The 18-Electron Rule and Its Exceptions

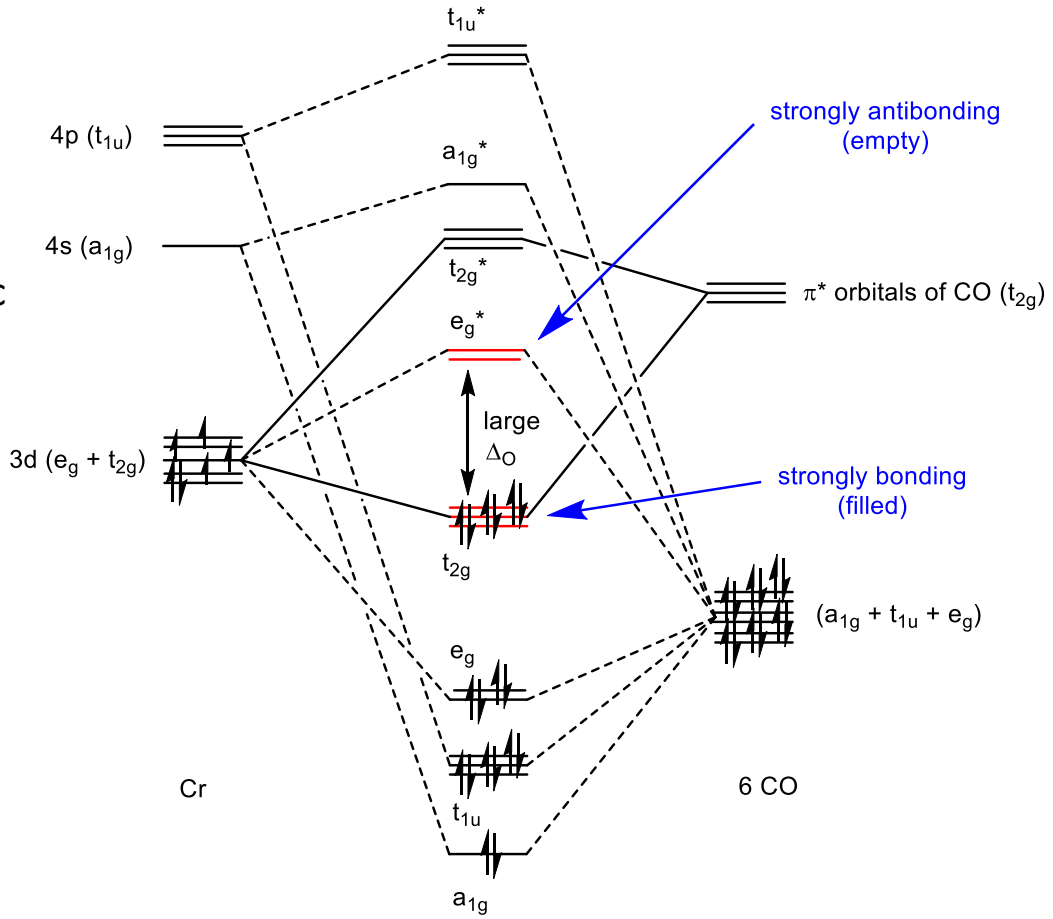
(1) Octahedral complexes → can be split into 3 categories:

	Number of Electrons	Description
A	18	18-electron rule *obeyed*
B	12-18	18-electrons *not exceeded*
C	12-22	18-electron rule *disobeyed*

A. Those that obey the 18 electron rule

- **Complexes with strong π-acceptor ligands**
  - (*e.g.* $[V(CO)_6]^-$, $[Cr(CO)_6]$, $[W(CO)_6]$, $[Mn(CO)_6]^+$)
  - t_{2g} strongly bonding ∴ filled
  - e_g^* strongly antibonding (due to synergic bonding) ∴ empty

- Complexes of strong π-acceptor ligands tend to obey the 18-electron rule irrespective of their coordination number (*e.g.* $[Fe(CO)_5]$, $[Fe(CO)_4]^{2-}$, $[Ni(PPh_3)_4]$).
- Note: d^8 and d^{10} configurations are exceptions to this rule (see later).



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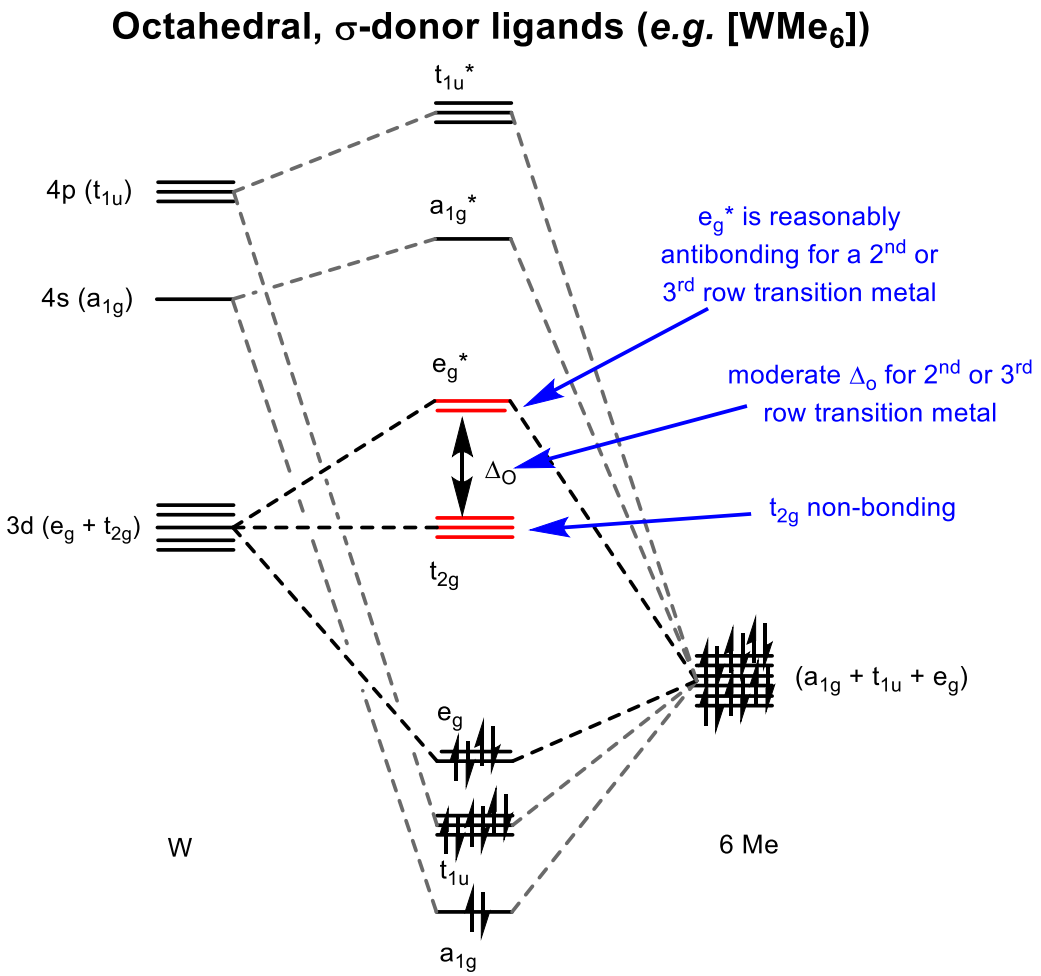
B. Octahedral complexes with 12-18 electrons

- **2nd and 3rd row TM complexes** (high in the spectrochemical series of metal ions)
- **σ-donor or π-donor ligands** (low to medium in the spectrochemical series)
- *e.g.* $[ZrF_6]^{2-}$ (Zr^{4+}, d^0, 12 e^-), $[PtF_6]^{2-}$ (Pt^{4+}, d^6, 18 e^-), $[OsCl_6]^{2-}$ (Os^{4+}, d^4, 16 e^-), $[WMe_6]$ (W^{6+}, d^0, 12 e^-), $[Zr(OH_2)_6]^{3+}$ (Zr^{3+}, d^1, 13 e^-)
  - t_{2g} non-bonding or weakly antibonding (because the ligands are either σ-donors or π-donors) ∴ t_{2g} can contain from 0 to 6 electrons
  - e_g* fairly strongly antibonding (because 2nd/3rd row TMs bond more effectively to the ligands) ∴ e_g* empty



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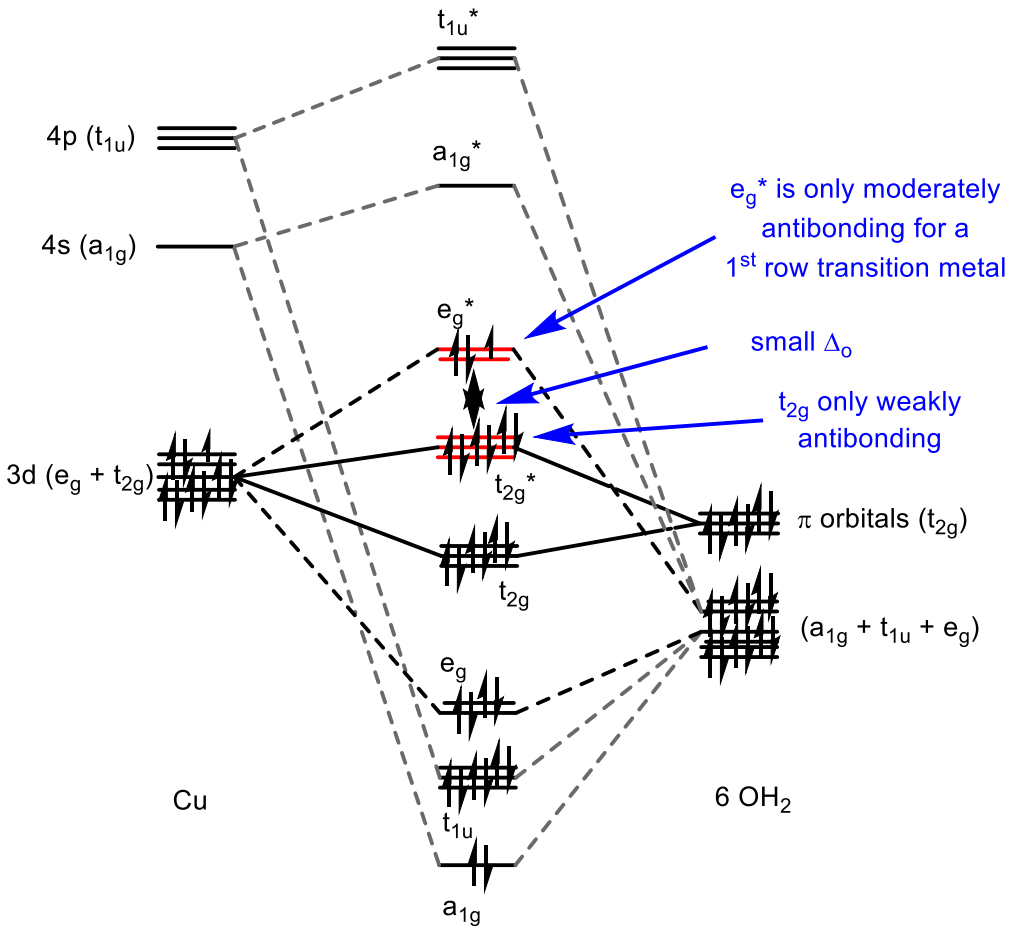
C. Octahedral complexes with 12-22 electrons

- **1st row TM complexes** (low in the spectrochemical series of metal ions)
- **σ-donor or π-donor ligands** (low to medium in the spectrochemical series)
- *e.g.* $[TiF_6]^{2-}$ (Ti^{4+}, d^0, 12 e^-), $[Co(NH_3)_6]^{3+}$ (Co^{3+}, d^6, 18 e^-), $[Cu(OH_2)_6]^{2+}$ (Cu^{2+}, d^9, 21 e^-)
  - t_{2g} non-bonding or weakly antibonding (because the ligands are either σ-donors or π-donors) ∴ t_{2g} can contain from 0 to 6 electrons
  - e_g* only weakly antibonding (because 1st row TMs don't bond as effectively to the ligands) ∴ e_g* can contain from 0 to 4 electrons

Octahedral, π-donor ligands (*e.g.* $[Cu(OH_2)_6]^{2+}$)



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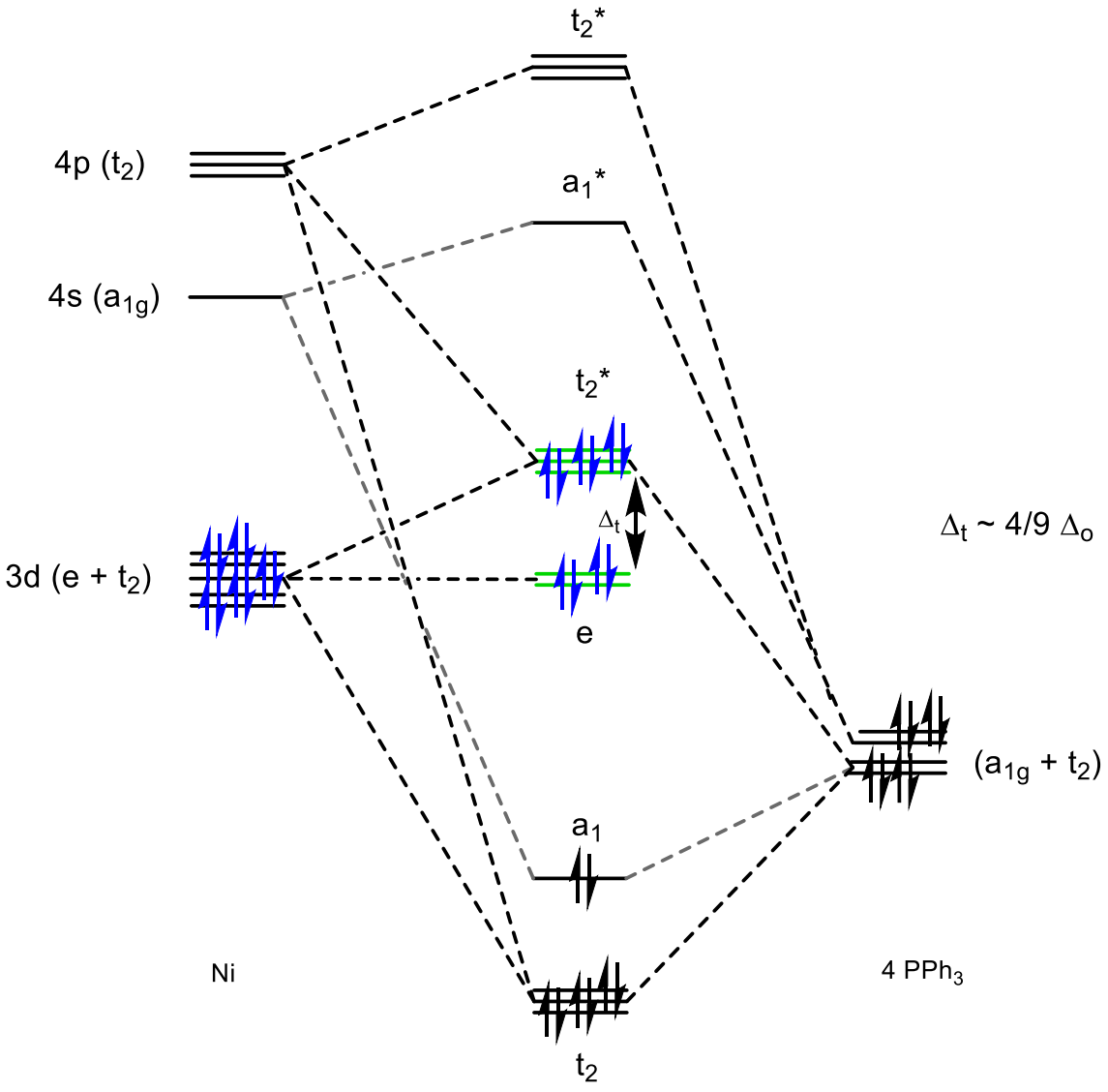
(2) Tetrahedral complexes:

- Tetrahedral complexes cannot exceed 18 electrons because there are no low lying MOs that can be filled to obtain tetrahedral complexes with >18 electrons. In addition, a transition metal complex with the maximum of 10 d-electrons, will receive 8 electrons from the ligands → a total of 18 electrons.
- Δ_t is small (~4/9 Δ_o), so there is no particular preference for the e or t_2 orbitals to be filled (can have 8-18 electrons) – similar to class C octahedral complexes.
- *e.g.* $[Ni(PPh_3)_4]$ (Ni^0, d^{10}, 18-electron complex)



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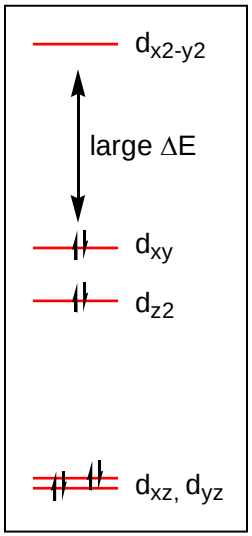
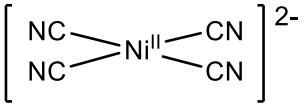
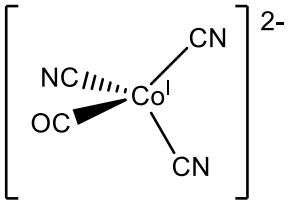
(3) Square planar complexes (d^8, 16 electrons):

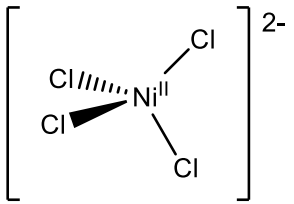


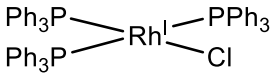
- d^8-metals with 4 ligands ∴ 16-electron complexes
- Common for metals and ligands high in the spectrochemical series
- **Rh^{I}, Ir^{I}, Pd^{II}, Pt^{II}, Au^{III}** almost always square planar, all of which are highly common oxidation states, except Au^{III}, which is quite oxidizing.
- Ni^{II} can be square planar, but only with strong π-acceptor ligands (because 1st row TMs are lower in the spectrochemical series than 2nd or 3rd row TMs).
- Co^{I} is almost never square planar because it is a first row transition metal in a low oxidation state (very low in the spectrochemical series for metals).
- d^8 Cu^{III} and Ag^{III} complexes are extremely rare and highly oxidising.
- d^8 Ru^0 and Os^0 are not square planar (2nd and 3rd row TMs but low in the spectrochemical series of metals because their oxidation state is zero).
- Cu^{II} d^9 complexes are sometimes square planar (*e.g.* $[Cu^{II}(py)_4]^{2+}$) – this may be considered an extreme form of Jahn-Teller distortion.

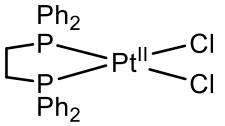
EXAMPLES:

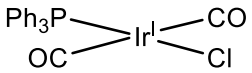


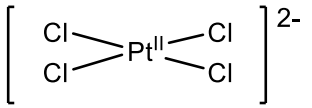












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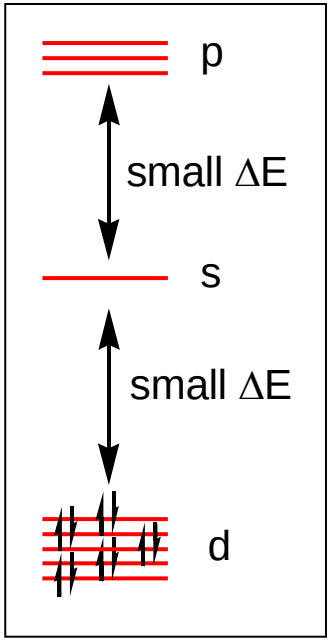
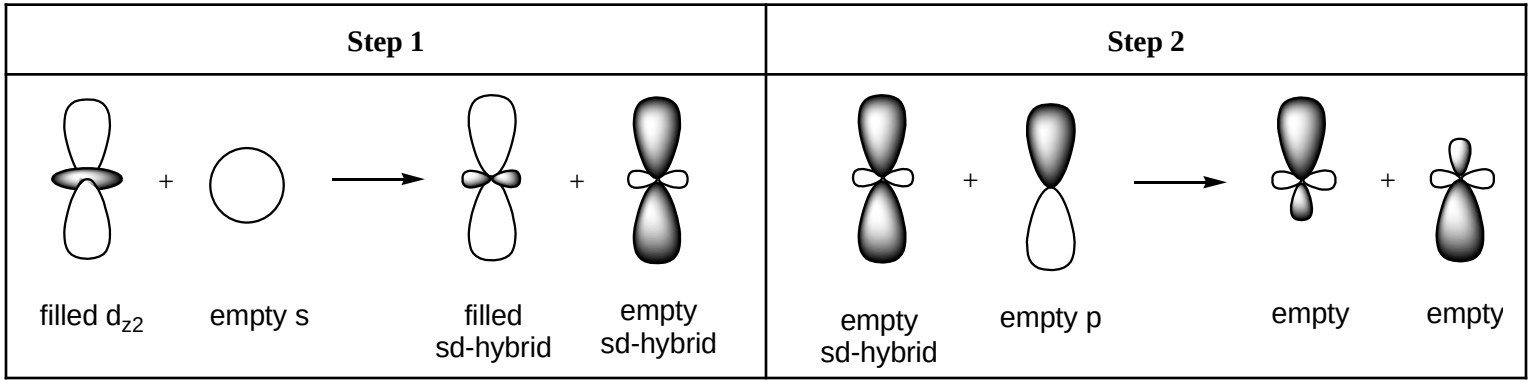
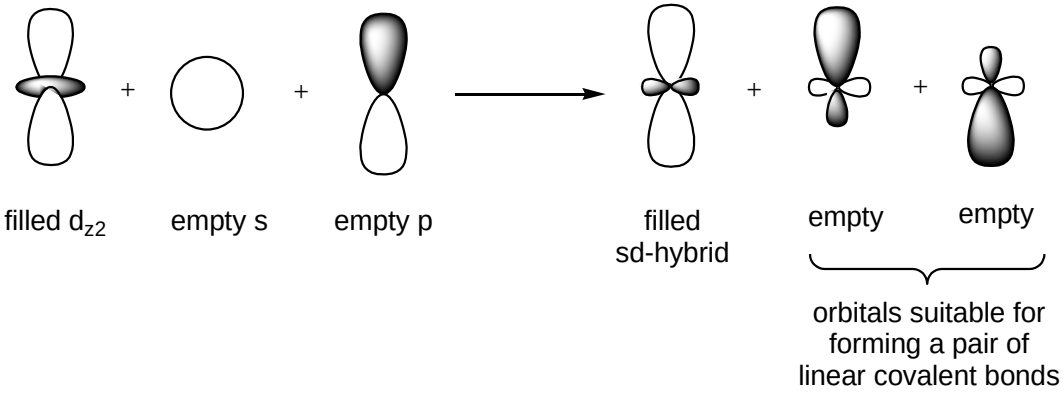
(4) Linear complexes (d^{10}, 14 electrons):



- d^{10} metals with 2 ligands ∴ 14-electron complexes
- Common for Ag^{I}, Au^{I} and Hg^{II}
- Less common for Cu^{I}, Zn^{II} and Cd^{II}
- For d^{10} complexes, there is a relatively small energy difference between the d, s and p orbitals (*e.g.* 5d, 6s and 6p for Au^{I}).
- This permits extensive hybridization between the d_{z2}, s and p_z orbitals as shown below:



Overall:



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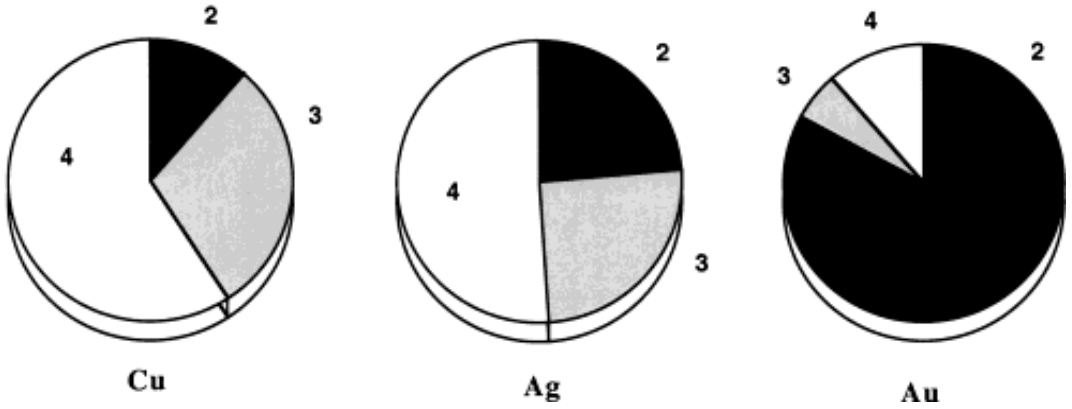
(4) Linear complexes (d^{10}, 14 electrons):

- More common for group 11 (Cu, Ag, Au) than group 12 (Zn, Cd, Hg) because the energy difference between the d, s and p-orbitals is smaller for group 11.
- More common for the heavier elements (Ag^{I}, Au^{I}, Hg^{II}).
- *e.g.* $[Ag(CN)_2]^-$, $[Ag(NH_3)_2]^+$, $[Cu(NH_3)_2]^+$, $[(R_3P)AuCl]$, $[HgMe_2]$, $[CdMe_2]$, $[ZnMe_2]$
- However, there are also lots of tetrahedral complexes of Ag^{I}, Au^{I}, Cu^{I}, Zn^{II}, Cd^{II} and Hg^{II} (*e.g.* 14 e^- linear $[(R_3P)AuCl]$ + 2 PR_3 ←→ 18 e^- tetrahedral $[(R_3P)_3AuCl]$).



- Distribution of coordination numbers for crystallographically characterized Cu^{I}, Ag^{I}, and Au^{I} compounds as found in the Cambridge Structural Database.
- Alvarez, S. *et al.*, *J. Am. Chem. Soc.* **2004**, 1465-1477.

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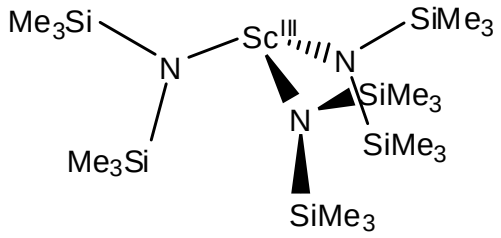
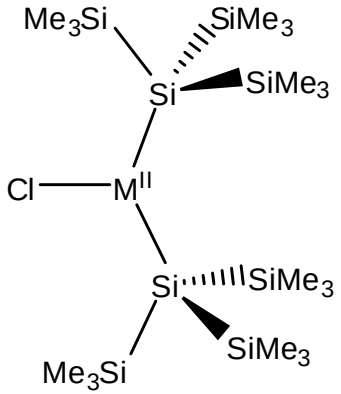
(5) Steric effects and early transition metal complexes:

- Steric effects can produce low-coordinate (not many ligands) complexes which often have <18 electrons.

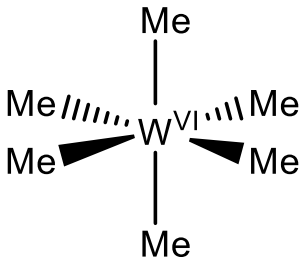


M = Sc^{3+} d^0 6 electrons

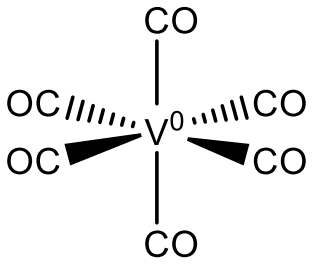


M = Cr^{2+} d^4 10 electrons
M = Mn^{2+} d^5 11 electrons
M = Fe^{2+} d^6 12 electrons

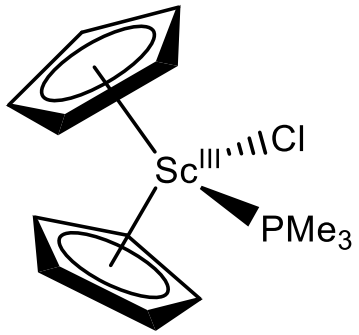
- For early-mid transition metals (*e.g.* d^0 metals) it is often not possible to fit the number of ligands around the metal that would be required to reach an electron count of 18.



W^{6+} d^0 12 electrons



V^0 d^5 17 electrons

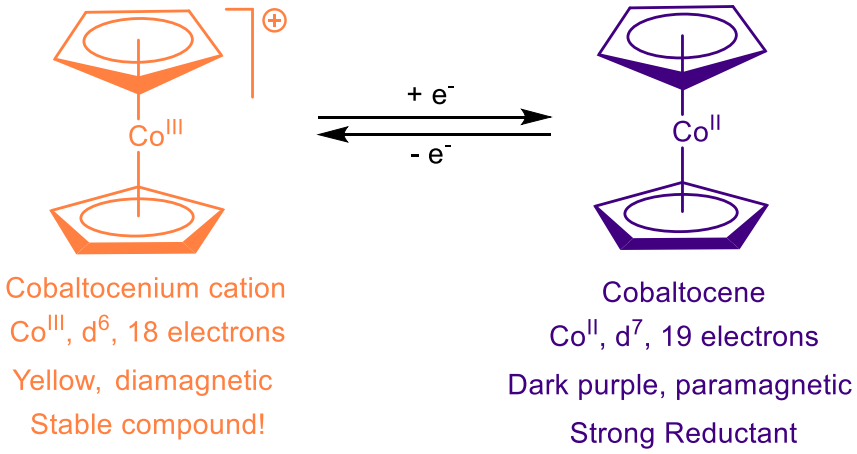


Sc^{3+} d^0 16 electrons

The 18-Electron Rule and Its Exceptions

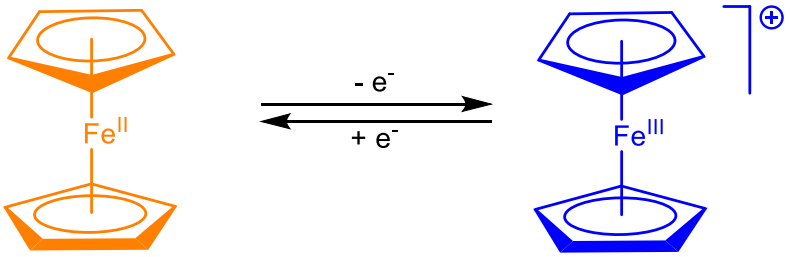
(6) Strong oxidants or reductants:

- Many 18 electron complexes can be reduced or oxidized to give 17 or 19 electron complexes. Such compounds are often good oxidizing or reducing agents (*i.e.* a preference to 'get back to being' 18-electron compounds).



Cobaltocenium cation
Co^{III}, d^6, 18 electrons
Yellow, diamagnetic
Stable compound!

Cobaltocene
Co^{II}, d^7, 19 electrons
Dark purple, paramagnetic
Strong Reductant



Ferrocene
Fe^{II}, d^6, 18 electrons
Orange, diamagnetic
Stable compound!

Ferrocenium cation
Fe^{III}, d^5, 17 electrons
Dark blue, paramagnetic
Oxidant