

Formalisms – Oxidation State & Electron Counting

Understanding the nature of the metal center is critical in understanding how it reacts.

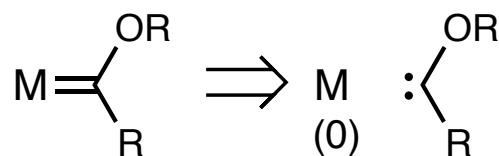
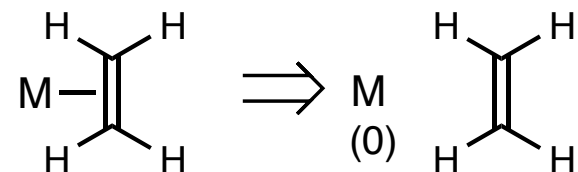
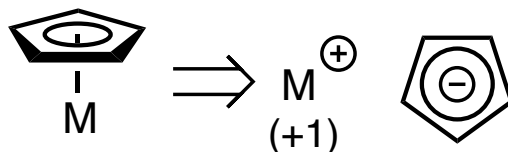
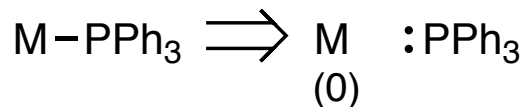
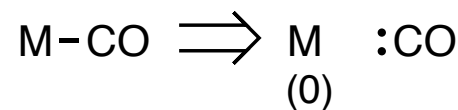
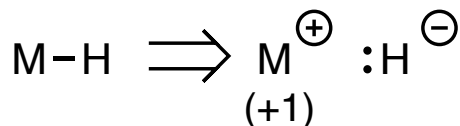
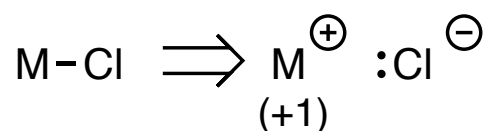
There are four things we need to know:

- (1) The oxidation state of the metal
- (2) The number of *d* electrons on the metal in that oxidation state
- (3) The coordination number of the metal
- (4) The availability (or lack thereof) of any coordination sites on the metal

Oxidation State – The charge left on the metal after *all* ligands have been removed in their *normal, closed shell*, configuration.

There are two ways to figure out the oxidation state. The one we will use involves breaking the metal–ligand bonds heterolytically with both electrons going with the ligand.

Examples:



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Now that we know the oxidation state of the metal we can figure out the d -electron count. This can be done easily by consulting the periodic table.

The $4s$ and $3d$ orbitals are very close in energy and for *complexes* of transition metals it is a good approximation that the d orbitals are filled first.

	Group #	4	5	6	7	8	9	10	11
First row	$3d$	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
Second row	$4d$	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag
Third row	$5d$	Hf	Ta	W	Re	Os	Ir	Pt	Au

oxidation state	{	0	4	5	6	7	8	9	10	–
		I	3	4	5	6	7	8	9	10
		II	2	3	4	5	6	7	8	9
		III	1	2	3	4	5	6	7	8
		IV	0	1	2	3	4	5	6	7

of d -electrons

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Why is knowing the number of *d*-electrons important?

18 electron rule – In mononuclear diamagnetic complexes, the total number of electrons in the bonding shell (the sum of the metal *d* electrons plus those contributed by the ligands) never exceeds 18. This determines the *maximum* number of ligands allowable for any metal in any oxidation state.

If a metal complex has 18 electrons in the bonding shell it is *coordinatively saturated*.

If a metal complex has fewer than 18 electrons it is *coordinatively unsaturated* and typically has at least one vacant coordination site.

In general, catalytic processes require the metal catalyst to have a vacant coordination site so that the substrate can bind.

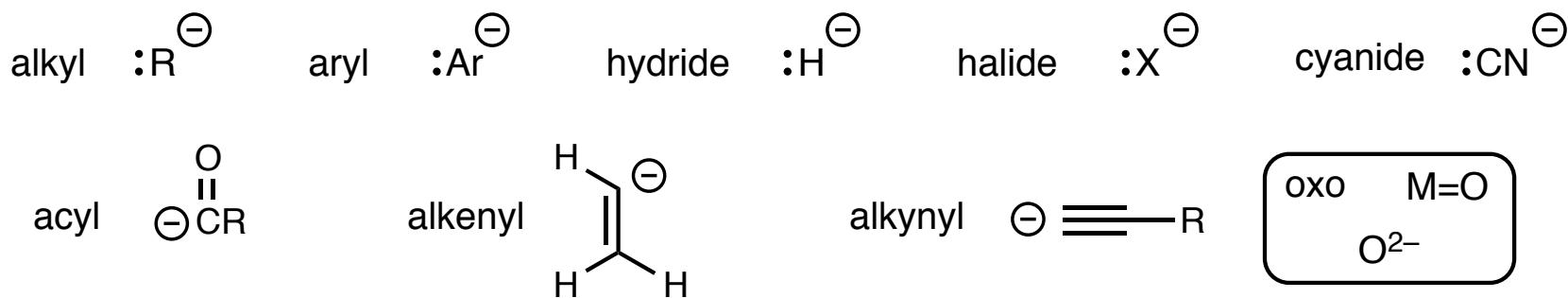
Knowing the oxidation state of the metal and the number of *d* electrons is only part of the story. In order to properly count the electrons in the bonding shell we also need to know how many electrons each ligand supplies. It is not always two.

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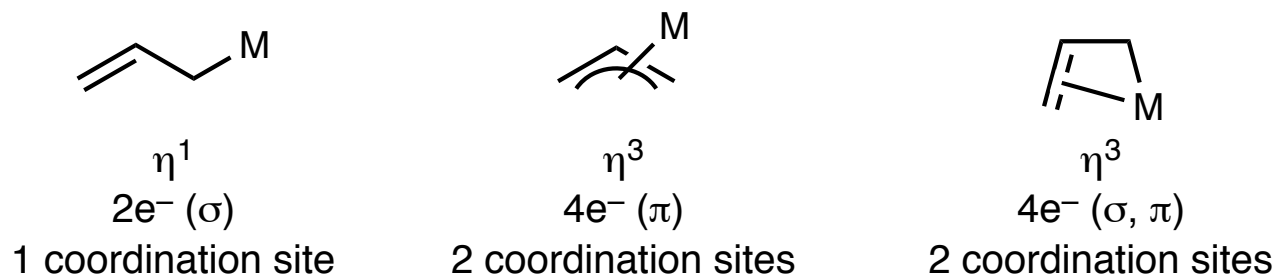
Classes of ligands – There are three classes of ligands: (1) *formal* anions (X-Type); (2) *formal* neutrals (L-Type); (3) *formal* cations.

All of these ligand classes have one pair of electrons for bonding the metal that are used to determine the metal's oxidation state. Often the ligand will also contain additional unsaturation that can donate additional electron pairs to the bonding shell. The manner in which these unsaturated ligands binds is called the "hapticity" (η).

Some Simple X-Type Donors – monohapto (η^1); only donate two electrons to bonding shell

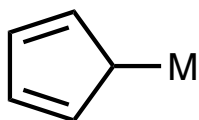


Allyl – X-Type ligand with multiple coordination modes; can donate 2 or 4 electrons



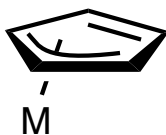
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Cyclopentadienyl – X-Type ligand with multiple coordination modes; can donate 2, 4, or 6 electrons



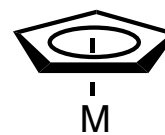
η^1
 $2e^-$

1 coordination site



η^3
 $4e^-$

2 coordination sites



η^5
 $6e^-$

3 coordination site
(most common)

Some common L-Type ligands and their hapticity

phosphine R_3P-M η^1 $2e^-$

amine R_3N-M η^1 $2e^-$

nitrile $RCN-M$ η^1 $2e^-$

carbonyl $OC-M$ η^1 $2e^-$

carbene $\begin{array}{c} X \\ \diagdown \\ C \\ \diagup \\ R \end{array} = M$ η^1 $2e^-$

alkene/alkyne $\begin{array}{c} || \\ -M \end{array}$ $\begin{array}{c} ||| \\ -M \end{array}$ η^2 $2e^-$

diene η^4 $4e^-$

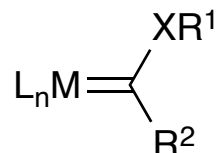
arene η^6 $6e^-$

Note: For polydentate ligands, count each attachment separately.

Carbene Complexes

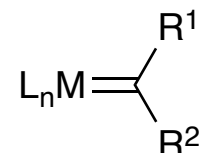
Several types are known. How they contribute to the overall electron counting is dependent on the substituents and metal involved.

Fischer carbenes



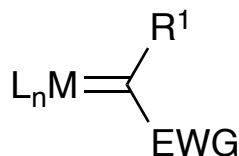
- X = O, NR, S
M = low-valent, middle or late transition metals
- L-type ligand
 - donating 2 electrons

Schrock carbenes



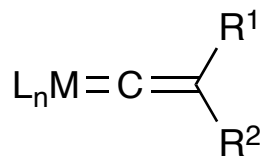
- R¹, R² = alkyl or H
M = high-valent carbonyl or middle transition metals
- 2X-type ligand (−2 charge)
 - donating 4 electrons

Carbenoids



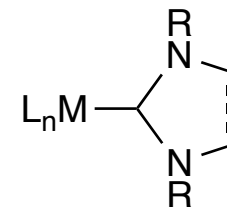
- L_nM = Rh₂(O₂CR)₄, N₄Ru,
(N₂O₂)Ru, or (N,N)Cu
- L-type ligand
 - donating 2 electrons

Vinylidenes



- R¹, R² = alkyl, aryl, or H
- L-type ligand
 - donating 2 electrons

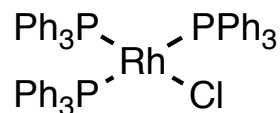
N-Heterocyclic carbenes



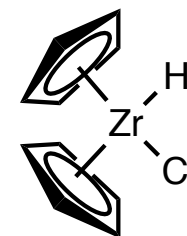
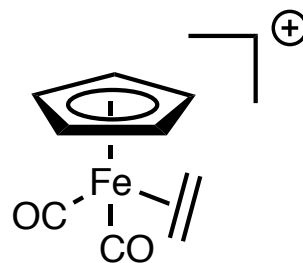
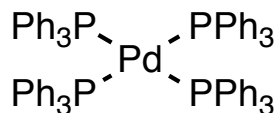
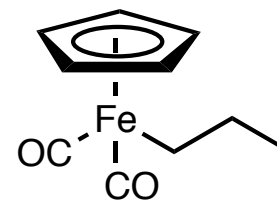
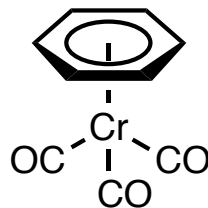
- R = alkyl or aryl
- generally a spectator ligand
 - L-type ligand
 - donating 2 electrons

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Examples – For each complex determine the oxidation state of the metal, the number of *d* electrons supplied by the metal, the overall electron count, and the number of vacant coordination sites.

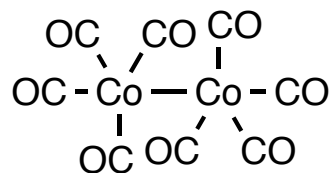


Wilkinson's catalyst



Schwartz's reagent

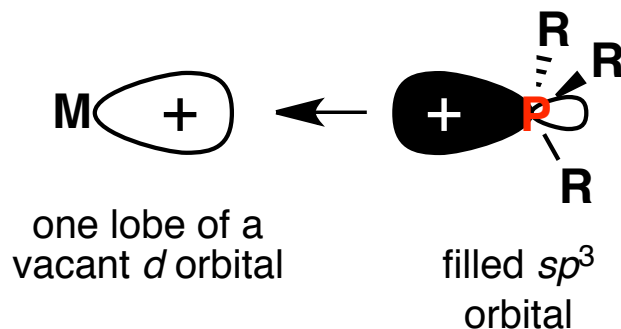
M–M bonds: contribute 1e to each metal



d Orbitals and Ligand Bonding

The 18 electron rule is predicated on the notion that it is the d orbitals of the metal that are responsible for ligand binding as well as engaging the substrate in chemistry (the substrate can be thought of as nothing more than a particularly reactive ligand). Therefore understanding how the d orbitals of a metal interact with the sp hybrid orbitals of the ligand and/or substrate is important.

σ -donor bonds – formed by overlap of filled sp hybrid orbitals (or π -bonding orbitals) of ligand with vacant d orbitals of the metal. Orbital symmetry should be kept in mind.

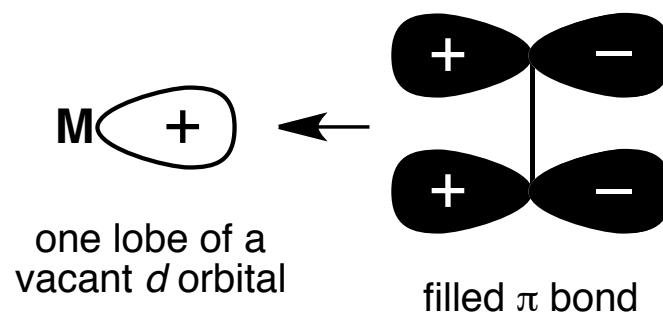


Ligands that are primarily σ -donors (e.g., R_3P , R_3N , H^- and R^-) *increase* electron density on the metal

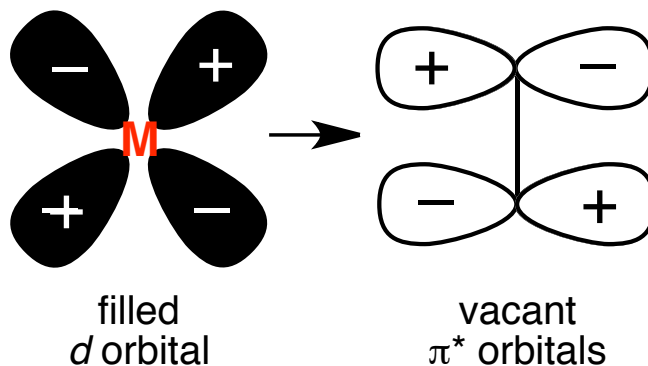
What about unsaturated ligands?

d Orbitals and Ligand Bonding

π -Bonds on the ligand can also serve as a σ -donor ligands



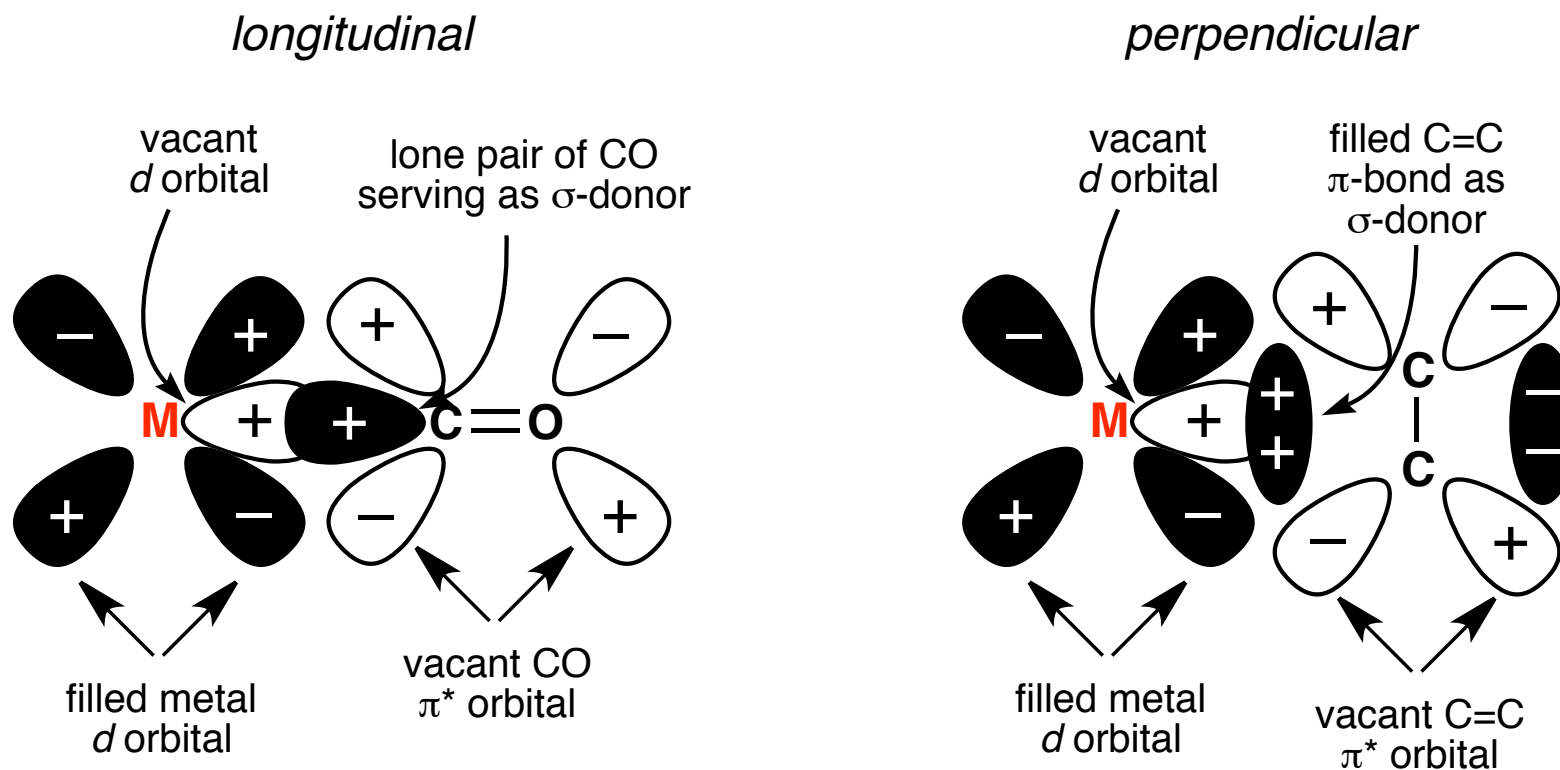
BUT...the π^* orbital also has the same symmetry and similar energy to the d orbitals



By this model, the metal is donating electron density to the ligand. This is known as "back bonding" and can act as an electron sink. Thus the electron density of the metal will *decrease*.

d Orbitals and Ligand Bonding

Two different types of backbonding are possible depending on the geometry of the ligand orbitals.



Bottom Line...because of these two bonding modes the electron density of the metal (and as a consequence its reactivity) can be tuned by varying the identity σ -donor ligands (add electron density) and π -acceptor ligands (remove electron density).

For this course I have chosen to focus more on the reactivity of metals rather than the structures. We will talk about ligand choices more when necessary.

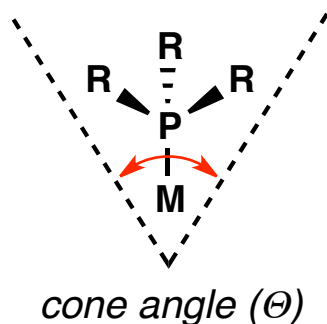
Phosphine Ligands

Phosphine ligands are frequently used ligands for organometallic reactions. While they can be somewhat difficult to synthesize and are often oxygen sensitive, they are highly tunable. Influences on the metal can be mediated by **electronics**, **cone angle**, **monodentate vs. bidentate**, and **bite angle**.

Electronics: The identity of the substituents around the phosphorus atom has a profound influence on how donating the ligand is.

		PR₃	ν_{CO} (cm⁻¹)	ν_{CO} (cm ⁻¹) is determined with Ni(CO) ₃ L and is a measurement of the amount of backbonding. More donating L, more backbonding and ν_{CO} decreases.
trialkylphosphine	triarylphosphine	P(<i>t</i> -Bu) ₃	2056	
		PCy ₃	2056	
		PMe ₃	2064	
		P(C ₆ H ₄ -4-OMe) ₃	2066	
phosphite	phosphoramidite	PPh ₃	2069	
		P(OMe) ₃	2079	
		P(OPh) ₃	2085	

Cone Angle: This is a measure of the three-dimensional steric influence a ligand has on the environment around the metal. It can be changed independently from electronics.

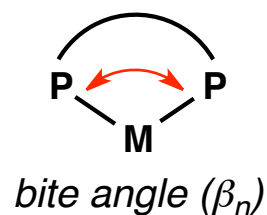


PR₃	θ	PR₃	θ	PR₃	θ
PH ₃	87	PHPh ₂	128	PPh(<i>t</i> -Bu) ₂	170
PF ₃	104	P(OPh) ₃	128	PCy ₃	170
P(OMe) ₃	107	PEt ₃	132	P(<i>t</i> -Bu) ₃	182
PMe ₃	118	PPh ₃	145	PPh ₃	145
PMe ₂ Ph	122	PPh ₂ (<i>t</i> -Bu)	157	P(<i>o</i> -tol) ₃	194
Ph ₂ PCH ₂ CH ₂ PPh ₂	123				

Hartwig, *Organotransition Metal Chemistry*, 2010, pp 37–38.

Phosphine Ligands

Bite Angle: This is a measure of the three-dimensional steric influence a ligand has on the environment around the metal. It can be changed independently from electronics.



Ligand	β_n	Ligand	β_n
dppm (1 , $n = 1$)	72	BISBI (5)	113 (92–155)
dppe (1 , $n = 2$)	84 (70–95)	TRANSPHOS (6)	111
dppp (1 , $n = 3$)	91	NORPHOS (7)	123 (110–145)
dppb (1 , $n = 4$)	98	DPEphos (8)	102 (86–120)
DIOP (2)	102 (90–120)	DBFphos (9)	131 (117–147)
BINAP (3)	92	Xantphos (10)	112 (97–135)
Me-DuPHOS (4)	83	dppf (11)	96

