

Electrophilic attack on Coordinated Ligands

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Organometallic complexes have at least one organic group and they can undergo various types of reactions. Incoming electrophile may react with or attack on either the **metal centre** or on one of the **coordinated ligands**. In this article, we exclusively examine the electrophilic attack on coordinated ligands.

Electrophilic attack on coordinated ligands is favoured when,

- (i) the metal centre is a strong π -base.
- (ii) the complex is negatively charged, or the metal centre is in a very low oxidation state.
- (iii) the coordinated ligands are good σ -donors.
- (iv) the metal complex is coordinatively saturated.

Let us look at reactions of transition metal complexes with electrophiles (E^+) such as proton (H^+), halogens (X_2), methylating agents (Me_3OBF_4), metal ions (*e.g.*, Hg^{2+}) and trityl ion, Ph_3C^+ . Bulky electrophiles are more likely to attack the surrounding ligands rather than the metal centre due to steric effects.

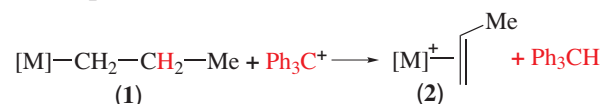
Electrophilic attack on η^1 -alkyl and aryl ligands

Coordinated η^1 -alkyl and aryl ligands (R) are often removed from the metal complex $[L_nMR]$ by reacting it with electrophiles such as acids (HX), halogens (X_2) and metal salts (HgX_2). Some examples are given below.

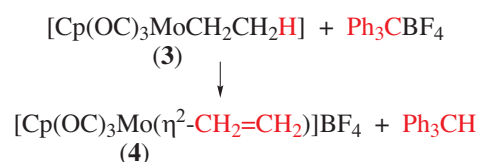
1. $[(\eta^5-Cp)_2VPh] + HBr \rightarrow [(\eta^5-Cp)_2VBr] + C_6H_6$
2. $[(\eta^5-Cp)_2ZrCl(Me)] + Cl_2 \rightarrow [(\eta^5-Cp)_2ZrCl_2] + MeCl$
3. $[(\eta^5-Cp)FePh(CO)_2] + HgCl_2 \rightarrow [(\eta^5-Cp)FeCl(CO)_2] + PhHgCl$
4. $[(\eta^5-Cp)_2TaMe_3] + Ph_3CBF_4 \rightarrow [(\eta^5-Cp)_2TaMe_2]BF_4 + Ph_3CMe$

η^1 -Alkyl ligands containing a β -hydrogen in (1)

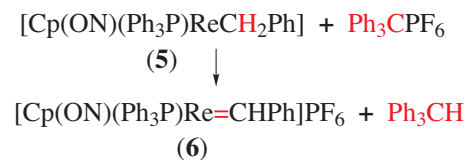
can be converted into a **coordinated olefin** as depicted in (2) *via* the abstraction of a **hydride ion**. This is an **electrophilic abstraction reaction**.



Alternatively, this process can be viewed as an oxidative addition of a C-H bond within the alkyl group to the metal centre, followed by elimination of hydride ion. For example, β -hydride abstraction from the ethyl complex (3) gives the cationic ethylene complex (4).

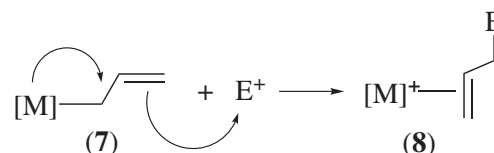


The complex (5) lacks an β -hydride, thus, an α -hydrogen is eliminated to give a **carbene-complex** (6) as shown below.

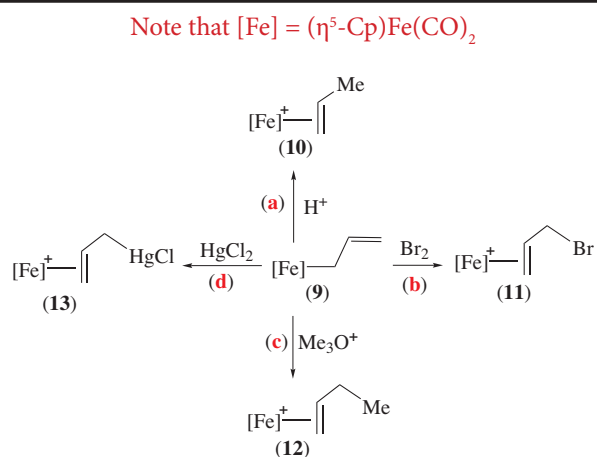


Electrophilic attack on η^1 -allyl ligands

Electrophilic attack on an η^1 -allyl group in (7) gives a cationic η^2 -olefin complex (8) as shown below.



This is an **electrophilic addition reaction**. The **hapticity** of the metal has increased by one unit. These reactions often generate a positive charge on the complex. Some of the electrophilic addition reactions of $[(\eta^5-Cp)Fe(CO)_2(\eta^1-CH_2CH=CH_2)]$ (9) are given in Scheme 1.

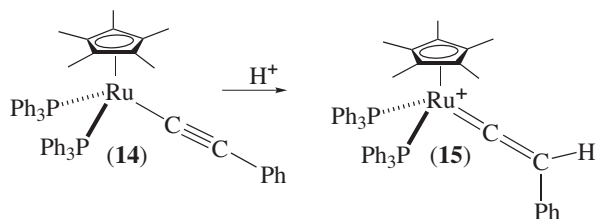


Scheme 1 Electrophilic reactions of (9)

- (a) Protonation of the η^1 -allyl group of (9) generates the ion with a coordinated olefin $[(\eta^5\text{-Cp})(\text{OC})_2\text{Fe}(\eta^2\text{-CH}_2\text{=CHMe})]^+$ (10).
- (b) Electrophilic attack of Br_2 on the η^1 -allyl group of (9) gives the complex ion $[\text{Cp}(\text{OC})_2\text{Fe}(\eta^2\text{-CH}_2\text{=CHCH}_2\text{Br})]^+$ (11).
- (c) Methylation of the η^1 -allyl group of (9) with Me_3O^+ gives the cationic complex $[\text{Cp}(\text{OC})_2\text{Fe}(\eta^2\text{-CH}_2\text{=CHCH}_2\text{Me})]^+$ (12).
- (d) Mercuriation of the η^1 -allyl group of (9) with HgCl_2 gives the cationic complex $[\text{Cp}(\text{OC})_2\text{Fe}(\eta^2\text{-CH}_2\text{=CHCH}_2\text{HgCl})]^+$ (13).

Electrophilic attack on η^1 -alkynyl ligands

Protonation of alkynyl-metal complexes gives complexes containing a **M=C bond**. For example, protonation of the complex $[(\eta^5\text{-Cp}^*)(\text{Ph}_3\text{P})_2\text{RuC}\equiv\text{CPh}]$ (14) gives $[(\eta^5\text{-Cp}^*)(\text{Ph}_3\text{P})_2\text{Ru}=\text{C}=\text{C}(\text{H})\text{Ph}]^+$ (15).



Problems

- Predict the product(s) of the following reactions.
 - $[\text{W}(\eta^6\text{-benzene})(\eta^6\text{-cht})] + \text{Ph}_3\text{CBF}_4 \rightarrow$
 - $[(\eta^5\text{-Cp}^*)(\text{OC})_3\text{W}(\eta^1\text{-CH}_2\text{CH=CH}_2)] + \text{H}^+ \rightarrow$
 - $[(\eta^5\text{-Cp}^*)(\text{OC})_2\text{Ru}(\eta^1\text{-C}_5\text{H}_5)] + \text{H}^+ \rightarrow$
 - $[(\eta^5\text{-Cp}^*)(\text{OC})_2\text{Ru}(\eta^1\text{-allyl})] + \text{C}_7\text{H}_7^+ \rightarrow$
 - $[(\eta^5\text{-Cp})(\text{PPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2)\text{Ru}(\text{C}\equiv\text{CR})] + \text{Me}_3\text{O}^+ \rightarrow$
 - $[(\eta^5\text{-Cp}^*)\text{Os}(\eta^1\text{-CH}_2\text{CH=CH}_2)(\text{PF}_3)_2] + \text{I}_2 \rightarrow$
- Comment on the following statements.
 - Electrophilic attack of Me^+ on a coordinated $\text{CH}_2=\text{CH}_2$ is facilitated if the metal is in low oxidation state.
 - Electrophilic attack of Me^+ on a coordinated $\text{CH}_2=\text{CH}_2$ is facilitated if the metal coordinated to poor σ -donor ligands.
 - Electrophilic attack of Me^+ is more facile on $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{C}\equiv\text{CPh})(\text{CO})]^+$ than $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{C}\equiv\text{CPh})(\text{CO})]$.
 - Electrophilic attack of Me^+ is more facile on $[\text{CpIr}(\eta^2\text{-CH}_2=\text{CH}_2)(\text{PF}_3)]$ than $[\text{CpIr}(\eta^2\text{-CH}_2=\text{CH}_2)(\text{PMe}_3)]$.
 - Electrophilic attack of Me^+ is less facile on $[(\eta^5\text{-C}_5\text{Me}_5)\text{IrMe}_2(\eta^2\text{-CH}_2=\text{CH}_2)]$ than $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\eta^2\text{-CH}_2=\text{CH}_2)(\text{PMe}_3)]$.