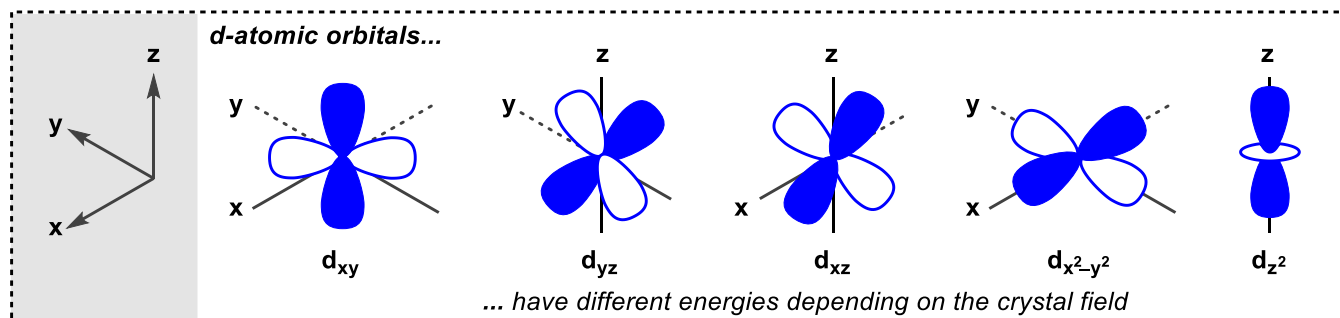


## Crystal Field Theory

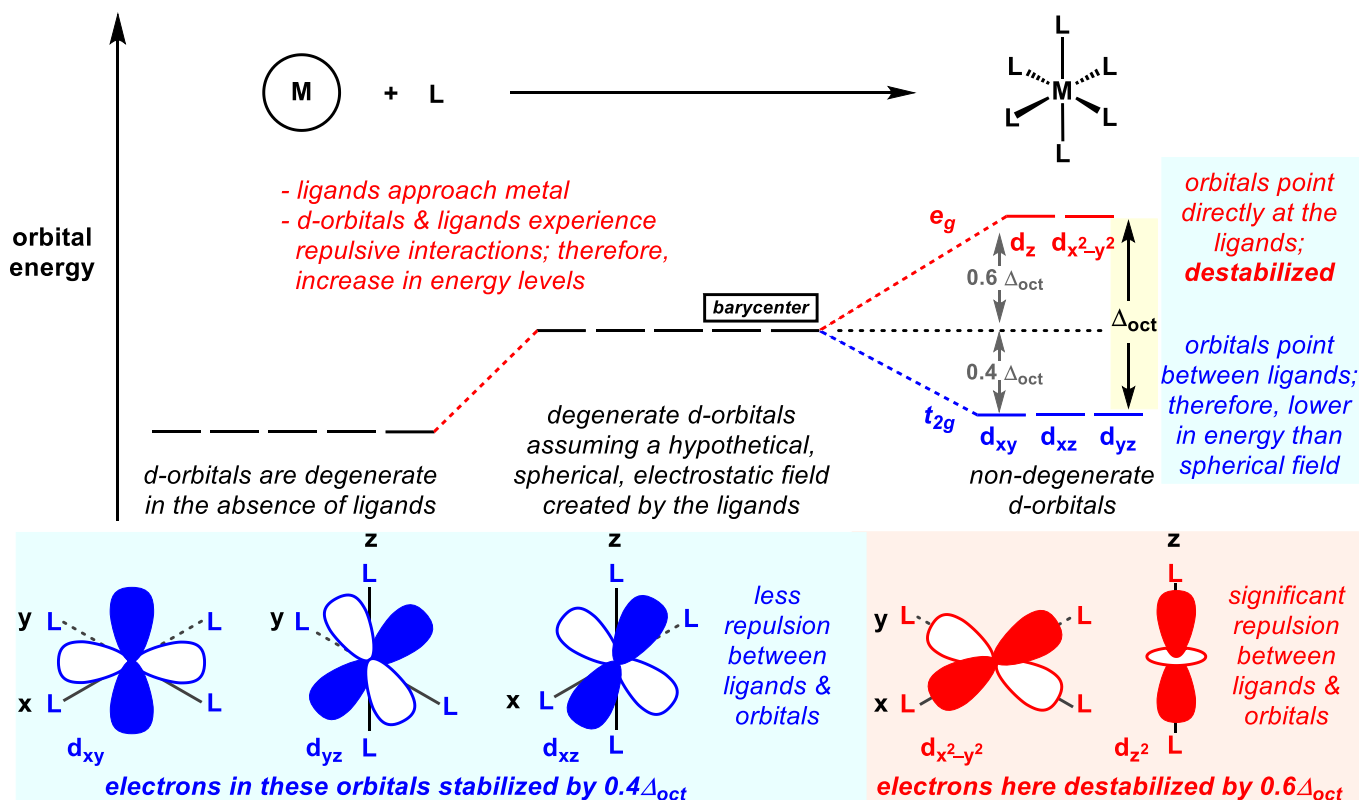
Crystal field theory predicts how the d-orbitals of transition metals are influenced by the ligand environment

- *d-orbitals are not degenerate*
- An **electrostatic model** that assumes all ligands to be point (negative) charges
  - As a consequence of the point charges, the d-orbitals in a metal complex are *not degenerate*;
  - The relative energies of the d-orbitals depend on the “crystal field” (the electrostatic field), which is governed by the ligand arrangement



- While there is attraction between the metal ion and ligand point charges, *there are repulsive interactions between the electrons in the d-orbitals and the ligands*
- An incredibly simple, but unrealistic, model for understanding structural, electronic, and magnetic properties — for synthetic organic chemists, it is useful for understanding why metal complexes adopt certain geometries
  - Resort to **ligand field theory** for a more rigorous treatment

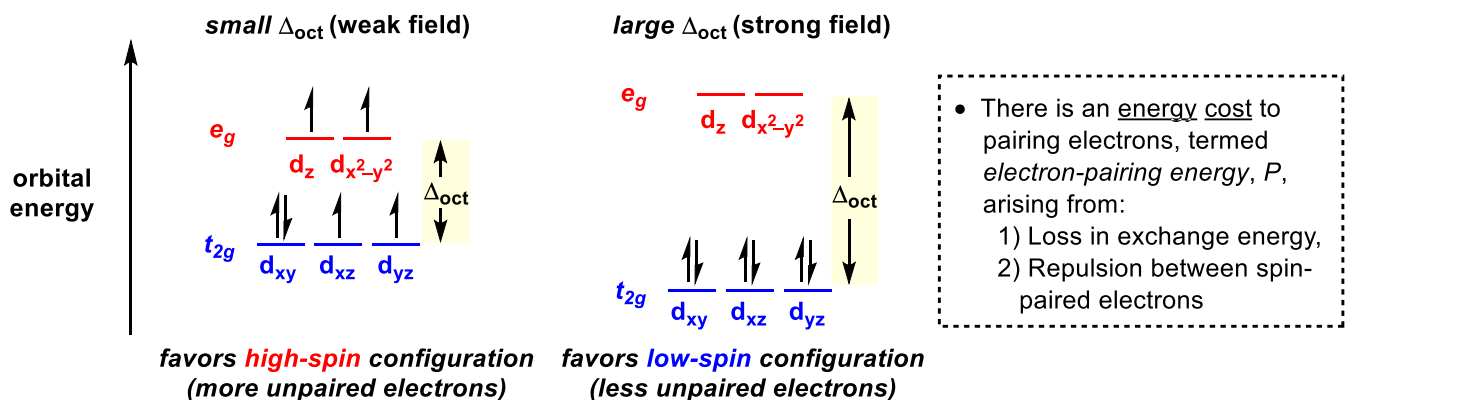
### A) Octahedral Crystal Field ( $O_h$ )



## Crystal Field Theory

- $\Delta_{\text{oct}}$  is the energy difference between the  $t_{2g}$  and  $e_g$  sets of orbitals (see Page 4 brief review)
  - Determined empirically (*i.e.*, via electronic absorption spectroscopy; easiest to determine for early transition metals with few  $t_{2g}$  electrons)
  - Magnitude of  $\Delta_{\text{oct}}$  affects whether a transition metal complex exhibits a high-spin or low-spin electron configuration:

*High-Spin vs Low-Spin Complexes (consider the following  $d^6$  arrangements):*



- Crystal field stabilization energy (CFSE) quantifies the stabilization attained from the crystal field with respect to the spherical field
  - The difference in energy between the  $d$ -electrons in the crystal field and those in the spherical field (barycenter; set to 0)

**High-spin  $d^6$  complex –  $t_{2g}^4 e_g^2$ :** CFSE =  $4(-0.4\Delta_{\text{oct}}) + 2(0.6\Delta_{\text{oct}}) = -0.4\Delta_{\text{oct}}$

**Low-spin  $d^6$  complex –  $t_{2g}^6 e_g^0$ :** CFSE =  $6(-0.4\Delta_{\text{oct}}) + 2P = -2.4\Delta_{\text{oct}} + 2P$

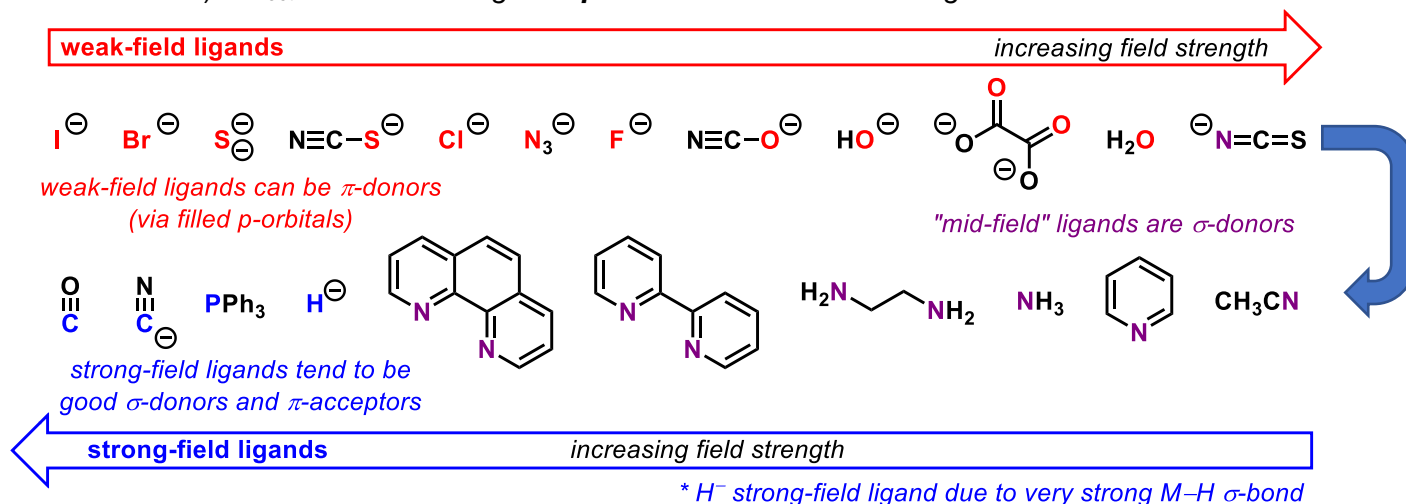
-  $\Delta_{\text{oct}}$  **large** for **low-spin** complexes ( $\Delta_{\text{oct}} > P$ )

-  $\Delta_{\text{oct}}$  small for **high-spin** complexes ( $\Delta_{\text{oct}} < P$ )

2 additional sets of paired electrons

- The strength of the crystal field influences the magnitude of  $\Delta_{\text{oct}}$ :  **$\Delta_{\text{oct}}(\text{weak field}) < \Delta_{\text{oct}}(\text{strong field})$** 
  - 3 factors affect  $\Delta_{\text{oct}}$ :

i)  $\Delta_{\text{oct}}$  increases along the **spectrochemical series** of ligands:



e.g.  $\Delta_{\text{oct}}\{[\text{Fe}(\text{OH}_2)_6]^{3+}\} = 13\,700\text{ cm}^{-1}$  vs  $\Delta_{\text{oct}}\{[\text{Fe}(\text{CN})_6]^{3-}\} = 35\,000\text{ cm}^{-1}$

## Crystal Field Theory

ii)  $\Delta_{\text{oct}}$  increases with increasing oxidation state:

Metal Complex	$\Delta_{\text{oct}}$	Metal Complex	$\Delta_{\text{oct}}$	Metal Complex	$\Delta_{\text{oct}}$
$[\text{Cr}(\text{OH}_2)_6]^{2+}$	14 100 $\text{cm}^{-1}$	$[\text{Fe}(\text{OH}_2)_6]^{2+}$	9 400 $\text{cm}^{-1}$	$[\text{Co}(\text{OH}_2)_6]^{2+}$	9 300 $\text{cm}^{-1}$
$[\text{Cr}(\text{OH}_2)_6]^{3+}$	17 400 $\text{cm}^{-1}$	$[\text{Fe}(\text{OH}_2)_6]^{3+}$	13 700 $\text{cm}^{-1}$	$[\text{Co}(\text{OH}_2)_6]^{3+}$	18 200 $\text{cm}^{-1}$

iii)  $\Delta_{\text{oct}}$  increases down a group of congeners:

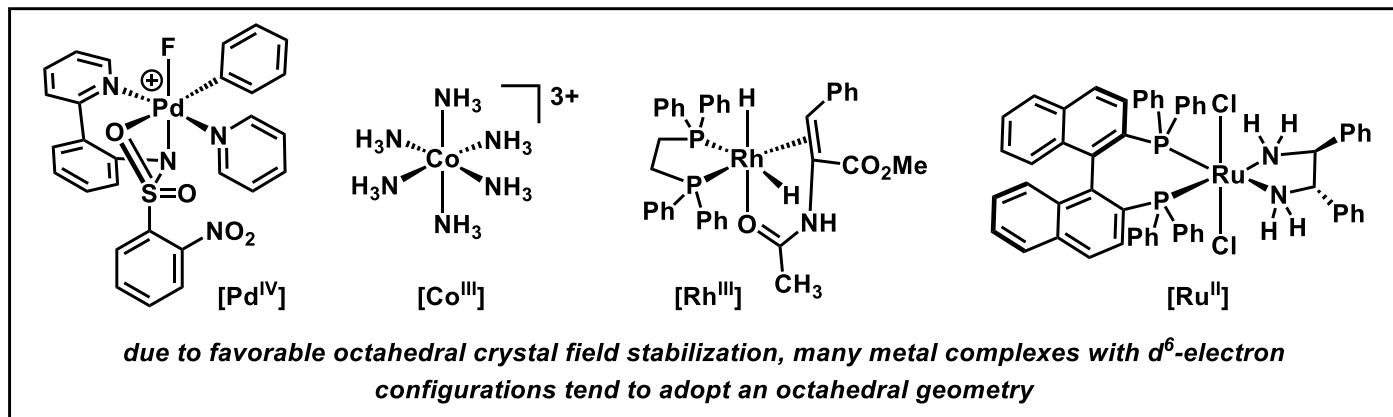
- There is no trend within a row of metals

Metal Complex	$\Delta_{\text{oct}}$
$[\text{Co}(\text{NH}_3)_6]^{3+}$	~22 000 $\text{cm}^{-1}$
$[\text{Rh}(\text{NH}_3)_6]^{3+}$	~ 34 000 $\text{cm}^{-1}$
$[\text{Ir}(\text{NH}_3)_6]^{3+}$	~ 42 000 $\text{cm}^{-1}$

- Empirically, there is a spectrochemical series of metal ions:

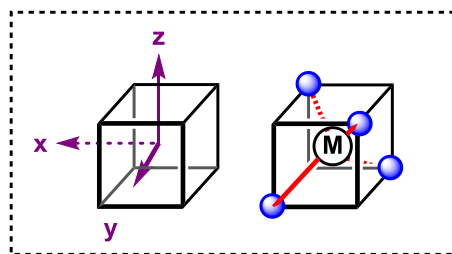
**Mn(II) < Ni(II) < Co(II) < Fe(III) < Cr(III) < Co(III) < Ru(III) < Mo(III) < Rh(III) < Pd(II) < Ir(III) < Pt(IV)**

*crystal field theory does not rationalize the order of the spectrochemical series*

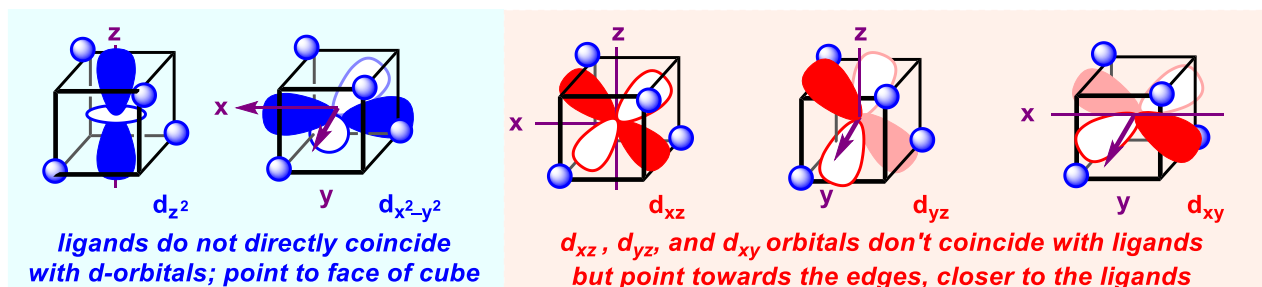


**B) Tetrahedral Crystal Field ( $T_d$ )** – crystal field diagram is the inversion of the  $O_h$  crystal field

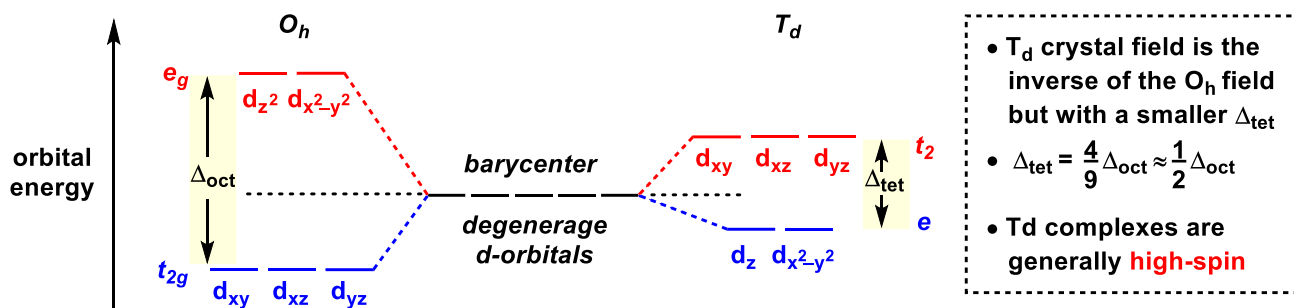
$d_{z^2}$  and  $d_{x^2-y^2}$  orbitals are stabilized with respect to the barycenter



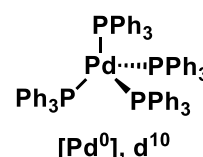
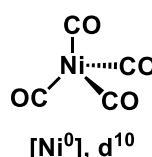
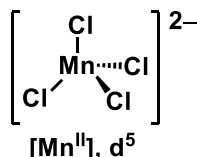
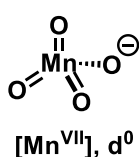
$d_{xz}$ ,  $d_{yz}$ , and  $d_{xy}$  orbitals are destabilized with respect to the barycenter



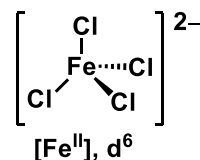
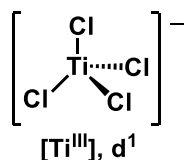
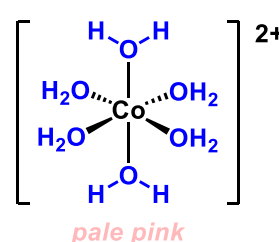
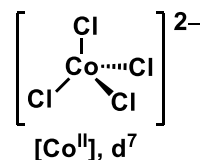
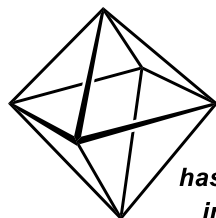
## Crystal Field Theory



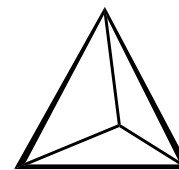
- $e \rightarrow t_2$  ( $T_d$ ) transitions require less energy than those of  $t_{2g} \rightarrow e_g$  ( $O_h$ ) transitions; therefore, tetrahedral complexes tend to be high spin and more brightly colored
- Complexes with  $d^0$ ,  $d^5$  (**high-spin**), and  $d^{10}$  electron configurations adopt tetrahedral geometries
  - When all the d-orbitals are equally-occupied, the  $T_d$  geometry of the metal-ligand complex arises from minimizing steric interactions



- $T_d$  complexes can arise from other **high-spin** d-electron configurations with weak-field ligands, except  $d^3$  and  $d^8$ :

**Drierite****Symmetry Labels** $e_g$  — — — $t_{2g}$  — — —

$O_h$ :  
has center of  
inversion

 $t_2$  — — — $e$  — — —

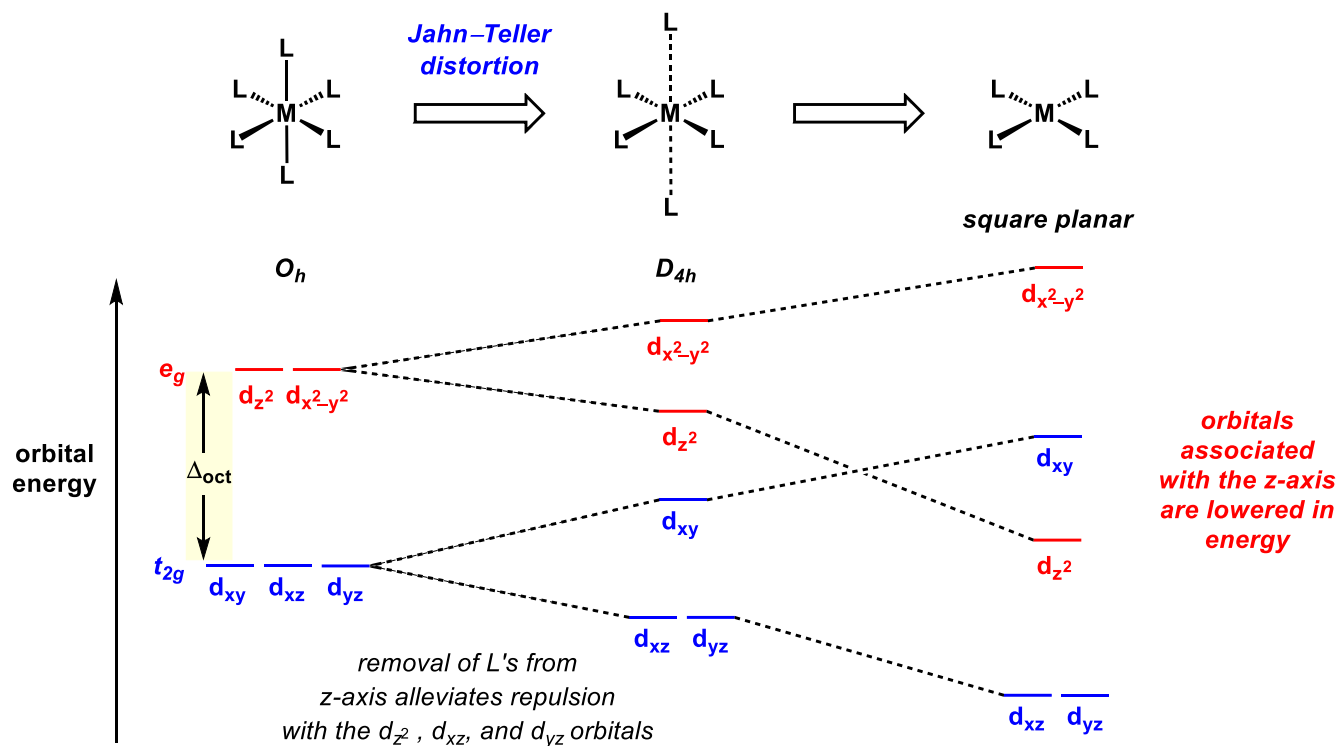
$T_d$ : no center of inversion

- $e$  and  $t$  refer to the **level of degeneracy**
  - a *doubly* degenerate set of orbitals is labelled  $e$
  - a *triply* degenerate set of orbitals is labelled  $t$
- $g$  is short for "*gerade*"; the alternative is  $u$  for "*ungerade*"
  - property of the wavefunction under the *inversion* operation
  - applicable *only* if the system exhibits symmetry via a center of inversion
- the octahedral geometry has a center of symmetry; therefore  $e_g$  and  $t_{2g}$
- the tetrahedral geometry does not have a center of symmetry; therefore  $e$  and  $t_2$

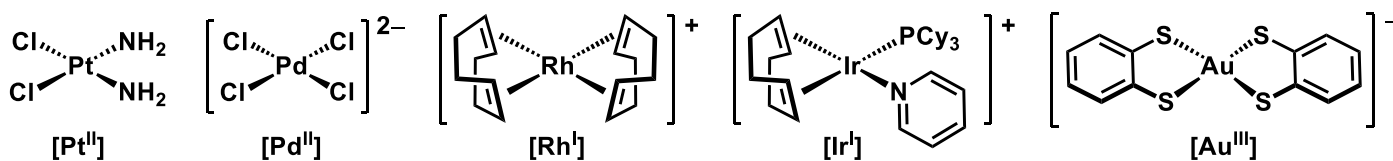
## Crystal Field Theory

### C) Square Planar Crystal Field

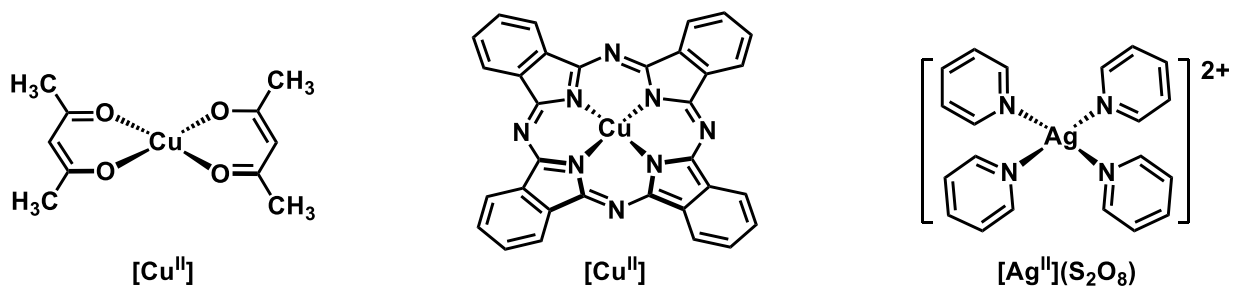
- The square planar crystal field orbital energy diagram can be derived from an octahedral complex by removing the axial ligands along the z-axis



- Most common with  $d^8$ -electron configurations:



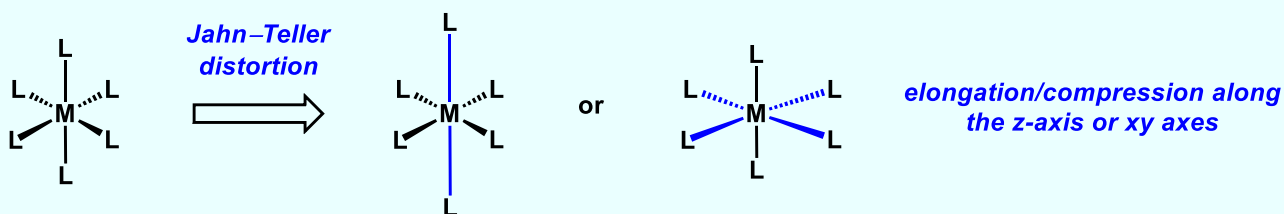
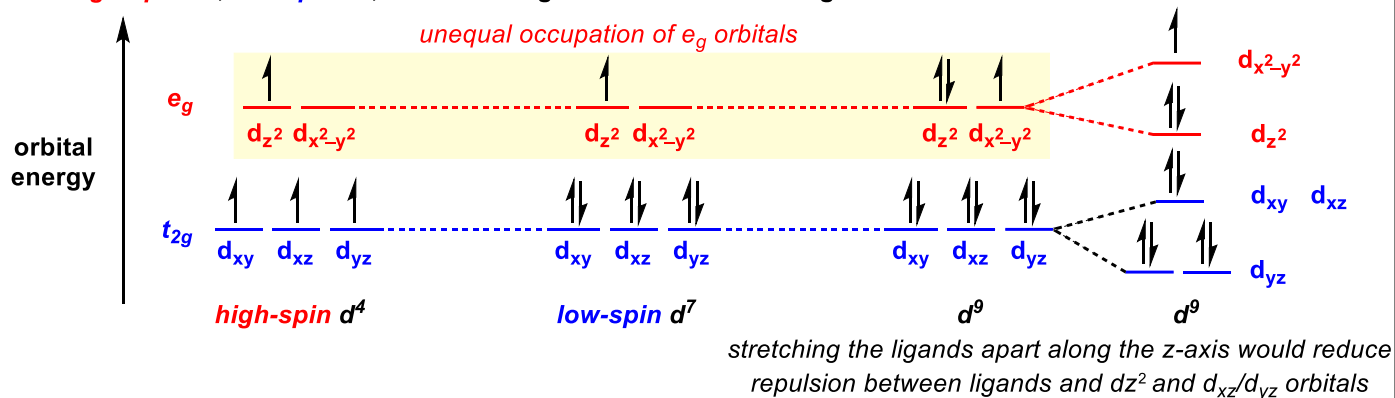
- Some  $d^9$ -complexes can adopt square planar geometries:



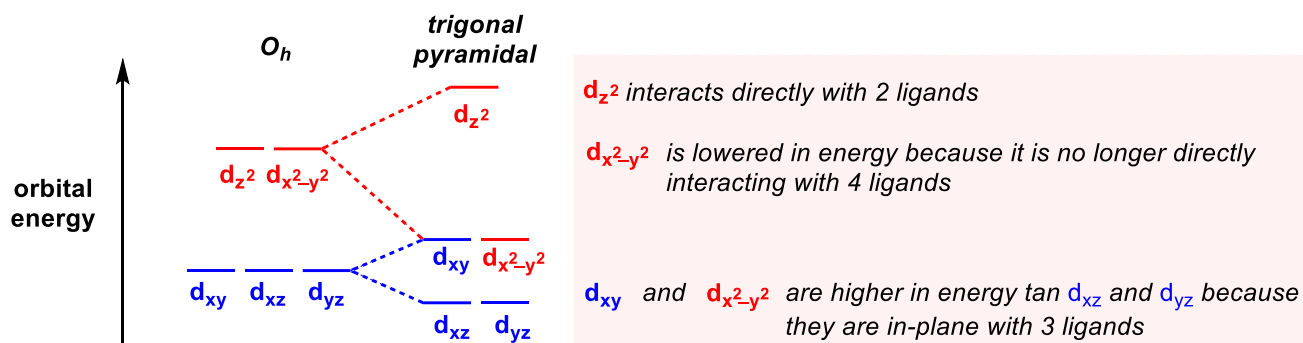
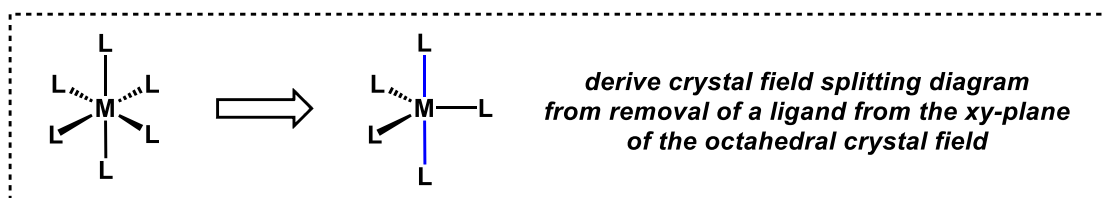
## Crystal Field Theory

### Jahn–Teller Distortions

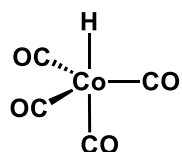
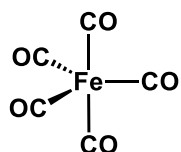
- degenerate sets of orbitals with unequal electron occupancy are unfavorable
- undergoes distortion to lower overall energies
- **high-spin**  $d^4$ , **low-spin**  $d^7$ , and  $d^9$ -configurations exhibit strong Jahn–Teller effects



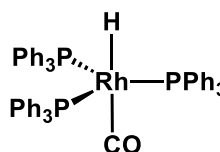
### D) Trigonal Bipyramidal Crystal Field



- Some  $d^8$ -complexes adopt trigonal bipyramidal structures:



*early hydroformylation catalyst*



*industrial hydroformylation catalyst*