

6.2: Synthesis and Stability

Learning Objectives

In this lecture you will learn the following

- Understand the role lead by ligands in stabilizing organometallic transition metal complexes.
- Know about various synthetic methods available for preparing the organometallic transition metal complexes.
- Understand the various factors like β -elimination and other bimolecular decomposition pathways that contribute to the observed instability of the organometallic transition metal complexes.
- Obtain insight about making stable organometallic transition metal complexes by suppression of the destabilizing factors mentioned.

Ligands play a vital role in stabilizing transition metal complexes. The stability as well as the reactivity of a metal in its complex form thus depend upon the number and the type of ligands it is bound to. In this regard, the organometallic carbon based ligands come in diverse varieties displaying a wide range of binding modes to a metal. In general, the binding modes of the carbon-derived ligands depend upon the hybridization state of the metal bound carbon atom. These ligands can thus bind to a metal in many different ways as depicted below. Lastly, these ligands can either be of (a) purely σ -donor type, or depending upon the capability of the ligand to form the multiple bonds may also be of (b) a σ -donor/ π -acceptor type, in which the σ -interaction is supplemented by a varying degree of π -interaction.

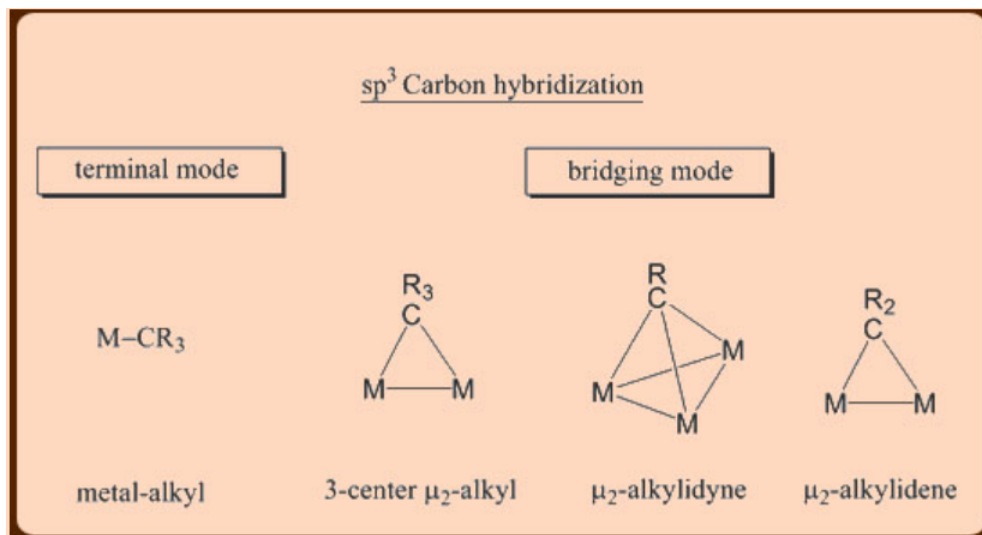


Figure 6.2.1

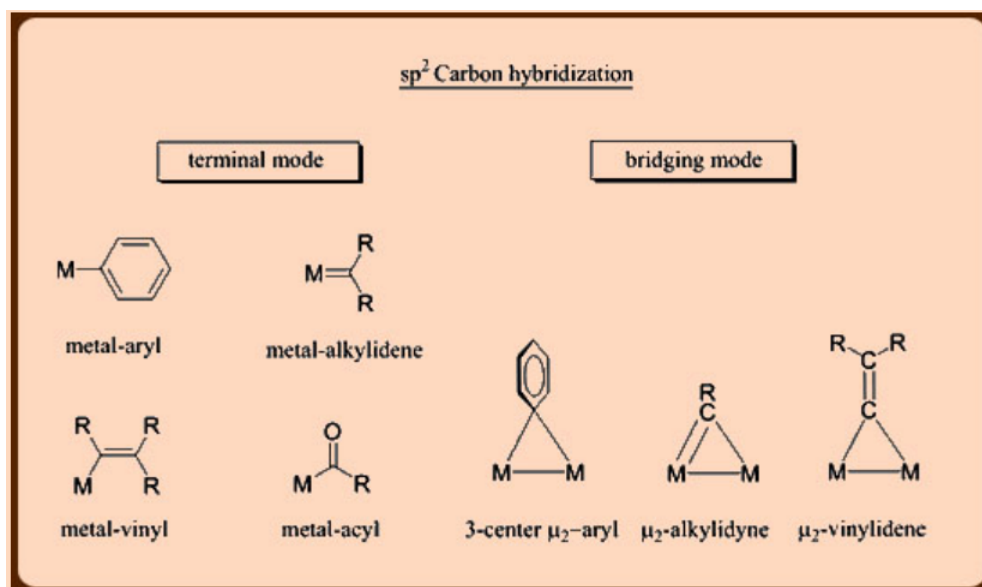


Figure 6.2.2

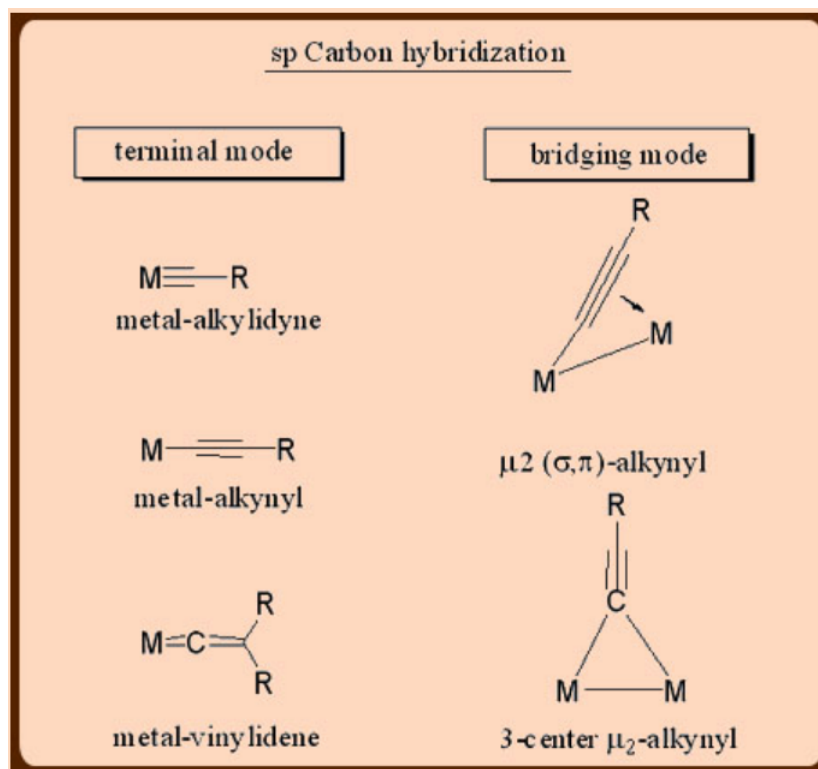


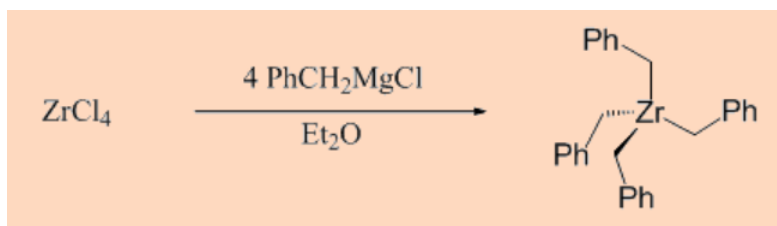
Figure 6.2.3

Preparation of transition metal-alkyl and transition metal-aryl complexes

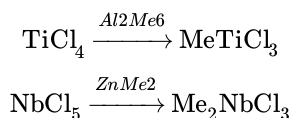
The transition metal-alkyl and transition-metal aryl complexes are usually prepared by the following routes discussed below,

a. Metathesis

This involves the reactions of metal halides with organolithium, organomagnesium, organoaluminium, organotin and organozinc reagents.

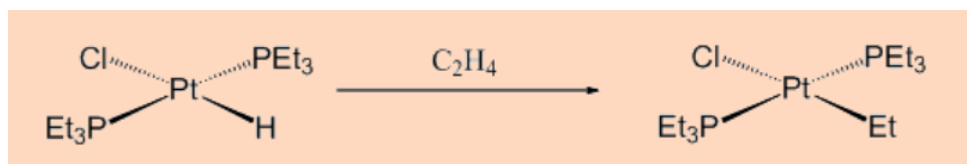


Of the different organoalkyl compounds listed above, the organolithium and organomagnesium compounds are strongly carbanionic while the remaining main group organometallics like the organoalkyl, organozinc and organotin reagents are relatively less carbanionic in nature. Thus, the main group organometallic reagents have attenuated alkylating power, that can be productively used in partial exchange of halide ligands.



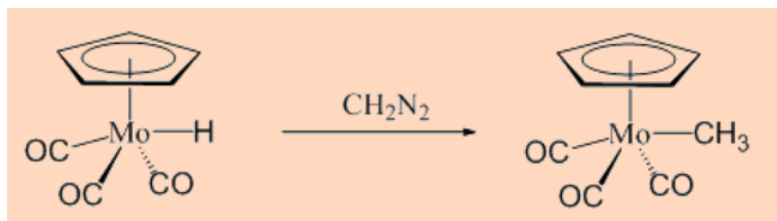
b. Alkene insertion or Hydrometallation

As the name implies, this category of reaction involves an insertion reaction between metal hydride and alkene as shown below. These type reactions are relevant to certain homogeneous catalytic processes in which insertion of an olefin to M–H bond is often observed.



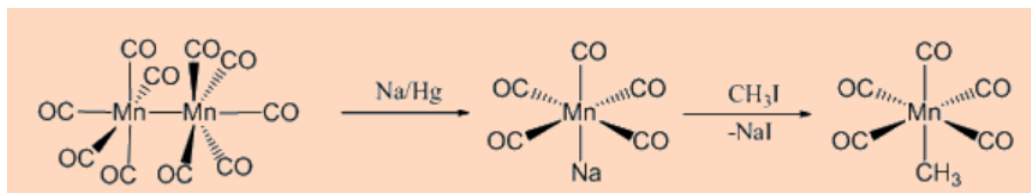
c. Carbene insertion

This category represents the reaction of metal hydrides with carbenes.



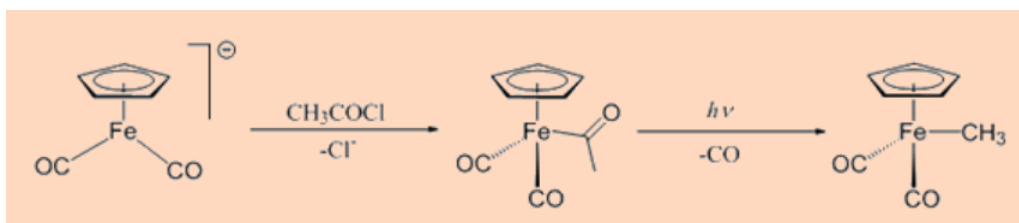
d. Metallate alkylation reaction

This category represents the reaction of carbonylate anions with alkyl halides as shown below.



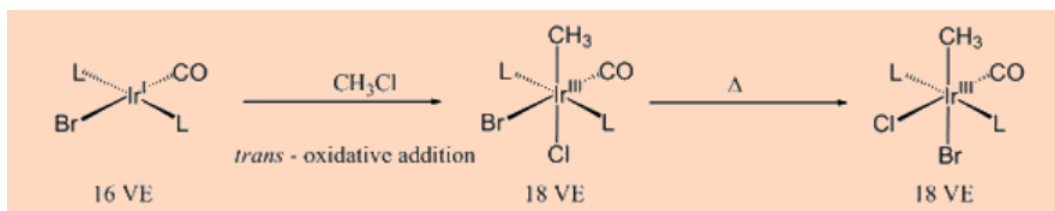
e. Metallate acylation reaction

This category involves the reaction of carbonylate anions with acyl halides



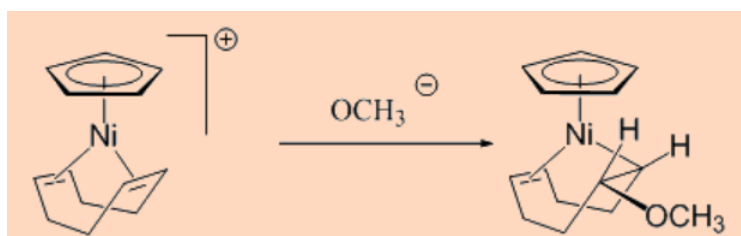
f. Oxidative addition reaction

Many unsaturated 16 VE transition metal complexes having d^8 or d^{10} configuration undergo oxidative addition reactions with alkyl halides. The oxidative addition reactions proceed with the oxidation state as well as coordination number of the metal increasing by +2.



g. Addition reaction

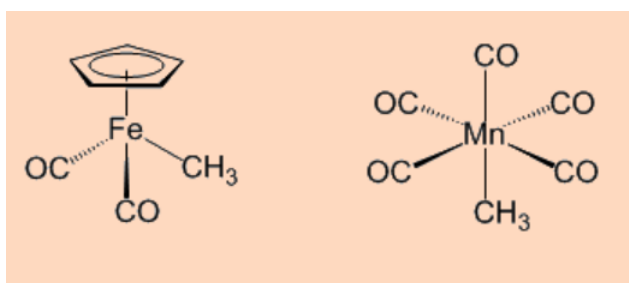
This category involves the reaction of an activated metal bound olefin complex with a nucleophile as shown below.



Thermodynamic Stability and Kinetic Lability

The transition metal organometallic compounds are often difficult to synthesize under ordinary laboratory conditions and require stringent experimental protocols involving the exclusion of air and moisture for doing so. As a consequence, many homoleptic binary transition metal-alkyl and transition metal-aryl compounds like, Et_2Fe or Me_2Ni cannot be made under normal laboratory conditions. More interestingly, most of the examples of transition metal-aryl and transition metal-alkyl compounds, known in the literature, invariably contain additional ligands like $\eta^5\text{-C}_5\text{H}_5$, CO, PR_3 or halides.

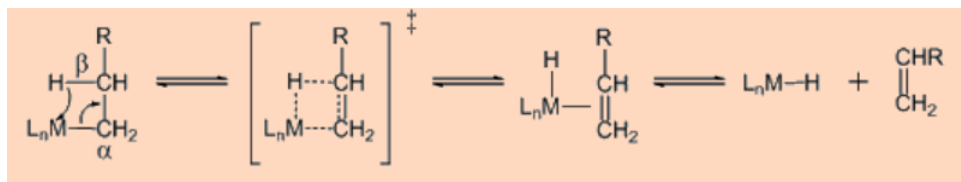
For example,



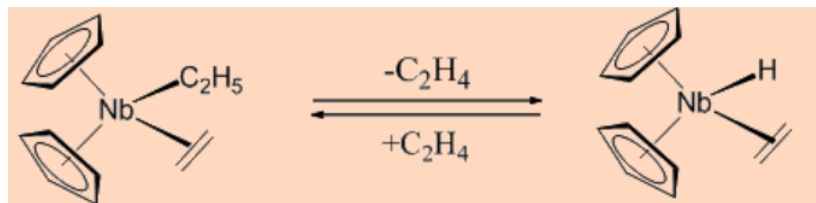
Transition metal-carbon (TM-C) bond energy values are important for understanding the instability of transition metal organometallic compounds. In general, the TM-C bonds are weaker than the transition metal-main group element (TM-MGE) bonds (MGE = F, O, Cl, and N) and more interestingly so, unlike the TM-MGE bond energies, the TM-C bond energy values increase with increasing atomic number. The steric effects of the ligands also play a crucial role in influencing the TM-C bond energies and thus have to be given due consideration.

Contrary to the popular belief, the difficulty in obtaining transition metal-aryl and transition metal-alkyl complexes does primarily arise from the thermodynamic reasons but rather the kinetic ones. β -elimination is by far the most general decomposition

mechanism that contribute to the instability of transition metal organometallic compounds. β -elimination results in the formation of metal hydrides and olefin as shown below.



β -elimination can also be reversible as shown below.



The instability of transition metal organometallic compounds can arise out of kinetic lability like in the case of the β -elimination reactions that trigger decomposition of these complexes. Thus, the suppression of the decomposition reactions provides a viable option for the stabilization of the transition metal organometallic complexes. The β -elimination reactions in transition metal organometallic complexes may be suppressed under any of the following three conditions.

a. Formation of the leaving olefin becomes sterically or energetically unfavorable

In the course of β -elimination, this situation arises when the olefinic bond is formed at a bridgehead carbon atom or when a double bond is formed with the elements of higher periods. For instance, the norbornyl group is less prone to decomposition by β -elimination because that would require the formation of olefinic double bond at a bridgehead carbon atom in the subsequent olefin, *i.e.* norbornene, and which is energetically unfavorable.

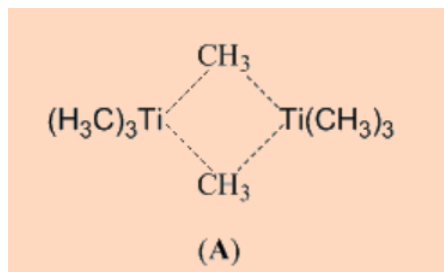


b. Absence of β -hydrogen atom in organic ligands

Transition metal bound ligands that do not possess β -hydrogen cannot decompose by β -elimination pathway and hence such complexes are generally more stable than the ones containing β -hydrogen atoms. For example, the neopentyl complex, $\text{Ti}[\text{CH}_2\text{C}(\text{CH}_3)_3]_4$ (m.p. 90 °C), and the benzyl complex, $\text{Zr}(\text{CH}_2\text{Ph})_4$ (m.p. 132 °C), exhibit higher thermal stability as both of the neopentyl and benzyl ligands lack β -hydrogens.

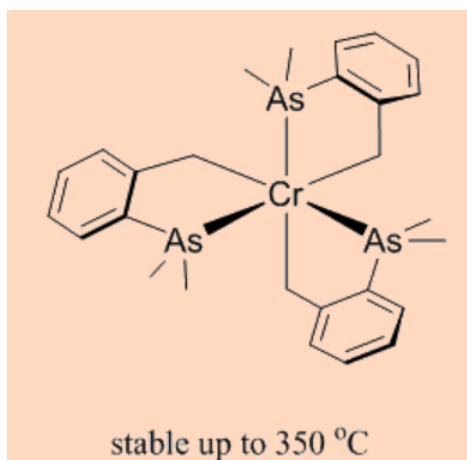
c. Central metal atom is coordinatively saturated

Transition metal organometallic complexes in which the central metal atom is coordinatively saturated tend to be more stable due to the lack of coordination space available around the metal center to facilitate β -elimination reaction or other decomposition reactions. Thus, the absence of free coordination sites at the metal is crucial towards enhancing the stability of the transition metal organometallic complexes. For example, $\text{Ti}(\text{Me})_4$, which is coordinatively unsaturated can undergo a bimolecular decomposition reaction *via* a binuclear intermediate (**A**), is unstable and exhibits a decomposition temperature of -40 °C. On the contrary, $\text{Pb}(\text{Me})_4$, that cannot undergo decomposition by such bimolecular pathway, is more stable and distills at 110 °C at 1 bar atmospheric pressure.



The $\text{Ti}(\text{Me})_4$ decomposes by dimerization involving the formation of $\text{Ti}-\text{C}$ ($3c-2e$) bonds. For $\text{Pb}(\text{Me})_4$, such bimolecular decomposition pathway is not feasible, as being a main group element it has higher outer d orbital for extending the coordination number. If the free coordination site of $\text{Ti}(\text{Me})_4$ is blocked by another ligand, as in $[(\text{bipy})\text{Ti}(\text{Me})_4]$, then the thermal stability of the complex, $[(\text{bipy})\text{Ti}(\text{Me})_4]$, increased significantly. Other bidentate chelating ligands like *bis*(dimethylphosphano)ethane (dmpe) also serve the same purpose.

Coordinative saturation thus brings in kinetic stabilization in complexes. For example, $\text{Ti}(\text{Me})_4$ is extremely reactive as it is coordinatively unsaturated, while $\text{W}(\text{Me})_6$ is relatively inert for reasons of being sterically shielded and hence, coordinatively saturated. Thus, if all of the above discussed criteria for the suppression of β -elimination are taken care of, then extremely stable organometallic complexes can be obtained like the one shown below.



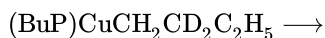
Problems

1. Arrange the following compounds in the order of their stability.

- $\text{Ti}(\text{Et})_4$
- $\text{Ti}(\text{Me})_4$ and
- $\text{Ti}(\text{6-norbornyl})_4$

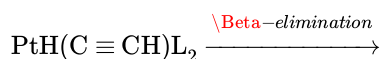
Ans: $\text{Ti}(\text{Et})_4 < \text{Ti}(\text{Me})_4 < \text{Ti}(\text{6-norbornyl})_4$

2. Predict the product of the reaction given below.



Ans: Equi molar amounts of $(\text{Bu}_3\text{P})\text{CuD}$ and $\text{CH}_2=\text{CDC}_2\text{H}_5$

3. Will the compound β -eliminate,



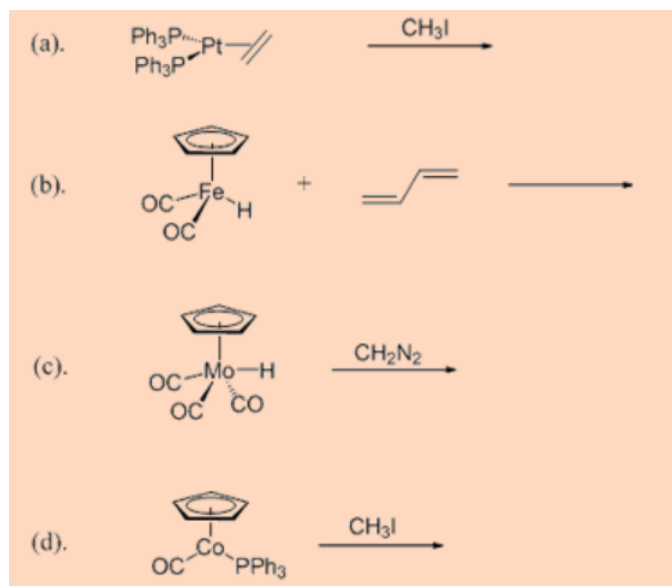
(a). readily, (b). slowly and (c). not at all.

Explain your answer with proper reasoning.

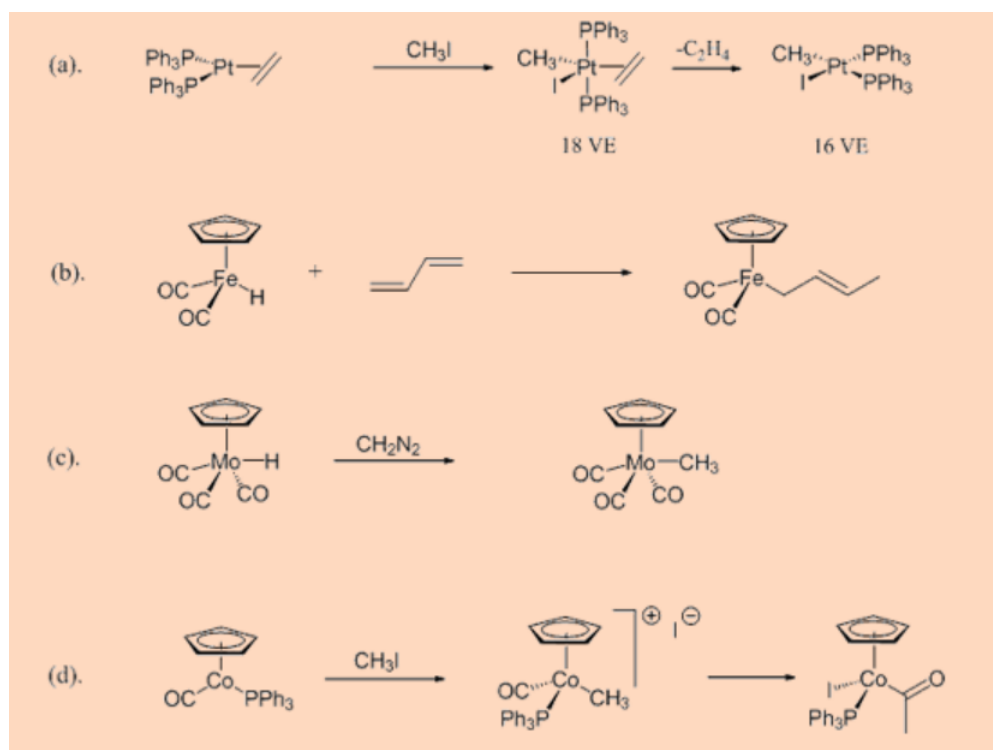
Ans: Not at all as the β -hydrogens are pointing away from the metal and cannot participate in β -elimination reaction.

Self Assessment test

1. Write the product(s) of the reactions.



Ans:



Summary

Ligands assume a pivotal role in the stabilization of the organometallic transition metal complexes. There are several methods available for the preparation of the organometallic transition metal complexes. The observed instability of the organometallic transition metal complexes can be attributed to two main phenomena namely β -elimination and bimolecular decomposition reaction that severely undermine the instability of these complexes. The suppression of these decomposition pathway thus pave way for obtaining highly stable organometallic transition metal complexes.

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