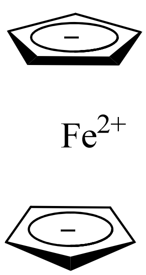
1. For all complexes listed below, determine

a) metal oxidation state
b) total number of electrons contributed from metal
c) total number of electrons contributed from the ligand set
d) total electron count of the complex

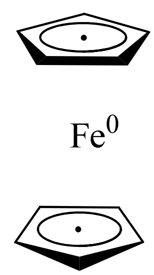
Please note: use the ionic model unless asked otherwise and comment on any complexes that do not obey the 18VE rule or have CN < 6.

i) $(\eta^5\text{-Cp})_2Fe$

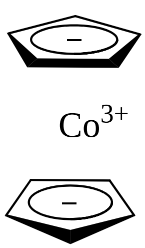


Ionic Model
Metal oxidation state: 2+
Metal electron count: 6
Ligand electron count: 6 + 6
Total electron count: 18

Covalent Model
Metal oxidation state: 0
Metal electron count: 8
Ligand electron count: 5 + 5
Total electron count: 18

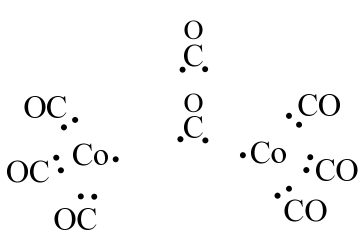


ii) $[(\eta^5\text{-Cp})_2Co]^+$



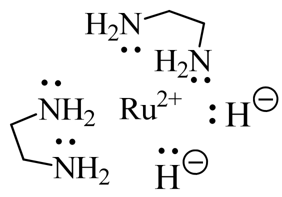
Ionic Model
Metal oxidation state: 3+
Metal electron count: 6
Ligand electron count: 6 + 6
Total electron count: 18

iii) $Co_2(CO)_8$



Ionic Model
Metal oxidation state: 0
Metal electron count: 9
Ligand electron count: 2 + 2 + 2 + 1 + 1 + 1 (inc Co-Co)
Total electron count: 18

iv) $Ru(\eta^2\text{-en})_2H_2$



Ionic Model

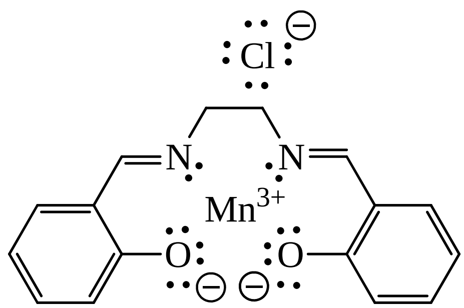
Metal oxidation state: 2+

Metal electron count: 6

Ligand electron count: 2 + 2 + 2 + 2 + 2 + 2

Total electron count: 18

v) $Mn(\eta^4\text{-salen})Cl$



Ionic Model

Metal oxidation state: 3+

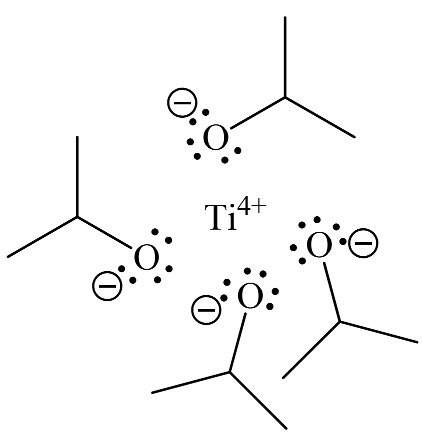
Metal electron count: 4

Ligand electron count (S only): 2 + 2 + 2 + 2 + 2

Total electron count: 14

A total electron count at the metal of just 14 electrons is predicted using the ionic model but only considering σ-bonds. Both oxide and chloride ligands are capable of π-donation to the empty metal orbitals making up the 4 extra electrons to comply with the 18VE rule. The nature of this π-donation can be deciphered using the molecules point group symmetry, the corresponding character table and the method of systematic reduction of non-shifted/inverted π-vectors.

vi) Ti(*iso*-propoxide)$_4$



Ionic Model

Metal oxidation state: 4+

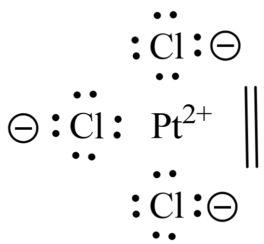
Metal electron count: 0

Ligand electron count (σ only): 2 + 2 + 2 + 2

Total electron count: 8

A total electron count at the metal of just 8 electrons is predicted using the ionic model but only considering σ-bonds. Each isopropoxide ligand is capable of π-donation to the empty metal orbitals making up the 10 extra electrons to comply with the 18VE rule. The nature of this π-donation can be deciphered using the molecules point group symmetry, the corresponding character table and the method of systematic reduction of non-shifted/inverted π-vectors.

vii) $[PtCl_3(\eta^2\text{-ethene})]^-$



Ionic Model

Metal oxidation state: 2+

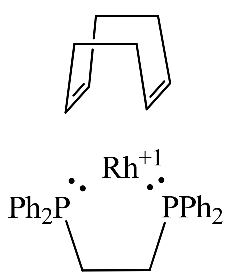
Metal electron count: 8

Ligand electron count (σ only): 2 + 2 + 2 + 2

Total electron count: 16

This is a square planar d^8 complex thus the dz^2 orbital is filled preventing axial coordination and therefore precluding a CN=6 geometry in favor of CN=4. As a result of the reduced coordination number, a total electron count at the metal of 16 electrons is predicted. This prediction only considers σ-bonds however when in fact each chloride ligand is capable of π-donation to the unfilled metal orbitals making up the 2 extra electrons to comply with the 18VE rule. The nature of this π-donation can be deciphered using the molecules point group symmetry, the corresponding character table and the method of systematic reduction of non-shifted/inverted π-vectors.

xiii) $Rh(\eta^4\text{-cod})(\eta^2\text{-dppe})]^+$



Ionic Model

Metal oxidation state: +1

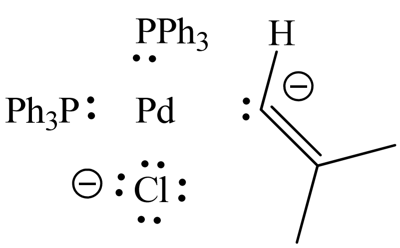
Metal electron count: 8

Ligand electron count: 8

Total electron count: 16

This is a square planar d^8 complex thus the dz^2 orbital is filled preventing axial coordination and therefore precluding a CN=6 geometry in favor of CN=4. As a result of the reduced coordination number, a total electron count at the metal of 16 electrons is predicted. This prediction only considers σ-bonds. The ligand set does not contain and π-donating moieties capable of making up the 2 extra electrons to comply with the 18VE rule and is thus a coordinatively unsaturated 16 electron species.

ix) $Pd(PPh_3)_2\{CHC(CH_3)_2\}Cl$



Ionic Model

Metal oxidation state: 2+

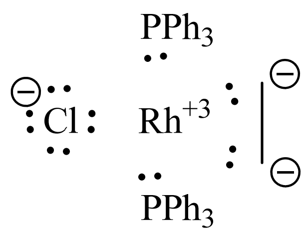
Metal electron count: 8

Ligand electron count (σ only): 2 + 2 + 2 + 2

Total electron count: 16

This is a square planar d^8 complex thus the dz^2 orbital is filled preventing axial coordination and therefore precluding a CN=6 geometry in favor of CN=4. As a result of the reduced coordination number, a total electron count at the metal of 16 electrons is predicted. This prediction only considers σ-bonds however when in fact the chloride ligand is capable of π-donation to the unfilled metal orbitals making up the 2 extra electrons to comply with the 18VE rule. The nature of this π-donation can be deciphered using the molecules point group symmetry, the corresponding character table and the method of systematic reduction of non-shifted/inverted π-vectors.

x) $Rh(CO)(PPh_3)_2(C_2H_2)$



<u>Ionic</u> <u>Model</u>

Metal oxidation state: 3+

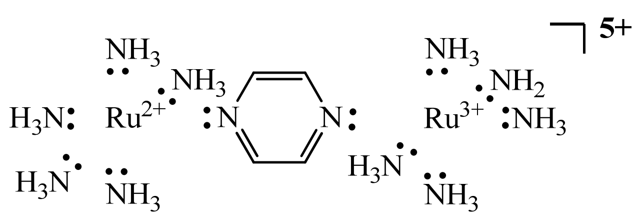
Metal electron count: 6

Ligand electron count (σ only): 10

Total electron count: 16

This is a square planar d^8 complex thus the dz^2 orbital is filled preventing axial coordination and therefore precluding a CN=6 geometry in favor of CN=4. As a result of the reduced coordination number, a total electron count at the metal of 16 electrons is predicted. This prediction only considers σ-bonds however when in fact the chloride ligand is capable of π-donation to the unfilled metal orbitals making up the 2 extra electrons to comply with the 18VE rule. The nature of this π-donation can be deciphered using the molecules point group symmetry, the corresponding character table and the method of systematic reduction of non-shifted/inverted π-vectors.

xi) $[(NH_3)_5Ru(\mu\text{-pyrazine})Ru(NH_3)_5]^{5+}$



<u>Ionic</u> <u>Model</u>

1st Metal oxidation state: 2+

Metal electron count: 6

Ligand electron count: 2 + 2 + 2 + 2 + 2 + 2

Total electron count: 18

<u>Ionic</u> <u>Model</u>

2nd Metal oxidation state: 3+

Metal electron count: 5

Ligand electron count: 2 + 2 + 2 + 2 + 2 + 2

Total electron count: 17

This represents an unusual example. With a completely neutral ligand set, the overall 5+ charge must be shared between both metal centers. As this is a symmetric system the obvious choice would be to share charge equally as +2.5 on each metal center. Alternatively, the charge may be distributed as +2 and +3 as above. Without conducting detailed experimental investigations (UV-vis-NIR/Xray/computational/electrochemical/ etc.) it is difficult to state the true nature of charge localization in this complex. Thus, either answer would suffice.

2. Relative to a spherical ligand field, in a transition metal complex of O_h symmetry
The e_g orbitals have lobes that point at the ligands and so will increase in energy.
The t_{2g} orbitals have lobes that lie between ligands and so will decrease in energy.

3. High coordination numbers are favored by
i) high ~~or low~~ oxidation states
ii) ~~small or~~ large atomic radii
iii) small ~~or bulky~~ ligands

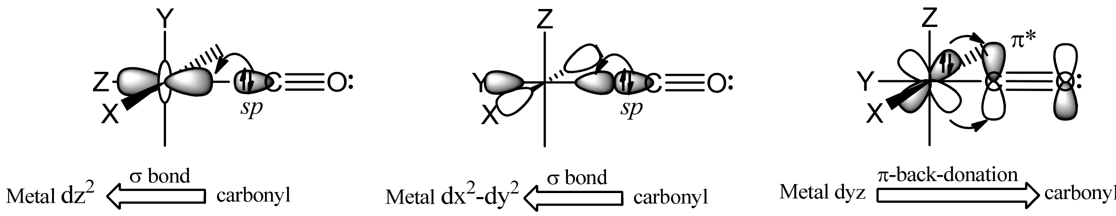
4. High spin Δ_O electronic configurations are favored by
i) low ~~or high~~ oxidation states
ii) first, ~~second or third~~ row transition metals
iii) weak ~~or strong~~ field ligands

5. The magnitude of Δ_o depends most strongly upon which 3 of the following components
i) the metal ion
ii) the attaching ligands
iii) the counterion
iv) the solvent
v) the metal oxidation state

6. MO theory is a method for determining molecular structure in which electrons are not assigned to individual bonds between atoms, but are treated as moving under the influence of the nuclei in the whole molecule. Ligand field theory (LFT) represents an application of molecular orbital (MO) theory to transition metal complexes.
For effective overlap to occur between metal atom orbitals and the SALC's there are two important requisites. Please select these requisites from the following list:

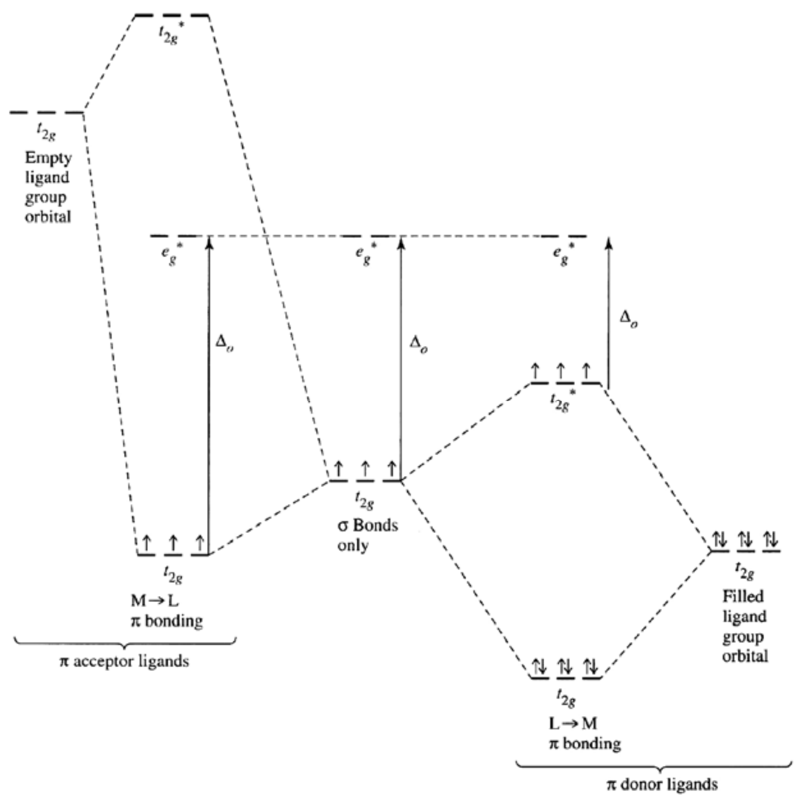
i) Shape
ii) Energy
iii) Symmetry
iv) Size
v) Occupancy

7. Draw the σ and π bonding interactions for a metal carbonyl bond. Very briefly explain why this interaction weakens the CO bond strength.



π-back donation is a synergistic effect. The stronger the σ-donation the more electron rich the metal center becomes, and subsequently the greater the π-back donation to the ligand π^* orbitals. Upon occupation of the ligand π^* orbitals the order of the CO bond is reduced to b.o.<3. This is elegantly observed in the stretching frequency of the CO bond *v*(CO) using FTIR spectrsocopy.

8. For an O_h complex draw the influence π-acceptor and π-donor bonding interactions on the frontier orbitals.



π acceptor ligands result in M→L π bonding, a larger Δ_o favoring low spin configurations with an increased stability. π donor ligands result in L→M π bonding, a smaller Δ_o favoring high spin configurations and a decreased stability.

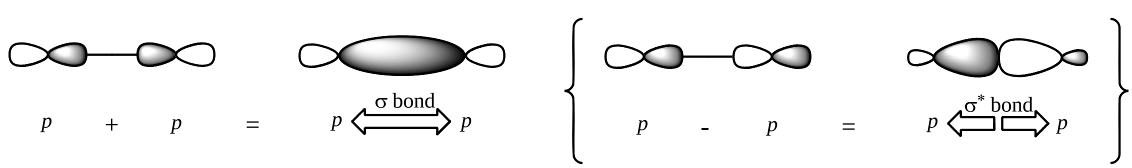
9. Explain the below trend in CO bond vibrational frequency *v*(CO) using the Dewar-Chatt-Duncanson model.

	***v*(CO) cm^{-1}**
$[Ti(CO)_6]^{2-}$	**1748**
$[V(CO)_6]^{-}$	**1859**
$Cr(CO)_6$	**2000**
$[Mn(CO)_6]^{+}$	**2100**
$[Fe(CO)_6]^{2+}$	**2204**

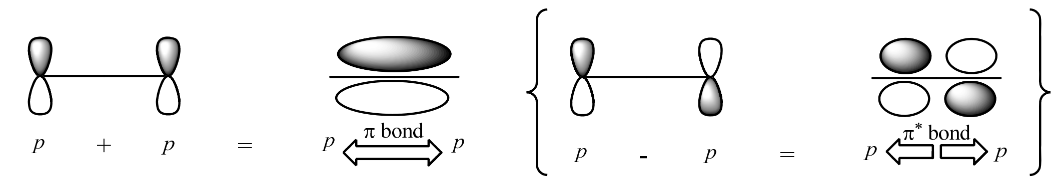
- all complexes have CN = 6 and are of O_h symmetry.
- all complexes are metal hexacarbonyls
- all complexes have 6 *d*-valence electrons

As we progress from Ti(2-) to V(-) to Cr(0) to Mn(1+) to Fe(2+) the electron count on the nuclei is identical however the proton count at the central nuclei increase resulting in a net increase in electronegativity as we follow the above trend. The increase in electronegativity reduces the extent of π-back-donation from the central metal d_{xy} , d_{xz} and d_{yz} orbitals such that population of the t_{2g} π^* ligand SALC orbitals is reduced. Reduced population of the t_{2g} π^* ligand SALC orbitals on CO therefore gives rise to a higher bond order between carbon and oxygen (somewhere between 2 and 3). This can be observed via an increase in the *v*(CO) stretching frequency in the IR spectrum. This is most obvious, for example, if we compare the least electronegative metal center Ti(2-) where *v*(CO) = 1748 cm^{-1} relative to the most electronegative metal given in Fe(2+) where *v*(CO) = 2204 cm^{-1}.

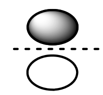
10. Using any combination of *s*, *p* or *d* orbitals please demonstrate overlap resulting in
i) a σ–bond has no nodal planes at the internuclear axis and is thus symmetric with respect to C_2 rotation about the bond axis, e.g.



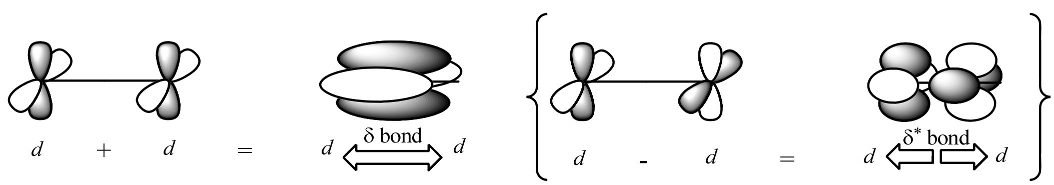
ii) a π–bond is characterized by a single nodal plane at the internuclear axis and is thus asymmetric with respect to C_2 rotation about this axis, e.g.



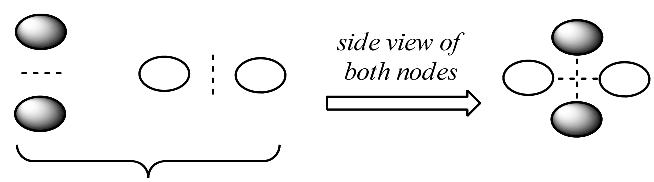
(side view - 1 node on bonding axis)



iii) a δ–bond has two nodal planes at the internuclear axis (one containing the internuclear axis and a second perpendicular to this axis).



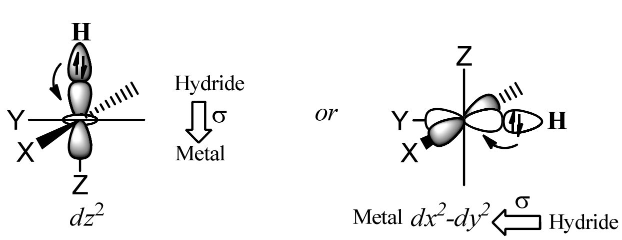
(side view - 2 nodes)



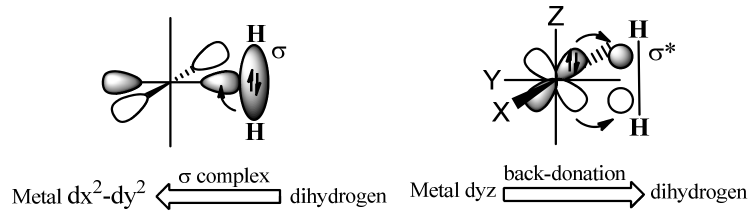
each node viewed independently

11. Using molecular orbitals draw the bonding scheme for the following classes of metal carbene complex, inclusive of any π-bonding:

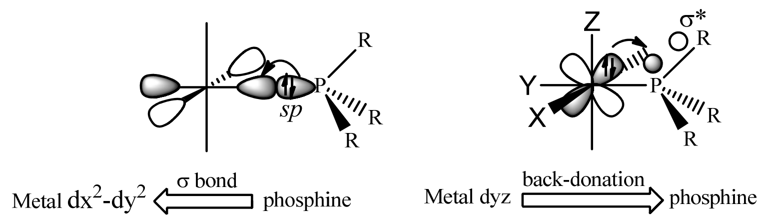
i) Metal hydride



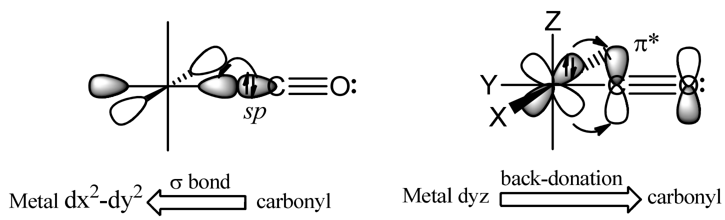
ii) Metal dihydrogen complex



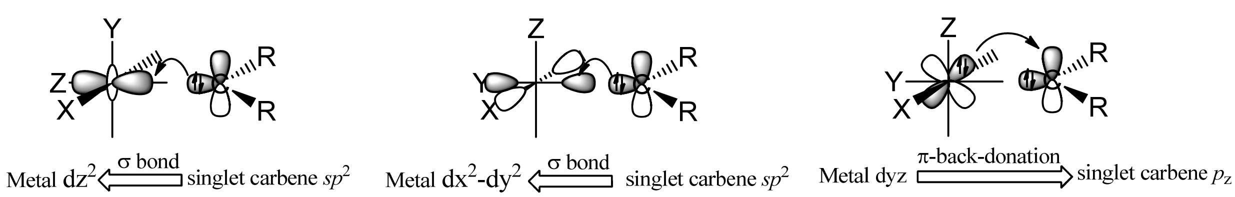
iii) Metal phosphine



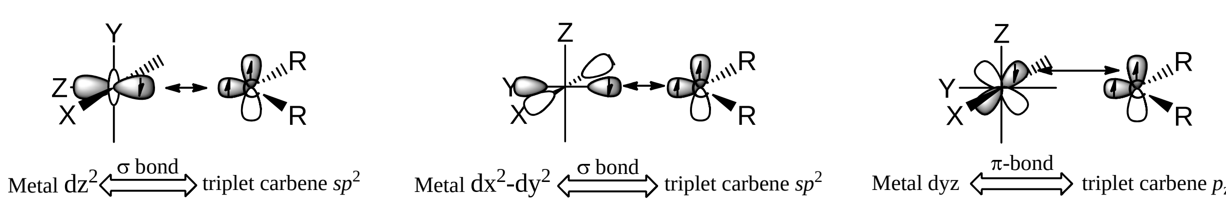
iv) Metal carbonyl



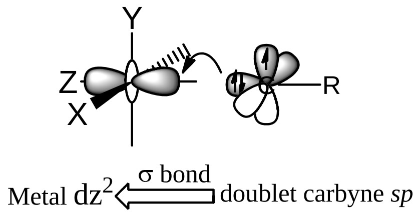
v) Fischer carbene

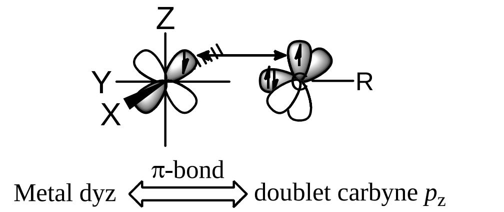


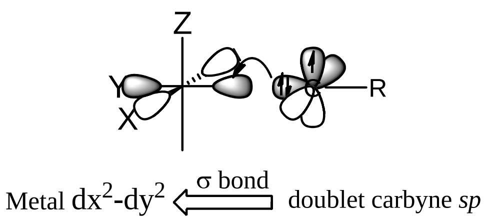
vi) Schrock carbene

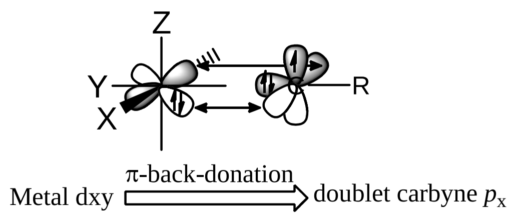


vii) Fischer carbyne

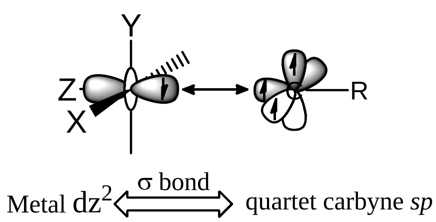


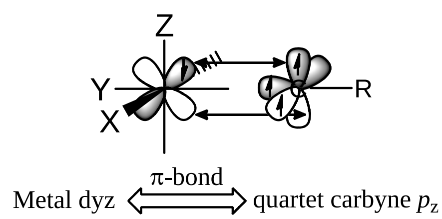


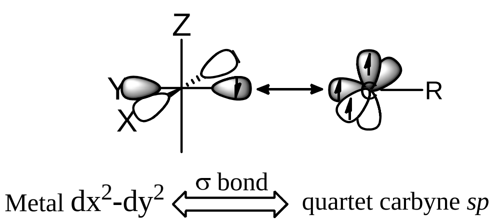


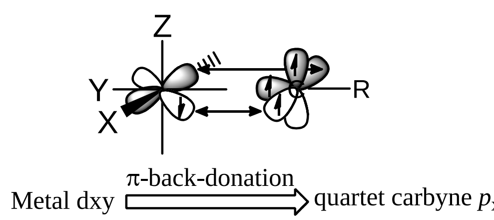


viii) Schrock carbyne

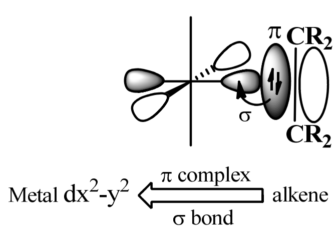


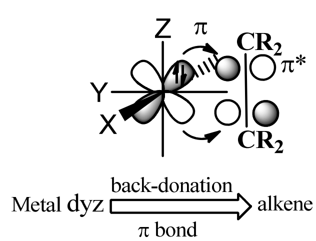




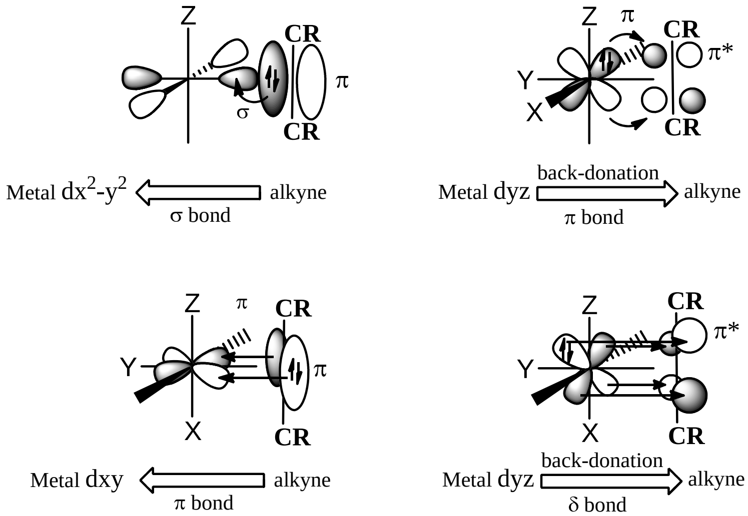


ix) Metal alkene

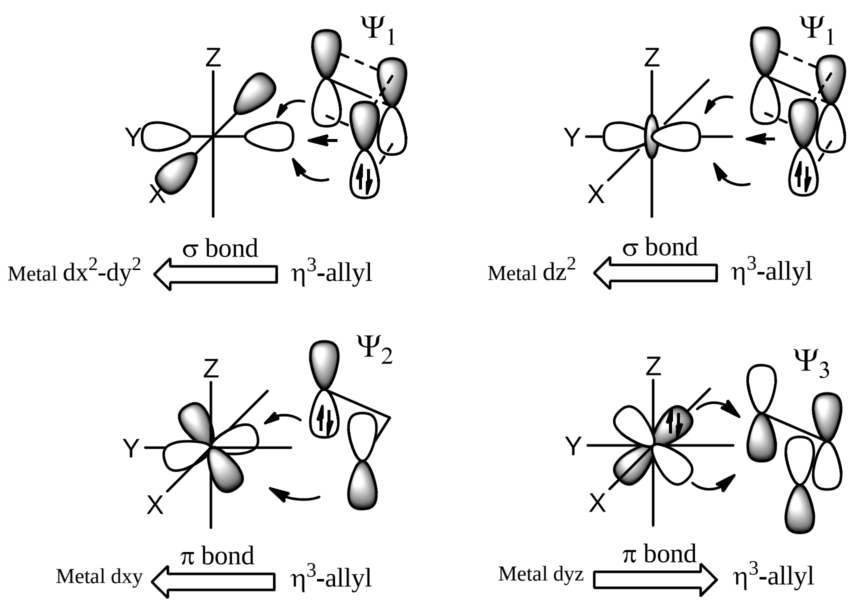




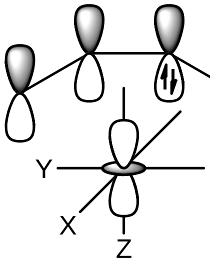
x) Metal alkyne



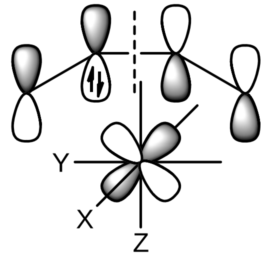
xi) Metal allyl



xii) Metal butadiene



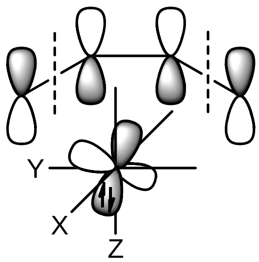
Ψ_1



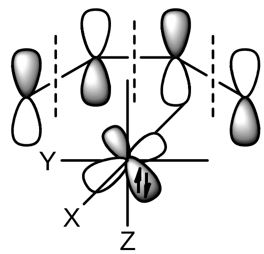
Ψ_2

Metal dz^2 ⇐ (σ bond) η^4-butadiene Ψ_1

Metal dyz ⇐ (π bond) η^4-butadiene Ψ_2



Ψ_3

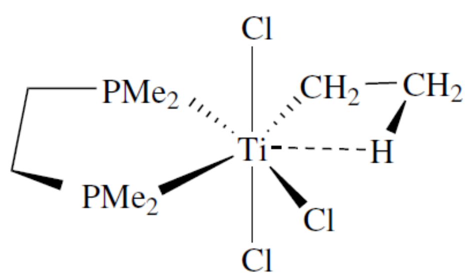


Ψ_4

Metal dx^2-dy^2 ⇒ (π bond) η^4-butadiene Ψ_3

Metal dz^2 ⇒ (δ bond) η^4-butadiene Ψ_4

12. How is the M….H bond described in the below complex? Is the C-H σ^* bond occupied?



The M….H bond is described as an "agostic bond" or "agostic interaction". This complex contains Ti^{4+} which has valence shell of d^0, thus there are no metal electrons available for back donation to the C-H σ^* bond. As a result the C-H bond is not destabilized upon formation of the agostic bond and is perfectly stable for this complex. [Note, for future reference; if *d* electrons were available for back donation to the C-H σ^* bond a metal(alkene)(hydride) would likely be formed due to destabilization and effective cleavage of the C-H bond. This is a process known as β-elimination].

13. State the multiplicity of the free ligand for each of the carbene complexes listed below.
Spin, S = *n*(1/2) where *n* is the number of unpaired electrons.
Multiplicity, M = 2S + 1

Fischer carbyne	*n* = 1; S = 1/2; M = 2 = doublet
Schrock carbene	*n* = 2; S = 2; M = 3 = triplet
Schrock carbyne	*n* = 3; S = 3/2; M = 4 = quartet
Fischer carbene	*n* = 0; S = 0; M = 1 = singlet

14. Using the Tolman map below describe similarities/differences between any 3 sets of ligands.

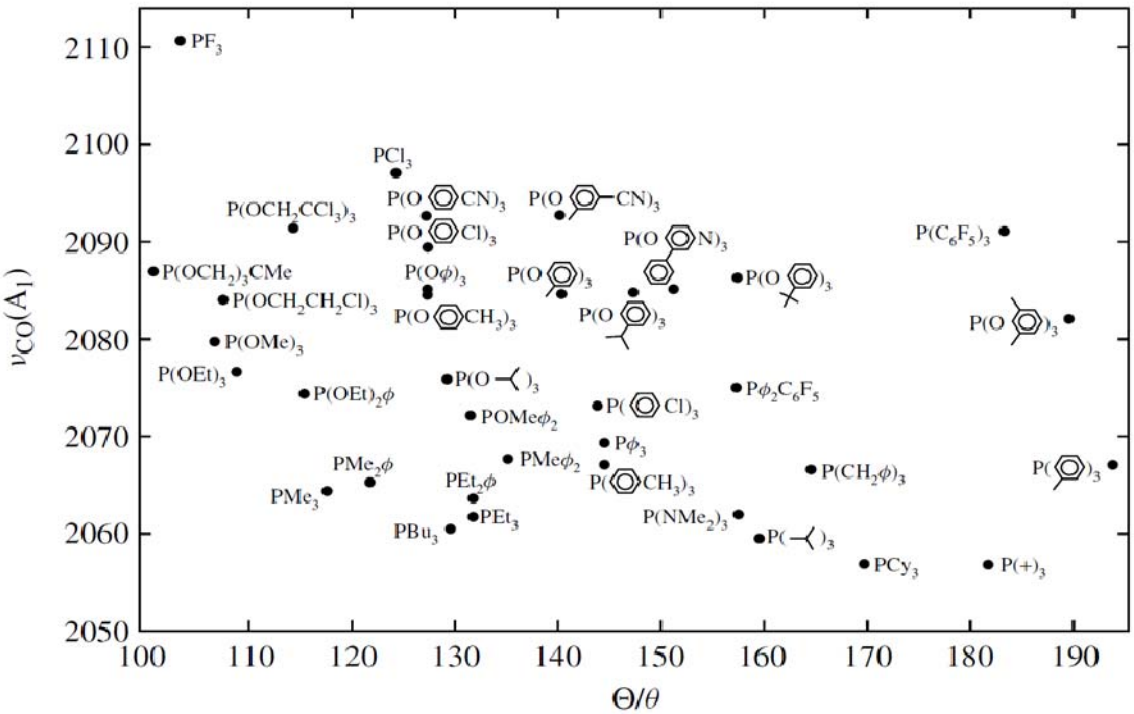
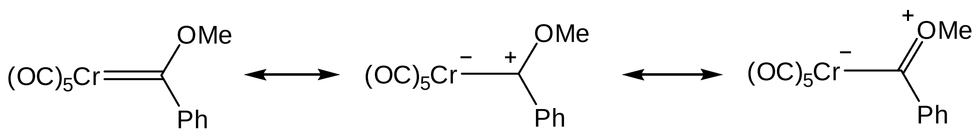
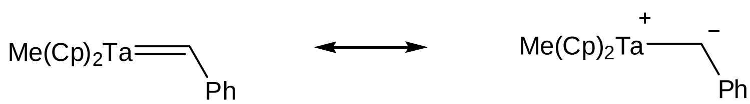


FIGURE 4.4 Electronic and steric effects of common P-donor ligands plotted on a map according to Tolman (ν in cm^{-1}, θ in degrees).

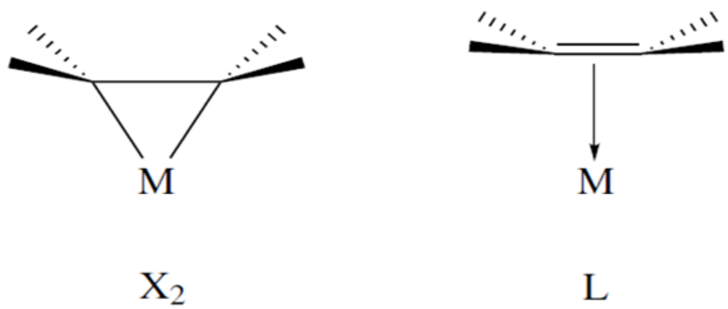
PF_3 and $P(OCH_3)_3$ have similar cone angles (100-105°). PF_3 is more electron withdrawing due to the greater electronegativity of the F atom which lowers the P–F π-accepting σ^* orbital. This reduces π-back donation to the *trans* CO ligand resulting in a larger CO bond order and a higher frequency *v*(CO) stretch (2110 vs 2080 cm^{-1}). Likewise, $P(Tol)_3$ and $P(4\text{-}ClPh)_3$ have a similar cone angle (145°) but the Cl substituent is electron withdrawing resulting in a larger CO bond order and a higher frequency *v*(CO) stretch (2065 vs 2075 cm^{-1}). Similarly, $P(^tBu)_3$ and $P(C_6F_5)_3$ have a similar cone angle (180-185°) but the perfluorobenzene substituent is both π-delocalized and electron withdrawing resulting in a lower energy π-accepting σ^* orbital and subsequently a larger CO bond order and a higher frequency *v*(CO) stretch (2055 vs 2095 cm^{-1}).

15. Draw resonance structures for the following two complexes.

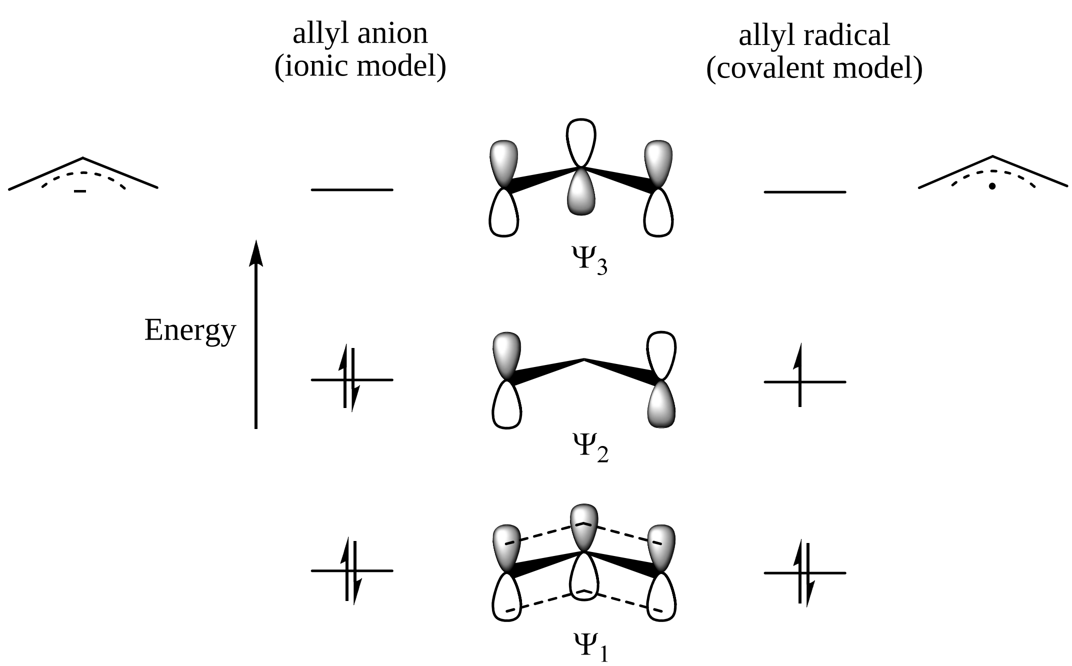




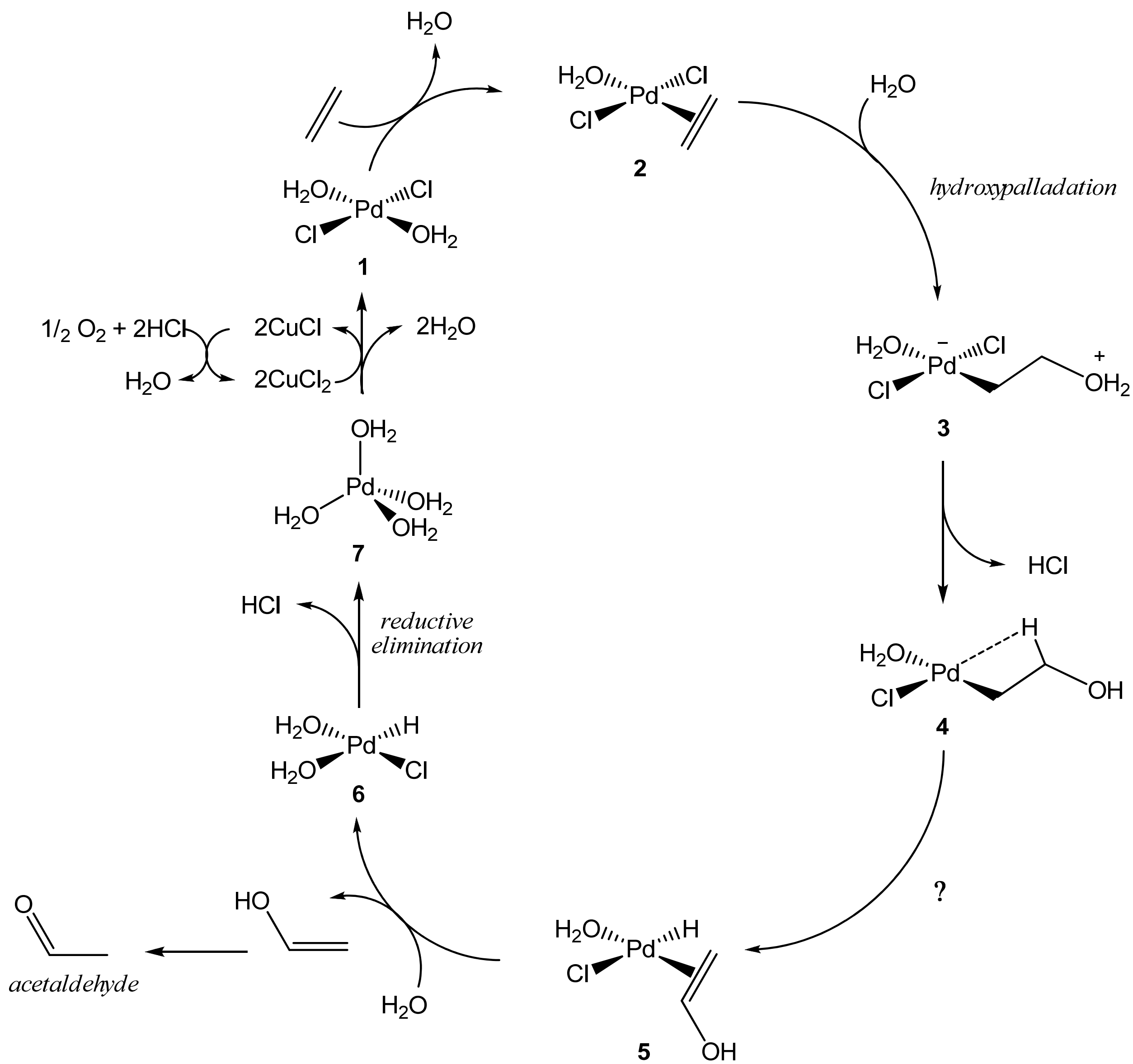
16. Draw the X_2 and L bonding modes of a metal-alkene complex.



17. Complete the following diagram by drawing lobes and nodes of each orbital and filling electrons.

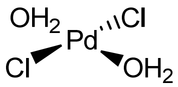


18. Below is the catalytic cycle describing the *Wacker oxidation* reaction, which is used to produce *ca*. 4 million tons of *acetaldehyde,* annually. Using the ionic model, determine the metal oxidation state and total valence electron count of each Pd complex (**1** – **7**). What is the role of the $CuCl_2$ complex?



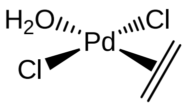
CH 611 Advanced Inorganic Chemistry – Synthesis and Analysis

Practice problems



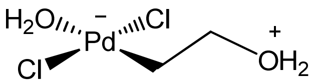
1

Metal oxidation state: +2
Total electron count: 16 electron



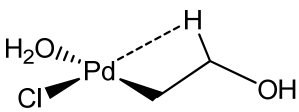
2

Metal oxidation state: +2
Total electron count: 16 electron



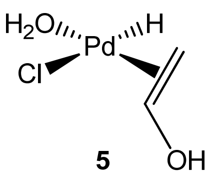
3

Metal oxidation state: 2+
Total electron count: 16 electron



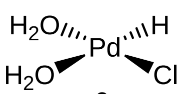
4

Metal oxidation state: 2+
Total electron count: 14 electron



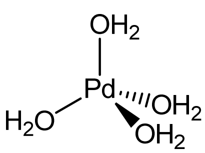
5

Metal oxidation state: 2+
Total electron count: 16 electron



6

Metal oxidation state: 2+
Total electron count: 16 electron



7

Metal oxidation state: 0
Total electron count: 18 electron

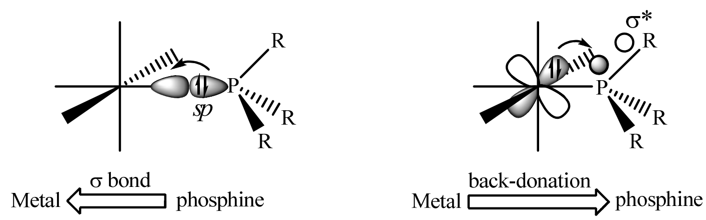
The $CuCl_2$ reagent is used as a co-catalyst to regenerate Pd(II) from Pd(0) to re-initiate the catalytic cycle

$$2Cu(II) + Pd(0) \rightarrow 2Cu(I) + Pd(II)$$

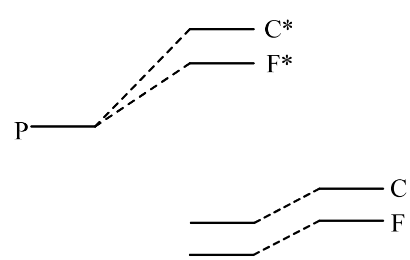
19. Using MO models for metal carbonyl and metal phosphine complexes explain the difference observed in v(CO) by FTIR spectroscopy for the *trans*-CO ligand of the following complexes.

$v(\mathrm{CO})_{\mathrm{trans}} = 2056\ \mathrm{cm}^{-1}$ $v(\mathrm{CO})_{\mathrm{trans}} = 2111\ \mathrm{cm}^{-1}$

The M-P bond can be represented with a particular geometry in a generic representation as is shown below. A σ–bond is formed from donation of the lone pair on the P atom (*sp* orbital) to one of the empty e_g metal orbitals (dz^2 or dx^2-dy^2) and back-bonding occurs from one of the filled t_{2g} set of metal orbitals (*dxy*, *dxz* or *dyz*) to the P–R anti-bonding σ^*-orbitals.

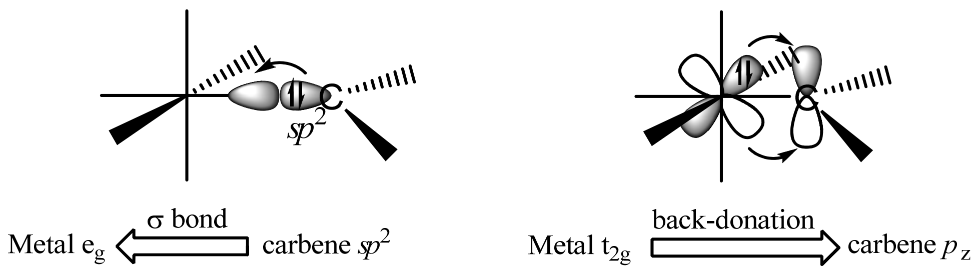


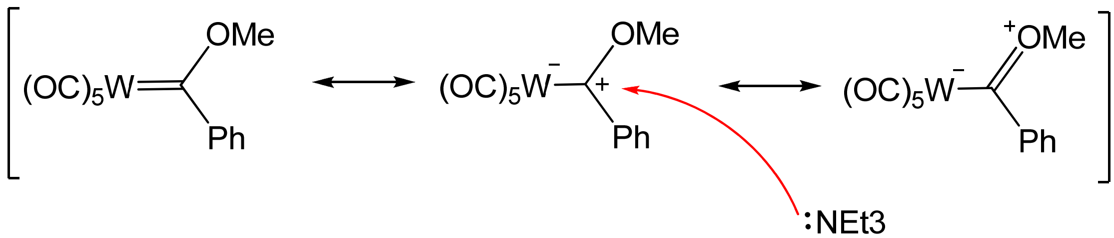
The PF_3 ligand has a lower energy σ* ligand orbital than the $P(^tBu)_3$ ligand due to the greater electronegativity of F *vs.* C. Therefore the PF_3 ligand is a better π-acceptor than the $P(^tBu)_3$ ligand. As a result of this energy difference (shown in MO diagram below) the PF_3 ligand has a greater back-donation from the Ni metal than the $P(^tBu)_3$ ligand and thus decreases the back-donation to the *trans* CO ligand relative to the analogous $P(^tBu)_3$ complex. This decreased back-donation to the *trans* CO ligand in the PF_3 complex results in a stronger C≡O bond and a higher energy stretching frequency in the IR spectrum.



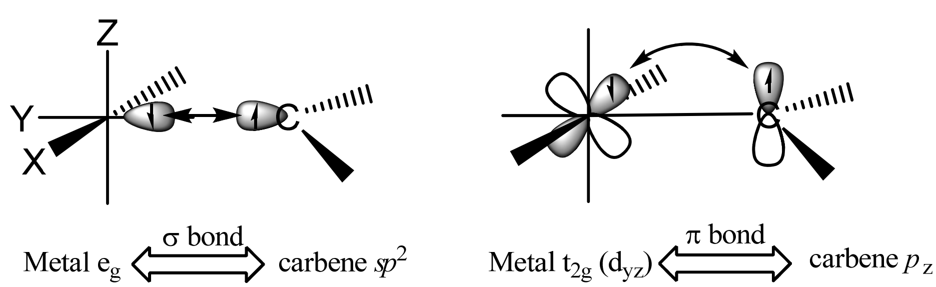
20. Using an MO bonding picture and resonance structures explain the reactivity of the following complexes:

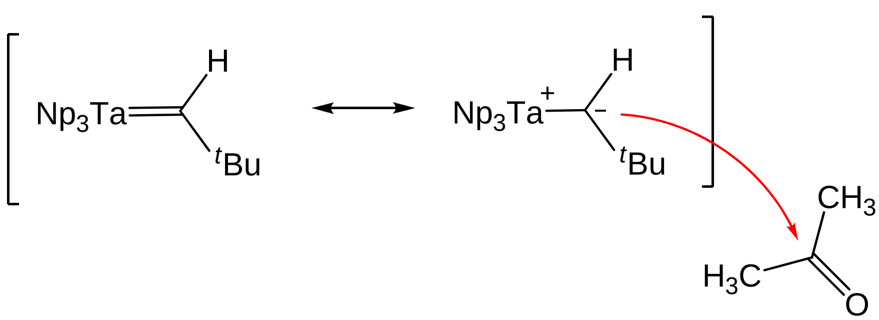
i) $(CO)_5W{=}C(OMe)Ph$ and Et_3N:



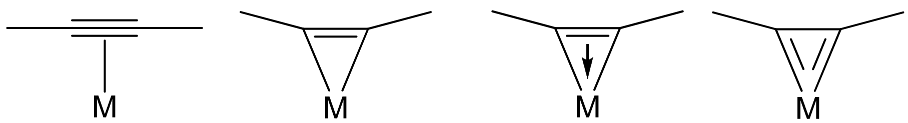


ii) $(Np)_3Ta{=}CH(^tBu)$ and $(CH_3)_2C{=}O$



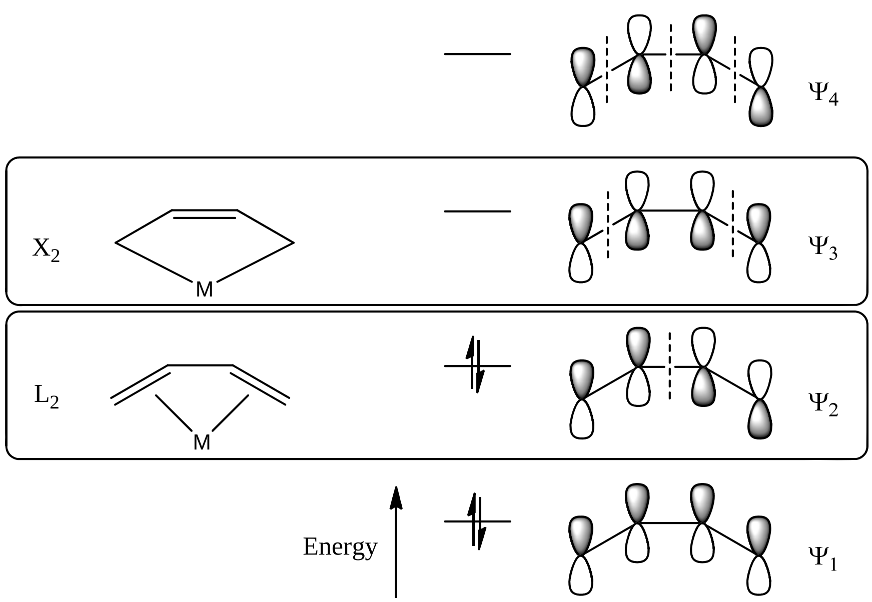


21. For the following bonding modes of the alkyne ligand complete the table below indicating the charge of the ligand and the number of electrons donated (in both the ionic and covalent models). Also describe the bonding using the L_aX_b formalism.



hapticity:	η^2	η^2	η^2	η^2
Ionic model:	**2e (0)**	**4e (2-)**	**6e (2-)**	**8e (4-)**
Covalent model:	**2e (0)**	**2e (0)**	**4e (0)**	**4e (0)**
L_mX_n:	**L**	**X_2**	**LX_2**	**X_4**

22. Using a molecular orbital bonding scheme and the ligand atomic orbitals describe how transition metal back-bonding to the butadiene ligand can favor the X_2 bonding mode over the L_2 bonding mode.



The HOMO (Ψ_2) is fully occupied in the butadiene ligand and forms a π-bond with an empty metal *d* orbital of appropriate symmetry and energy. The LUMO (Ψ_3) orbital is empty and available for π-back donation from a filled metal orbital of appropriate symmetry and energy. As can be seen in the schematic above, occupation of the LUMO (Ψ_3) via π-back donation will increase the bond order between C_2–C_3 and decrease the bond order between C_1–C_2 and C_3–C_4 of the butadiene ligand. Thus π-back donation favors the MX_2 bonding motif.