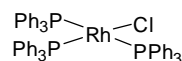


## Electron Counting

Description of a transition metal

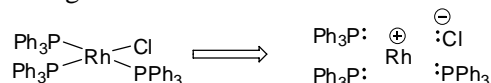
- 1) Formal Oxidation State
- 2) d Electron Configuration
- 3) Total Electron Count at the Metal
- 4) Coordination Number

Consider Wilkinson's Catalyst:



Assignment of Oxidation State

- Remove ligands in closed shell configuration
- The charge on the metal is the oxidation state [Rh(I)]



*d*-Electron count ( $d^n$ )

$n$  = Valence of neutral metal – charge on the metal  
 Rh(0) has 9 valence electrons, so Rh(I) has (9-1= 8)  
 Rh(I) has 8 d-electrons and is said to be  $d^8$

Total electron count

The total electron count at the metal is given by:  
 (metal electrons + ligand electrons). In this case:  
 the phosphines and chloride are all 2 e<sup>-</sup> donors so,  
 Total e<sup>-</sup> = 8 + 2 + 2 + 2 + 2 = **16 e<sup>-</sup>**

Coordination number

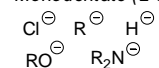
$$CN = (\# \text{ of monodentate}) + 2(\# \text{ of bidentate}) + \dots$$

In the example Rh is 4-coordinate. Other cases may be less obvious.

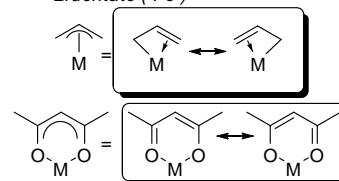
Common Ligands

Anionic Ligands

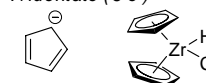
Monodentate (2 e<sup>-</sup>)



Bidentate (4 e<sup>-</sup>)

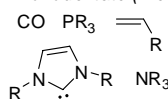


Tridentate (6 e<sup>-</sup>)

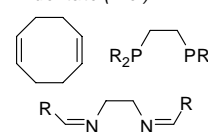


Neutral Ligands

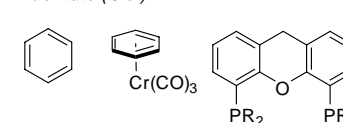
Monodentate (2 e<sup>-</sup>)



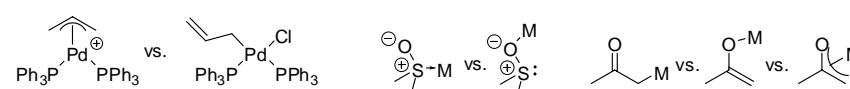
Bidentate (4 e<sup>-</sup>)



Tridentate (6 e<sup>-</sup>)



Variable coordination modes



Coordination number and electron count dictate geometry.

$d^6$ , 6 coordinate metal = octahedral

$d^8$ , 3-coordinate = T-shaped

$d^8$ , 4-coordinate metal = square planar

$d^8$ , 5-coordinate metal = square pyramidal or trigonal bipyramidal

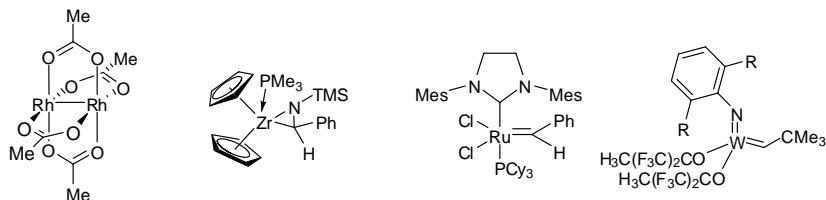
$d^{10}$ , 3-coordinate metal = trigonal planar

$d^{10}$ , 4-coordinate metal = tetrahedral

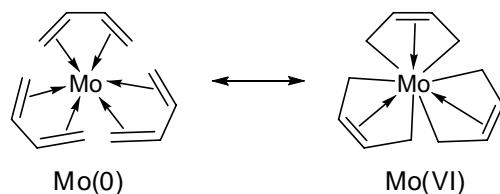
Coordination mode and electron count affect reactivity

$d^6$ , 6 coordinate metal is **substitutionally inert**

## Practice



## Where "formal" oxidation state fails

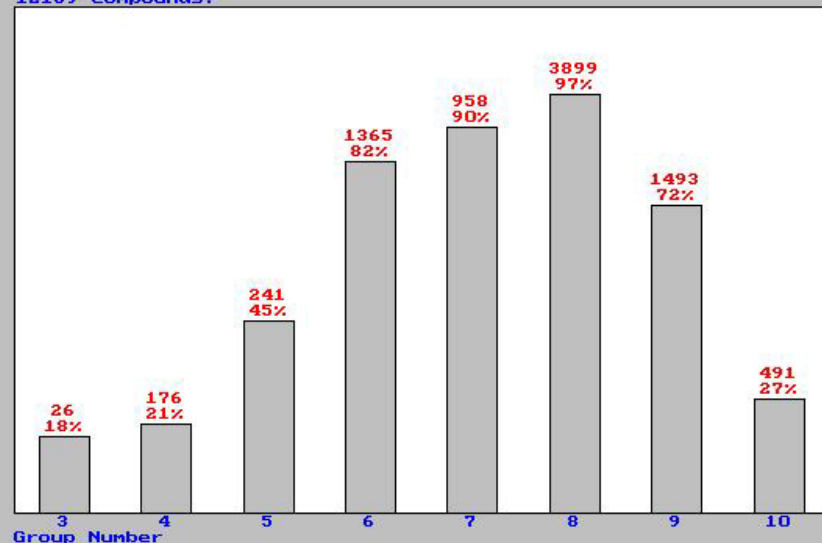


In fact, formal oxidation states often do not correlate with ionization energies : Green, M. L. H. *J. Organometallic Chemistry* **1995**,500, 127-148.

Consider  $WMe_6$  :the calculated charge on W is +0.4 not +6

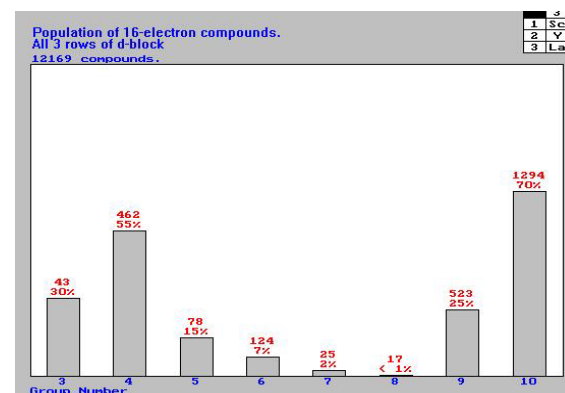
## On the 18 e- "rule":

Population of 18-electron compounds.  
All 3 rows of d-block  
12169 compounds.



Graphs generated by the program mlx (Version 1), Copyright©Cary Zachmanoglou, 1998 which was graciously provided by Professor Ged Parkin, Columbia University

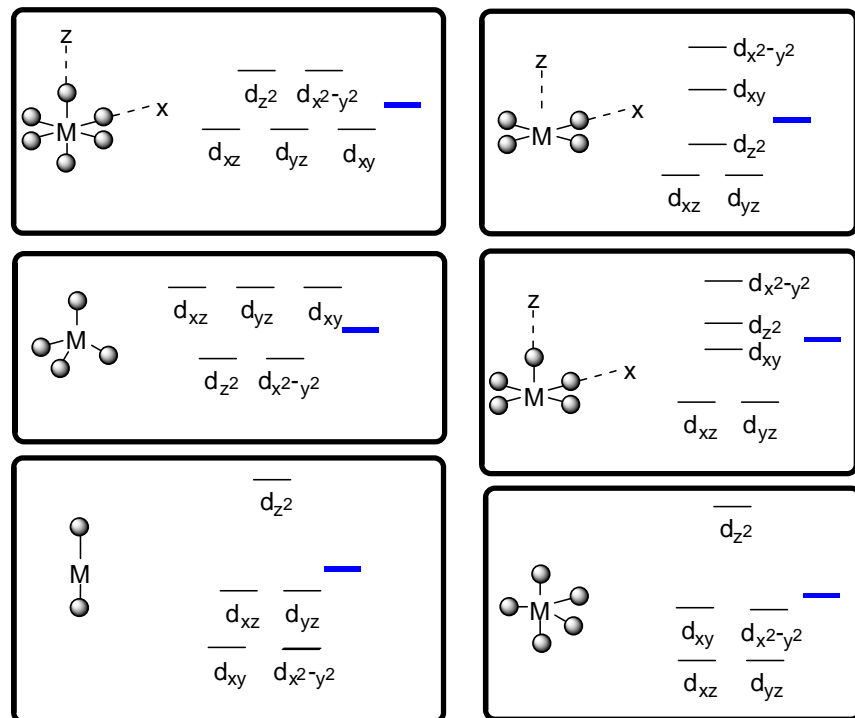
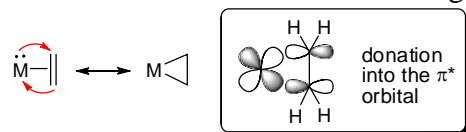
The 18 e- rule works well for groups 6-8, but in general you should regard 18 e- as a maximum (not as you view the octet rule)



= 16 e- compounds

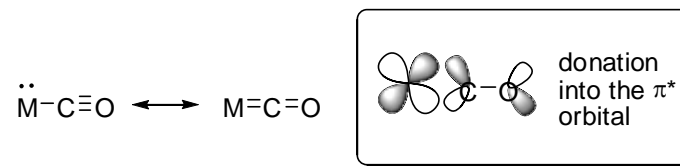
## Where do the electrons go?

Approximate d-orbital MO's for common coordination geometries.

**Note: Metals have lone pairs that are often not shown**These lone pairs can be involved in  $\pi$ -backbonding

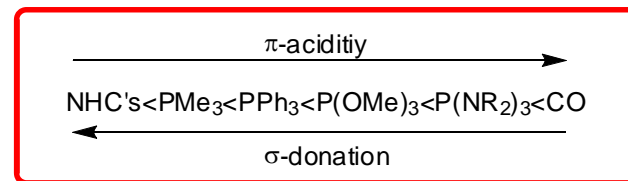
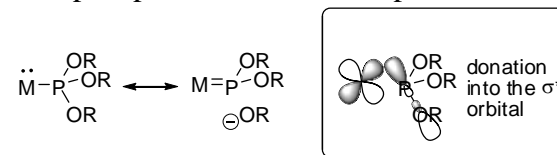
Backbonding in metal alkene complexes

- 1) lengthens the C-C bond
- 2) makes carbons more tetrahedral
- 3) formally oxidizes the metal by 2 e-

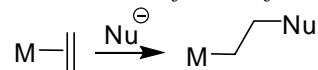


complex	$\nu_{CO}$ cm <sup>-1</sup>
$H_3C-C \equiv O^+$	2299
$:C \equiv O^{\ominus}$	2143
$Ni(CO)_4$	2060
$Ni(CO)_3PPh_3$	2068, 1990
$Ni(CO)_3P^tBu_3$	2056, 1971
$(O_3C)Ni$ (cyclopentadienyl)	2049, 1965
$Co(CO)_4^{\ominus}$	1890
$Fe(CO)_4^{2\ominus}$	1770

increasing backbonding

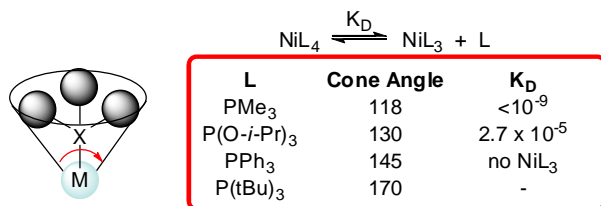
**Consequence of backbonding:**  $HCo(CO)_4$  is as acidic as HCl!Phosphines and phosphites can be  $\pi$ -acceptors

What type of ligand would be best for the following reaction?

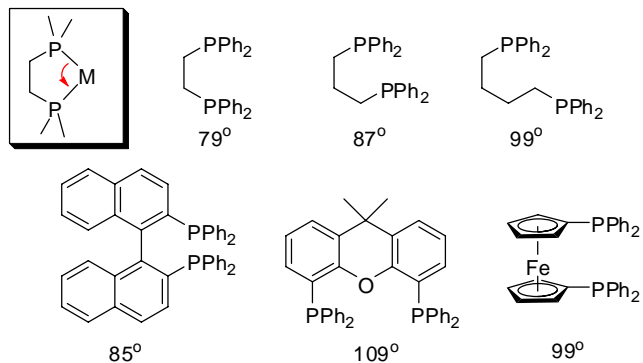


### Other ligand effects

The size of a ligand can dramatically influence substitution reactions at the metal. One convenient measure of ligand size is its **Cone Angle**. The cone angle is essentially the area that is blocked by the ligand. See Tolman, C. A. *Chem. Rev.* **1977**, 313.



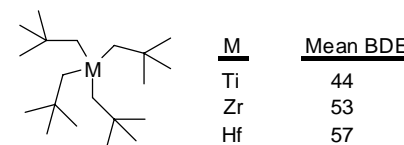
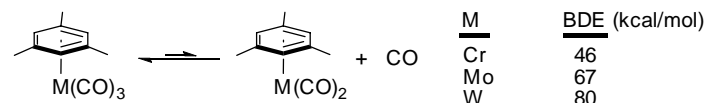
**Bite Angle:** The angle produced when a chelating ligand binds to a metal center. van Leeuwen, P. W. N. M. *Dalton* **2003**, 1890.



**Natural bite angle:** Preferred chelation angle of ligand regardless of metal valence angles. Casey, C. P. *Israel J. Chem.* **1990**, 299.

### Bond Strengths

Note: In the d-block bond strengths increase by row. This is due to better overlap with the larger d-orbitals. 3<sup>rd</sup> row > 2<sup>nd</sup> row > 1<sup>st</sup> row

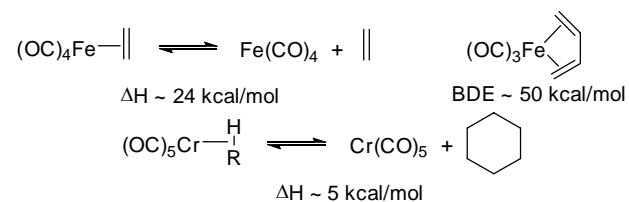


Calibration : BDE(CH<sub>3</sub>-I) = 58 kcal/mol

	(OC) <sub>4</sub> Mn-X	Ir(III)-X
H	55(4)	60(2)
CH <sub>3</sub>	37(1)	46(3)
Ph	41(3)	-56
Ac	31(3)	45(3)
I	47(2)	45(2)
Cl	70(2)	71(4)
(CO) <sub>4</sub> Mn	~23	

Mn: Skinner, *Orgmet* 1982, 1166

Ir: Blake et. al. *JACS* 1979, 74; *JACS* 1981, 5768



*While BDE's decrease going down a row in the d-block, Atomic size does not.*

Element	Atomic radius	Ionic radius (IV)
Ti	1.40 Å	0.56 Å
Zr	1.55 Å	0.73 Å
Hf	1.55 Å	0.72 Å
Ni	1.35 Å	0.62 Å
Pd	1.40 Å	0.76 Å
Pt	1.35 Å	0.76 Å

*d-orbitals do not shield the nuclear charge well, so elements decrease in size going to the right.*

**Lanthanide contraction:** *electrons in f-orbitals shield the nucleus more poorly than d-orbitals, so many of the 3<sup>rd</sup> row d-block elements are smaller than their 2<sup>nd</sup> row analogs.*