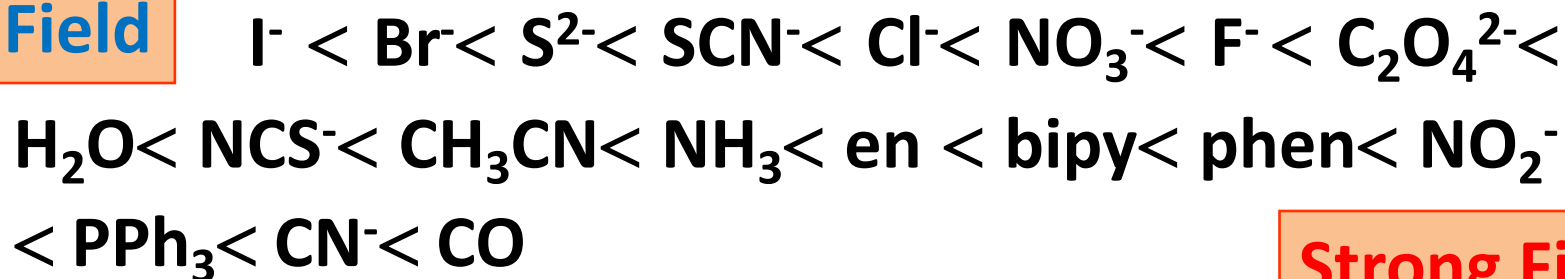# Effect of Ligands on Δ: Spectrochemical Series

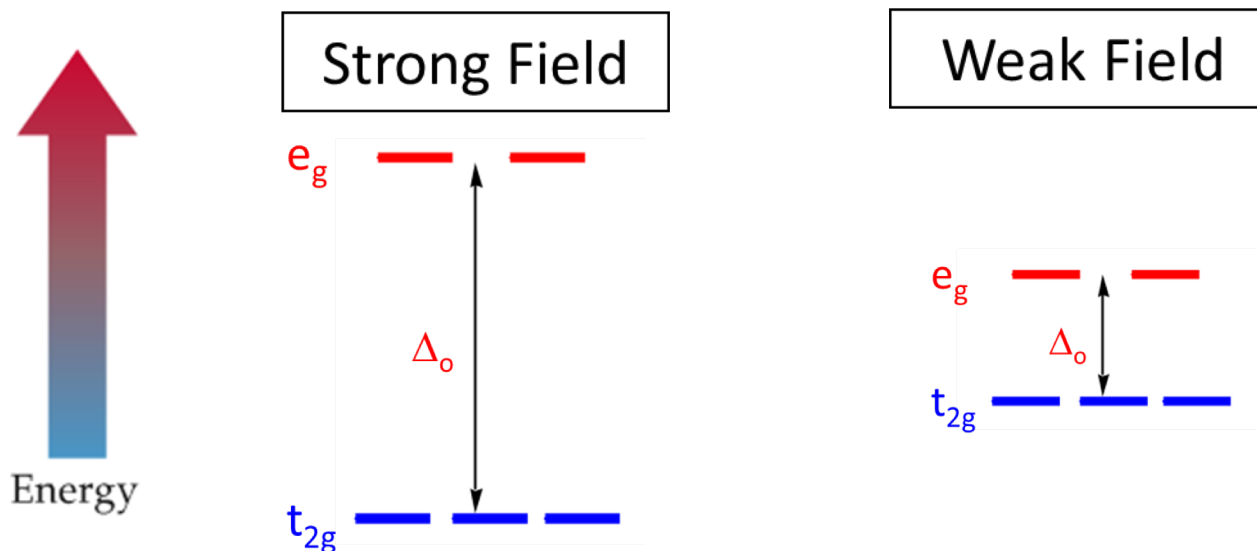❑ An arrangement of ligands according to their increasing ability to split the *d*-orbitals or crystal field splitting parameter (Δ).

❑ Experimentally determined.

Weak Field

$$I^- < Br^- < S^{2-} < SCN^- < Cl^- < NO_3^- < F^- < C_2O_4^{2-} <$$

$$H_2O < NCS^- < CH_3CN < NH_3 < en < bipy < phen < NO_2^-$$

$$< PPh_3 < CN^- < CO$$

Strong Field

Analysis of the Spectrochemical Series

❑ **Spectrochemical Series cannot be entirely explained by Crystal Field Theory (CFT). Examples: why neutral molecules such as H_2O are stronger ligands than halides; why PPh_3 and CO are strong field ligands.**

❑ **Orbital interactions need to be invoked to rationalize the order of ligands. Thus, covalency is incorporated into CFT resulting in the Ligand Field Theory.**

❑ **We will not discuss detailed Molecular Orbital treatment but will focus on Ligand Field Theory as a tool to understand important concepts pertaining to the bonding in coordination compounds.**

Observation: I^- < Br^- < Cl^- < F^- (Ligand Field strength)

❑ **In terms of CFT, the fluoride ion being much smaller, can approach closer to the metal ion thereby increasing the electronic repulsion leading to higher Δ.**
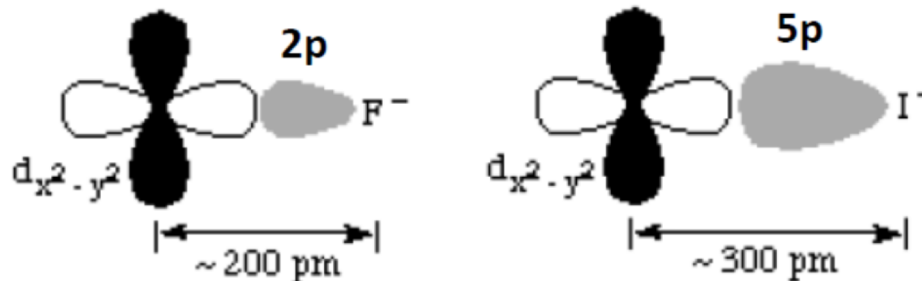
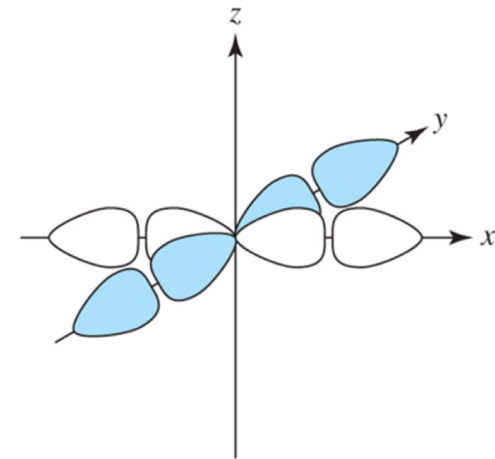# Analysis of the Spectrochemical Series

Observation: $F^- <$ OH$^- <$ O$^{2-} <$ H$_2$O (Ligand Field strength)

❑ To explain the above series, let's look at the bonding modes between the ligand and the metal. We will consider simplified diagrams for clarity.

❑ Initially, the ligands can be viewed as having a hybrid orbital or a *p* orbital pointing toward the metal to make σ bonds.

❑ This is referred to as σ donation from the ligand to the metal.

❑ Hence, all ligands are "σ donors".

❑ However, some ligands *may have* additional orbitals that can interact with other orbitals on the metal.

❑ Ligand Field Theory provides insights into these additional interactions as the reasons for the different strengths of ligands.

Sigma bonding interaction between two ligand orbitals and metal d_{z^2} orbital

Sigma bonding interaction between four ligand orbitals and metal $d_{x^2 - y^2}$ orbital
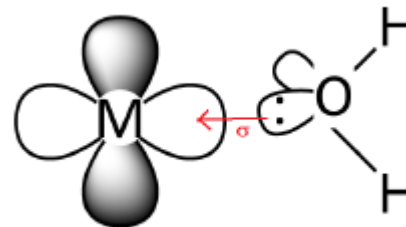
Analysis of the Spectrochemical Series

Observation: F$^-$ < OH$^-$ < O^{2-} < H$_2$O (Ligand Field strength)

❑ **Ligands which have filled *p* orbitals may act as π donors by interacting with suitable metal orbitals.**

Interaction between d$_{xy}$ of metal and p$_y$ of halide:
Reduces positive charge on metal
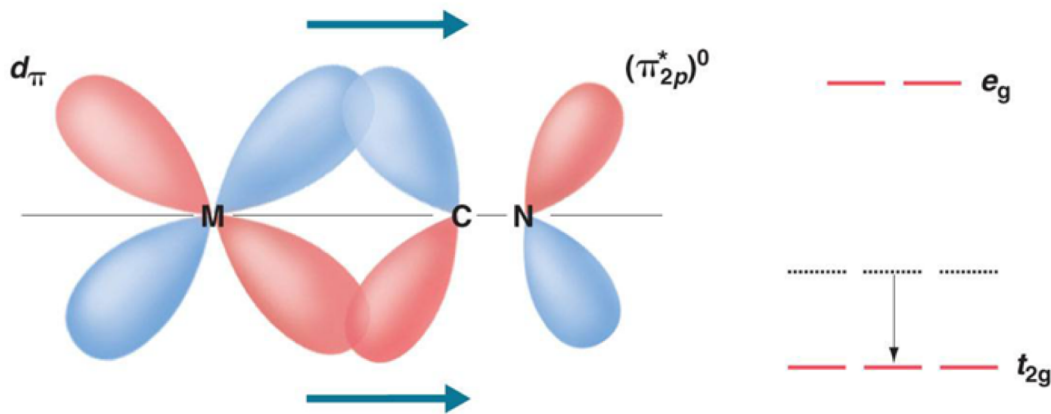Reduces Δ
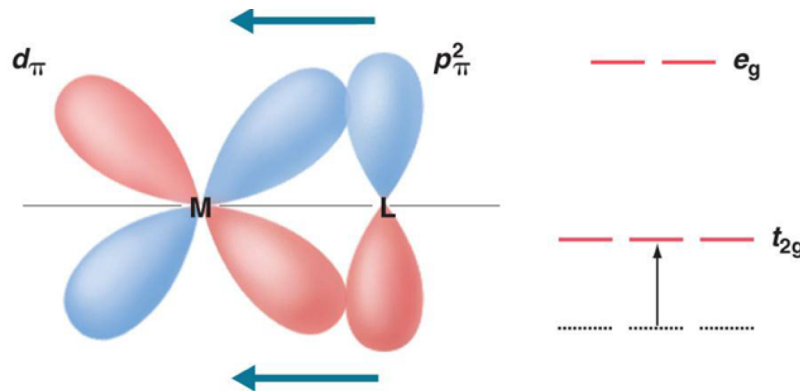
❑ **Water acts only as a sigma-donor ligand.**

Analysis of the Spectrochemical Series

Observation: PPh$_3$, CN$^-$, CO are strong field ligands

- [ ] **Ligands which have empty *p* or *d* orbitals may act as π acceptors by interacting with suitable metal orbitals.**
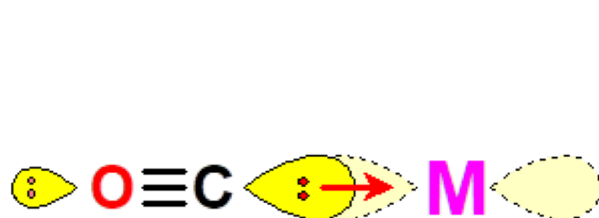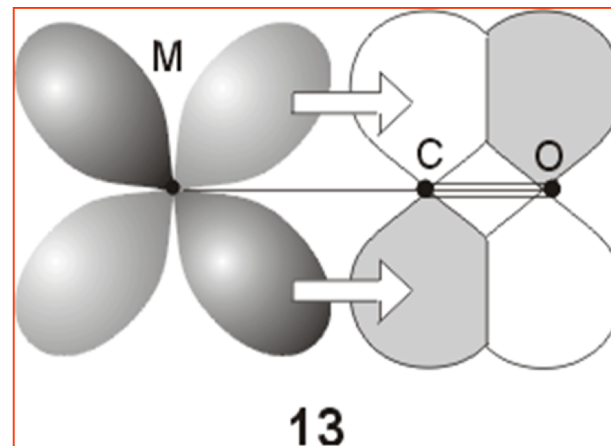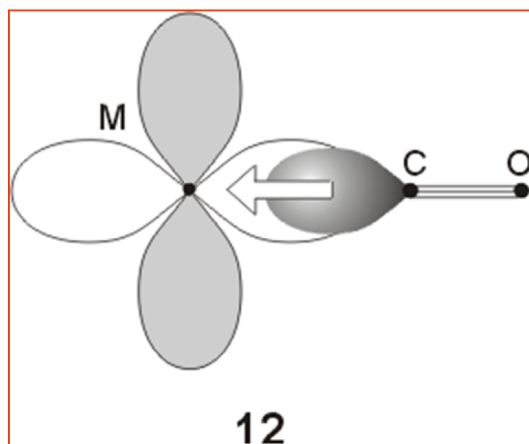
π-back-bonding of ligand with d$_{xy}$ orbital
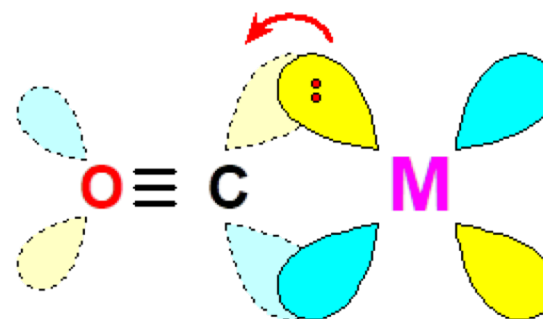Increases positive charge on metal
Increases Δ

dπ-pπ back donation (back bonding)

Analysis of the Spectrochemical Series

❑ **CO also has available π* orbitals for back bonding.**

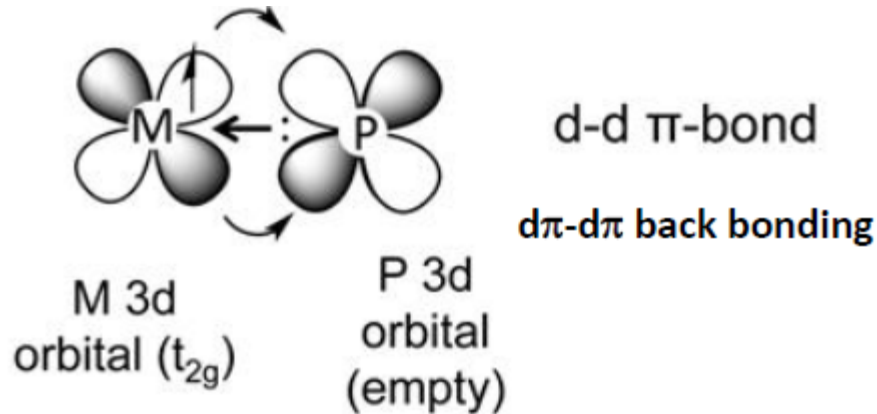CO-M sigma bond

M to CO pi backbonding

Analysis of the Spectrochemical Series

❑ **PPh$_3$ has dπ orbitals for back bonding.**

M 3d orbital (t$_{2g}$)   P 3d orbital (empty)

d-d π-bond

dπ-dπ back bonding

❑ **Accepts electrons from filled metal d-orbital to empty d-orbital of P in PPh$_3$ (π-back bonding)**

❑ **In low oxidation states, the electron density on the metal ion is very high.**

❑ **To stabilize low oxidation states, we require ligands, which can simultaneously bind the metal center and also withdraw electron density from it.**

Summary of Ligand Bonding Modes

1. All ligands are σ donors. In general, ligands that engage solely in σ bonding are in the middle of the spectrochemical series.

2. Ligands with filled *p* or *d* orbitals can also serve as π donors. This results in a smaller value of Δ_o.

3. Ligands with empty *p, d* or π* orbitals can also serve as π acceptors. This results in a larger value of Δ_o.

$$I^- < Br^- < Cl^- < F^- < H_2O < NH_3 < PPh_3 < CO$$

π donor< weak π donor<σ only< π acceptor

Examples of donor and acceptor ligands

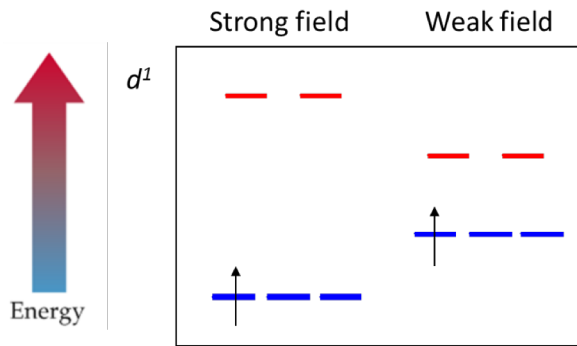| Sigma donor	Pi donor*	Pi acceptor*
H_2O	RO^-, R_2N^-	CO, olefin
NR_3	F^-, Cl^-	CN^-
	$RCOO^-$	PR_3

These ligands also act as σ donors.

Significance of Spectrochemical Series

❑ Lets try to populate the t_{2g} and e_g orbitals for octahedral complexes of different metals (varying number of *d*-electrons).
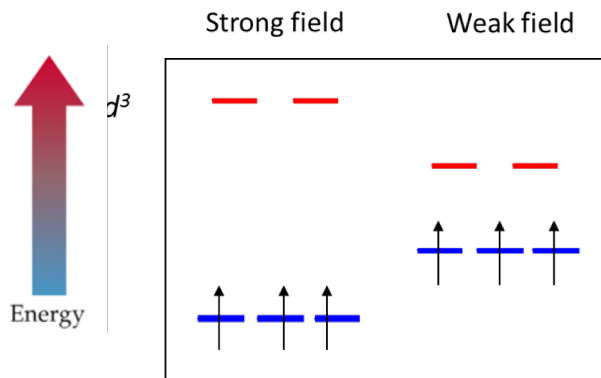
❑ *d¹*-system: no impact of strong field or weak field ligand

❑ *d²*-system: no impact of strong field or weak field ligand
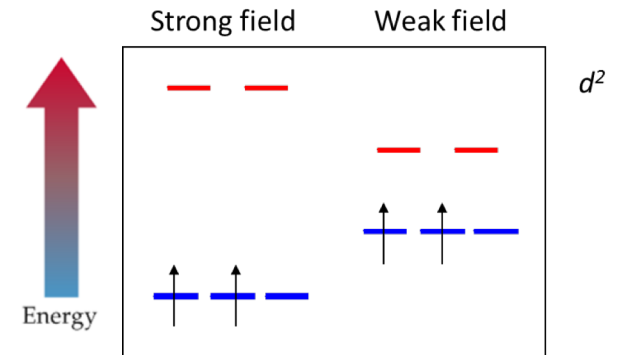
❑ *d³*-system: no impact of strong field or weak field ligand

❑ *d⁴*-system: **Two choices depending on the ligand**