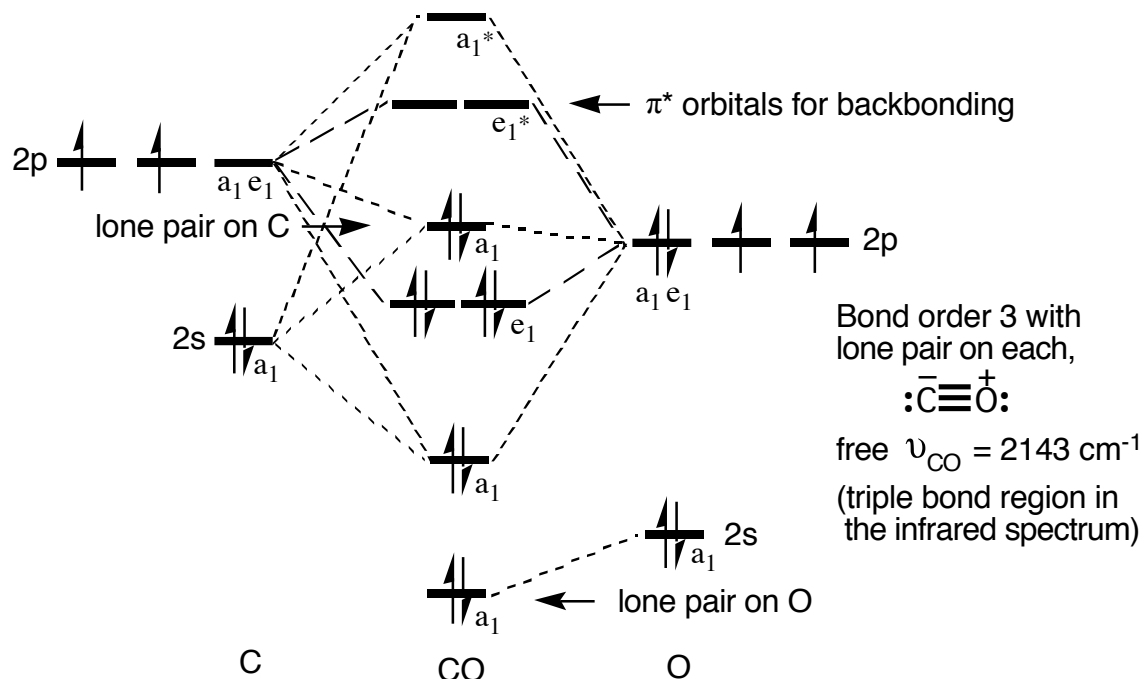
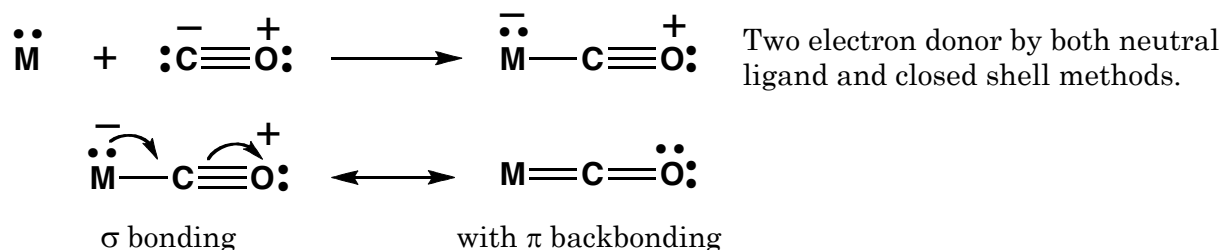


Ligands and Electron Counting

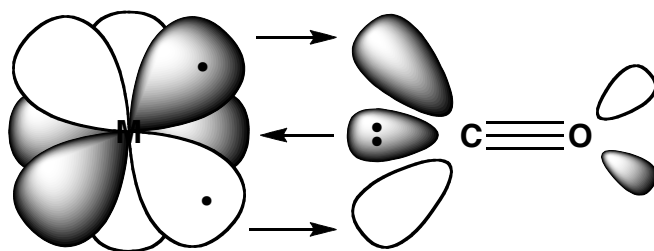
Carbon Monoxide (strong field ligand so tends to follow EAN rule)



Terminal geometry (*sp* hybrid carbon, linear geometry)



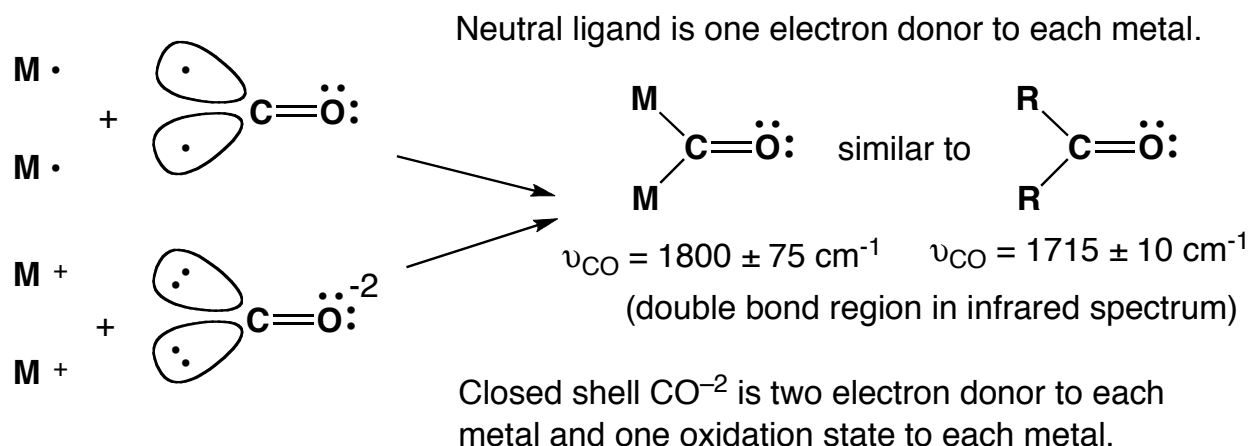
CO is a good π acid (or π acceptor) ligand, accepts electron density from metal into π^* orbital, and stabilizes low metal oxidation states by removing electrons from the metal. The π backbonding also enhances the σ bonding (synergistic).



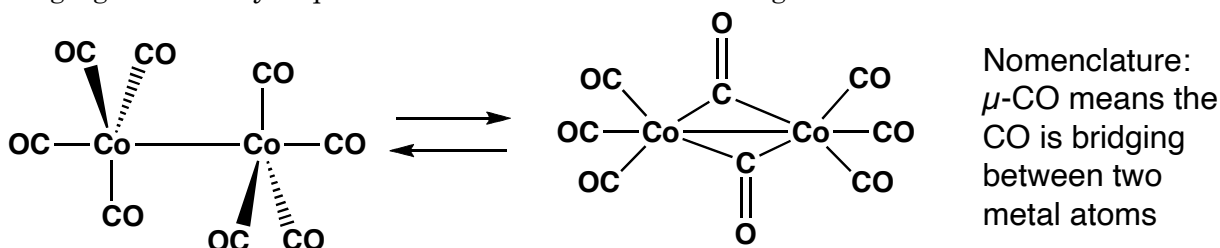
One of a mutually perpendicular set of π orbitals is shown

π backbonding fills both π^* orbitals, the CO bond order decreases, and the $\nu_{\text{CO}} = 2000 \pm 100 \text{ cm}^{-1}$ (the more π backbonding by other ligands and the more electronegative the other ligands, the higher the ν_{CO}).

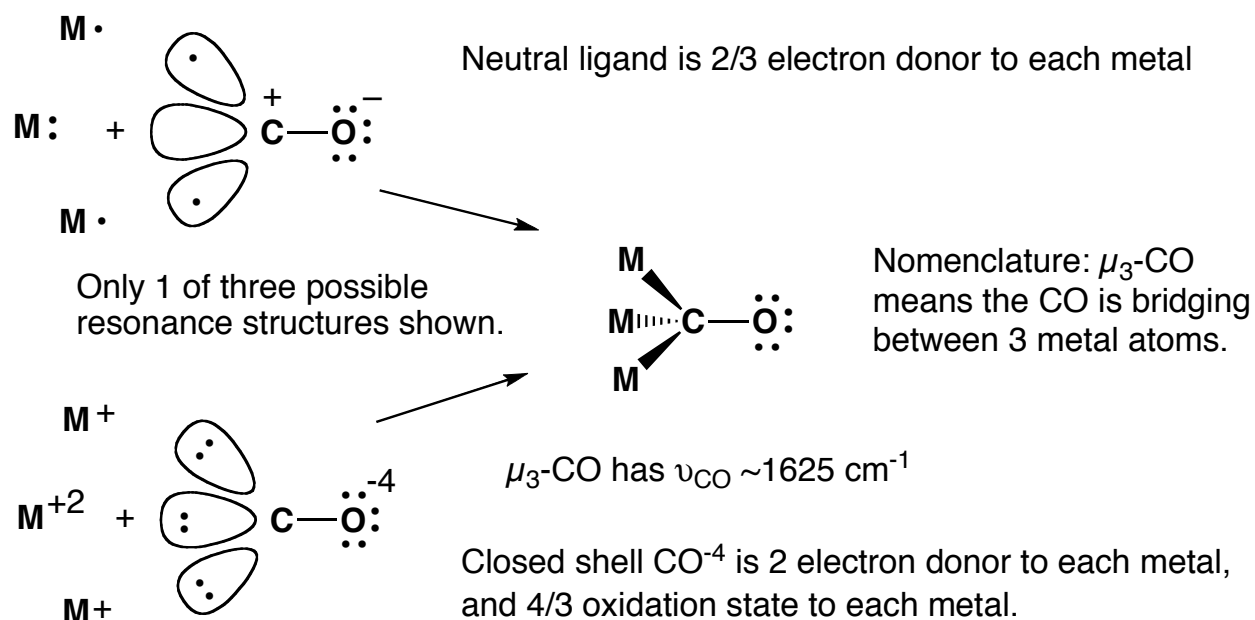
Bridging geometry (sp^2 hybrid carbon, 120° angle)



Bridging CO usually requires M-M bond to hold metals together.



Triply bridging geometry (sp^3 hybrid carbon, tetrahedral geometry)



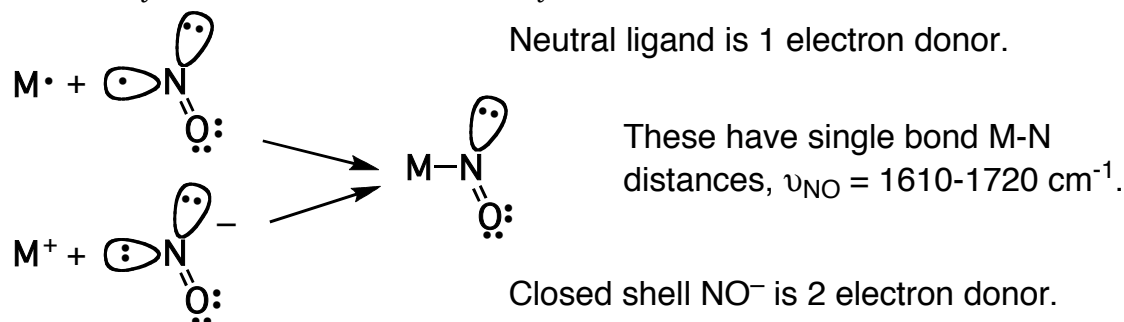
Formal charges written above atoms indicate the number of protons versus electrons belonging to an atom, and assumes that all electron bond pairs are shared equally (one electron of each bond pair belongs to each atom).

Determination of oxidation states, however, must be done using the closed shell ligand method of counting.

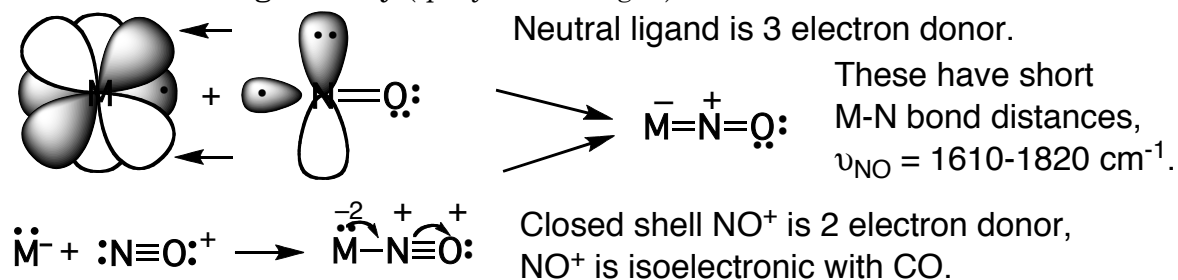
Nitric Oxide, $\cdot\ddot{\text{N}}=\ddot{\text{O}}:$, MO bond order 2.5, $\nu_{\text{NO}} = 1860 \text{ cm}^{-1}$

Terminal bent geometry (sp^2 hybrid nitrogen, 120° angle)

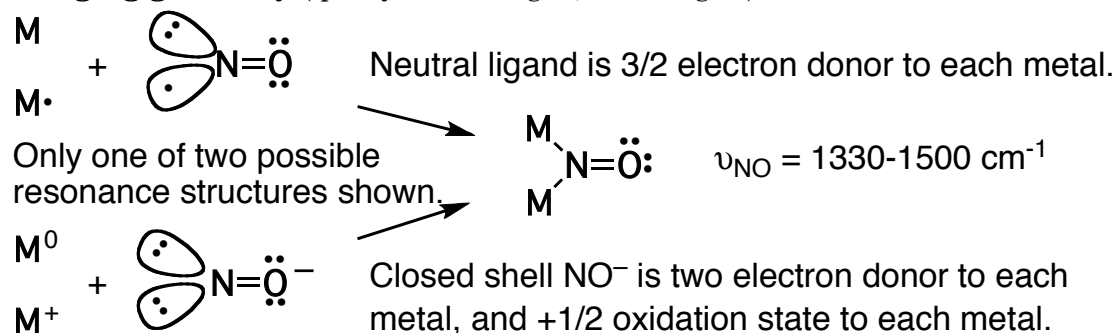
Favored by transition metals with many electrons.



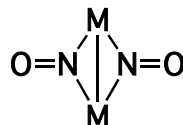
Terminal linear geometry (sp hybrid nitrogen) MOST COMMON



Bridging geometry (sp^2 hybrid nitrogen, 120° angles)



Bridging usually happens in pairs.

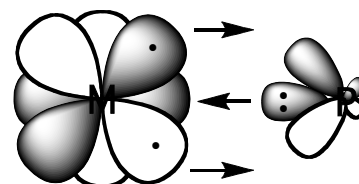


Neutral ligand pair of bridging NO donates 3 electrons to each metal.

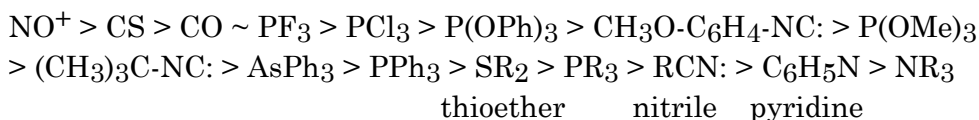
Closed shell pair of bridging NO gives 4 electrons and $+1$ charge to each metal.

Phosphines

PR_3 , just like $:\text{NH}_3$, is a two electron donor by both neutral and closed shell ligand methods. PMe_3 is a good σ -donor and stabilizes high metal oxidation states, but PF_3 is a good π -acceptor (using P-F σ^* orbitals) and stabilizes low metal oxidation states.

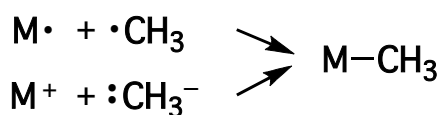


π -acid series



Carbon Ligands

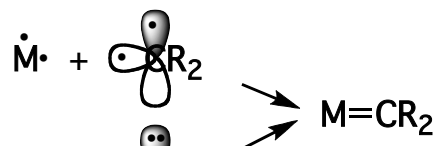
Carbane, sp^3 hybridization



Neutral ligand is one electron donor.

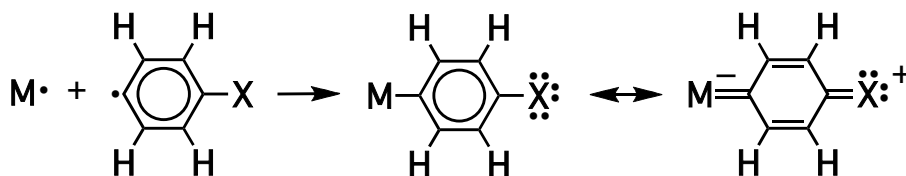
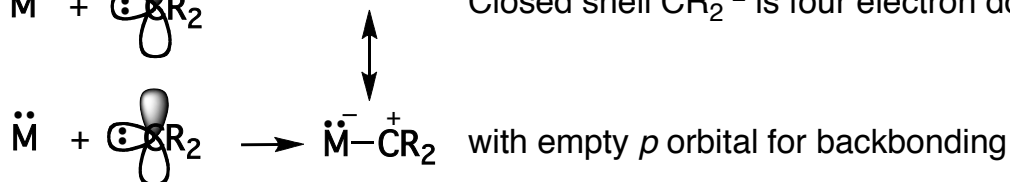
Closed shell CH_3^- is two electron donor.

Carbene, sp^2 hybridization

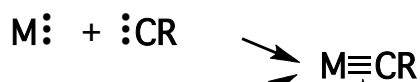


Neutral ligand is two electron donor.

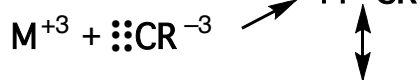
Closed shell CR_2^{2-} is four electron donor.



Carbyne, sp hybridization



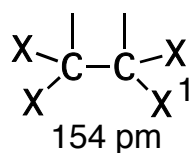
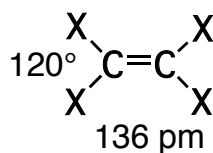
Neutral ligand is 3 electron donor.



Closed shell CR^{3-} is 6 electron donor.

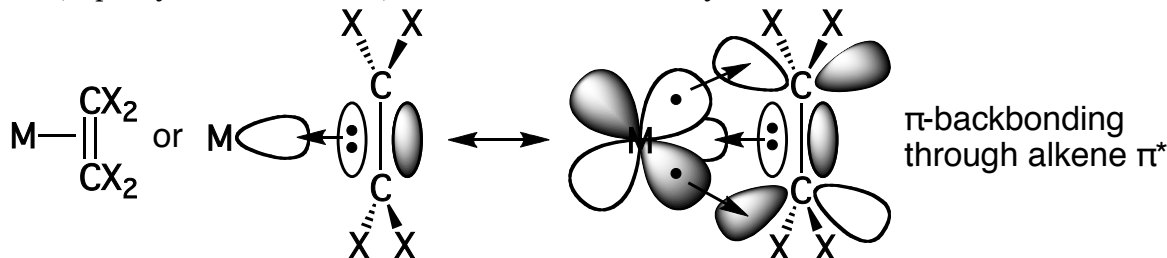


Alkenes
(olefins)



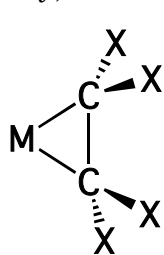
Alkane
(for comparison)

σ -donor, sp^2 hybridized carbon, is two electron donor by either method.

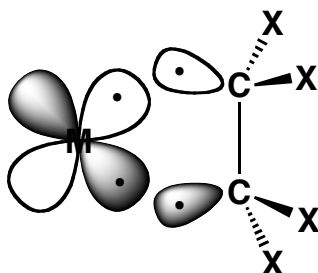


Coordinated alkenes are activated toward nucleophilic substitution, especially if the complex is positively charged and/or the metal has a high positive oxidation state.

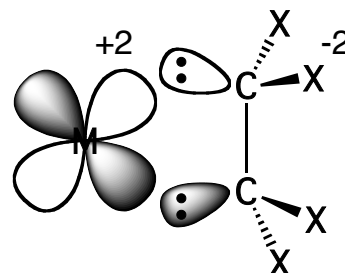
Alternatively, alkenes can be counted as a bidentate alkane.



π -donor,
 sp^3 hybridized carbon



Neutral ligand is
two electron donor.

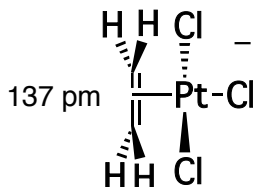


Closed shell $C_2X_4^{-2}$ is
four electron donor.

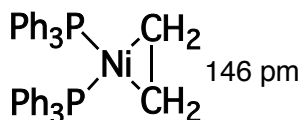
Nomenclature: these are "metallocyclopropanes" since include M in the count of the number of "carbons."

As electronegativity of X increases

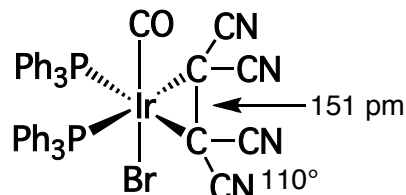
- C-C bond length increases
- X bends away from metal (out of $CX_2= CX_2$ plane)



Is this square planar Pt(II) or
trigonal bipyramidal Pt(IV)?



Is this trigonal Ni(0) or
square planar Ni(II)?



Is this trigonal bipyramidal
Ir(I) or octahedral Ir(III)?

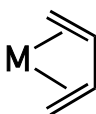
Oxidation state uses closed shell formalism and has little reality with actual charges on the atoms, especially since many ligands have both donor and acceptor properties.

Nomenclature: hapto or η is the number of carbons bonded to the metal



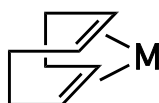
η^2

2 electron
ethylene



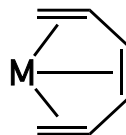
η^4

4 electron
1,3-butadiene



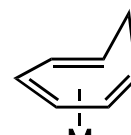
η^4

4 electron
cyclooctadiene



η^6

6 electron
1,3,5-
hexatriene

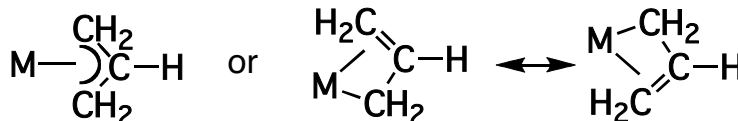


η^6

6 electron
cycloheptatriene

Can draw
a single
line to the
 π system.

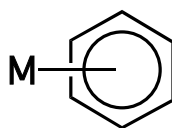
η^3 -allyl (allyl is also occasionally observed with η^1 bonding)



Allyl ligand is tipped slightly so middle carbon is a little farther from metal.

Neutral ligand is three electron donor. Closed shell $C_3H_5^-$ is four electron donor.

Aromatic systems



η^6 -benzene

Example: $\text{Cr}(\text{C}_6\text{H}_6)_2$

Six electron donor by both methods.
Ring is deactivated for electrophilic substitution, can do nucleophilic substitution.



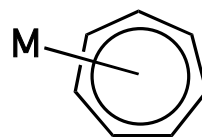
η^5 -cyclopentadienyl, C_5H_5 or Cp

Example: FeCp_2

Neutral ligand is 5 electron donor.

Closed shell Cp^- is 6 electron donor.

Ring undergoes electrophilic substitution.



η^7 -tropylium, C_7H_7

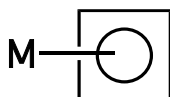
Example: $\text{Mo}(\text{C}_7\text{H}_7)(\text{CO})_3^+$

Neutral ligand is 7 electron donor.

Closed shell C_7H_7^+ is 6 electron donor.

Ring undergoes nucleophilic substitution.

Without metal neither of these is aromatic in organic chemistry



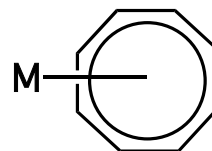
η^4 -cyclobutadiene, C_4H_4

Example: $\text{Fe}(\text{C}_4\text{H}_4)(\text{CO})_3$

Neutral ligand is 4 electron donor.

Closed shell $\text{C}_4\text{H}_4^{-2}$ is 6 electron donor.

Ring undergoes electrophilic substitution.



η^8 -cyclooctatetraene, C_8H_8 or COT

Example: $\text{Mo}(\text{COT})(\text{CO})_3^+$

Neutral ligand is 8 electron donor.

Closed shell $\text{C}_8\text{H}_8^{+2}$ is 6 electron donor.

Nomenclature: Metallocene or sandwich if metal atom between two planar polyhapto rings.

Summary: η^n are n electron neutral ligand donors.

Aromatic rings are six electron closed shell donors.

Alkynes

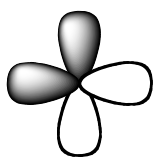


sp hybridization, linear,

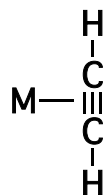
120 pm bond distance,

$\nu_{\text{CC}} = 2170 \text{ cm}^{-1}$

(triple bond region)



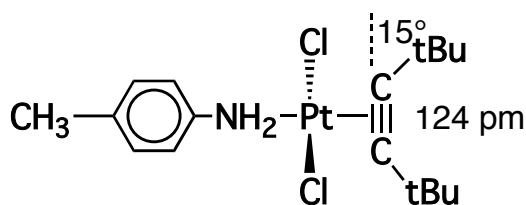
End view



Two electron donor (like alkene)
by both methods.

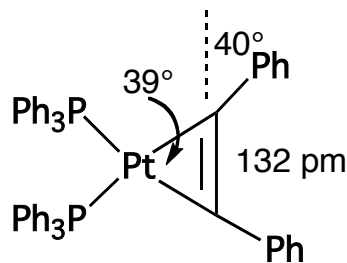
Just as for alkene, there are also π^* orbitals for π backbonding with metal d orbitals.

As electronegativity of alkyne substituents increases the C-C bond length increases and the alkyne deviates from linear geometry:



$\nu_{\text{CC}} = 2020 \text{ cm}^{-1}$

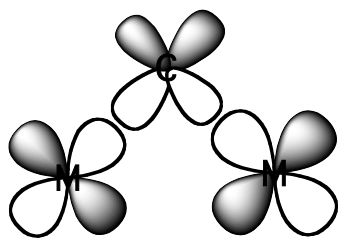
Is this square planar Pt(II)
or trigonal bipyramidal Pt(IV)?



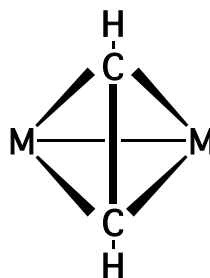
$\nu_{\text{CC}} = 1750 \text{ cm}^{-1}$

Is this trigonal Pt(0) or square planar Pt(II)?
Is this a metallocyclopropene?

Bridging Alkyne



Side view



Top view

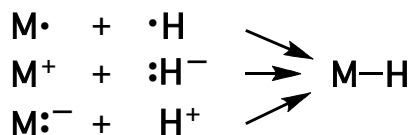
Acetylene
perpendicular to
and above the
M-M bond.

Neutral ligand is two electron donor to each metal.

Closed shell $C_2H_2^{-4}$ is four electron donor to each metal.

146 pm C-C bond distance in $(H_2C_2)Co_2(CO)_6$.

Hydride, M-H



Neutral ligand $H\cdot$ is one electron donor.

Closed shell H^- is two electron donor.

Acidic H^+ is zero electron donor.

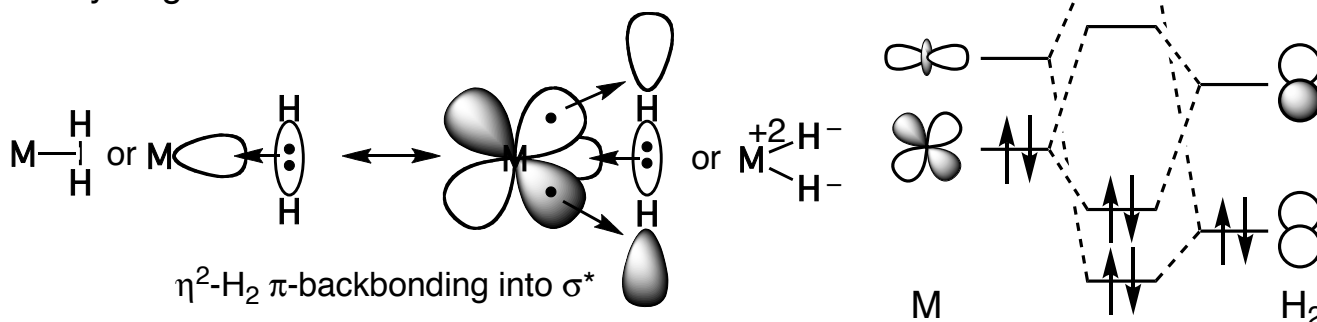
Ambiguity of oxidation states

Trans. Met. Chem., 1, 112 (1965)

	1H chemical shift*	Acidity in water
$HMn(CO)_5$	-17.5 ppm	$K_a = 8 \times 10^{-8}$
$H_2Fe(CO)_4$	-20.8	$K_{a1} = 4 \times 10^{-5}$ $K_{a2} = 4 \times 10^{-14}$
$HCo(CO)_4$	-20.7	$K_a = 1$ (strong acid!)

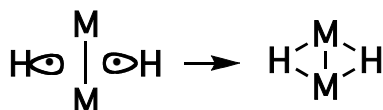
*Neat solution (all three are liquids at RT). Values typical for hydride.

Dihydrogen



Redrawn from *Chem. Comm.*, (2012) 48, 11481-11503.

Electron deficient, μ -H

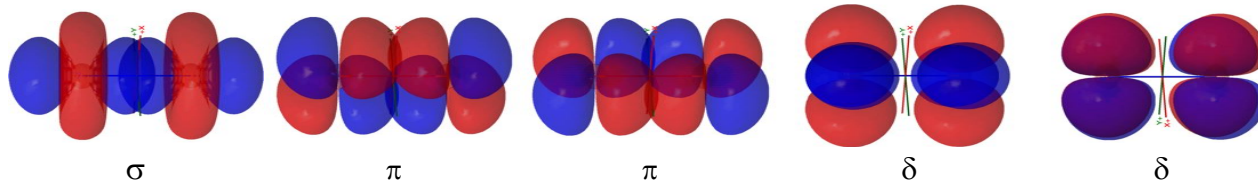
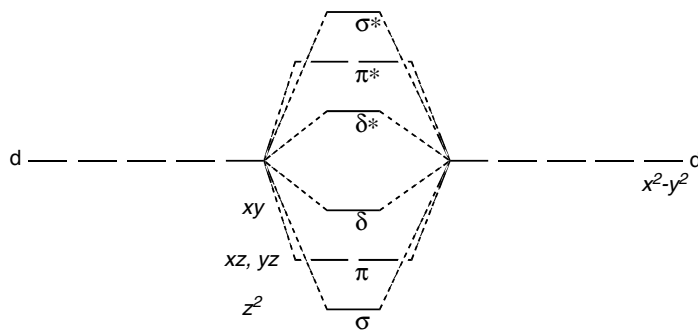


Neutral ligand $H\cdot$ is one electron donor,
divided between two metals.

Closed shell H^- is two electron donor,
divided between two metals.

M-M bonds

1. Requires d electron for each bond (low metal oxidation state)
2. Requires orbitals with sufficient extension (second and third row transition metals preferred)
3. d orbitals can make 1 σ , 2 π , and 2 δ bonds (but x^2-y^2 bonding to square planar ligands makes it not available for δ bonding, unless metal sp bonding to ligands with linear coordination).
 σ overlap > π overlap > δ overlap.

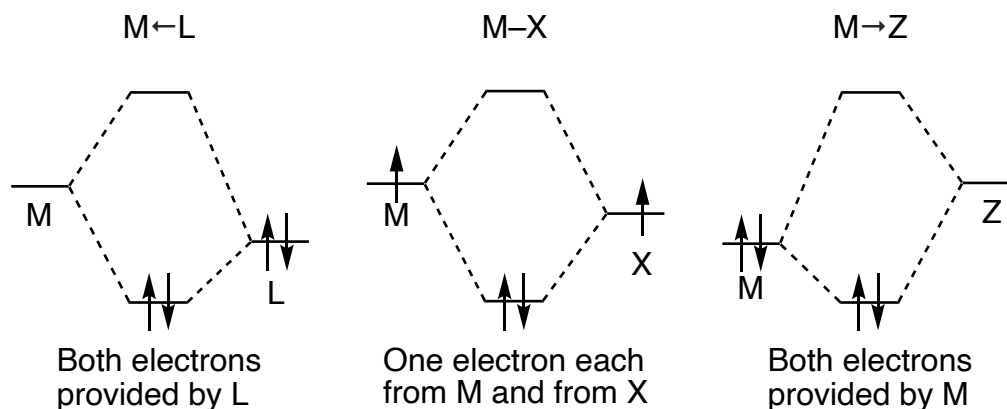


Recognizing metal-metal bonds

1. Internuclear separation: Compare metal-metal distance with 2 times covalent radius, but varies 20 pm with ligands.
2. Geometry changes: metal displacement or eclipsed ligand conformation?
3. Magnetic susceptibility: bonding electrons are paired.
4. Electron counting if π back-bonding ligands.

Covalent Bond Classification (LXZ)

This scheme uses the neutral ligand counting based on whether the neutral ligand contributes two (L), one (X) or zero (Z) electrons to the bond.



Redrawn from *Chem. Comm.*, (2012) 48, 11481-11503.

For example, CO, PR₃, NH₃, H₂O, carbenes and alkenes are L ligands and H, Cl, Br, F, OH, CH₃ are X ligands and BR₃, AlR₃ are Z ligands. Cp is considered an L₂X ligand. Why? (If the overall complex is charged, the charge is sometimes assigned to a ligand to give the *equivalent neutral class*. For each positive charge, one L → X and, if no L ligand is present, X → Z; for each negative charge, one X → L and, if no X ligand is present, L → LX.)