P.G. SEMESTER-IV

Elective Course-1a

Inorganic Chemistry Special

Unit -1 (a) Alkyl and Aryl Transition Metal Complexes

Topic: Decomposition Pathways of Alkyl and Aryl Transition Metal Complexes

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DECOMPOSITION PATHWAYS OF TRANSITION METAL ALKYL AND ARYL COMPLEXES

Transition metals σ-hydrocarbyls, due to their coordinative unsaturation are not kinetically stable and this origins severe facile pathways for their decomposition and strong reactivity. These paths are classified as-

1. Migration of a substituent (generally hydrogen) from a σ-bonded hydrocarbyl to the metal
2. Intermolecular reductive elimination and
3. Homolytic fission M-C bond

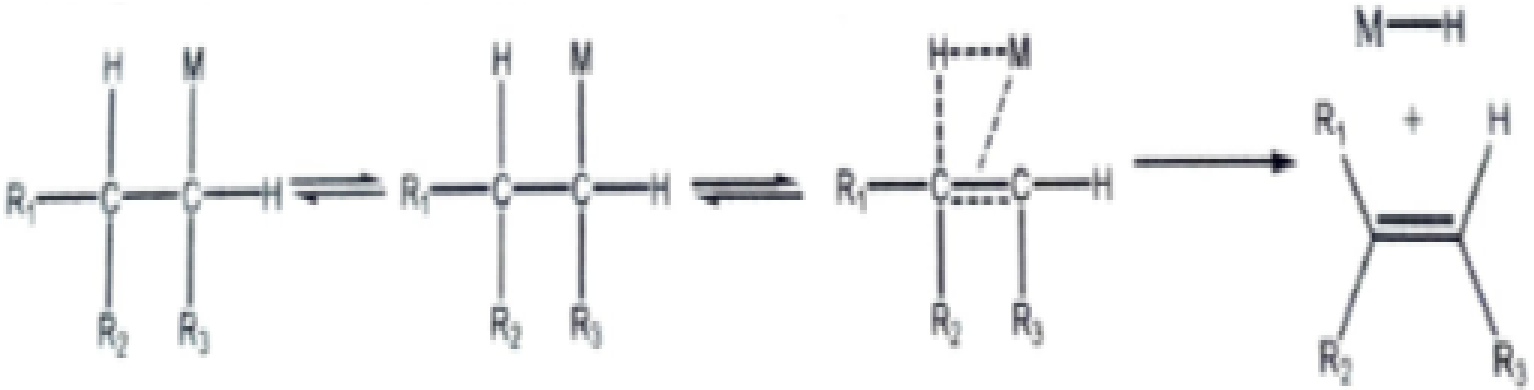
1. Migration of a substituent (generally hydrogen) from a σ-bonded hydrocarbyl to the metal:

It occurs via 3 types of mechanisms-

i. **β-elimination**

The most facile route for the decomposition, preferred by transition metal alkyls is through the so called hydride transfer accompanied with alkene elimination. This typye of recation involves transfer of one hydrogen atom from the second or β-carbon

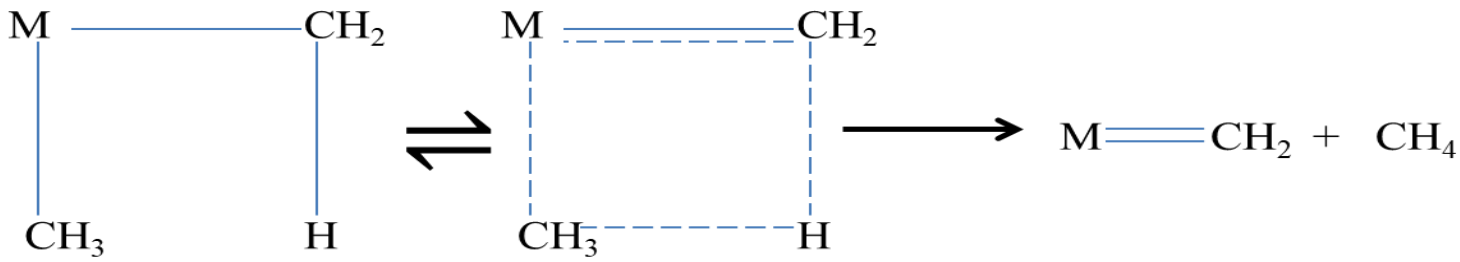
atom of the alkyl chain to the metal, increasing ts coordination number. Resulting intermediate hydrido-alkene complex tends to loose alkene upon formation of metal-hydride, which in some cases may decompose to metal and hydrogen too.



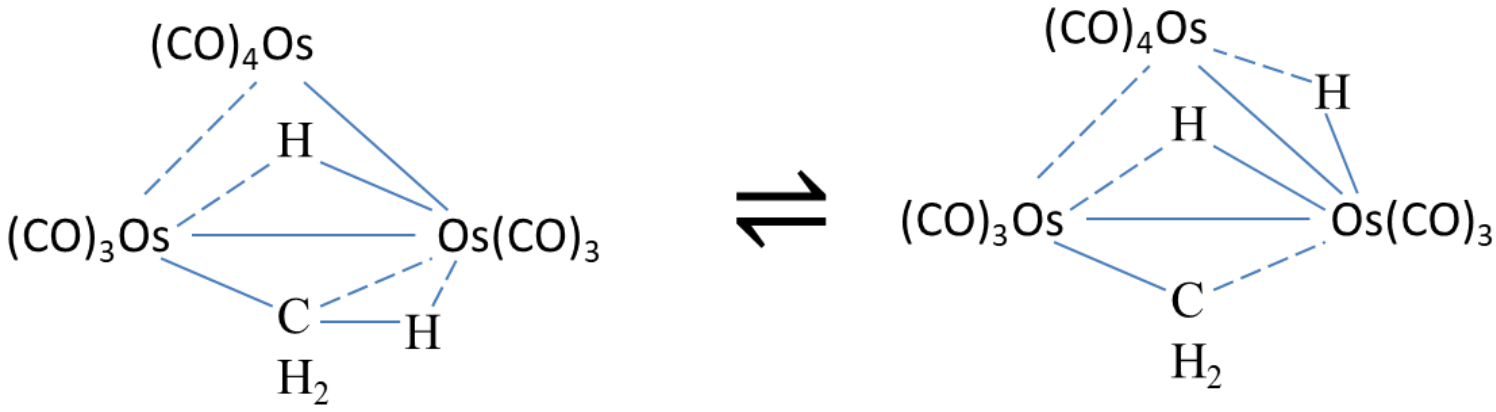
ii. α-elimination

This pathway is much less observed for transition metal hydrocarbyls and main examples involve metal-methyls. However, these are of considerable synthetic utility in main group hydrocarbyls and involves the transfer of a substituent 'R' from the α-carbon atom to the metal. Binary permethyls, example $TaMe_5$, $WaMe_6$ and $ReMe_6$ are unstable and decompose explosively with the formation of methane via four-centered transition state. This plays a key role towards synthesis of alkylidene complexes.

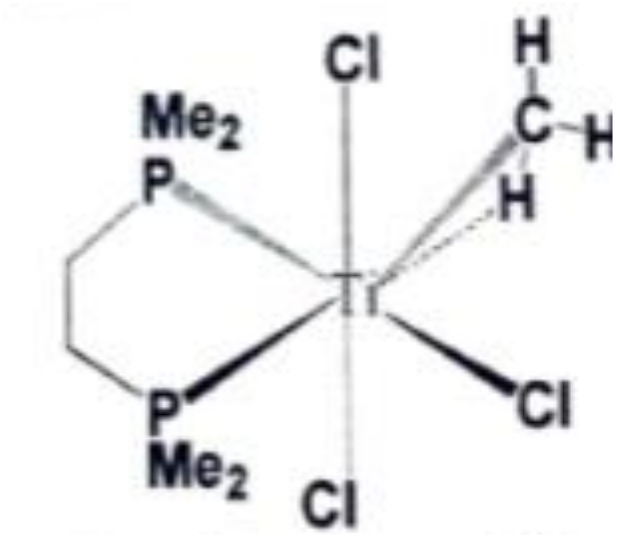
Several metal benzyl and neopentyls especially of titanium and tantalum are known to decompose by this mechanism.



Another mechanism of α-elimination involves " agnostic" hydrogens (C-H-M) which are actually covalently bonded both to a carbon atom and a transition metal atom.



Crystallographic analysis shows that, when a methyl group is attached to a d0- metal centre, having less than 18-electron environment, one of the C-H bonds of that methyl group gets distorted to the extent that it gets into the bonding distance with the metal. Such strong interactions between metal and C-H group are known to play key role towards cyclometallation and alkene polymerization reactions.



iii. **γ-elimination-** It has been observed for some main group hydrocarbyls but it is rare in transition metal chemistry.

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