The 18-Electron Rule and Its Exceptions
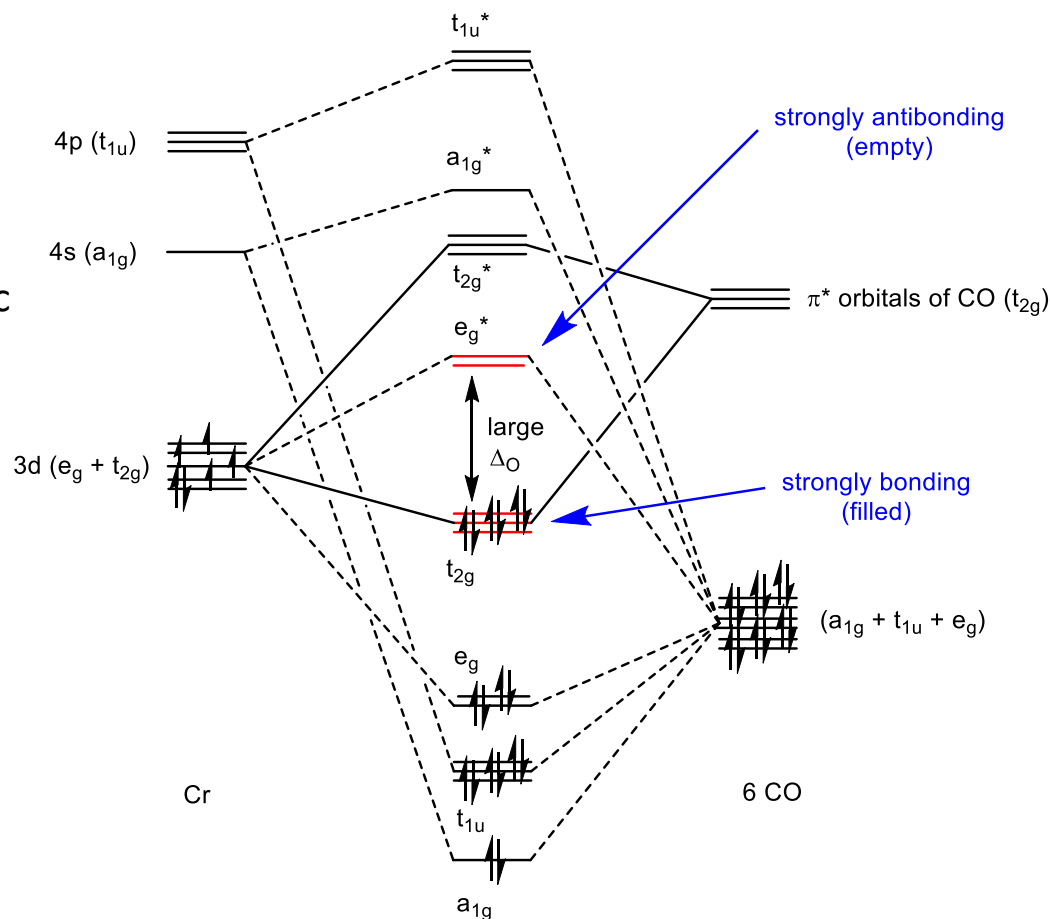
(1) Octahedral complexes → can be split into 3 categories:

	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).

t_{1u}^*

4p (t_{1u})

a_{1g}^*

4s (a_{1g})

t_{2g}^*

strongly antibonding (empty)

e_g^*

π^* orbitals of CO (t_{2g})

large Δ_O

3d ($e_g + t_{2g}$)

t_{2g}

strongly bonding (filled)

e_g

($a_{1g} + t_{1u} + e_g$)

Cr

6 CO

t_{1u}

a_{1g}

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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) $\therefore$ 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) $\therefore$ e_g* empty
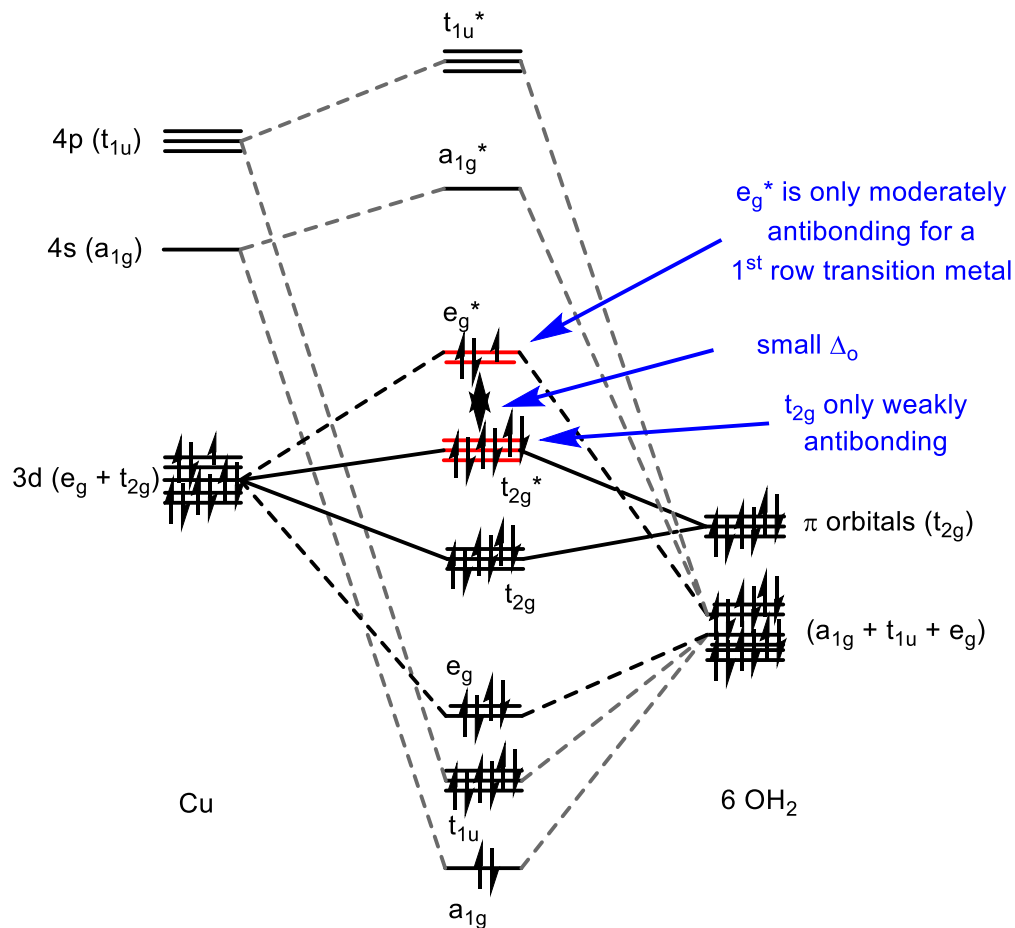
Octahedral, σ-donor ligands (*e.g.* $[WMe_6]$)

e_g* is reasonably antibonding for a 2nd or 3rd row transition metal

moderate Δ_o for 2nd or 3rd row transition metal

t_{2g} non-bonding

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Octahedral, π-donor ligands (*e.g.* $[Cu(OH_2)_6]^{2+}$)
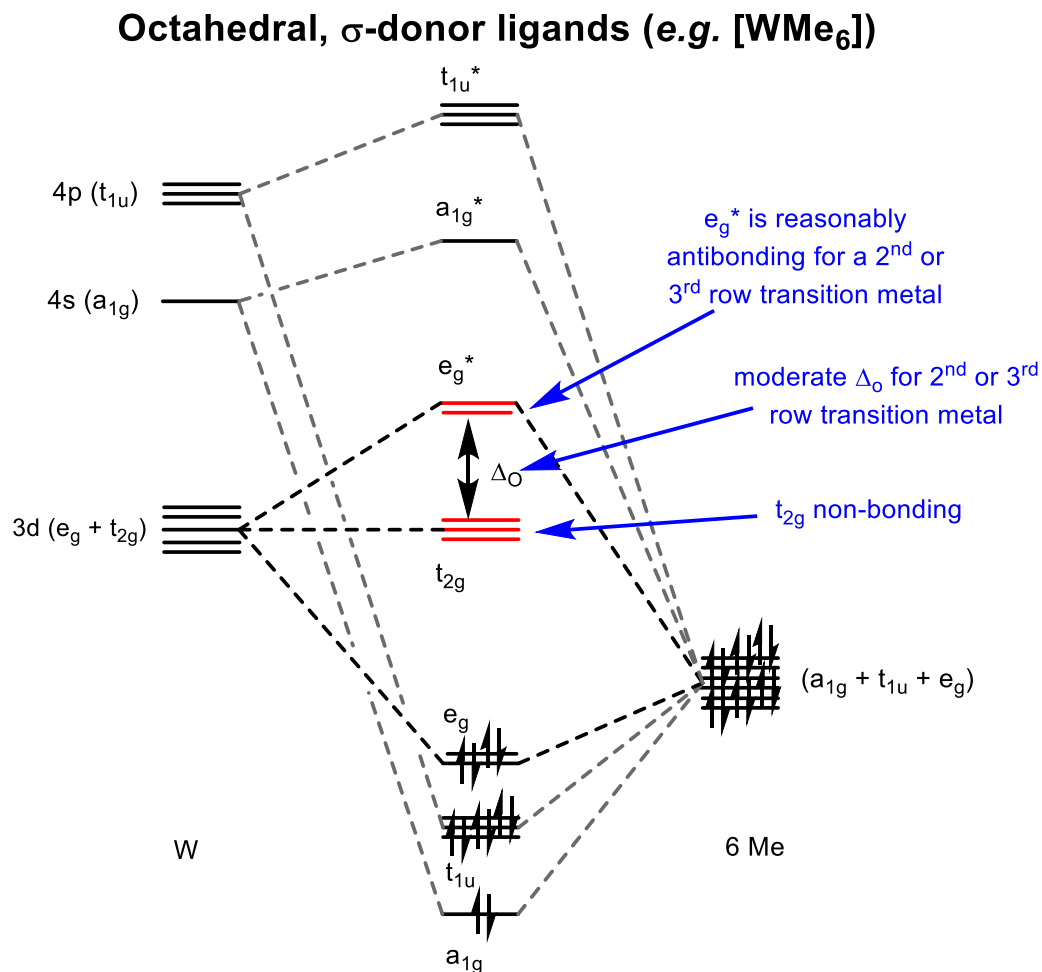
C. Octahedral complexes with 12-22 electrons

- **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) $\therefore t_{2g}$ can contain from 0 to 6 electrons
  - e_g^* only weakly antibonding (because 1st row TMs don't bond as effectively to the ligands) $\therefore e_g^*$ can contain from 0 to 4 electrons


e_g^* is only moderately antibonding for a 1st row transition metal

small Δ_o

t_{2g} only weakly antibonding

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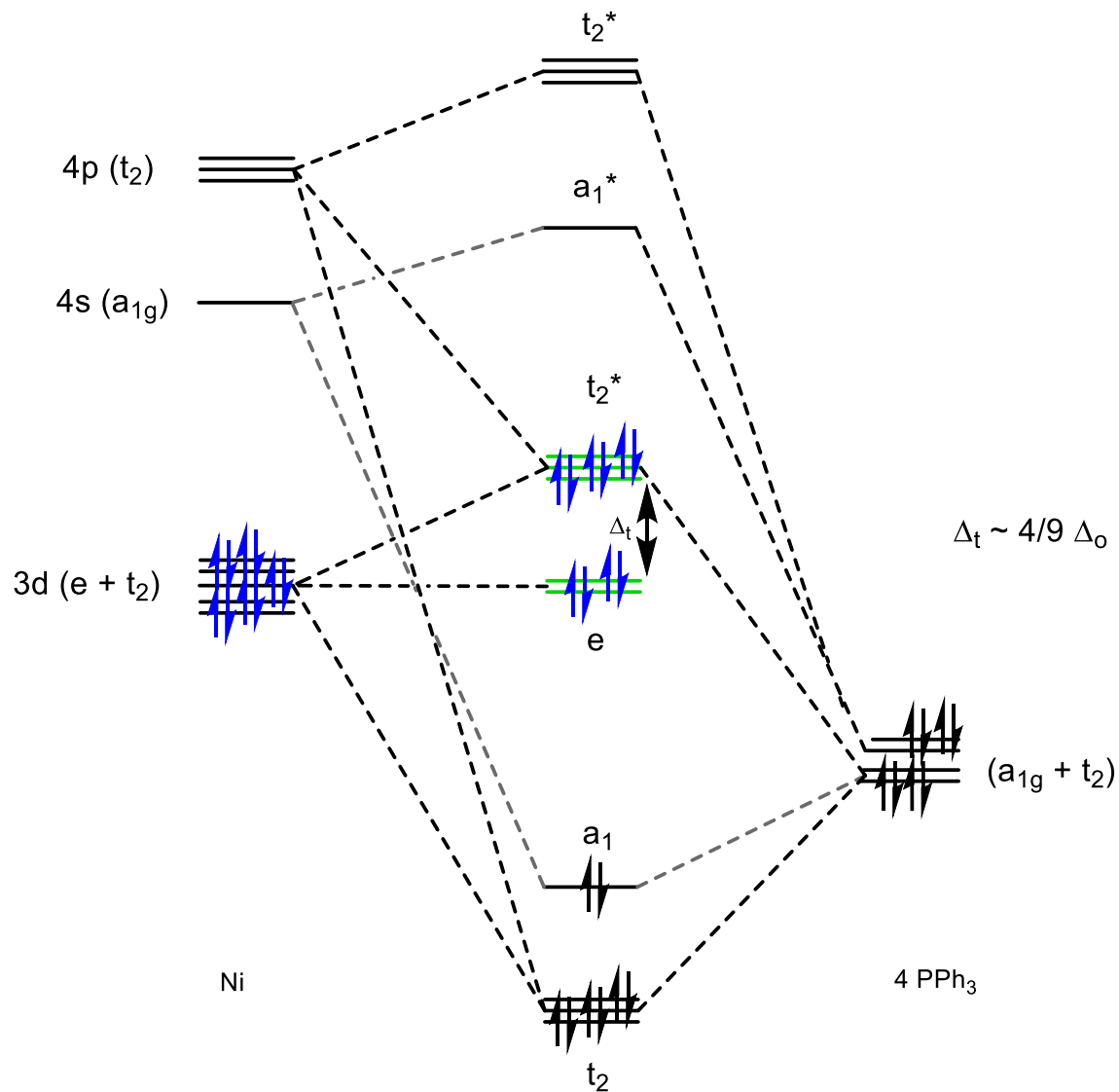
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(3) Square planar complexes (d^8, 16 electrons):

- d^8-metals with 4 ligands $\therefore$ 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.

$d_{x^2-y^2}$

large ΔE
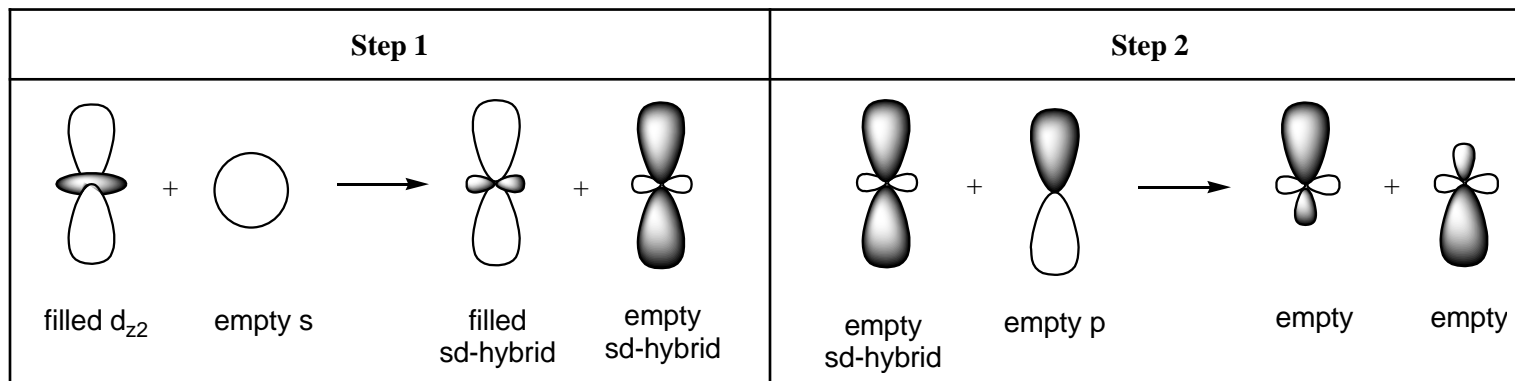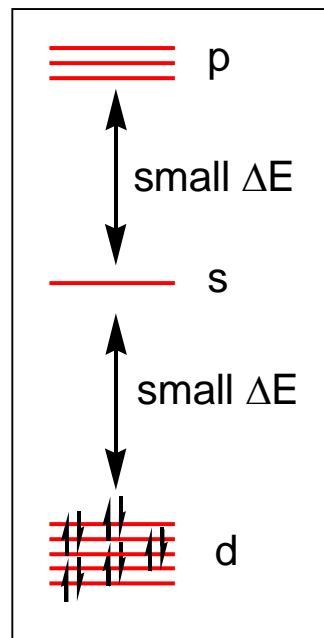
d_{xy}

d_{z^2}

d_{xz}, d_{yz}
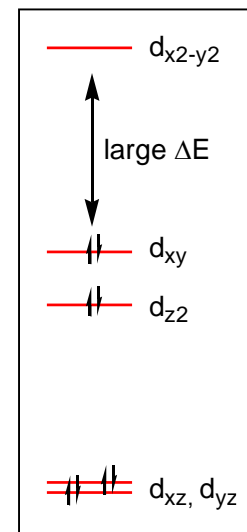
EXAMPLES:
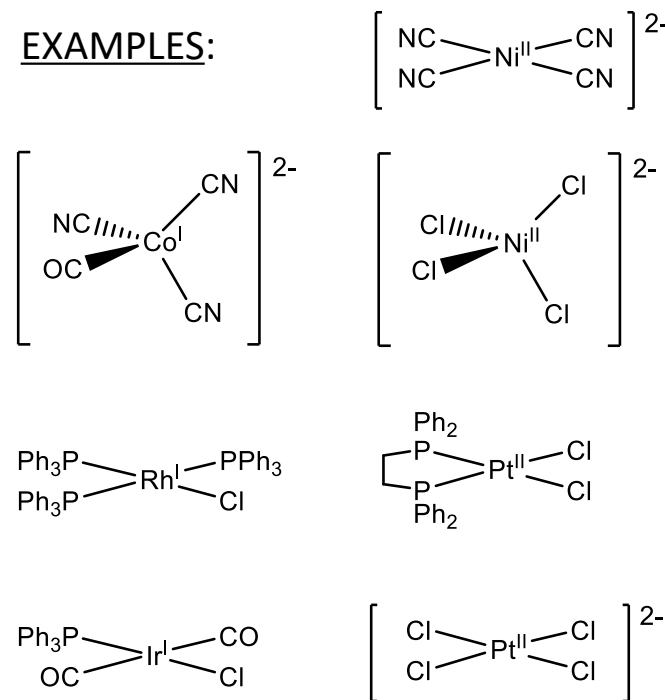
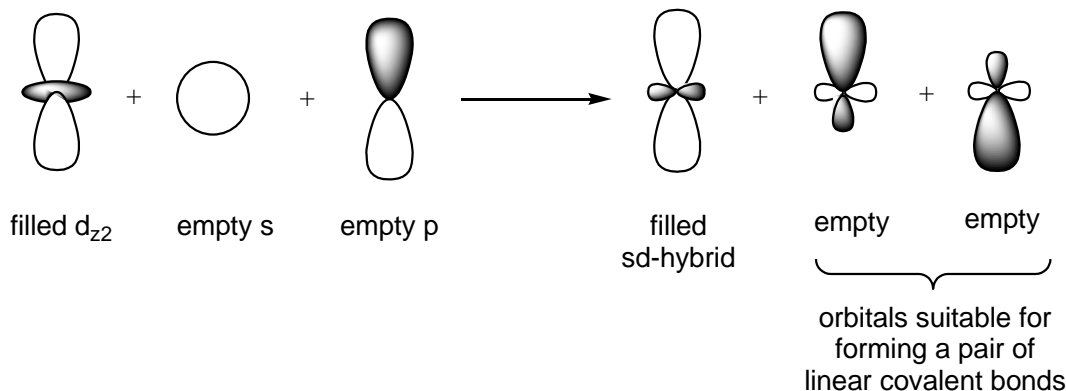# The 18-Electron Rule and Its Exceptions

(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:

Step 1	Step 2
filled d_{z2} + empty s → filled sd-hybrid + empty sd-hybrid	empty sd-hybrid + empty p → empty + empty

Overall:

filled d_{z2} + empty s + empty p → filled sd-hybrid + empty + empty

orbitals suitable for forming a pair of linear covalent bonds

p

small ΔE

s

small ΔE

d

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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$_3$P)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$_3$P)AuCl] + 2 PR$_3$ ←→ 18 e$^-$ tetrahedral [(R$_3$P)$_3$AuCl]).
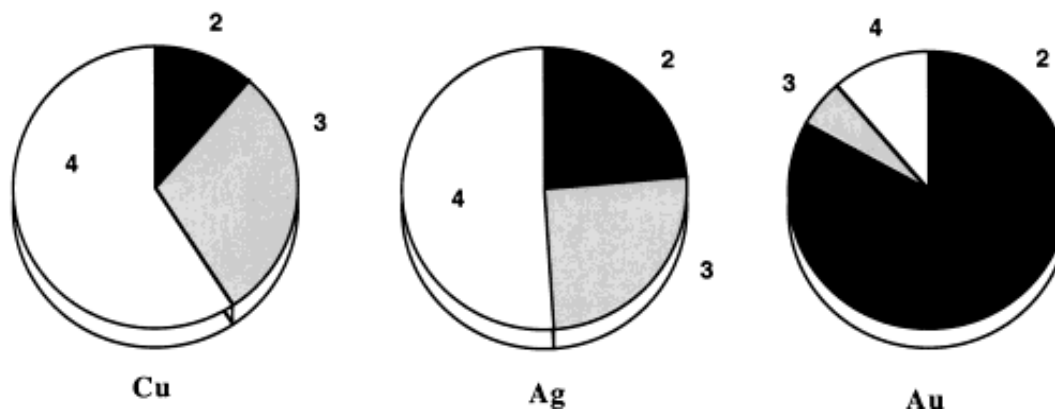

- Distribution of coordination numbers for crystallographically characterized Cu^I, Ag^I, and Au^I compounds as found in the Cambridge Structural Database.
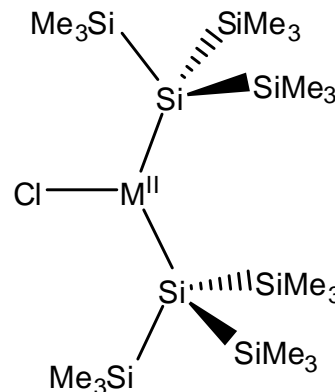- Alvarez, S. *et al.*, *J. Am. Chem. Soc.* **2004**, 1465-1477.

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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.
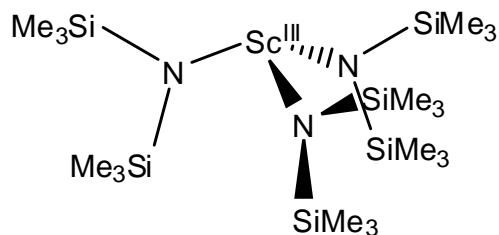
$M = Sc^{3+}$ d^0 6 electrons
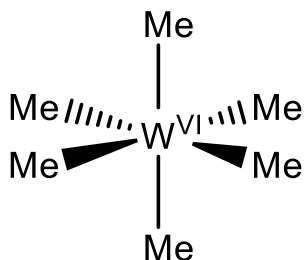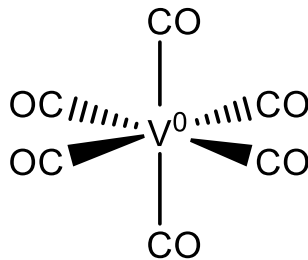
$M = Cr^{2+}$ d^4 10 electrons
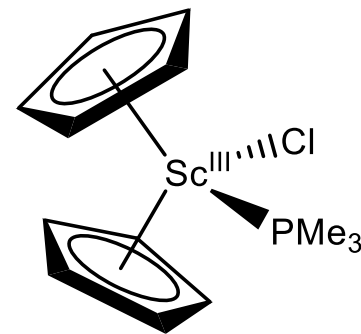$M = Mn^{2+}$ d^5 11 electrons
$M = Fe^{2+}$ d^6 12 electrons

- 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

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(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!

$+ e^-$ / $- e^-$

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

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

$- e^-$ / $+ e^-$

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