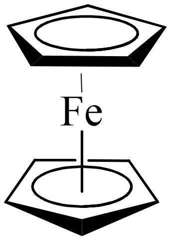
1. For all complexes listed below, determine

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

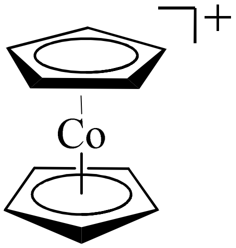
Please note: use the ionic model unless asked otherwise and comment on any complexes that do not obey the 18VE rule or have CN < 6.

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



Ionic Model	Covalent Model
Metal oxidation state:	Metal oxidation state:
Metal electron count:	Metal electron count:
Ligand electron count:	Ligand electron count:
Total electron count:	Total electron count:

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



Ionic Model

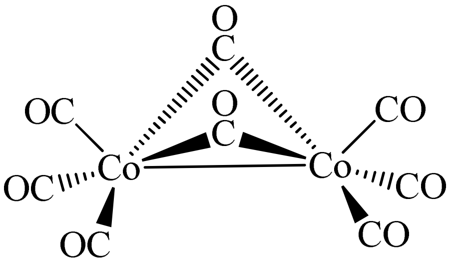
Metal oxidation state:

Metal electron count:

Ligand electron count:

Total electron count:

iii) $Co_2(CO)_8$



Ionic Model

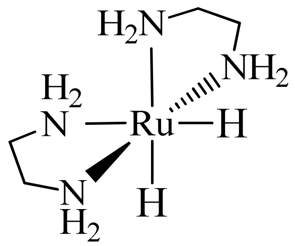
Metal oxidation state:

Metal electron count:

Ligand electron count:

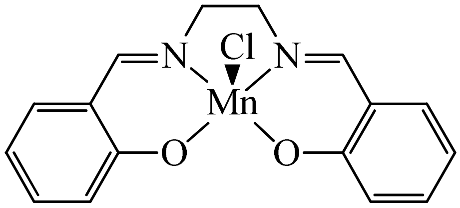
Total electron count:

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



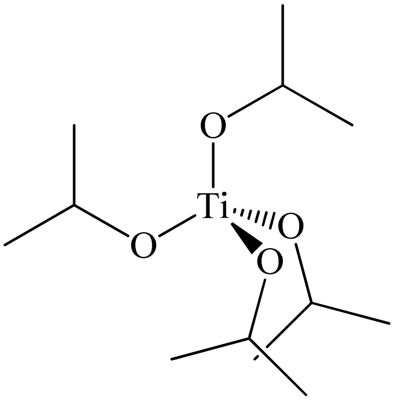
Ionic Model
Metal oxidation state:
Metal electron count:
Ligand electron count:
Total electron count:

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



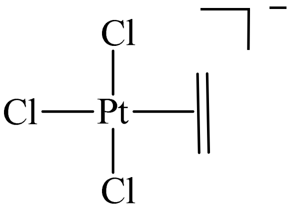
Ionic Model
Metal oxidation state:
Metal electron count:
Ligand electron count:
Total electron count:

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



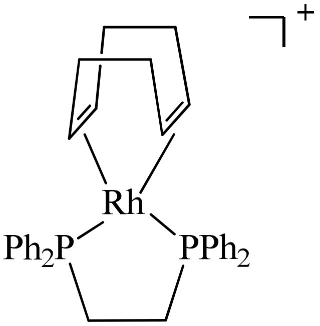
Ionic Model
Metal oxidation state:
Metal electron count:
Ligand electron count:
Total electron count:

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



Ionic Model
Metal oxidation state:
Metal electron count:
Ligand electron count:
Total electron count:

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



Ionic Model

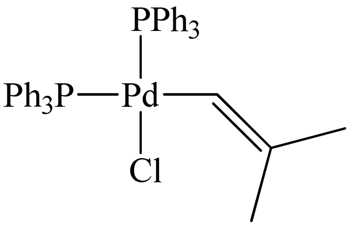
Metal oxidation state:

Metal electron count:

Ligand electron count:

Total electron count:

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



Ionic Model

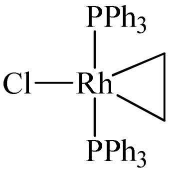
Metal oxidation state:

Metal electron count:

Ligand electron count:

Total electron count:

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



Ionic Model

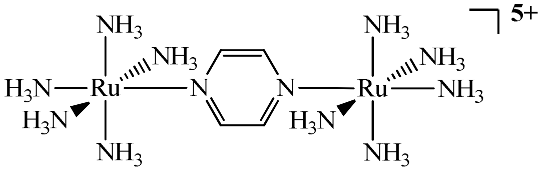
Metal oxidation state:

Metal electron count:

Ligand electron count:

Total electron count:

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



Ionic Model

1st Metal oxidation state:

Metal electron count:

Ligand electron count:

Total electron count:

Ionic Model

2nd Metal oxidation state:

Metal electron count:

Ligand electron count:

Total electron count:

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 __________ in energy.
The t_{2g} orbitals have lobes that lie between ligands and so will __________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.

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

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**

10. Using any combination of *s*, *p* or *d* orbitals please demonstrate overlap resulting in
i) a σ–bond

ii) a π–bond

iii) a δ–bond

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

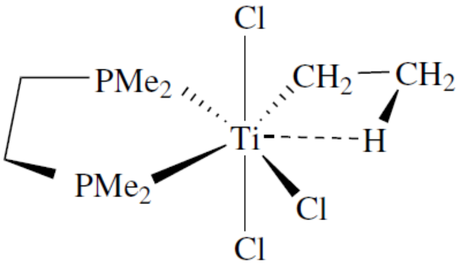
ix) Metal alkene

x) Metal alkyne

xi) Metal allyl

xii) Metal butadiene

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



13. State the multiplicity of the free ligand for each of the carbene complexes listed below.

Fischer carbyne
Schrock carbene
Schrock carbyne
Fischer carbene

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

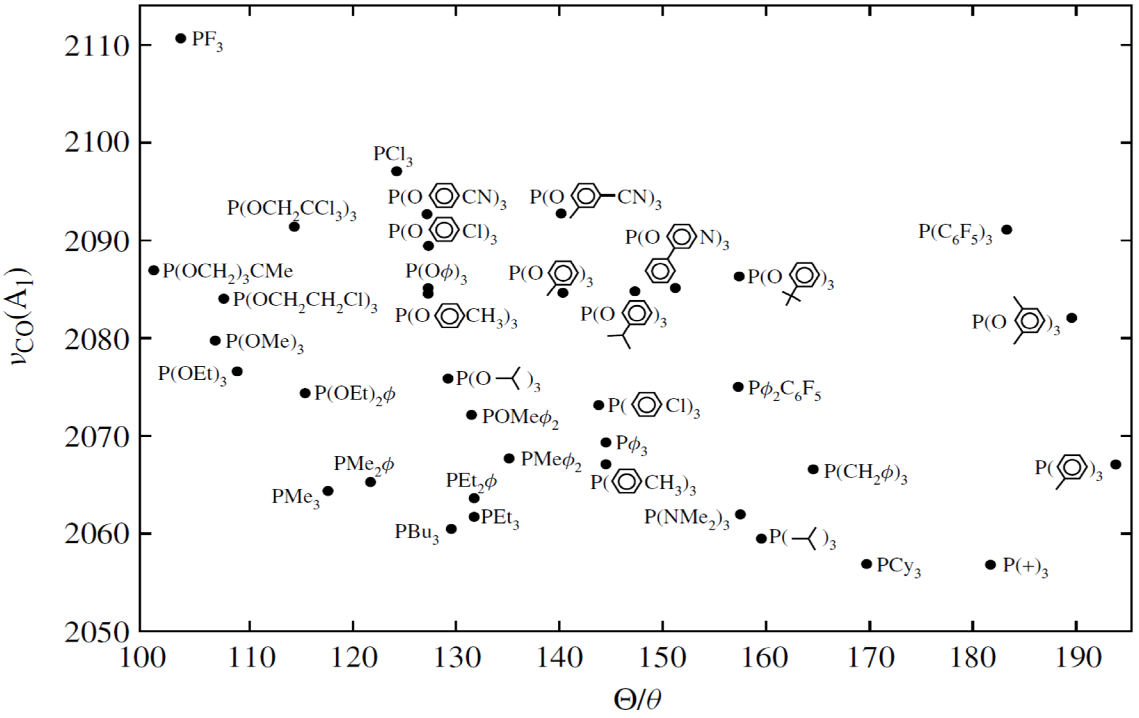
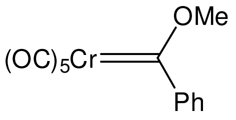
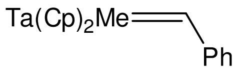


FIGURE 4.4 Electronic and steric effects of common P-donor ligands plotted on a map according to Tolman (ν in cm^{-1}, θ in degrees).

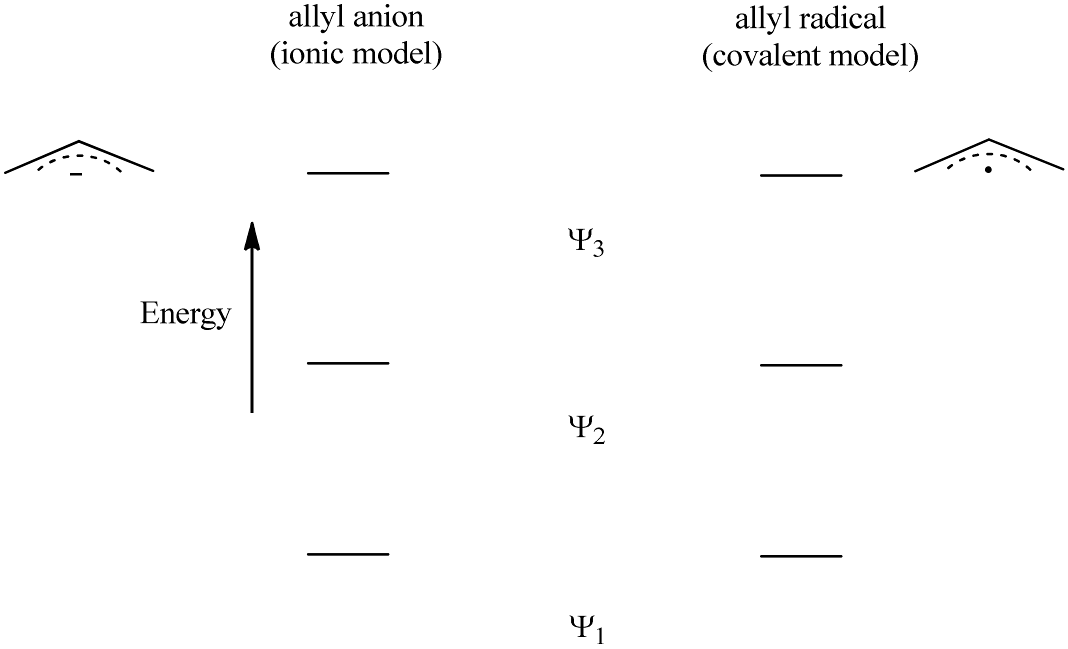
15. Draw resonance structures for the following two complexes.



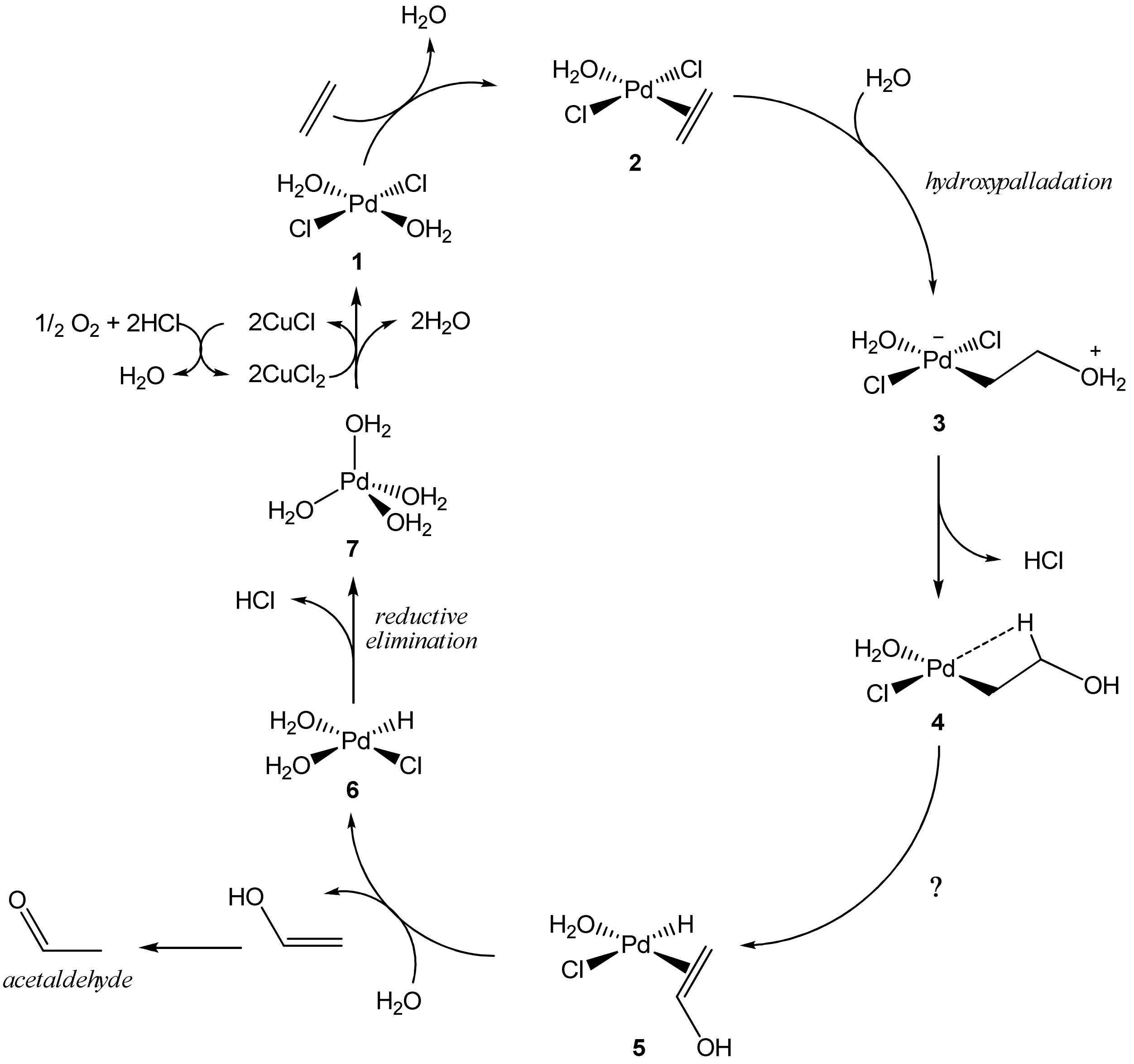


16. Draw the X_2 and L bonding modes of a metal-alkene complex.

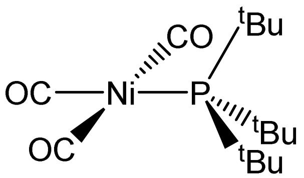
17. Complete the following diagram by drawing lobes and nodes of each orbital and filling electrons.



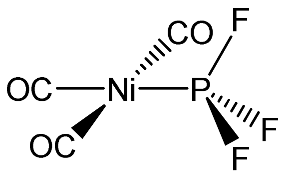
18. Below is the catalytic cycle describing the *Wacker oxidation* reaction, which is used to produce *ca*. 4 million tons of *acetaldehyde* annually. Using the ionic model, determine the metal oxidation state and total valence electron count of each Pd complex (**1** – **7**). What is the role of the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


H_2O
2
H_2O
hydroxypalladation
1
$1/2\ O_2 + 2HCl$
2CuCl
$2H_2O$
H_2O
$2CuCl_2$
3
HCl
7
HCl
reductive elimination
4
6
?
acetaldehyde
H_2O
5

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.



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



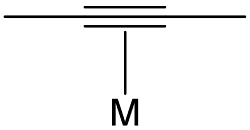
$\nu(\mathrm{CO})_{\mathrm{trans}} = 2111\ \mathrm{cm}^{-1}$

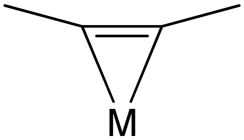
20. Using an MO bonding picture and resonance structures explain the reactivity of the following complexes:

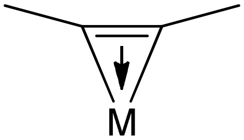
    i) $(CO)_5W{=}C(OMe)Ph$ and Et_3N:

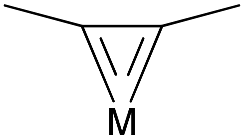
    ii) $(Np)_3Ta{=}CH(^t\mathrm{Bu})$ and $(CH_3)_2C{=}O$

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:

Ionic model:

Covalent model:

L_mX_n:

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.