

Coordination Chemistry II: Jahn-Teller, Square Planar Complexes, Orbital Overlap Method, and Electron Counting

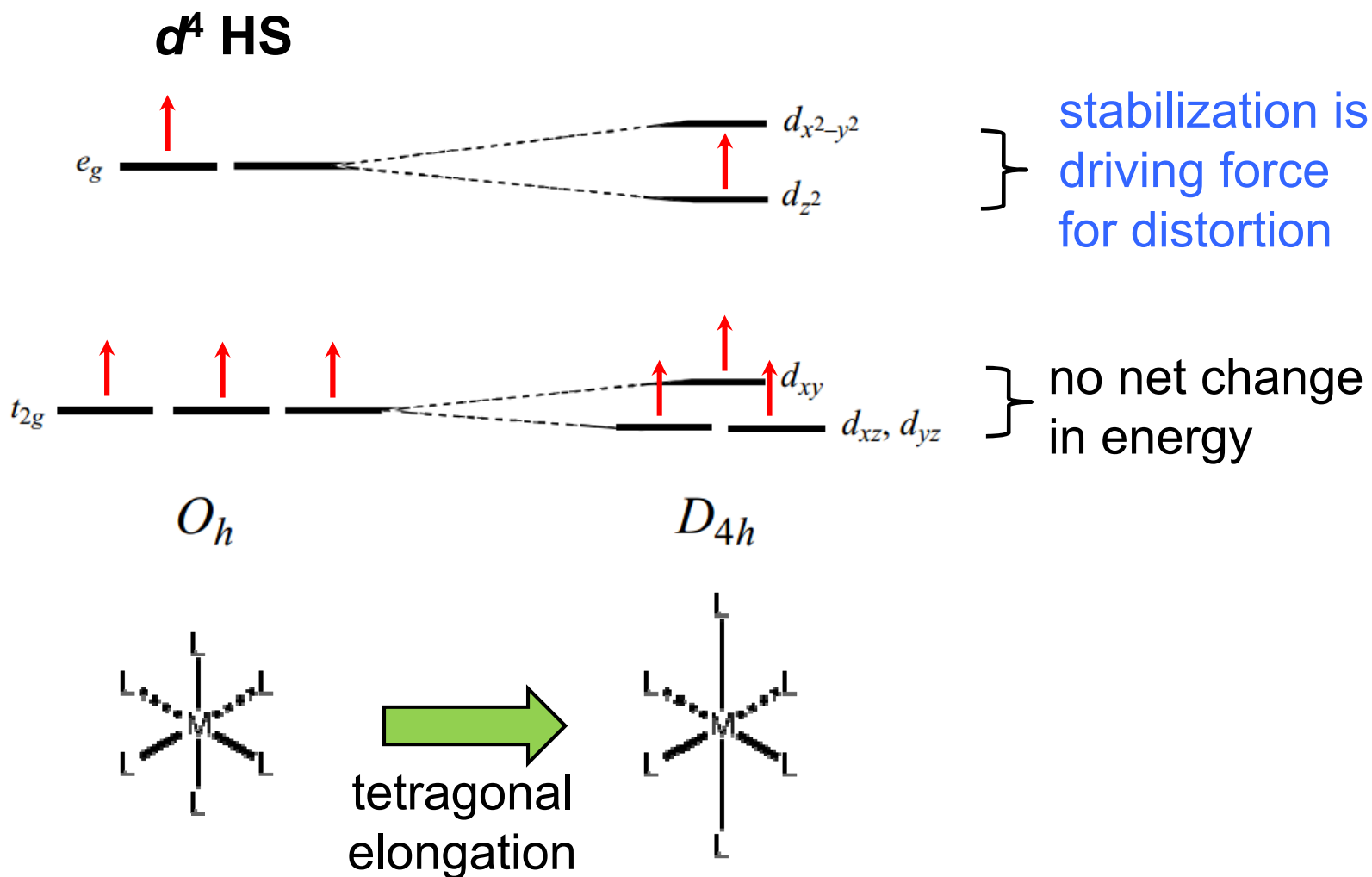
Chapter 10 and Section 13.3

Monday, November 30, 2015

Jahn-Teller Distortions

Jahn-Teller Theorem: electron configurations with *unequal occupancy of degenerate orbitals* are not stable.

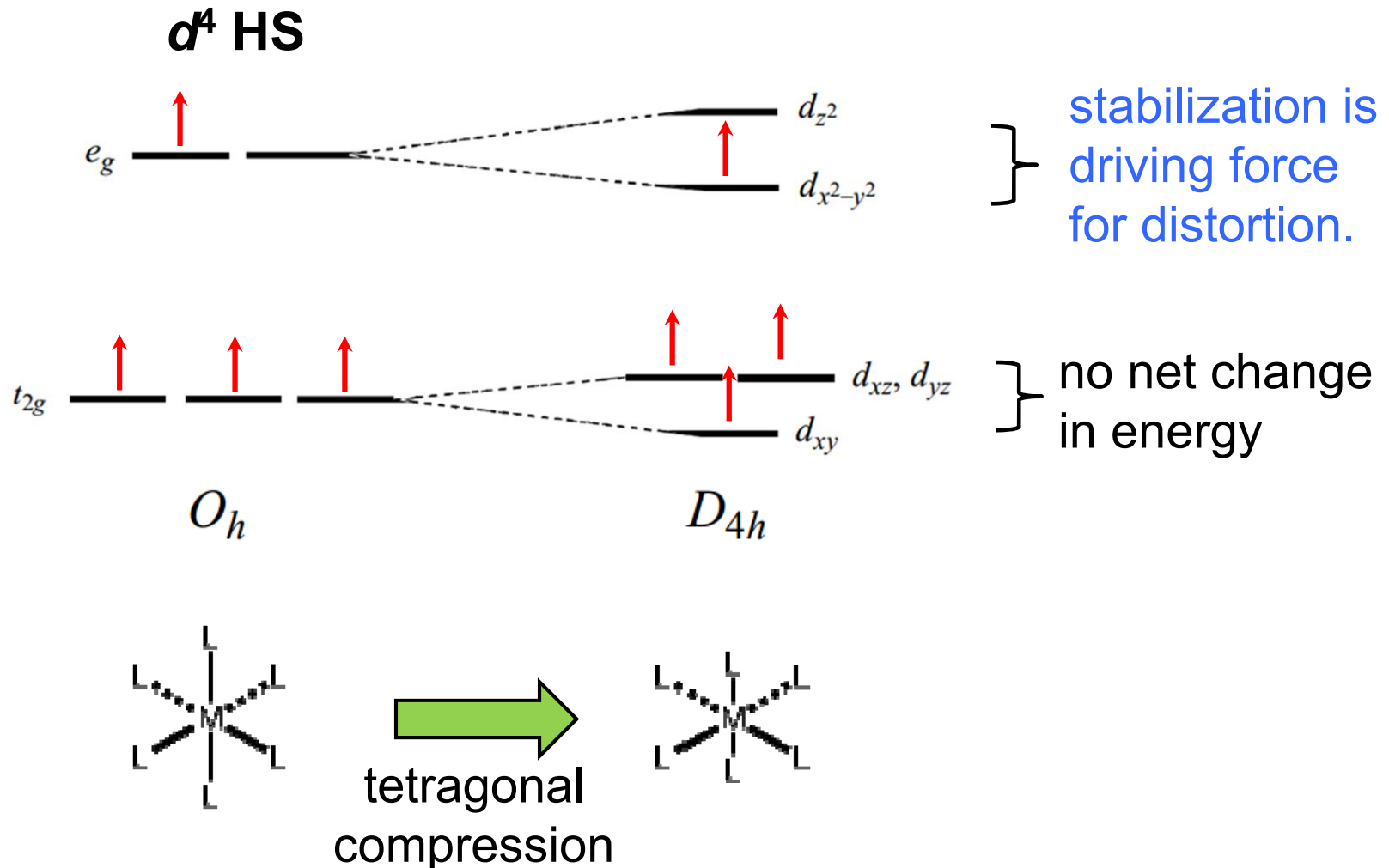
A complex with such a configuration will undergo a *Jahn-Teller distortion* to lower its energy.



Jahn-Teller Distortions

Jahn-Teller Theorem: electron configurations with *unequal occupancy of degenerate orbitals* are not stable.

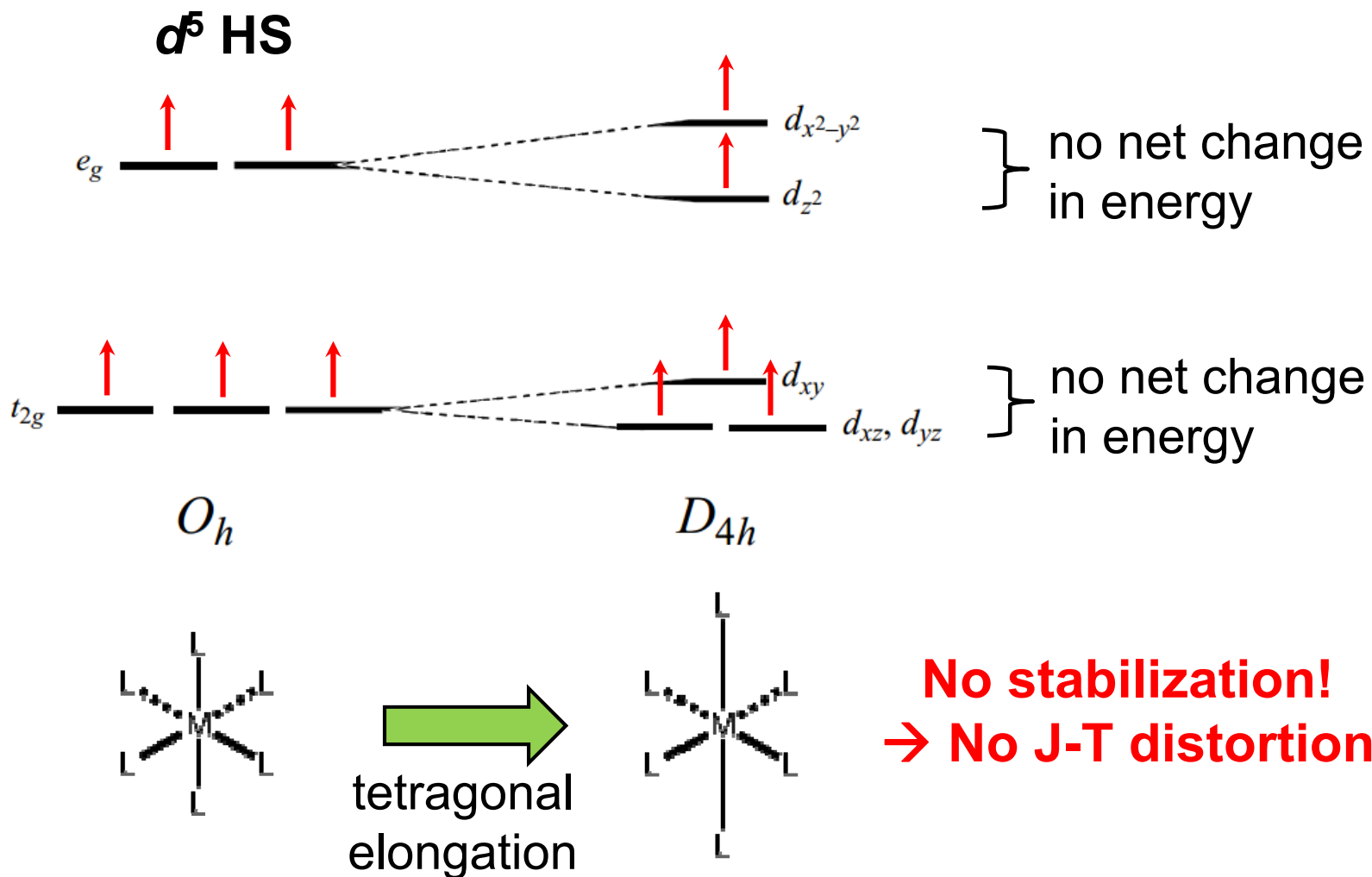
Various types of distortions are possible (tetragonal, trigonal, etc.).



Jahn-Teller Distortions

Jahn-Teller Theorem: electron configurations with *unequal occupancy of degenerate orbitals* are not stable.

Only some complexes can lower their energy by distorting:



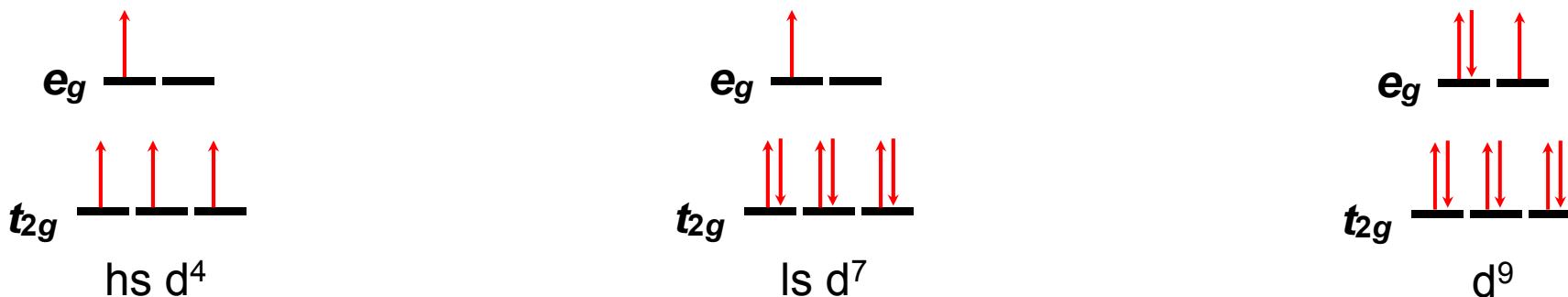
Occurrence of Jahn-Teller Effects

Partially occupied e_g orbitals ($M-L \sigma^*$) lead to more pronounced distortions than partially-occupied t_{2g} orbitals (non-bonding).

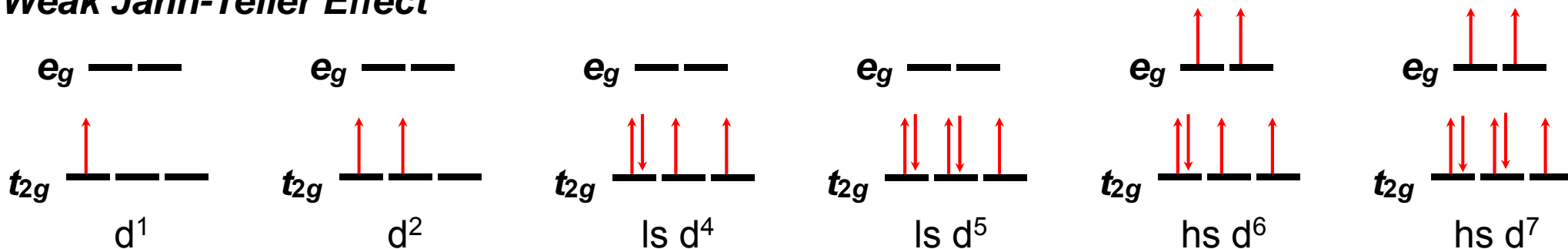
Number of Electrons	1	2	3	4	5	6	7	8	9	10
High-spin Jahn-Teller	w	w		s		w	w		s	
Low-spin Jahn-Teller	w	w		w	w		s		s	

w = weak Jahn-Teller effect expected (t_{2g} orbitals unevenly occupied); s = strong Jahn-Teller effect expected (e_g orbitals unevenly occupied); No entry = no Jahn-Teller effect expected.

Strong Jahn-Teller Effect

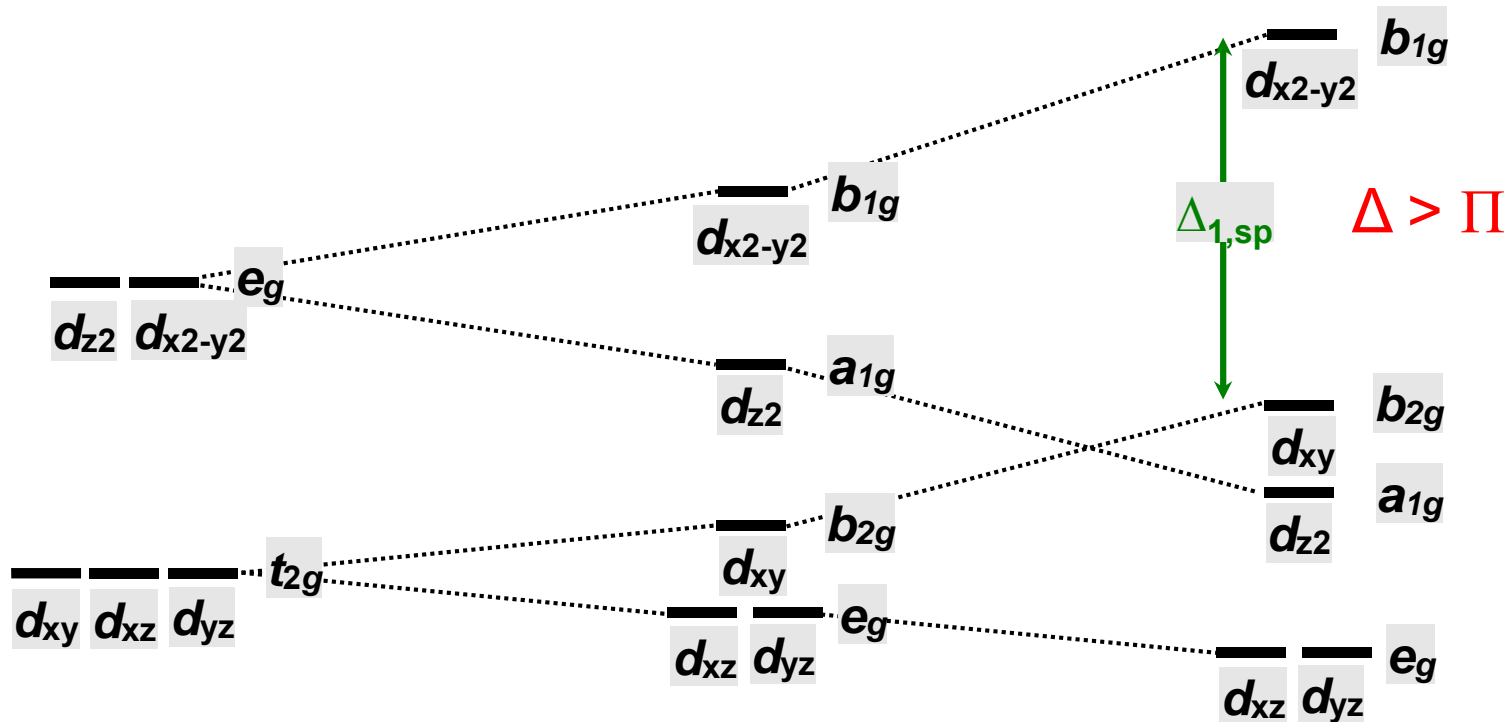


Weak Jahn-Teller Effect

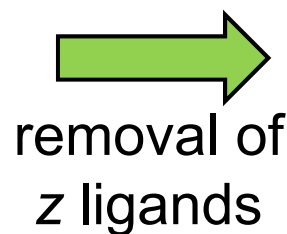
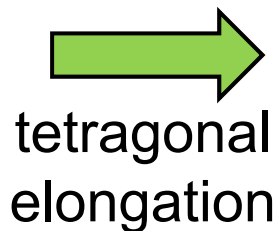


Square Planar Complexes

Consider a CFT diagram of a tetragonal elongation taken to its extreme:



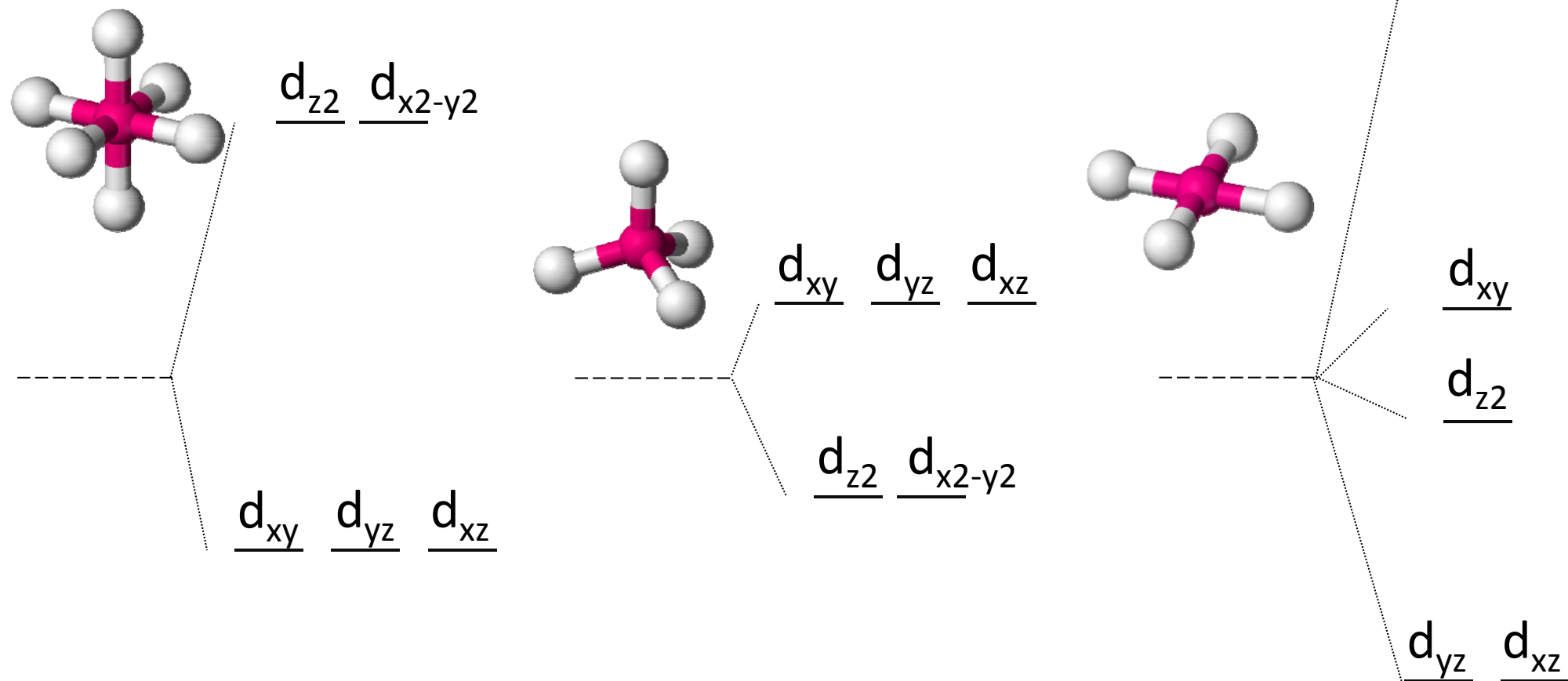
Octahedral



Square Planar

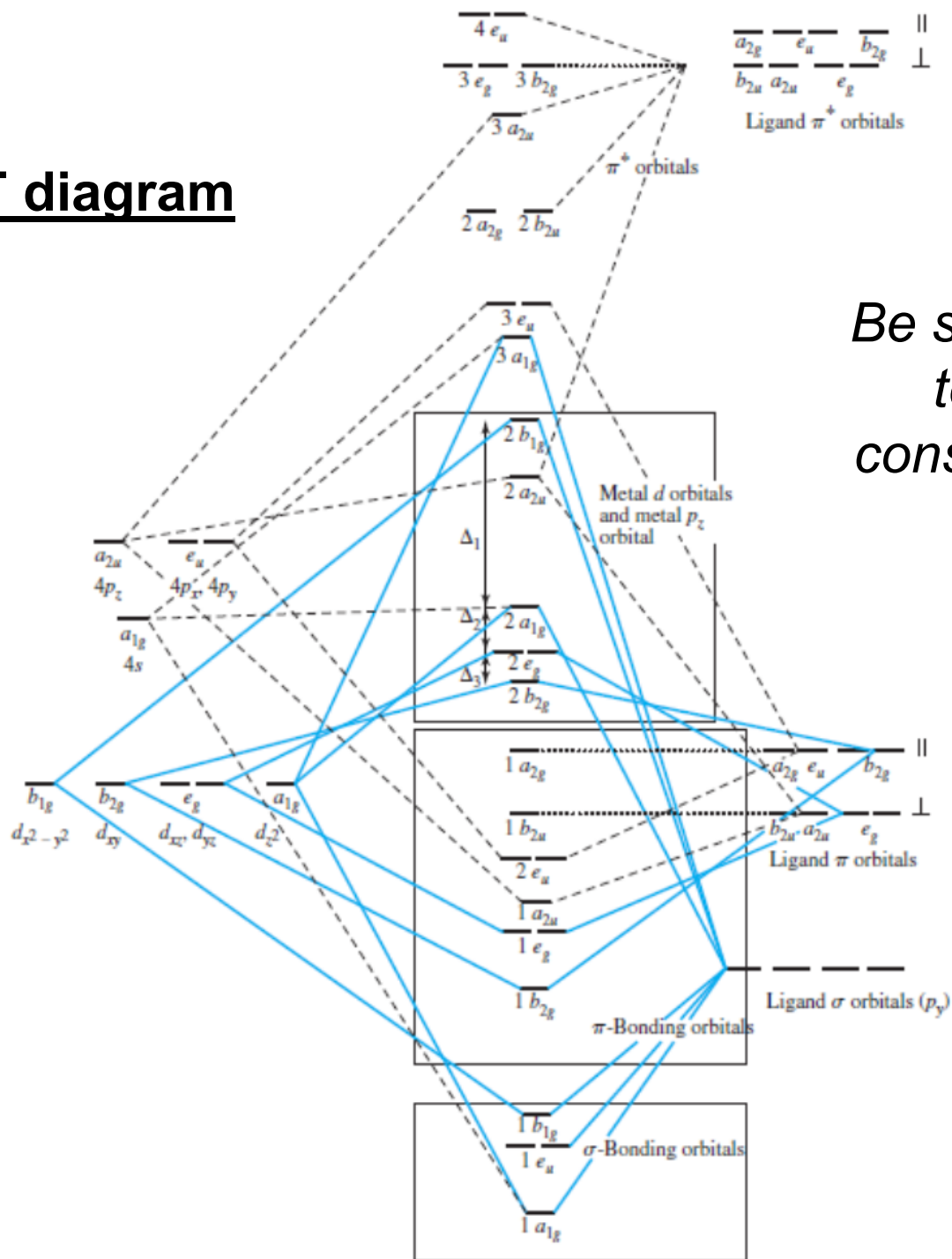
CFT of Square Planar Complexes

Occurs mostly for d^8
i.e., Pd^{2+} , Pt^{2+} , Ir^+ , Au^{3+}
(majority low spin)
Strong-field ligands



Square Planar Complexes

σ & π LFT diagram

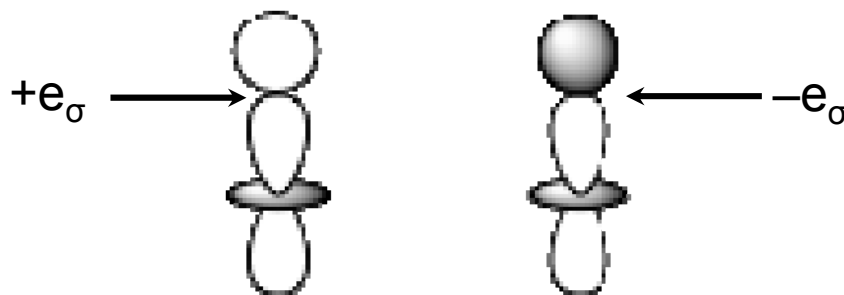


Be sure you know how to derive this by considering σ , π_{\parallel} , and π_{\perp} separately

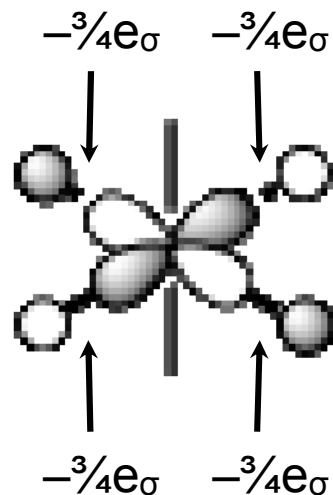
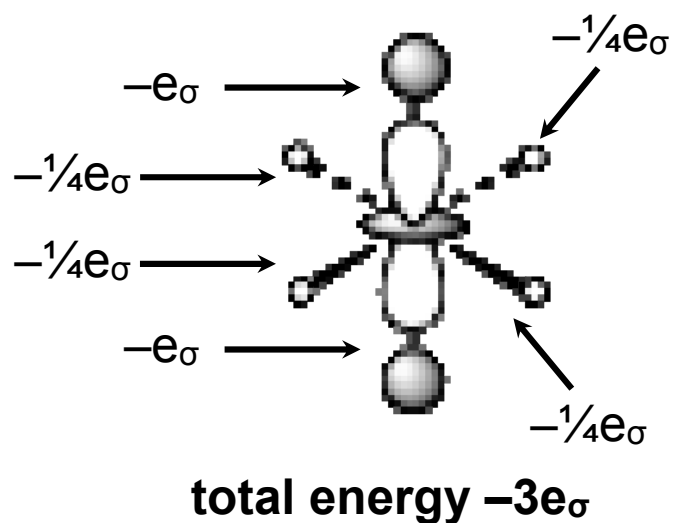
Angular Overlap Method

The AOM provides a way to estimate the impact of metal-ligand interactions on the energy of the d orbitals (only used on d orbitals!).

e_σ is a negative number because the in-phase or bonding interaction is favorable

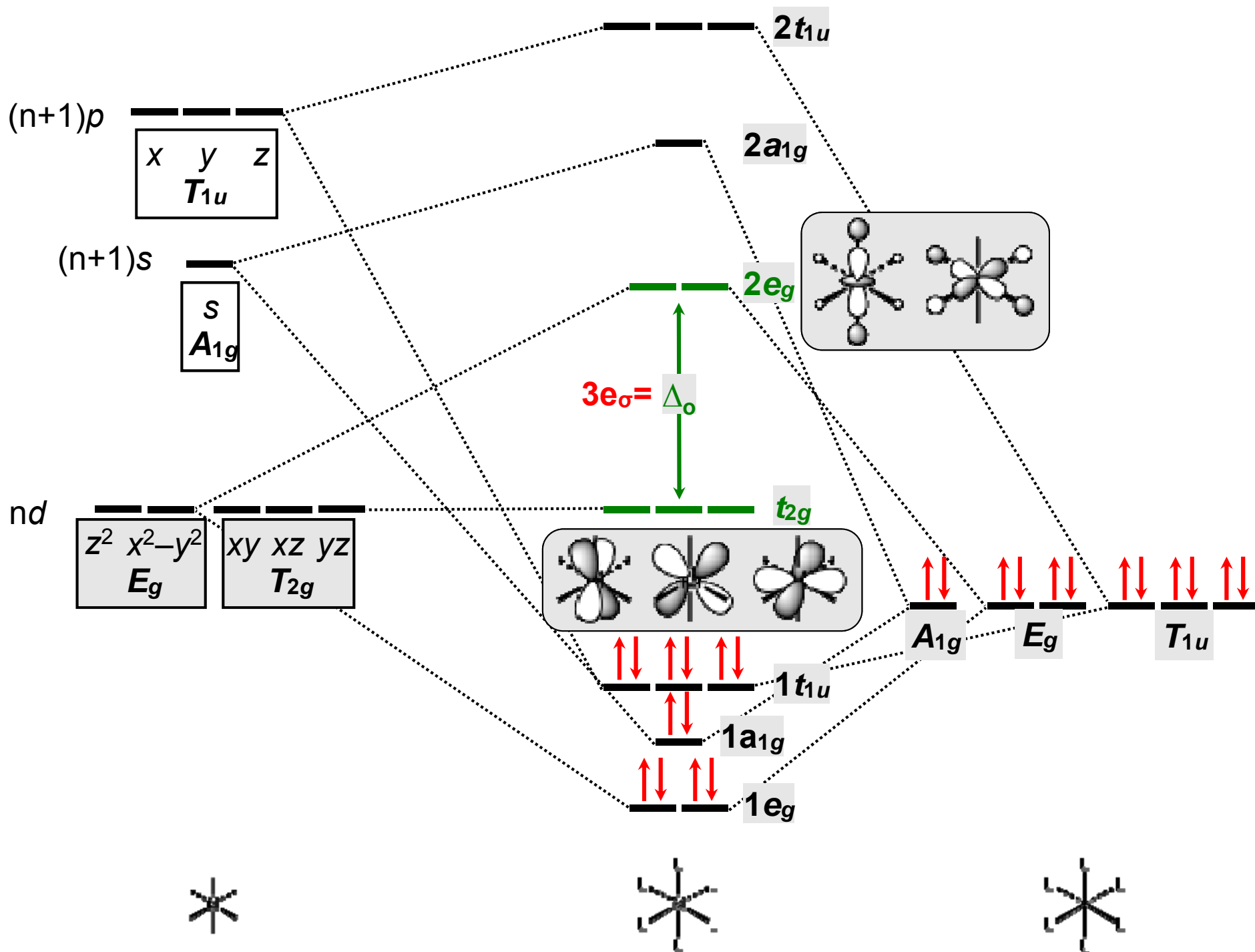


Remember for an octahedral complex in the σ -only case only the d_{z^2} and $d_{x^2-y^2}$ orbitals interact with ligands



total energy $-3e_\sigma$

σ -ML₆ Octahedral MO Diagram

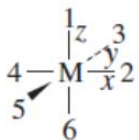
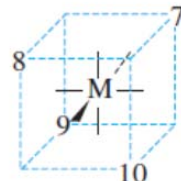
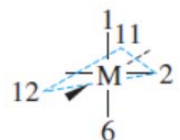


Using the AOM

The usefulness of the AOM is that it gives a good approximation of the energies of the metal *d* orbitals in different coordination geometries.

- the metal *d* orbitals are the frontier orbitals in most coordination complexes
- the AOM can be used to predict changes to the metal *d* orbitals if the coordination geometry is changed.

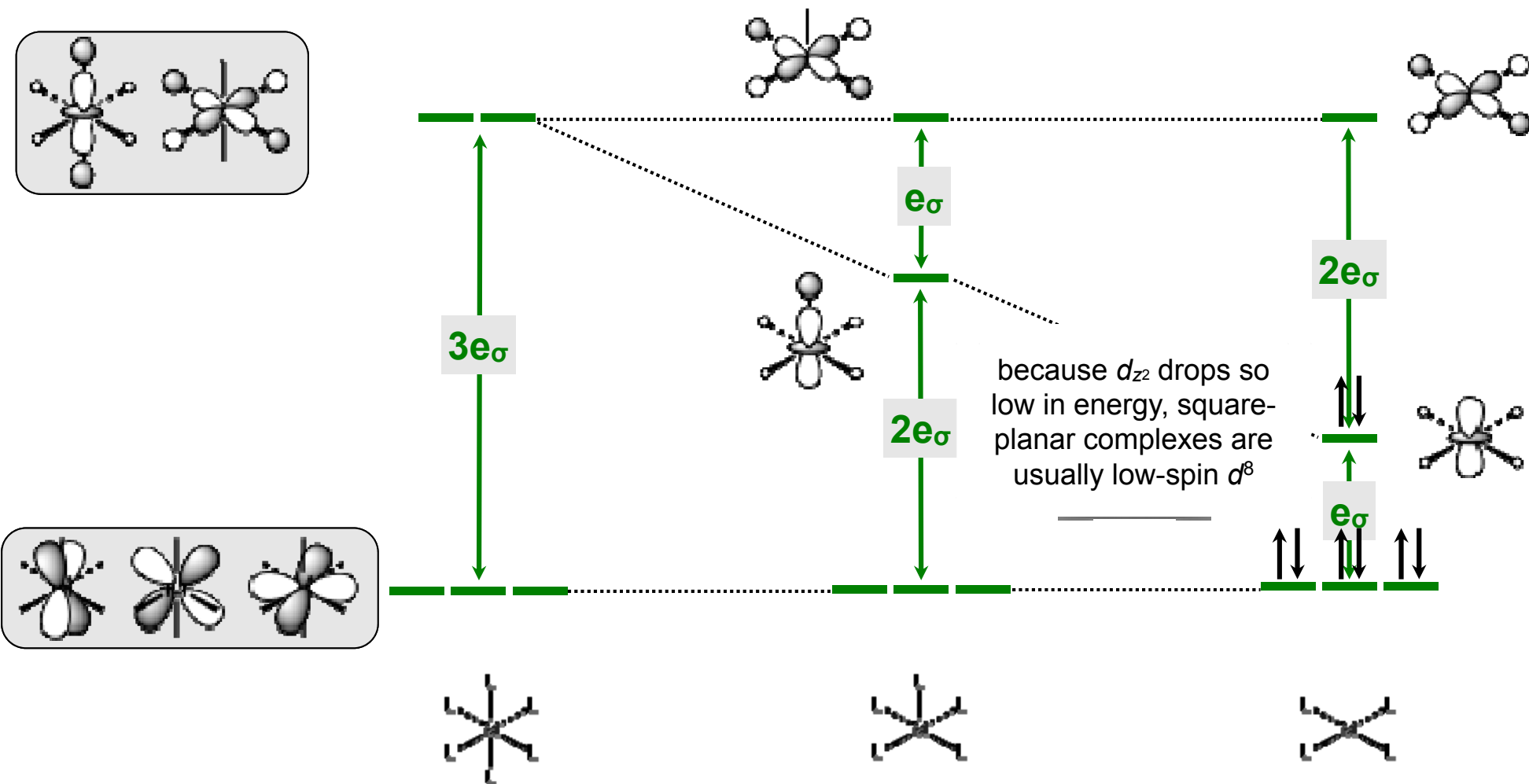
TABLE 10.10 Angular Overlap Parameters: Sigma Interactions

Octahedral Positions			Tetrahedral Positions			Trigonal Bipyramidal Positions		
								
Ligand Positions for Coordination Geometries			Sigma Interactions (in units of e_{σ}) Metal <i>d</i> Orbital					
CN	Shape	Positions	Ligand Position	z^2	x^2-y^2	xy	xz	yz
2	Linear	1, 6	1	1	0	0	0	0
3	Trigonal	2, 11, 12	2	$\frac{1}{4}$	$\frac{3}{4}$	0	0	0
3	T shape	1, 3, 5	3	$\frac{1}{4}$	$\frac{3}{4}$	0	0	0
4	Tetrahedral	7, 8, 9, 10	4	$\frac{1}{4}$	$\frac{3}{4}$	0	0	0
4	Square planar	2, 3, 4, 5	5	$\frac{1}{4}$	$\frac{3}{4}$	0	0	0
5	Trigonal bipyramidal	1, 2, 6, 11, 12	6	1	0	0	0	0
5	Square pyramidal	1, 2, 3, 4, 5	7	0	0	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$
6	Octahedral	1, 2, 3, 4, 5, 6	8	0	0	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$
			9	0	0	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$
			10	0	0	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$
			11	$\frac{1}{4}$	$\frac{3}{16}$	$\frac{9}{16}$	0	0
			12	$\frac{1}{4}$	$\frac{3}{16}$	$\frac{9}{16}$	0	0

Using the AOM

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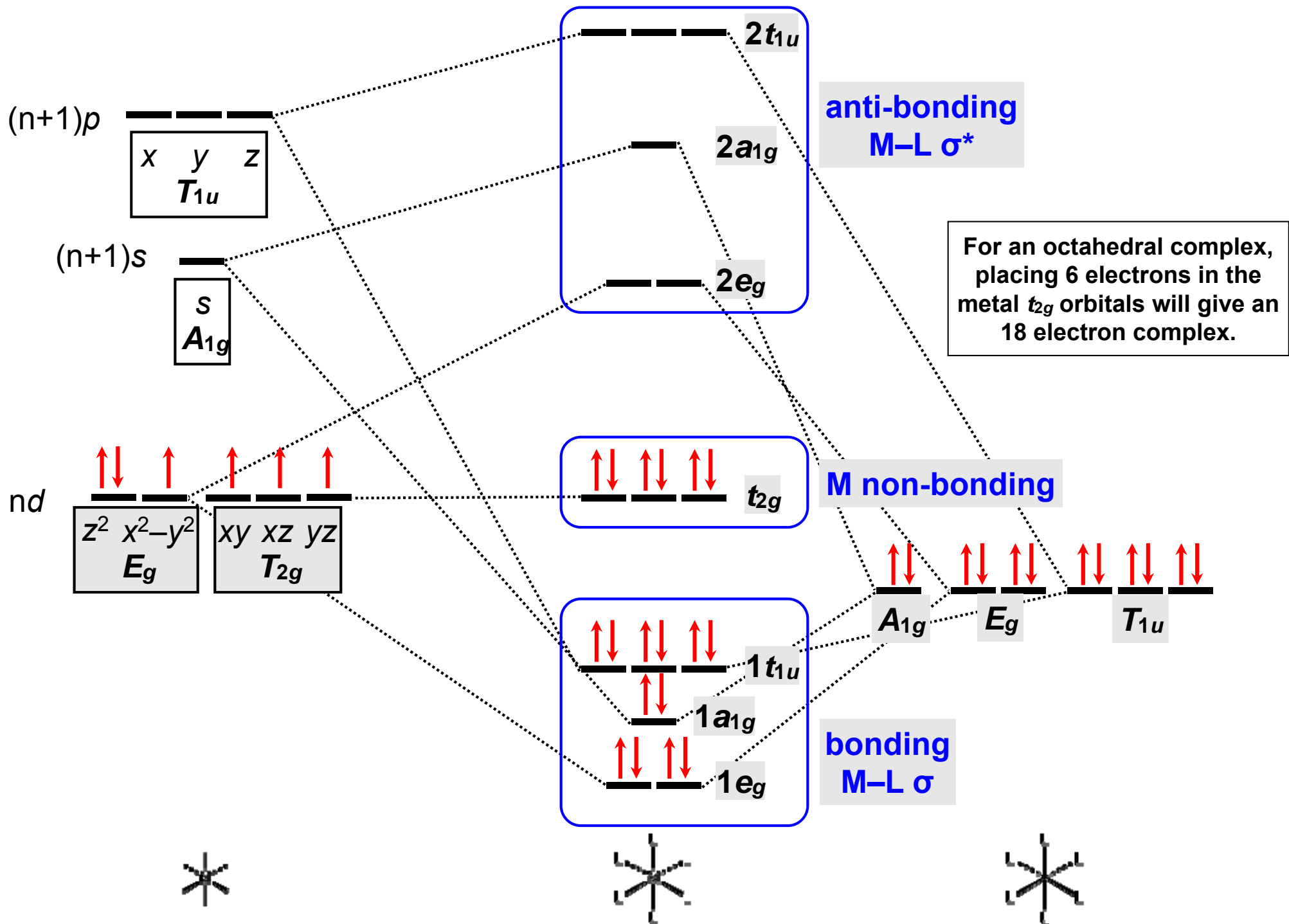


18 Electron Rule (Section 13.3)

The 18 electron rule is a loose formalism for describing stable electron configurations for some transition metal coordination complexes.

- 18 electrons is the maximum number of electrons that can be accommodated by the metal nd , $(n+1)s$, and $(n+1)p$ valence orbitals.
- really the 18 electron rule is an extension of the octet rule to include d orbitals
- the octet rule and the 18 electron rule are alternately known as the Effective Atomic Number (EAN) rule.

σ -Only ML_6 Octahedral MO Diagram



18 Electron Rule

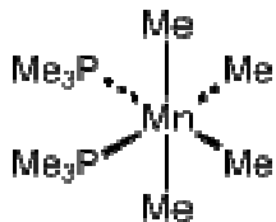
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There are two methods for determining the total valence electron count for a transition metal complex

- Donor-Pair (ionic) counting method – **every ligand coordinated to the metal is considered to be a Lewis Base (i.e., a two electron donor)**
 - $:\text{NH}_3$, $:\text{PR}_3$, etc, are neutral Lewis Bases
 - $:\text{Cl}^-$, $:\text{CH}_3^-$, etc, are anionic Lewis Bases

Donor-Pair Method - Example 1

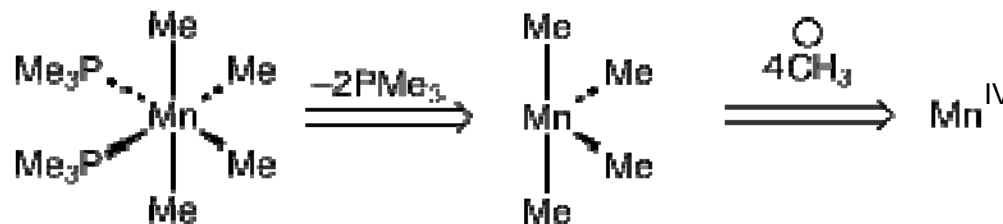


tetramethylbis(trimethylphosphane)manganese

1. Remove all ligands as Lewis bases (closed octet on donor atom)



2. Determine the charge left on the metal after removing the Lewis Base ligands.



in order to balance charge, the manganese must be 4+, this is the metal *oxidation state*

3. Using the metal oxidation state, determine the number of metal *d* electrons

#*d* electrons = #valence electrons in neutral metal – metal oxidation state

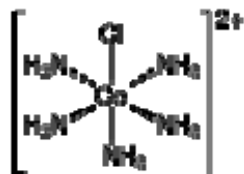
$$\#d \text{ electrons} = 7 - (+4) = 3$$

4. Add the number of metal *d* electrons to the number of electrons donated by the ligands to get the total valence electron count.

2 :PMe ₃	4 e ⁻
4 :CH ₃ ⁻	8 e ⁻
Mn ^{IV}	3 e ⁻
	15 e ⁻

So we'd say that MnMe₄(PMe₃)₂ is a *d*³ Mn^{IV} 15-electron complex

Donor Pair Method - Example 2

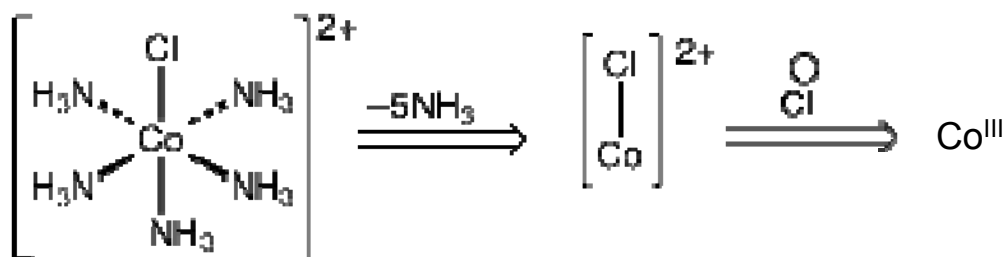


pentaamminechlorocobalt (2+)

1. Remove all ligands as Lewis bases (closed octet on donor atom)



2. Determine the charge left on the metal after removing the Lewis Base ligands.



in this case the charge from removing the Cl⁻ must be added to the overall charge on the complex, giving us Co^{III}

3. Using the metal oxidation state, determine the number of metal *d* electrons

#*d* electrons = #valence electrons in neutral metal – metal oxidation state

$$\#d \text{ electrons} = 9 - (+3) = 6$$

4. Add the number of metal *d* electrons to the number of electrons donated by the ligands to get the total valence electron count.

5 :NH ₃	10 e ⁻
1 :Cl ⁻	2 e ⁻
Co ^{III}	6 e ⁻
	18 e ⁻

So [Co(NH₃)₅Cl]²⁺ is a *d*⁶ Co^{III} 18-electron complex

18 Electron Rule

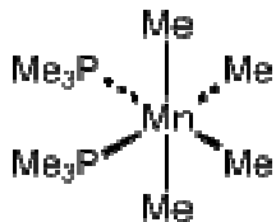
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 - $:\text{Cl}^-$, $:\text{CH}_3^-$, etc, are anionic Lewis Bases
- **Neutral Ligand counting method** – every ligand coordinated to the metal is considered to be a neutral species
 - $:\text{NH}_3$, $:\text{PR}_3$, etc, are neutral two-electron donors to the metal
 - $\cdot\text{Cl}$, $\cdot\text{CH}_3$, etc, are neutral one-electron donors to the metal

Neutral Ligand Method - Example 1



tetramethylbis(trimethylphosphane)manganese

1. Remove all ligands as neutral fragments, which leaves a neutral metal



2. Add up the electrons donated by the neutral ligands and on the neutral metal to get the total valence electron count



Notice we again determine that $\text{MnMe}_4(\text{PMe}_3)_2$ is a 15 electron complex

3. We still need to determine the metal oxidation state.

metal OS = #one-electron donor ligands + charge on the complex

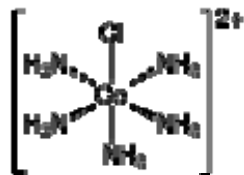
$$\text{metal OS} = 4 + (+0) = +4 \quad \boxed{\text{Mn}^{\text{IV}}}$$

4. Now, using the metal oxidation state, determine the number of metal *d* electrons

#*d* electrons = #valence electrons in neutral metal – metal oxidation state

$$\#d \text{ electrons} = 7 - (+4) = 3$$

Neutral Ligand Method - Example 2



pentaamminechlorocobalt (2+)

1. Remove all ligands as neutral fragments, which leaves a neutral metal



2. Add up the electrons donated by the neutral ligands and on the neutral metal to get the total valence electron count

5 :NH ₃	10 e ⁻
1 ·Cl	1 e ⁻
Co ⁰	9 e ⁻
<hr/>	
	20 e ⁻
+2 charge	-2 e ⁻
<hr/>	
	18 e ⁻

We forgot to account for the charge on the complex, which is 2+

3. Determine the metal oxidation state.

metal OS = #one-electron donor ligands + charge on the complex

$$\text{metal OS} = 1 + (+2) = 3 + \boxed{\text{Co}^{\text{III}}}$$

4. Using the metal oxidation state, determine the number of metal *d* electrons

#*d* electrons = #valence electrons in neutral metal – metal oxidation state

$$\#d \text{ electrons} = 9 - (+3) = 6$$

18 Electron Rule

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Emphasizes metal oxidation state and
d electron count

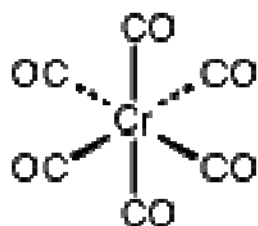
Useful for all coordination complexes

- Neutral Ligand counting method – **every ligand coordinated to the metal is considered to be a neutral species**
 - :NH₃, :PR₃, etc, are neutral two-electron donors to the metal
 - ·Cl, ·CH₃, etc, are neutral one-electron donors to the metal

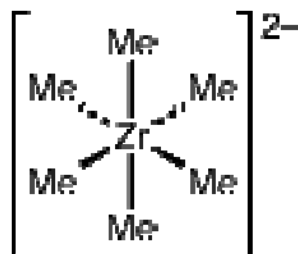
Emphasizes EAN

Useful for organometallic and other
electron-rich complexes

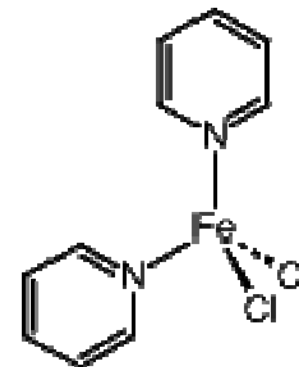
Examples to try...



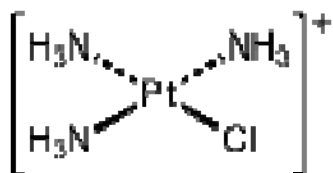
hexacarbonylchromium
 d^6 , Cr^0
18 electron complex



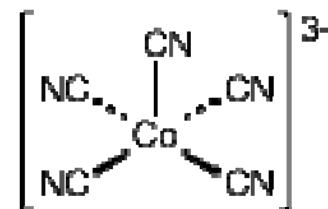
hexamethylzirconate ($2-$)
 d^0 , Zr^{4+}
12 electron complex



dichlorobis(pyridine)iron
 d^6 , Fe^{2+}
14 electron complex



triamminechloroplatinum ($1+$)
 d^8 , Pt^{2+}
16 electron complex



pentacyanocobaltate ($3-$)
 d^7 , Co^{2+}
17 electron complex

Remember, you should get the same oxidation state, d -electron count, and total valence electron count regardless of which counting method you use!