

B Organometallic Concepts, Terminology and Nomenclature

Handout:

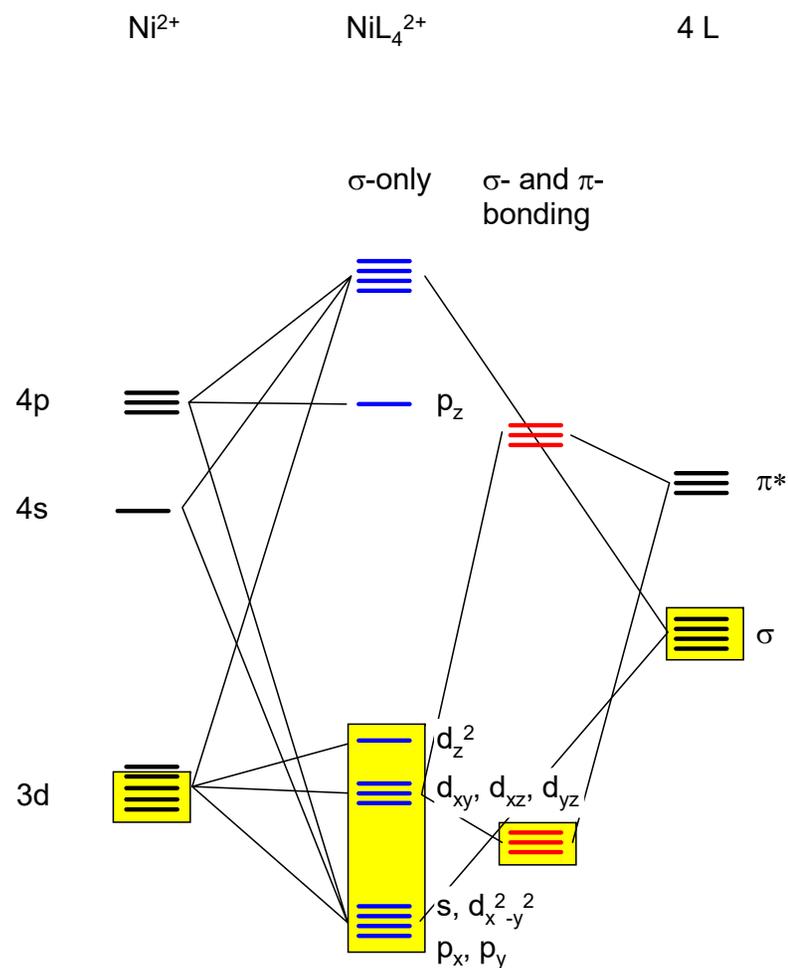
'Electron Counting, Formal Oxidation States and the 18 Electron Rule in Transition Metal Chemistry'

The 18 Electron Rule offers *predictive power*.

- ◆ stable vs. unstable complexes
- ◆ likely reactivity patterns
 - $< 18 e^-$ add ligands, can be reduced
 - $> 18 e^-$ lose ligands, can be oxidized
- ◆ viability of catalytic intermediates or cycles
 - species of less than $18 e^-$ (or $16 e^-$ for d^8) are unlikely to exist in high concentrations
 - species with electron counts more than two less than the stable configuration are unlikely to play a role

Stable 16 e⁻ complexes: square planar d⁸ metal centres

NB: some poetic license has been taken in this diagram. Strictly speaking the orbitals grouped together are NOT actually degenerate - they are merely close in energy. Also note that the LUMO may be one of the σ^* orbitals (often assumed to be the antibonding combinations with dx^2-y^2 character); nevertheless, this diagram emphasizes the point that the $4p_z$ metal valence orbital is not used to in the bonding and hence a maximum 16 e⁻ count arises.



Things to note about stable 16 e- counts:

- ◆ applies to complexes **WITH** and **WITHOUT** π -acceptor ligands
 - unlike the case of octahedral 18 e⁻ complexes, π -acceptors have a minor impact on the HOMO-LUMO gap (see the Figure above).
- ◆ applies to some of the most important catalytic metals:
Ni²⁺, Pd²⁺, Pt²⁺ and Rh⁺, Ir⁺
- ◆ even though the complexes are < 18 e⁻ they still undergo oxidative-addition in which a pair of electrons is formally donated by the metal centre (it is oxidized): this apparent contradiction in behaviour is because the pair of electrons in d_{z^2} is fairly high in energy.

Nomenclature and Terminology

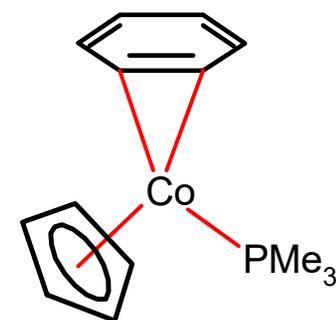
η^x **eta designation** – also called the ***hapto number*** or ***hapticity***:

the **x** superscript indicates the number of **'points of contact'** between the ligand and metal.

For organic ligands this is also the number of electrons donated in a neutral counting scheme:

η^1	1e ⁻	eg.	alkyl or aryl (yl)
η^2	2e ⁻		alkene (ene)
η^3	3e ⁻		allyl
η^4	4e ⁻		diene
η^5	5e ⁻		cyclopentadienyl
η^6	6e ⁻		arene

Thus an η^2 -benzene complex is only coordinated to the metal along one edge of the benzene ring and only donates two electrons:



For other types of ligands, the η^x designation does not relate to the number of electrons donated:

Egs. η^1 -OR $1e^-$, $3e^-$ or even $5e^-$ donor

η^2 -acac usually a $3e^-$ donor

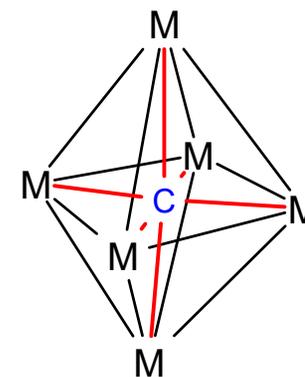


Bridging ligands: μ^x designation

x designates the number of metal centres bridged by the ligand

μ without a superscript implies μ^2

Eg. μ^6 -carbides are known in cluster species



'metallo' vs. 'metalla'

metallo: designates a metal 'on' the ring not 'in' the ring eg. Ferrocene

metalla: designates a metal 'in' the ring structure naming by analogy to hydrocarbon rings

Egs.

