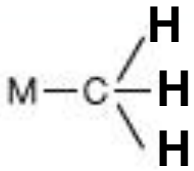
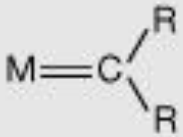
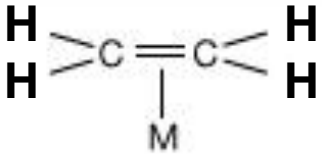
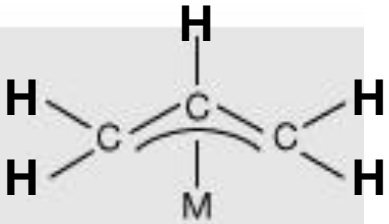
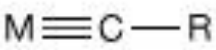
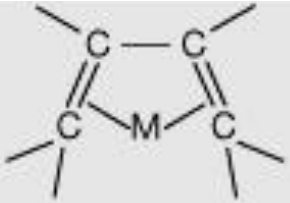
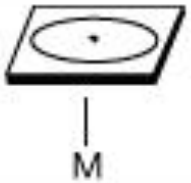
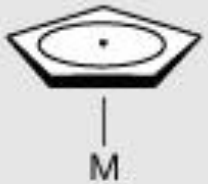
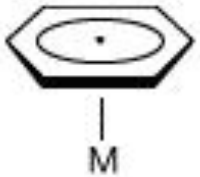
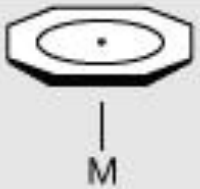
Common Organic Ligands

methyl, alkyl CH_3, CH_2R	
alkylidene (carbene)	
alkene $H_2C = CH_2$	
π-allyl C_3H_5	
alkylidyne (carbyne) C — R	

1,3-butadiene C_4H_6	
cyclobutadiene C_4H_4	
cyclopentadienyl C_5H_5 (Cp)	
benzene C_6H_6	
cyclooctatetraene C_8H_8 (cot)	

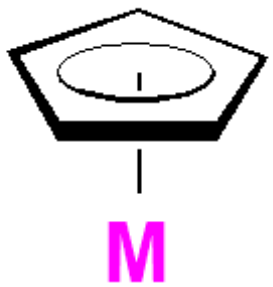
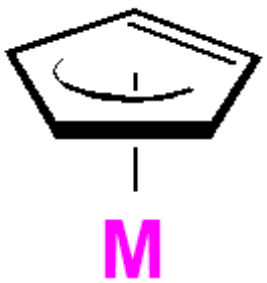
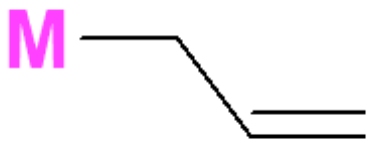
Carbon Monoxide (CO) is also an important ligand

Terminology: Hapticity

η^x

"eta-*x*" was originally developed to indicate how many ***contiguous*** donor atoms of a π-system were coordinated to a metal center. ***Hapticity*** is another word used to describe the bonding mode of a ligand to a metal center. An η^5-cyclopentadienyl ligand, for example, has all five carbons of the ring bonding to the transition metal center.

η^x values for all-carbon based ligands where the x value is odd usually indicate ***anionic*** carbon ligands (e.g., η^5-Cp, η^1-CH_3, η^1-allyl or η^3-allyl, η^1-$CH{=}CH_2$). The # of electrons donated (ionic method of electron counting) by the ligand is usually equal to $x + 1$. Even η^x values usually indicate ***neutral*** carbon π-system ligands (e.g., η^6-C_6H_6, η^2-$CH_2{=}CH_2$, η4-butadiene, η^4-cyclooctadiene). The # of electrons donated by the ligand in the even (*neutral*) case is usually just equal to *x*.

			
η^5-Cp	η^3-Cp	η^3-allyl	η^1-allyl

Common Ligands and Electrons Contributed

- Electron Counting

a) Common organometallic ligands are assigned an electron count and charge; those that are commonly ions are treated as such

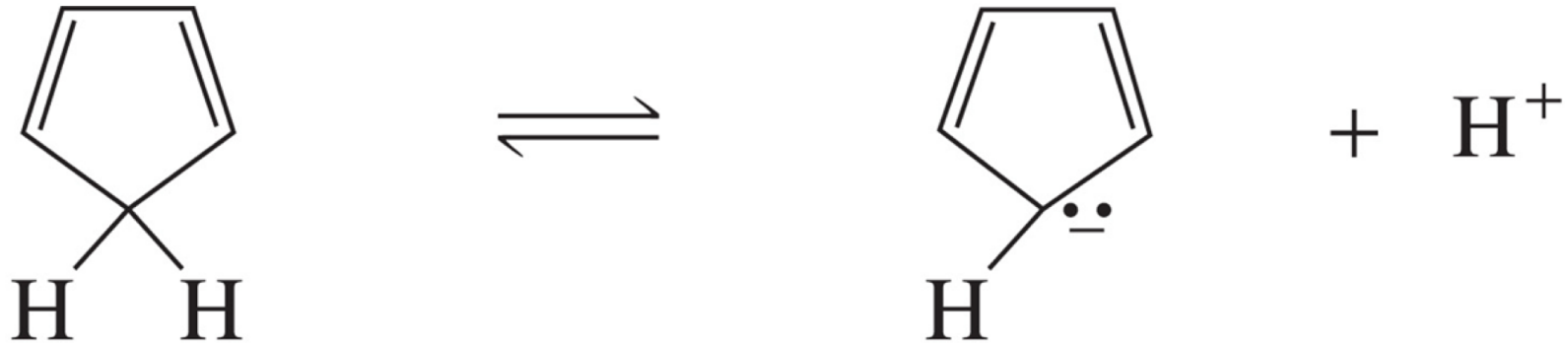
b) The overall charge on the complex must equal the total charge on ligands plus the charge on the metal; this helps determine d-electron count of metal

c) Add up all electrons from metal d orbitals and ligands to find total e-count

Ligand	*Method A*
H	2 (H^-)
Cl, Br, I	2 (X^-)
OH, OR	2 (OH^-, OR^-)
CN	2 (CN^-)
CH_3, CR_3	2 (CH_3^-, CR_3^-)
NO (bent M—N—O)	2 (NO^-)
NO (linear M—N—O)	2 (NO^+)
CO, PR_3	2
NH_3, H_2O	2
=CRR' (carbene)	2
$H_2C{=}CH_2$ (ethylene)	2
CNR	2
=O, =S	4 (O^{2-}, S^{2-})
η^3-C_3H_5 (π-allyl)	2 ($C_3H_5^+$)
≡CR (carbyne)	3
≡N	6 (N^{3-})
Ethylenediamine (en)	4 (2 per nitrogen)
Bipyridine (bipy)	4 (2 per nitrogen)
Butadiene	4
η^5-C_5H_5 (cyclopentadienyl)	6 ($C_5H_5^-$)
η^6-C_6H_6 (benzene)	6
η^7-C_7H_7 (cycloheptatrienyl)	6 ($C_7H_7^+$)

Varying Hapticity = Varying Electron Contribution

- Consider the cyclopentadienyl anion.
- How do we get the cyclopentadienyl anion? How to understand its structure?



cyclopentadiene

$pK_a = 15$

cyclopentadienyl anion

$CH_3CH_3 \rightleftharpoons CH_3\ddot{\bar{C}}H_2 + H^+$

ethane

$pK_a > 60$

ethyl anion

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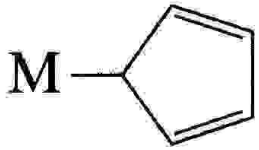
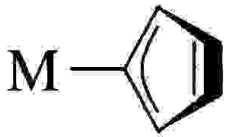
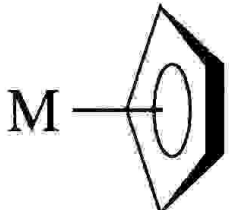
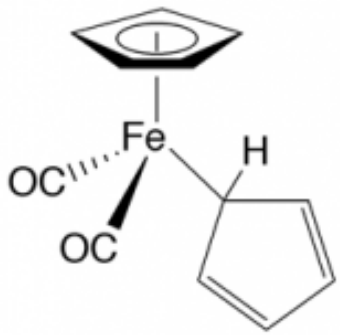
Varying Hapticity = Varying Electron Contribution

Number of bonding positions	*Formula*	*Name*	
1	η^1-C_5H_5	monohaptocyclopentadienyl 2 electron donor	
3	η^3-C_5H_5	trihaptocyclopentadienyl 4 electron donor	
5	η^5-C_5H_5	pentahaptocyclopentadienyl 6 electron donor	

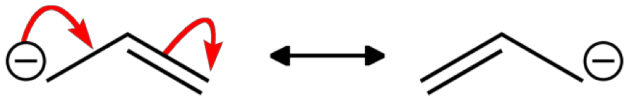
η^5-cyclopentadienyl

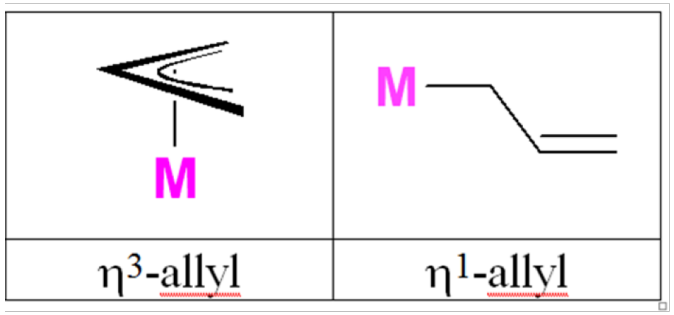


η^1-cyclopentadienyl

A molecule can have the Same ligand in different hapticities.

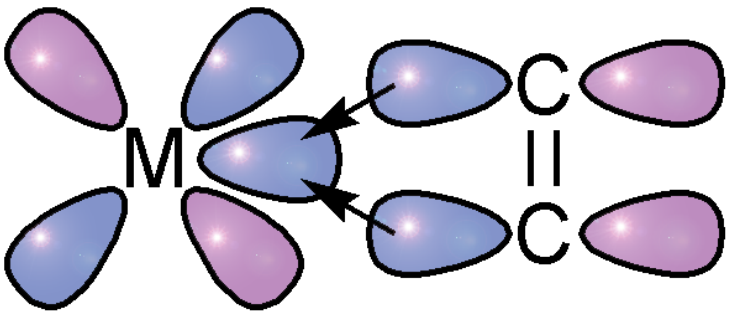
The allyl anion has similar attributes



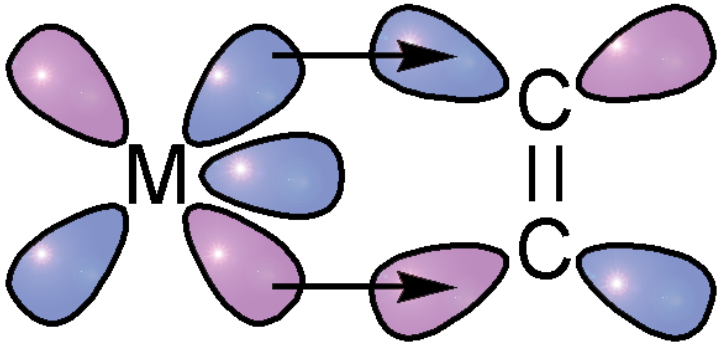


η^3-allyl	η^1-allyl
4 electron donor	2 electron donor

Dewar-Chatt-Duncanson Model for Metal-Alkene Bonding

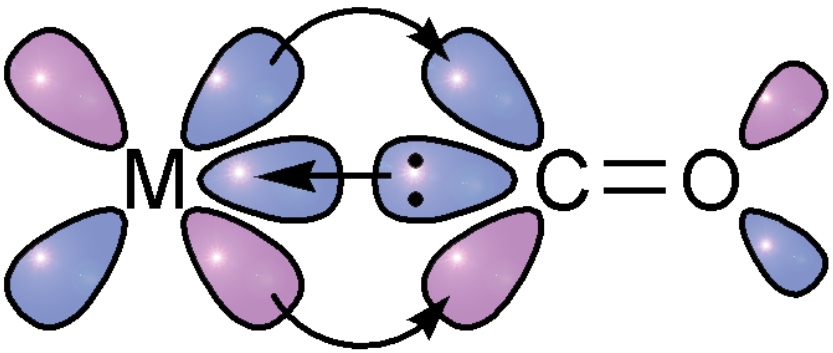


σ-component:
C-C π → empty metal orbital



π-component:
occupied metal d → empty C-C π*

Note the similarity to CO ligands...

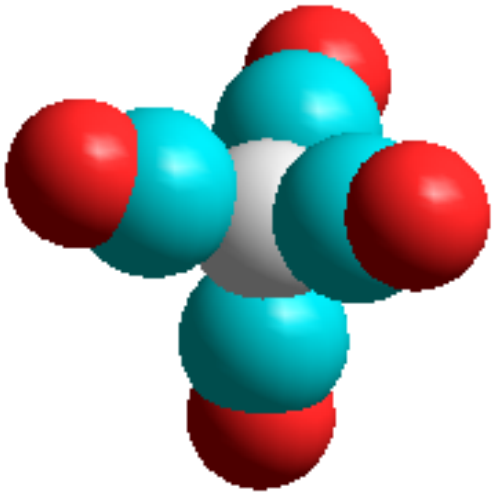


σ-component: donation of C lone pair

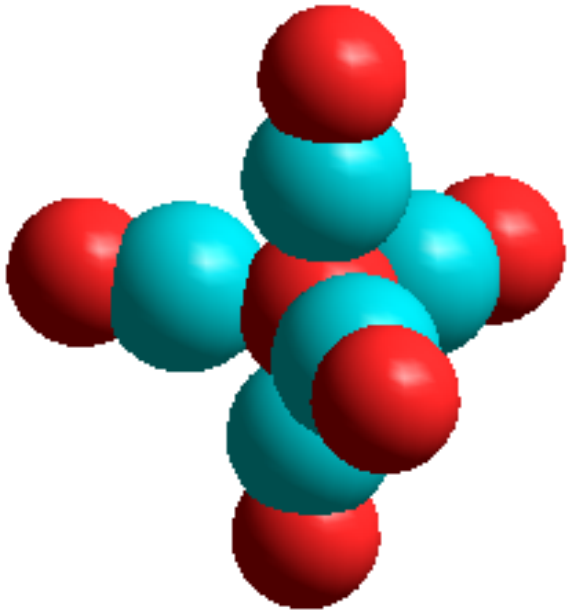
π-component: backbonding into CO π*

Metal-Carbonyl Complexes

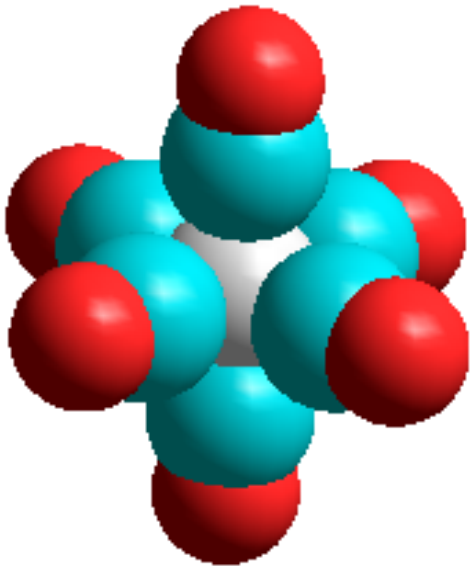
- The carbonyl ligand forms a huge number of complexes with metal ions, most commonly in low oxidation states, where it binds to the metal through its C-donor, as in the complexes below, where all the metal ions are zero-valent:



$[Ni(CO)_4]$



$[Fe(CO)_5]$



$[Cr(CO)_6]$

Metal-Carbonyl Complexes: 18 Electron Rule

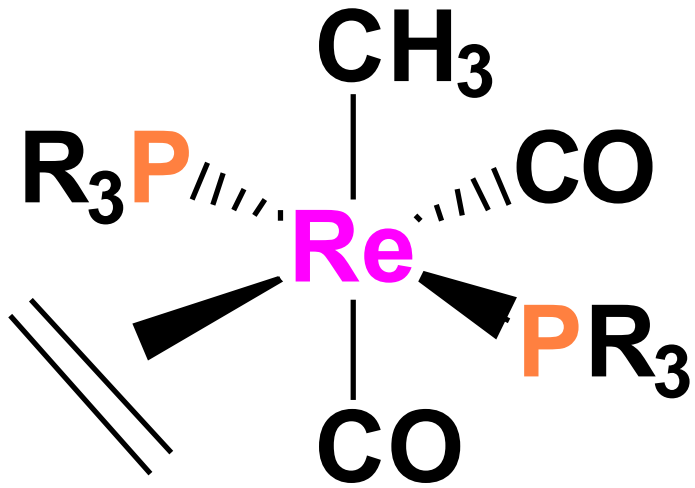
- Why in the above complexes Ni(0) has four C≡O groups attached to it, Fe(0) five C≡O, and Cr(0) six C≡O?

- The eighteen electron rule allows us to explain this observation.

- The charge on the complexes is zero. Since CO is a neutral molecule, the metals are in the zero oxidation state.

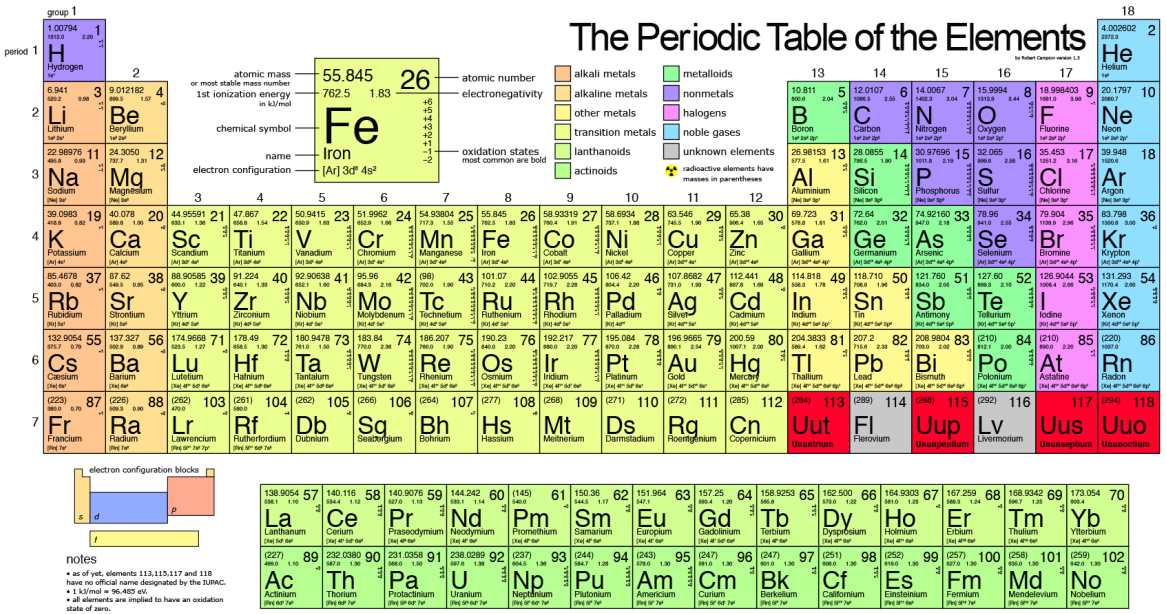
$[Ni(CO)_4]$	$[Fe(CO)_5]$	$[Cr(CO)_6]$
Ni(0) = d^{10}	Fe(0) = d^8	Cr(0) = d^6
4 x CO = 8	5 x CO =10	6 x CO = 12
18 e	18e	18e

Example: A Simple Case

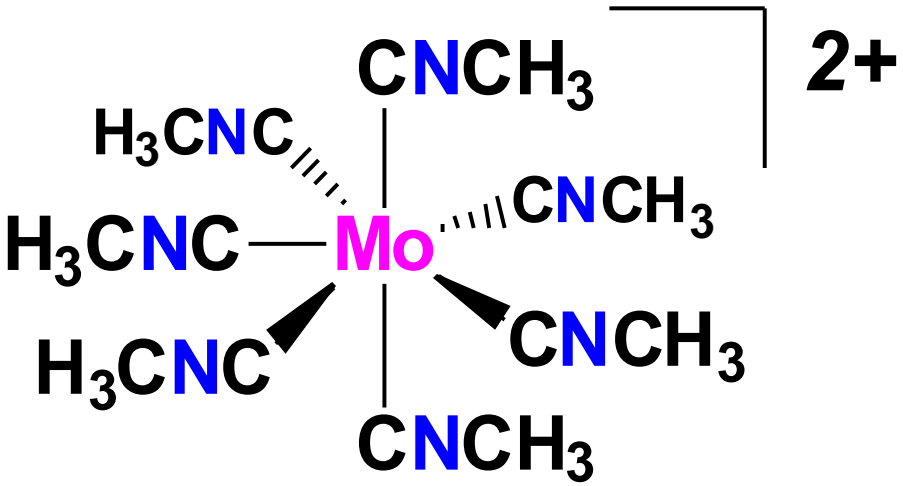


1) There is no overall charge on the complex
2) There is one anionic ligand (CH_3^-, methyl group)
3) The Re metal atom must have a +1 charge to compensate for the one negatively charged ligand. So the Re is the in the +1 oxidation state. We denote this three different ways: Re(+1), Re(I), or Re^{I}.

Re(+1)	d^6
2 PR_3	4e-
2 CO	4e-
CH_3^-	2e-
$CH_2{=}CH_2$	2e-
Total:	18e-

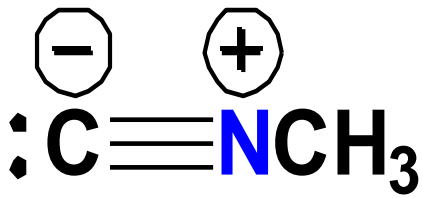


Example: Simple Case with Somewhat Unusual Ligand



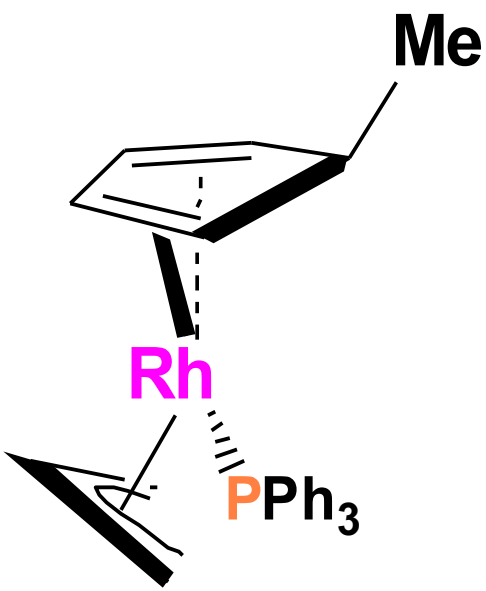
Mo(+2)		d^4
7 $CNCH_3$		14e-
	Total:	18e-

1) There is a +2 charge on the complex
2) The $CNCH_3$ (methyl isocyanide) ligand is neutral, but lets check the Lewis Dot structure to make sure that is correct:

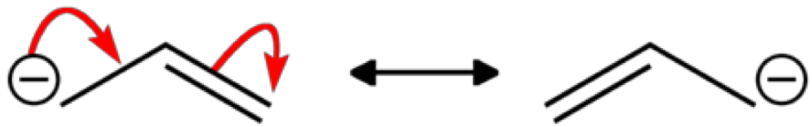


3) Because there is a +2 charge on the complex and all neutral ligands present, the Mo has a +2 charge & oxidation state.

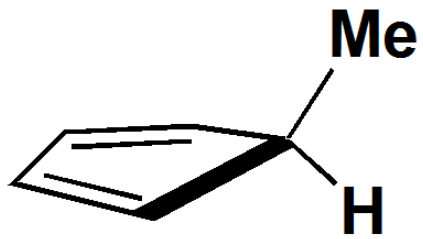
Example: Somewhat Tricky!



1) There is no overall charge on the complex
2) There is one anionic ligand ($C_3H_5^-$, allyl)



3) The top ligand is NOT a $MeCp^-$! It is a neutral diene that has a H attached to the methyl-substituted ring carbon. This is a neutral 4e- donor.

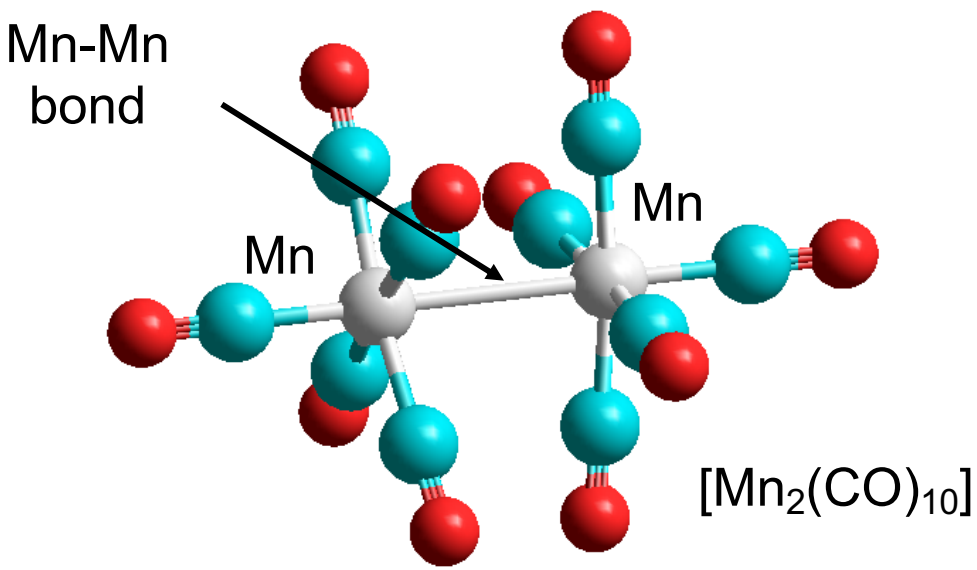


4) Because the complex is neutral and there is one anionic ligand present, the Rh atom must have a +1 charge to compensate for the one negatively charged ligand. So the Rh atom is in the +1 oxidation state.

Rh(+1)	d^8
PR_3	2e-
η^4-C_5H_5Me	4e-
η^3-$C_3H_5^-$	4e-
Total:	18e-

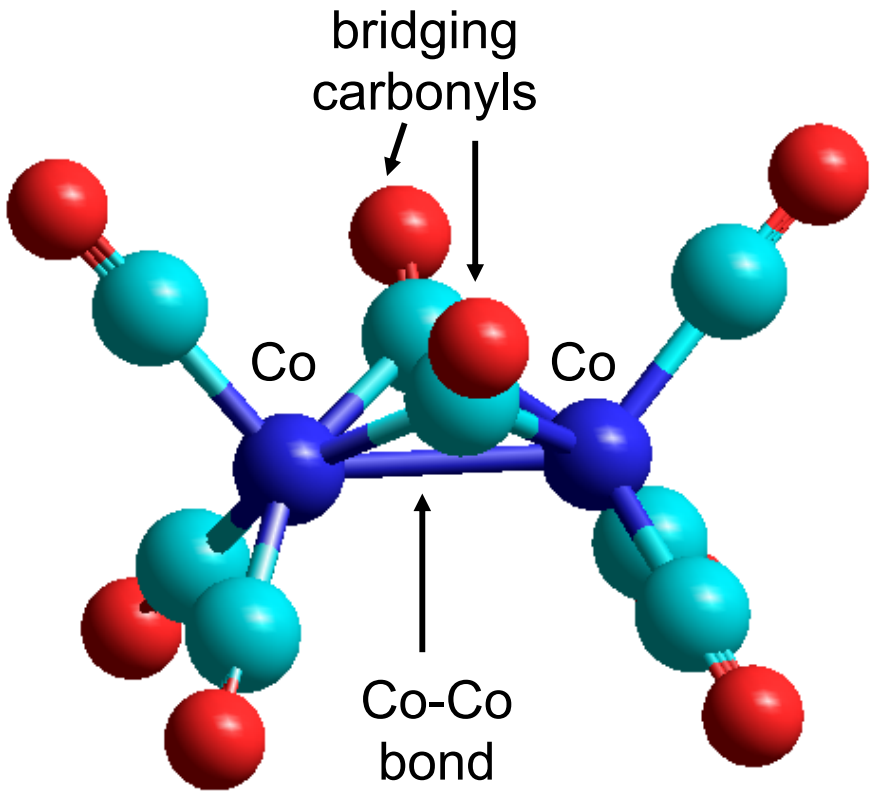
18 Electron Rule Explains Some Observations

- The compound $Mn_2(CO)_{10}$ exists but $Mn(CO)_5$ does not.
- A species such as $[Mn(CO)_5]$ would have only 17 e.
- Each Mn contributes one electron to the valence shell of the other Mn, giving the metal-metal bonded species $[(CO)_5Mn\text{-}Mn(CO)_5]$. To check on the 18e rule, we look at one metal at a time:

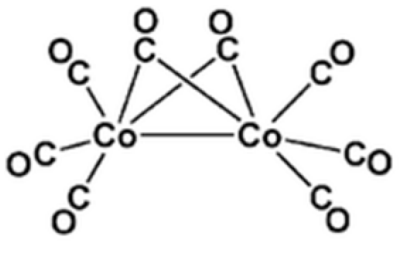


Mn(0)	=	d^7
5 C≡O	=	10
Mn-Mn	=	1
		18 e

Bridging Carbonyl Ligands



$[Co_2(CO)_8]$

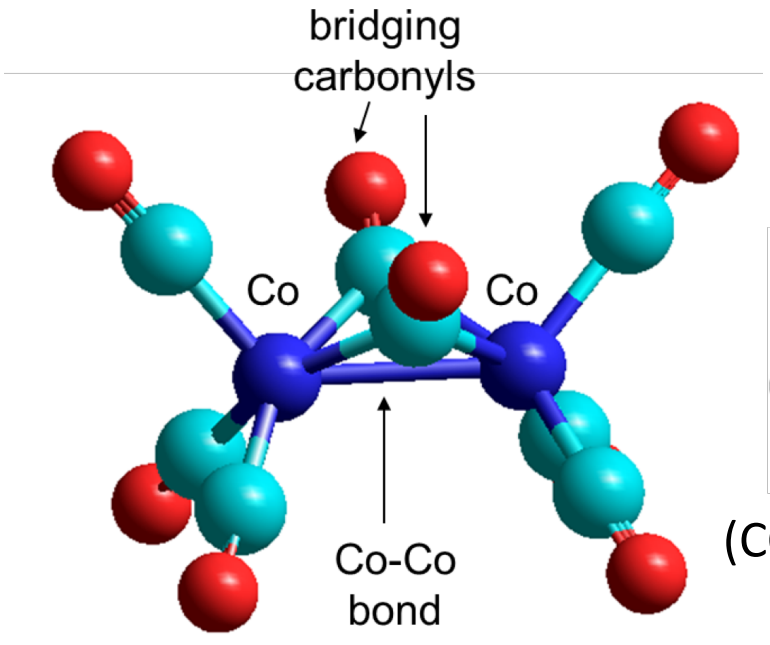


- Carbonyls may form bridges between two metals, where they donate one electron to each metal in working out the 18 electron rule.
- In $[Co_2(CO)_8]$, each Co has three terminal CO's, two bridging CO's, and a Co-Co bond:

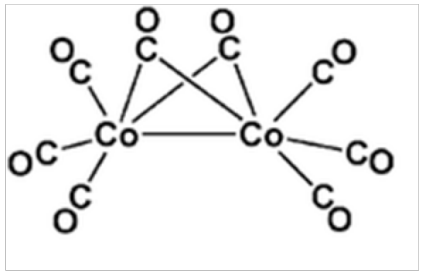
Co(0)	=	d^9
3 CO's	=	6
2 bridge CO's	=	2
Co-Co bond	=	1
		18 e

Terminolgy for Bridging Ligands

μ_x **"mu-*x*" is the nomenclature used to indicate the presence of a bridging ligand between two or more metal centers. The *x* refers to the number of metal centers being bridged by the ligand. Usually most authors omit *x* = 2 and just use μ to indicate that the ligand is bridging the simplest case of two metals.**



$[Co_2(CO)_8]$



$(CO)_3Co(\mu\text{-}CO)_2Co(CO)_3$