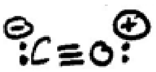
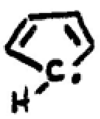
18 ELECTRON RULE [EFFECTIVE ATOMIC NUMBER (EAN) RULE]

In 1927, Sidwick thought that the coordination compounds should reach the noble gas structure in order to gain a stable structure. He suggested the theory called the 18-electron rule by saying that there should be 18 valence electrons around the central atom in most of the stable coordination compounds. The valence shells of transition metals consist of nine valence orbitals (one s orbital, three p orbitals and five d orbitals). These orbitals are filled with a total of 18 electrons. In the EAN rule, thermodynamically stable transition metal compounds contain 18 valence electrons comprising of the metal electrons plus the electrons supplied by the ligands. If the EAN of the central metal is equal to the number of electrons in the nearest noble gas [36 (Kr), 54 (Xe), 86 (Rn)] then the complex possess greater stability. By this rule, carbonyl, nitrozyl, olefin (π) and metallocene complexes can be described.

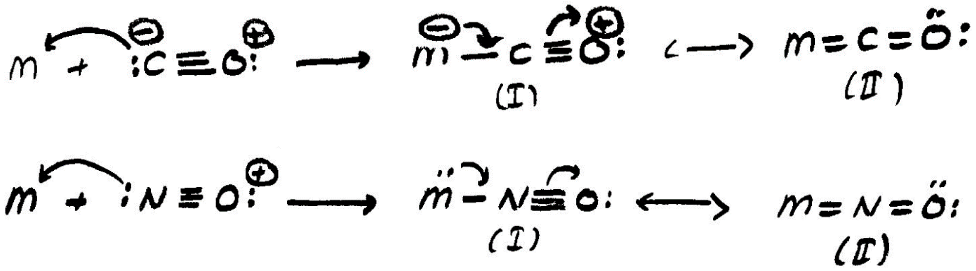
Ligand	***Electron contribution***
Hydrogen	*1*
Alkyl, aryl	*1*
carbonyl 	*2*
nitrosyl 	*3*
Cl^-, PR_3, NR_3	*2*
Olefin (per double bond)	*2*
allyl  *(C_3H_5)*	*3*
Cyclopentadienyl  *(C_5H_5)*	
Benzene	*6*
Cycloheptatrienyl  *(C_7H_7)*	*7*
Vinyl 	*3*

In order to comply with the EAN rule, transition metals can be grouped into three classes:

1. *<u>Group coordination compounds</u>: Central atom has a low or a medium valency. The interaction between the ligands and the d orbitals of the central atom is a weakness σ interaction.*

2. *<u>Group coordination compounds</u>: Central atom has a higher valency. The interaction between the ligands and the d orbitals of the central atom is a strong σ interaction.It is mostly seen in the complexes of 2nd and 3rd order transition metals.*

3. *<u>Group coordination compounds</u>: Central atom has a low valency. The interaction between the ligands and the central atom is strong. There is π interaction between the d orbitals of the central atom and the ligands along with the σ interaction.*



Central atom	*Atomic number*	*Complex*	*Electron contribution from ligands*	*Total number of valence electrons*	*EAN*
Cr	24	$[Cr(CO)_6]$	12	6+12=18	24+12=36 [Kr]
Fe	26	$[Fe(CN)_6]^{4-}$	12	6+12=18	24+12=36 [Kr]
Fe	26	$[Fe(CO)_5]$	10	8+10=18	26+10=36 [Kr]
Co	27	$[Co(NH_3)_6]^{3+}$	12	6+12=18	24+12=36 [Kr]
Ni	28	$[Ni(CO)_4]$	8	10+8=18	28+8=36 [Kr]
Cu	29	$[Cu(CN)_4]^{3-}$	8	10+8=18	28+8=36 [Kr]
Pd	46	$[Pd(NH_3)_6]^{4+}$	12	6+12=18	42+12=54 [Xe]
Pt	78	$[PtCl_6]^{2-}$	12	6+12=18	74+12=86 [Rn]
Fe	26	$[Fe(CN)_6]^{3-}$	12	5+12=17	23+12=35
Ni	28	$[Ni(NH_3)_6]^{2+}$	12	8+12=20	26+12=38
Pd	46	$[PdCl_4]^{2-}$	8	8+8=16	44+8=52
Pt	78	$[Pt(NH_3)_4]^{2+}$	8	8+8=16	76+8=84

WERNER COMPLEXES

$[Co(NH^3)_6]^{3+}$

$Co:27e^-$

$Co^{3+}:24e^-$

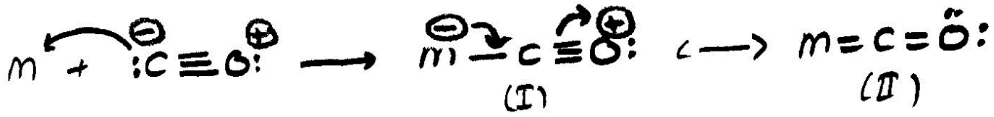
$24+6x2=36e^-$ (Kr)

$Co:9e^-$

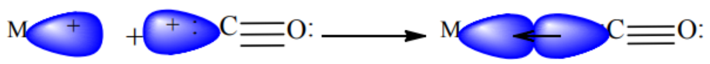
$Co^{3+}:6e^-$

$6+6x2=18e^-$

CARBONYL COMPLEXES (METAL CARBONYLS)

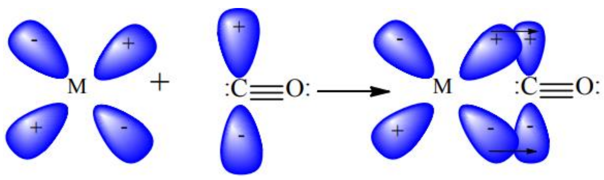


Formation of dative σ-bond: The overlapping of empty hybrid orbital (a blend of d, s and p orbitals) on metal atom with the filled hybrid orbital (HOMO) on carbon atom of carbon monoxide molecule results into the formation of a M←CO σ-bond.



Formation of a M←CO σ-bond in metal carbonyls

Formation of π-bond by back donation: This bond is formed because of overlapping of filled dπ orbitals or hybrid dpπ orbitals of metal atom with low-lying empty (LUMO) orbitals on CO molecule.



Formation of M→CO π-bond by back donation in metal carbonyls

If the atomic number of the central atom is double digit number;

$Fe(CO)_5$

Fe:26e^-

Fe^0:26e^-

26+5x2=36e^-(Kr)

Fe:8e^-

Fe^0:8e^-

8+5x2=18e^-

If the atomic number of the central atom is single digit number;

a) The complex can get dimerization.

b) The complex can receive electrons.

c) The complex receive radicals.

$${}_{25}Mn + 5CO \longrightarrow Mn(CO)_5$$

Mn:25e^-

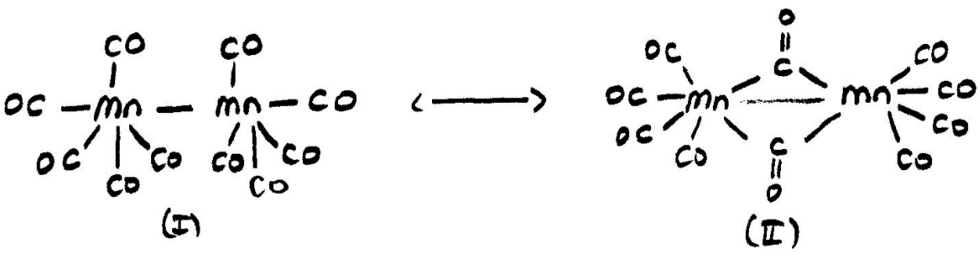
Mn^0=25e^-

25+5x2=35e^- (unstable)

a) $2Mn + 10\ {:}\overset{\ominus}{C}{\equiv}\overset{\oplus}{O}{:} \longrightarrow Mn_2(CO)_{10}$

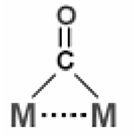
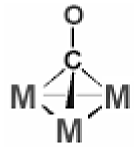
$$2Mn = 2\times25 = 50e^-$$
$$10\,CO = 10\times2 = 20e^-$$
$$Mn{-}Mn = 2e^-$$
$$+\ \overline{72e^-}$$

For 1 Mn: 36e^- (Kr)



Which of these structures [(I) or (II)] will occur depends on the size of the metal atom. The larger the metal atom, the more linear structure is preferred. It is difficult to be a bridge between two large metal atoms for CO. Because the metal-C bonds to be formed by the bridge will have to be too long.

Which of these structures will occur can be found by IR spectroscopy:

	Free CO	*Terminal CO*	*μ^2-bridging CO*	*μ^3-bridging CO*
	O≡C	O≡C→M		
ν_{CO} IR (cm^{-1})	*2143*	*1850-2100*	*1700-1850*	*1600-1730*

b) $Mn + 5CO \longrightarrow Mn(CO)_5 \xrightarrow{+e^-} [Mn(CO)_5]^- \xrightarrow{Na^+} Na[Mn(CO)_5]$

$[Mn(CO)_5]^-$ $\quad [Mn(CO)_5] \xrightarrow{Na} Na^+[Mn(CO)_5]^-$

$Mn^{\ominus} + :\overset{\ominus}{C}\equiv O:^{\oplus} \longrightarrow Mn^{2-}-C\equiv O^{\oplus} \longleftrightarrow \overset{(-)}{Mn}=C=\ddot{O}:$

c) $Mn(CO)_5 +$
- $\cdot Cl \longrightarrow [Mn(CO)_5Cl]$
- $\cdot H \longrightarrow [HMn(CO)_5]$
- $\cdot X \longrightarrow [Mn(CO)_5X]$
- $\cdot CH_3 \longrightarrow [Mn(CO)_5CH_3]$

$M_2(CO)_x + 2Na \longrightarrow 2Na[M(CO)_{x/2}]$
$\quad + I_2 \longrightarrow 2[M(CO)_{x/2}I]$
$\quad + H_2 \longrightarrow 2[HM(CO)_{x/2}]$

$M(CO)_x + Na \longrightarrow Na[M(CO)_x]$

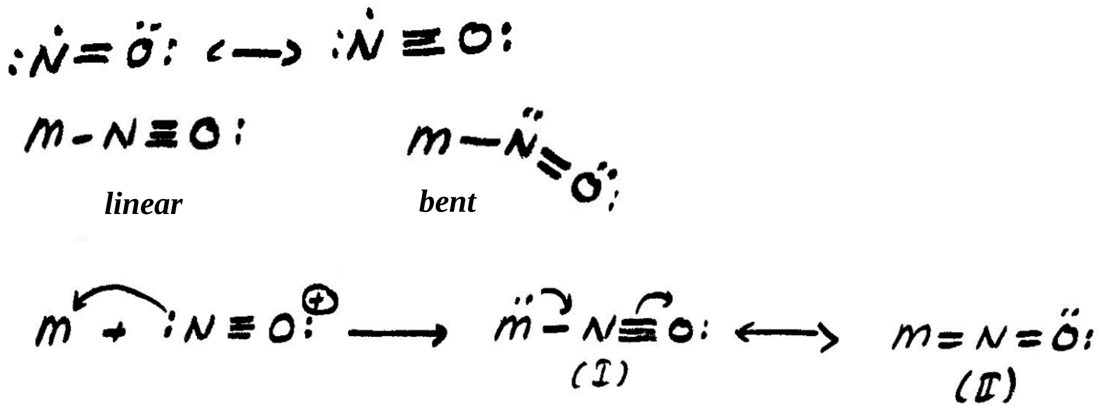
$M(CO)_xBr + Na[M(CO)_x] \longrightarrow M_2(CO)_{2x} + NaBr$

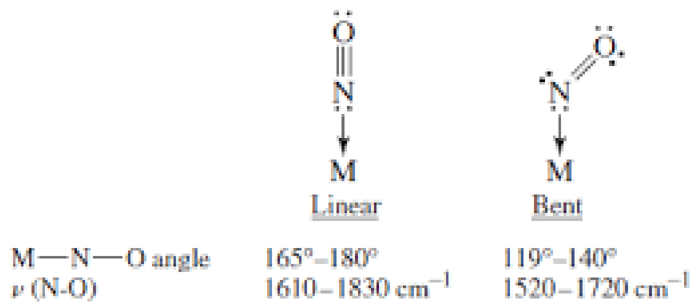
$[M(CO)_x]^- + H^+ \longrightarrow [HM(CO)_x]$

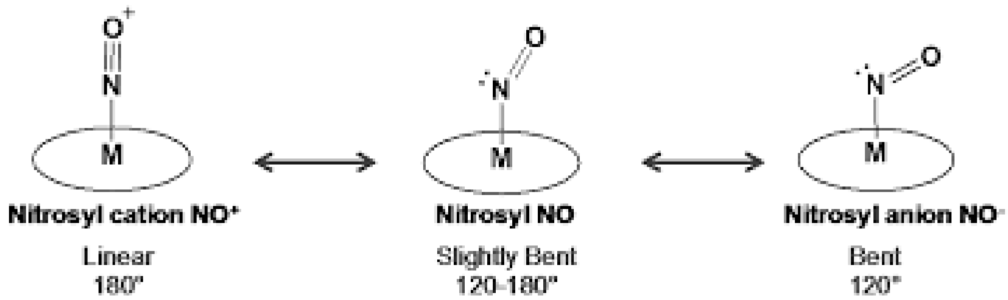
		polynuclear	
mononuclear	**dinuclear**	**threenuclear**	**tetranuclear**
$Cr(CO)_6$	$Mn_2(CO)_8$	$Te_3(CO)_{12}$	$Co_4(CO)_{12}$
$Mo(CO)_6$	$Re_2(CO)_8$	$Fe_3(CO)_{12}$	$Rh_4(CO)_{12}$
$W(CO)_6$	$Fe_2(CO)_8$	$Ru_3(CO)_{12}$	$Ir_4(CO)_{12}$
$Fe(CO)_5$	$Co_2(CO)_8$	$Os_3(CO)_{12}$	
$Ru(CO)_5$	$Rh_2(CO)_8$		
$Os(CO)_5$	$Ir_2(CO)_8$		
$Ni(CO)_4$			

NITROSIL COMPLEXES

NO binds to a transition metal in two ways:







$Cr(NO)_4$

$Cr: 24e^-$

$Cr^0: 24e^-$

$24+4x3=36e^-$ (Kr)

$Cr: 6e^-$

$Cr^0: 6e^-$

$6+4x3=18e^-$

DINITROGEN COMPLEXES

N_2 (dinitrojen), is both a weak σ-donor and a weak π-receptor ligand since there is no dipole moment. In complexes, N_2 binds in a wide variety of ways to the metal atom.

Terminal binding

Head-tail-bridge binding

Terminal binding

Head-tail-bridge binding

DIOXYGEN COMPLEXES

Both dioxygen (O_2) and dinitrogen (N_2) complexes are important in relation to biological systems. Reactions that O_2 binds to transition metals as ligands are reversible. By increasing the temperature or reducing the partial pressure of O_2, the dioxygen leaves the structure. This reversibility is important in biological systems. O_2 carriage of hemoglobin is based on the reversible property of dioxygen complexes. In some complexes, O_2 is considered to be O_2^- in some complexes and O_2^{-2} in some complexes.

superoxo monomeric

superoxo dimeric

peroxo chelate

peroxo dimeric