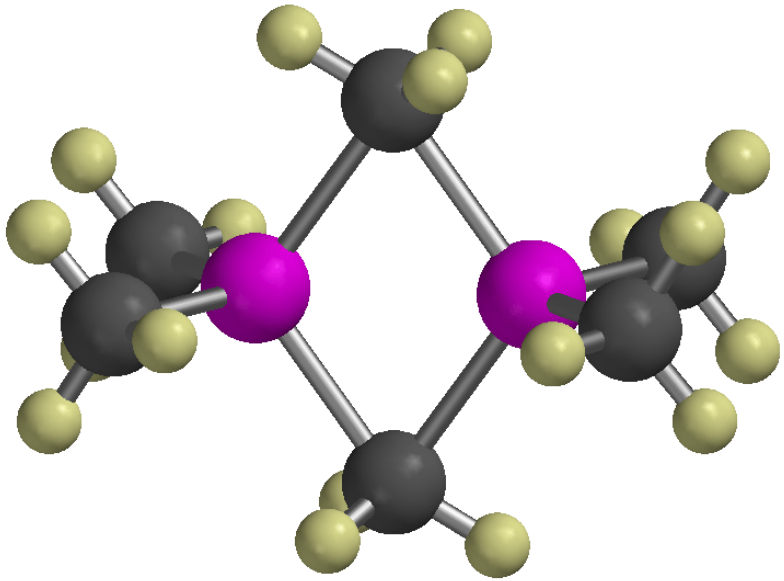
Organometallic chemistry



421 chem

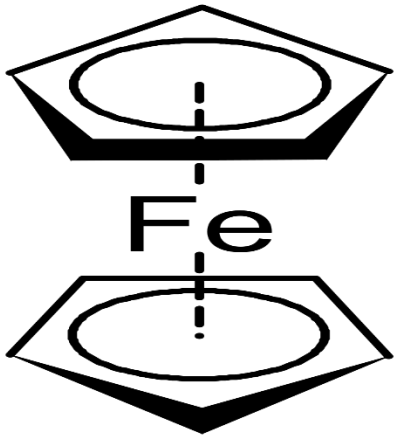
Dr.Amal AlFawaz

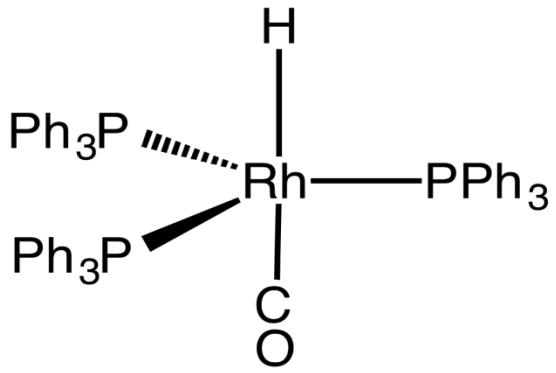
Organometallic chemistry 424 chem Credit Hour: 2 Actual Hour: 2 Class Hour: Wensday 1:00-3:00 and Class Room: A022	**الكيمياء العضو معدنيه 424 كيم** الساعات المعتمده:2 الساعات الفعليه:2 وقت المحاضرات: الأربعاء الساعة 3:00-1:00 قاعه المحاضرات :A022
Professor of the course: Dr.Amal AlFawaz Office Hours:Tues:11:30-12:30 Office Room: 5 T 254 e-mail: amalf@ksu.edu.sa	**استاذه المقرر: د.امال الفواز** الساعات المكتبيه: الثلاثاء 12:30-11:30 المكتب: 5 T 254 e-mail: amalf@ksu.edu.sa
Aims of the Course: • The course aims to give the student the basic principles of organometallic compounds such as their definition, classification, stability, and applications. Understanding the difference between organometallic and non-organometallic compound. Defining the different type of bonding between metals and organic fragment • The study of the transition metal organometallic complexes in terms of the18 electrons rule and types of ligands and types of reactions for the organometallic complexes with emphasis on ligand substitution, oxidative addition, reductive elimination, insertion and elimination reactions as well as catalytic activity • Short brief about the main gr[illegible]rganometallic complexes such as Li and Mg organometallic comple[illegible]	**اهداف المقرر:** * يهدف المقرر الى تعريف الطالبات بالمفاهيم الأساسية للمعقدات العضومعدنيه كتعريفها وتصنيفها وثباتها وتطبيقاتها. فهم الفرق بين المعقدات العضوالمعدنيه والغير عضومعدنيه. والتعريف بانواع الروابط بين المعادن والشقوق العضويه. * دراسه المعقدات العضو معدنيه للعناصر الانتقاليه من حيث قاعده ال 18 الكترون وانواع المتصلات وكذلك انواع التفاعلات العضومعدنيه مثل تفاعلات استبدال المتصلات وتفاعلات الاضافه التاكسديه والحذف الاختزالي وتفاعلات الادخال والهدم بالاضافه الى النشاط الحفزي. * نبذه مختصره عن المعقدات العضو معدنيه لعناصر المجموعات الرئيسيه.

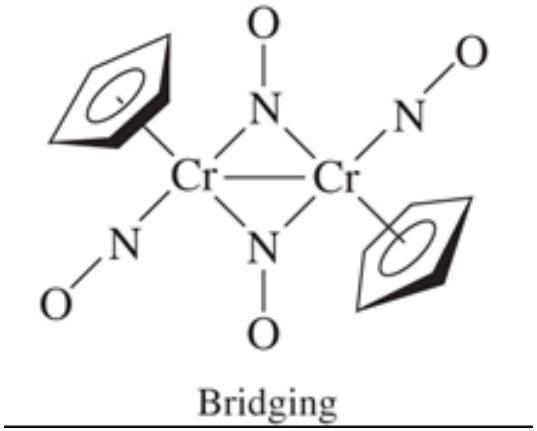
Topics to be cover in the course: • Identification of organometallic complexes and Properties of bond between metals and carbon • Principles of the 18 electron rule and the ligand rule • Types of ligands and natural of the olefins and CO,PPh3 bonds with metallic ions • Sigma and Bi- transition metals complexes • Fundamental organometallic reactions complexes (ligand substitution, oxidative addition, reductive elimination, insertion and elimination reactions) • Catalytic role of the transition metallic complexes • main group organometallic complexes	**المواضيع التي ستدرس في المقرر:** * تعريف المعقدات العضو معدنيه وكذلك خواص الرابطة بين المعدن والكربون وثباتها . * تطبيق قاعده ال 18 الكترون وحساب عدد الكترونات المعقد وكذلك عدد الأكسدة للمعدن والاستثناء لقاعده ال 18 الكترون * دراسة انواع المتصلات والقواعد التي تحكمها مع تطبيق امثله على انواع المتصلات مثل متصلة * دراسة معقدات السيجما والباي للمعقدات العضو معدنيه للمعادن الانتقالية. * الانواع الأساسية للتفاعلات العضو معدنيه مثل تفاعلات استبدال المتصلة وتفاعلات الإضافة التأكسدية والحذف الاختزالي وكذلك تفاعلات الادخال والهدم. * دراسة النشاط الحفزي للمعقدات العضو معدنيه * دراسة مختصره للمعقدات العضو معدنيه للمجموعات الرئيسية تصنيفها وطرق تحضيرها ومثال لكل مجموع.
Grading: • Two 60 min Exams: 40% • Final Exam (2 hrs): 40% • Homework: 10% • 2 in-class Quizzes: 10%	**تقسيم الدرجات:** * امتحانين 60 دقيقه: %40 * الأمتحان النهائي %40 * الواجبات المنزليه: %10 * امتحانين قصيرين: %10
Required Textbooks • Principle of Organometallic Chemistry, Green, Coates, edit Powell and Wade. English • The Organometallic Chemistry of the Transition Metals, Crabtree, 4 Crabtree th ed., 2006	**المراجع المطلوبه** • Principle of Organometallic Chemistry, Green, Coates, edit Powell and Wade. English • The Organometallic Chemistry of the Transition Metals, Crabtree, 4 Crabtree th ed., 2006

The definition of Organometllic complexes

- **organometallic compounds**, chemical compounds containing at least one chemical bond between a carbon atom of an organic molecule and a metal M-C, including alkaline, alkaline earth, and transition metals, and sometimes broadened to include metalloids like boron, silicon, and tin, as well.



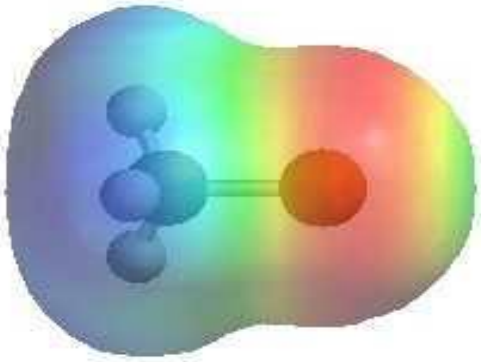




Importance of organometallic complexes

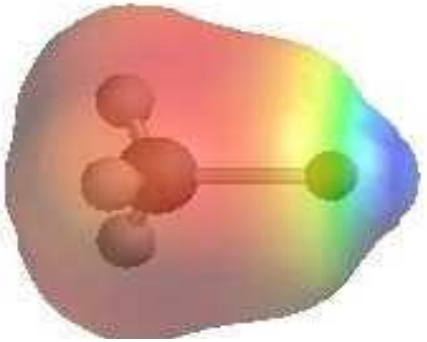
- Organometallic compounds provide a source of **nucleophilic carbon** atoms which can react with electrophilic carbon to form a new carbon-carbon bond. This is very important for the synthesis of complex molecules from simple starting materials.
- Organometallic chemistry is the basis of ***homogeneous catalysis***, which is the method of choice for clean and efficient synthesis of fine chemicals, pharmaceuticals and many larger-scale chemicals.

Reactivity of organometallic complexes



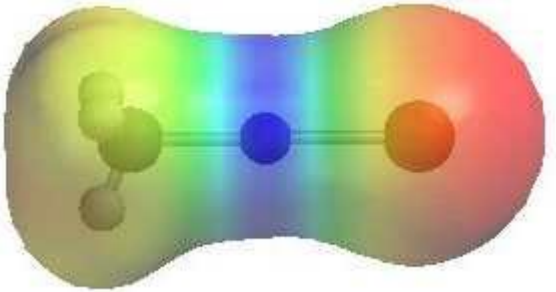
methyl chloride

CH_3Cl



methyllithium

CH_3Li



methylmagnesium bromide

CH_3MgBr

•The images show the electrostatic potentials for methyl chloride, methyl lithium and methyl magnesium bromide.

The more **red** an area is, the higher the electron density and the more **blue** an area is, the lower the electron density.In the alkyl halide, the methyl group has lower electron density (**blue**), and is an **electrophile**.

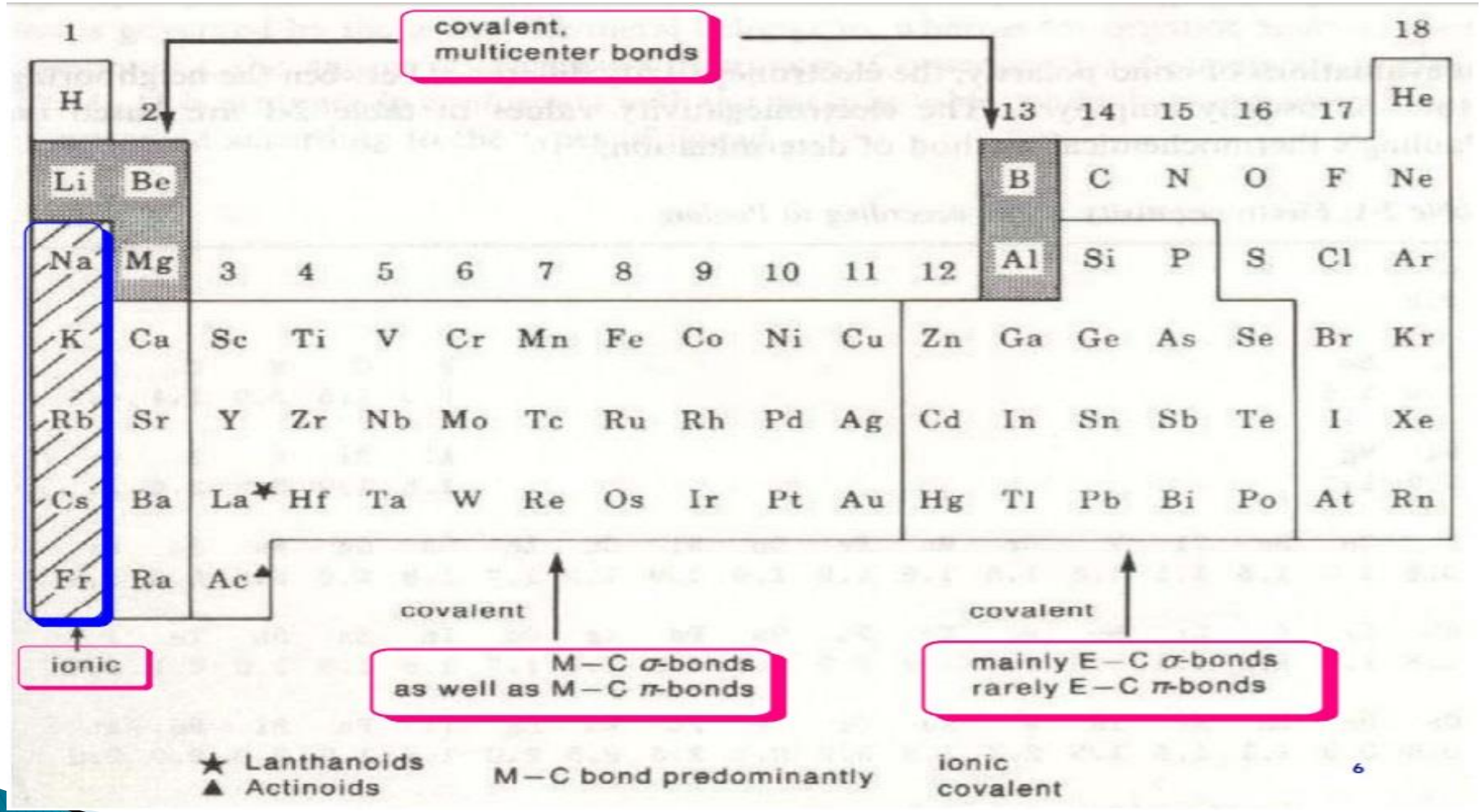
•In methyl lithium, the methyl group has higher electron density (**red**) and is a **nucleophile**.

•In methyl magnesium bromide, the methyl group is less electron rich that methyl lithium.

Therefore, organometallic compounds react as electron rich or anionic carbon atoms *i.e.* as carbanions, which means they will function as either **bases** or **nucleophiles**.

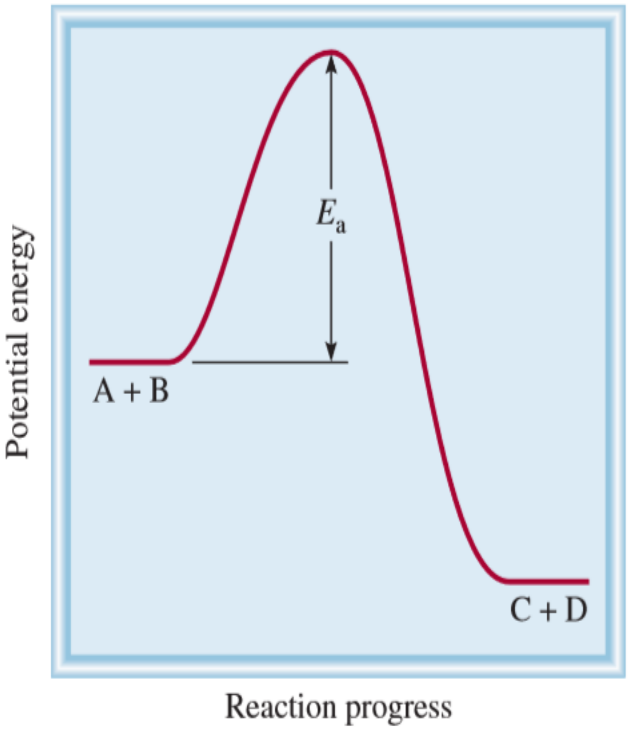
It is reasonable to think of these organometallic compounds as $\mathbf{R^-\ M^+}$

Types of bonding in organometallic complexes



Stability of organometallic complexes

- Thermal stability.
- Oxidation resistance.
- Hydrolysis resistance.
- Basicity.



Classifications of ligands

Metal-ligand bonding can be divided into three basic classes:

- σ- donor

e.g. H, CH_3 (or any alkyl or aryl group, R), H_2O, NH_3, NR_2 (bent)

- σ - donor, π acceptor (sometimes referred to as 'π-acceptors' or 'π-acids')

e.g. CO, CN, NO, H_2, C_2H_4, N_2, O_2, PR_3, BR_2

- σ - donor, π donor (sometimes referred to as 'π donors')

e.g. F, Cl, Br, I, O, OR, S, SR, N, NR_2(linear), NR (bent and linear), P,η^3-C_3H_5, η^5-C_5H_5, η^6-C_6H_6

- In terms of bond strength the σ-bond is much more important than π-bonding (donor or acceptor)

Classifications of ligands

Cationic 2e- donor: NO^+ (nitrosyl)

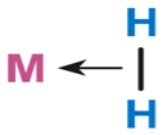
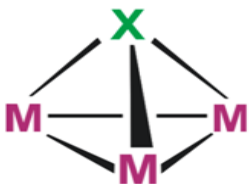
Neutral 2e- donors: PR_3 (phosphines), CO (carbonyl), $R_2C{=}CR_2$ (alkenes), RCºCR (alkynes, can also donate 4 e-), NºCR (nitriles)

Anionic 2e- donors: Cl^- (chloride), Br^- (bromide), I^- (iodide), CH_3^- (methyl), CR_3^- (alkyl), Ph^- (phenyl), H^- (hydride)
The following can also donate 4 e- if needed, but initially count them as 2e- donors (unless they are acting as bridging ligands): OR^- (alkoxide), SR^- (thiolate), NR_2^- (inorganic amide), PR_2^- (phosphide)

Anionic 4e- donors: $C_3H_5^-$ (allyl), O^{2-} (oxide), S^{2-} (sulfide), NR^{2-} (imido), CR_2^{2-} (alkylidene)
and from the previous list: OR^- (alkoxide), SR^- (thiolate), NR_2^- (inorganic amide), PR_2^-

Anionic 6e- donors: Cp^- (cyclopentadienyl), N^{3-} (nitride)

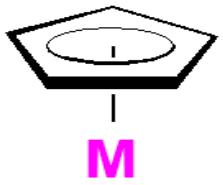
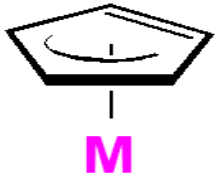
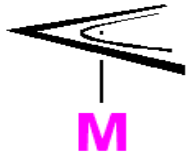
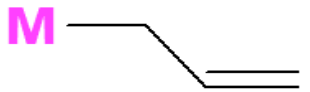
Classifications of ligands

Ligand Name	Bonding Type	Formal Charge	Electrons Donated
Molecular Hydrogen: H_2		0	2
Hydride: H^-		-1	2
Hydride: H^-		-1	2
Halide: X^-		-1	2
Halide: X^- μ bridging		-1	4 (2 to each M)
Halide: X^- μ_3 bridging		-1	6 (2 to each M)

Classification of ligands

- η^x "eta-*x*" was originally developed to indicate how many *contiguous* donor atoms of a p-system were coordinated to a metal center. Hapticity is another word used to describe the bonding mode of a ligand to a metal center. An h^5-cyclopentadienyl ligand, for example, has all five carbons of the ring bonding to the transition metal center.

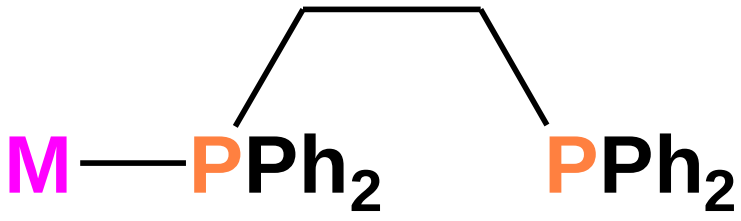
- η^x values for all-carbon based ligands where the x value is odd usually indicate *anionic* carbon ligands (e.g., η^5-Cp, η^1-CH3, η^1-allyl or η^3-allyl, η^1-CH=CH2). The # of electrons donated (ionic method of electron counting) by the ligand is usually equal to $x + 1$. Even η^x values usually indicate *neutral* carbon p-system ligands (e.g., η^6-C6H6, η^2-CH2=CH2, η4-butadiene, η^4-cyclooctadiene). The # of electrons donated by the ligand in the even (*neutral*) case is usually just equal to *x*.

			
η^5-Cp	η^3-Cp	η^3-allyl	η^1-allyl

Classification of ligands

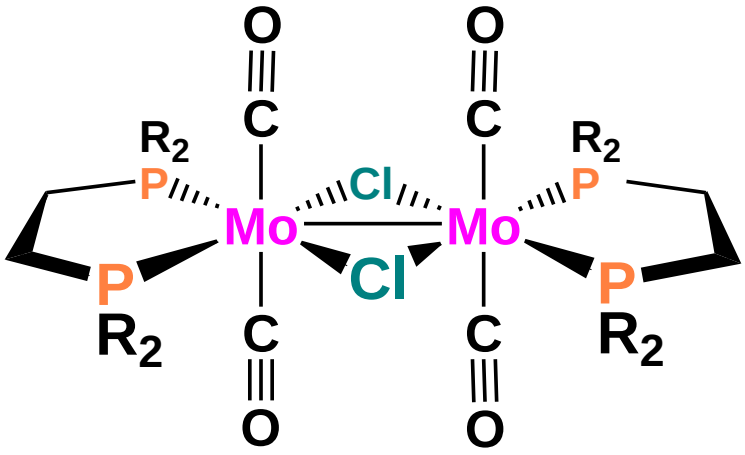
- κ^x "kappa-*x*" was developed to indicate how many *non*-*contiguous* donor atoms of a ligand system were coordinated to a metal center.
- This usually refers to non-carbon donor atoms, but can include carbons.

A κ^1-dppe ($Ph_2PCH_2CH_2PPh_2$) ligand, for example, has only one of the two phosphorus donors bonded to the transition metal center.



Classification of ligands

- μ^x “mu-*x*” is the nomenclature used to indicate the presence of a **bridging ligand** between two or more metal centers. The *x* refers to the number of metal centers being bridged by the ligand. Usually most authors omit *x* = 2 and just use m to indicate that the ligand is bridging the simplest case of two metals.



18 Electron Rule

- **The vast majority of stable diamagnetic organometallic compounds have 16 or 18 valence electrons due to the presence of the five *d* orbitals which can hold 10 more electrons relative to C, O, N, etc.**
- ***Electron counting* is the process of determining the number of valence electrons about a metal center in a given transition metal complex. To figure out the electron count for a metal complex:**
- **1) Determine the oxidation state of the transition metal center(s) and the metal centers resulting *d*-electron count. To do this one must:**
  - **a) note any overall charge on the metal complex**
  - **b) know the charges of the ligands bound to the metal center (ionic ligand method)**
  - **c) know the number of electrons being donated to the metal center from each ligand (ionic ligand method)**
- **2) Add up the electron counts for the metal center and ligands**
- **18 e- counts are referred to as *saturated*, because there are no empty low-lying orbitals to which another incoming ligand can coordinate. Electron counts lower than 18e- are called *unsaturated* and can electronically bind additional ligands unless the coordination site is sterically blocked.**

Exceptions to the 18-Electron "Rule"

d^3	d^4	d^5	d^6	d^7	d^8	d^9	d^{10}	$d^{10}s^1$
21 Sc Scandium	22 Ti Titanium	23 V Vanadium	24 Cr Chromium	25 Mn Manganese	26 Fe Iron	27 Co Cobalt	28 Ni Nickel	29 Cu Copper
39 Y Yttrium	40 Zr Zirconium	41 Nb Niobium	42 Mo Molybdenum	43 Tc Technetium	44 Ru Ruthenium	45 Rh Rhodium	46 Pd Palladium	47 Ag Silver
57 La Lanthanum	72 Hf Hafnium	73 Ta Tantalum	74 W Tungsten	75 Re Rhenium	76 Os Osmium	77 Ir Iridium	78 Pt Platinum	79 Au Gold

Early Transition Metals

16e- and sub-16e- configurations are common

Coordination geometries higher than 6 relatively common

Middle Transition Metals

18e- configurations are common

Coordination geometries of 6 are common

d^6

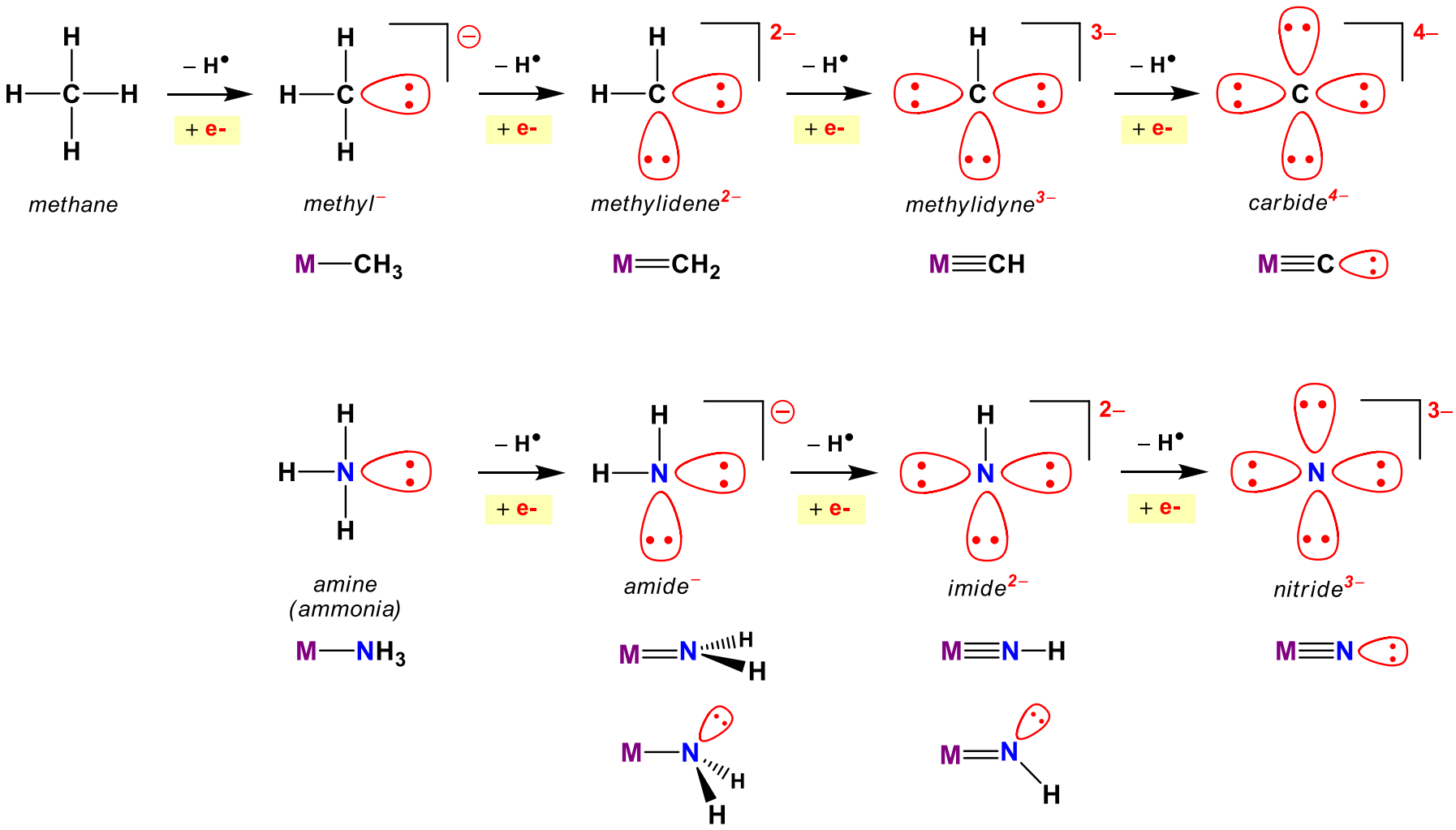
Late Transition Metals

16e- and sub-16e- configurations are common

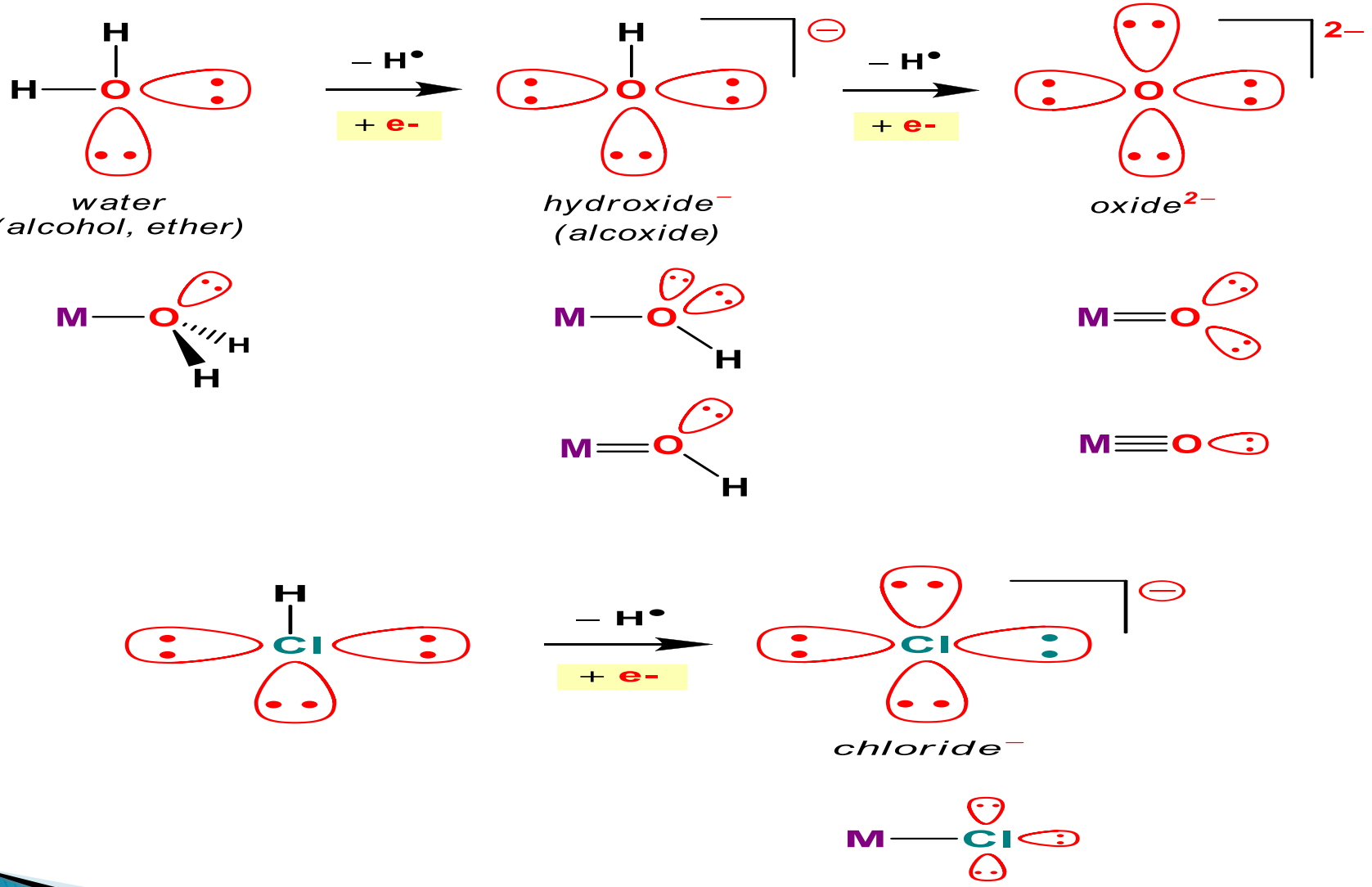
Coordination geometries of 5 and lower are common:

d^8 = square planar

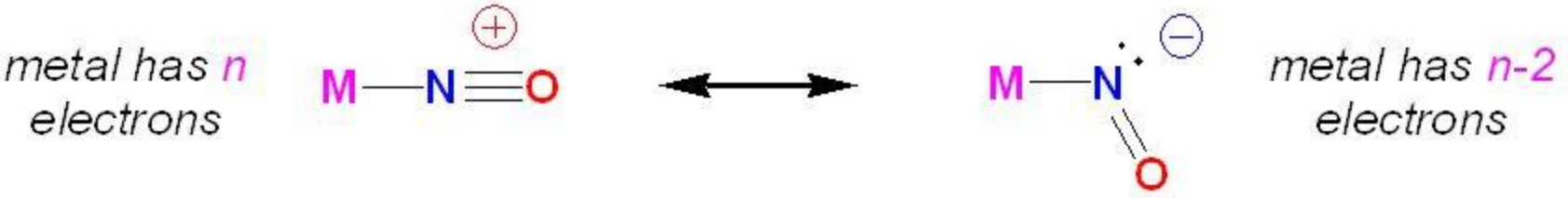
Ligands, Charges, and Donor #'s



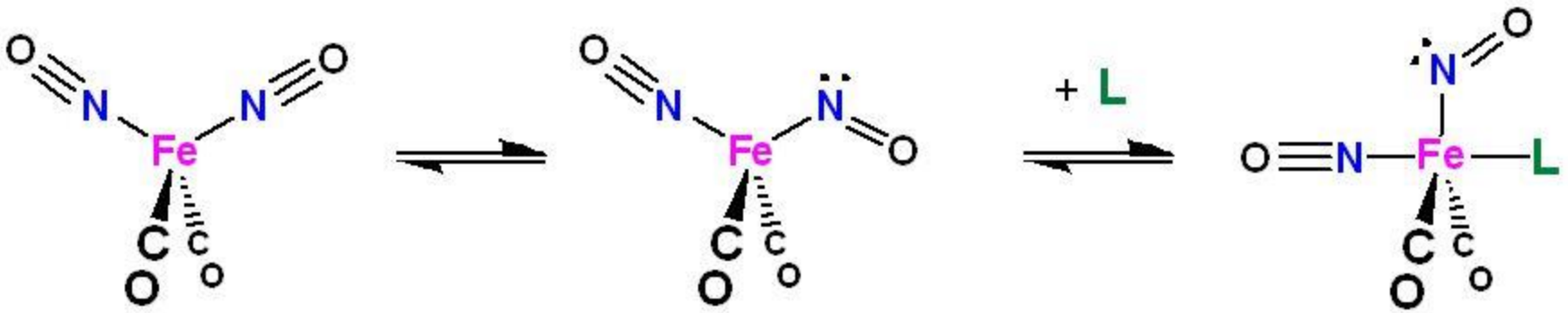
Ligands, Charges, and Donor #'s



We usually count the nitrosyl ligand as a cationic 2e- donor, isoelectronic with CO. But it can adopt an anionic 2e- configuration with a bent coordination geometry:



The nitrosyl ligand can shift from linear to bent, cationic to anionic, and open up a coordination site on the metal by essentially oxidizing it (shuttling 2e- from the metal to the NO^+ turning it into NO^-). The linear NO^+ form can usually be easily differentiated from the bent anionic form by IR spectroscopy because of the large change in NO bond order (triple to double bond).



How many electrons does NO donate?

Linear:

i) 1 electron goes *from NO to the metal, giving NO+ + M-.*

ii) NO+ is then isolectronic with CO, and donates 2 electrons *from NO to metal*

2+1 = 3, so NO is a 3-electron donor.

Bent:

i) 1 electron goes *from metal to NO, giving NO- + M+.*

ii) NO- is then isolectronic with O2, and donates 2 electrons *from NO to metal*

-1 + 2 = 1, so NO is a 1-electron donor

Strategy for determining bent or linear, electron count and oxidation state:

1) Remove NO (neutral) from complex and calculate electron count and oxidation state of remaining fragment.

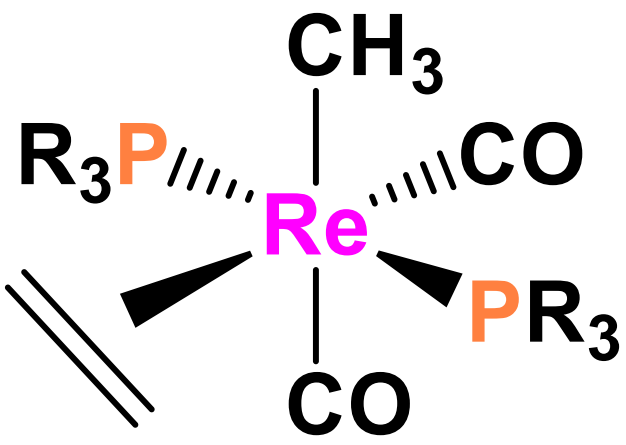
2) Add 1 or 3 electrons per NO to increase electron count to 18 (or as close as possible without exceeding 18). You now have the total electron count at the metal and the MNO geometry.

3) Determine the metal oxidation state of the complex including the NO ligand(s) and consider linear NO to be NO+ and bent NO to be NO-.

Example:

Mn(CO)4(NO)	**18**	**-I**	**8**
Co(NH3)5(NO)2+	**18**	**III**	**6**
RuCl(NO)2(PPh3)2	**17**	**I**	**7**

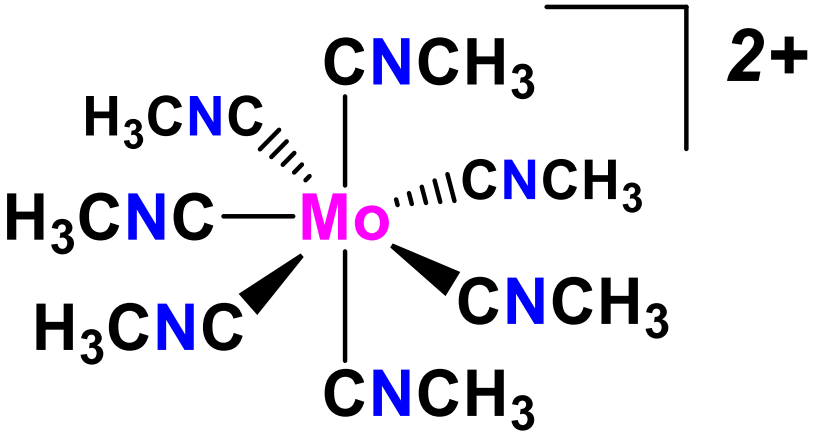
e-counting Examples: Simple



1) There is no overall charge on the complex
2) There is one anionic ligand (CH_3^-, methyl group)
3) The Re metal atom must have a +1 charge to compensate for the one negatively charged ligand. So the Re is the in the +1 oxidation state. We denote this three different ways: Re(+1), Re(I), or Re^I.

Re(+1)	**d^6**
2 PR_3	**4e-**
2 CO	**4e-**
CH_3^-	**2e-**
CH_2=CH_2	**2e-**
Total:	**18e-**

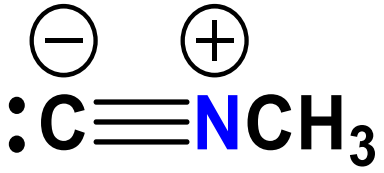
e-counting Examples: Simple *(but semi-unusual ligand)*



Mo(+2)		d^4
7 $CNCH_3$		14e-
	Total:	18e-

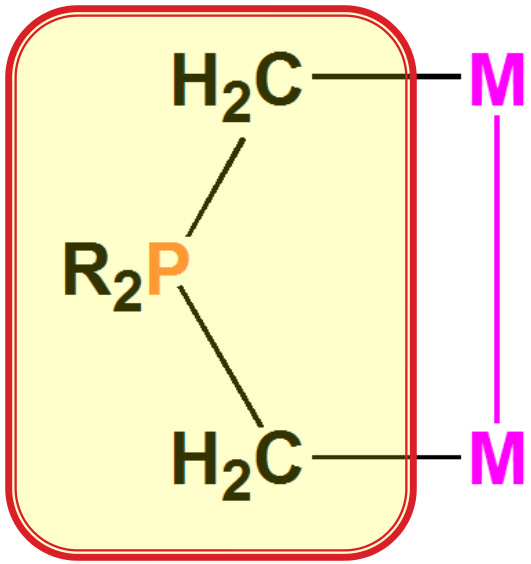
1) There is a +2 charge on the complex

2) The $CNCH_3$ (methyl isocyanide) ligand is neutral, but lets check the Lewis Dot structure to make sure that is correct:

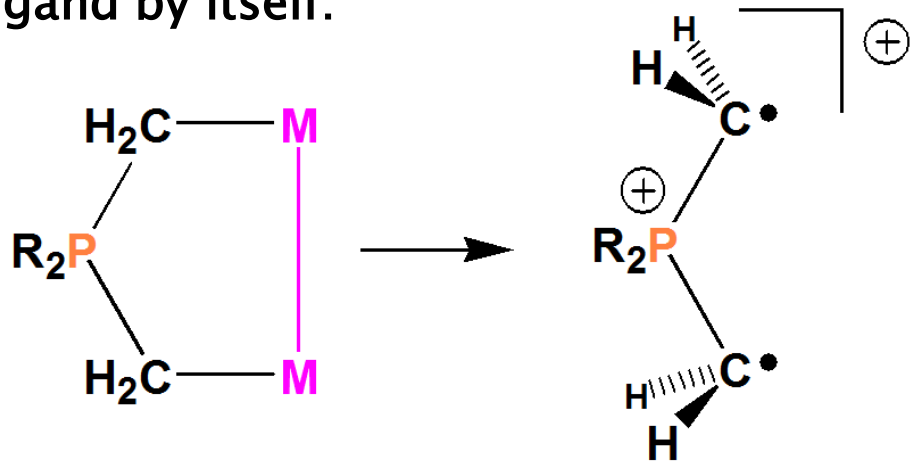


3) Because there is a +2 charge on the complex and all neutral ligands present, the Mo has a +2 charge & oxidation state.

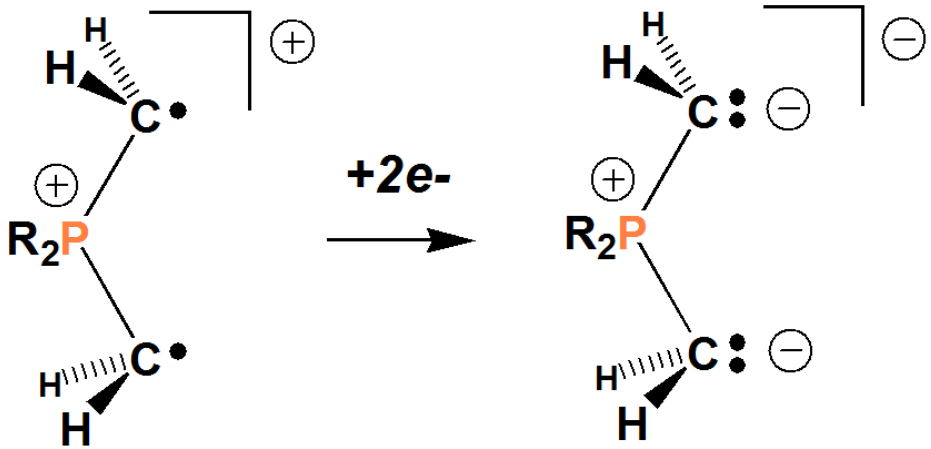
e-counting Examples: Ligand Analysis



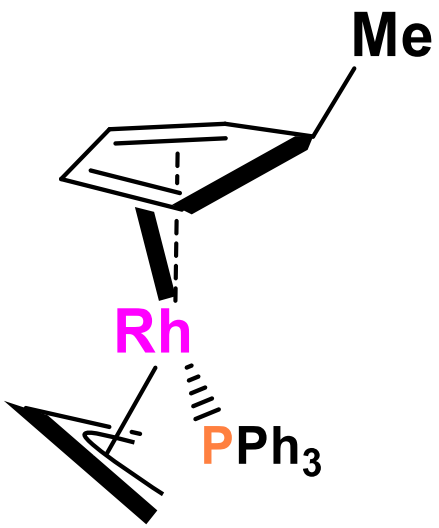
1) Remove the metal atom(s) and examine the ligand by itself:



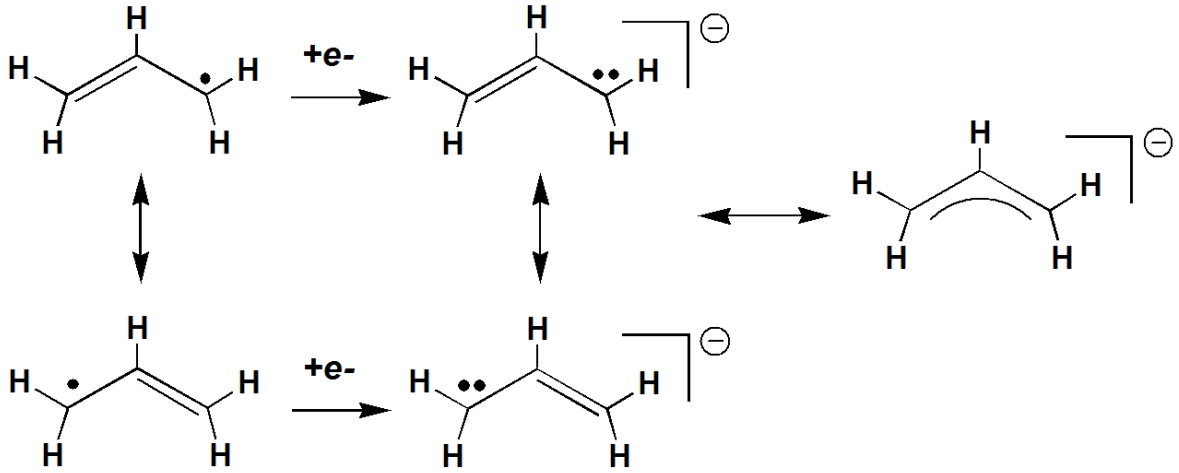
2) If the donor atoms have an odd # of e–'s, add enough to get an even # and (usually) a filled octet. As you add e–'s don't forget to add negative charges!!



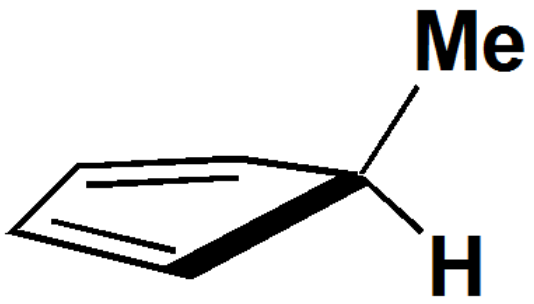
e-counting Examples: Tricky System

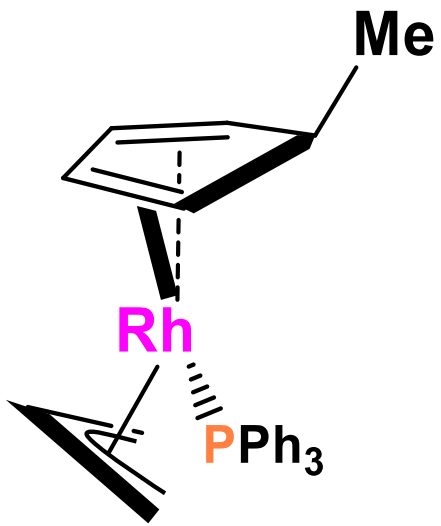


1) There is no overall charge on the complex
2) There is one anionic ligand ($C_3H_5^-$, allyl)



3) The top ligand is NOT a $MeCp^-$! It is a neutral diene that has a H attached to the methyl-substituted ring carbon. This is a neutral 4e- donor.

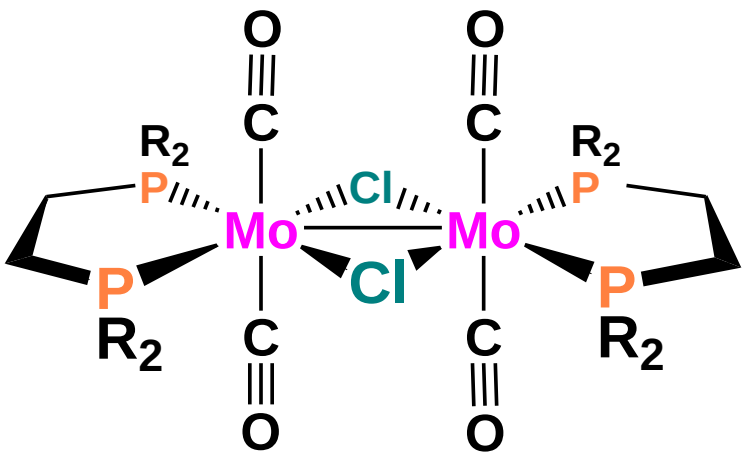




3) Because the complex is neutral and there is one anionic ligand present, the Rh atom must have a +1 charge to compensate for the one negatively charged ligand. So the Rh atom is in the +1 oxidation state.

Rh(+1)	**d^8**
PR_3	**2e-**
η^4-C_5H_5Me	**4e-**
η^3-$C_3H_5^-$	**4e-**
Total:	**18e-**

e-counting Examples: M-M Bonded System



Mo(+1)	d^5
$2PR_3$	4e-
2CO	4e-
$2\mu\text{-}Cl^-$	4e-
Sub-total:	*17e-*
Mo-Mo	1e-
TOTAL:	18e-

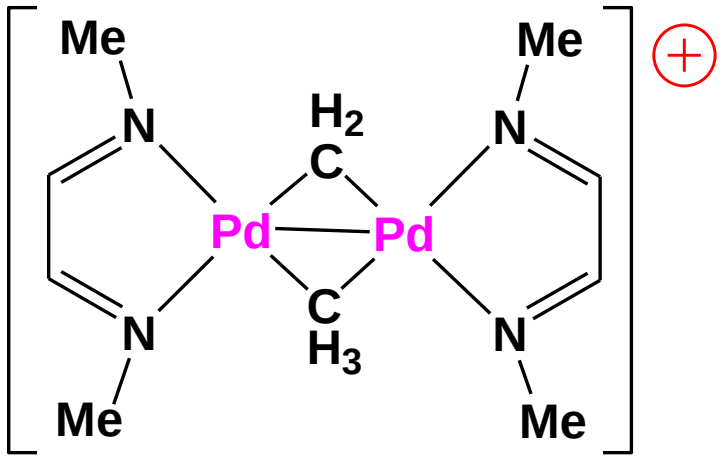
1) Generally treat metal–metal (M–M) bonds to be simple covalent bonds with each metal contributing 1e– to the bond. If you have two metal atoms next to one another and each has an odd electron–count, pair the odd electrons to make a M–M bond.

2) Bridging ligands, like halides, with at least 2 lone pairs almost always donate 2e– to each metal center.

3) Oxidation state determination: Total of two anionic ligands for two metal centers (overall complex is neutral). Thus each metal center needs to have a +1 oxidation state to balance the anionic ligands.

Very Common Mistake: Students determining the oxidation state for complexes with 2 or more metal centers often add up all the anionic ligands and then figure out the oxidation state for only one of the metal centers based on this.

e-counting Examples: M-M Bonded System

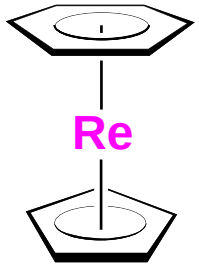


Ligand analysis: The chelating N ligand is a bis-imine, is neutral, with each N atom donating 2e-. Two <u>different</u> bridging ligands – an anionic CH_3^- (methyl group) and a dianionic CH_2^{2-} (carbene or alkylidene). The CH_3^- only has one lone pair of electrons, so it has to split these between the two metals (1e- to each). The CH_2^{2-} alkylidene ligand, on the other hand, has 2 lone pairs & donates 2e- to each M.

Oxidation state analysis: Total of 3 negative charges on the ligands (anionic methyl, dianionic alkylidene) and a positive charge on the complex. Therefore the <u>two</u> Pd centers must have a TOTAL of a +4 charge, or a +2 charge (oxidation state) on each.

Pd(+2)	d^8
2 imines	4e-
μ-CH_3^-	1e-
μ-CH_2^{2-}	2e-
Sub-total:	*15e-*
Pd-Pd	1e-
TOTAL:	16e-

e-counting Problems:

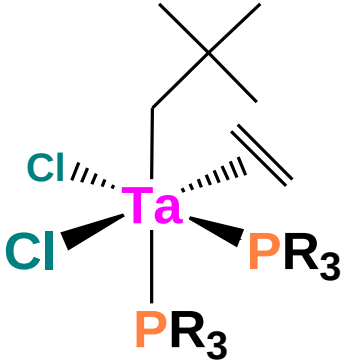


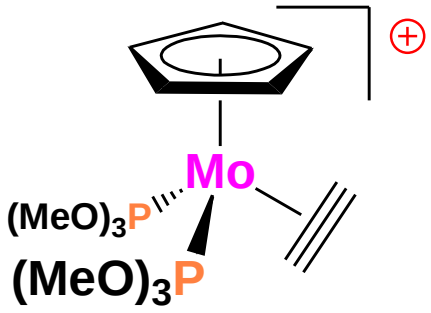
Re(+1) → d^6

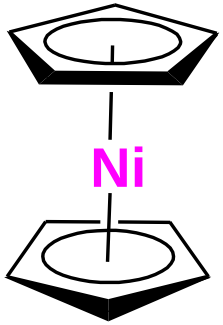
η^6-benzene → 6

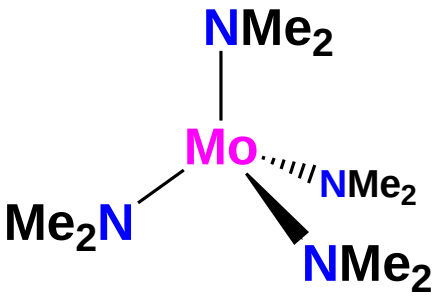
η^5-Cp$^-$ → 6

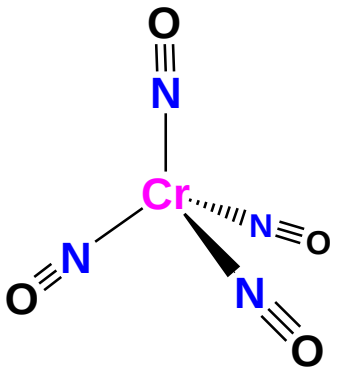
18

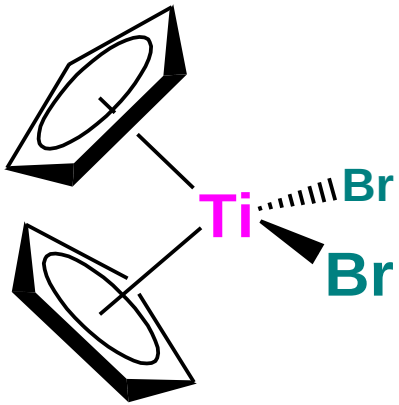


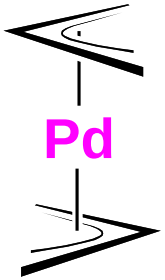


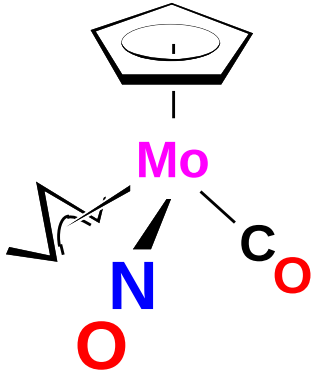


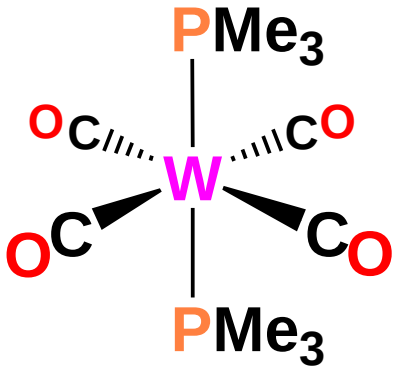


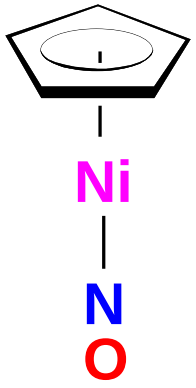


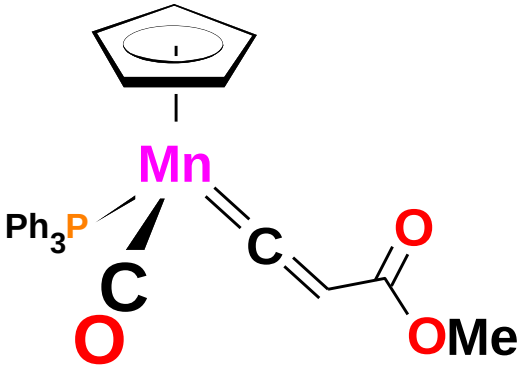

Ti
Br
Br


Pd

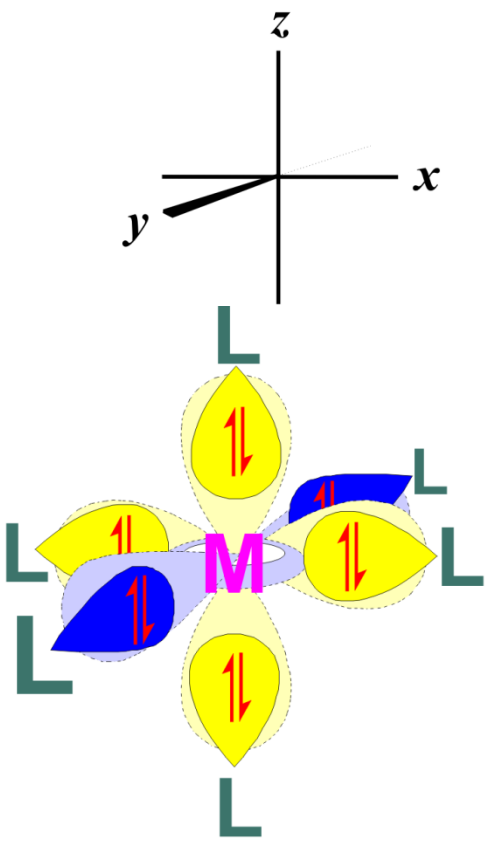

Mo
C
O
N
O

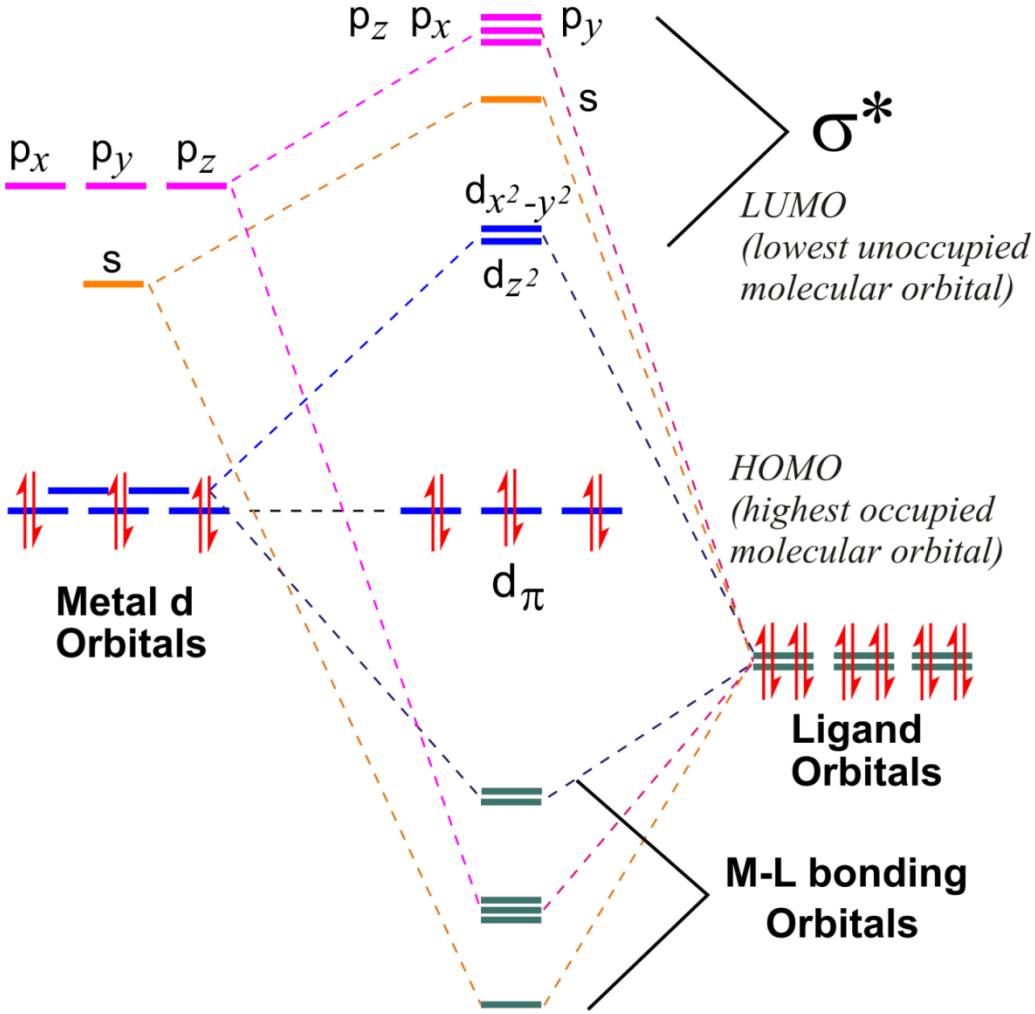

PMe3
OC
CO
W
OC
CO
PMe3


Ni
N
O

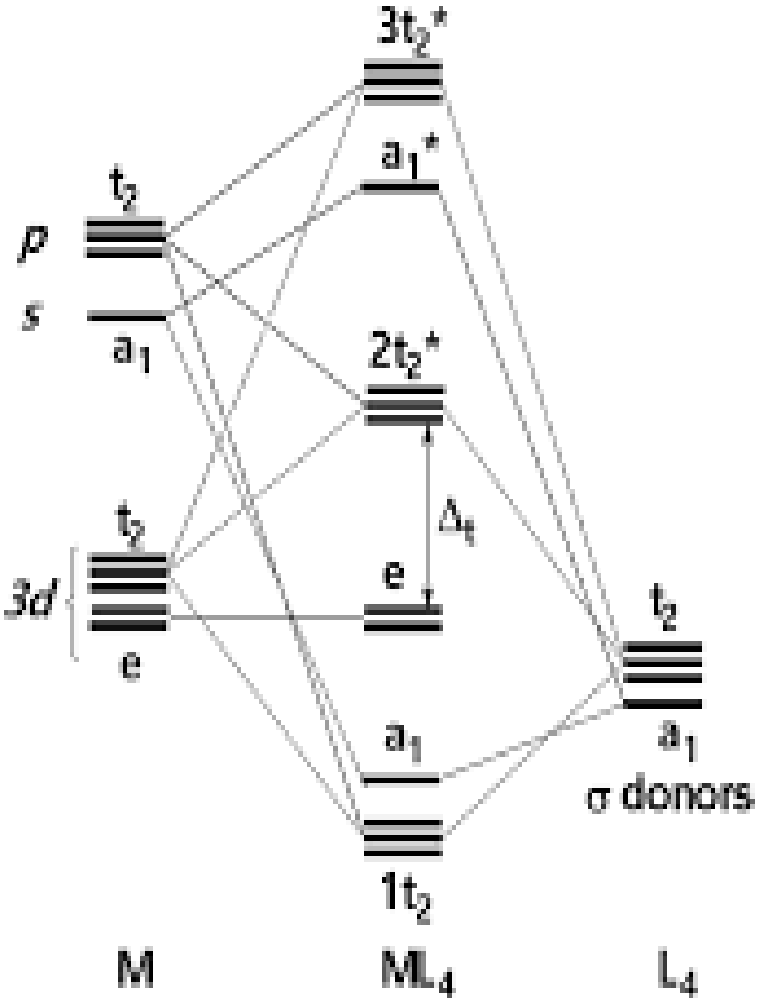

Mn
Ph3P
C
O
C
O
OMe

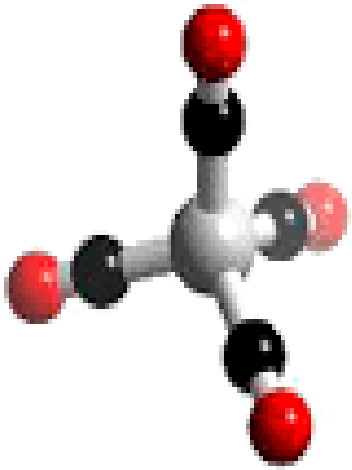
Stability of 18 e or 16e complexes according to MO theory





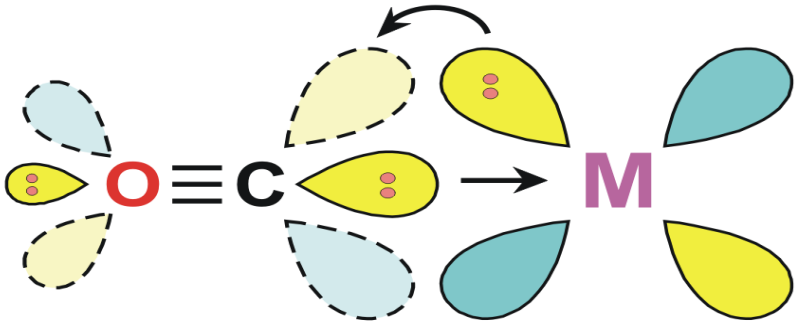
Stability of 18 e or 16e complexes according to MO theory





Carbonyl Ligands - C≡O

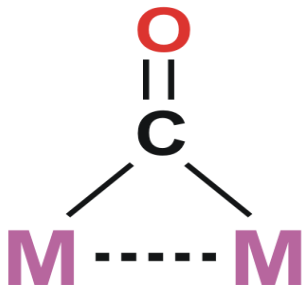
empty π-acceptor orbitals on carbonyl*

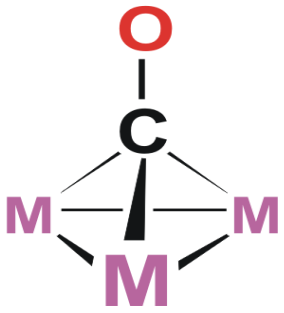


powerful π-acceptor ligand!

excellent ligand, therefore, for stabilizing electron-rich low-valent metal centers

Standard Bonding Modes:





terminal mode

$2e^-$ neutral donor

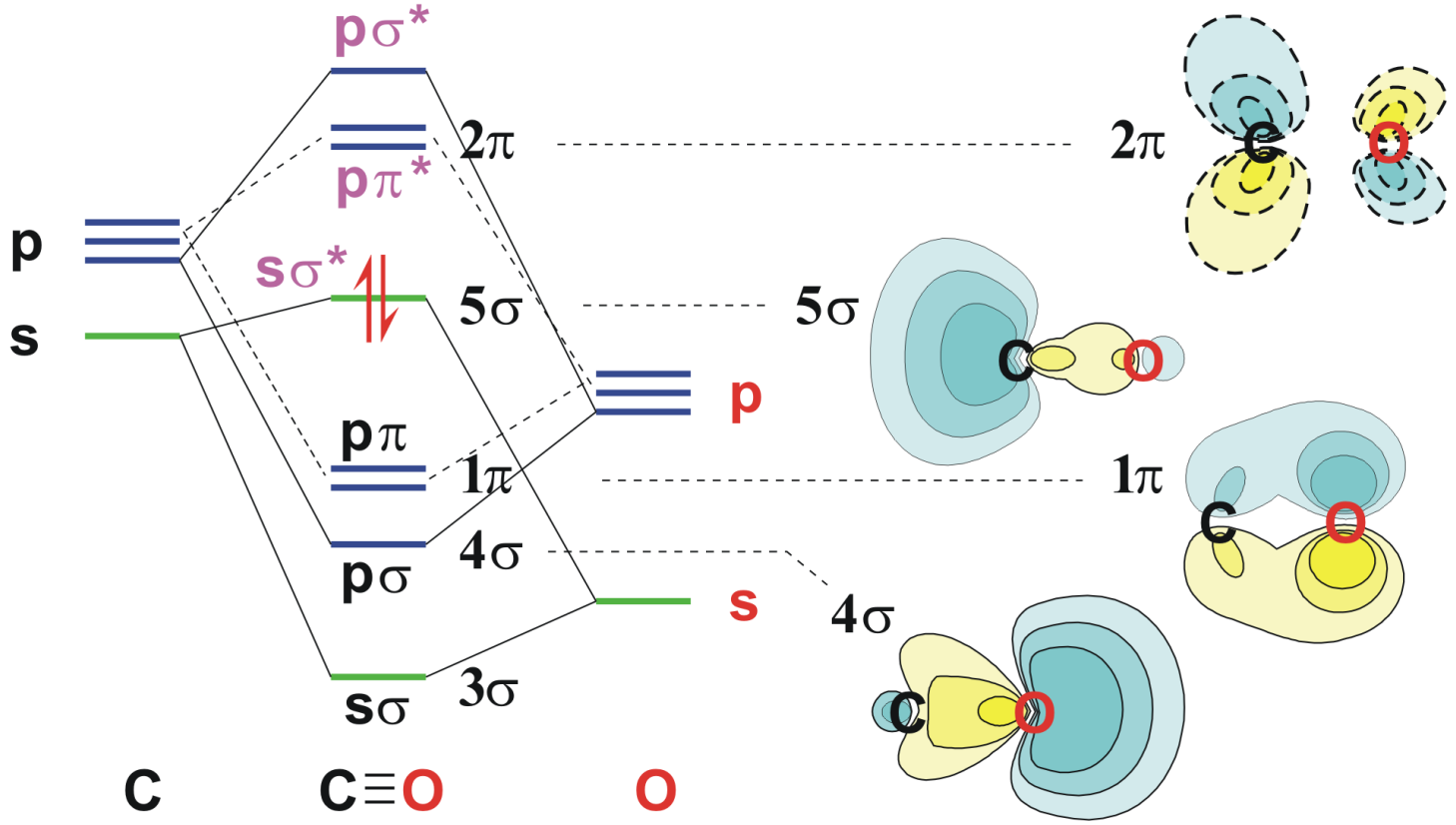
μ_2– bridging mode

$2e^-$ neutral donor

μ_3– bridging mode

$3e^-$ neutral donor

Molecular Orbital (MO) Diagram

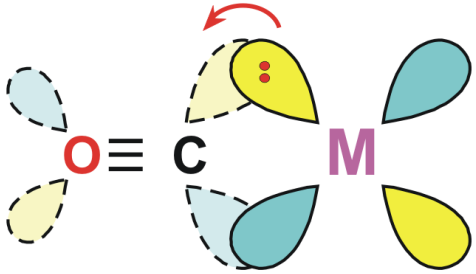


Experimental Data Supporting Nature of MO's in CO

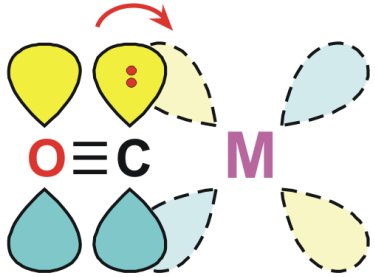
Species	Config	C-O Å	ν_{CO} cm^{-1}	Comment
CO	$(5\sigma)^2$	1.13	2143	
	$(5\sigma)^1$	1.11	2184	5σ MO is weakly antibonding
CO*	$(5\sigma)^1(2\pi)^1$	S 1.24	1489	2π MO is strongly antibonding
		T 1.21	1715	

Three types (two of which are important) of CO-Metal bonding interactions:

CO-M sigma bond



M to CO pi backbonding

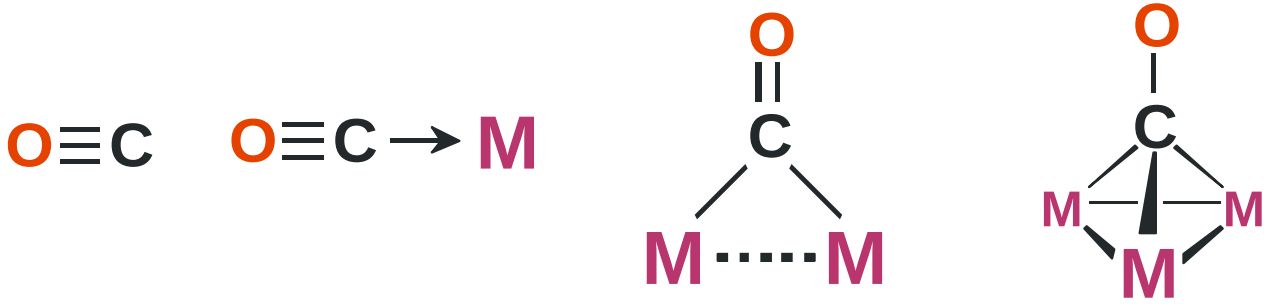


CO to M pi bonding
(rare)

M-C bond:	increases	increases	increases
C-O bond:	increases	decreases	decreases
ν_{CO} freq:	increases	decreases	decreases

Carbonyl Infrared (IR) Stretching Frequencies

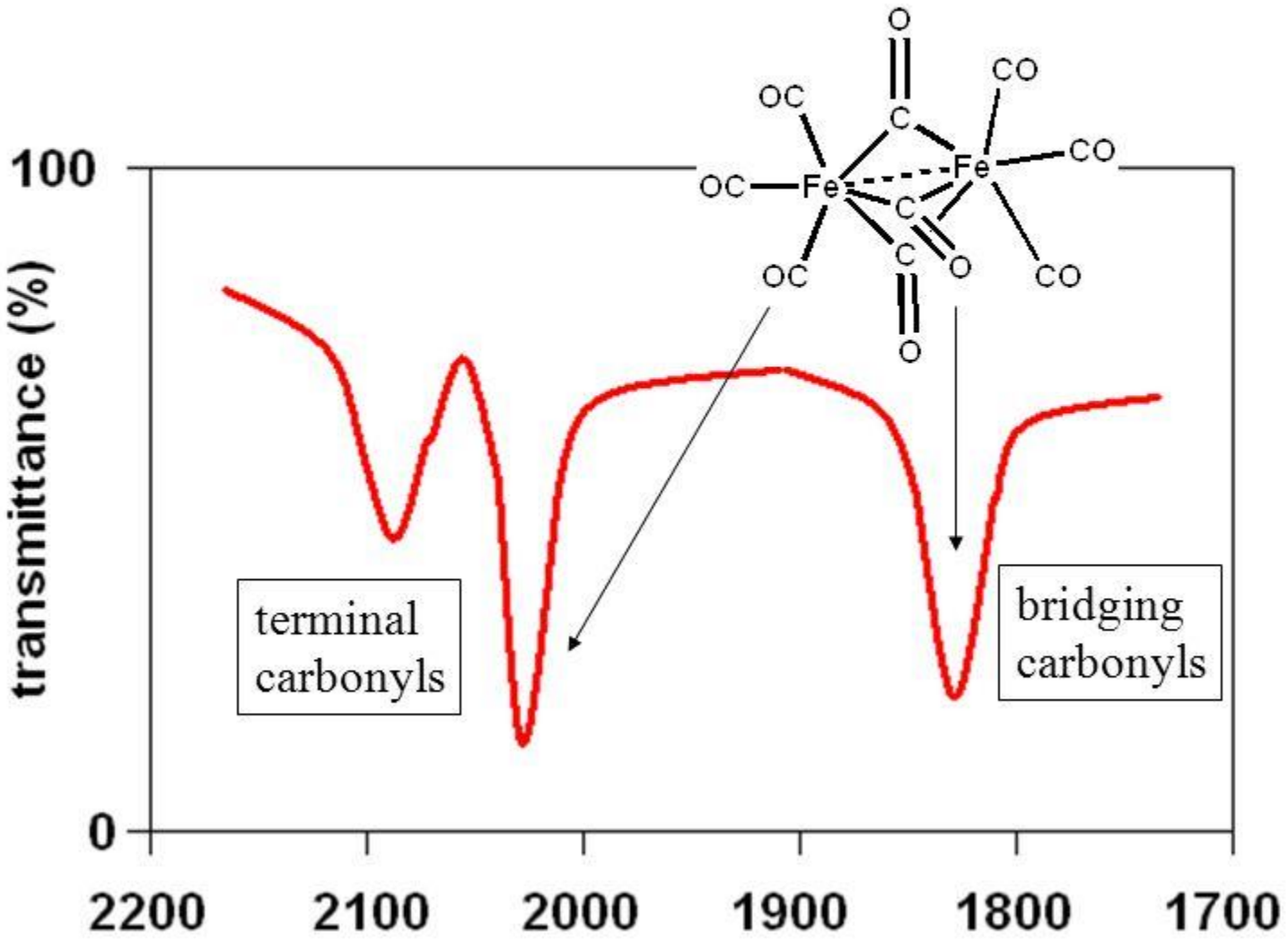
- The **position** of the carbonyl bands in the IR depends mainly on the bonding mode of the CO (terminal, bridging) and the amount of electron density on the metal being π-backbonded to the CO.
- The **number** (and intensity) of the carbonyl bands observed depends on the number of CO ligands present 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.



	free CO	*terminal mode*	μ_2 – *bridging*	μ_3 – *bridging*
ν_{CO} IR (cm^{-1})	2143	2120 - 1850	1850 - 1720	1730 - 1500

(for neutral metal complexes)

IR spectrum and bridging versus terminal carbonyls in $[Fe_2(CO)_9]$



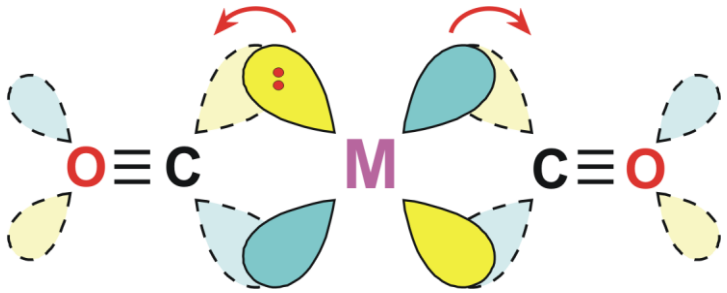
Electronic Effects on ν_{CO}

As the electron density on a metal center increases, more π-back bonding to the CO ligand(s) takes place. This further weakens the C-O bond by pumping more electron density into the formally empty carbonyl π^* orbital. This increases the M-CO bond strength making it more double-bond-like, i.e., the resonance structure
M=C=O assumes more importance.

d^x	Complex	ν_{CO} cm^{-1}
	free CO	2143
d^{10}	$[Ag(CO)]^+$	2204
	$Ni(CO)_4$	2060
	$[Co(CO)_4]^-$	1890
	$[Fe(CO)_4]^{2-}$	1790
	$[Mn(CO)_6]^+$	2090
d^6	$Cr(CO)_6$	2000
	$[V(CO)_6]^-$	1860

Ligand Electronic Effects on ν_{CO}

Complex	ν_{CO} cm^{-1}
$Mo(CO)_3(PF_3)_3$	2090, 2055
$Mo(CO)_3(PCl_3)_3$	2040, 1991
$Mo(CO)_3[P(OMe)_3]_3$	1977, 1888
$Mo(CO)_3(PPh_3)_3$	1934, 1835
$Mo(CO)_3(NCCH_3)_3$	1915, 1783
$Mo(CO)_3$(triamine)$_3$	1898, 1758
$Mo(CO)_3$(pyridine)$_3$	1888, 1746

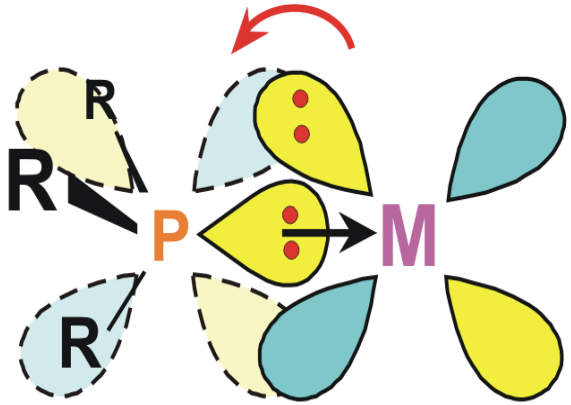


Based on CO IR stretching frequencies, the following ligands can be ranked from **best** π-acceptor to **worst**:

NO^+ > CO > PF_3 > RN≡C > PCl_3 > $P(OR)_3$ > PR_3 > RC≡N > NH_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

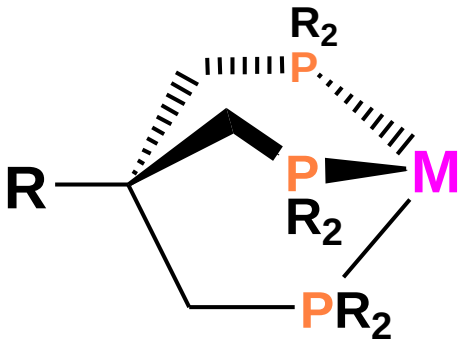
Phosphine ligands

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

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

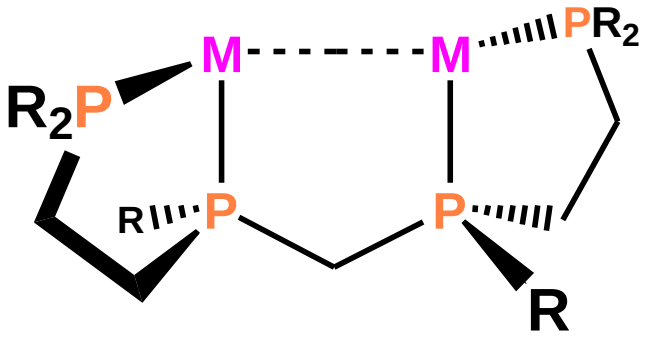
R = OR groups → phosphite

- large changes in the donor/acceptor properties of the phosphine (from excellent donor/poor π-acceptor to poor donor/excellent π-acceptor)
- large changes in the steric profile of the phosphine (from fairly small to enormous)
- generation of a large number of polydentate polyphosphines (bis-, tris-, tetra-, penta-, and hexaphosphine ligands are all known) that can adopt specific coordination geometries (cis-enforcing, facial tridentate, bridging, bridging and chelating, etc.)



M(η^3-tripod)

facial coordinating



racemic-M_2(P4)

binucleating phosphine

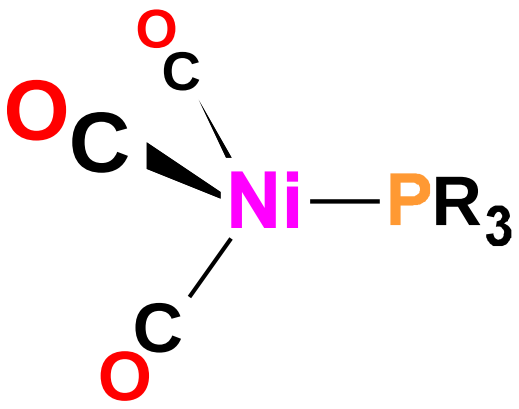
able to bridge and chelate 2 metals

Tolman's Cone Angle and Electronic Parameter

The electron-donating ability of a phosphine ligand was determined by measuring the ν_{CO} of a $Ni(CO)_3(PR_3)$ complex:

Lowest CO stretching frequency:

most donating phosphine

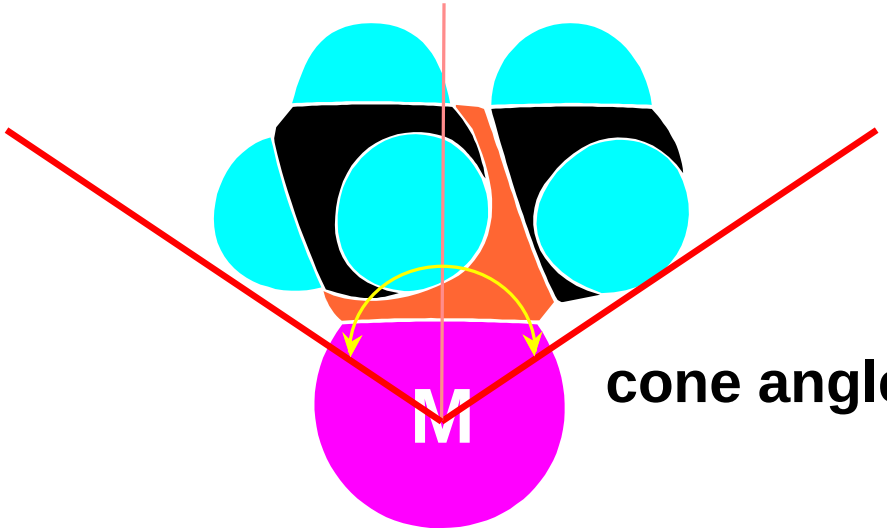


Highest CO stretching frequency:

least donating phosphine

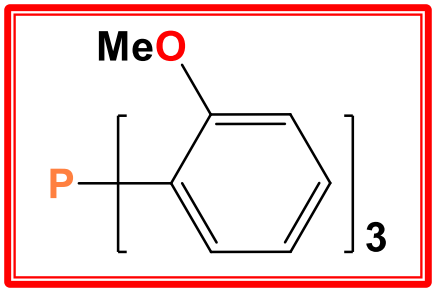
(best π-acceptor)

The size or steric bulk of a phosphine ligand was determined from simple 3-D space-filling models of the phosphine ligand coordinated to a Ni atom:

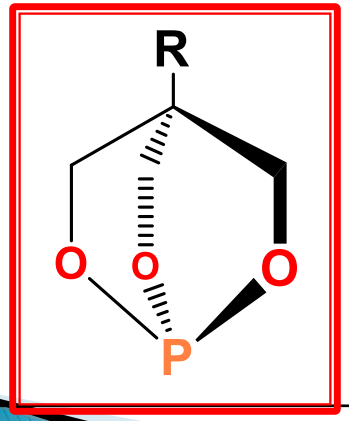


cone angle θ

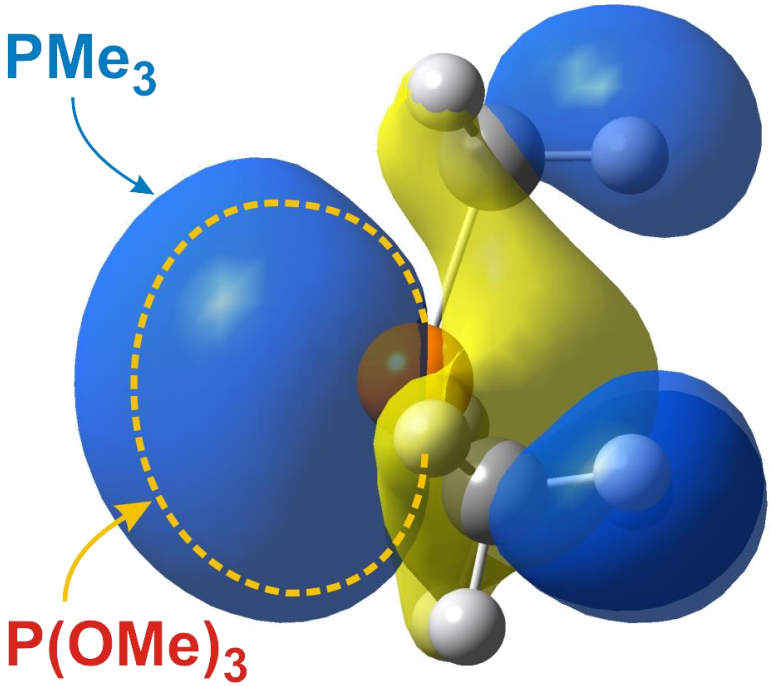
Tolman's Electronic Parameter ν (most donating to least)

PR_3	mixed	$P(OR)_3$	PX_3	ν, cm^{-1}
$P(t\text{-}Bu)_3$				2056.1
PCy_3				2056.4
$P(o\text{-}OMe\text{-}C_6H_4)_3$				2058.3
$P(i\text{-}Pr)_3$				2059.2
PBu_3				2060.3
PEt_3				2061.7
	PEt_2Ph			2063.7
PMe_3				2064.1
	PMe_2Ph			2065.3
$P(p\text{-}OMe\text{-}C_6H_4)_3$	$PPh_2(o\text{-}OMe\text{-}C_6H_4)$			2066.1
PBz_3				2066.4
$P(o\text{-}Tol)_3$				2066.6
$P(p\text{-}Tol)_3$	$PEtPh_2$			2066.7
	$PMePh_2$			2067.0
$P(m\text{-}Tol)_3$				2067.2
	$PPh_2(NMe_2)$			2067.3
	$PPh_2(2,4,6\text{-}Me\text{-}C_6H_2)$			2067.4
	$PPhBz_2$			2067.6
	$PPh_2(p\text{-}OMe\text{-}C_6H_4)$			2068.2
	PPh_2Bz			2068.4
PPh_3				**2068.9**

$P(CH=CH_2)_3$	$PPh_2(p\text{-}F\text{-}C_6H_4)$		2069.5
	$PPh(p\text{-}F\text{-}C_6H_4)_2$		2070.0
$P(p\text{-}F\text{-}C_6H_4)_3$			2071.3
	$PPh_2(OEt)$		2071.6
	$PPh(O\text{-}i\text{-}Pr)_2$		2072.2
$P(p\text{-}Cl\text{-}C_6H_4)_3$			2072.8
	PPh_2H		2073.3
	$PPh(OBu)_2$		2073.4
$P(m\text{-}F\text{-}C_6H_4)_3$			2074.1
	$PPh(OEt)_2$		2074.2
	$PPh_2(C_6F_5)$		2074.8
		$P(O\text{-}i\text{-}Pr)_3$	2075.9
		$P(OEt)_3$	2076.3
	$PPhH_2$		2077.0
		$P(OMe)_3$	2079.5
	$PPh(OPh)_2$		2079.8
		PPh_2Cl	2080.7
		PMe_2CF_3	2080.9
		$P(O\text{-}2,4\text{-}Me\text{-}C_6H_3)_3$	2083.2
		$P(OPh)_3$	2085.3
		$P(OCH_2)_3CR$	2086.8
	$P(C_6F_5)_3$		2090.9
			2097.0
			2110.8



PMe_3 vs. $P(OMe)_3$: The methyl groups are considered to be electron donating making the P center more electron-rich. The methoxy groups are σ electron-withdrawing due to the electronegative oxygen atoms, making the P center more electron deficient. The results from Density Functional Theory (DFT) calculations on both are shown below. Note the higher energy of the P lone pair (highest occupied molecular orbital, HOMO), greater spatial extent (generally better overlap with metal d-orbitals), and lower positive charge on P for PMe_3 relative to $P(OMe)_3$.

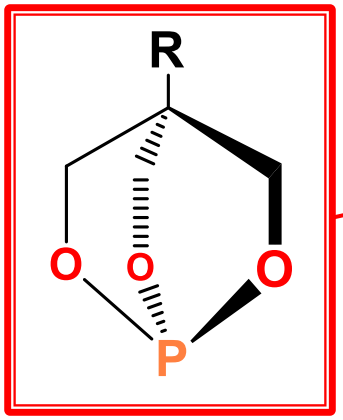


PMe_3
HOMO = –5.03 eV
Charge on P = +0.22

$P(OMe)_3$
HOMO = –7.40 eV
Charge on P = +0.75

MO plot of the lone pair orbital (HOMO) for PMe_3. Dashed outline indicates the spatial extent of the lone pair for $P(OMe)_3$.

Tolman's Cone Angle θ (smallest to largest)



PR_3	mixed	$P(OR)_3$	PX_3	θ (°)
			PH_3	87
	$PPhH_2$	$P(OCH_2)_3CR$		101
			PF_3	104
	$Me_2PCH_2CH_2PMe_2$	$P(OMe)_3$		107
		$P(OEt)_3$		109
	$P(CH_2O)_3CR$			114
	$Et_2PCH_2CH_2PEt_2$			115
PMe_3				118
	$Ph_2PCH_2PPh_2$			121
		PMe_2CF_3	PCl_3	124
	$Ph_2PCH_2CH_2PPh_2$			125
	PPh_2H	$P(OPh)_3$		128
			PBr_3	131
PEt_3, PPr_3, PBu_3	$PPh_2(OMe)$			132
	PEt_2Ph, $PMePh_2$			136
	$Cy_2PCH_2CH_2PCy_2$			142
PPh_3				145

	$PPh_2(t\text{-Bu})$		157
	$PPh_2(C_6F_5)$		158
$P(i\text{-Pr})_3$			160
PBz_3			165
PCy_3	$PPh(t\text{-Bu})_2$		170
		$P(O\text{-}t\text{-Bu})_3$	175
$P(t\text{-Bu})_3$			182
	$P(C_6F_5)_3$		184
$P(o\text{-Tol})_3$			194
$P(\text{mesityl})_3$			212

Commonly Used Monodentate Phosphines

PPh_3 (145°, medium donor), triphenylphosphine, tpp "The KING"

- air-stable, white crystalline material, no odor to speak of

Increasing σ-Donor Ability:

$PMePh_2$ (136°), PMe_2Ph (122°), PMe_3 (118°), PEt_3 (132°)

$P(Cy)_3$ (170°) tricyclohexylphosphine, $P(t\text{-}Bu)_3$ (182°)

- the alkyl phosphines are strong σ-donors; low MW ones usually colorless liquids, somewhat to very air-sensitive, horrible smelling (unless very high MW and non-volatile)

Poor σ-Donors, Good π-Acceptors:

Phosphites: $P(OMe)_3$ (107°), $P(OEt)_3$ (110°), $P(OPh)_3$ (128°)

- phosphites are relatively poor σ-donors, but can be fairly good π-acceptor ligands (about half as good as CO); low MW ones are usually colorless liquids, higher MW compounds are white solids; usually air-stable but moisture sensitive; sometimes sweet smelling

PF_3 (104°) } v. poor donor; strong π-acceptor, almost as good as CO

Problem: **For each of the following pairs of metal complexes, which should have the *highest* average carbonyl IR stretching frequency.**

a) $CpFeBr(CO)_2$ -or- $CpRuCl(CO)(PMe_3)$

b) $MnCl(CO)_5$ -or- $Cr(CO)_6$

c) $(\eta^3\text{-allyl})Co(PPh_3)(CO)_2$ -or- $(\eta^3\text{-allyl})Co(PMe_3)(CO)_2$

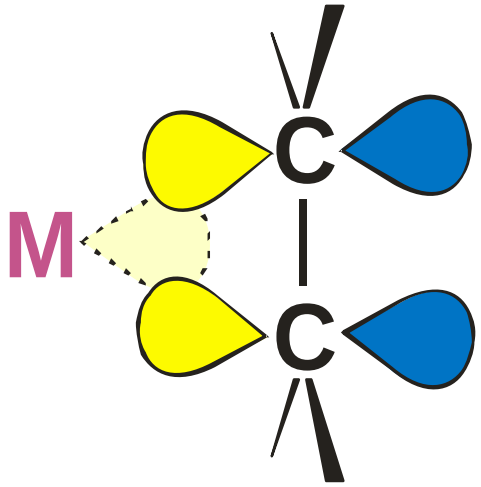
Problem: **Order the following phosphines from smallest to largest:**

$P(OEt)_3$ PPh_3 PPr_3 PCl_3 $PPhCy_2$

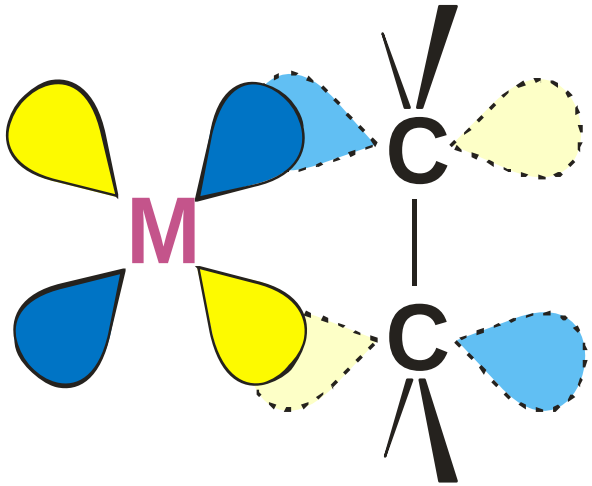
Problem: **Order the following phosphines from best to worst π-acceptor:**

$P(OEt)_3$ PPh_3 PPr_3 PCl_3 $PPhCy_2$

Alkenes/Alkynes ligand



σ-donation via the filled alkene π-system

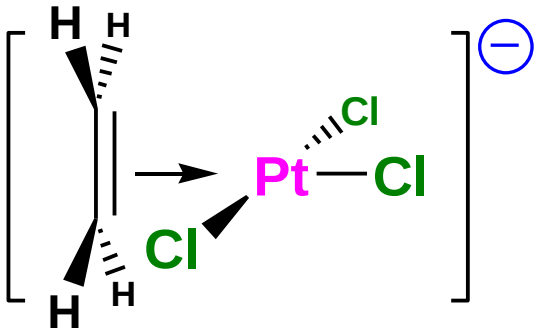


π-back donation via the empty alkene π-system*

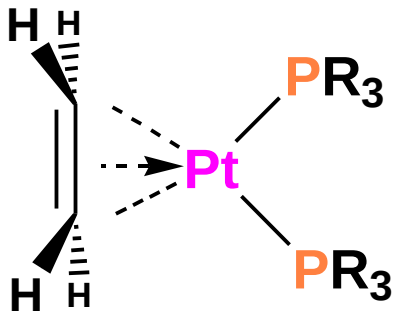
Dewar-Chatt-Duncanson bonding model (1953)

Alkenes are typically relatively weakly coordinating ligands. They are also extremely important substrates for catalytic reactions. The strongest alkene-metal bonds occur with third row metals (as with almost all ligands) and when one can get more π-backbonding to occur.

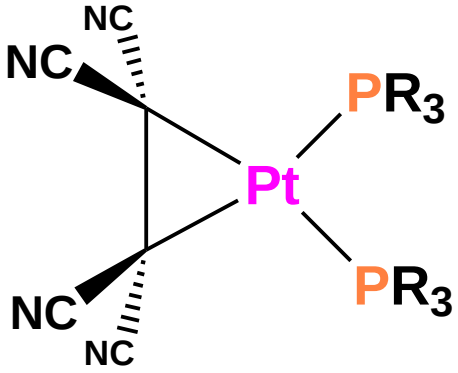
The amount of π-backbonding depends strongly on how electron-rich the metal center is and whether or not there are electron-withdrawing groups on the alkene to make it a better acceptor ligand.



Pt(2+)
C=C = 1.37Å
Zeiss's Salt

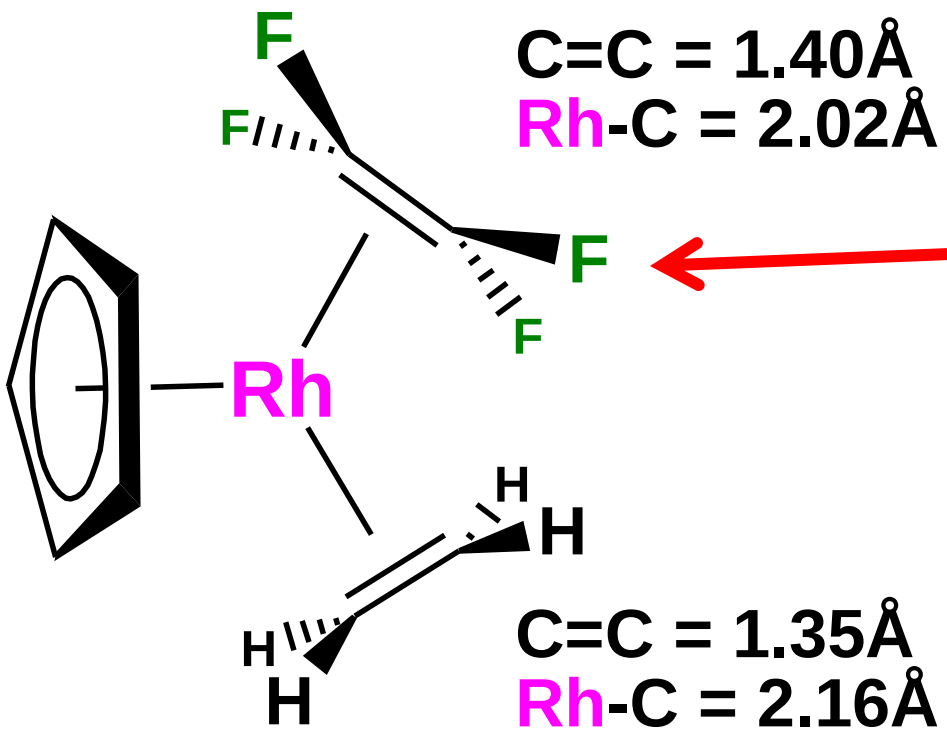


Pt(0)
C=C = 1.43Å



Pt(+2)
C--C = 1.49Å
metallocyclopropane

If the metal is electron-rich enough and/or if there are electron-withdrawing groups on the alkene, one can actually get a formal oxidation of the metal via the transfer of 2e- to the alkene to form a dianionic metallocyclopropane ligand that is now coordinated via two anionic alkyl σ-bonds (thus the assignment of Pt(+2)).



C=C = 1.40Å
Rh-C = 2.02Å

C=C = 1.35Å
Rh-C = 2.16Å

The electron-withdrawing fluorine groups on the $F_2C=CF_2$ alkene makes it a better π-acceptor ligand. This *weakens* the C=C bond, but ***strengthens*** the alkene-metal bond.

Electronic Effects

Ethylene Complex	νC=C (cm^{-1})
Free Ethylene	1623
$[Ag(H_2C{=}CH_2)_2]^+$	1584
$Fe(CO)_4(H_2C{=}CH_2)$	1551
$[Re(CO)_4(H_2C{=}CH_2)_2]^+$	1539
$[CpFe(CO)_2(H_2C{=}CH_2)]^+$	1527
$Pd_2Cl_4(H_2C{=}CH_2)_2$	1525
$[PtCl_3(H_2C{=}CH_2)]^-$	1516
$CpMn(CO)_2(H_2C{=}CH_2)$	1508
$Pt_2Cl_4(H_2C{=}CH_2)_2$	1506
$CpRh(H_2C{=}CH_2)_2$	1493

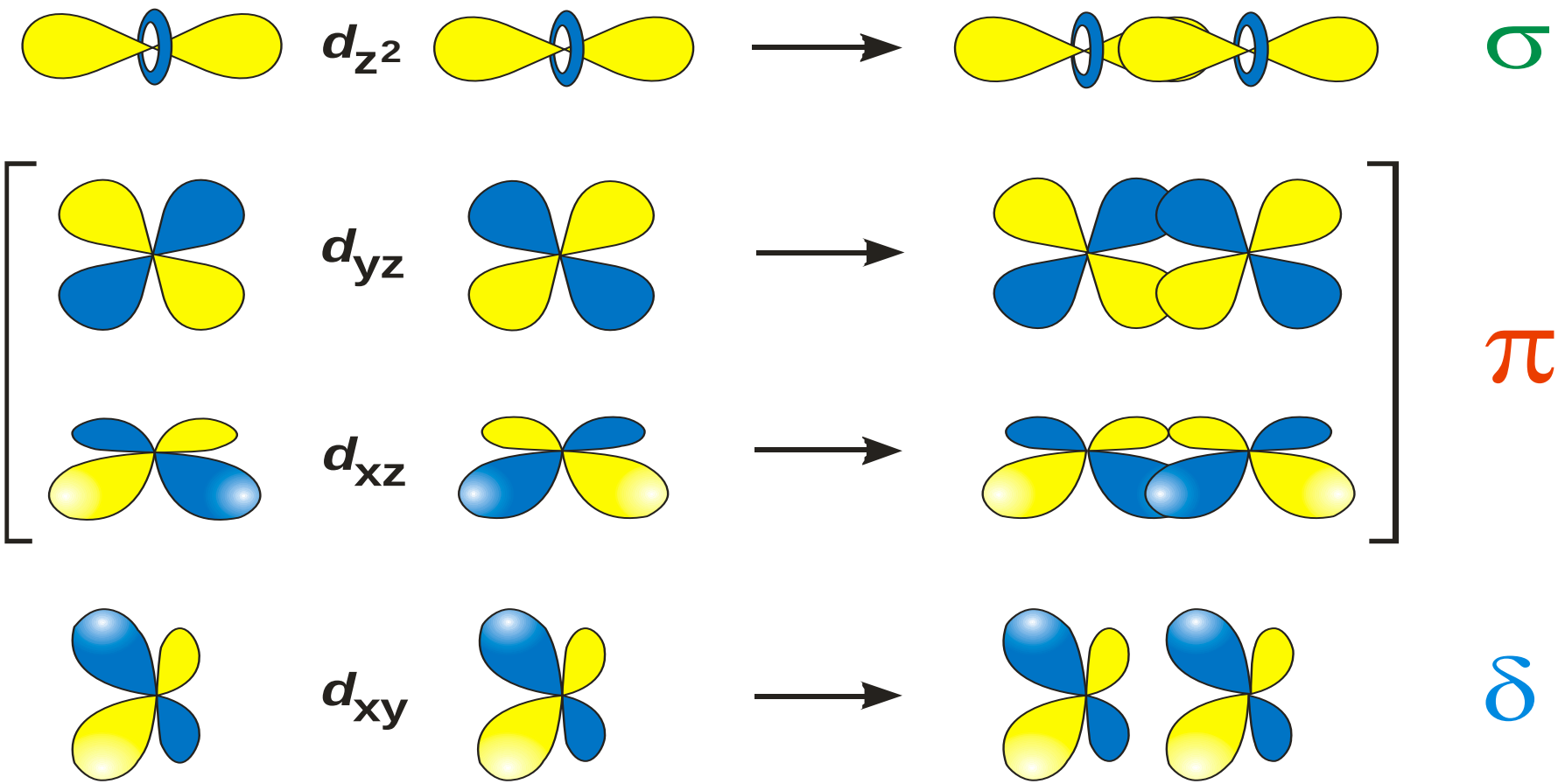
Metal-Metal Bonding

Covalent: Electron precise bonds. M-M bond counts as one e- from each metal center. Most common type of M-M bonding.

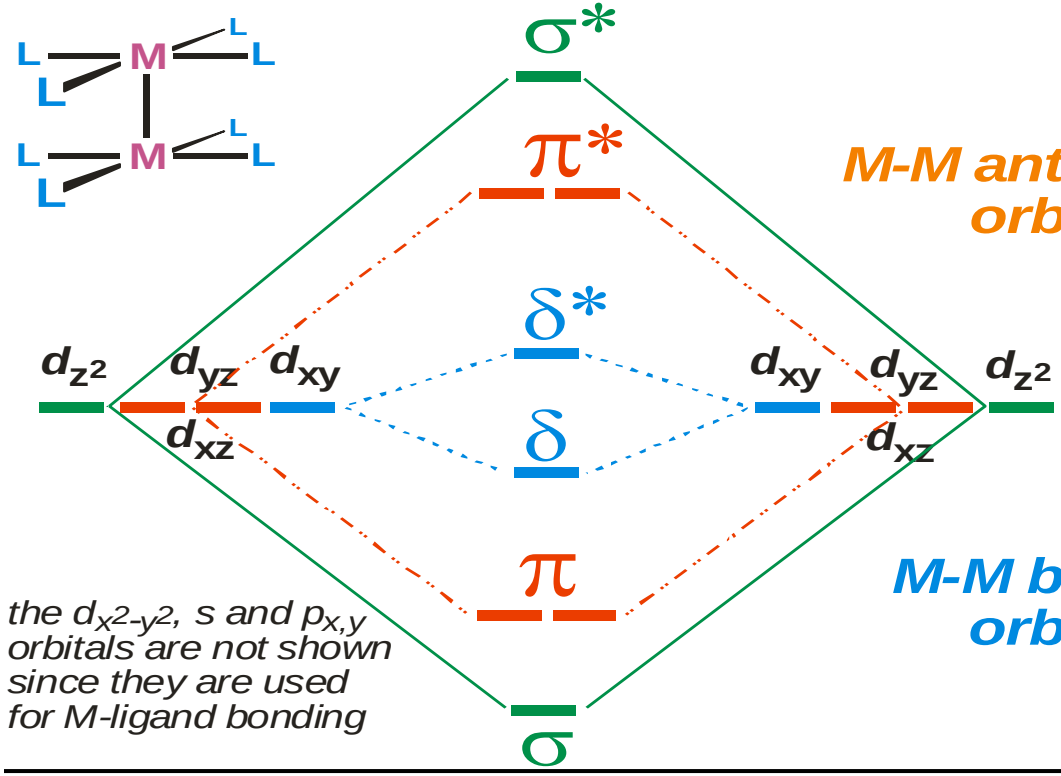
Dative: Where one metal uses a filled *d* orbital "lone pair" to coordinate to an empty orbital on a second, more unsaturated metal. Most dative bonding situations can also be electron-counted as covalent bonds.

Symmetry: Weak metal-metal interactions caused by molecular orbital symmetry interactions of filled & empty M-M bonding and/or antibonding orbitals. Typically seen for d8 metals. Not at all common.

Metal-Metal Bonding

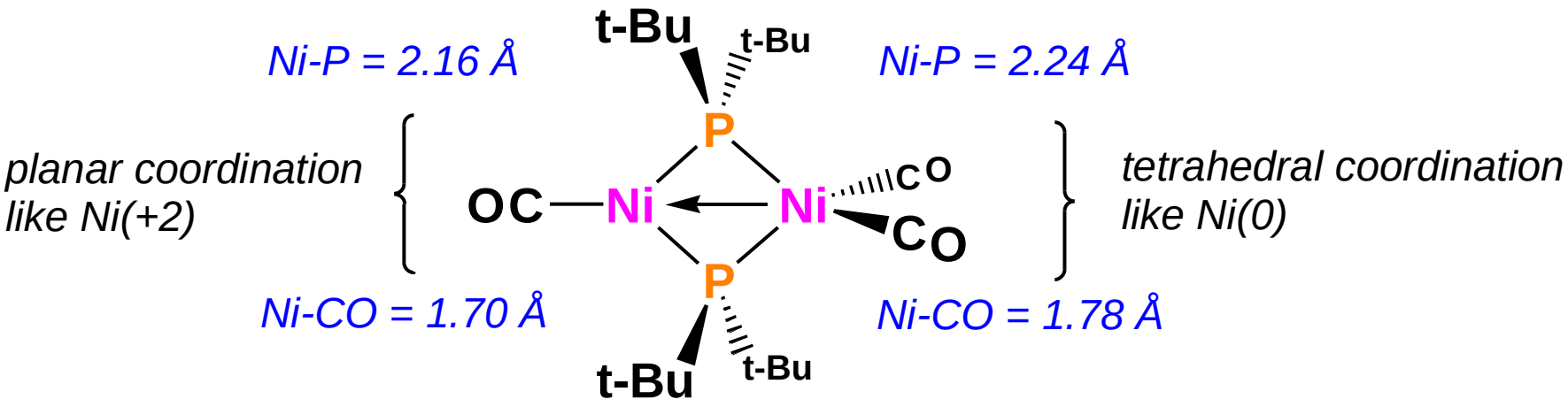


the $d_{x^2-y^2}$ orbitals (not shown) are used for M-L bonding



Electron Count	Resulting M-M Bond
$d^1 - d^1$	Single bond
$d^2 - d^2$	Double bond
$d^3 - d^3$	Triple bond
$d^4 - d^4$	Quadruple bond *optimum*
$d^5 - d^5$	Triple bond
$d^6 - d^6$	Double bond *(M-L bonding usually dominates)*
$d^7 - d^7$	Single bond
$d^8 - d^8$	No bond *(symmetry interaction)*

Dative M-M Bonds (unsymmetrical M-M bonded complexes)

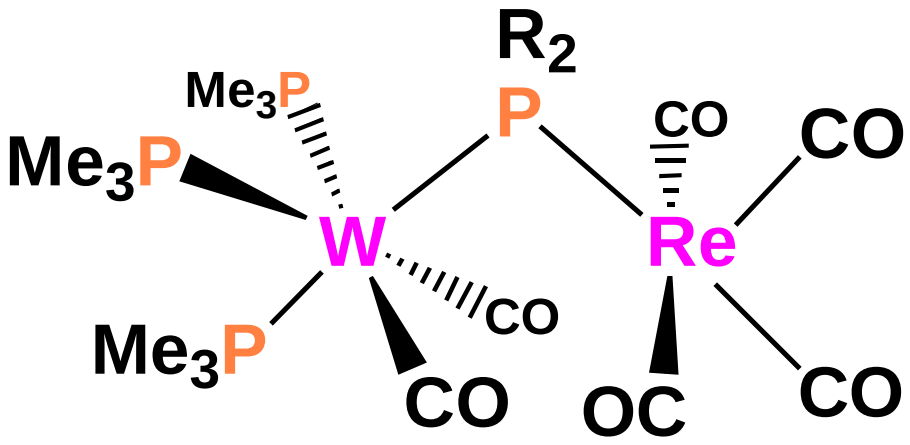


Ni-Ni = 2.41 Å

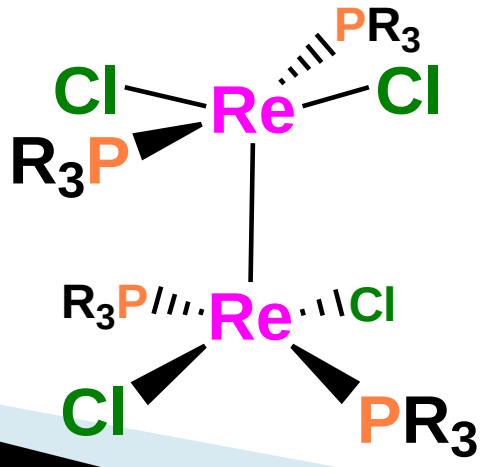
Covalent M-M Bonding			
Left Ni		**Right Ni**	
Ni(+1)	d^9	Ni(+1)	d^9
$[\mu\text{-}PR_2]^-$	2e-	$[\mu\text{-}PR_2]^-$	2e-
$\mu\text{-}PR_2$	2e-	$\mu\text{-}PR_2$	2e-
CO	2e-	2CO	4e-
M-M	1e-	M-M	1e-
Total	**16e-**	**Total**	**18e-**

Dative			
Left Ni		**Right Ni**	
Ni(+2)	d^8	Ni(0)	d^{10}
$2[\mu\text{-}PR_2]^-$	4e-	$2\mu\text{-}PR_2$	4e-
CO	2e-	2CO	4e-
Ni←Ni(0)	2e-		
Total	**16e-**	**Total**	**18e-**

Problem: Electron-count the following complex using both the covalent and dative M-M bonding methods:



Problem: Electron-count the following complex. What is the order of the Re-Re bond? Why wouldn't it be appropriate to use the dative bond method for this complex?



Ligand Substitution Rxns

$$ML_n + xP \rightleftharpoons ML_{n-x}P_x + xL$$

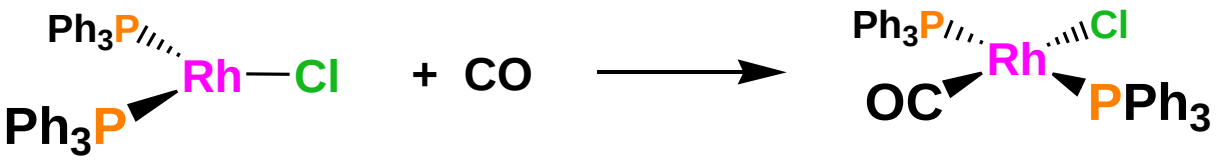
The mechanism of this substitution will almost always depend on whether the parent ML_n complex is coordinatively saturated or not!

Saturated Complex: Dissociative Pathway!

Unsaturated Complex: Associative Pathway (usually)
Dissociative pathway (sometimes)

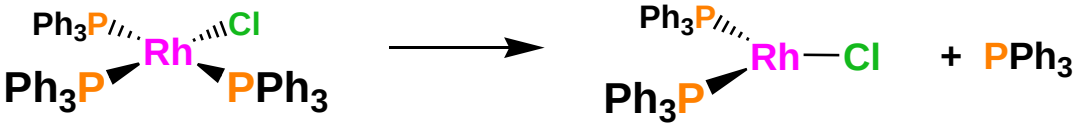
Most of the substitutions we will study will involve 2e- pathways. Odd e- or radical pathways are known, but less common.

Ligand Addition (association): this is when an incoming ligand coordinates to a metal center that has one or more empty orbitals available.

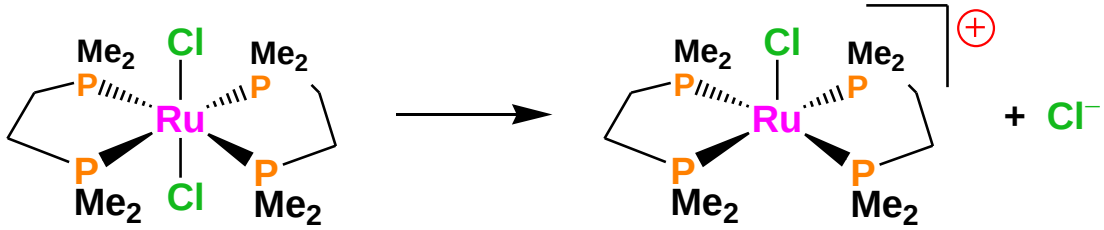


This Rh(+1) complex is d^8 and only 14e-. Adding a ligand takes one to the more stable 16e- square-planar complex.

Ligand Dissociation: this is when a ligand coordinated to a metal dissociates (falls off). The probability of a specific ligand dissociating depends on how strongly or weakly it is coordinated to the metal center and steric effects.

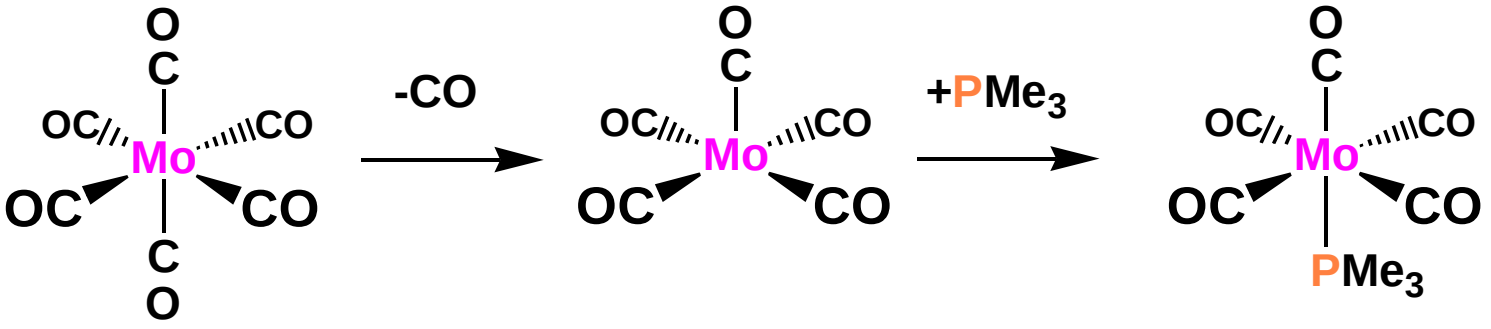


The steric hindrence of the three bulky PPh_3 ligands favors dissociation of one to form the 14e- $RhCl(PPh_3)_2$ complex. The moderate electron-donating ability of the PPh_3 ligand (not a strongly coordinating ligand) makes this fairly facile.



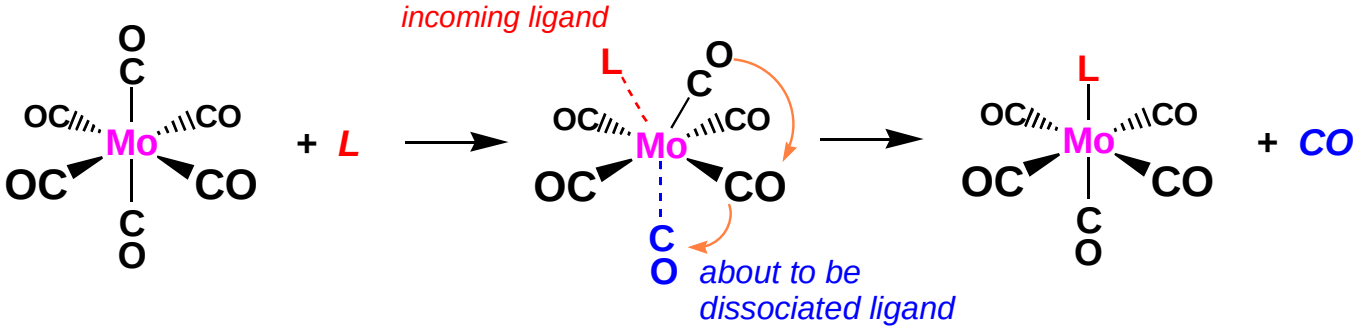
The strongly donating ability of the dmpe ligands combined with their strong chelate effect makes it difficult to dissociate one of the PMe_2 arms. In this case the Cl- anion is the one that dissociates, leaving a cationic complex behind. The two dmpe ligands donate enough electron-density to the Ru center to make it reasonable to dissociate a Cl-.

A **ligand substitution** can occur either by an ***associative*** or ***dissociative*** route. The exact mechanism depends in large part on the electron-count of the metal complex undergoing the ligand substitution. The simplest case is when one is dealing with an **18e-** metal complex. In this case one almost always has a ***dissociative substitution***.



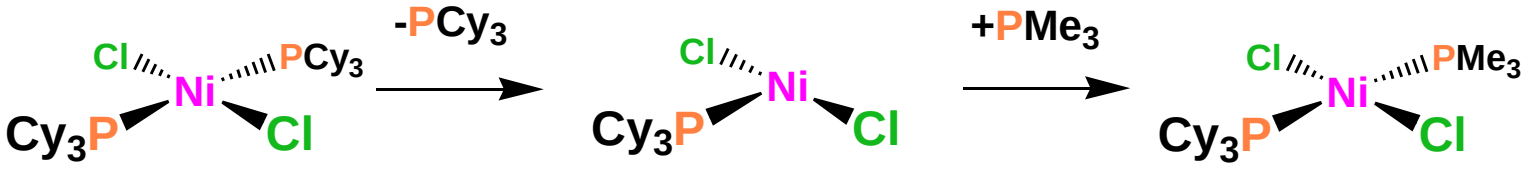
18e- saturated complex *16e- unsaturated complex* *18e- saturated complex*

Almost NO evidence for this type of rxn:



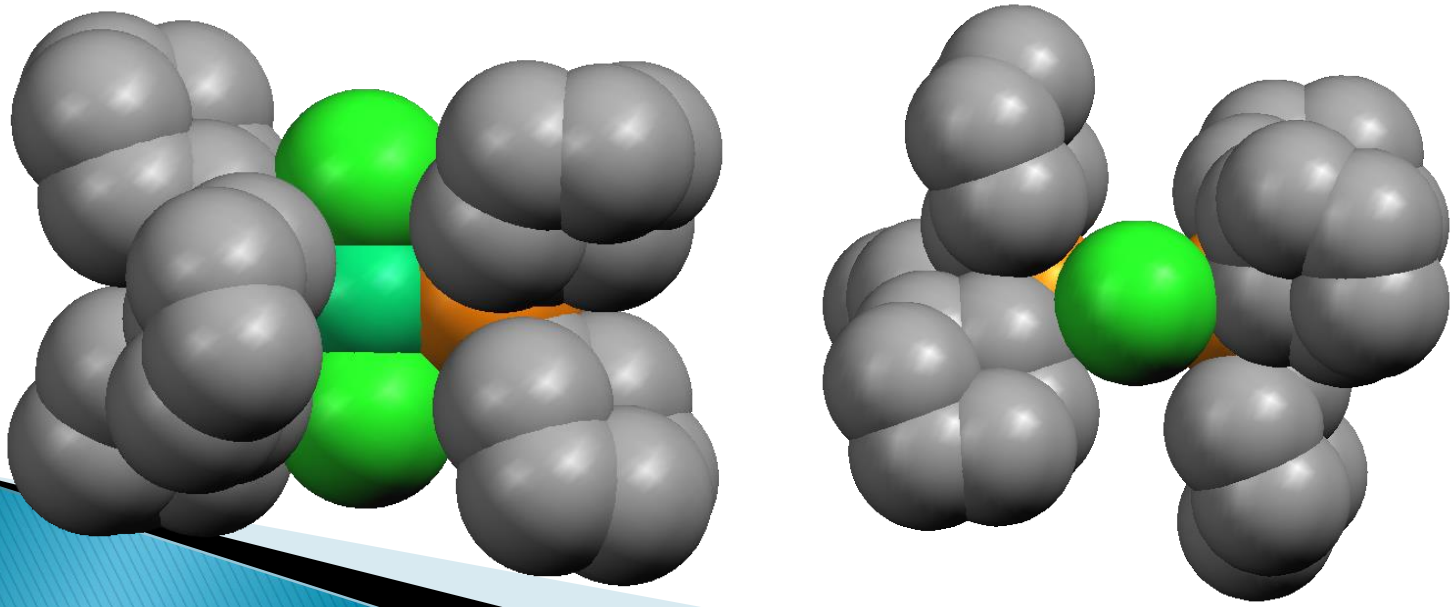
18e- complex ***20e- transition state with added ligand*** ***18e- complex***

Dissociative substitution can also occur in 16e- (or in very unusual cases, lower electron count systems) complexes. These cases either involve sterically bulky ligands that block the open coordination site, or third row square planar d^8 complexes like Pt(+2) where there are strong electronic factors that limit the coordination of an additional ligand to the empty axial site.



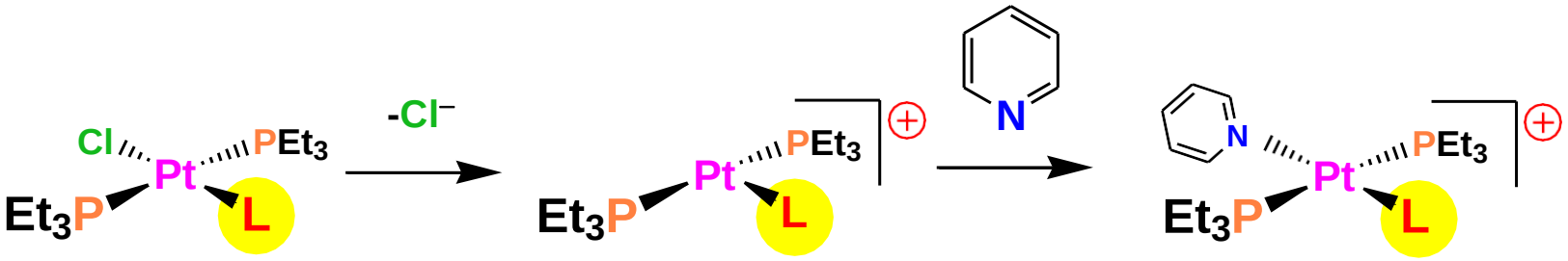
16e- unsaturated complex | *14e- unsaturated complex* | *16e- unsaturated complex*

The large PCy_3 ligands sterically block access to the empty axial p_z orbital



Trans Effect

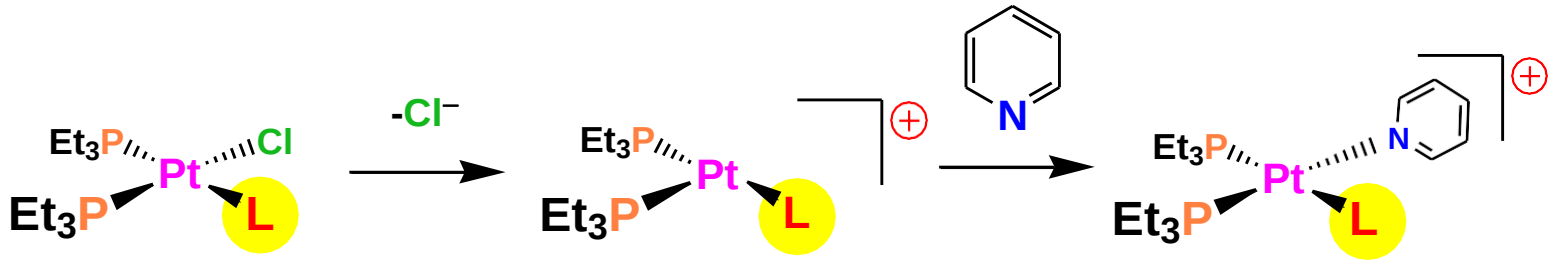
The ***trans effect*** concerns the electronic effect of one ligand on another ligand when they are ***trans*** (opposite) to one another. The classical *trans* effect involves two σ-donating ligands *trans* to one another.



Relative rate of substitution based on *trans* ligand :

Cl^- = 1, Ph^- = 100, CH_3^- = 10^3, H^- = 10^4

There is a *cis* effect, but it is much weaker and basically ignored:



Relative rate of substitution based on *cis* ligand :

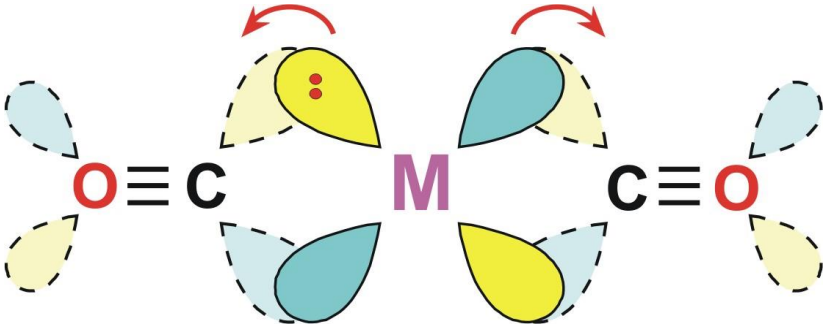
Cl^- = 1, Ph^- = 2, CH_3^- = 4, H^- = 4

Note that when most chemists talk about the *trans* effect they are referring to the σ-σ type of *trans* effect, where a strong σ-donor weakens the σ-donating ligand *trans* to it.

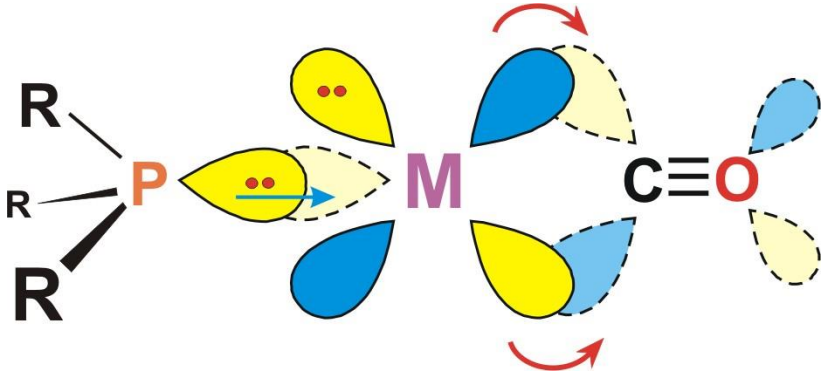
Do NOT overestimate the importance of the *trans*-effect. There are other forms that have different effects.

π-Acceptor *Trans* Effects

Trans effects that involve π-backbonding ligands. CO ligands represent the most common type.

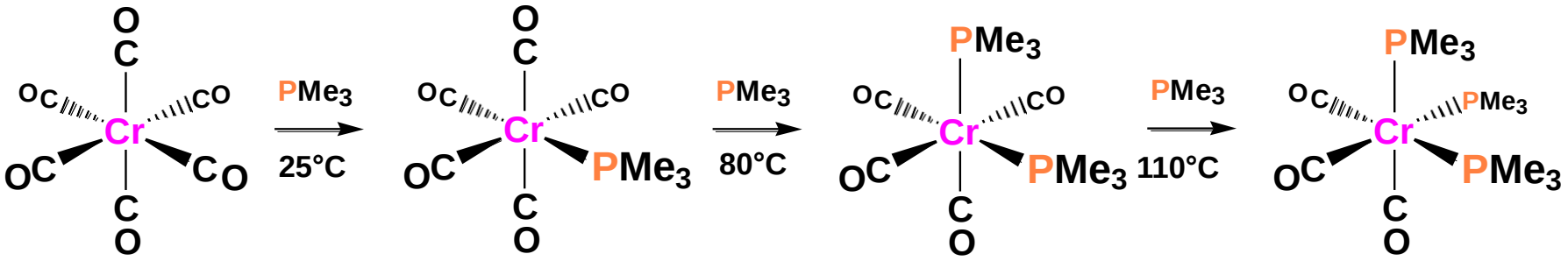


π-backbonding to a metal is ***weakened*** when it is *trans* to another good π-backbonding ligand



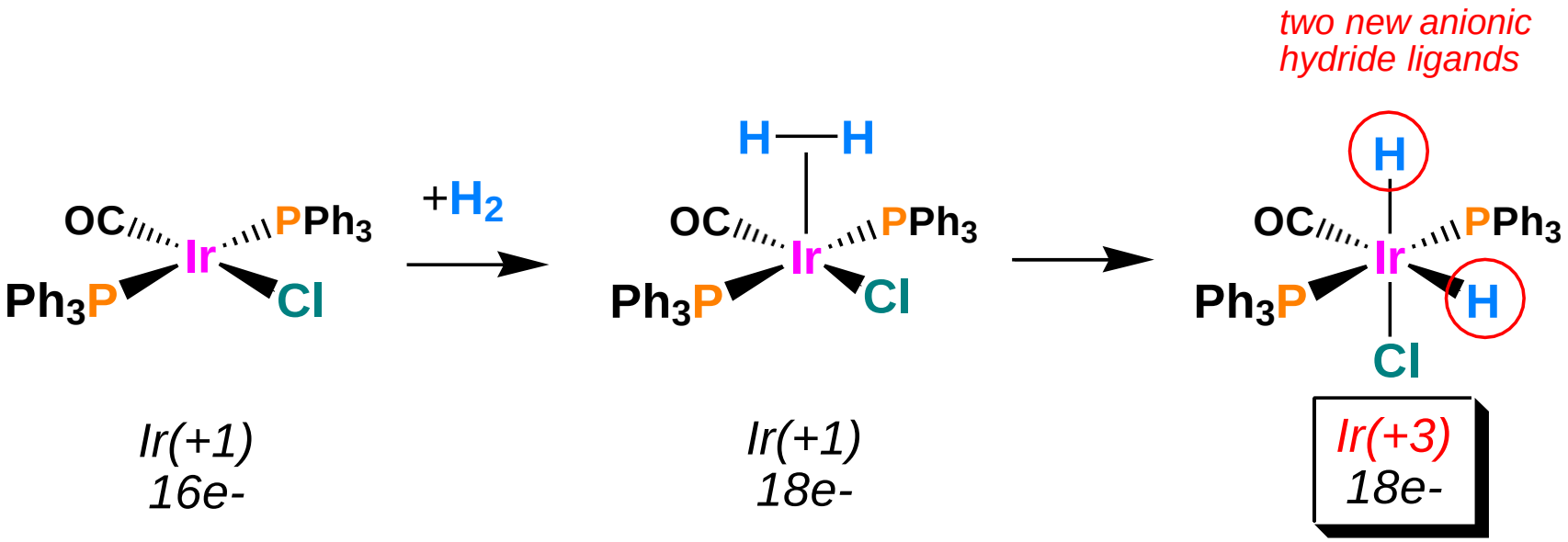
π-backbonding to a metal is ***strengthened*** when it is *trans* to a good σ-donating ligand that can't π-backbond

Problem: Consider the following series of substitution reactions.



As one replaces each CO ligand with a PMe_3, the next CO substitution is progressively more and more difficult requiring higher temperatures and longer times. Once one forms $Cr(CO)_3(PMe_3)_3$, it is extremely difficult to replace another carbonyl ligand. Why? Give all the major reasons?

Oxidative Addition/Reductive Elimination



There are three main classes of molecules (substrates) that can perform oxidative additions to metal centers:

- Non-Electrophillic
- Non-Electrophillic “Intact”
- Electrophillic

Non-electrophillic: these molecules do NOT contain electronegative atoms and/or are not good oxidizing agents. These molecules usually require the presence of an **empty orbital** on the metal in order for them to pre-coordinate prior to being activated for the oxidative addition rxn.

H_2, C-H bonds, Si-H bonds, S-H bonds,
B-H bonds, N-H bonds, S-S bonds, C-C bonds, etc.

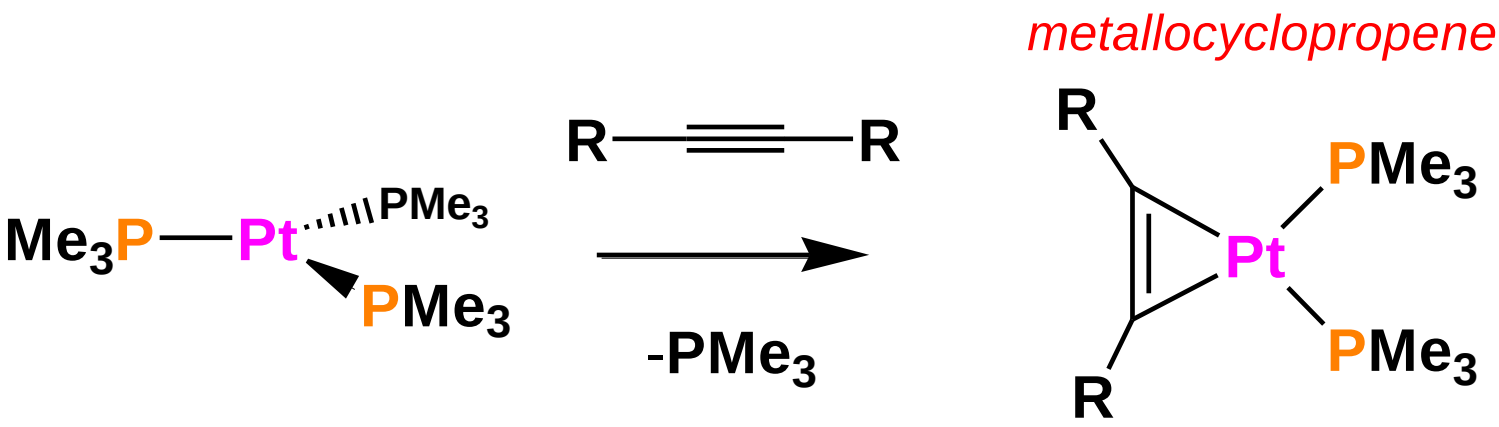
H_2 is by far the most important for catalytic applications, followed by Si-H bonds, B-H, N-H, and S-H bonds.

C-H bond activation and functionalization is very important, but still not practical.

Non-electrophillic "Intact": these molecules may or may not contain electronegative atoms, but they do need to have a **double** or **triple bond** present. One also needs a metal center with an **empty orbital** (16e- or lower count) in order to pre-coordinate the ligand before the oxidative addition occurs.

Typical "intact" ligands that can perform an oxidation addition without fragmenting apart are (O_2 can also act as an **electrophillic** substrate):

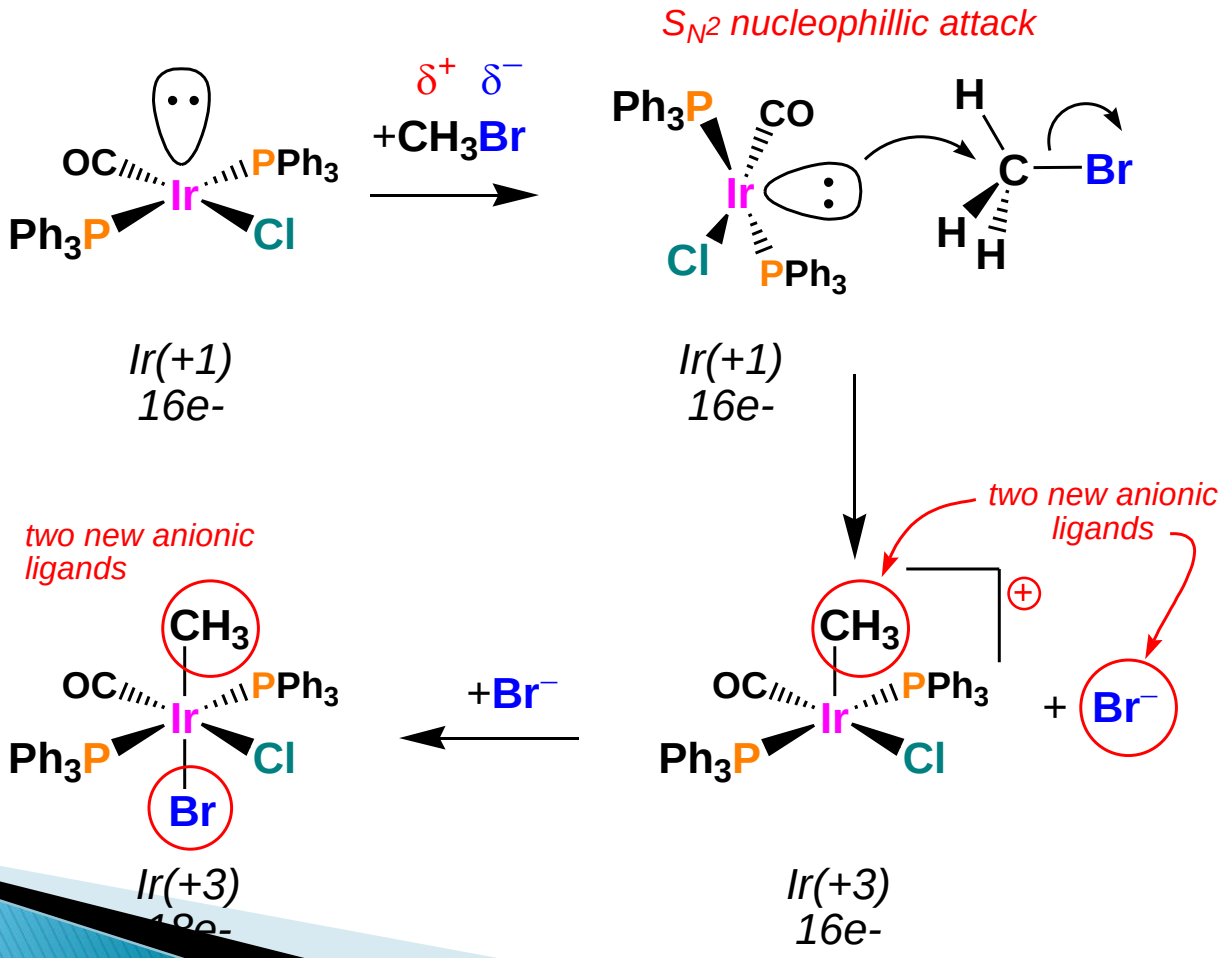
alkenes, alkynes, and O_2



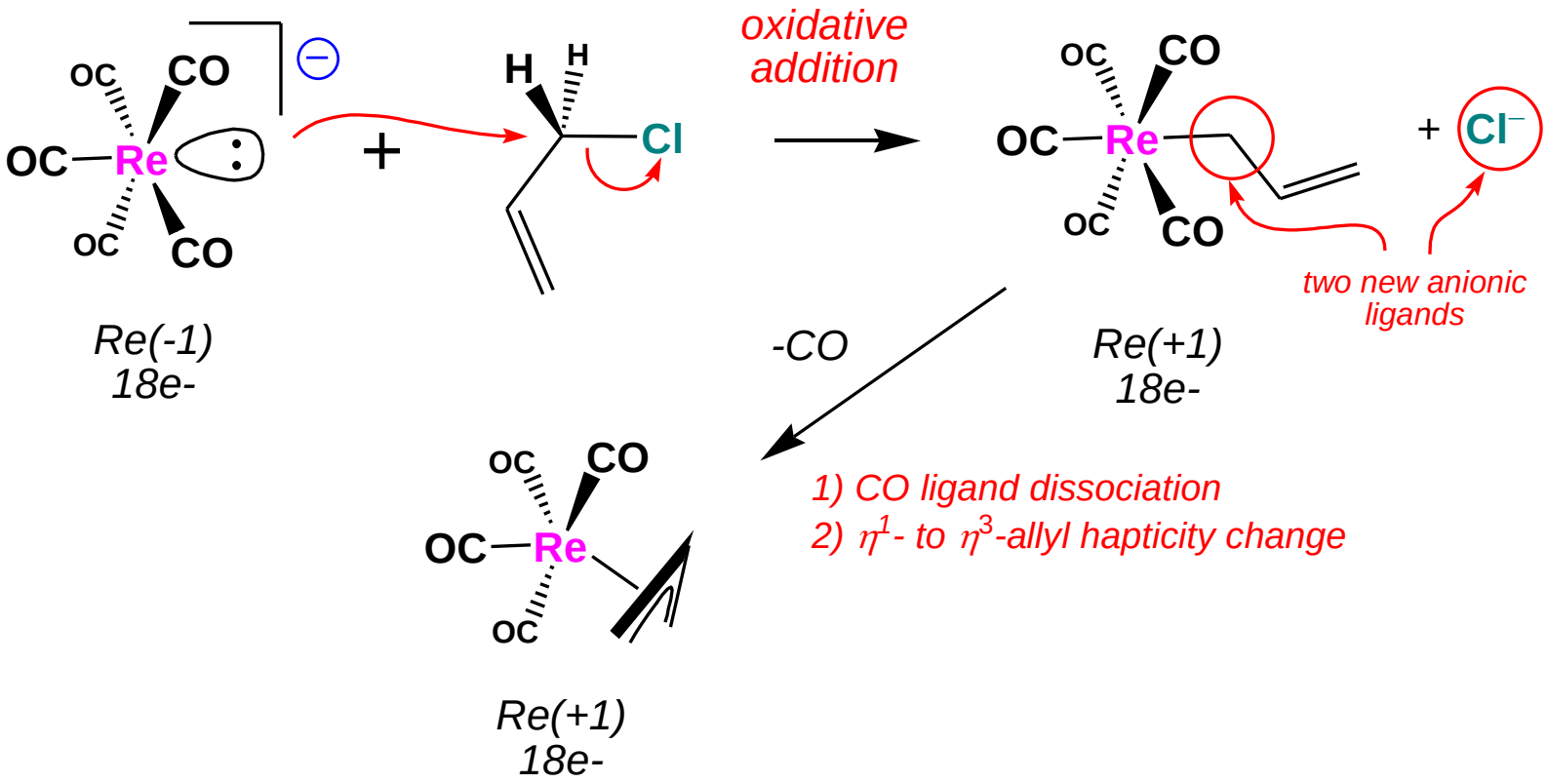
Electrophillic: these molecules ***do*** contain electronegative atoms and are good oxidizing agents. They are often considered to be *"reactive"* substrates.

These molecules do ***NOT*** require the presence of an **empty orbital** (18e- is OK) on the metal center in order to perform the oxidative addition rxn.

X_2 (X = Cl, Br, I), R-X, Ar-X, H-X, O_2, etc.



In the case of a starting **18e-** complex (shown below) only ***one*** of the two anionic ligands (usually the strongest binding) generated from the oxidative addition will end up coordinated to the metal unless a separate substitution reaction occurs.



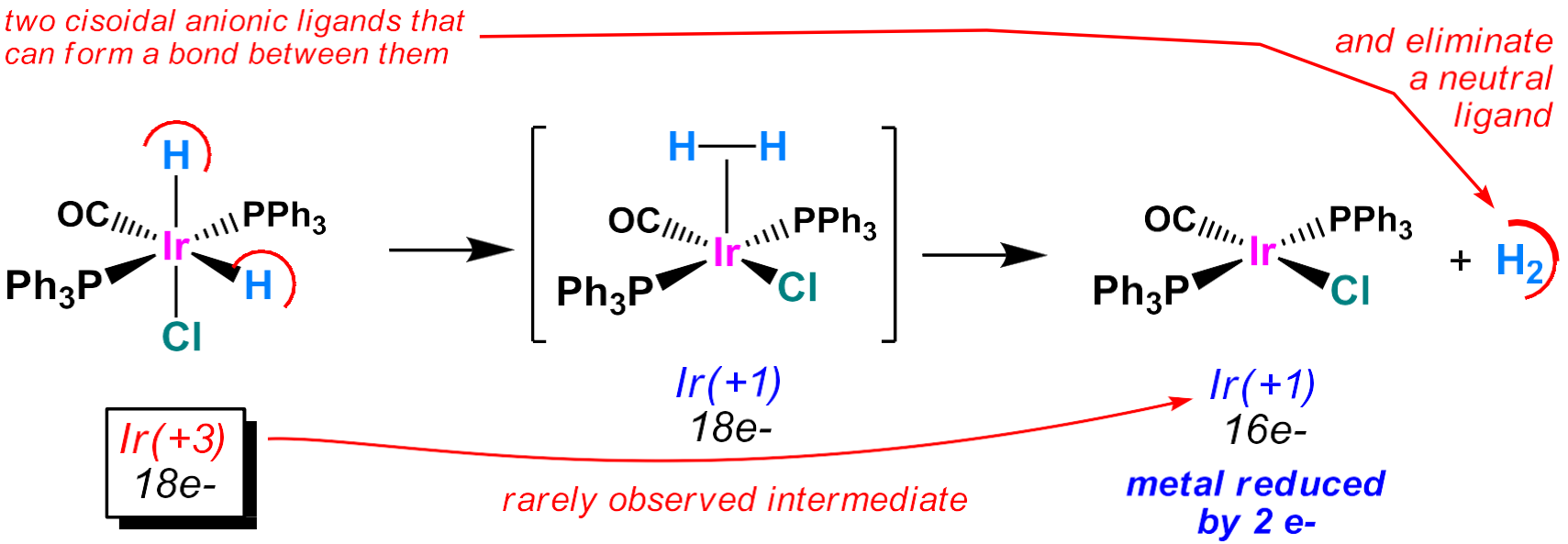
WARNING:

d^0 metals can ***NOT*** do ***oxidative additions***!!

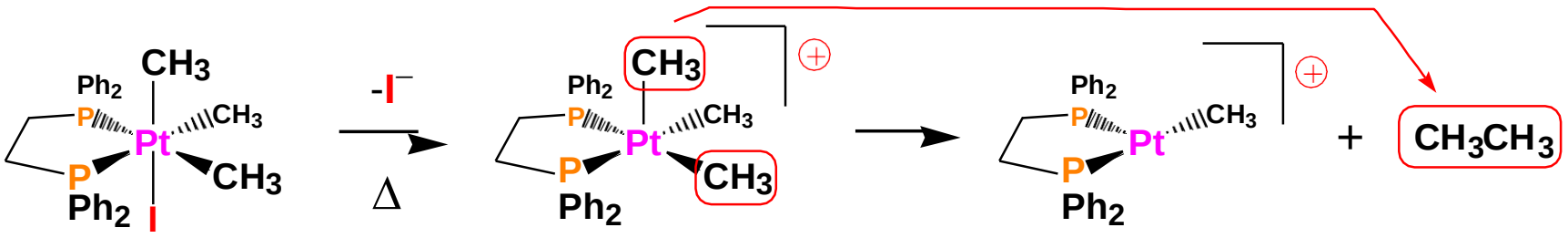
So always electron count the starting and final metal complexes to check out the overall electron-count, metal oxidation state and *d*-electron count!

Reductive Elimination

A ***reductive elimination*** reaction is the reverse of an oxidative addition. It is a reaction in which **two cisoidal anionic ligands** on a metal center couple together. Each anionic ligand pushes one electron back onto the metal center (in the case of a monometallic complex) to reduce it by 2e-. The coupled anionic ligands then usually fall off the metal center as a **neutral** molecule.



While reductive elimination can occur from saturated 18e- complexes (so long as the two ligands that you want to reductively eliminate are **cisoidal** to one another), it has been shown that reductive elimination can be promoted by a ligand dissociation generating an unsaturated and more electron-deficient metal center.

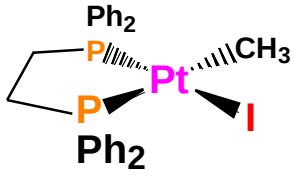


Pt(+4)
18e-

Pt(+4)
16e-

Pt(+2)
14e-

+I⁻

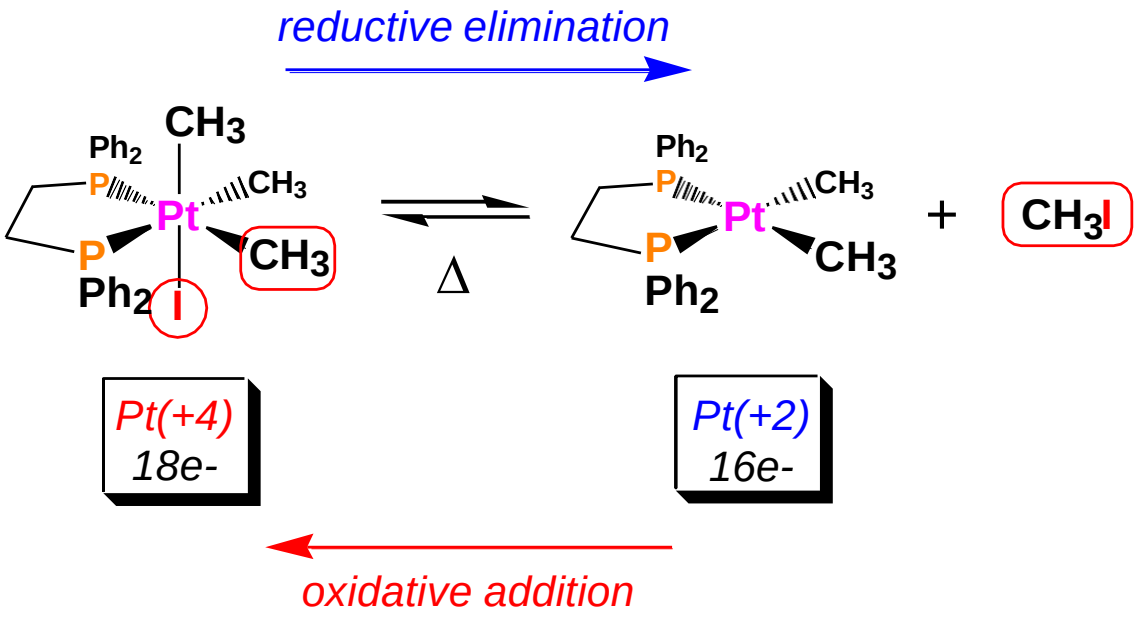


Pt(+2)
16e-

The dissociation of the I- generates a cationic unsaturated complex. This is electron deficient enough to help promote the reductive elimination of ethane (CH_3CH_3).

Goldberg, J. Am. Chem. Soc. ***1995****, 117, 6889-6896*

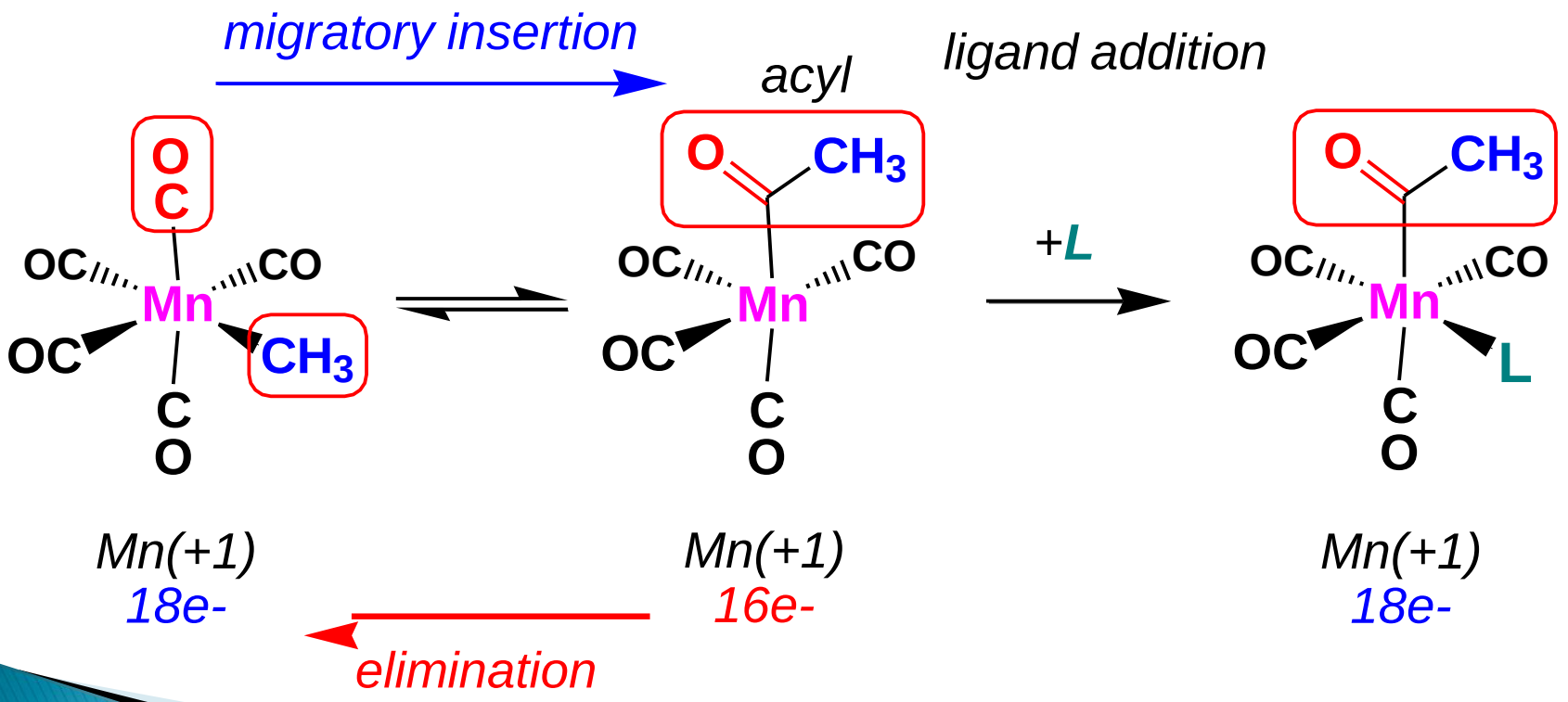
In studying the above system, it was also found that one could have reductive elimination of CH_3I from the starting 18e- complex. This reaction, however, is very reversible due to the high reactivity of CH_3I for doing an oxidative addition back reaction with the electron-rich neutral Pt(+2) complex to make the Pt(+4) octahedral compound.



The reductive elimination of the CH_3I is kinetically favored. This is because the orbitals around the iodide anion are spherically symmetric and this makes it much easier to overlap with the alkyl group orbital to perform the reductive elimination. The sp^3 directed orbitals on the two CH_3 groups are more difficult to overlap in order to get the reductive elimination to occur. But the reductive elimination of the CH_3CH_3 is thermo-dynamically considerably more favorable and the back oxidative addition much more difficult.

Migratory Insertion & Elimination Rxns

A ***migratory insertion*** reaction is when a **cisoidal anionic and neutral** ligand on a metal complex couple together to generate a new coordinated **anionic** ligand**.** This new anionic ligand is composed of the original neutral and anionic ligands now bonded to one another.***There is <u>NO</u> change in the oxidation state or d electron-count of the metal center.***



General Features of Migratory Insertions:

1) No change in formal oxidation state (exception: alkylidenes)

2) The two groups that react must be cisoidal to one another

3) A vacant coordination site is generated by the migratory insertion. Therefore, a vacant site is required for the back elimination reaction (e.g., β-hydride elimination). A trapping ligand is often needed to coordinate to the empty site formed from a migratory insertion in order to stop the back elimination reaction.

4) Migratory insertions are usually favored on more electron-deficient metal centers.

The following are common **anionic** and **neutral** ligands that can do ***migratory insertion*** reactions with one another:

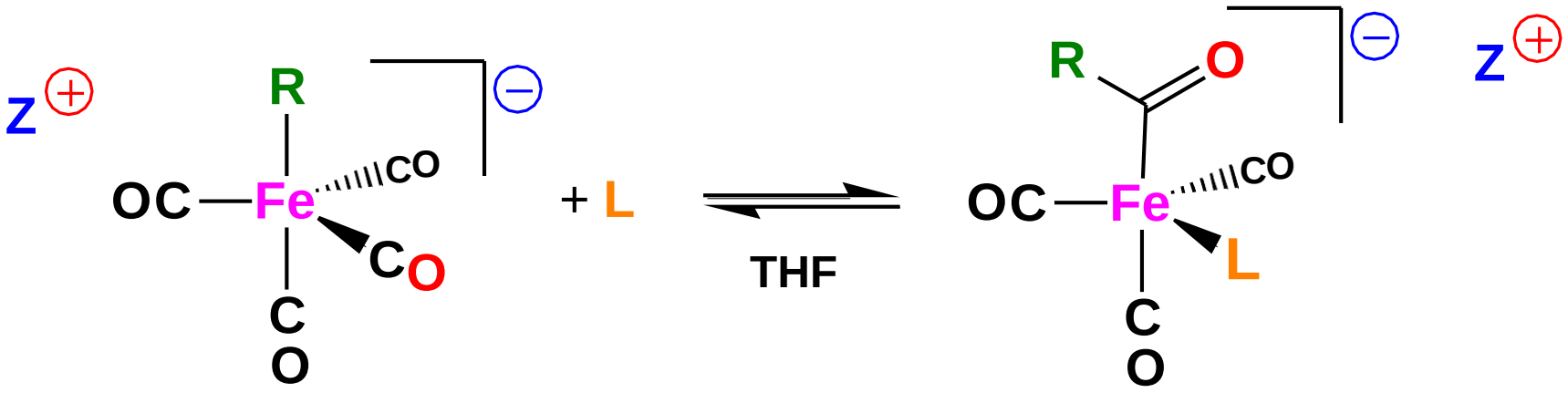
Anionic: H^-, R^- (alkyl), Ar^- (aryl), $acyl^-$, O^{2-} (oxo)

Neutral: CO, alkenes, alkynes, carbenes

CO and alkyl migratory insertions (as shown on previous slide) are extremely important and are often generically referred to as **carbonylation** reactions.

Hydride and CO migratory insertions to produce formyl groups are not common due to the *thermodynamic instability* of the formyl-metal interaction.

Some Electronic effects



best Lewis acid - can coordinate to electron-rich CO ligands and drain off some e- density

Z^+ = Li^+ > Na^+ > $(Ph_3)_2N^+$

strongest coordinating ligand - best trapping ligand

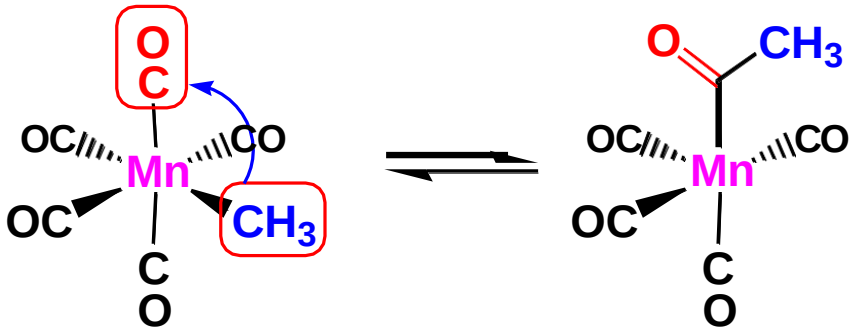
L = PMe_3 > $PPhMe_2$ > PPh_2Me > CO

most electron-rich alkyl group makes the best nucleophile for migrating to the electron-deficient CO

R = n-alkyl$^-$ > $PhCH_2^-$

Migration vs. Insertion

Migration

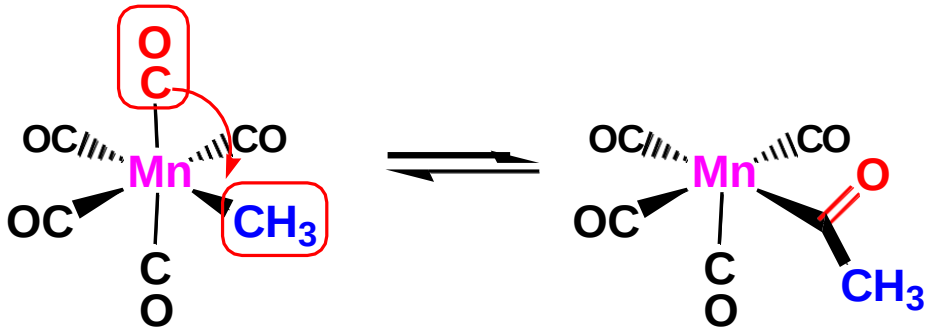


Mn(+1)
18e-

Mn(+1)
16e-

a MIGRATION rxn involves the anionic ligand doing a nucleophillic-like attack on the neutral ligand. This involves the anionic ligand moving to the site where the neutral ligand is coordinated. An empty coordination site is left behind.

Insertion

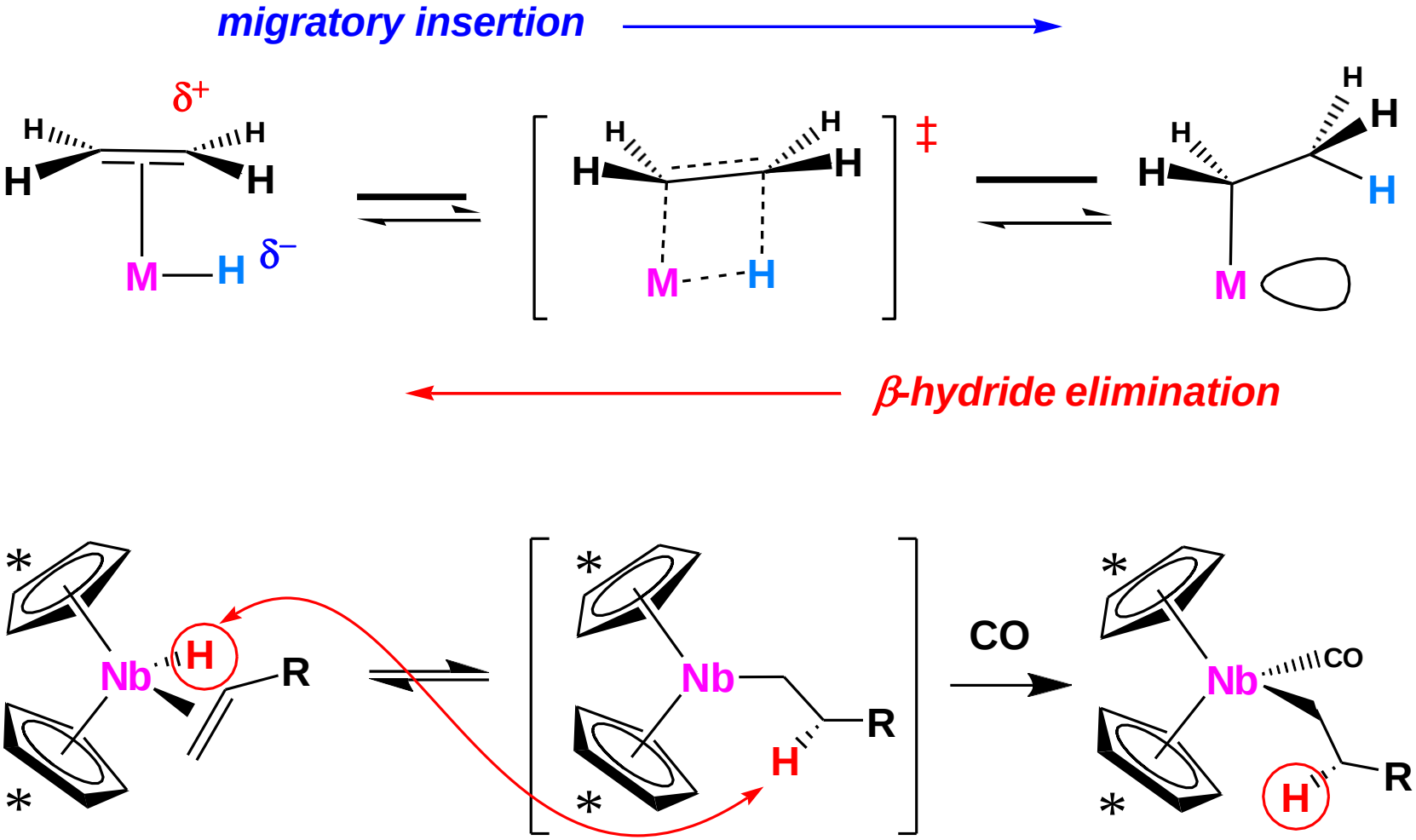


Mn(+1)
18e-

Mn(+1)
16e-

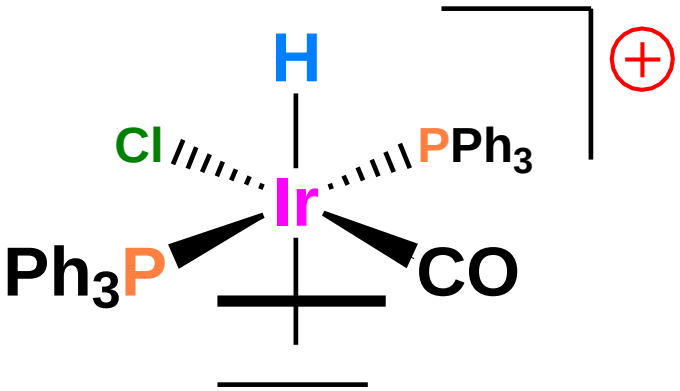
an INSERTION rxn involves the neutral ligand moving over to where the anionic ligand is coordinated and "inserting" into the anionic ligand-metal bond to generate the new anionic ligand. An empty coordination site is left behind from where the neutral ligand originally was located.

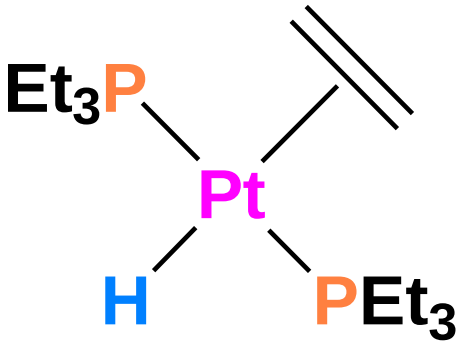
Alkene Migratory Insertion – β-Hydride Elimination



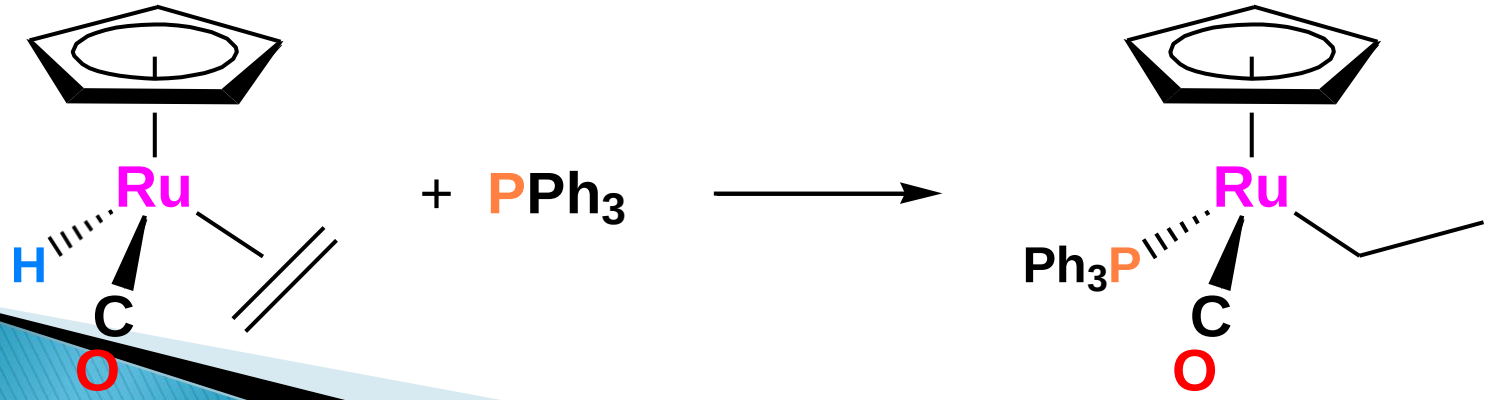
NMR irradiation of the Nb-hydride resonance affects the NMR resonance for the alkyl hydride, demonstrating that they are connected by the migratory insertion mechanism

Problem: **Why don't either of the complexes shown below do alkene-hydride migratory insertions at room temperature?**

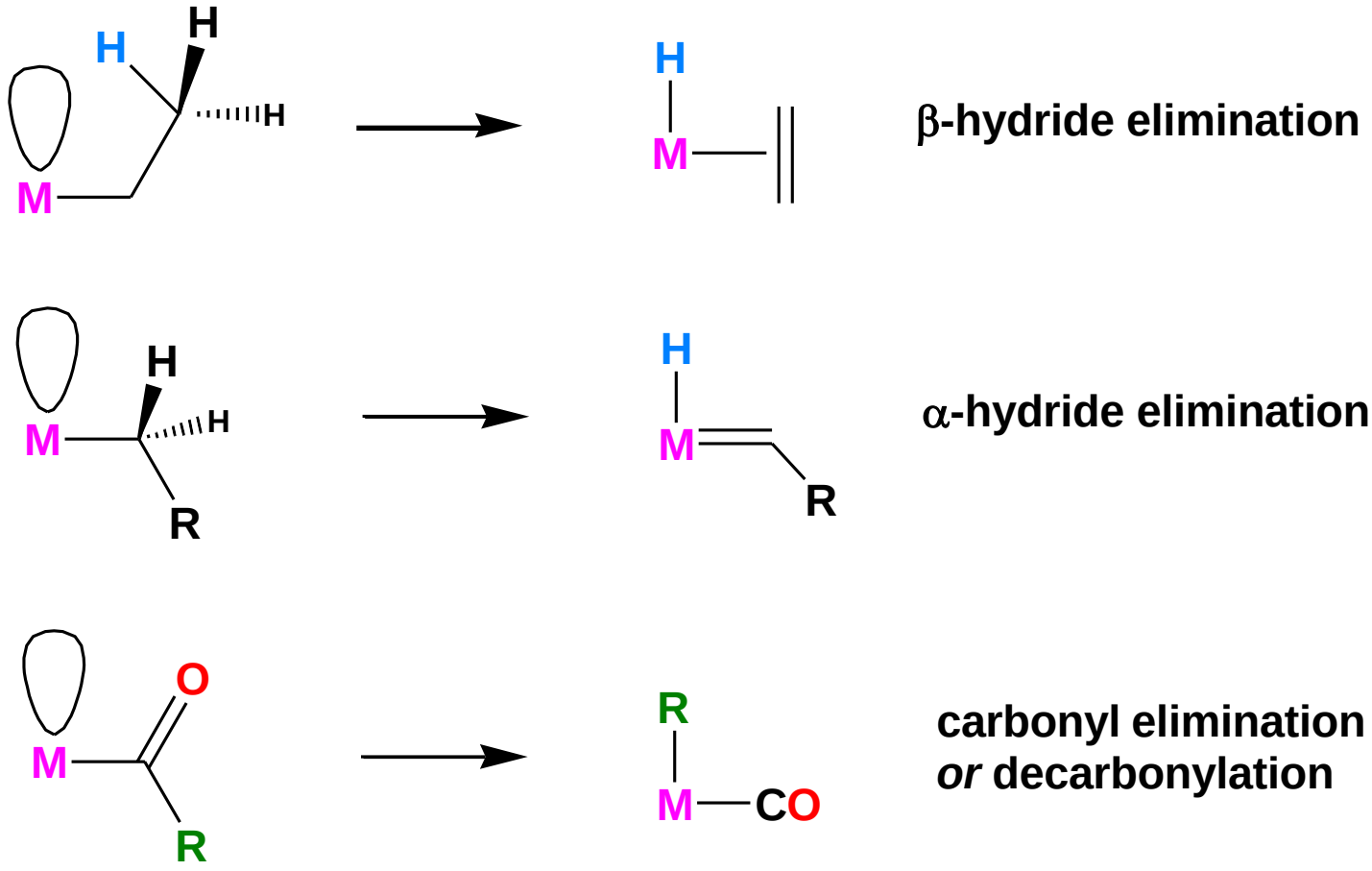




Problem: **Sketch out and label the two mechanistic steps (in the correct order) that are occurring for the following reaction.**



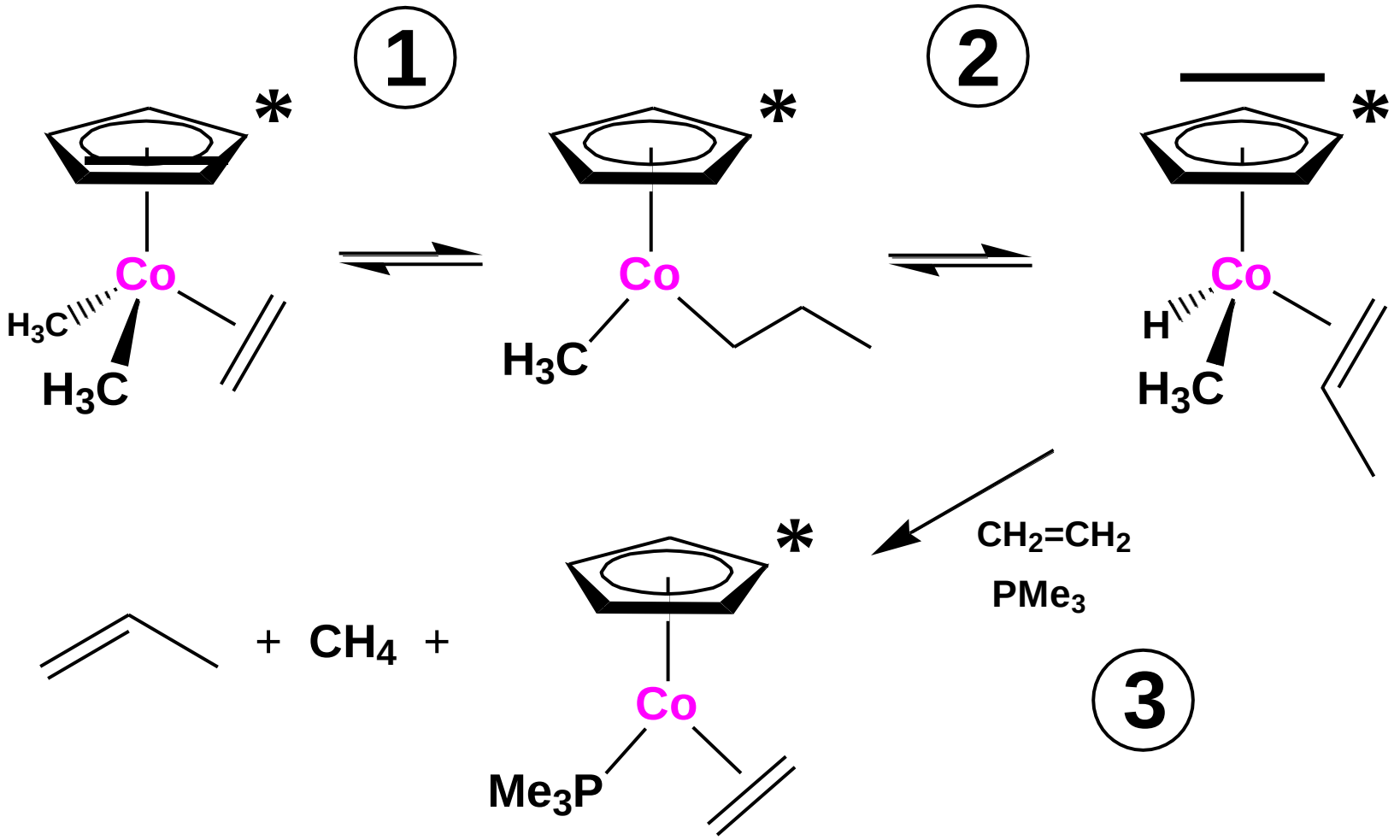
Eliminations



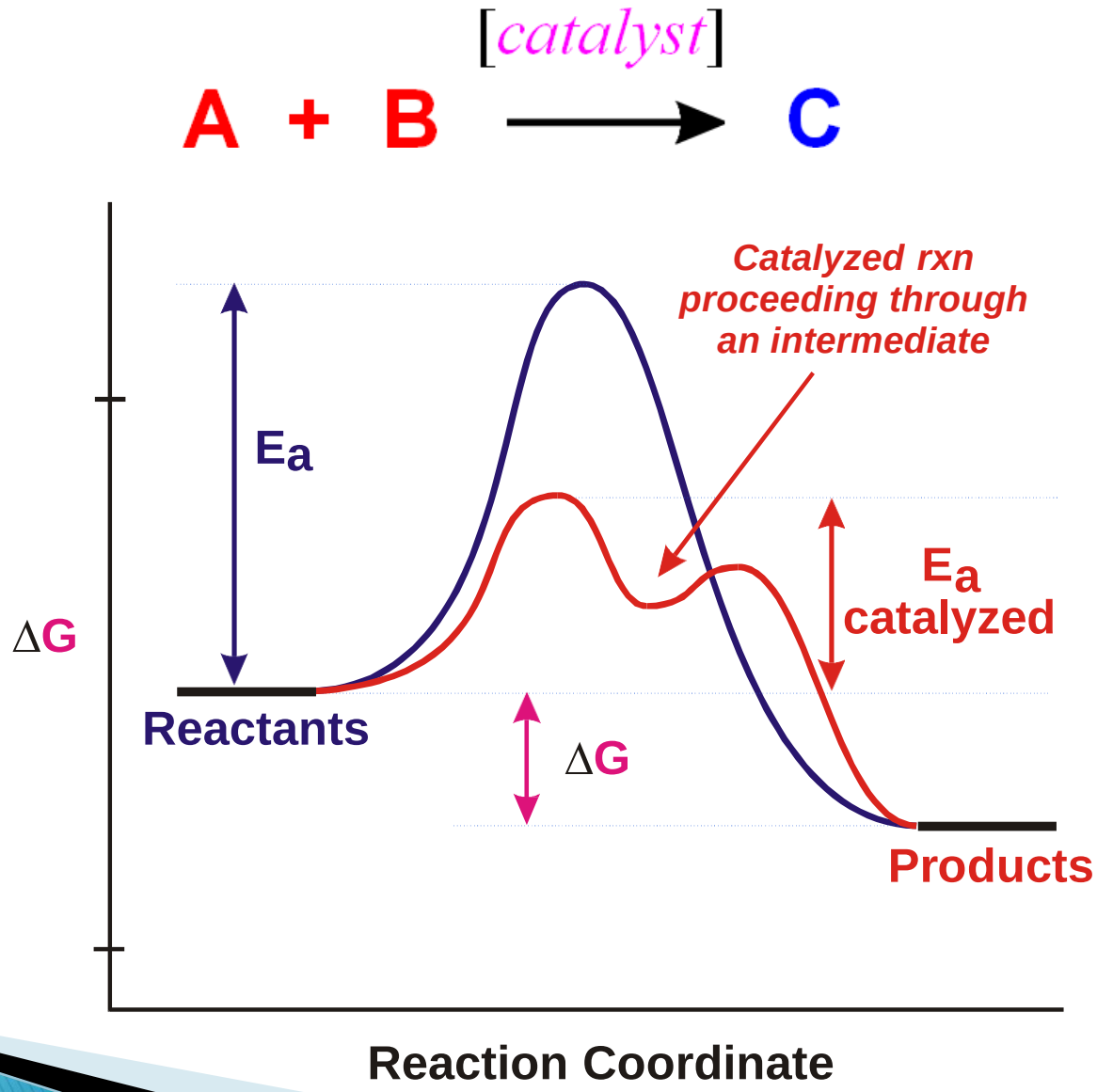
The key points are:

1) **No change in formal oxidation state (exception: alkylidenes)**
2) **You must have an empty orbital that is cisoidal to the group that you are doing an elimination reaction on. Alternatively, a cisoidal labile ligand that can easily dissociate to open up an empty orbital.**

Problem: **Identify each step in the following mechanism. Some steps may have several things occurring.**



Homogeneous Catalysis - Introduction



Advantages/Disadvantages of Homogeneous Catalysts Relative to Heterogeneous Catalysts

Good **homogeneous** catalysts are:

Good generally far more selective for a single product

far more active

far more easily studied from chemical & mechanistic aspects

far more easily modified for optimizing selectivity

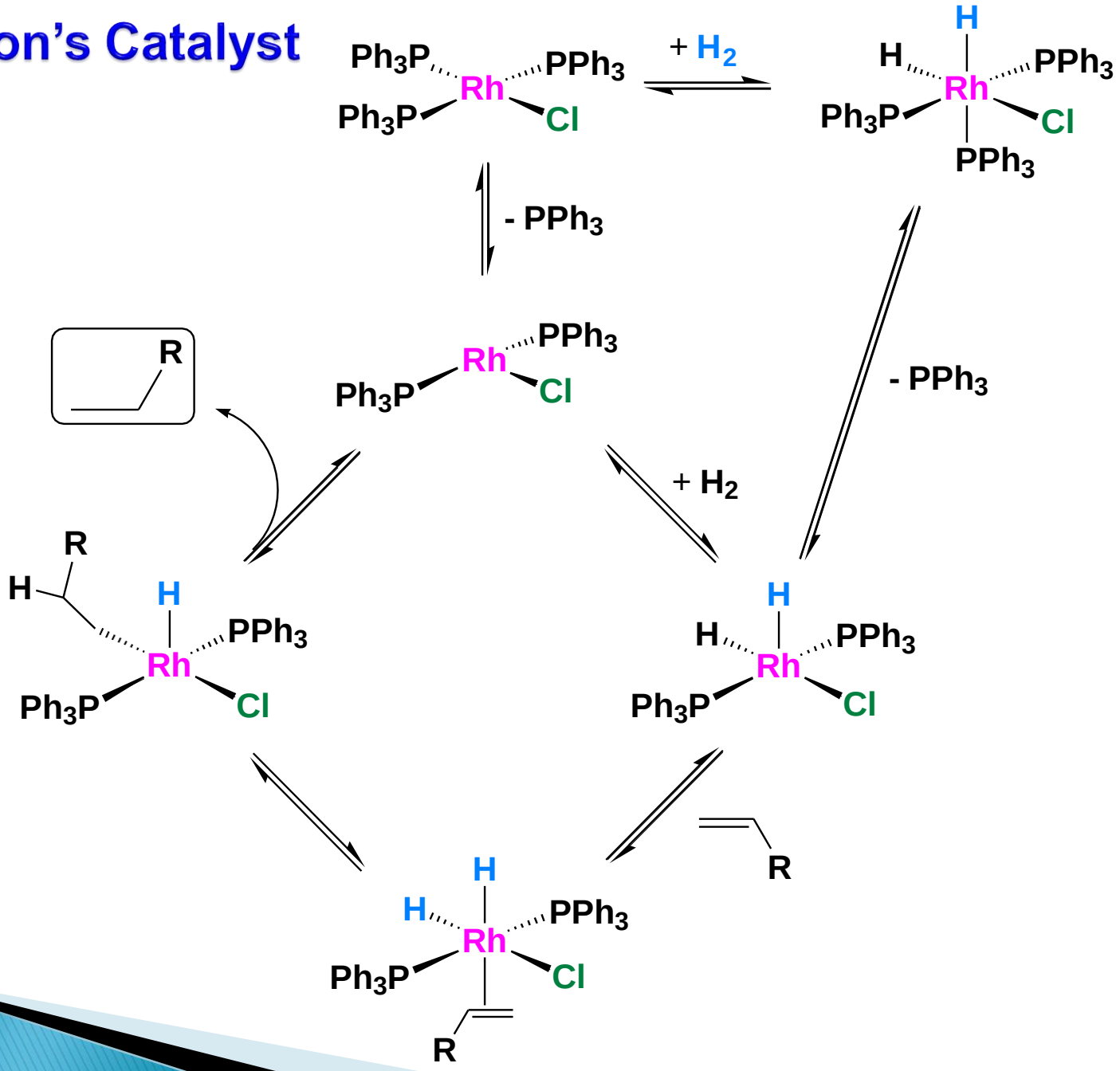
Bad far more sensitive to permanent deactivation

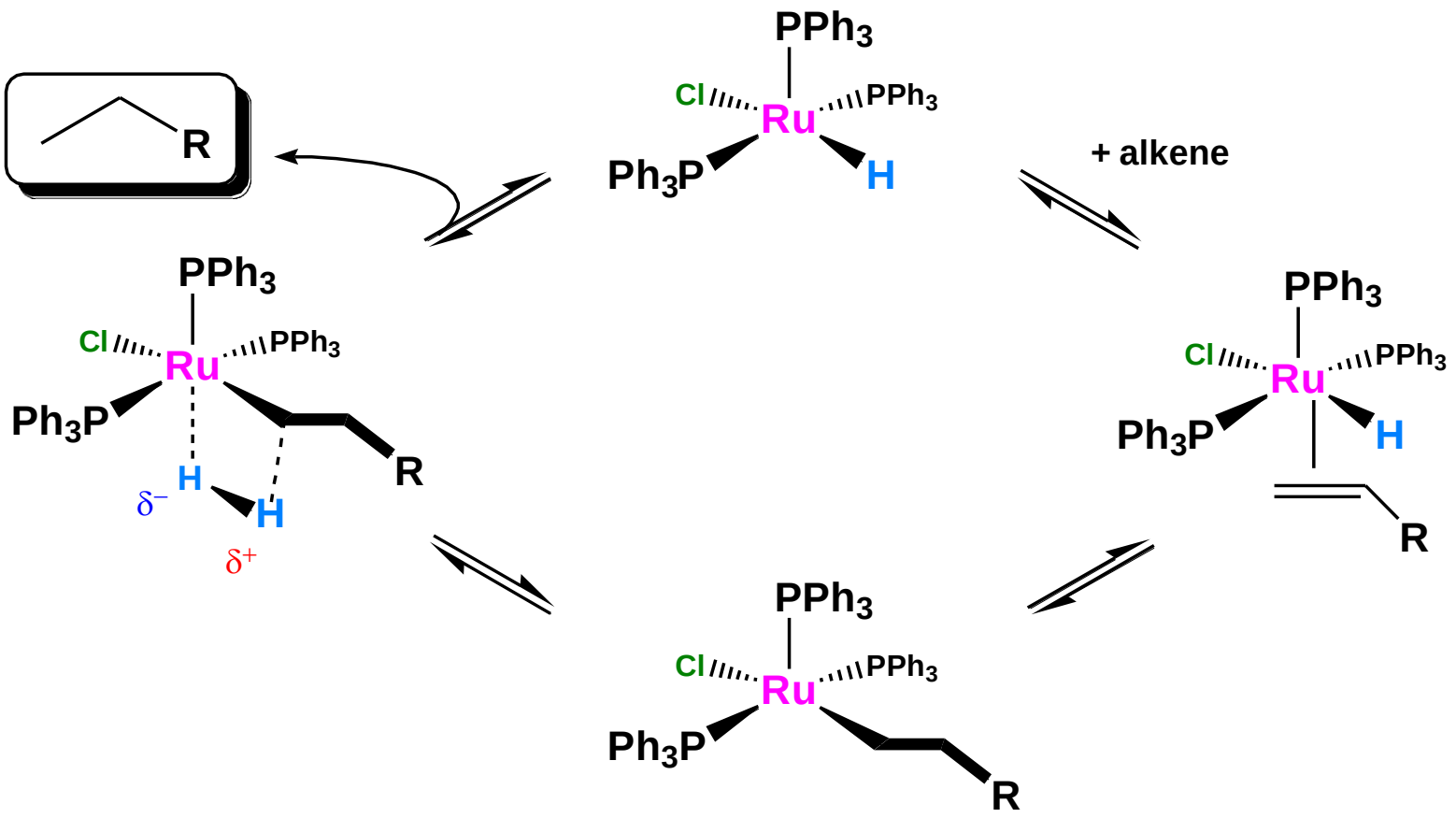
far more difficult for achieving product/catalyst separations

Heterogeneous catalysts dominate chemical and petro•chemical industry: ~ 95% of all chemical processes use ***heterogenous*** catalysts.

Homogenous catalysts are used when ***selectivity*** is critical and product-catalyst ***separation problems*** can be solved.

Wilkinson's Catalyst

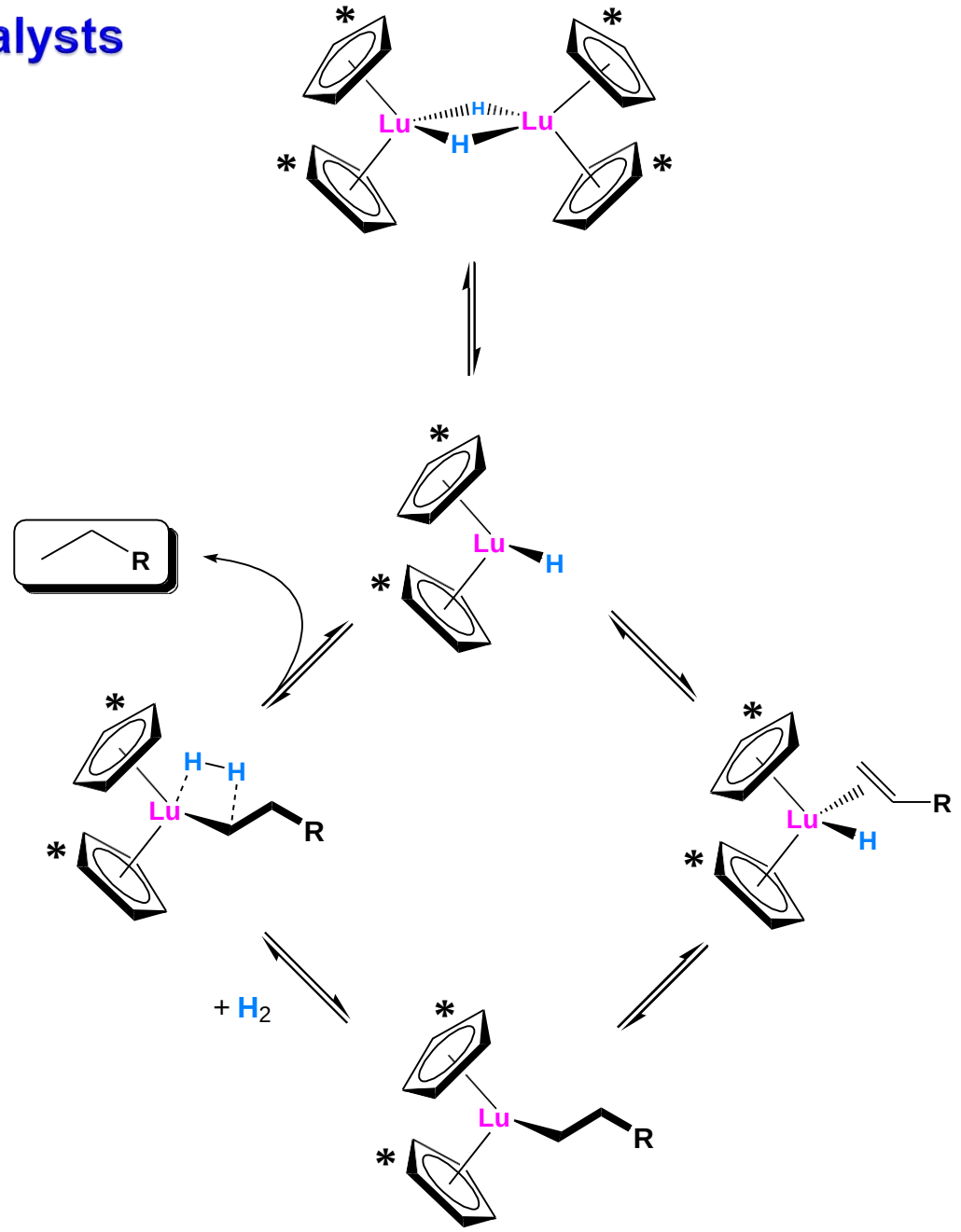



R
PPh3
Cl
Ru
PPh3
Ph3P
H
+ alkene
PPh3
Cl
Ru
PPh3
Ph3P
H
δ−
H
H
δ+
R
PPh3
Cl
Ru
PPh3
Ph3P
H
R
PPh3
Cl
Ru
PPh3
Ph3P
R

Lanthanide Hydrogenation Catalysts

Tobin Marks reported the extraordinary activity of $(Cp^*_2LuH)_2$ for the hydrogenation of alkenes and alkynes. The monometallic complex catalyzes the hydrogenation of 1-hexene with a TOF = 120,000 hr^{-1} at 1 atm H_2, 25ºC!!

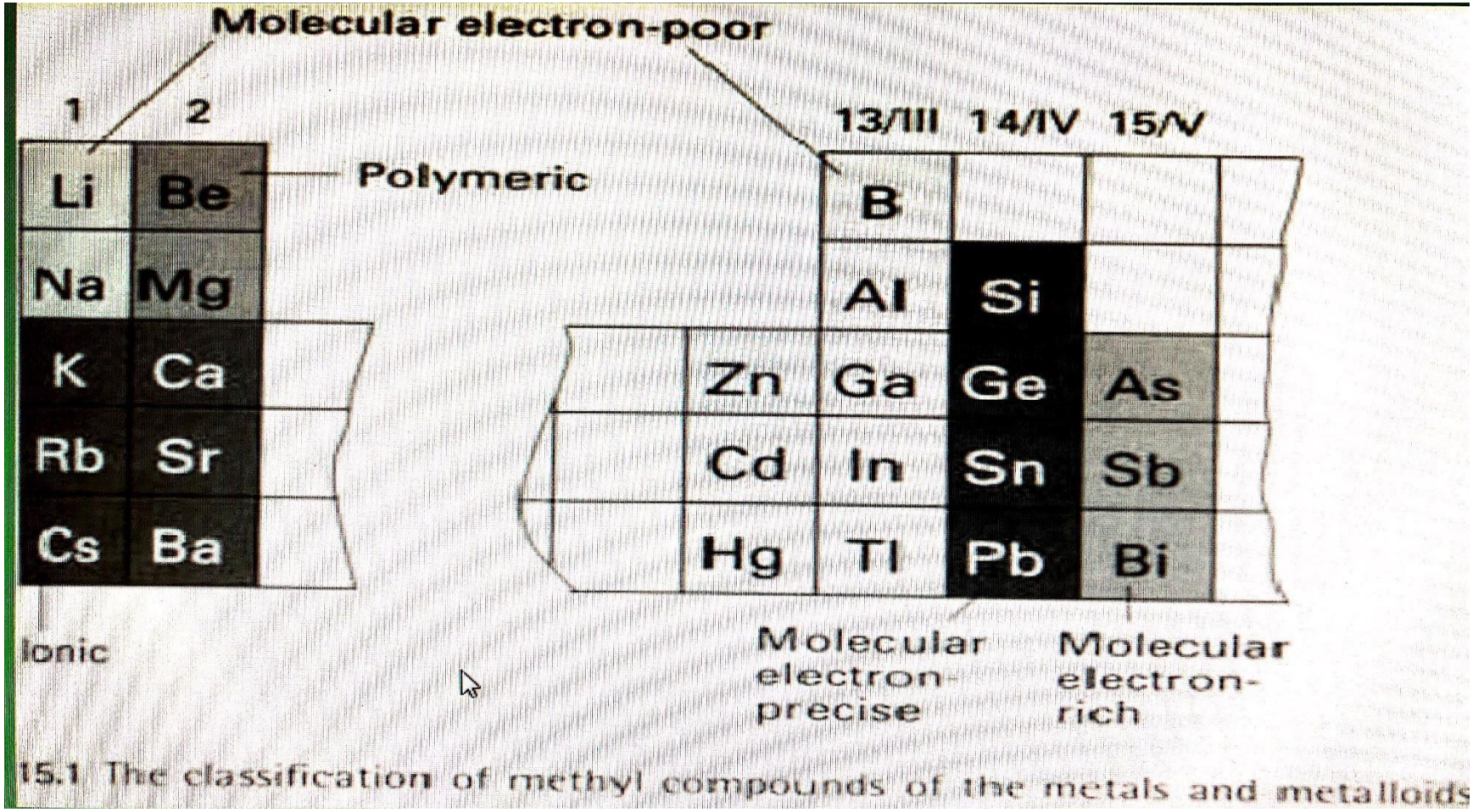
This is one of the most active hydrogenation catalysts known.



Main Group Organometallic Compounds

- Classification Based on type of metal-carbon bond •
- Ionic – most electropositive elements •
- Covalent –
- electron deficient: metals with less than half filled valency shells, form strongly polarizing cations –
- electron precise –
- electron rich

Classification



15.1 The classification of methyl compounds of the metals and metalloids

Main Group Metal–Carbon Bond Formation

- Reaction of metal with organic halogen compounds
- 2M + nRX → RnM + MXn (orRxMXy where x+y=n)
- Suitable for synthesis of organometallic compounds of the most electropositive elements.
- Metal exchange
- M + RM → RM + M
- Dependent on the difference in free energies of formation of the two species RM′ and RM Main Group Metal-Carbon Bond Formation
- Endothermic or weakly exothermic organometallic compounds should be the most versatile reagents RM′ in such reactions (ie compounds of Hg, Tl, Pb, Bi)

Main Group Metal–Carbon Bond Formation

Reactions of organometallic compounds with metal halides

- Most widely used and versatile of all laboratory methods

$$RM + MX \rightarrow RM + MX$$

- Organolithium and Grignard reagents most commonly used

- **Insertion of alkenes and alkynes into metal or nonmetal hydride bonds Hydroboration**

$$RCH{=}CH_2 + HB \Longrightarrow RCH_2CH_2B$$

Organolithium Compounds

- Small size and polarizing power of Li+ causes its compounds tohave more covalent character than other group members

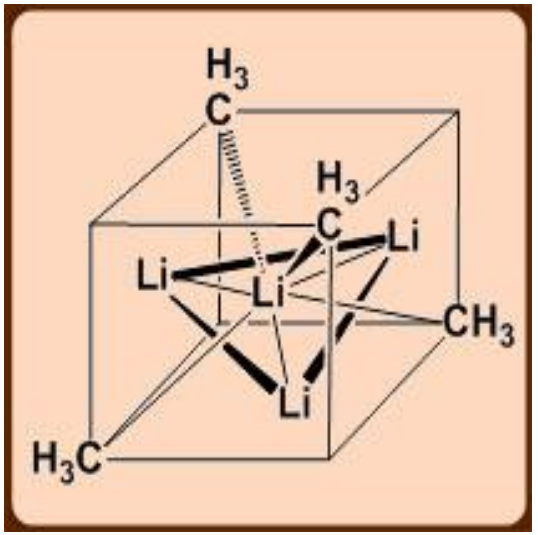
- Organolithium compounds more stable and less reactive than other organocompounds of group 1
- – Due to lower polarity

- Valuable in chemical synthesis due to:

- • High reactivity
- • Relatively easy preparation
- • Solubility in inert solvents
- • Used for the same kinds of synthesis as Grignard reagents

Organolithium Compounds

- Polar character causes strong association
- Geometry of coordination sphere is determined by steric effects (as in ionic structures) rather than
- interaction of electron pairs.
- Eg. Methyllithium consists of tetrameric aggregates
- in solid state and in solution $Li_4(CH_3)_4$



Organolithium Compounds

- Lithium alkyls
- Extremely reactive
- Sensitive to oxygen and moisture
- Dry apparatus and solvents must be used
- Air must be excluded (reactions carried out under argon or nitrogen

Organolithium Compounds

- Preparation:

- Metal–metal exchange (transmetallation)
- $2Li + HgR_2 \rightarrow 2LiR + Hg$ (Dry N_2, hydrocarbon solvent)

- Convenient route to vinyl and allyllithium compounds

- $4PhLi + (H_2C{=}CH)_4Sn \rightarrow 4H_2C{=}CHLi + Ph_4Sn$

- Metal – halogen exchange (halide abstraction)

- $RLi + PhI \rightarrow RI + PhLi$

Organolithium Reactivity

- Nucleophilic attack on multiple bonds

$$RLi + R'C{\equiv}CH \rightarrow LiC{\equiv}CR'$$

- React with aldehydes and ketones to form alcohols

$$RLi + R'CHO + H2O \rightarrow RCH(OH)R' + LiOH$$

- Carboxylic acid salts and acid chlorides to form ketones (after hydrolysis)

Organolithium Reactivity

- Reaction with halogens
  - $LiR + X_2 \rightarrow RX + LiX$ (Reduction)

- Addition Reactions
  - $BR_3 + LiR \rightarrow LiBR_4$

- Halide abstraction (nucleophilic substitution)
  - $LiR + BCl_3 \rightarrow BR_3 + 3LiCl$

- Proton abstraction (acid–base reaction)
  - $Li^{\delta+}\,{}^{-\delta}Bu + C_6F_5H \rightarrow BuH + C_6F_5Li$

Grignard Reagents

- Alkyl or aryl magnesium halides RMgX.
- Most important organometallic compounds.
- Commonly used in organic and inorganic synthesis
- Act as nucleophiles
- React readily with protic solvents and compounds with acidic protons

Grignard Reagents – Synthesis

- Action of alkyl or aryl halide on Mg
- $RX + Mg \rightarrow RMgX$
- Must be carried out in absence of moisture and oxygen
- polar aprotic solvent eg. diethyl ether or THF; inert atmosphere
- Reactivity of RX with Mg:
- $I > Br > Cl > F$
- Monomeric species exist in dilute solutions and in strong donor solvents
- In diethyl ether at high Mg concentrations, polymeric species exist
- Structure normally includes the solvent

Grignard Reagents

- Solution equilibria
  - Variety of species present in solution
  - Equilibria position dependent on

    - Steric and electronic nature of alkyl or aryl group
    - Nature of the halogen (size, electron donor power)
    - Nature of the solvent

    - Concentration
    - Temperature
    - Presence of impurities

Reactions

- Reaction with acid

- $RMgX + HX \rightarrow RH + MgX_2$

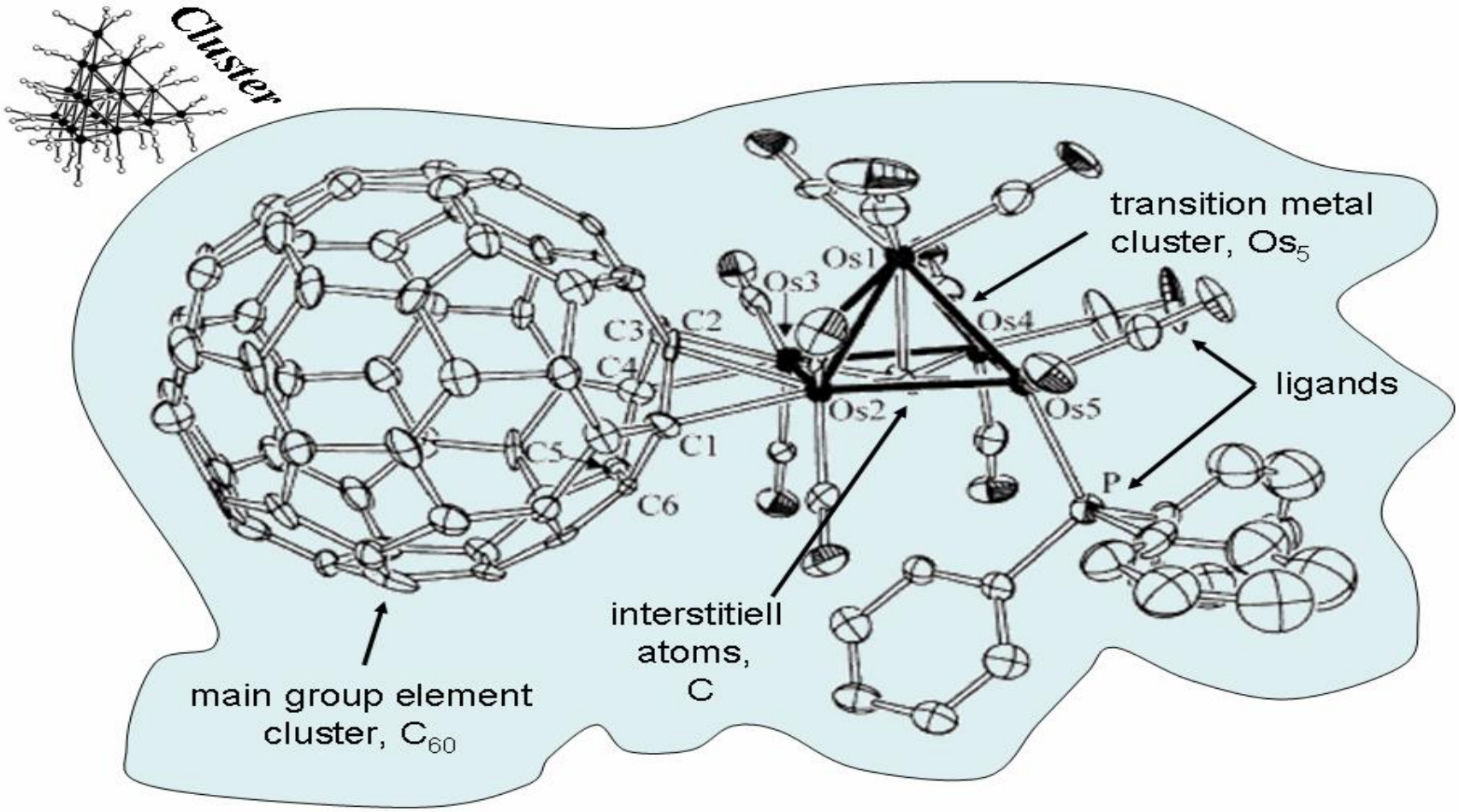
- Reaction with halogen

- $RMgX + X_2 \rightarrow RX + MgX_2$

- Reactions with halides

- $RMgX + BCl_3 \rightarrow BR_3$
- $RMgX + SnCl_4 \rightarrow SnR_4$

organometallic cluster

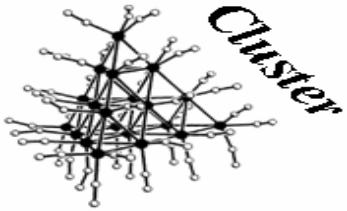


Electrons ⇦⇨Structure ⇦⇨ Stability ⇦⇨ Reactivity

1

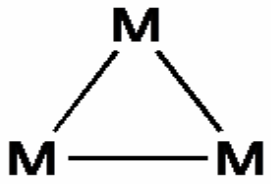
Angew. Chem. Int. Ed. 2000, 39, 1801

organometallic cluster



Definitions

Aggregation of at least three directly bonded metal atoms of the same or similiar type:

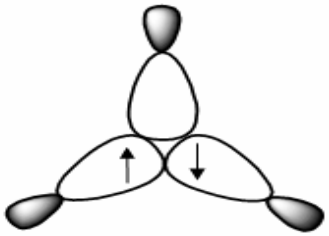


Closo cluster:
The cluster polyhedron has one shell and a closed and convex structure.

Deltahedron:
The cluster polyhedron has only triangular faces (from the greek letter Δ).

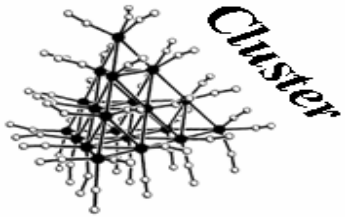
Electron precise cluster:
Each edge in the polyhedron represents a 2-center-2-electron bond (*2c2e*-bond).
Each cluster atom M reaches the 8 (M = main group element) or 18 (M = transition metal atom) valence electron configuration.

Electron deficient cluster:
a) Cluster with one 3-center-2-electron bonds (*3c2e*-bond) per M_3-triangle.
b) Cluster following the ***Wade-Mingos*** rules.



Cluster falling out of these two categories.

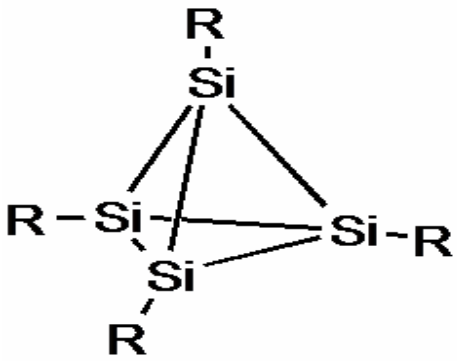
organometallic cluster



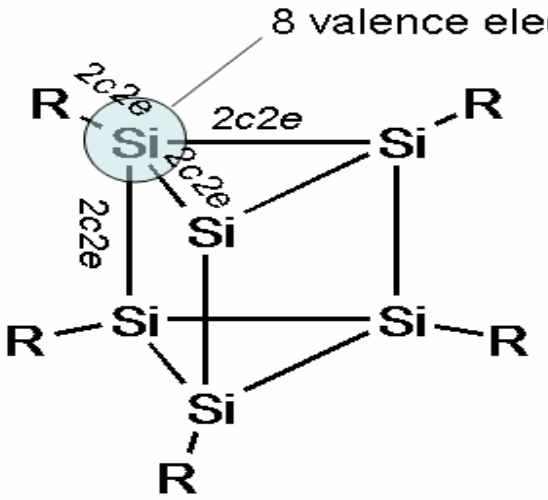
Electron precise cluster

Main group element cluster

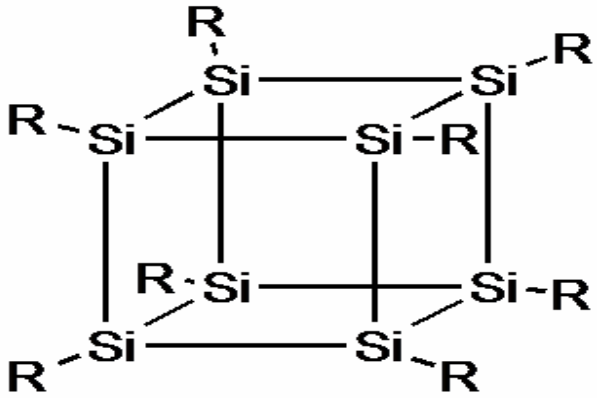
Examples:



tetrasilatetrahedrane

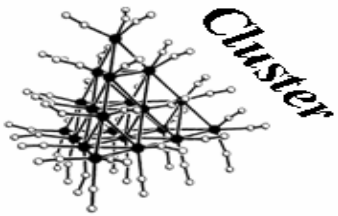


hexasilaprismane



octasilacubane

organometallic cluster



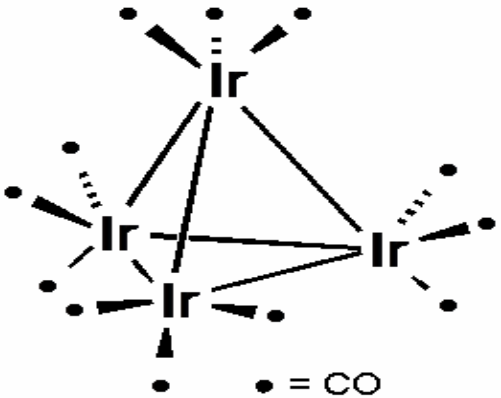
Electron precise cluster

Transition metal cluster:

Electron counting rules:

- Each cluster edge corresponds to a *2c2e* bond.
- Further electrons are provided by the cluster external ligands
- Uncharged metal atoms and uncharged ligands are assumed (covalent binding model).
- *Main group elements tend to obtain 8, transition metals 18 valence electrons*.

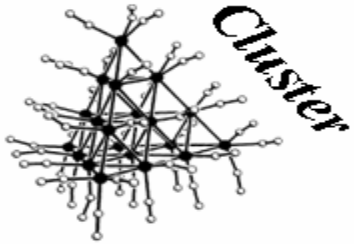
Example:
$[Ir_4(CO)_{12}]$



Electron count for each iridium atom:

Ir(0), d^9:	9 electrons
3 × CO:	6 electrons
3 × Ir-Ir bond:	3 electrons
total	18 electrons/Ir

organometallic cluster



Electron precise cluster

The ***Effective-Atomic-Number***-(EAN)-Rule:
gives the number of M-M bonds within the cluster

Main group element cluster:

b = ½ (8m – VEC)

Transition metal cluster:

b = ½ (18n – VEC)

Mixed cluster:

b = ½ [(8m +18n) – VEC]

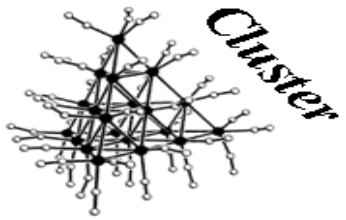
b = number of ***2c2e*** bonds = number of cluster ***edges***;

VEC = total **V**alence **E**lectron **C**ount of the cluster skeleton;

m = number of main group element atoms in the cluster frame work;

n = number of transition metal atoms in the cluster frame work;

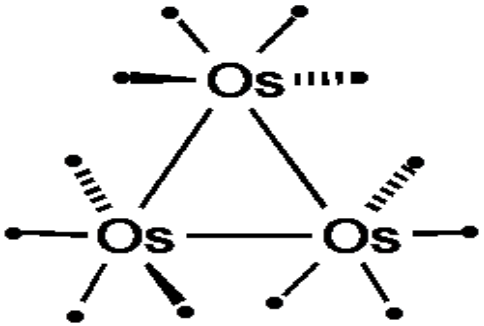
organometallic cluster



Electron precise cluster

The ***Effective-Atomic-Number***-(EAN)-Rule

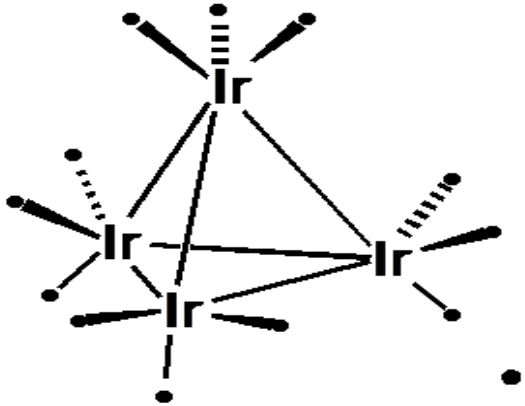
Examples (1):



electron counts:

3 × Os(0), d^8:	24 e
12 × CO:	24 e
VEC:	48 e

b = ½ [(18 × 3) – 48] = 3



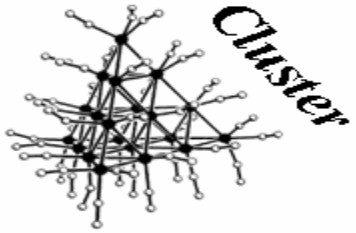
● = CO

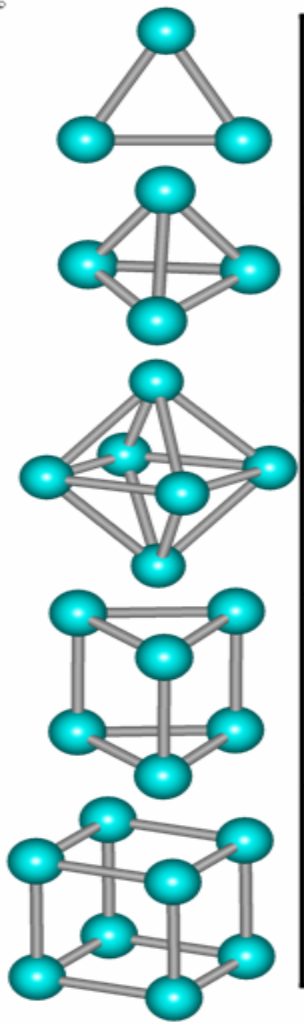
electron counts:

4 × Ir(0), d^9:	36 e
12 × CO:	24 e
VEC:	60 e

b = ½ [(18 × 4) – 60] = 6

organometallic cluster

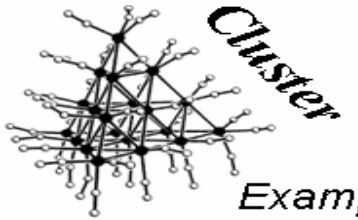




Valence Electron Counts, VEC

main group elements	transition metals
18	48
20	60
–	84
30	90
40	120

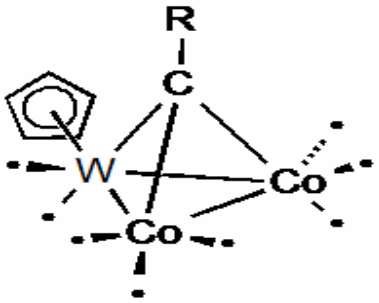
organometallic cluster



Electron precise cluster

The ***Effective-Atomic-Number***-(EAN)-Rule

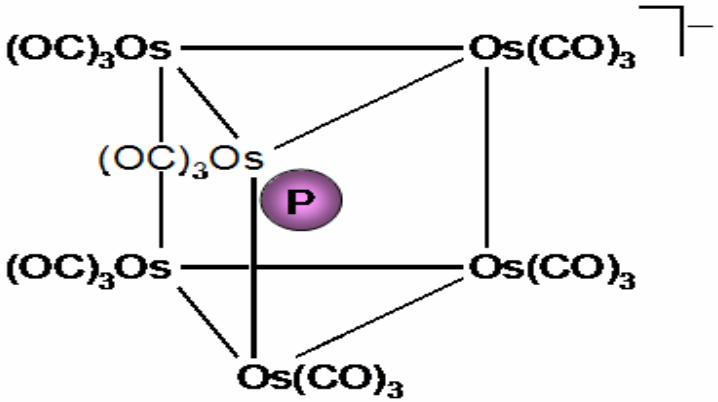
Examples (2):



electron counts:

1 × C:	4 e
2 × Co(0), d^9:	18 e
1 × W(0), d^6:	6 e
8 × CO:	16 e
1 × R:	1 e
1 × η^5-C_5H_5 (Cp):	5 e
VEC:	50 e

b = ½ [(18 × 3) + (1 × 8) – 50] = 6



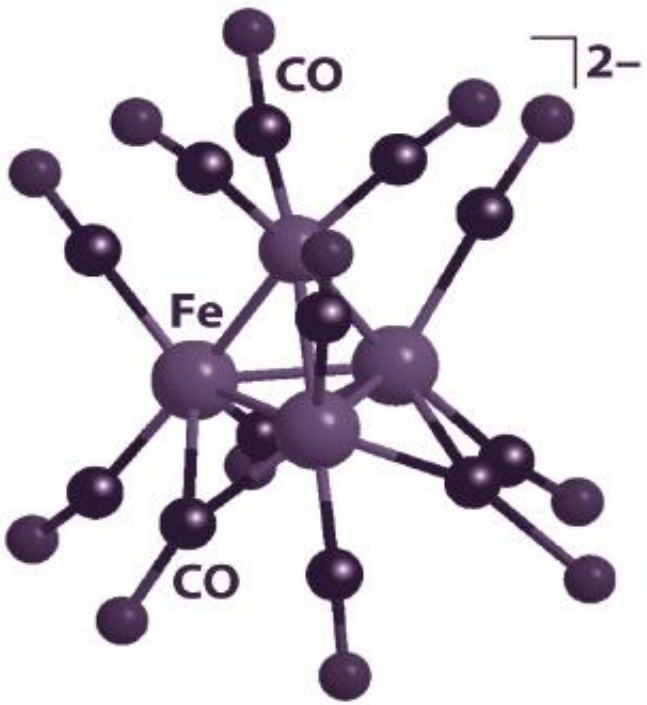
electron counts:

6 × Os(0), d^8:	48 e
18 × CO:	36 e
1 × P:	5 e
1 × neg. charge:	1 e
VEC:	90 e

b = ½ [(18 × 6) – 90] = 9

organometallic cluster

- Problems on clusters:
- $Os_5(CO)_{13}$
- $Os_6(CO)_{16}$
- $Co_4(CO)_{12}$
- $Os_3Ni_3Cp_3(CO)_9$
- $Ru_2Co_2(CO)_{13}$



3 $[Fe_4(CO)_{13}]^{2-}$

Structure 21-3
Shriver & Atkins Inorganic Chemistry, Fourth Edition

organometallic cluster

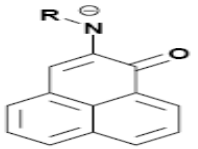
- Sketch out a structure showing the geometry about the metal center as accurately as possible and clearly show the electron counting for the complexes below. Phosphine ligand abbreviations are defined in your notes (see the phosphine ligand section).

i) $[CpFe(C_6H_6)]^+$

j) $Cp_2Nb(CH_3)(CH_2{=}CH_2)$

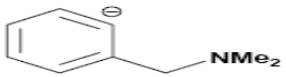
k) $CpOs(H)(Cl)(SiMe_3)(PR_3)$

l) $NiPh(PPh_3)(N{\sim}O)$ N~O ligand shown below



m) *cis*-$Re(CO)_3(bipy)(NR_2)$ bipy = bipyridine

n) $[Ru(C_6H_6)(C{\sim}N)(N{\equiv}CCH_3]^+$ C~N below



o) $Cp_2Fe_2(\mu\text{-}C{\equiv}C)(CO)_4$

p) $[Cp_2Fe]^+$

q) $(C_6H_6)Cr(CO)_3$

r) $Co_2(\mu\text{-}CO)_2(CO)_6$

Conclousion