclipsed conformation of $[Re_2Cl_8]^{2-}$



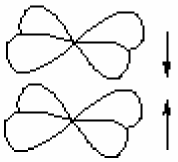
$d_{x^2-y^2}$ sp^2 hybrid orbitals of Re overlapping with orbitals of Cl in square planar geometry



d_{z^2} orbitals of the Re atoms overlapping to form sigma bond



d_{xz} and d_{yz} orbitals of Re overlapping to form two pi bonds



d_{xy} orbitals of Re overlapping to form a delta bond