

Agostic interaction and metallacycles

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Coordinatively unsaturated metal centers may interact with a C-H bond of a **coordinated ligand** and then undergo C-H bond activation or fission to form **metallacycles**.

Agostic interaction

An interaction that occurs between an unsaturated metal center and a C-H bond of a group attached to that metal center is called an **agostic interaction**. These interactions are denoted by a **half-headed arrow** (\rightarrow) as given in following examples.

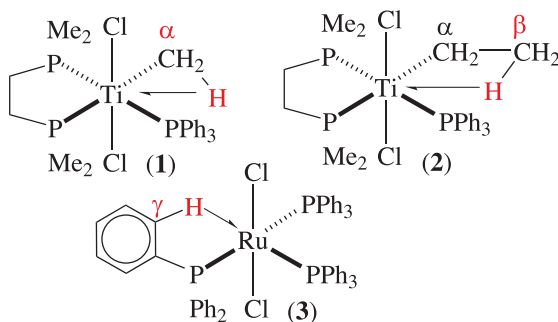
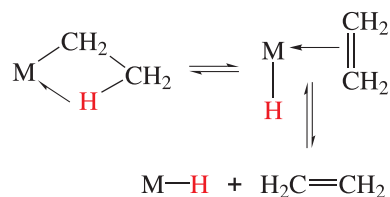


Figure 1: $[\text{TiCl}_3(\text{Me})(\text{dmpe})]$ (1) (agostic methyl); $[\text{TiCl}_3(\text{Et})(\text{dmpe})]$ (2) (agostic ethyl); $[\text{RuCl}_2(\text{PPh}_3)_3]$ (3) (agostic phenyl)

dmpe = bis(dimethylphosphino) ethane

Hydride abstraction

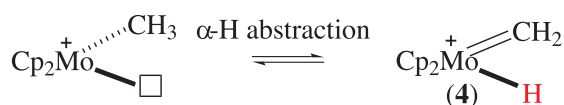
Sometimes, unsaturated metal centers may abstract a hydrogen from a coordinated organic group forming a metal hydride. For example, the $\text{M}-\text{CH}_2\text{CH}_3$ group can form a $\text{M}-\text{H}$ and a coordinated ethene molecule due to **β -hydride abstraction** and subsequent **elimination** of ethene as shown below.



Decomposition of alkyl-complexes is mainly occurred *via* β -hydride abstraction followed by elimination of an

organic molecule (*e.g.*, olefin). Thus, metal complexes which do not have a β -hydrogen (*e.g.*, $\text{C}\equiv\text{CR}$, CH_2Ph) are relatively stable.

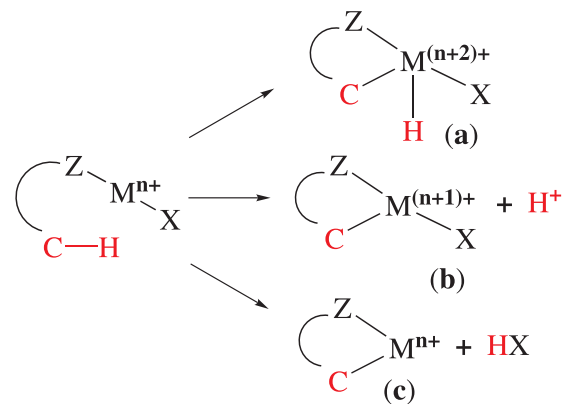
Metal-methyl ($\text{M}-\text{CH}_3$) complexes may undergo **α -hydride abstraction** to form **carbene** or **alkylidene** ($\text{M}=\text{CH}_2$) complexes. The complex $[\text{Cp}_2\text{MoH}(=\text{CH}_2)]^+$ (4) is formed *via* α -hydride abstraction by Mo of $[\text{Cp}_2\text{MoMe}]^+$; Cp = cyclopentadienyl.



Cyclometallation

The formation of a **metallacycle** with a **new M-C bond** *via* a C-X (X = H, halogen) bond fission of a coordinated ligand by the metal center is known as **cyclometallation**. This reaction can be considered as an **intramolecular reaction**. This cleavage of a C-H bond is also referred to as **C-H bond activation**. An alkyl group of a coordinatively unsaturated metal-alkyl complex could form weak **agostic interaction** before cleaving the C-H bond.

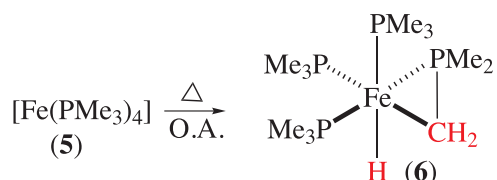
The possible path ways for C-H bond activation to form **metallacycles** are depicted in Scheme 1. Z is the coordinated atom (*e.g.*, C, N, P, O, S *etc.*).



Scheme 1: Possible reaction paths for C-H bond activation of a coordinated ligand by a metal. (a) Oxidative addition of a C-H bond; (b) C-H bond activation with a loss of H^+ ion; (c) C-H bond activation followed by a loss of HX molecule.

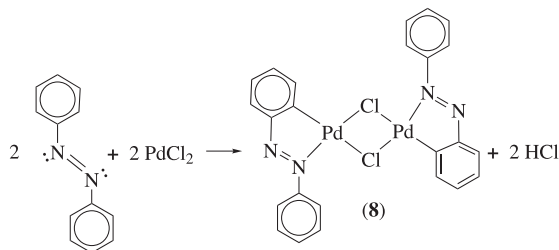
Aliphatic (sp^3 -hybridised) C-H bonds are quite unreactive towards chemical reagents. However, these bonds can be activated (or cleaved) by metal centers when they are brought closer to a metal center by means of prior coordination through a donor atom present in the ligand.

The C-H bond activation of a **methyl** group of a coordinated PMe_3 of $[\text{Fe}(\text{PMe}_3)_4]$ (5) gives a 3-membered metallacycle (6) as shown below.

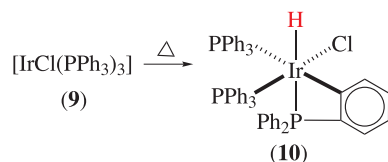


Chelate assisted activation of **aryl** C-H bonds (carbon is sp^2 -hybridised) forms stable metallacycles. In azobenzene, $\text{PhN}=\text{NPh}$ (7), the *ortho*-C-H bond of the Ph group is forced to interact with the Pd center to form a metallacycle. Thus, this process is referred to as **orthometallation**.

The reaction between (7) and PdCl_2 gives the cyclometallated chloride bridged Pd(II) dimer $[\text{Pd}(\text{C}_6\text{H}_4\text{N}=\text{NPh})(\mu\text{-Cl})_2]$ (8). It is the first example of cyclometallation reaction reported by A. C. Cope in 1965.

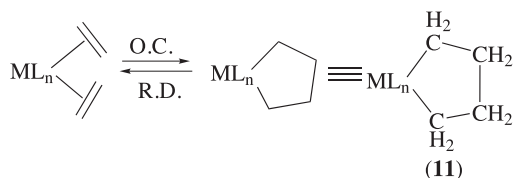


Upon heating, one of the *ortho*-C-H bond of PPh_3 ligand of the complex $[\text{IrCl}(\text{PPh}_3)_3]$ (9) oxidatively adds to the Ir(I) center giving the complex (10) or its isomers with a 4-membered ring.



Oxidative Coupling (O.C.)

Coupling of two alkenes (*e.g.*, $\text{CH}_2=\text{CH}_2$) at a metal center gives a 5-membered **metallacycle** $[\text{LnM}(\text{CH}_2)_4]$ (11) as shown below.



During this process, the oxidation state of the metal has increased by two units, thus it is an oxidation reaction. Two olefins are combined at the metal; thus, it is a coupling reaction. The reverse process is known as reductive decoupling (R.D.) or reductive cleavage and it is not very commonly observed.

Problems

1. Orthometallation of $[\text{RhMe}(\text{PPh}_3)_3]$ gives the complex (A) and a methane molecule (*via* reductive elimination). Draw the structure of (A).
2. Dimethyl hydrazone, $\text{PhC}(=\text{NNMe}_2)\text{Me}$, undergoes orthometallation with Na_2PdCl_4 to give a chloride bridged Pd(II) dimer (B) containing a 5 membered ring. Draw the structure of (B).
3. $[(\eta^5\text{-C}_5\text{Me}_5)\text{RhH}(\text{Ph})\{\text{PMe}_2(\text{CH}_2\text{Ph})\}]$ undergoes orthometallation to give the complex (C) and a benzene molecule. Draw the structure of (C).
4. One mole of $[\text{Fe}(\text{CO})_5]$ reacts with two moles of tetrafluoroethene ($\text{CF}_2=\text{CF}_2$) to give the 16e Fe(II) metallacycle (D). (D) takes up a CO molecule to form the 18e complex (E). Draw the structures of (D) and (E).