Metal Alkyls / Aryl Complexes

M. Sc. Chemistry 4th Sem (Ia)

Ph. D. Course Work/NET/JRF CSIR

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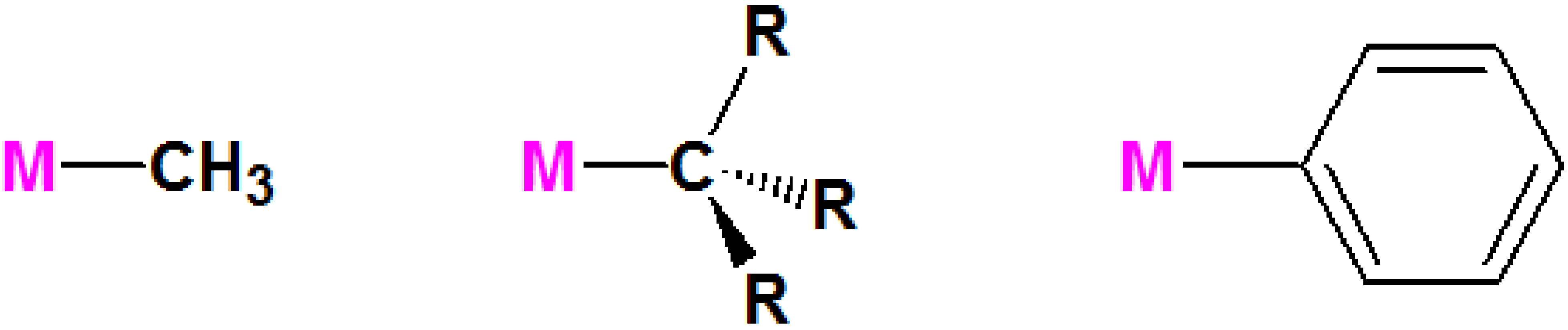
Metal Alkyls or Aryl Complexes

Compounds of metal with alkyl radical are called metal alkyls while those with aryl are called metal aryls. It contains direct M-C bond.



Anionic
2 e- donors

Where C comes from alkyl or aryl radical and it acts as ligand. It may be generally sigma donor. It may be homoleptic (if ligands are same) or hetroleptic (if ligands are different) aryl group are same than it is known as homoleptic if ligands are different than it is hetroleptic. It may be symmetrical or a symmetrical when ligands are same than it a symmetrical. If ligands are different than it is unsymmetrical. Similarly it may be mono nuclear or poly nuclear.

Donor Capacity

Alkyls are typically very **strong** anionic sigma donors, (second only to hydrides). They have virtually no pi-acceptor ability. Increasing the carbon substitution (replacing hydrogens with hydrocarbon groups, methyl ⟶ ethyl ⟶ isopropyl) usually increases the donor strength, but steric factors can come into play and weaken the metal-alkyl bond (e.g., t-butyl groups are often too sterically hindered to bind well). Replacing the hydrogens with fluorine atoms (very electron withdrawing) dramatically reduces the donor ability of the alkyl (aryl). For example, CF_3^- and $C_6F_5^-$ are not very strong donors. Metal alkyls are also typically quite to extremely reactive to molecular O_2, water, and a variety of other ligands and reagents. As with hydrides, they play a very important and active role in catalysis.

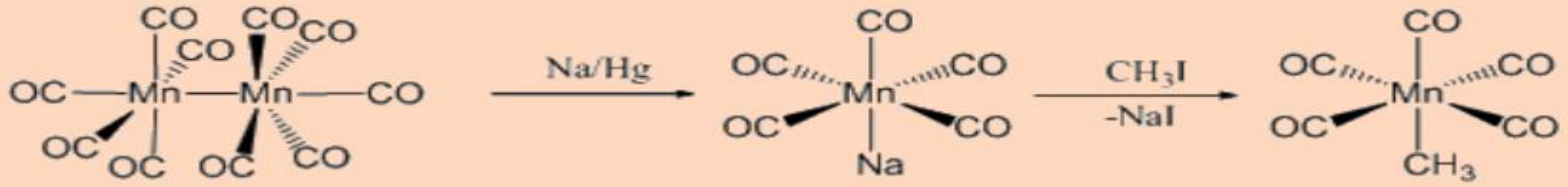
Alkyl anion stabilized to different extent depending on the electronegativity of the metal involved and also the nature of hybridization of alkyl ligand

Routes of Synthesis

The transition metal−alkyl and transition−metal aryl complexes are usually synthesized by the following routes.

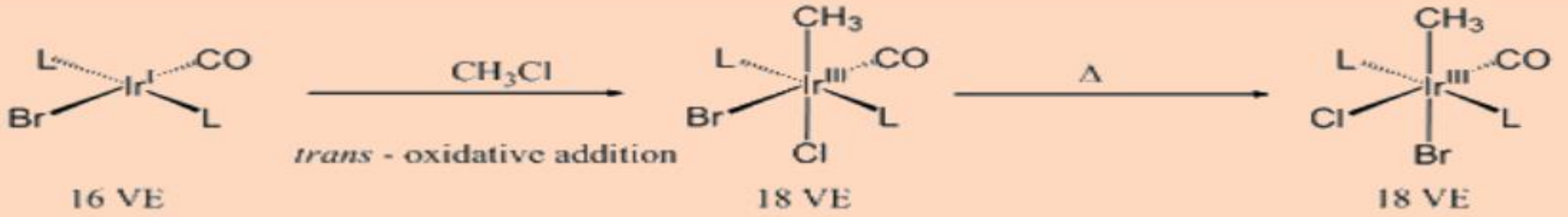
Metallate alkylation reaction

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



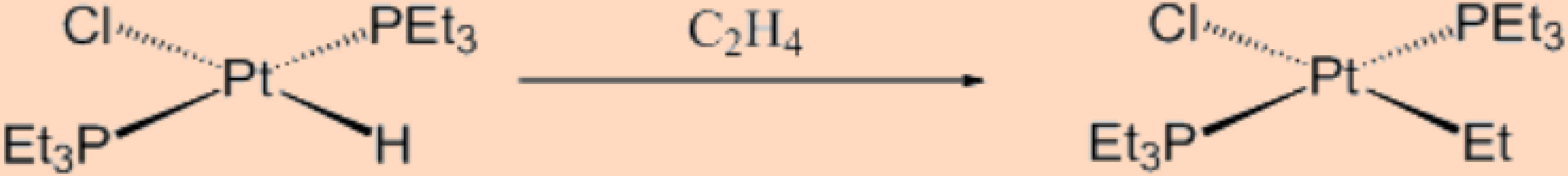
Oxidative addition reaction

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.



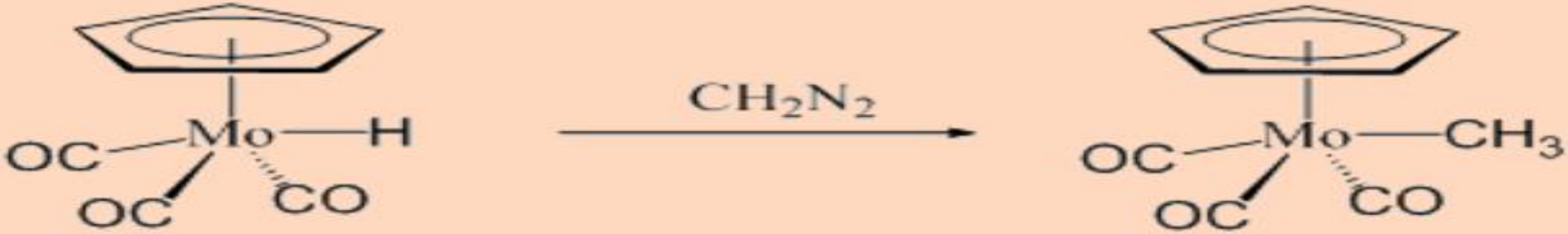
Alkene insertion or Hydrometallation

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.



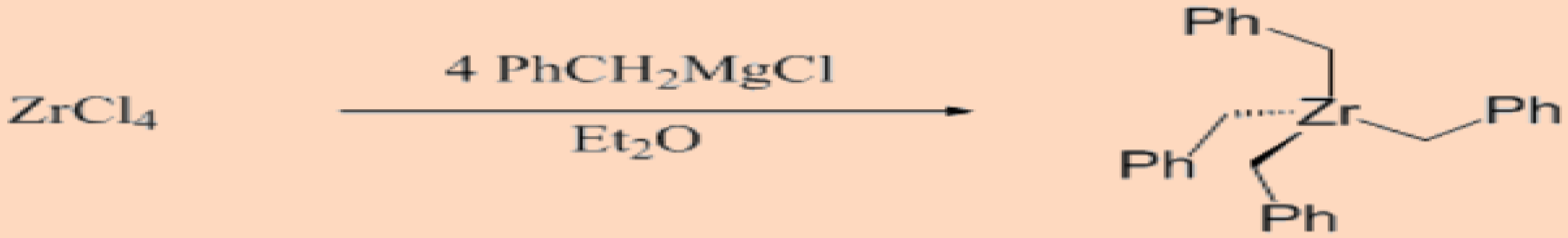
Carbene insertion

This category represents the reaction of metal hydrides with carbenes.



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.

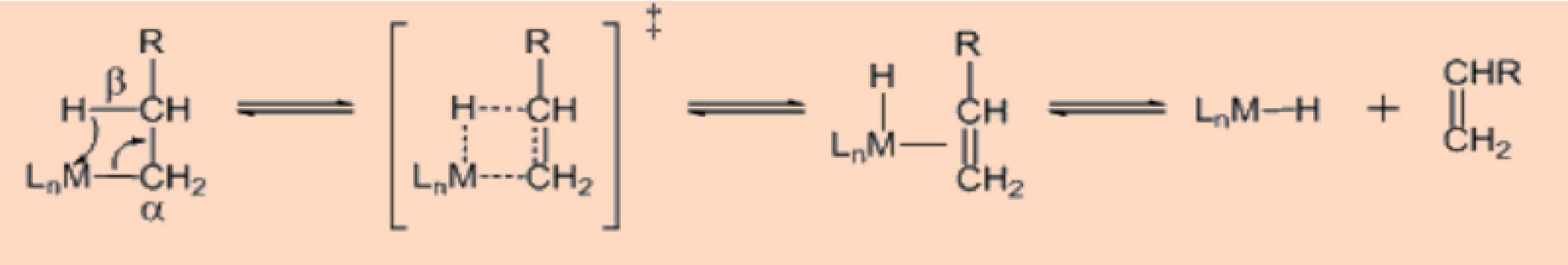
$$TiCl_4 \xrightarrow{Al2Me6} MeTiCl_3$$

$$NbCl_5 \xrightarrow{ZnMe2} Me_2NbCl_3$$

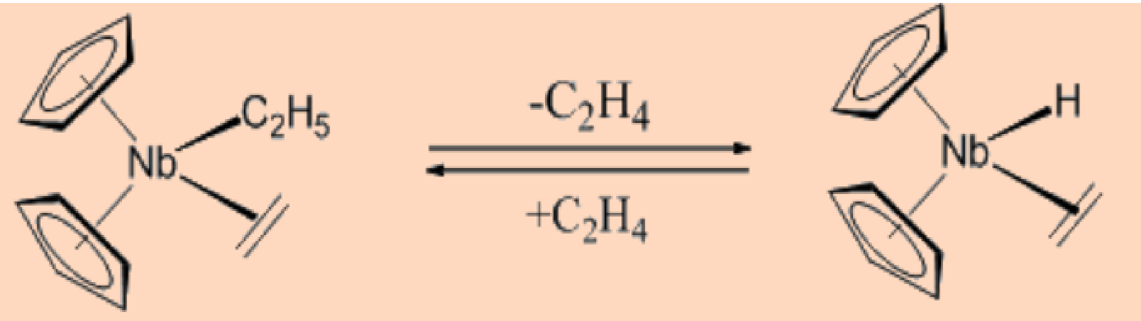
Thermodynamic Stability and Kinetic Lability

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.



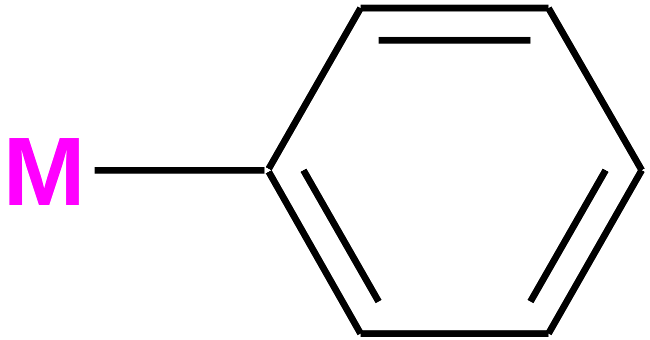
β−elimination can also be reversible as shown below.



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 conditions.

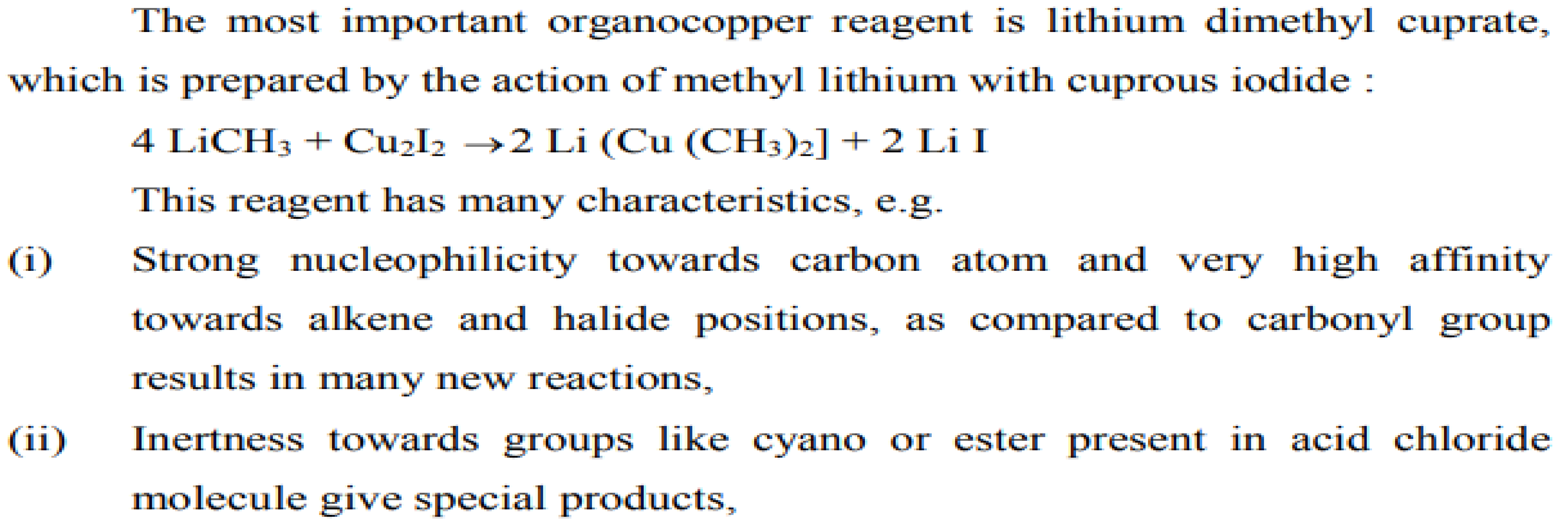
Metal Aryl

Aryl ligands are relatively strong anionic two electron donors, essentially just like alkyls. Since they cannot easily B-hydride eliminate (formation of the benzyne intermediate is typically too unstable), metal aryl complexes are usually relatively stable compared to alkyls with B-hydrogens. But “stable” is a relative term since transition metal aryl complexes are usually quite air-sensitive. Aryls do have the potential for both pi-donation and pi-back bonding through the filled aryl p-orbitals and empty p* antibonding orbitals. This can provide additional stability to a metal complex, depending on whether the metal needs additional electrons from the ligand or wants to dump excess electron density onto the ligand.



Organo Copper in Organic Synthesis

Organocopper chemistry is very important in organometallic chemistry due to it has been used as reagent where it acts as nucleophile. the chemical reactivity displayed by the cuprate reagents is due to a powerful nucleophilicity toward carbon, along with a strong preference for reaction at alkene or halide site compared to carbonyl groups.



The most important organocopper reagent is lithium dimethyl cuprate, which is prepared by the action of methyl lithium with cuprous iodide :

$$4\ LiCH_3 + Cu_2I_2 \rightarrow 2\ Li\ (Cu\ (CH_3)_2] + 2\ Li\ I$$

This reagent has many characteristics, e.g.

(i) Strong nucleophilicity towards carbon atom and very high affinity towards alkene and halide positions, as compared to carbonyl group results in many new reactions,

(ii) Inertness towards groups like cyano or ester present in acid chloride molecule give special products,

(iii) In, α,β- unsaturated carbonyl systems, it selectively attaches with β-Carbon atom,

(iv) It has special ability to replace various types of halogen atoms by methyl group,

(v) It reacts with allytic acetate by SN-1 reaction.

(vi) Reacts with epoxides to form open ring alkylated alcohols, and

(vii) It adds to acetylene-esters

The specific reactions of LiCu Me_2 with reference to organic synthesis, are :

1. Halogen Substitution

(i) trans $PhCH = CH\,Br + Li\,Cu\,me_2 \rightarrow$ trans $PhCH = CH\,Me$

(ii) $C_6H_5I + Li\,Cu\,me_2 \rightarrow C_6\,H_5\,Me$

(iii) $C_5H_{11}\,Br + Li\,[Cu\,Bu^t{}_2] \rightarrow But\,(CH_2)_4\,CH_3$

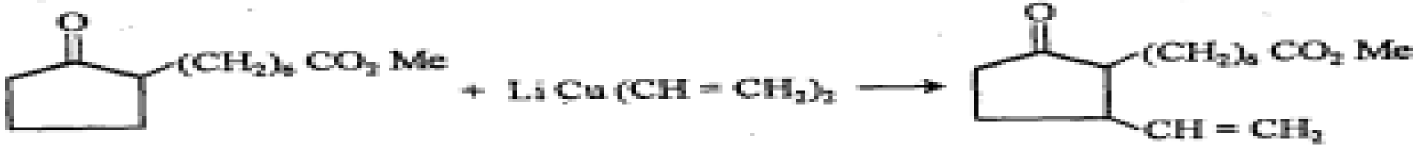
(iv) 

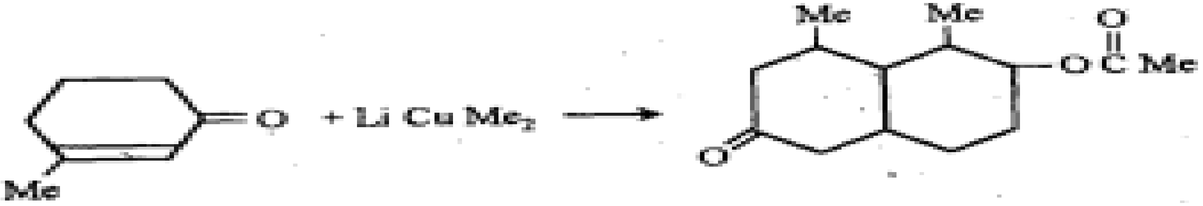
(v) 

2. Conjugated Additions

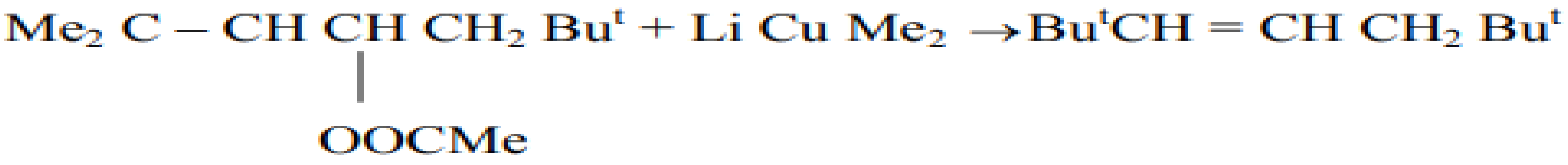
(i) 

$$Me\,CH = CH\,\overset{O}{\overset{\|}{C}}\,Me + Li\,Cu\,Me_2 \rightarrow Me_2\,CH\,CH_2\,\overset{O}{\overset{\|}{C}}\,Me$$

(ii) 

(iii) 

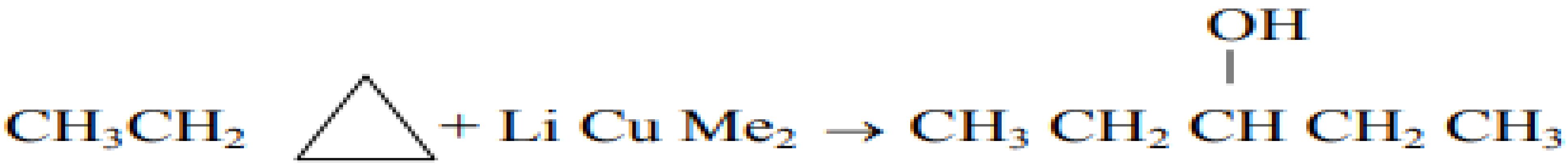
3. Alkylation of Allyl Acetate



$$Me_2\,C - CH\,\underset{\underset{OOCMe}{|}}{CH}\,CH_2\,Bu^t + Li\,Cu\,Me_2 \rightarrow Bu^tCH = CH\,CH_2\,Bu^t$$

4. Alkylation of Epoxides

(i)



(ii)

5. Formation Ketone from Acid- Chloride

(i)

$$N \equiv C(CH_2)_{10}\overset{\overset{O}{\|}}{C}\,Cl + Li\,Cu\,Me_2 \rightarrow N \equiv C(CH_2)_{10}\overset{\overset{O}{\|}}{C}\,Me$$

(ii) $Bu^t\,C\,Cl + Li\,Cu\,Pr^4{}_2 \rightarrow Bu^t\,C\,pr^t$

Thanks