

# Fundamentals You Need to Know:

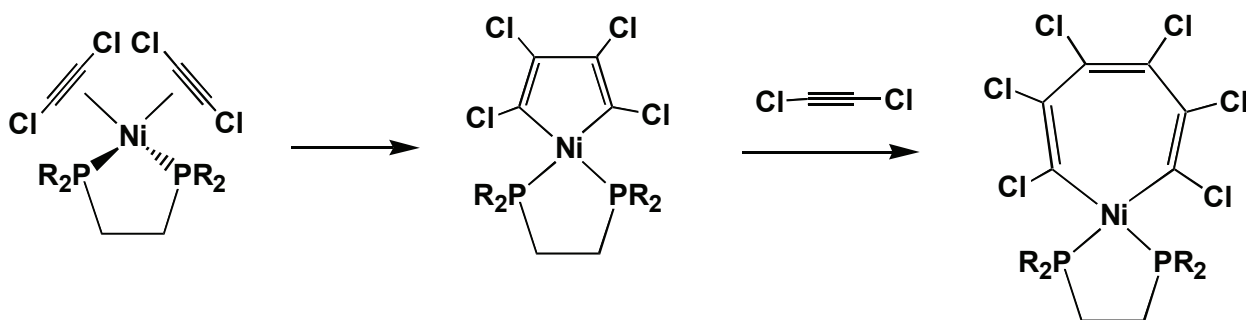
## 1. Electronegative/Electropositive concepts

Where do the positive and negative partial charges in a molecule reside? This is important for determining how much e- density will be donated from a ligand to a metal and where a nucleophile or electrophile will attack for chemical reactions.

## 2. Lewis dot structures and valence electron counts

Important for determining the number of electrons on a ligand and what the charge of the ligand is. We almost always deal with ligands with even # of electrons. If a ligand has an odd # of electrons we add additional electrons to get to an even # – often to form a closed shell electron configuration with a formal negative charge.

## 3. Organic line notation for drawing structures



## 4. Three-dimensional transition metal structures



# General Trends for the Transition Metals

**Group 8 Metals**

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

## Early Transition Metals

*low electronegativities*

*higher oxidation states*

*“harder” metal centers*

***OXOPHILIC!!***

## Late Transition Metals

*higher electronegativities*

*lower oxidation states*

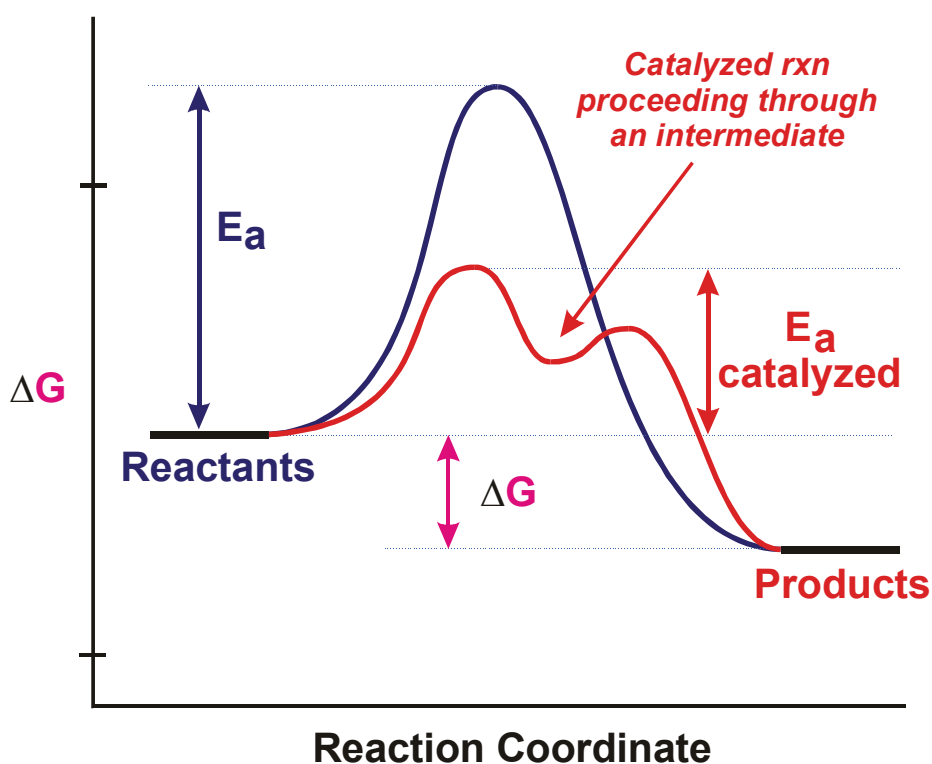
*“softer” metal centers*

# Transition Metal Catalysis



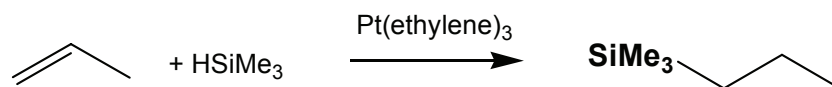
A catalyst is a substance that increases the rate of rxn without itself being consumed (but it is involved!) in the reaction. After the rxn is finished you should be able to recover the catalyst from the rxn mixture unchanged. A catalyst speeds up the rate at which a chemical reaction reaches equilibrium. The overall thermodynamics of the rxn is **NOT** changed by the catalyst. Therefore, very **endothermic** (*non-spontaneous*) reactions are usually **NOT** suitable for catalytic applications.

A catalyst provides a **lower energy pathway** for the production of **products** from **reactants**, thus allowing the rxn to proceed **faster**. It lowers the **activation energy** for a rxn (**kinetics**) – it does **NOT** change the **thermodynamics** of a rxn.

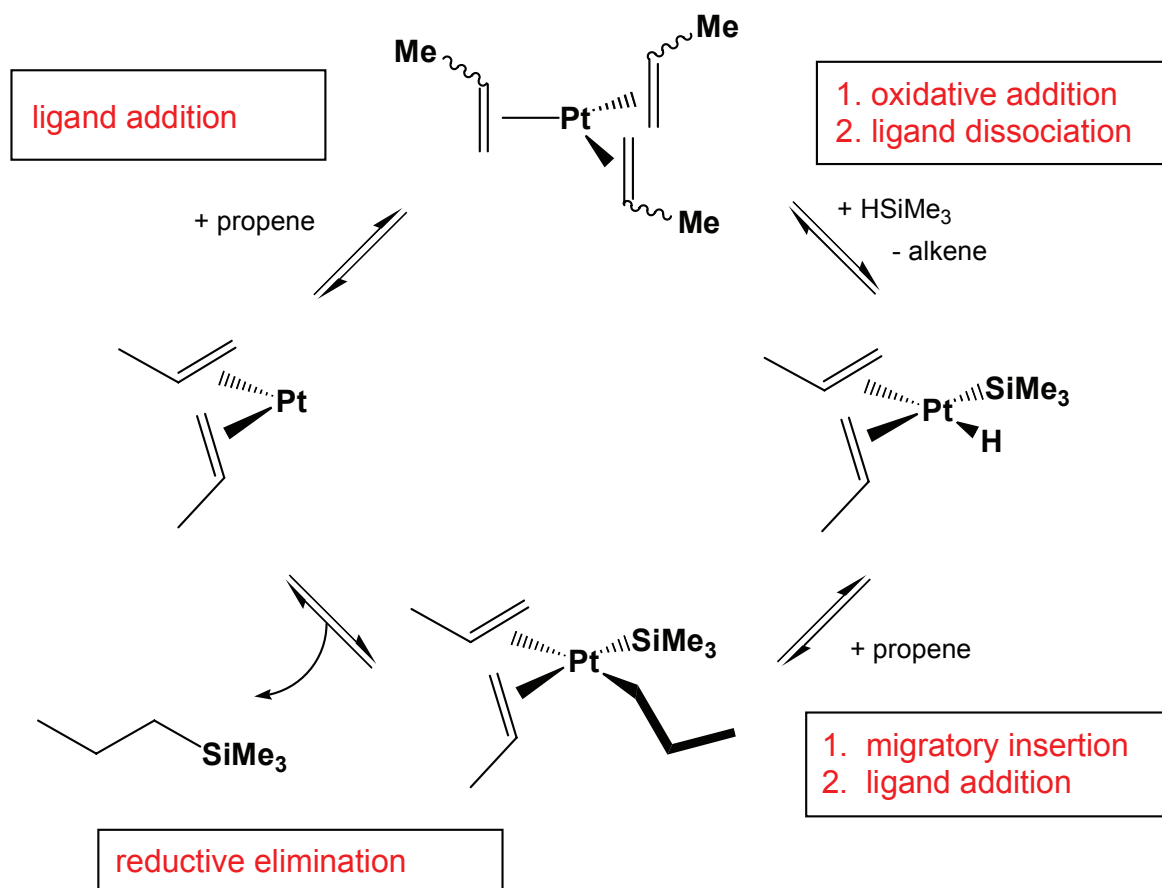


A catalyst provides an **alternate mechanism** (or pathway) for the **reactants** to be transformed into **products**. The catalyzed mechanism has an **activation energy** that is lower than the original uncatalyzed rxn. An excellent catalyst will lower the activation energy the most.

An example of a Pt-catalyzed reaction is shown below:



### Hydrosilylation



Note that there are different numbers of **ligands** (a generic name for anything that bonds to a metal center) on the metal. Too many is bad, too few is bad. How can you tell how many to use?? **Electron counting** is the key, which will be presented later in this chapter.

There are two broad classes of catalysts:

**Heterogeneous Catalysis:** Technically speaking this is when the catalyst is in a different phase than the reactants and products. Practically, it is usually when the catalyst is a solid and the reactants and products are liquids or gases. On a solid catalyst, only the surface of the catalyst is where the reaction will occur – so the more surface area available the more catalysis can occur. Industry makes extensive use of heterogeneous catalysts due to the ease of separating products from the catalyst.

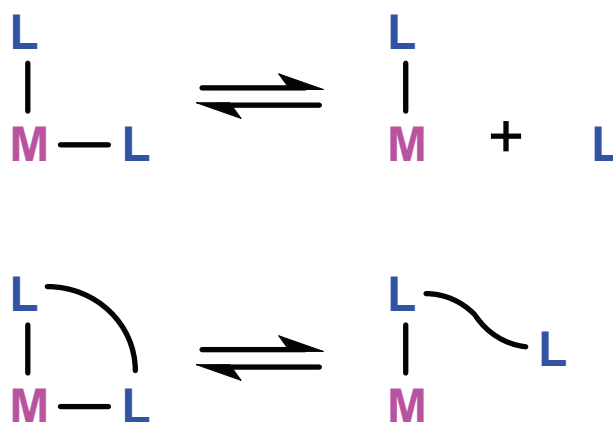
**Homogeneous Catalysis:** This is when the catalyst is in the same phase as the reactants & products. Practically, this is usually in the liquid or solution phase. Homogeneous catalysts are usually molecules dissolved in solution. Industry only uses homogeneous catalysts when selectivity is important due to problems associated with separating liquid products from the catalysts solution.

And one area of combined catalyst:

**Supported Catalysts:** This is what would normally be a homogeneous catalyst, but it is bound to (or supported by) a polymer, silica, or other insoluble phase. Industrial reactors employ “fluidized beds” of the catalysts.

## Some Important Ligand Nomenclature

**Chelate Effect** “chelate” is from the Greek meaning “claw” or to grab on to. The chelate effect or chelation is one of the most important ligand effects in transition metal coordination chemistry. Since most metal-ligand bonds are relatively weak compared to C-C bonds, M-L bonds can often be broken rather easily, leading to dissociation of the ligand from the metal. Consider the two metal ligand complexes shown below:

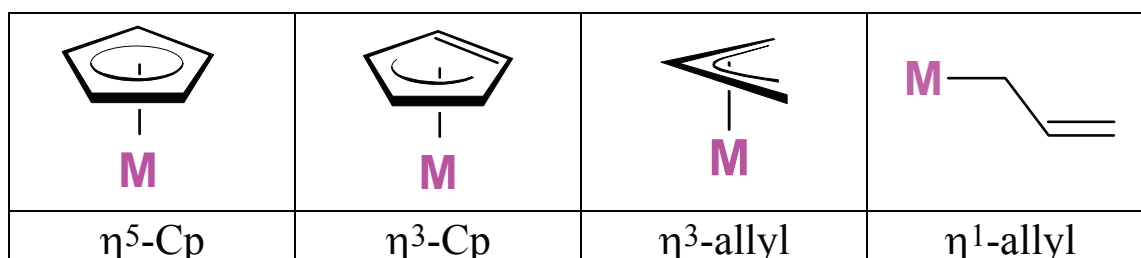


The second metal complex is much less likely to lose one of the ligands due to the bridging group that holds the ligands in proximity to the metal center. From a **kinetic viewpoint**, if one of the ligands dissociates, it will remain close enough to the metal center to have a high probability of re-coordinating before another ligand can get in and bind. From a **thermodynamic viewpoint**, by tethering two donor ligands together, one removes the entropic driving force for dissociating a ligand and thus making more particles in solution (more disorder).

The chelate effect can be extremely dramatic. There are cases known where the presence of a chelate will **change the equilibrium constant by a factor of  $10^{10}$**  favoring the coordinated form of the ligand to the metal over the dissociated form. Naturally, the longer and more flexible the bridging group in a chelating ligand, the less dramatic the chelating effect. It is possible to design ligands with sterically enforced chelates.

$\eta^x$  “eta- $x$ ” was originally developed to indicate how many carbons of a  $\pi$ -system were coordinated to a metal center. **Hapticity** is another word used to describe the bonding mode of a ligand to a metal center. You will occasionally see  $h^x$  used instead of  $\eta^x$ , although this is usually an error caused by forgetting to turn a regular font **h** into the *symbol* font on most word processors in order to get a Greek  $\eta$ . An  $\eta^5$ -cyclopentadienyl ligand, for example, has all five carbons of the ring bonding to the transition metal center.

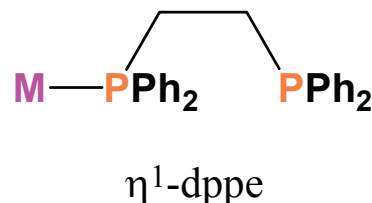
$\eta^x$  values for carbon ligands where the  $x$  value is **odd** usually indicate **anionic** carbon ligands (e.g.,  $\eta^5$ -Cp,  $\eta^1$ -CH<sub>3</sub>,  $\eta^1$ -allyl or  $\eta^3$ -allyl,  $\eta^1$ -CH=CH<sub>2</sub>). The # of electrons donated (ionic method of electron counting) by the ligand is usually equal to  $x + 1$ . **Even**  $\eta^x$  values usually indicate **neutral** carbon  $\pi$ -system ligands (e.g.,  $\eta^6$ -C<sub>6</sub>H<sub>6</sub>,  $\eta^2$ -CH<sub>2</sub>=CH<sub>2</sub>,  $\eta^4$ -butadiene,  $\eta^4$ -cyclooctadiene). The # of electrons donated by the ligand in the **even (neutral)** case is usually just equal to  $x$ .



The nomenclature, however, has been generalized by most in the organometallic field to include non-carbon ligands when there is some question as to the bonding mode (or hapticity) of the ligand donor atoms to the metal. For example, the bisphosphine Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub> (dppe) is normally a chelating ligand, but there are metal complexes known where only one of the phosphine atoms is coordinated to the metal center and the other is “dangling.”



The nomenclature for such a singly coordinated bisphosphine ligand would be:  $M(\eta^1\text{-dppe})$  -- meaning that only one of the two possible phosphorus atoms is bonded to the metal. Note that in cases like this, having an odd hapticity does NOT mean that the ligand is anionic (it is, however, a 2 electron donor!). When dppe is coordinated in its normal chelating mode, one usually omits the  $\eta^2$ -designation, as this is considered redundant. Note that some authors use  $\kappa^x$  instead of  $\eta^x$  when referring to non-carbon ligands.



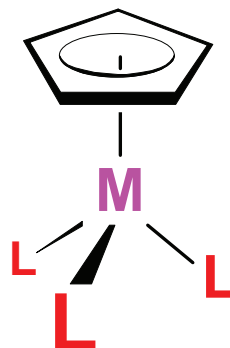
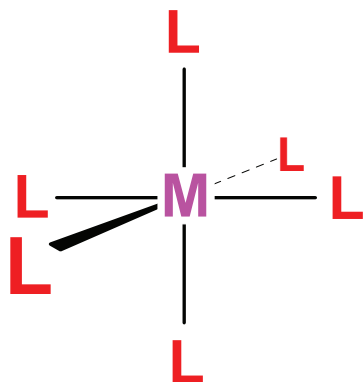
$\mu_x$  “mu-x” is the nomenclature used to indicate the presence of a **bridging ligand** between two or more metal centers. The  $x$  refers to the number of metal centers being bridged by the ligand. Usually most authors omit  $x = 2$  and just use  $\mu$  to indicate that the ligand is bridging the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

**Ordering** There is no set method of naming or ordering the listing of metal and ligands in a metal/ligand complex that most authors follow. There are IUPAC formalisms, but hardly anyone follows them. There are some qualitative rules that most authors seem to use in American Chemical Society (ACS) publications:

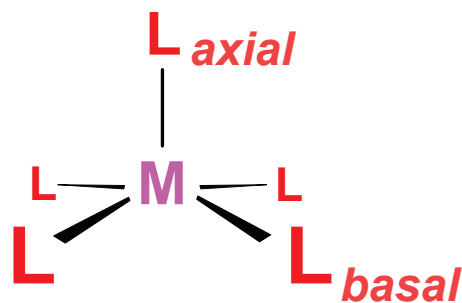
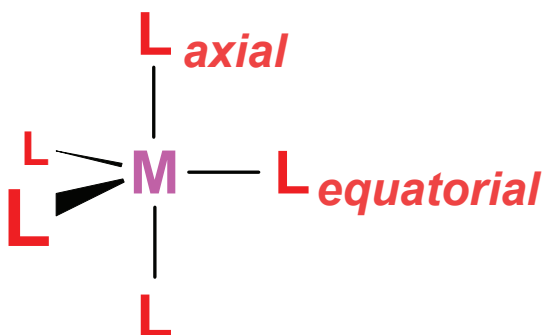
- 1) in formulas with Cp (cyclopentadienyl) ligands, the Cp usually comes first, followed by the metal center:  $\text{Cp}_2\text{TiCl}_2$
- 2) other anionic multi-electron donating ligands are also often listed in front of the metal.
- 3) in formulas with hydride ligands, the hydride is sometimes listed first. Rules # 1 & 2, however, take precedence over this rule:  
 $\text{HRh}(\text{CO})(\text{PPh}_3)_2$  and  $\text{Cp}_2\text{TiH}_2$
- 4) bridging ligands are usually placed next to the metals in question, then followed by the other ligands (note that rules 1 & 2 take precedence):  $\text{Co}_2(\mu\text{-CO})_2(\text{CO})_6$ ,  $\text{Rh}_2(\mu\text{-Cl})_2(\text{CO})_4$ ,  $\text{Cp}_2\text{Fe}_2(\mu\text{-CO})_2(\text{CO})_2$

## Common Coordination Geometries

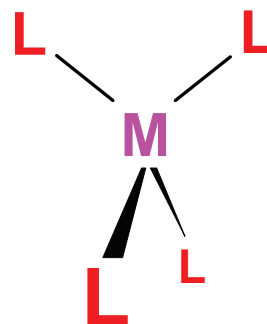
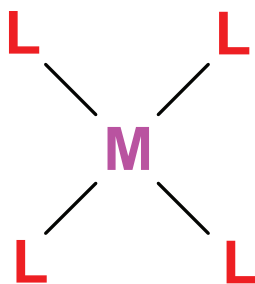
6-Coordinate: *Octahedral* ( $90^\circ$  &  $180^\circ$  angles)



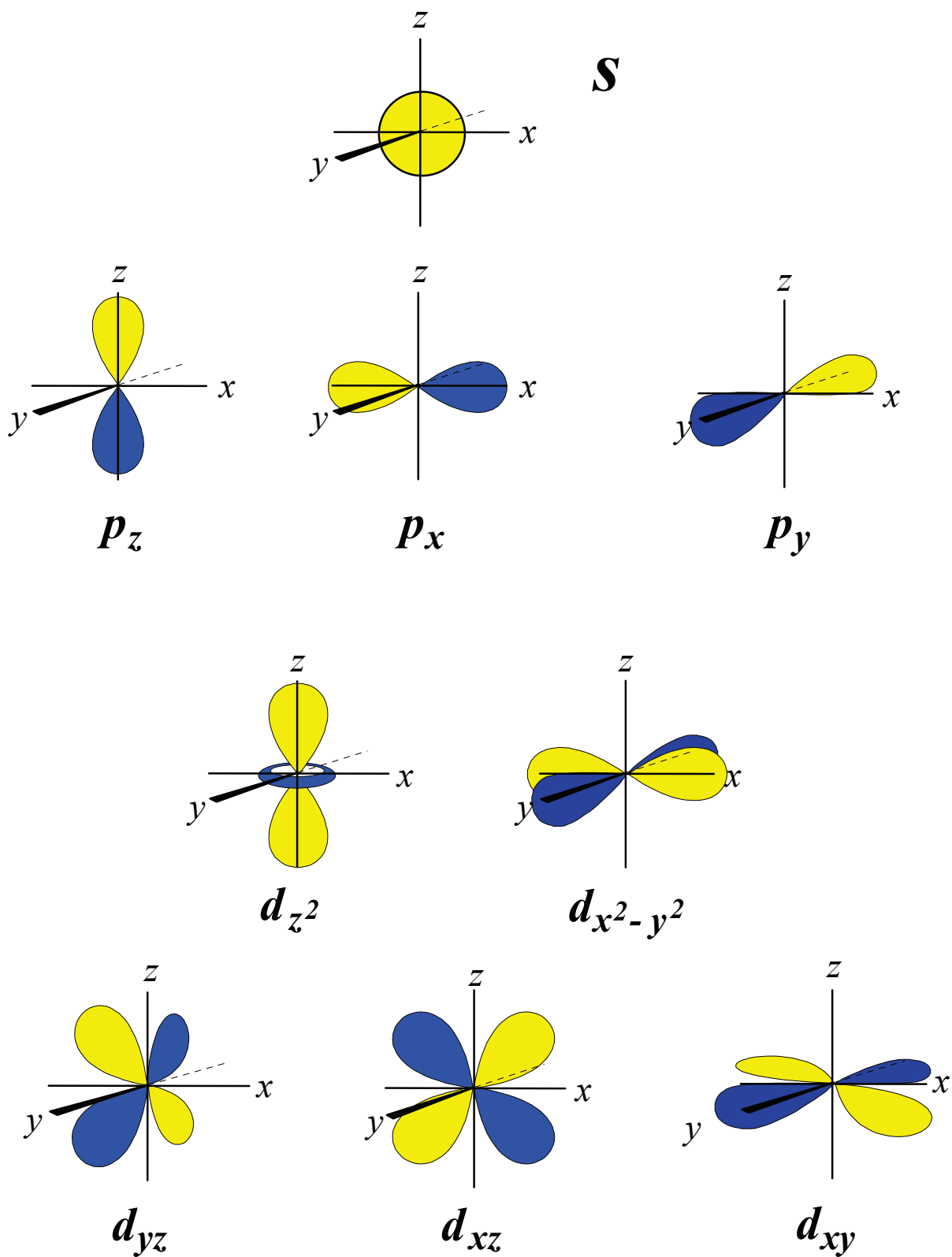
5-Coordinate: *Trigonal Bipyramidal or Square Pyramidal*  
 ( $90^\circ$  &  $120^\circ$ )                      ( $\sim 100^\circ$  &  $90^\circ$ )

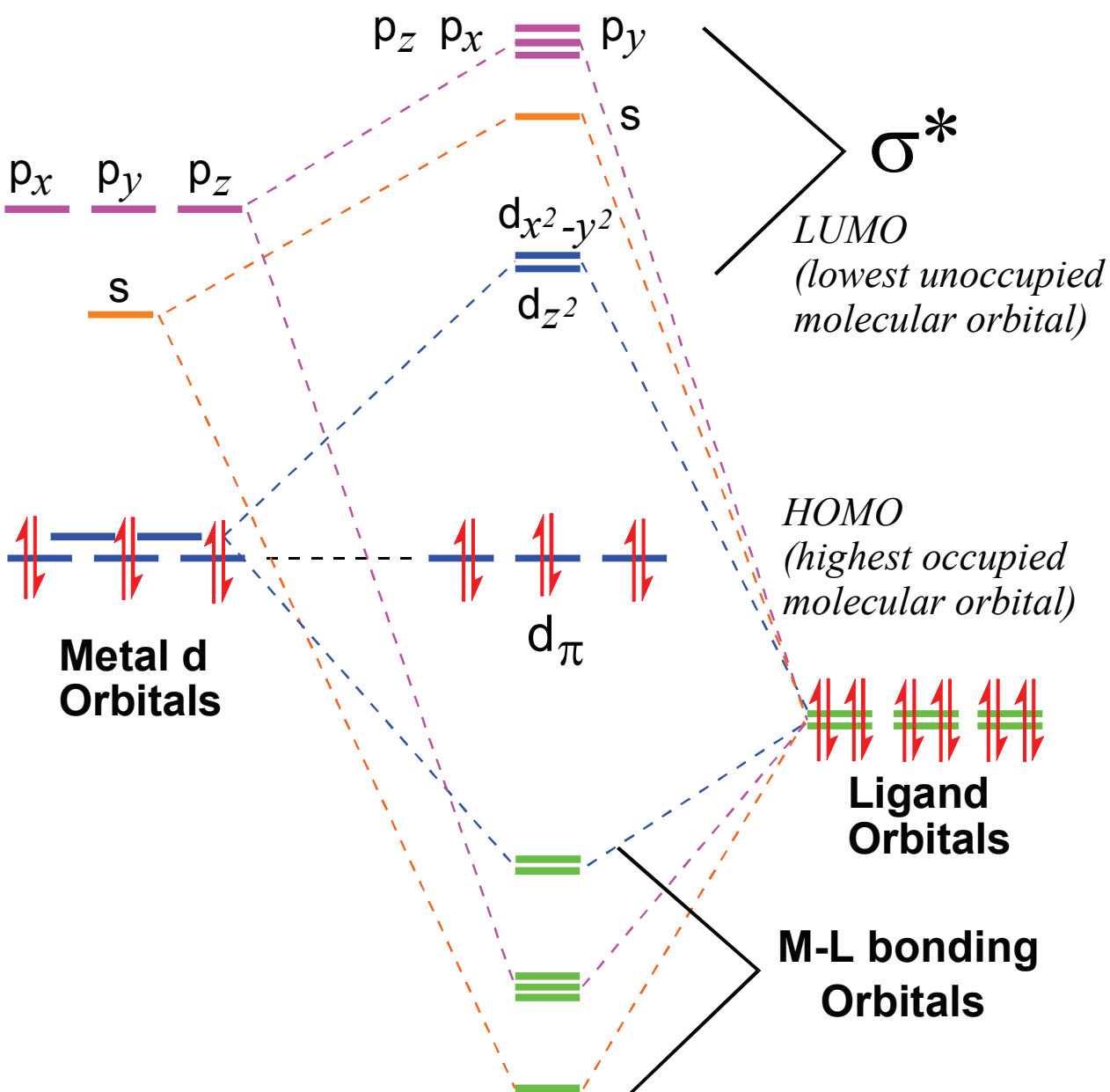
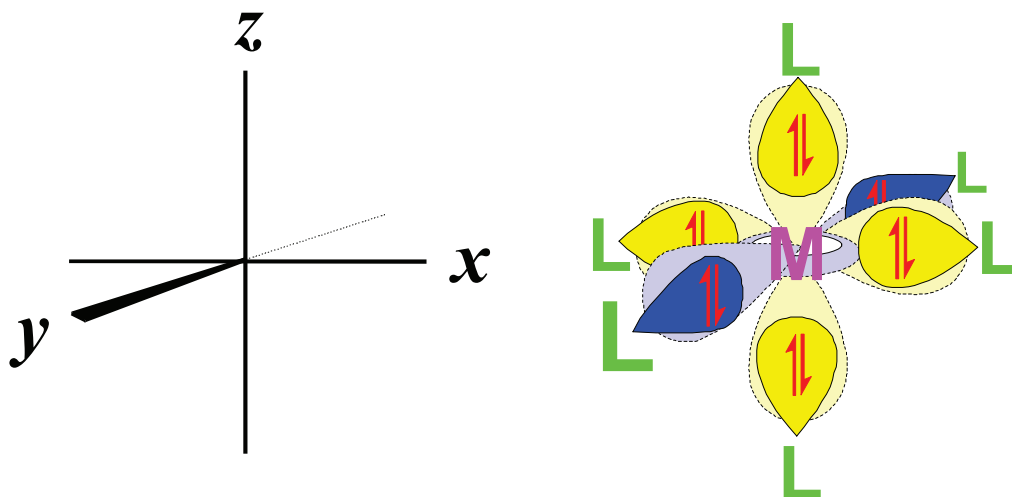


4-Coordinate: *Square Planar or Tetrahedral*  
 ( $90^\circ$  &  $180^\circ$ )                      ( $109^\circ$ )



# Bonding and Molecular Orbitals





# 18 Electron "Rule"

Organic compounds, of course, follow the **8 electron rule**: there can only be a maximum of 8 valence electrons around a carbon center.

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 determine 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

Complexes with 18 e<sup>-</sup> counts are referred to as **saturated**, because there are no empty low-lying orbitals to which another incoming ligand can coordinate. Complexes with counts lower than 18e<sup>-</sup> are called **unsaturated** and can electronically bind additional ligands.

## Exceptions to the 18e “Rule”

Group 8 Metals

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

### Early Transition Metals

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

*Coordination geometries higher than 6*

### Middle Transition Metals

*18e configurations are common*

*Coordination geometries of 6 are common*

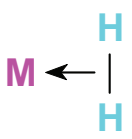
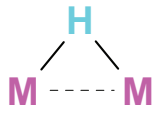
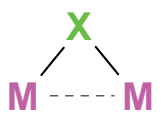
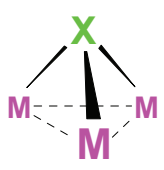
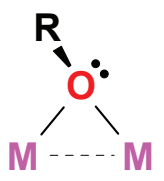
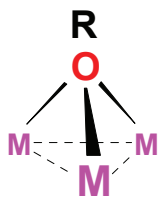
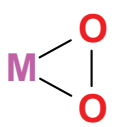
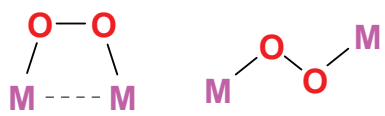
### Late Transition Metals

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

*Coordination geometries of 5 or lower*

*$d^6$*

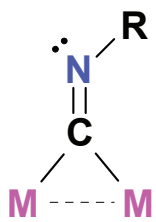
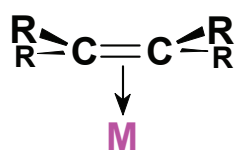
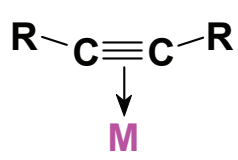
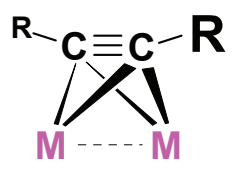

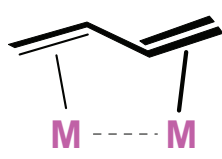
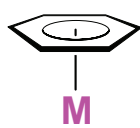
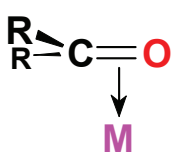
## Ligands, Bonding Types, Charges, and Electron Donor Numbers

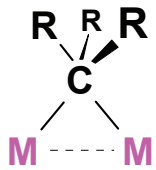
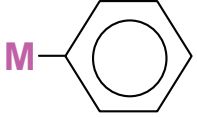
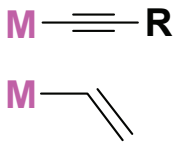

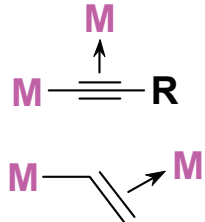
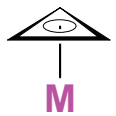

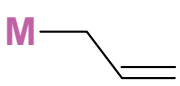

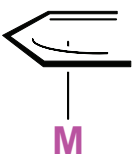
Ligand Name	Bonding Type	Formal Charge	Electrons Donated
Molecular Hydrogen: H <sub>2</sub>		0	2
Hydride: H <sup>-</sup>	M-H	-1	2
Hydride: H <sup>-</sup>		-1	2
Halide: X <sup>-</sup>	M-X	-1	2
Halide: X <sup>-</sup> μ bridging		-1	4 (2 to each M)
Halide: X <sup>-</sup> μ <sub>3</sub> bridging		-1	6 (2 to each M)
Alkoxide, thiolate: OR <sup>-</sup> , SR <sup>-</sup>	M-OR	-1	2 or 4
Alkoxide, thiolate: OR <sup>-</sup> , SR <sup>-</sup> μ bridging		-1	4 (2 to each M)
Alkoxide, thiolate: OR <sup>-</sup> , SR <sup>-</sup> μ <sub>3</sub> bridging		-1	6 (2 to each M)
Peroxide: O <sub>2</sub> <sup>2-</sup> η <sup>2</sup>		-2	4
Peroxide: O <sub>2</sub> <sup>2-</sup> μ <sub>2</sub> bridging		-2	4 (2 to each M)

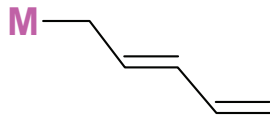
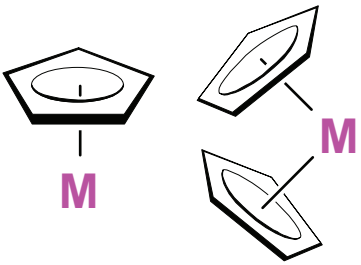
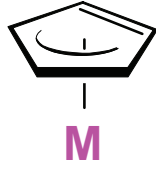
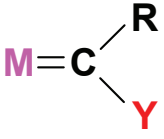
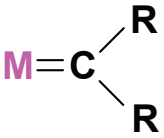
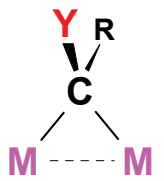
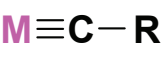
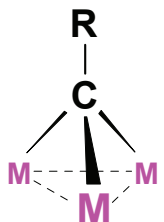
Oxide, sulfide: $O^{2-}$ , $S^{2-}$	$M=O:$ $M\equiv O:$	-2	4 6
Oxide, sulfide: $O^{2-}$ , $S^{2-}$ $\mu$ bridging		-2	4 (2 to each M)
Oxide, sulfide: $O^{2-}$ , $S^{2-}$ $\mu_3$ bridging		-2	6 (2 to each M)
Amine, phosphine, arsine: $NR_3$ , $PR_3$ , $AsR_3$	$M-NR_3$ $M-PR_3$	0	2
Amide, phosphide: $NR_2^-$ , $PR_2^-$		-1	2 4
Amide, phosphide: $NR_2^-$ , $PR_2^-$ $\mu$ bridging:		-1	4 (2 to each M)
Imido: $NR^{2-}$	$M=N-R$ $M\equiv N-R$	-2	4 (bent) 6 (linear)
Imido: $NR^{2-}$ $\mu$ bridging		-2	4 or 6 (2 or 3 to each M)
Imido: $NR^{2-}$ $\mu_3$ bridging		-2	6 (2 to each M)
Nitride, phosphide: $N^{3-}$ , $P^{3-}$	$M\equiv N:$	-3	6



Nitride, phosphide: $\text{N}^{3-}$ , $\text{P}^{3-}$ , $\mu$ bridging		-3	4 or 6 (2 or 3 to each M)
Nitride, phosphide: $\text{N}^{3-}$ , $\text{P}^{3-}$ , $\mu_3$ bridging		-3	6
Nitrosyl: $\text{N}\equiv\text{O}^+$ <i>linear form</i>	$\text{M}-\text{N}\equiv\text{O}$	+1	2
Nitrosyl: $\text{N}\equiv\text{O}^-$ <i>bent form</i>		-1	2
Nitrosyl: $\text{N}\equiv\text{O}^+$ $\mu$ bridging		+1	1 to each metal
Nitrosyl: $\text{N}\equiv\text{O}^+$ $\mu_3$ bridging		+1	1 to each metal
Carbonyl: $\text{C}\equiv\text{O}$	$\text{M}-\text{C}\equiv\text{O}$	0	2
Carbonyl: $\text{C}\equiv\text{O}$ $\mu, \eta^2$ mode		0	2 to each metal
Carbonyl: $\text{C}\equiv\text{O}$ $\mu$ bridging		0	1 to each metal
Carbonyl: $\text{C}\equiv\text{O}$ $\mu_3$ bridging		0	1 to each metal

Isocyanide: $C\equiv N-R$	$M-C\equiv N-R$	0	2
Isocyanide: $C\equiv N-R$ $\mu$ bridging		0	1 to each metal
Alkene: $R_2C=CR_2$ $\eta^2$ bonding mode		0	2
Alkyne: $RC\equiv CR$ $\eta^2$ bonding mode		0	2 or 4
Alkyne: $RC\equiv CR$ $\mu$ bridging		0	2 to each metal
Dienes: $R_2C=CH-CH=CR_2$ $\eta^4$ bonding mode		0	4
Dienes: $R_2C=CH-CH=CR_2$ $\mu$ bridging		0	2 to each metal
Benzene: $C_6H_6$ $\eta^6$ bonding mode		0	6
Ketones, aldehydes: $\eta^2$ bonding mode		0	2
Alkyl: $CH_3^-$ , $CH_2R^-$ $\eta^1$ bonding mode	$M-CR_3$	-1	2

Alkyl: $\text{CH}_3^-$ , $\text{CH}_2\text{R}^-$		-1	2 (1 to each M) <i>assuming no agostic M-H interactions</i>
Aryl: $\text{C}_6\text{H}_5^-$ $\eta^1$ terminal		-1	2
Alkenyl (vinyl), alkynyl: $\text{CH}=\text{CH}_2^-$ , $\text{C}\equiv\text{CH}^-$ $\eta^1$ terminal		-1	2
Alkenyl (vinyl): $\text{CH}=\text{CH}_2^-$ $\eta^2$ terminal		-1	4
Alkenyl (vinyl), alkynyl: $\text{CH}=\text{CH}_2^-$ , $\text{C}\equiv\text{CH}^-$ $\mu, \eta^2$ terminal		-1	4 (2 to each M)
Cyclopropenyl: $\text{C}_3\text{H}_3^+$ $\eta^3$ terminal		+1	2
Allyl: $\text{C}_3\text{H}_5^-$ $\eta^3$ terminal		-1	4
Allyl: $\text{C}_3\text{H}_5^-$ $\eta^1$ terminal		-1	2
Pentadienyl: $\text{C}_5\text{H}_7^-$ $\eta^5$ terminal		-1	6
Pentadienyl: $\text{C}_5\text{H}_7^-$ $\eta^3$ terminal		-1	4

<b>Pentadienyl: <math>C_5H_7^-</math></b> $\eta^1$ terminal		-1	2
<b>Cyclopentadienyl: <math>C_5H_5^-</math></b> $\eta^5$		-1	6
<b>Cyclopentadienyl: <math>C_5H_5^-</math></b> $\eta^3$		-1	4
<b>Carbene: <math>=CYR</math></b> <i>where Y is a substituent capable of <math>\pi</math> interaction with the carbene carbon atom</i>		0	2
<b>Alkylidene: <math>=CR_2^{2-}</math></b> <i>where no substituents capable of <math>\pi</math> bonding to the carbene carbon atom are present</i>		-2	4
<b>Carbene: <math>=CYR</math> or <math>=CR_2^{2-}</math></b> $\mu$ bridging		-2	2 to each metal
<b>Carbyne or Alkyidyne: <math>\equiv CR^{3-}</math></b>		-3	6
<b>Carbyne or Alkyidyne: <math>\equiv CR^{3-}</math></b> $\mu_3$ bridging		-3	2 to each metal

## How do I Figure Out Ligand Charges & Donor #'s)?? (without memorizing that !#&!@%\$\* entire list)

First, you should know the charges and donor # for the **common** ligands (this will significantly speed up your counting):

**Cationic 2e- donor:**  $\text{NO}^+$  (nitrosyl), cyclopropenium,  $\text{C}_3\text{H}_3^+$

**Neutral 2e- donors:**  $\text{PR}_3$  (phosphines),  $\text{CO}$  (carbonyl),  $\text{R}_2\text{C}=\text{CR}_2$  (alkenes),  $\text{RC}\equiv\text{CR}$  (alkynes, can also donate 4 e-),  $\text{N}\equiv\text{CR}$  (nitriles)

**Anionic 2e- donors:**  $\text{Cl}^-$  (chloride),  $\text{Br}^-$  (bromide),  $\text{I}^-$  (iodide),  $\text{CH}_3^-$  (methyl),  $\text{CR}_3^-$  (alkyl),  $\text{Ph}^-$  (phenyl),  $\text{H}^-$  (hydride)

*The following can also donate 4 e- if needed, but initially count them as 2e- donors (unless they are acting as bridging ligands):*  $\text{OR}^-$  (alkoxide),  $\text{SR}^-$  (thiolate),  $\text{NR}_2^-$  (inorganic amide),  $\text{PR}_2^-$  (phosphide)

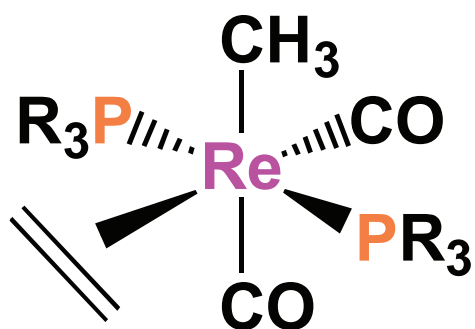
**Anionic 4e- donors:**  $\text{C}_3\text{H}_5^-$  (allyl),  $\text{O}^{2-}$  (oxide),  $\text{S}^{2-}$  (sulfide),  $\text{NR}^{2-}$  (imide),  $\text{CR}_2^{2-}$  (alkylidene)

*and from the previous list:*  $\text{OR}^-$  (alkoxide),  $\text{SR}^-$  (thiolate),  $\text{NR}_2^-$  (inorganic amide),  $\text{PR}_2^-$

**Anionic 6e- donors:**  $\text{Cp}^-$  (cyclopentadienyl),  $\text{O}^{2-}$  (oxide)

Please note that we are using the **Ionic Method** of electron-counting. 95% of inorganic/organometallic chemists use the ionic method. The ionic method assigns formal charges to the metal and ligands in order to keep the ligands with an even # of electrons and (usually) a filled valence shell. There is also the **neutral method** that considers everything to be neutral. Synthetically, the ionic method generally makes more sense and the one that we will use in this course.

## Simple Example:

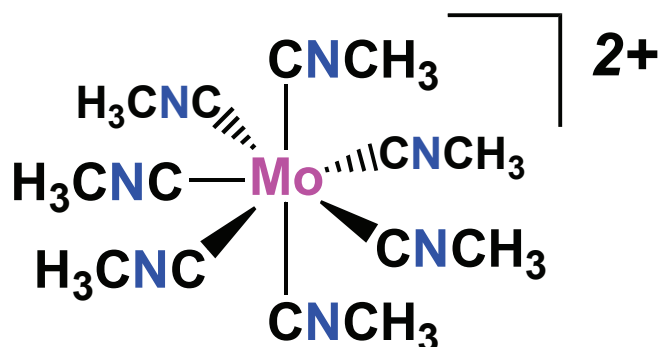


- 1) There is no overall charge on the complex
- 2) There is one anionic ligand ( $\text{CH}_3^-$ , methyl group)
- 3) Since there is no overall charge on the complex (it is neutral), and since we have one anionic ligand present, the Re metal atom must have a +1 charge to compensate for the one negatively charged ligand. The +1 charge on the metal is also its oxidation state. So the Re is in the +1 oxidation state. We denote this in two different ways:  $\text{Re}(+1)$ ,  $\text{Re}(\text{I})$ , or  $\text{Re}^{\text{I}}$ . I prefer the  $\text{Re}(+1)$  nomenclature because it is clearer. Most chemistry journals, however, prefer the Roman numeral notation in parenthesis after the element.

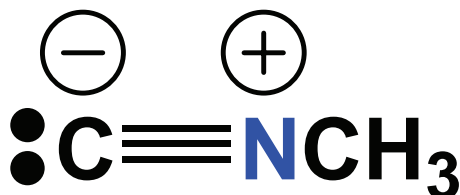
Now we can do our electron counting:

$\text{Re}(+1)$	$d^6$
$2 \text{ PR}_3$	$4e^-$
$2 \text{ CO}$	$4e^-$
$\text{CH}_3^-$	$2e^-$
$\text{CH}_2=\text{CH}_2$	$2e^-$
<b>Total: <math>18e^-</math></b>	

## Next Electron-Counting Example:



- 1) There is a +2 charge on the complex
- 2) The  $\text{CNCH}_3$  (methyl isocyanide) ligand is neutral, but let's check the Lewis Dot structure to make sure that is correct:



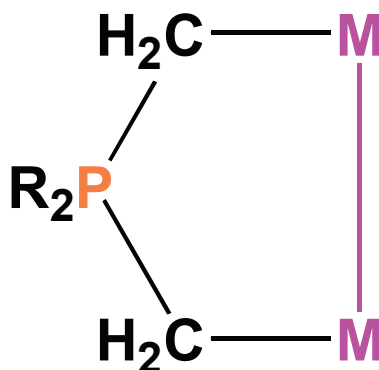
Nitrogen is normally trivalent, that is, it wants to have 3 chemical bonds to it. When it has 4 bonds, one more than usual, the nitrogen atom is assigned a formal *positive* charge. Carbon, on the other hand, is tetravalent and almost always wants 4 bonds. In isocyanides, however, we only have 3 bonds to the C. To keep an even number of electrons around the C we add an extra electron and the carbon gains a formal *negative* charge.

- 3) Since there is a +2 charge on the complex, and since we have all neutral ligands present, the Mo has a +2 charge & oxidation state.

Now we can do our electron counting:

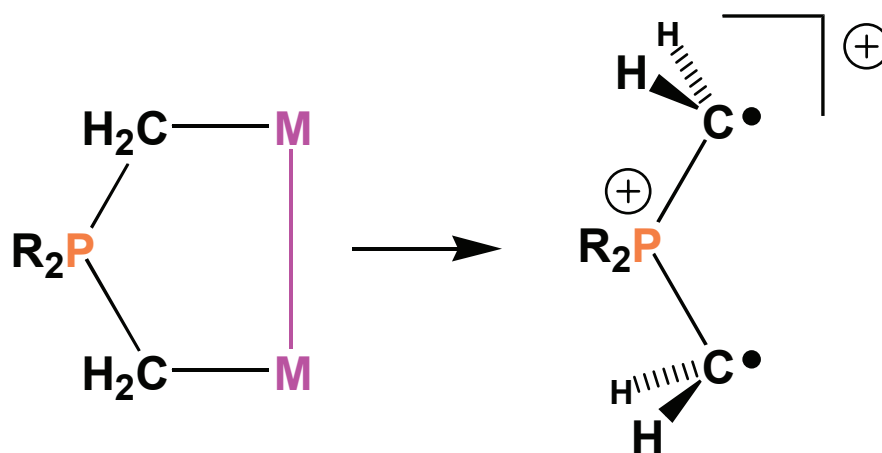
$\text{Mo}(+2)$	$d^4$
$7 \text{ CNCH}_3$	$14e^-$
$\text{Total: } 18e^-$	

## More Complicated Ligand Analysis:



How do we figure out the charge and electron donor ability of this weird ligand??

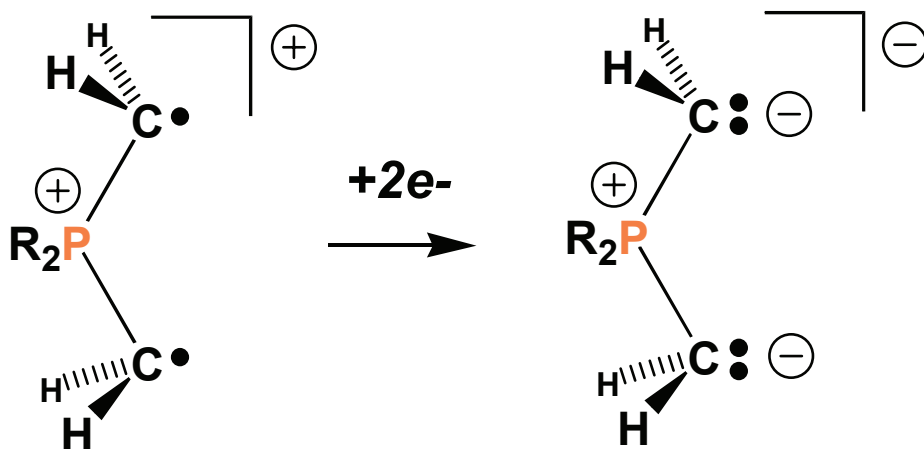
1) Remove the metal atoms and examine the ligand by itself:



Phosphorus is trivalent and since it has four bonds to it, there is a formal positive charge assigned to the atom. Each carbon is currently neutral and has an odd electron.



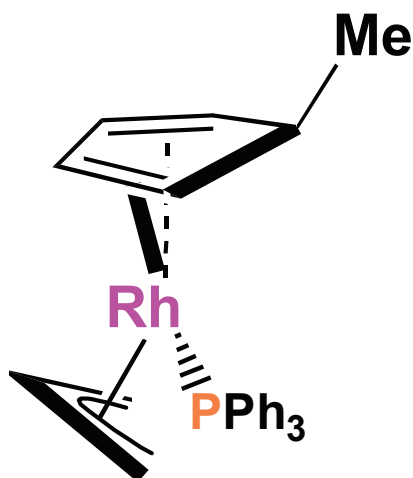
2) We always want the ligand in the ionic method of ligand electron counting to have an *even # of electrons*. IF the ligand atom has an odd # of electrons, add enough electrons to get to an even # (and usually a filled valence shell). This usually means adding one electron. In this specific case we have two carbon atoms each which needs an additional electron to give a lone pair that can donate to the metal center:



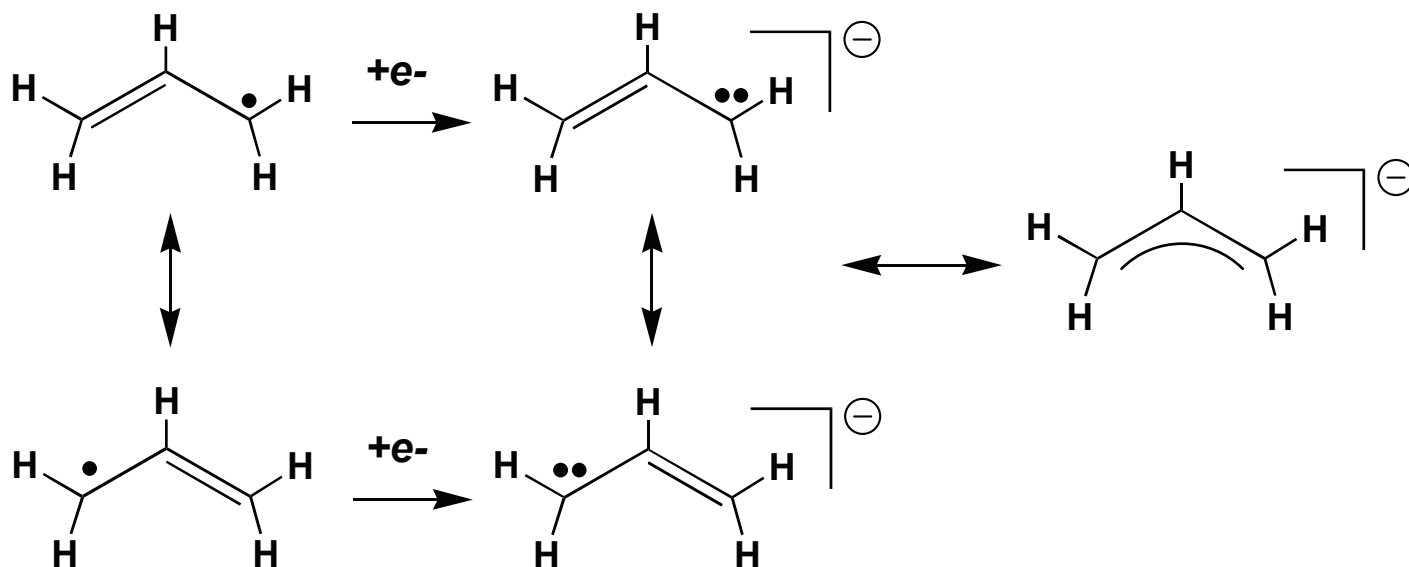
Adding two electrons to this ligand generates two anionic carbon donor centers. *But remember that we have a positive charge on the phosphorus atom*, which although not involved in bonding to the metal, is part of the overall charge of the ligand. So two negative charges and one positive charge (on the phosphorus) yields a net negative charge on this ligand. Each carbon can donate 2 e<sup>-</sup> to each metal center.

This strange ligand is called a phosphorus di-ylide and is a strongly donating ligand for bridging two metal centers.

## More Complicated Metal Compound Analysis:

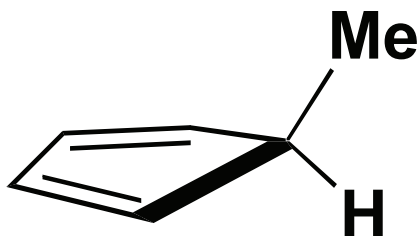


- 1) There is no overall charge on the complex
- 2) There is one anionic ligand ( $\eta^3\text{-C}_3\text{H}_5^-$ , allyl).



**Rule of Thumb:**  $\pi$ -based carbon ligands that have odd number attachments to the metal center are usually anionic (except for CO and CNR [isocyanide] ligands) and donate one more electron than the number of carbons bonded to the metal center. So our  $\eta^3\text{-C}_3\text{H}_5^-$ , allyl ligand is anionic and donates 4e<sup>-</sup> to the metal center.

The  $C_5H_5Me$  ligand is NOT a simple anionic cyclopentadienyl ligand. It is a neutral ligand with two alkenes that each act as neutral  $2e^-$  donors to the metal:



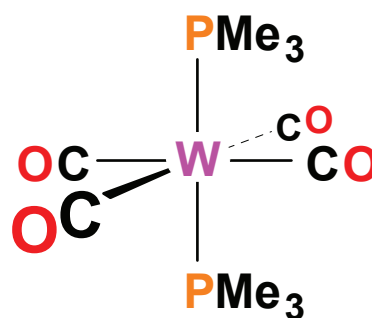
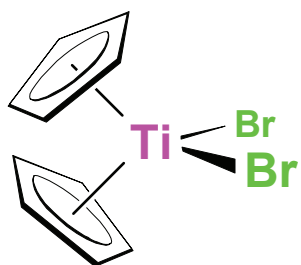
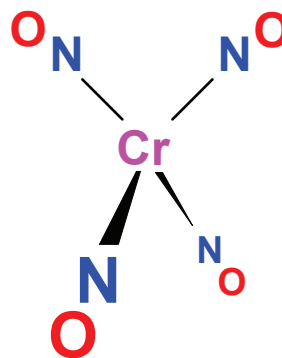
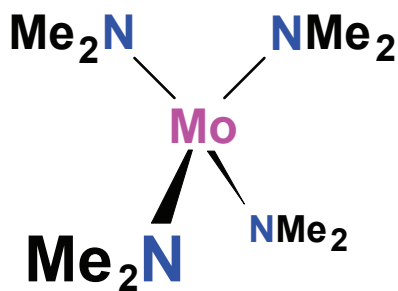
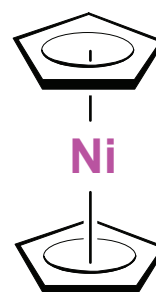
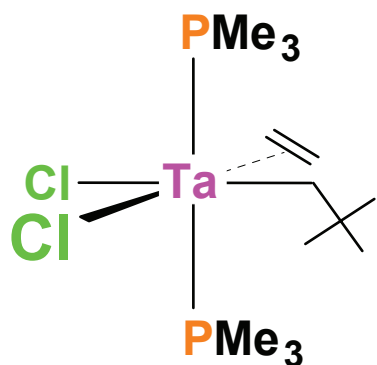
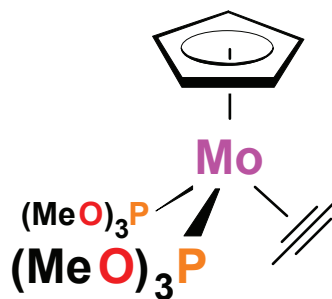
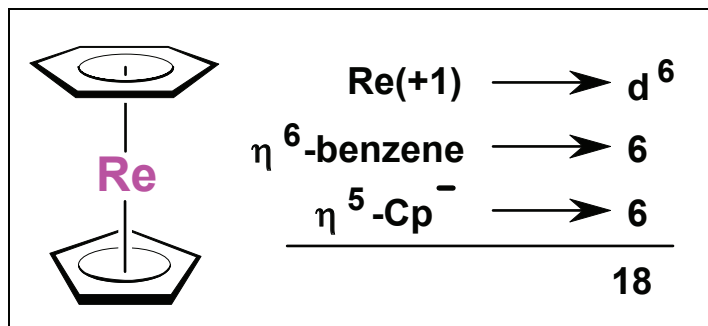
If you work out the Lewis Dot structure for this ligand you get an even # of electrons so there is no need to add an electron to get an anionic ligand. Note that it is EASY to forget that there is a H on the Cp carbon that has the methyl group attached if you are not thinking about organic line notation.

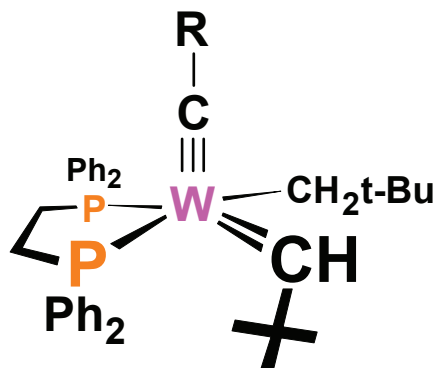
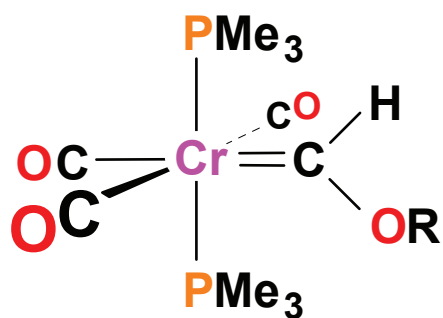
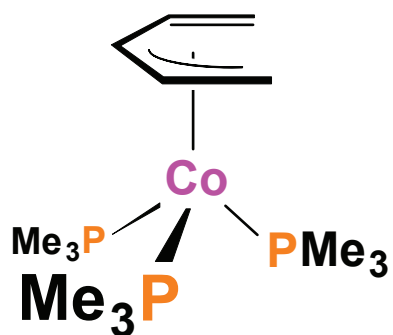
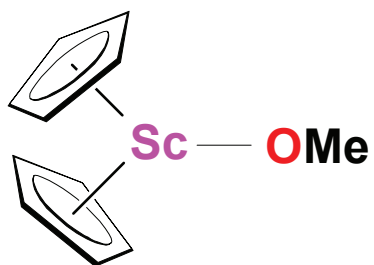
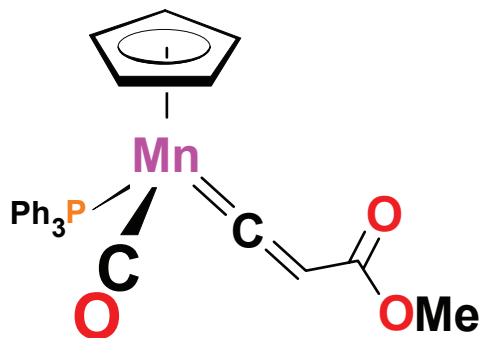
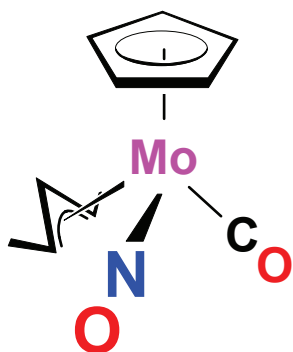
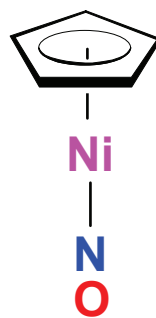
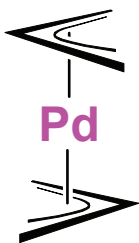
- 3) Since there is no overall charge on the complex (it is neutral), and since we have one anionic ligand present, the Rh atom must have a +1 charge to compensate for the one negatively charged ligand. So the Rh atom is in the +1 oxidation state.

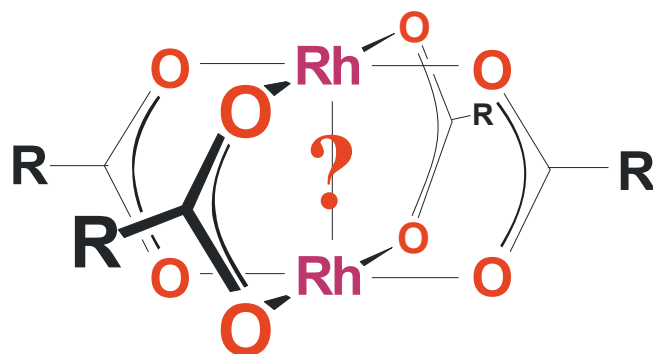
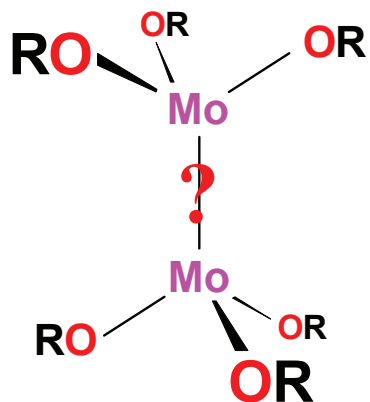
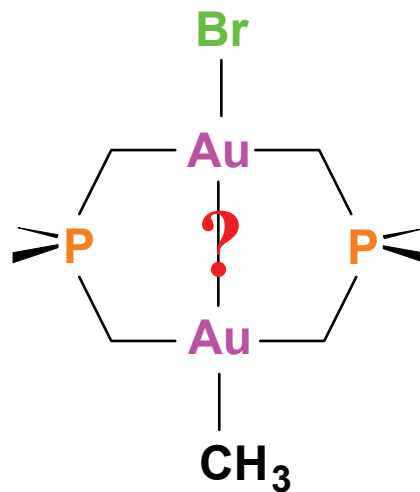
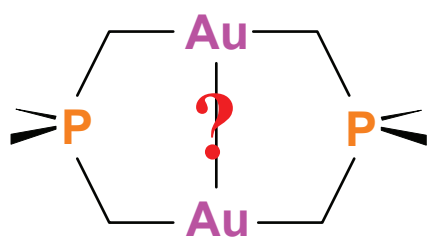
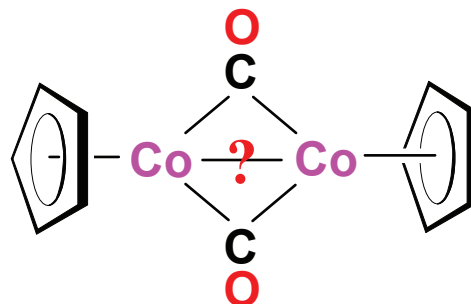
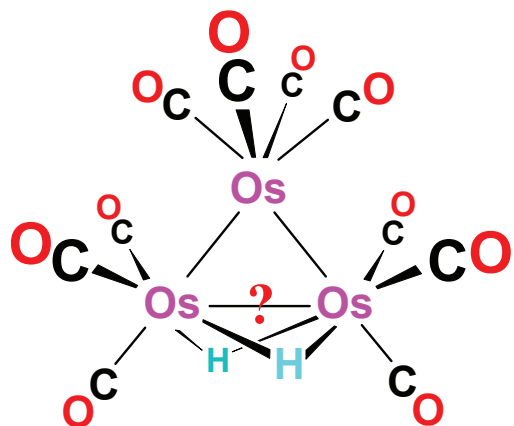
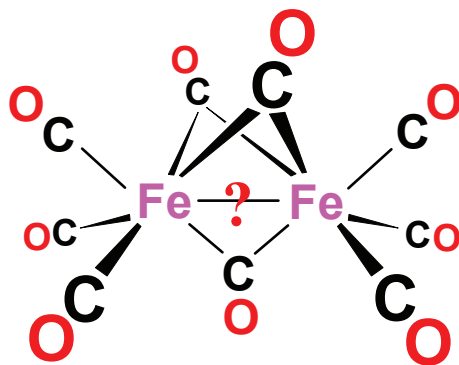
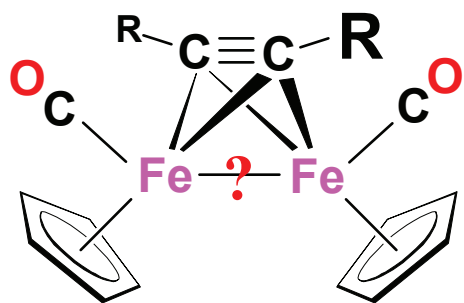
Now we can electron-count:

<b>Rh(+1)</b>	<b><math>d^8</math></b>
$PR_3$	$2e^-$
$\eta^4-C_5H_5Me$	$4e^-$
$\eta^3-C_3H_5^-$	$4e^-$
<hr/>	
Total:	$18e^-$

# Problems in Electron Counting







# Why is Electron Counting Important??

Cotton & Wilkinson, 3<sup>rd</sup> Edition (1972)

792

## CHEMISTRY OF THE TRANSITION ELEMENTS

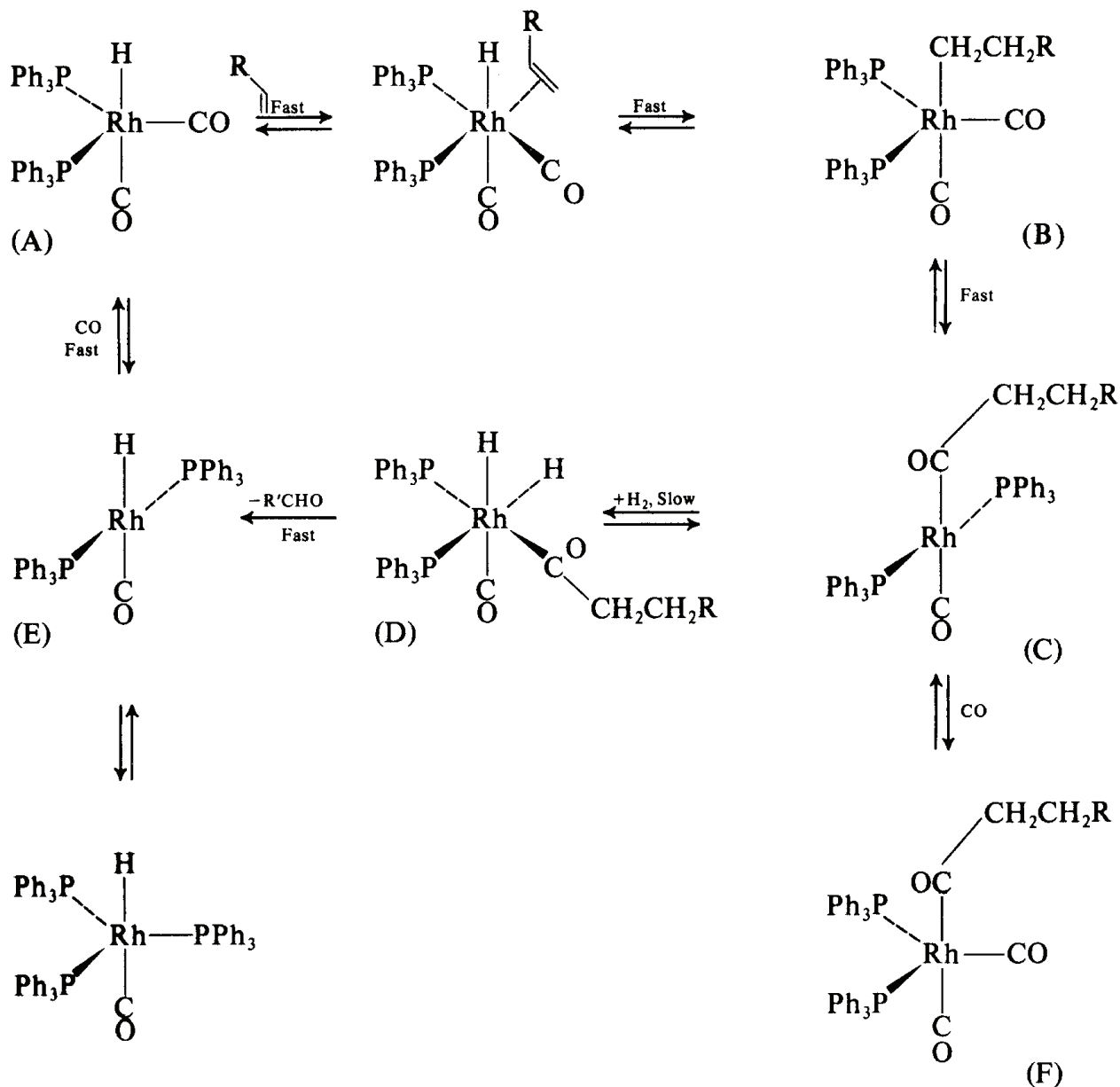


Fig. 24-B-2. Catalytic cycle for the hydroformylation of alkenes involving triphenylphosphine rhodium complex species. Note that the configurations of the complexes are not known with certainty.