UNIVERSITY OF DELAWARE

Chem 634

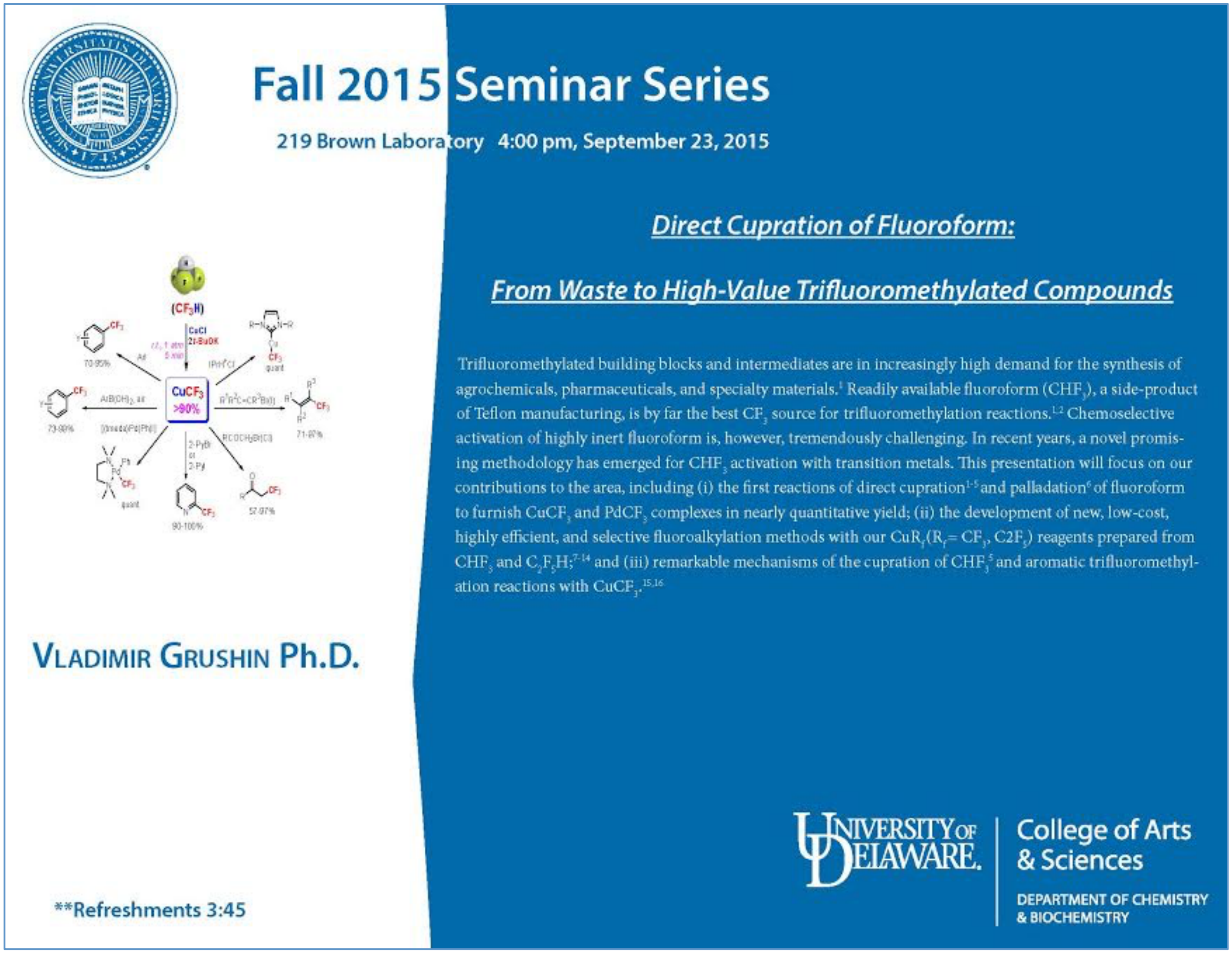
Introduction to Transition Metal Catalysis

Reading: Heg Ch 1–2
CS-B 7.1, 8.2–8.3, 11.3
Grossman Ch 6

Announcements

- Problem Set 1 due Thurs, 9/24 at beginning of class
- Office Hour: Wed, 10:30-12, 220 BRL

Announcements



Fall 2015 Seminar Series

219 Brown Laboratory 4:00 pm, September 23, 2015

Direct Cupration of Fluoroform:

From Waste to High-Value Trifluoromethylated Compounds

Trifluoromethylated building blocks and intermediates are in increasingly high demand for the synthesis of agrochemicals, pharmaceuticals, and specialty materials.[1] Readily available fluoroform (CHF_3), a side-product of Teflon manufacturing, is by far the best CF_3 source for trifluoromethylation reactions.[1,2] Chemoselective activation of highly inert fluoroform is, however, tremendously challenging. In recent years, a novel promising methodology has emerged for CHF_3 activation with transition metals. This presentation will focus on our contributions to the area, including (i) the first reactions of direct cupration[1-5] and palladation[6] of fluoroform to furnish $CuCF_3$ and $PdCF_3$ complexes in nearly quantitative yield; (ii) the development of new, low-cost, highly efficient, and selective fluoroalkylation methods with our CuR_f ($R_f = CF_3$, $C2F_5$) reagents prepared from CHF_3 and C_2F_5H;[7-14] and (iii) remarkable mechanisms of the cupration of CHF_3[5] and aromatic trifluoromethylation reactions with $CuCF_3$.[15,16]

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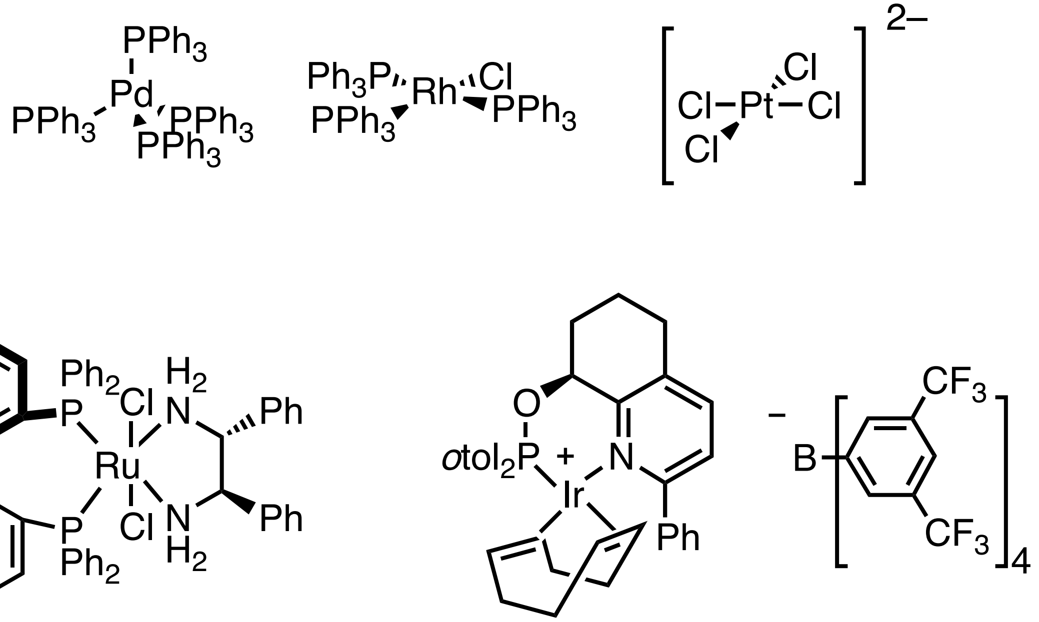
UNIVERSITY OF DELAWARE | College of Arts & Sciences
DEPARTMENT OF CHEMISTRY & BIOCHEMISTRY

**Refreshments 3:45

Organometallic Complexes

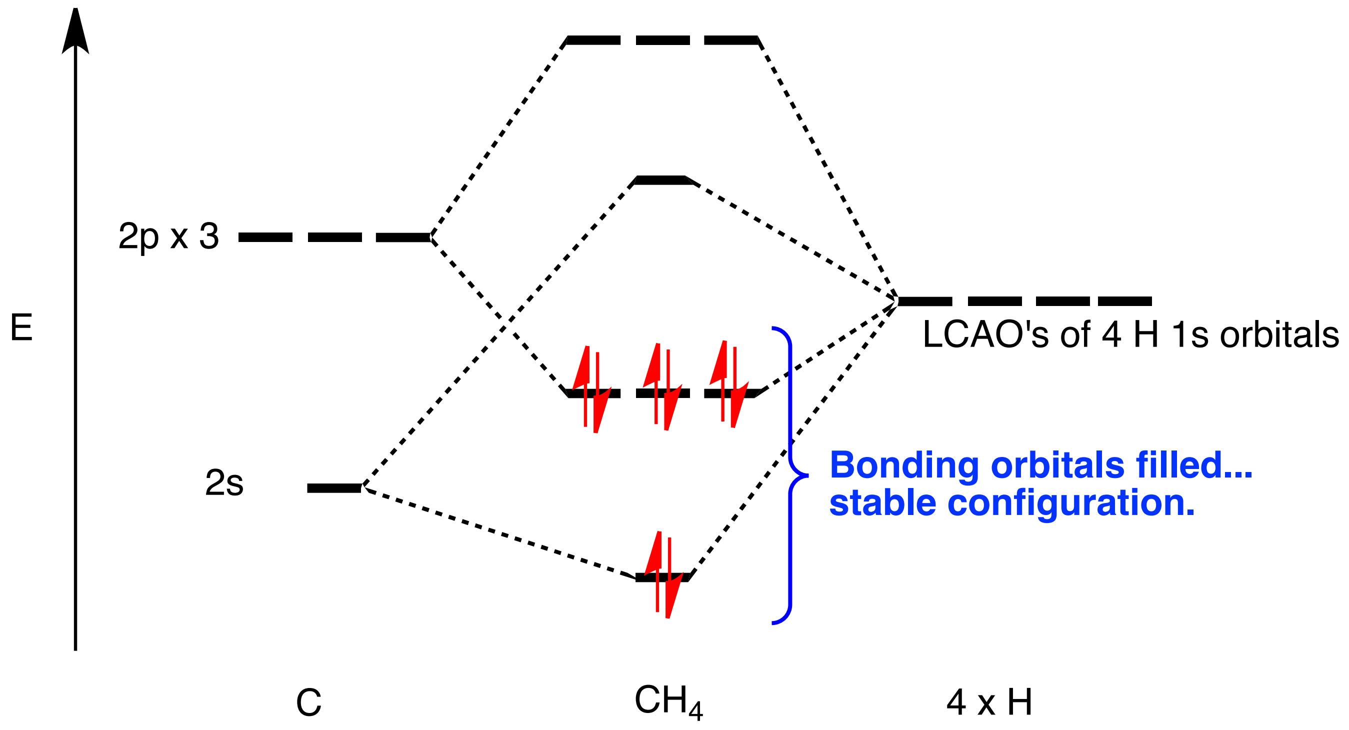


M^0	III	IV	V	VI	VII	VIII	IX	X	XI	XII
	d^3	d^4	d^5	d^6	d^7	d^8	d^9	d^{10}	d^{10}s^1	d^{10}s^2
1st row	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
2nd row	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
3rd row	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg

early dividing line late

How Many Valence Electrons?

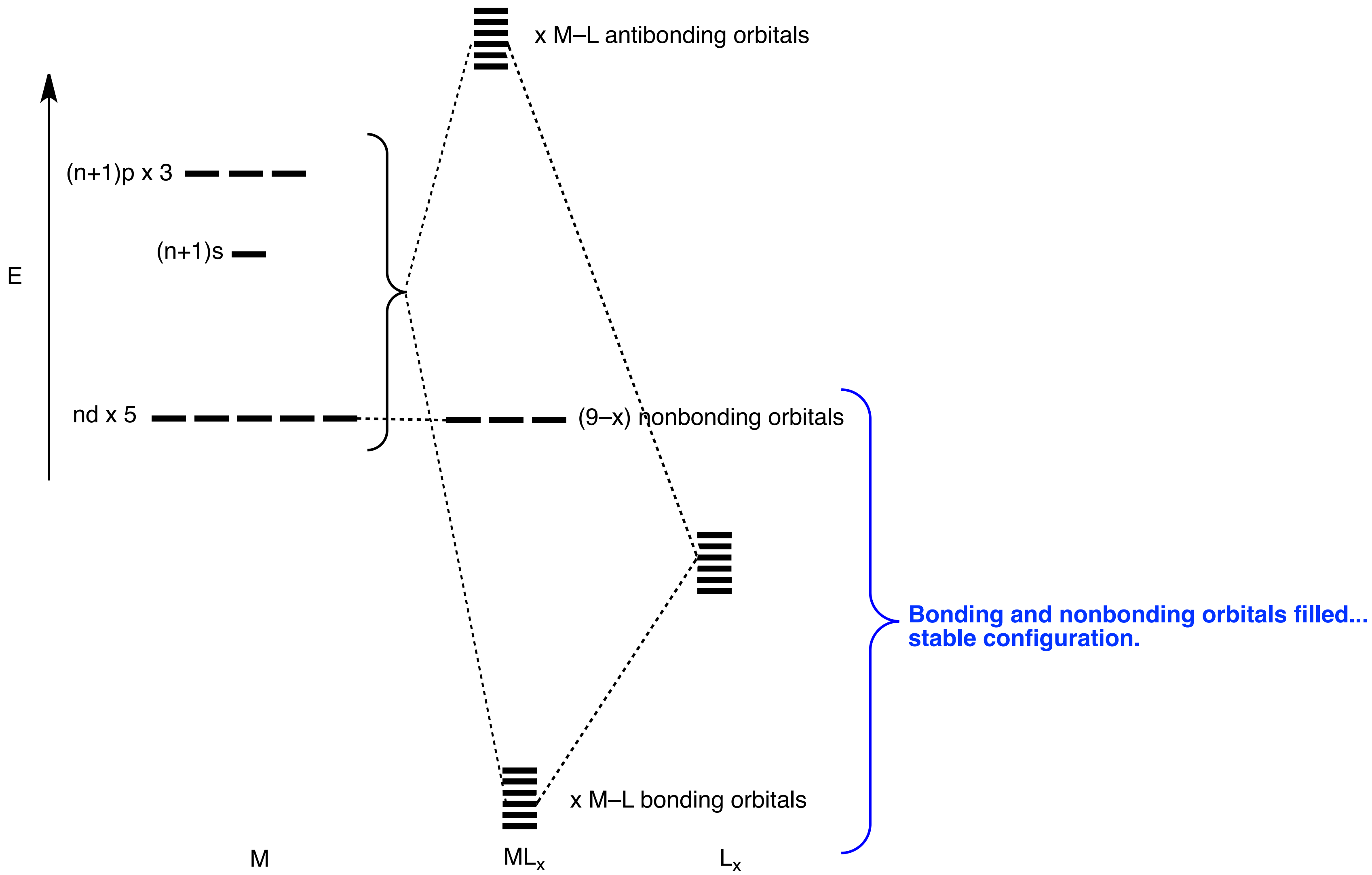
Consider CH_4… Recall the Octet Rule



Bonding orbitals filled...
stable configuration.

How Many Valence Electrons?

Transition metals have 5 d orbitals (plus s & 3 p's)!

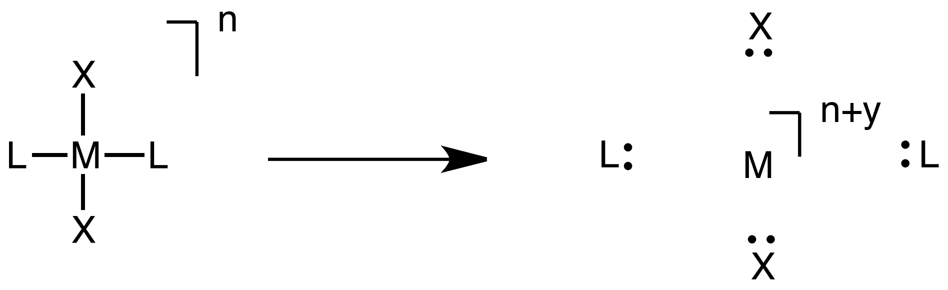


Bonding and nonbonding orbitals filled... stable configuration.

Determining Electron Count of TM Complex

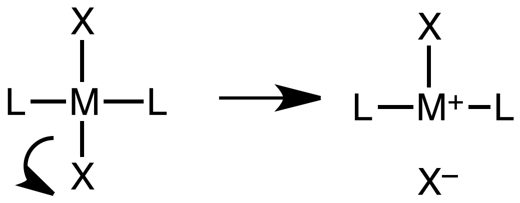
Ionic Method: All ligands are dissociated with their electrons.

L-type ligands = neutral, 2 e⁻ donor
X-type ligands = anionic 2 e⁻ donor



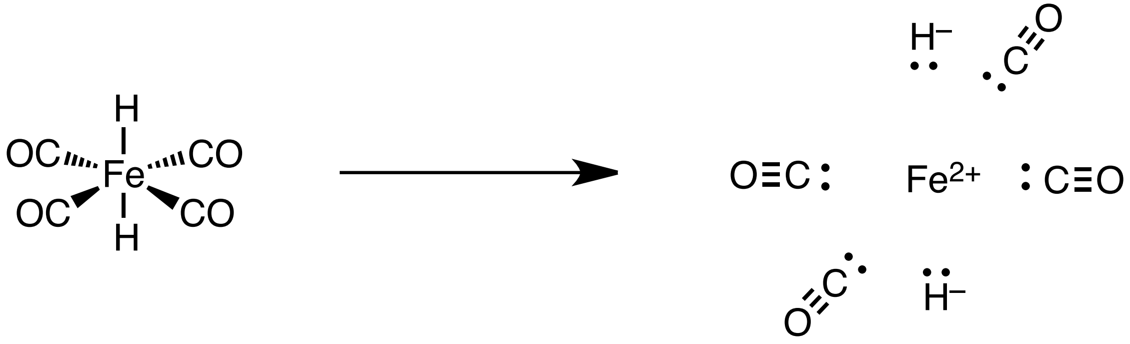
where y = number of x-type ligands

mnemonic:



Electron counting is a formalism.

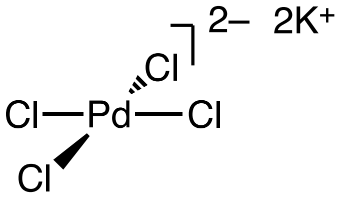
Example of Ionic Method Electron Counting



4 X CO	4 X $2e^-$	$8e^-$
2 X $H^–$	2 X $2e^-$	$4e^-$
Fe(2+) (d^6)		$6e^-$
		$18e^-$

Note: Both Ionic and Neutral Methods give the same electron count, but differ in how they treat the metal center.

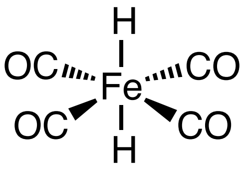
Charged Complexes



4 X Cl^-	4 X $2e^-$	$8e^-$
Pd(2+) (d8)		$8e^-$
		$16e^-$

Oxidation State

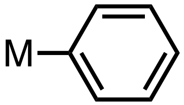
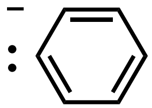
- Formalism to account for “oxidation state” of metal center.
- This is only a formalism, in reality electrons (and thus charge) are shared over both the ligand and metal.
- Nonetheless, oxidation state guides understanding of metal reactivity.
- Using ionic method of electron counting arrives directly at metal oxidation state.
- Example:



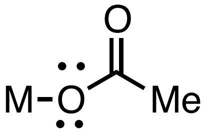
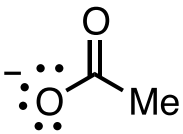
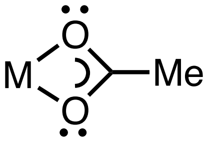
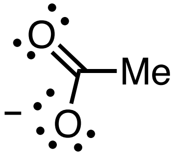
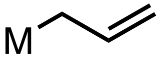
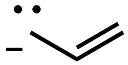
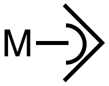
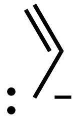
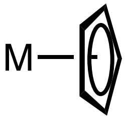
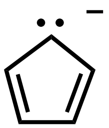
4 X CO	4 X $2e^-$	$8e^-$
2 X H^-	2 X $2e^-$	$4e^-$
Fe(2+) (d^6)		$6e^-$
		$18e^-$

Oxidation State = Fe(II)

Examples of X-type Ligands

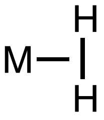
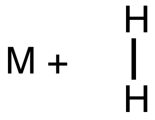
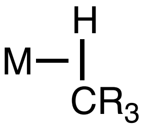
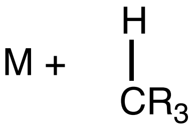
Ligand	**Complex**	**Disconnection**	**ligand charge**	**ligand e$^-$**
hydride	$M-H$	$M^+ + \overset{-}{:H}$	-1	2
halide	$M-\ddot{\underset{\cdot\cdot}{Cl}}:$	$M^+ + \overset{-}{:\ddot{\underset{\cdot\cdot}{Cl}}:}$	-1	2
alkyl	$M-CR_3$	$M^+ + \overset{-}{:CR_3}$	-1	2
aryl (σ bound)		$M^+ +$ 	-1	2
acetylide	$M-\equiv-R$	$M^+ + \overset{-}{:}\equiv-R$	-1	2
silane	$M-SiR_3$	$M^+ + \overset{-}{:SiR_3}$	-1	2
amido	$M-\ddot{N}R_2$	$M^+ + \overset{-}{:\ddot{N}R_2}$	-1	2
alkoxide	$M-\ddot{\underset{\cdot\cdot}{O}}R$	$M^+ + \overset{-}{:\ddot{\underset{\cdot\cdot}{O}}R}$	-1	2

Examples of X-type Ligands (More Complex)

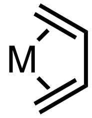
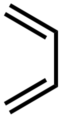
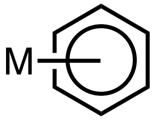
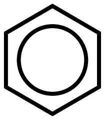
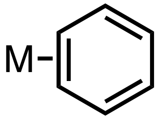
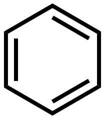
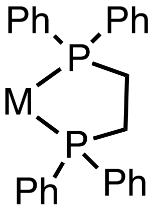
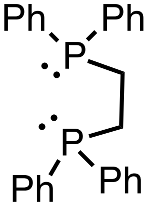
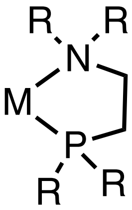
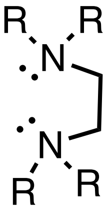
Ligand	**Complex**	**Disconnection**	**ligand charge**	**ligand e^-**
acetate (η1)		M^+ + 	-1	2
acetate (η3)		M^+ + 	-1	4
allyl (η1)		M^+ + 	-1	2
allyl (η3)		M^+ + 	-1	4
cyclopentadienyl (Cp)		M^+ + 	-1	6

- ***η*** (eta) denotes "hapticity" = how many atoms of ligand are bond to metal from single donor site.

Examples of 2e⁻ Donor "L"-type Ligands

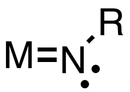
Ligand	Complex	Disconnection	ligand charge	ligand e$^-$
phopshine	$M-PPh_3$	$M +\ :PPh_3$	0	2
amine	$M-NEt_3$	$M +\ :NEt_3$	0	2
nitrile	$M-N\equiv CR$	$M +\ :N\equiv CR$	0	2
sigma bond (H–H)	 $M-\overset{H}{\underset{H}{\vert}}$	 $M +\ \overset{H}{\underset{H}{\vert}}$	0	2
sigma bond (C–H)	 $M-\overset{H}{\underset{CR_3}{\vert}}$	 $M +\ \overset{H}{\underset{CR_3}{\vert}}$	0	2
alkene	$M-\Vert$	$M +\ \Vert$	0	2
carbonyl	$M-C\equiv O$	$M +\ :C\equiv O:$	0	2
ether	$M-\ddot{O}R_2$	$M +\ :\ddot{O}R_2$	0	2

“L”-type Ligands Donating More than $2e^-$

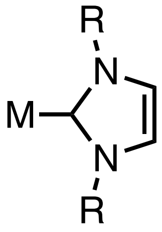
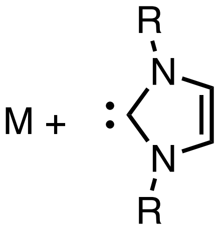
Ligand	**Complex**	**Disconnection**	**ligand charge**	**ligand e^-**
diene		M + 	0	4
arene (η6)		M + 	0	6
arene (η2)		M + 	0	2
bisphosphine (κ^2)		M + 	0 2 X 2e– L-type ligands	4
diamine (κ^2)		M + 	0 2 X 2e– L-type ligands	4

- κ (kappa) denotes “denticity” = how many binding sites of a polydentate ligand are bound .

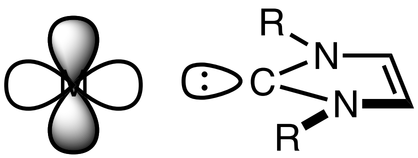
X_2 *Ligands*

Ligand	**Complex**	**Disconnection**	**ligand charge**	**ligand e⁻**
triplet carbenes (alkylidines)	$M{=}CR_2$	$M^{2+} + CR_2^{2-}$	-2	4
oxo	$M{=}O$	$M^{2+} + O^{2-}$	-2	4
imido (bent)	 $M{=}NR$	$M^{2+} + NR^{2-}$	-2	4

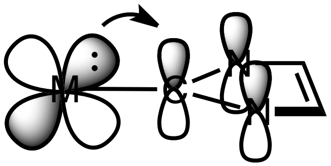
NHC-Ligands

Ligand	**Complex**	**Disconnection**	**ligand charge**	**ligand e^-**
N-heterocyclic carbenes			0	2

Sigma Bond

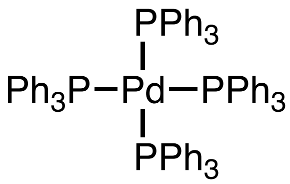


Pi-Backbond



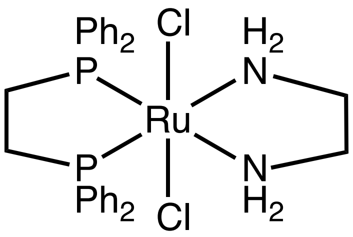
18 Electron "Rule"

Many, **but not all**, stable, isolatable TM complexes are 18e⁻ complexes.



$$\mathrm{Ph_3P{-}}\overset{\mathrm{PPh_3}}{\underset{\mathrm{PPh_3}}{\mathrm{Pd}}}\mathrm{{-}PPh_3}$$

Pd = group 10
10e- + 8e- = 18e-



Ru = group 8
+2 = d^6
6+12 = 18

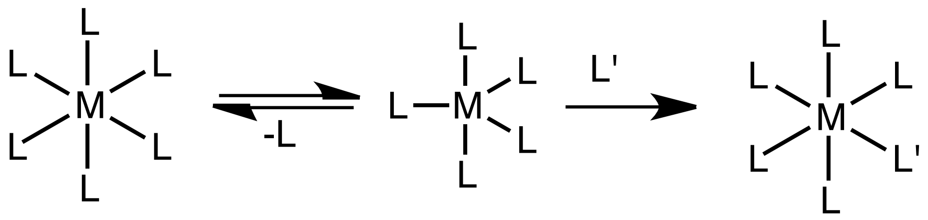
NOTE: 18e⁻ "rule" is more of a suggestion. Many of the most interesting, i.e. reactive, complexes do not follow this "rule".

Basic Organometallic Mechanisms

- To understand transition metal catalysis, we need to understand something about the mechanisms by which the catalysts operate.

- Many TM catalyzed reactions proceed via a series of elementary steps.

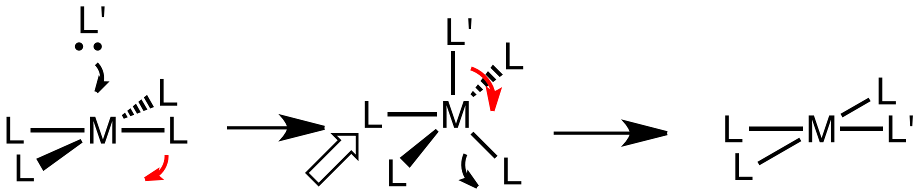
Dissociative Ligand Substitution



common with:

- coordinately saturated
- 18e- complexes

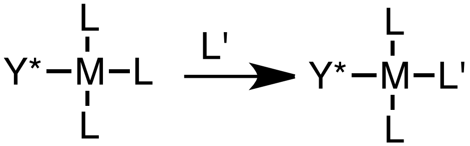
Associative Ligand Substitution



equatorial ligand w/
strongest pi-interactions

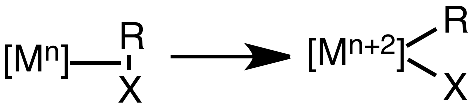
common with:

- 16 e- complexes
- requires open coordination site



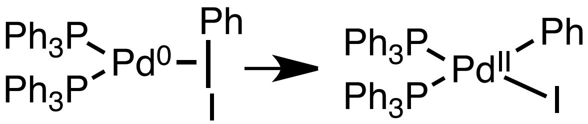
trans effect

Oxidative Addition

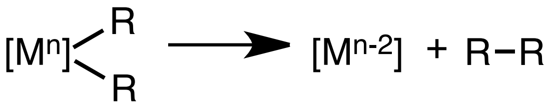


- formal oxidation state of metal center increases by two
- favored by electron-rich metal centers

Example:

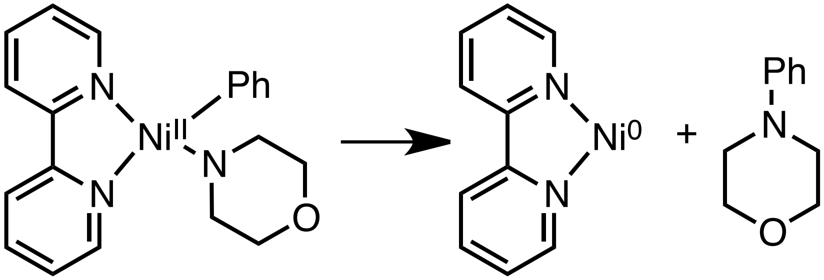


Reductive Elimination

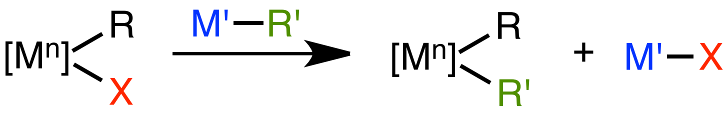


- formal oxidation state of metal center decreases by two
- promoted by electron poor metal centers
- large ligands accelerate process
- microscopic reverse of oxidative addition

Example:

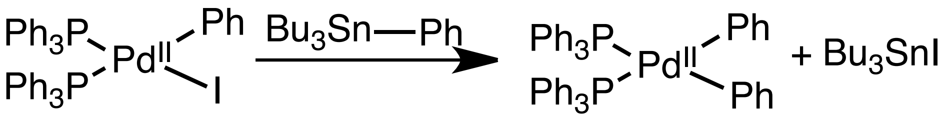


Transmetallation

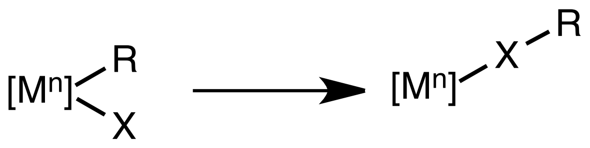


- Exchange of ligands between different metal centers
- No change in oxidation state at metals
- Exact mechanisms are complex, some are still unknown.

Example:

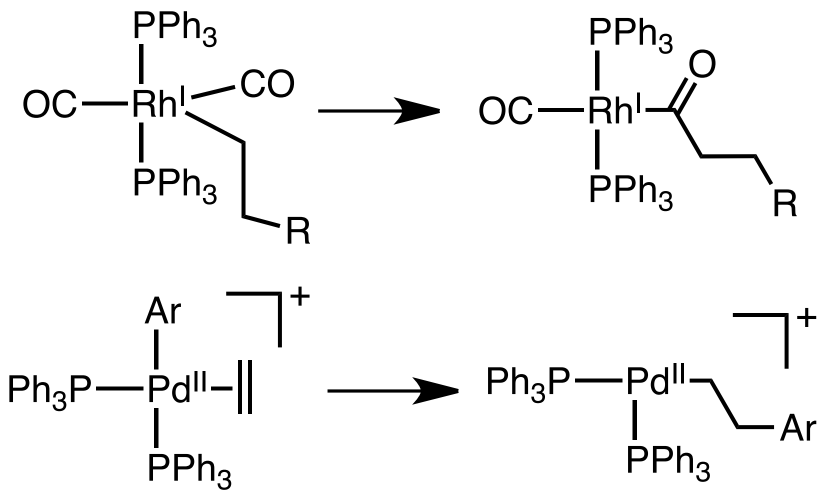


Migratory Insertion

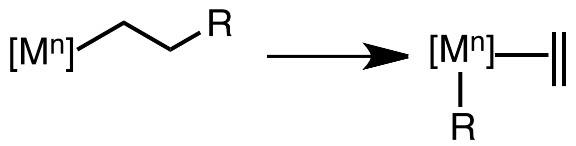


- Ligand inserts into adjacent metal-ligand bond
- No net change of oxidation state at the metal

Examples:

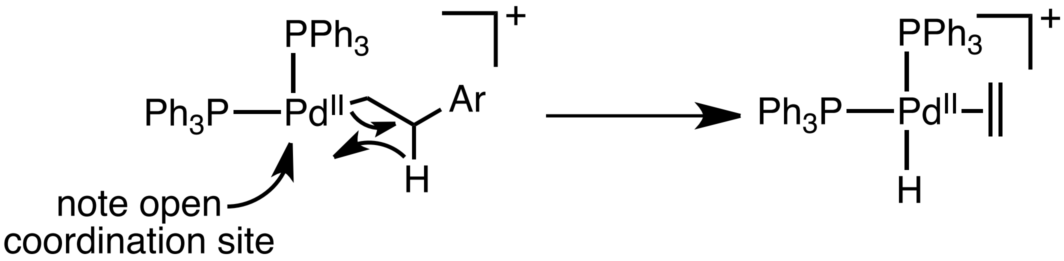


β-Elimination



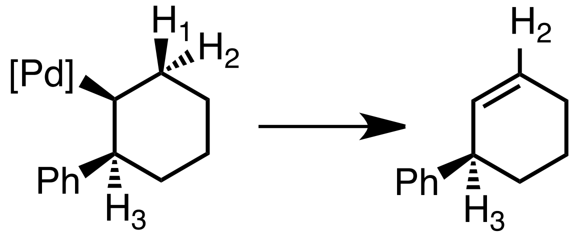
- Microscopic reverse of migratory insertion
- No net change of oxidation state at the metal
- Most often observed as β-hydride elimination from alkyl ligand
- Requires open coordination site on the metal center

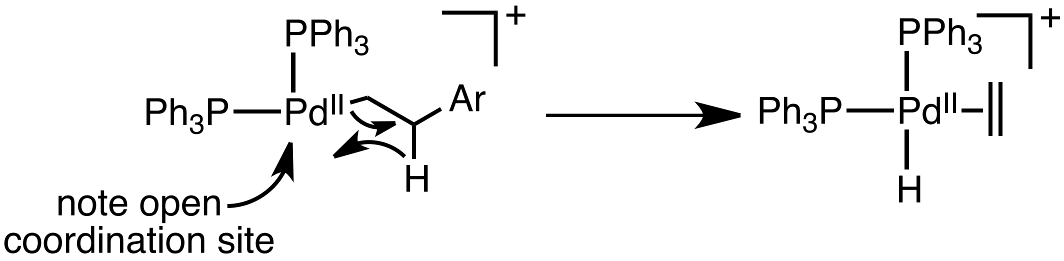
Example:



β-Elimination

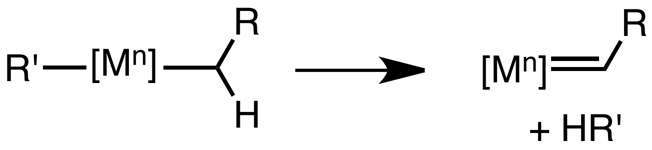
Note: most of the time, β-hydride elimination is superfacial. This is because the mechanism is inner-sphere, involving formation of a metal-hydride bond.



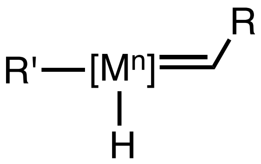


note open coordination site

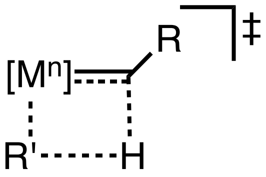
α-Elimination



Via:

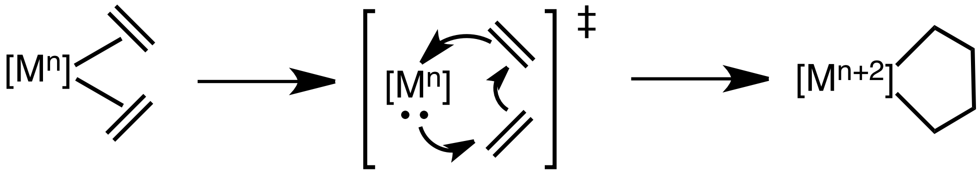


or:

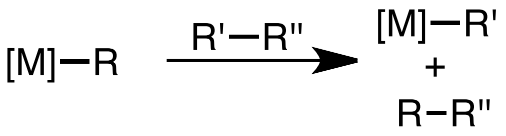


not common in organic synthesis

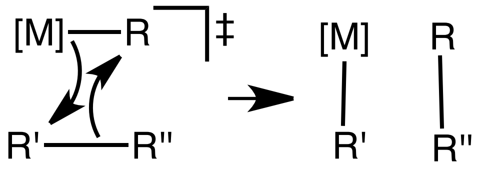
Oxidative Coupling/Cyclization



σ−Bond Metathesis



Via:

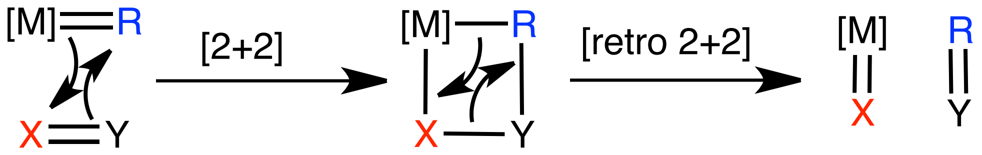


Common mechanism of C-H bond activation.

π−Bond Metathesis

$$[M]{=}R \xrightarrow{X{=}Y} [M]{=}X + R{=}Y$$

via:



Common in alkene metathesis.