

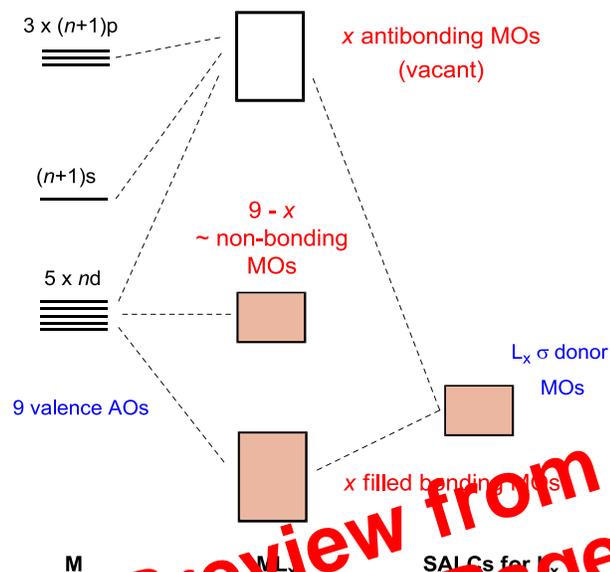
1. **Include theoretical, thermodynamic and kinetic perspectives on stability, limitations, uses and the 16/14 electron rules.** Make reference to examples of your own choice and some of the following compounds: $W(CO)_4(PMe_3)_2$, $(5-C_5H_5)_2TiCl_2$, $Mo(CO)_5\{CPh(OEt)\}$, $(5-C_5H_5)_2Co$, $Ti(CH_2Ph)_4 [RhCl_2(CO)_2]$, $Hg(CO)_2^{2+}$, $Cr(NO)_4$, $Cr(6-C_8H_8)(CO)_3$, $Ce(8-C_8H_8)_2$, $Fe(4-C_8H_8)(CO)_3$, $Re_2(CO)_{10}$, $Ir_4(CO)_{12}$, $[(5-C_5H_5)Fe(CO)]_4$

When does the 18-electron rule work?

It was devised for mid-low oxidation state metals with π -acceptor ligands, such as CO, for 2nd & 3rd row compounds. It doesn't work for lanthanide or actinide-based organometallic compounds as they have valence f-orbitals, as well as the s, p, and d orbitals of the transition metals.

What is the 18-electron rule?

If all of the metal-ligand bonding & low-energy non-bonding d-orbitals are filled and the antibonding orbitals are unoccupied, then a kinetically stable complex will result.



Transition metals have **9 valence MOs** (5 x d, 1 x s, 3 x p)

In any σ -only complex, there will be x -bonding and x -antibonding MOs.

This gives $(9-x)$ non-bonding/weakly antibonding MOs, of mostly d-character on the metal.

Filling x bonding & $(9-x)$ nonbonding MOs - leaving the antibonding MOs vacant - requires **18 electrons**.

How do we determine the valence electron count of a metal complex?

1. Take the total number of metal valence electrons for the neutral atom (aka the group number).
2. Add the electrons donated by the ligands in their *neutral* forms.
3. Add/subtract electrons for any net anionic (negative) or cationic (positive) charges.
4. Add electrons for any metal-metal bonds, providing there are sufficient d electrons. The number of metal-metal bonds present in a compound can be predicted according to the 18-electron rule.

Complications

This does not explain why not all transition metals follow this rule, or why there is an equivalent 16-electron rule.

It is disobeyed for:

- Some octahedral (ML_6) complexes
- Square planar ($D_{4h} ML_4$) complexes
- Early transition metals
- Sterically encumbered compounds

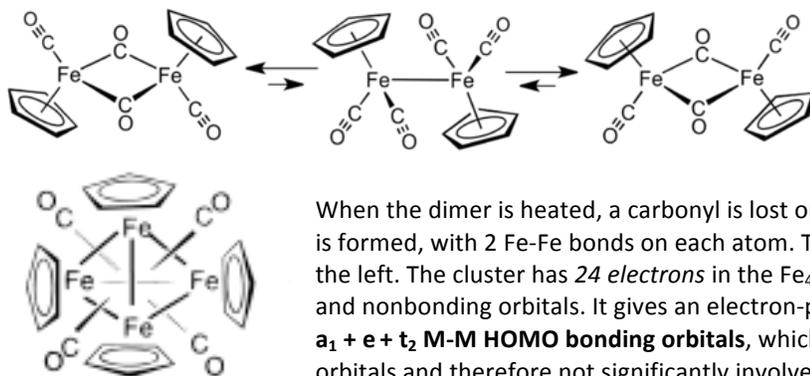
[RhCl(PPh₃)₃] – Wilkinson’s Catalyst

Wilkinson’s catalyst acts as an **alkene hydrogenation catalyst**.



It loses a ligand, forming the T-shaped 14-valence electron Rh(+1) centre, prior to the oxidative addition of H₂. It has to lose the PPh₃ ligand as it is quite bulky, and prevents the ready addition of H₂ to form a 6-coordinate RhCl(PPh₃)₃(H)₂. This is **ligand dissociation**.

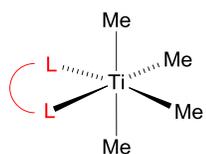
(η⁵-C₅H₅)Fe₂(CO)₄ – King’s Dimer/Tetramer



The King’s compound is also called Fp₂, or ‘fip dimer’. In solution it exists in *three* isomeric forms: cis, trans and unbridged, with the cis and trans isomers being the most abundant. The isomers interconvert – **fluxionality** (as left).

When the dimer is heated, a carbonyl is lost on each Fe atom and a **tetra-cluster** of T_d symmetry is formed, with 2 Fe-Fe bonds on each atom. This has the formula Cp₄(CO)₄Fe₄ and is shown to the left. The cluster has 24 electrons in the Fe₄ cluster molecular orbitals, which fill the bonding and nonbonding orbitals. It gives an electron-precise structure with **12 bonding electrons** in the **a₁ + e + t₂ M-M HOMO bonding orbitals**, which are also involved in backbonding to the CO π* orbitals and therefore not significantly involved in M-M bonding.

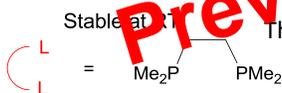
[TiCl₃(dmpe)Et]



This is an example of a kinetically stabilized transition metal alkyl by **blocking vacant coordination sites with donor ligands**.

The dmpe ligand blocks the vacant coordination sites, and inhibits β-H elimination. This involves an increase in the coordination number and an increase in the valence electron count.

Therefore, TiMe₃ is unstable about -50°C, but the dmpe adduct is stable at room temperature.



dmpe
(1,2-bis(dimethylphosphino)ethane)

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