

Organometallic chemistry

Organometallic compounds (metal organyls, organometallics) are defined as materials which possess direct, more or less polar bonds $M^{\delta+}-C^{\delta-}$ between metal and carbon atoms. In addition to the traditional metals, lanthanides, actinides, and semimetals, elements such as boron, silicon, arsenic, and selenium are considered to form organometallic compounds, e.g. organoborane compounds such as triethylborane (Et_3B).

Organometallic chemistry is the study of organometallic compounds. Since many compounds without such bonds are chemically similar, an alternative may be compounds containing **metal-element** bonds of a largely covalent character. Organometallic chemistry combines aspects of inorganic chemistry and organic chemistry.

18-Electron Rule

➤ The 18e rule: characterizing and predicting the stability of metal complexes.

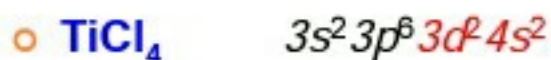
Valence shells of a M_T can accommodate **18** electrons: 2 in each of the five *d* orbitals (**10** in total); 2 in each of the three *p* orbitals (**6** in total); and **2** in the *s* orbital.

Combination of these atomic orbitals with ligand orbitals: **9** MOs which are either *metal-ligand bonding* or *non-bonding*. (There are also some higher energy *anti-bonding orbitals*). The complete filling of these nine lowest energy orbitals with electrons, whether those electrons originate from the metal or from any ligand, is the basis of the **18-electron rule**.

Electrons donated by common fragments

Neutral	Positive	Negative	Ligands
1	0	2	H; X (F, Cl, Br, I); alkyl
2	–	–	CH ₂ =CH ₂ , CO, phosphane, etc.
3	2	4	π -ally, cyclopropenyl, NO
4	–	–	diolefin
4		6	Cyclobutdiene
5	–	6	cyclopentadienyl
6	–	–	Arene, triolefin
7	6	–	Tropylium (C ₇ H ₇ ⁺)
8	–	10	cyclooctatetraene

Examples:



Neutral counting: Ti 4e, Cl 1e; $4+4(1) = 8$ valence electrons

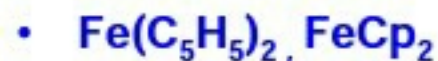
Ionic counting: Ti⁴⁺ 0e, Cl⁻ 2e; $0+4(2) = 8$ valence electrons

Conclusion: Having only 8e (vs. 18 possible), we can anticipate that TiCl₄ will be a good Lewis acid. Indeed, it reacts (in some cases violently) with water, alcohols, ethers, amines.



Neutral counting: Fe 8e, CO 2e, $8 + 2(5) = 18$ valence electrons

Conclusion: This is a special case, all fragments being neutral. Since this is an 18-electron complex, Fe(CO)₅ is a stable compound.



Neutral counting: Fe 8e, C₅H₅ 5e: $8 + 2(5) = 18$ electrons

Ionic counting: Fe²⁺ 6e, C₅H₅⁻ 6e: $6 + 2(6) = 18$ electrons

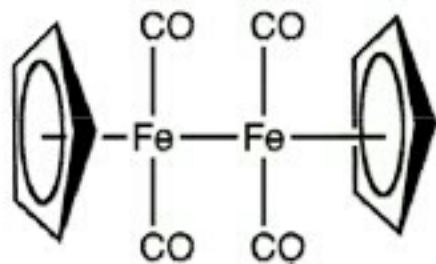
Conclusion: Ferrocene is expected to be a stable compound.

o $[\text{CpFe}(\text{CO})_2]_2$

Neutral counting:

$$\text{Cp } 5 + \text{Fe } 8 + 2 \text{ CO } 4 + \text{Fe-Fe } 1 = 18$$

Counting electrons for just one iron center can be done by considering the other iron as contributing 1 electron to the count.



o $\text{CpFe}(\text{CH}_3)(\text{CO})_2$

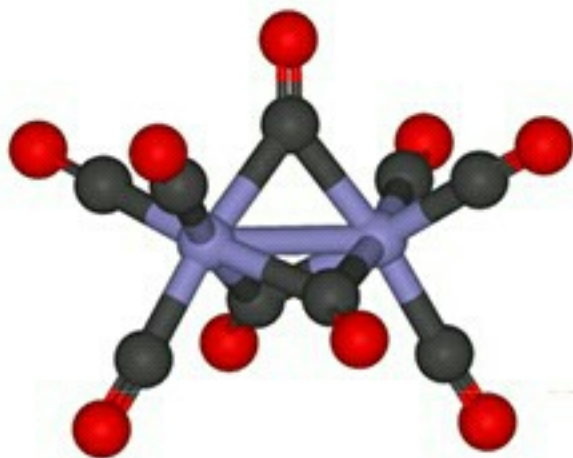
Neutral counting:

$$\text{Cp } 5 + \text{Fe } 8 + \text{CH}_3 \text{ } 1 + 2 \text{ CO } 4 = 18$$

o $\text{Fe}_2(\text{CO})_9$

Neutral counting:

$$3 \text{ CO } 6 + 3 \mu\text{-CO } 3 + \text{Fe } 8 + \text{Fe-Fe } 1 = 18$$



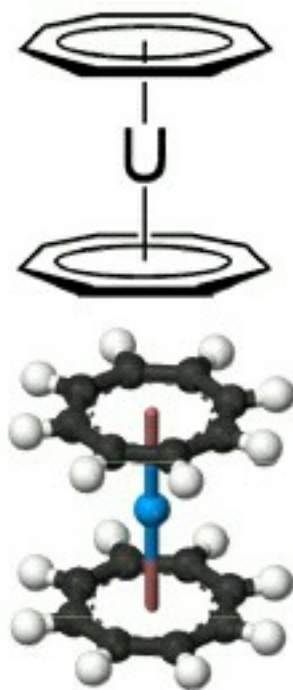
Hapticity

The term **hapticity** is used to describe how a group of *contiguous* atoms of a ligand are coordinated to a central atom. Hapticity of a ligand is indicated by the Greek character 'eta', η .

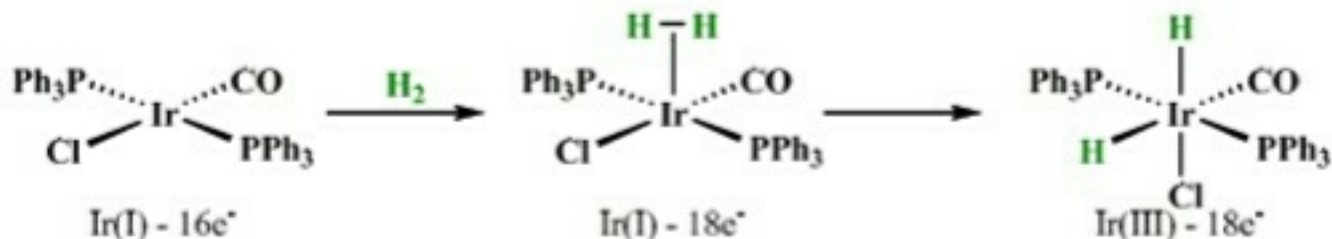
η^n : n = the number of contiguous atoms of the ligand that are bound to the metal.

☞ The term is usually employed to describe ligands containing extended π -systems or where agostic bonding is not obvious from the formula.

- **Ferrocene:** bis(η^5 -cyclopentadienyl)iron
- **Zeise's salt:** $\text{K}[\text{PtCl}_3(\eta^2\text{-C}_2\text{H}_4)]\cdot\text{H}_2\text{O}$
- **Uranocene:**
bis(η^8 -1,3,5,7-cyclooctatetraene)uranium
- $\text{W}(\text{CO})_3(\text{PPr}^i_3)_2(\eta^2\text{-H}_2)$
- $\text{IrCl}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2(\eta^2\text{-O}_2)$



Oxidative Addition



Non-electrophilic: Such molecules do not contain electro-negative atoms and/or are not good oxidizing agents. They are often considered to be “non-reactive” substrates. These molecules generally require the presence of an empty orbital on the metal center in order for them to pre-coordinate prior to being activated for the oxidative addition reaction.

Examples: H₂, C-H bonds, Si-H bonds, S-S bonds, C-C bonds

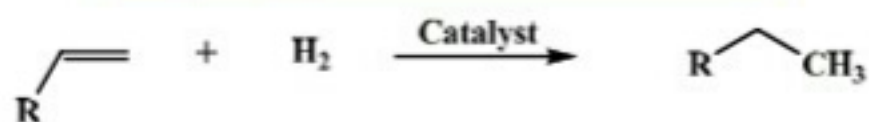
Electrophilic: Such molecules do contain electro-negative atoms and are good oxidizing agents. They are often considered to be “reactive” substrates. These molecules do not require the presence of an empty orbital (18e⁻ is OK) on the metal center in order to perform the oxidative addition reaction.

Examples: X₂ (X = Cl, Br, I), R-X, Ar-X, H-X, O₂

The most common substrates used are

R-X (alkyl halides), Ar-X (aryl halides), and H-X.

Hydrogenation of Alkenes



The most commonly used catalyst is the Wilkinson's Catalyst



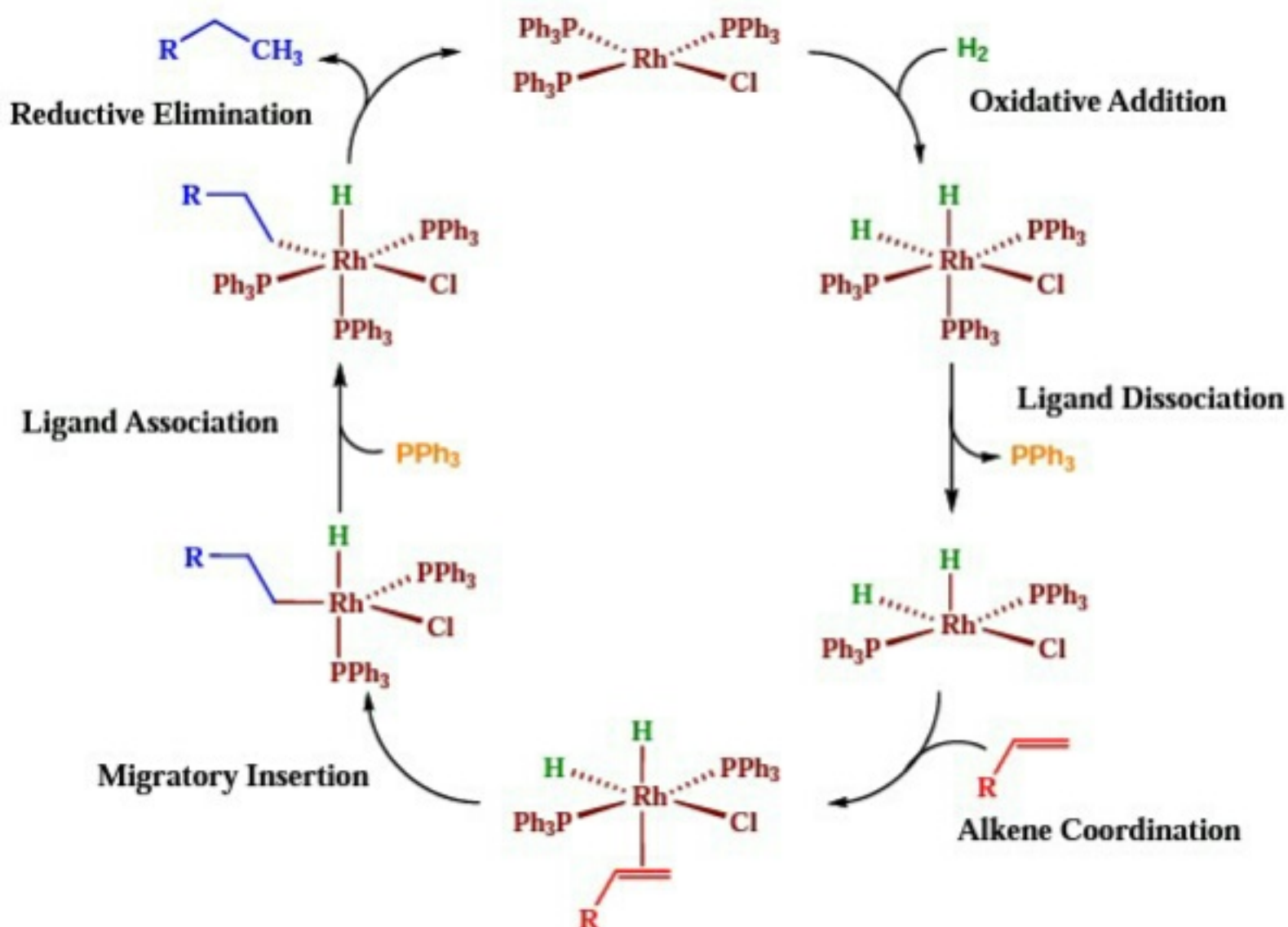
Many alkenes are hydrogenated with hydrogen at 1atm pressure or less.

Wilkinson's catalyst is highly sensitive to the nature of the phosphine ligand and the alkene substrate.

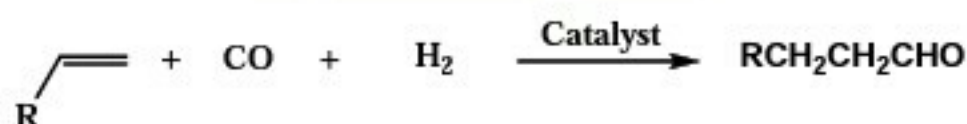
Analogous catalysts with alkyl phosphine ligands are inactive

Highly hindered alkenes and ethylene are not hydrogenated by the catalyst

Wilkinson's Catalyst



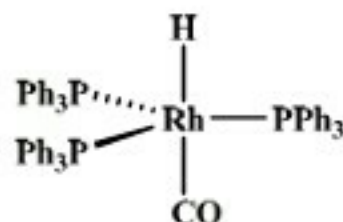
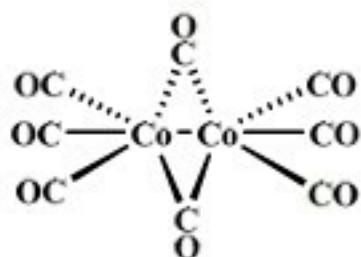
Hydroformylation



A less common, but more appropriate name is hydrocarbonylation

Both cobalt and rhodium complexes are used as catalysts.

Alkene isomerization, alkene hydrogenation and formation of branched aldehydes are the possible side reactions.



Cobalt catalysts operate at 150 °C and 250 atm, whereas Rhodium catalysts operate at moderate temperatures and 1 atm.

Rhodium catalysts promote the formation of linear aldehydes. Cobalt catalysts do so if modified with alkylphosphine ligands.

Hydroformylation

