

2017 Lecture 2 September 5, 2017



Transition metals are tuned by their ligands

Classification of Ligands

Metal Oxidation States

Electron Counting

Primary Classes of Ligands for Organometallic Chemistry:

- ◆ Carbon Monoxide (Carbonyls)
- ◆ Phosphines
- ◆ Cyclopentadienide
- ◆ Halides and Hydrides and Carbanions

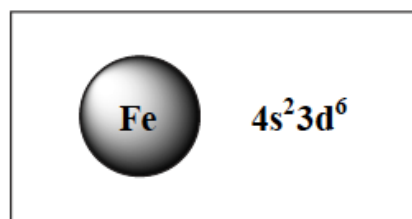
The Transition Metals

1													13	18
H													B	He
Li														Ne
Na													Al	Ar
	3	4	5	6	7	8	9	10	11	12				
K	Sc	Ti $4s^2 3d^2$ $3d^4$	V $4s^2 3d^3$ $3d^5$	Cr $4s^1 3d^5$ $3d^6$	Mn $4s^2 3d^5$ $3d^7$	Fe $4s^2 3d^6$ $3d^8$	Co $4s^2 3d^7$ $3d^9$	Ni $4s^2 3d^8$ $3d^{10}$	Cu	Zn	Ga		Kr	
Rb	Y	Zr $5s^2 4d^2$ $4d^4$	Nb $5s^1 4d^4$ $4d^5$	Mo $5s^1 4d^5$ $4d^6$	Tc $5s^2 4d^5$ $4d^7$	Ru $5s^1 4d^7$ $4d^8$	Rh $5s^1 4d^8$ $4d^9$	Pd $5s^0 4d^{10}$ $4d^{10}$	Ag	Cd	In		Xe	
Cs	La	Hf $6s^2 5d^2$ $5d^4$	Ta $6s^2 5d^3$ $5d^5$	W $6s^2 5d^4$ $5d^6$	Re $6s^2 5d^5$ $5d^7$	Os $6s^2 5d^6$ $5d^8$	Ir $6s^2 5d^7$ $5d^9$	Pt $6s^1 5d^9$ $5d^{10}$	Au	Hg	Tl		Rn	
		EARLY → LATE												

Transition metals (d-block metals):
elements that can have a partially filled d valence shell. Typically group 4-10 metals.*

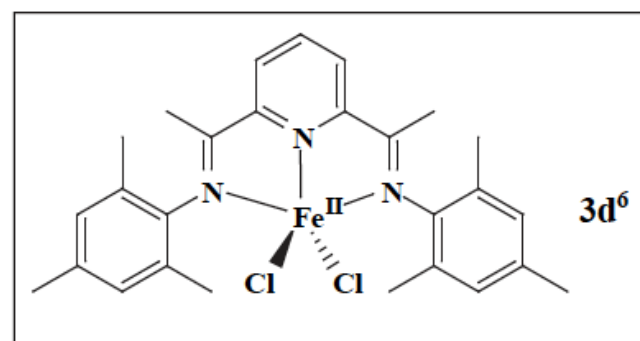
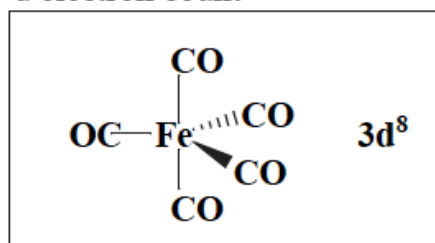
* d electrons in group 3 are readily removed via ionization, those in group 11 are stable and generally form part of the core electron configuration.

valence (d) electron count:



for free (gas phase) transition metals: (n+1)s is below (n)d in energy (recall: n = principal quantum #).

for complexed transition metals: the (n)d levels are below the (n+1)s and thus get filled first. note that group # = d electron count



for oxidized metals, subtract the oxidation state from the group #.

Ref. : Christina White UCIU

d¹ d² d³ d⁵ d⁵ d⁶ d⁷ d⁸ d⁹ d¹⁰

4s ²	21 Sc 44.9559 Scandium	22 Ti 47.867 Titanium	23 V 50.9415 Vanadium	24 Cr 51.9961 Chromium	25 Mn 54.938 Manganese	26 Fe 55.845 Iron	27 Co 58.9332 Cobalt	28 Ni 58.6934 Nickel	29 Cu 63.546 Copper	30 Zn 65.4089 Zinc
5s ²	39 Y 88.9058 Yttrium	40 Zr 91.224 Zirconium	41 Nb 92.9064 Niobium	42 Mo 85.94 Molybdenum	43 Tc 98 Technetium	44 Ru 101.07 Ruthenium	45 Rh 102.9055 Rhodium	46 Pd 106.42 Palladium	47 Ag 107.8682 Silver	48 Cd 112.411 Cadmium
6s ²	71 Lu 174.967 Lutetium	72 Hf 178.49 Hafnium	73 Ta 180.9497 Tantalum	74 W 183.84 Tungsten	75 Re 186.207 Rhenium	76 Os 190.23 Osmium	77 Ir 192.217 Iridium	78 Pt 195.084 Platinum	79 Au 196.9666 Gold	80 Hg 200.59 Mercury

Early Transition Metals

low electronegativities

higher oxidation states

“harder” metal centers

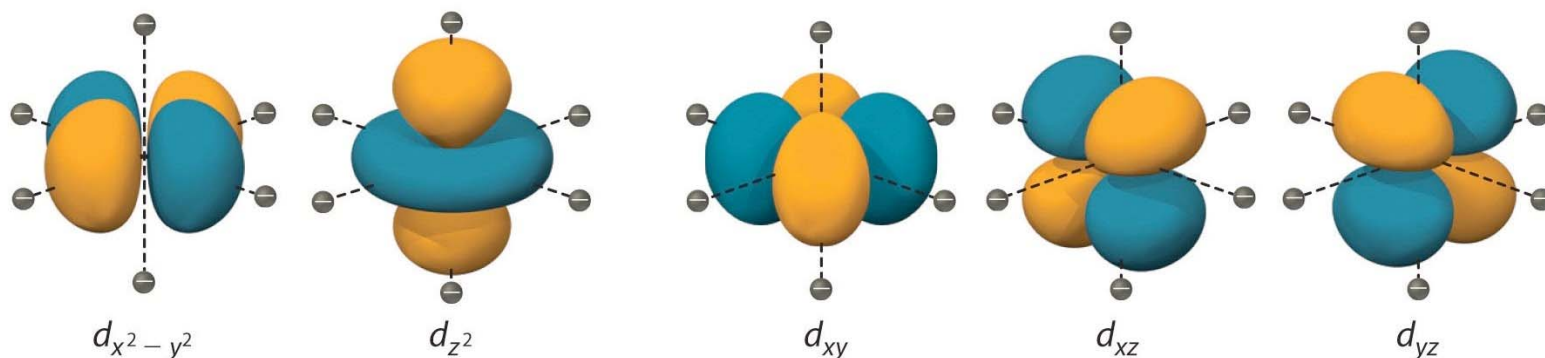
OXOPHILIC!!

Late Transition Metals

higher electronegativities

lower oxidation states

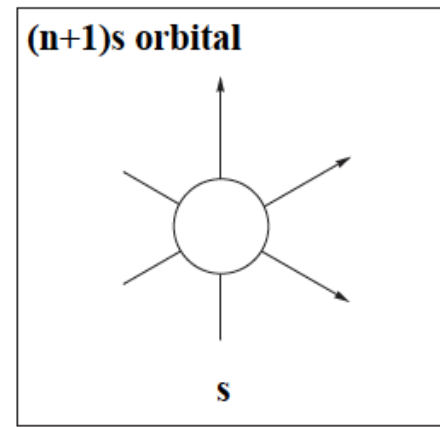
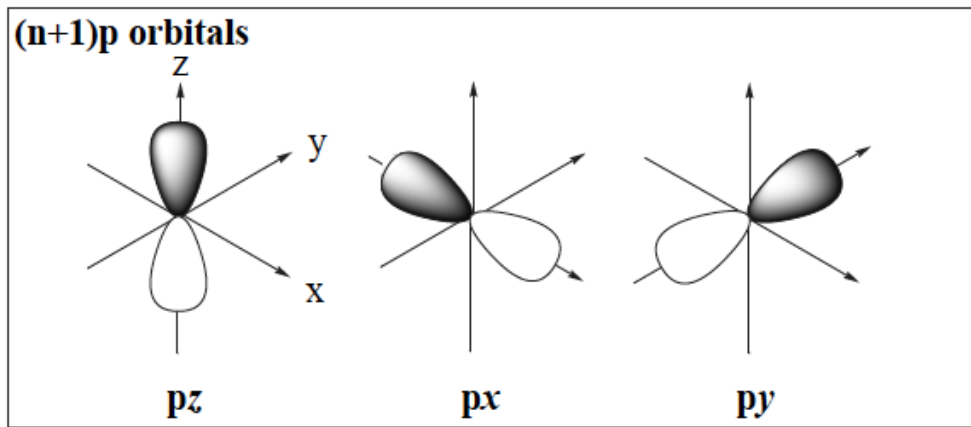
“softer” metal centers



d^1 d^2 d^3 d^5 s^1d^5 d^6 d^7 d^8 d^9 d^{10}

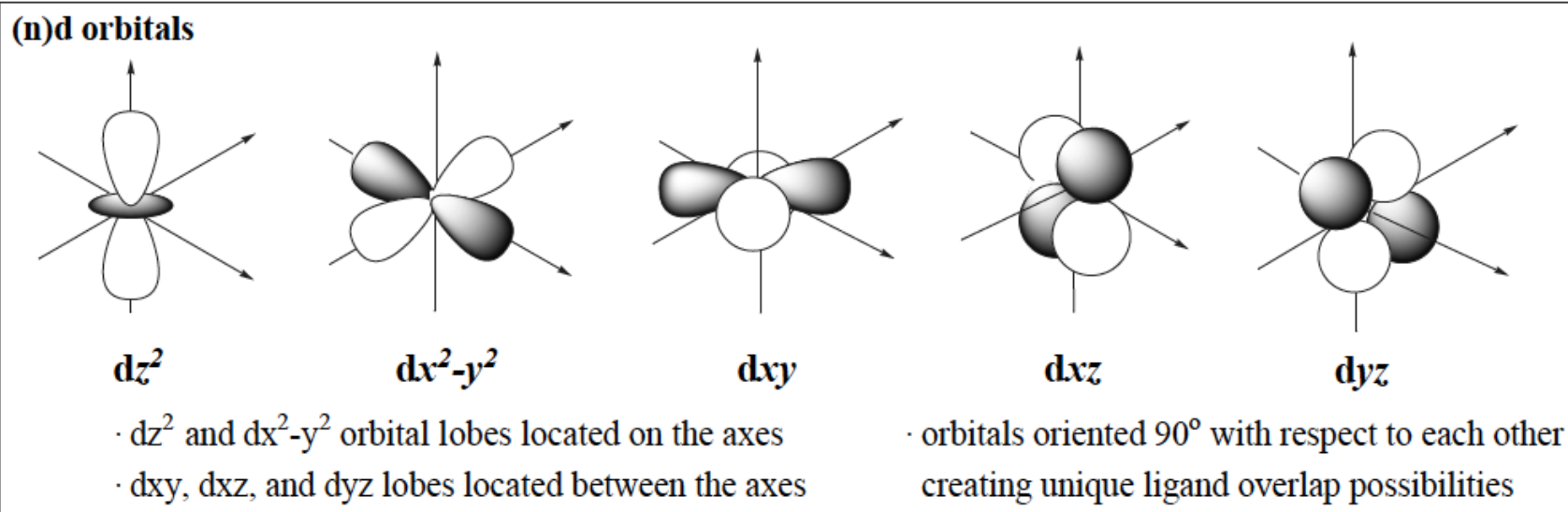
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Transition Metal Valence Orbitals



- **9 Valence Orbitals:** upper limit of 9 bonds may be formed. In most cases a maximum of 6 σ bonds are formed and the remaining d orbitals are non-bonding. It's these non-bonding d orbitals that give TM complexes many of their unique properties.

- **18 electron rule:** upper limit of 18 e⁻ can be accommodated w/out using antibonding molecular orbitals (MO's).

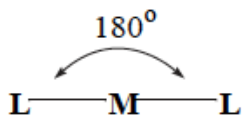


Common Geometries for TM Complexes

Coordination number (CN): The number of ligands (L) bonded to the same metal (M).

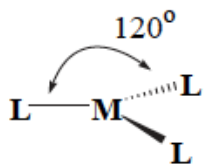
Sterics. to a 1st approximation, geometry of TM complexes determined by steric factors (VSEPR -valence shell electron pair repulsion). The M-L bonds are arranged to have the maximum possible separation around the M.

$CN = 2, ML_2$:



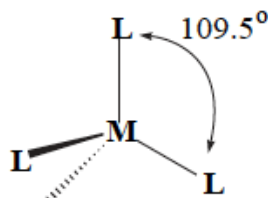
linear

$CN = 3, ML_3$:



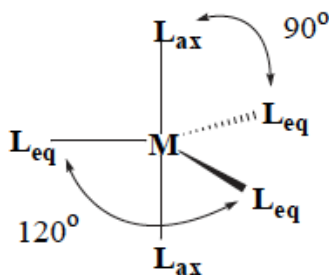
trigonal planar

$CN = 4, ML_4$:



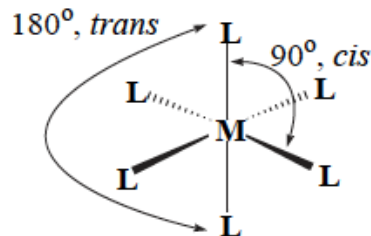
tetrahedral

$CN = 5, ML_5$:



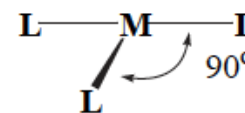
trigonal bipyramidal

$CN = 6, ML_6$:

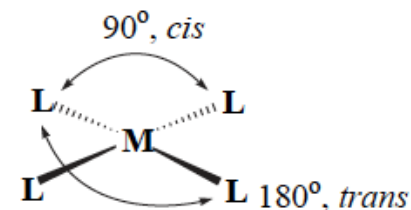


octahedral

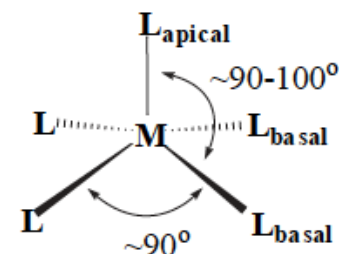
Electronics: d electron count combined with the complex electron count must be considered when predicting geometries for TM complexes with non-bonding d electrons. Often this leads to sterically less favorable geometries for electronic reasons (e.g. $CN = 4, d^8, 16 e^-$ strongly prefers square planar geometry).



T-shaped



square planar

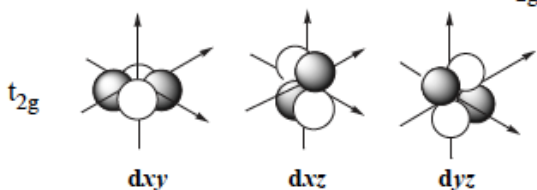
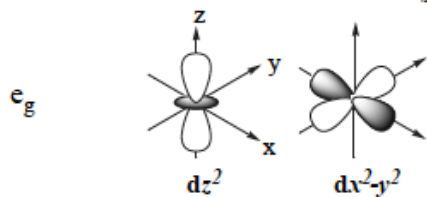
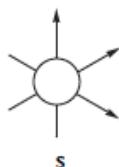
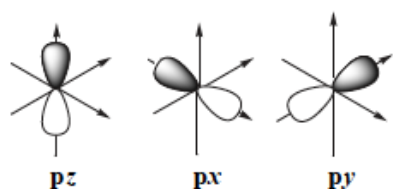


square pyramidal

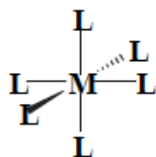
Ref. : Christina White UCIU

MO Description of σ bonding in ML_6

Metal Valence Orbitals



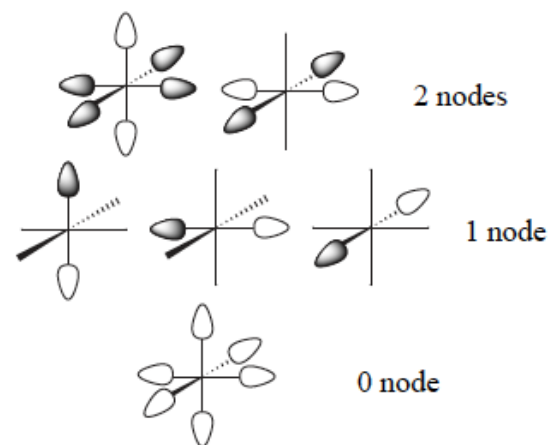
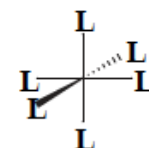
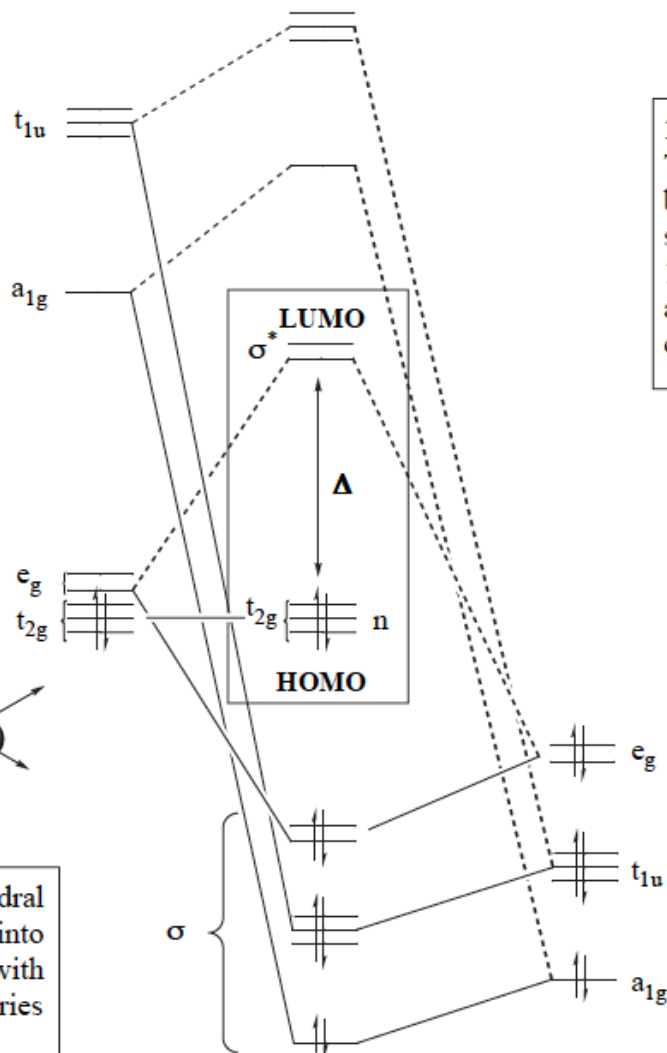
Mulliken symbols: in an octahedral environment, the degenerate d orbitals split into orbitals of t_{2g} and e_g symmetries. Orbitals with different symbols have different symmetries and cannot interact.



Linear Combinations of Ligand σ Donor Orbitals

18 e- Rule:

The octahedral geometry is strongly favored by d^6 metals (e.g. Fe (II), Ru (II), Rh(III)). A stable electronic configuration is achieved at $18 e^-$, where all bonding (mostly L character) and non-bonding orbitals (mostly M d character) are filled.



Overview of Transition Metal Complexes

1. The coordinate covalent or dative bond applies in $L:\rightarrow M$
2. Lewis bases are called LIGANDS—all serve as σ -donors
some are π -donors as well, and some are π -acceptors
3. Specific coordination number and geometries
depend on metal and number of d-electrons
4. HSAB theory useful $[ML_nX_m]^z$
 - a) Hard bases stabilize high oxidation states
 - b) Soft bases stabilize low oxidation states

Classification of Ligands: The L, X, Z Approach

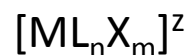
Malcolm Green : The CBC Method (or Covalent Bond Classification) used extensively in organometallic chemistry.

- L** ligands are derived from charge-neutral precursors: NH_3 , amines, N-heterocycles such as pyridine, PR_3 , CO, alkenes etc.
- X** ligands are derived from anionic precursors: halides, hydroxide, alkoxide alkyls—species that are one-electron neutral ligands, but two electron donors as anionic ligands. [EDTA](#)⁴⁻ is classified as an L_2X_4 ligand, features four anions and two neutral donor sites. C_5H_5 is classified an L_2X ligand.
- Z** ligands are RARE. They accept two electrons **from** the metal center. They donate none. The “ligand” is a Lewis Acid that accepts electrons rather than the Lewis Bases of the X and L ligands that donate electrons.

5. Oxidation State

Here, z = charge on the complex unit.

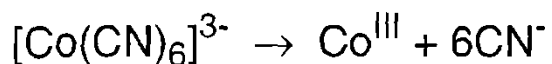
$$\text{ox. state} = z - \sum_N \text{L charge}$$



ligand removed from complex with closed shell configuration

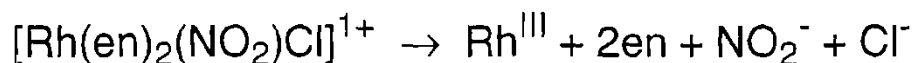
examples:

octahedral

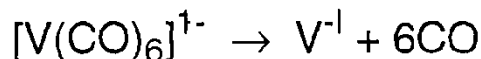
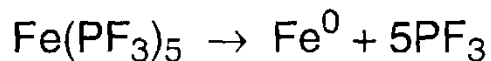


positive oxidation states usually written as Roman numerals

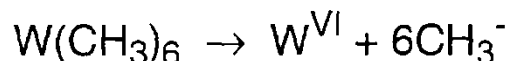
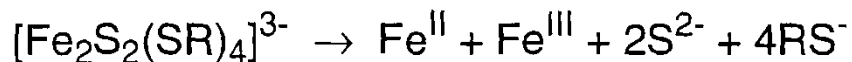
Square
pyramidal



Trigonal bi-
pyramidal

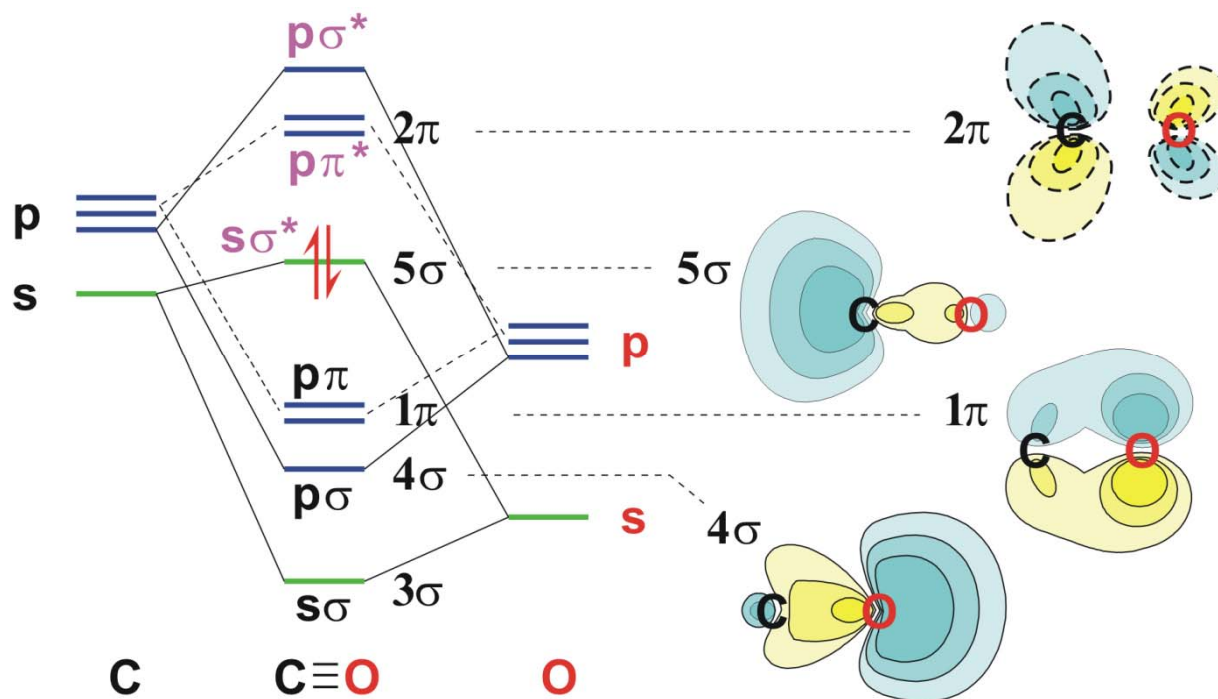


Tetrahedral

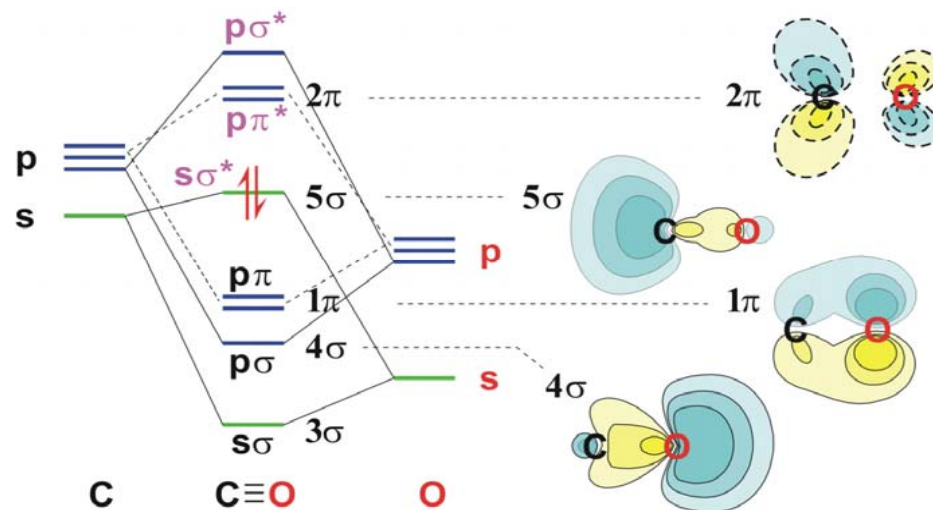


An oxidation state is a formalism which affords that d^n configuration consistent with molecular properties.

Carbon Monoxide or Carbonyl: MO description



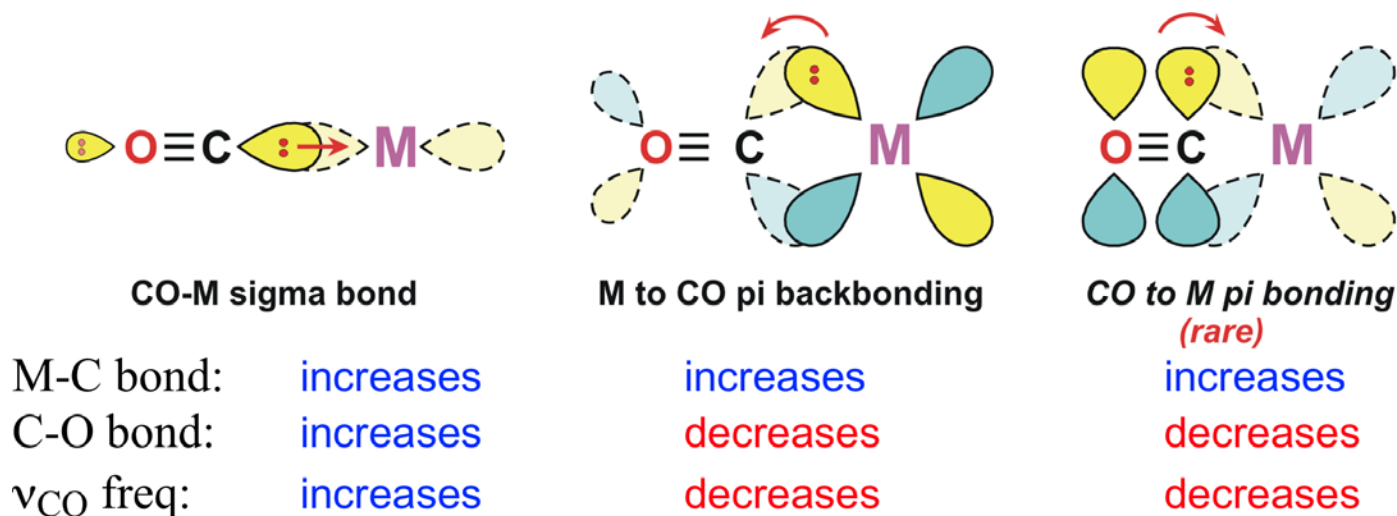
How do we know?



Experimental Data Supporting Nature of MO's in CO

Species	Config	C-O Å	ν_{CO} cm ⁻¹	Comment
CO	(5σ) ²	1.13	2143	
CO ⁺	(5σ) ¹	1.11	2184	5σ MO is weakly antibonding
CO*	(5σ) ¹ (2π) ¹	S 1.24	1489	2π MO is strongly antibonding
		T 1.21	1715	

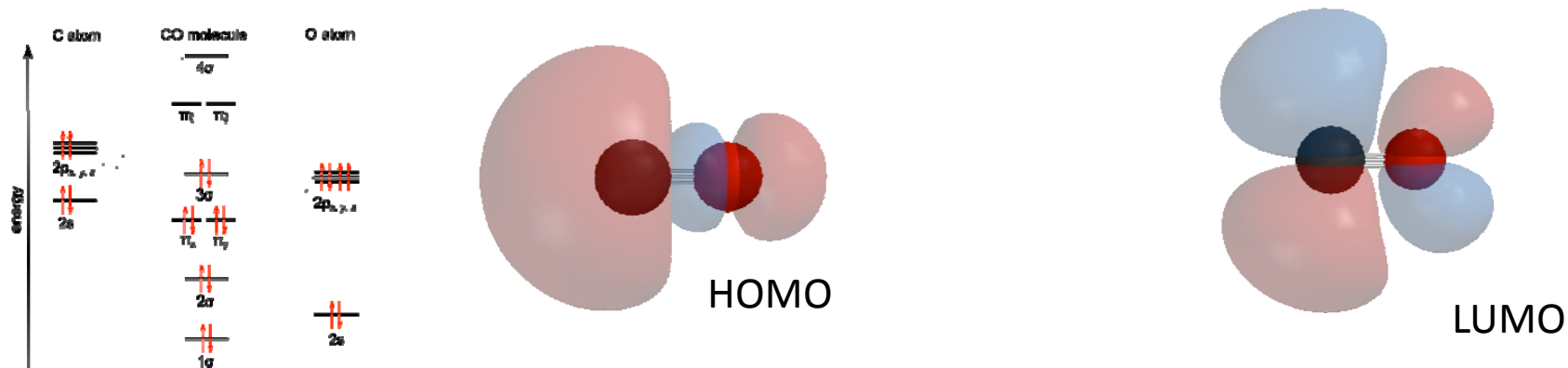
The M-C bond in Metal Carbonyls



Carbonyl IR Stretching Frequencies

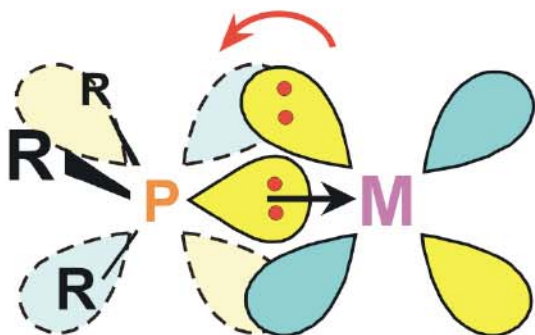
- The **position** of the carbonyl bands in the IR depends mainly on the **bonding mode** of the CO (terminal, bridging) and the **amount of electron density on the metal being π -backbonded to the CO**.
- The **number** (and intensity) of the carbonyl bands one observes depends on the **number of CO ligands present** and the **symmetry** of the metal complex. There are also secondary effects such as Fermi resonance and overtone interactions that can complicate carbonyl IR spectra.

Ligands of Organometallic Chemistry. Homoleptic complexes from CO and PR_3 .



Phosphine Ligands – PR_3

empty d orbitals on phosphine can act as π -acceptor orbitals } not very important unless R-groups are electron-withdrawing

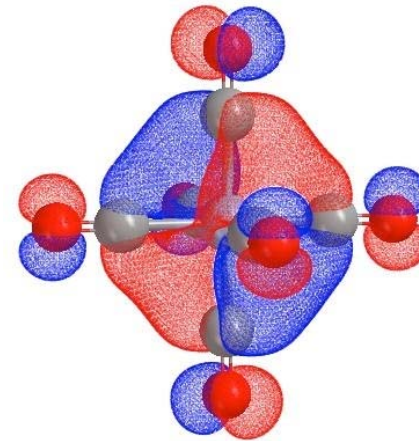
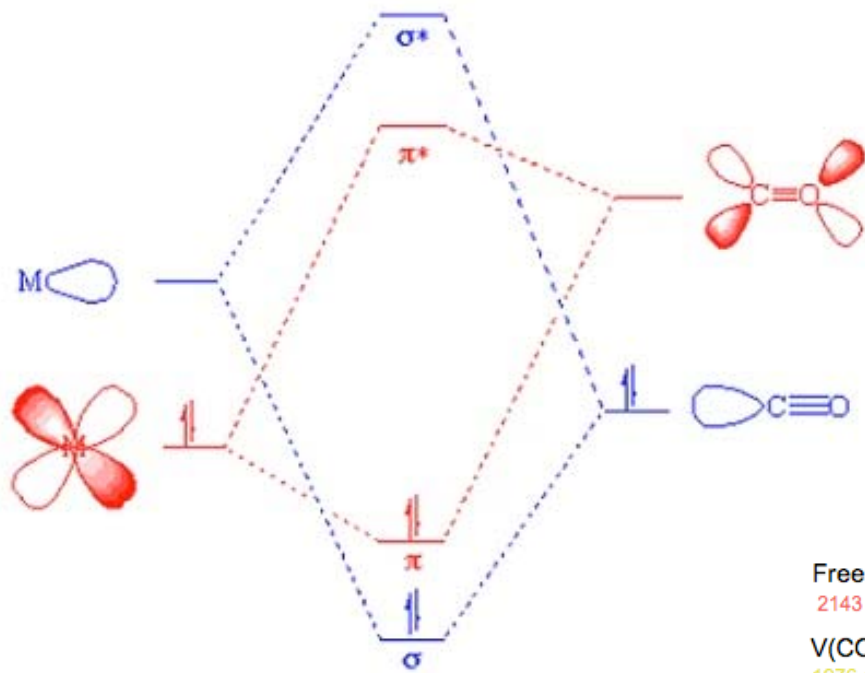


neutral $2e^-$ donor

Phosphine ligands

excellent soft-donor ligands with a wide variety of easily adjusted steric and electronic factors

R = carbon groups { phosphine (US)
phosphane (Germany/Europe)



Free CO
2143 cm^{-1}

$\text{V}(\text{CO})_6$
1976 cm^{-1}

$[\text{Ti}(\text{CO})_6]^{2-}$
1747 cm^{-1}

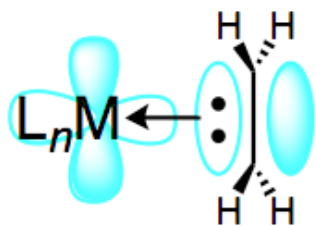
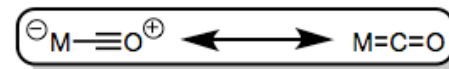
$\text{Cr}(\text{CO})_6$
2000 cm^{-1}

$\text{Mn}_2(\text{CO})_{10}$
2013 cm^{-1}

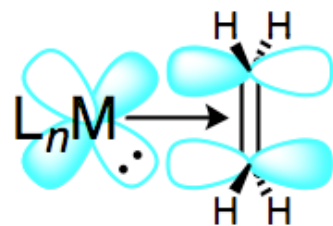
$\text{Fe}(\text{CO})_5$
2023 cm^{-1}

$\text{Co}_2(\text{CO})_8$
2044 cm^{-1}

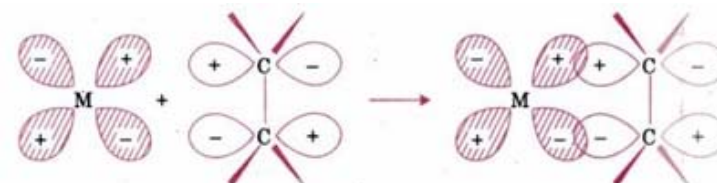
$\text{Ni}(\text{CO})_4$
2057 cm^{-1}



Filled π orbital
Empty d orbital



Filled metallic HOMO
Empty π^* orbital



Back-Bonding

The molecular orbital view of alkene-metal bonding.

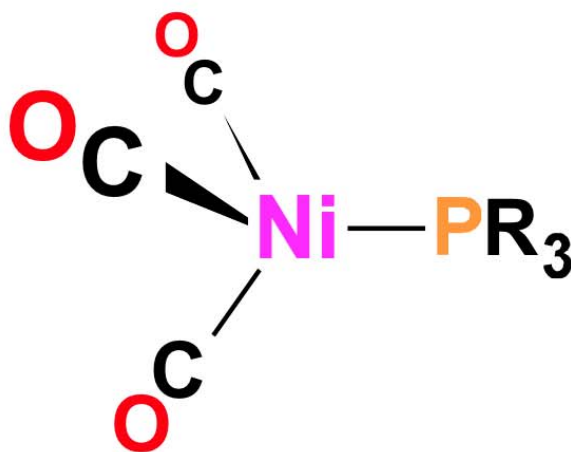


CO as a Reporter Ligand via IR Stretching Frequencies

Tolman Electronic Parameter for Ligand Donor Ability

Lowest CO stretching
frequency:

*most donating
phosphine*



Highest CO stretching
frequency:

*least donating
phosphine
(best π -acceptor)*

Tolman electronic parameter

2) Strong π acceptor ligands will compete with CO for the electron back donation and C-O stretch frequency will remain high

Weak back donation \rightarrow High C – O stretch

The IR frequencies represent a reliable yardstick for the electronic properties of a series of P ligands toward a particular metal, M.

$\text{CrL}(\text{CO})_5$ or $\text{NiL}(\text{CO})_3$ as examples; L = $\text{P}(\text{t-Bu})_3$ as reference

The electronic parameter, χ (chi) for other ligands is simply defined as the difference in the IR frequencies of the symmetric stretch of the two complexes

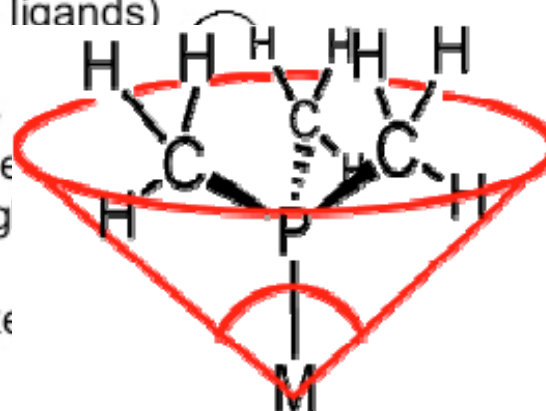
<u>Ligand, PR_3, R=</u>	<u>χ (chi)</u>	<u>IR Freq (A_1) of $\text{NiL}(\text{CO})_3$ in cm^{-1}</u>
T-Bu	0	2056
N-Bu	4	2060
4- $\text{C}_6\text{H}_4\text{NMe}_3$	5	2061
Ph	13	2069
4- $\text{C}_6\text{H}_4\text{F}$	16	2072
CH_3O	20	2076
PhO	29	2085
$\text{CF}_3\text{CH}_2\text{O}$	39	2095
Cl	41	2097
$(\text{CF}_3)_2\text{CHO}$	54	2110
F	55	2111
CF_3	59	2115

Tolman's steric parameter

B. Steric Effects

1) Cone angle (Tolman's parameter, θ) (Monodentate ligands)

From the metal center, located at a distance of 2.28 Å from the phosphorus atom in the appropriate direction, a cone is constructed which embraces all the atoms of the substituents on the P atom, even though ligands never form a perfect cone.



angle

Sterically, more bulky ligands give less stable complexes. Crystal structure determination, angles smaller than θ values would suggest.

Thermochemistry: heat of formation of metal-phosphine adducts.

When electronic effects are small, the heats measured are a measure of the steric hindrance in the complexes.

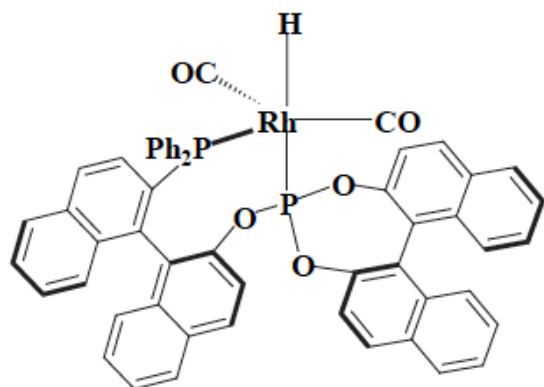
Heats of formation decrease with increasing steric bulk of the ligand.

Ligand, PR_3 ; R =	H	θ value =	87
	CH_3O		107
	n-Bu		132
	PhO		128
	Ph		145
	i-Pr		160
	C_6H_{11}		170
	t-Bu		182

Electron Counting

Step 1: Determine the oxidation state of the metal.

To do this, balance the ligand charges with an equal opposite charge on the metal. This is the metal's formal oxidation state.

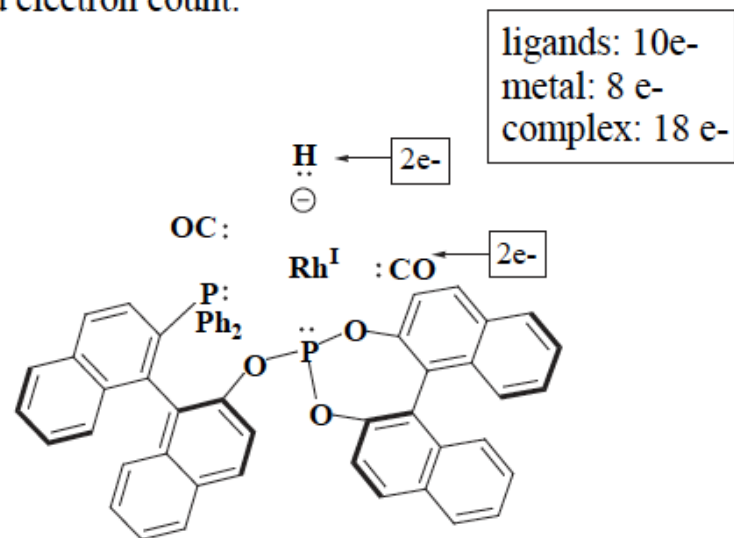
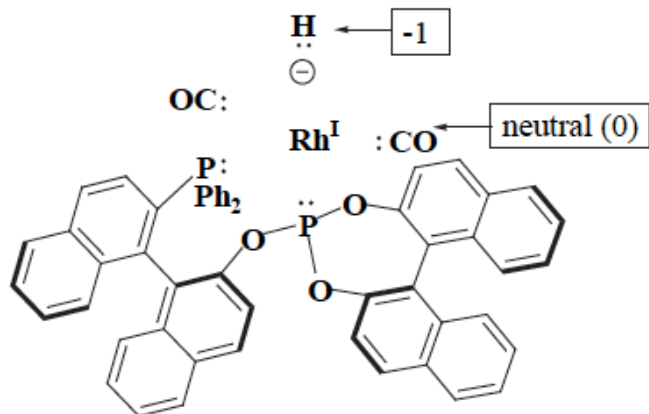


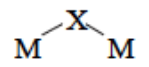
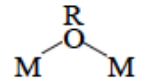
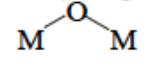
Step 2: Determine the d electron count. Recall: subtract the metal's oxidation state from its group #.

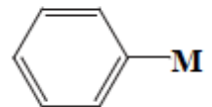
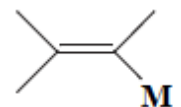
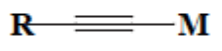
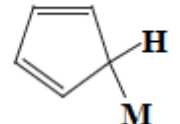

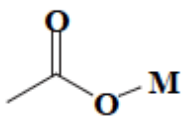
9	
Co 3d ⁹	
Rh 4d ⁹	Rh^I = d⁸
Ir 5d ⁹	

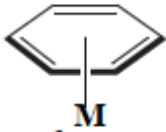
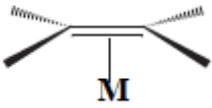
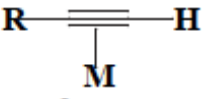

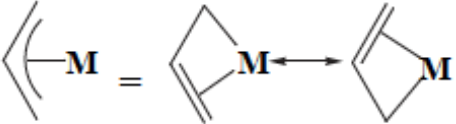
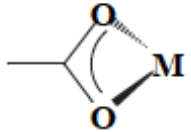
To determine ligand charges, create an ionic model by assigning each M-L electron pair to the more electronegative atom (L). This should result in stable ligand species or ones known as reaction intermediates in solution.

Step 3: Determine the electron count of the complex by adding the # of electrons donated by each ligand to the metal's d electron count.



η^1 ligands (monodentate):	Formal charge	# of e-donated
H (hydride)	-1	2
CH ₃ (alkyl)	-1	2
CO	0	2
X (halides)	-1	2
μ -X (bridging)	-1	4
		(2/metal)
OR (terminal alkoxide)	-1	2
μ -OR (bridging)	-1	4
		(2/metal)
OR ₂ (ether)	0	2
O ₂ (superoxide)	-1	2
O (terminal oxo)	-2	4
μ -O (bridging)	-2	4
		(2/metal)
PR ₂ (phosphide)	-1	2
PR ₃ (phosphine)	0	2
NR ₂ (amide)	-1	2
NR ₃ (amine)	0	2
imines	0	2
nitriles	0	2
NO (nitrosyl) linear	+1	2

η^1 -coordination	Formal charge	# of e-donated
 η^1 -aryl	-1	2
 η^1 -alkenyl	-1	2
 η^1 -alkynyl	-1	2
 η^1 -Cp (cyclopentadienyl)	-1	2
 η^1 -allyl	-1	2
 η^1 -acetate	-1	2

η^x -coordination	Formal charge	# of e-donated
 η^6 -arene	0	6
 η^2 -alkene	0	2
 η^2 -alkyne	0	2
 η^5 -Cp (cyclopentadienyl)	-1	6
 η^3 -allyl	-1	4
 η^2 -acetate	-1	4

Ferrocene: $(\eta^5-C_5H_5)_2Fe$

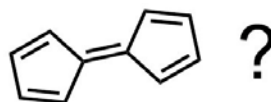
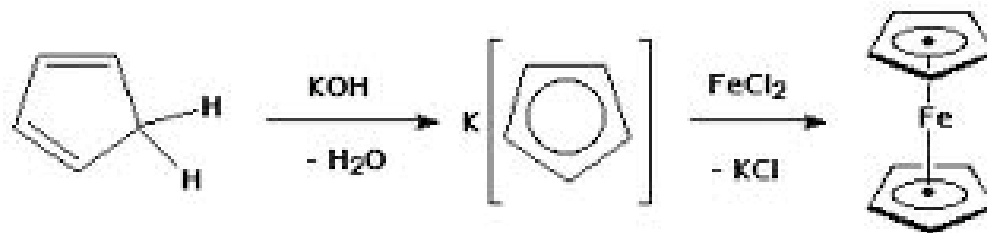


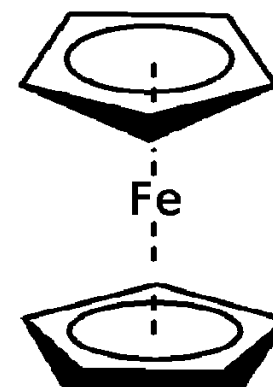
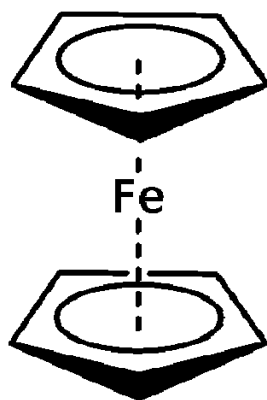
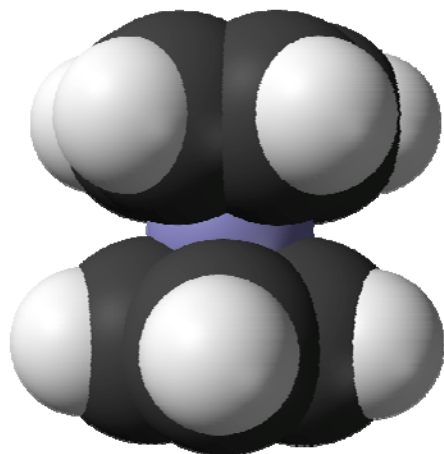
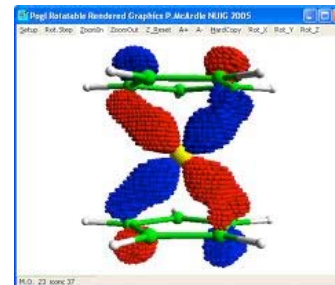
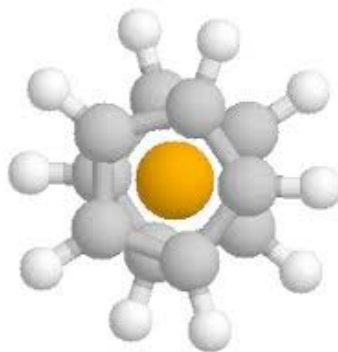
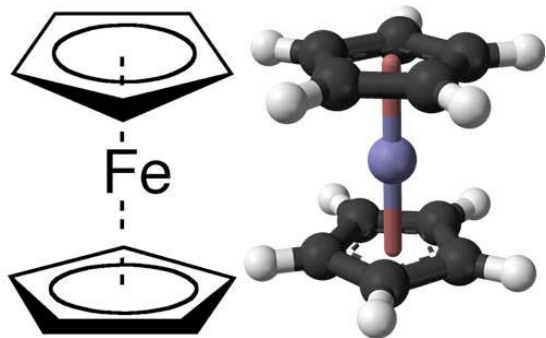
Photo credit: wikipedia.org

?

mpt: 172° C; bpt: 250° C !! No decomposition.

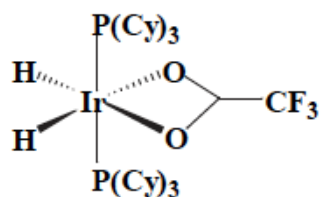
https://www.youtube.com/watch?v=H6_E6C_e_fg

Ferrocene: $(\eta^5-C_5H_5)_2Fe$



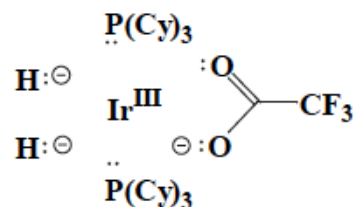
What symmetry element distinguishes the two?

Electron Counting II

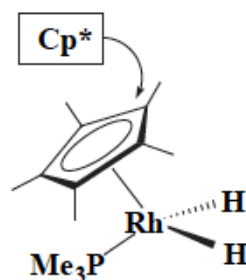


Crabtree's dehydrogenation catalyst

Crabtree *JACS* 1987 (109) 8025.

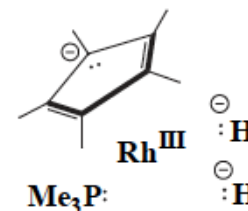


ligands: 12e-
metal: d^6 , 6e-
complex: 18 e-

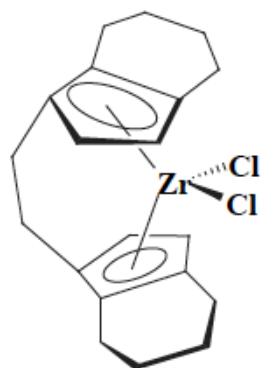


Bergman:
direct observation
of C-H \rightarrow C-M

Bergman *OM* 1984 (3) 508.

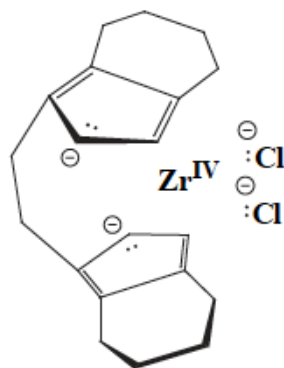


ligands: 12e-
metal: d^6 , 6e-
complex: 18 e-

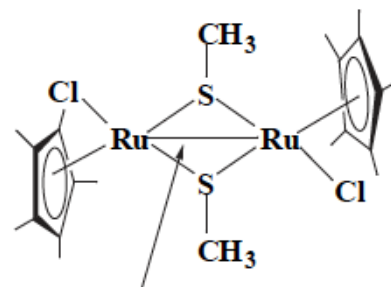


Brintzinger catalyst

Brintzinger *JOMC* 1985 (228) 63.



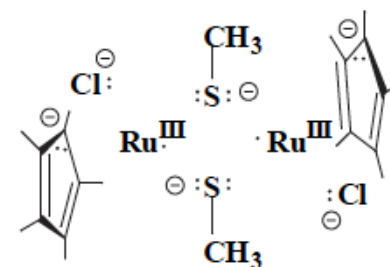
ligands: 16e-
metal: d^0 , 0e-
complex: 16 e-



Ru-Ru bond = 2 e-
note: metal oxidation
state doesn't change

Hidai catalyst for
propargylic substitution

Hidai *JACS* 2002 (124) 7900



Ru 1	Ru 2
ligands: 12 e-	ligands: 12 e-
metal: d^5 , 5e-	metal: d^5 , 5e-
Ru 2: 1 e-	Ru 1: 1 e-
complex: 18 e-	complex: 18 e-