

the propagation step thereby terminating the radical chain reaction, e.g., hydroquinone (HQ), 4-*tert*-

butylcatechol (TBC), 4-methoxyphenol, 2,6-di-*tert*-butyl-4-methylphenol (BHT), etc.

Alkyl Metal Complexes

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An alkyl-metal complex has at least one Metal Carbon (M-C) σ - or π -bond. Grignard reagent (RMgX) and LiR are the most common alkyl-metal reagents used in organic synthesis. ZnEt₂ and EtZnI are the first metal alkyls prepared by Edward Frankland in 1848.

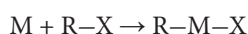
Synthetic routes to metal alkyls (M-R)

There are many ways to synthesize metal-alkyls. Here, the appropriate aliphatic, alkenyl, alkynyl, and aryl groups are considered as alkyl groups (R).

1. By reacting a metal directly with RX

This can be considered as an oxidative addition of an organic halide to a zerovalent metal.

With divalent metals



Some examples are given below.

- $Mg + PhI \rightarrow PhMgI$ (Grignard reagent)
- $Zn + EtI \rightarrow EtZnI$
- $Hg + CH_2=CHCH_2I \rightarrow CH_2=CHCH_2HgI$
- $Ca + MeI \rightarrow MeCaI$

Note that structures of some of these reagents are not *monomeric*.

With monovalent metals

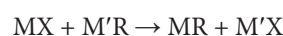


The order of the reactivity of organic halides is as follows.



2. via Transmetallation

Alkylating agents (containing transferable alkyl groups) can be used to prepare other organometallic compounds as shown below.



Magnesium, lithium, aluminium and mercury alkyls are some of the common alkylating agents. This transfer of an alkyl group from one metal to another is known as **transmetallation**.

Some reactions are given below.

- $[PtBr_2(PPh_3)_2] + 2 EtMgBr \rightarrow [PtEt_2(PPh_3)_2]$
- $TiCl_3 + 3 LiMe \rightarrow TiMe_3 + 3 LiCl$
- $[Cp(OC)_2RuBr] + HgPh_2 \rightarrow [Cp(OC)_2RuPh] + PhHgBr$
- $[Cp(OC)_2RuBr] + LiMe \rightarrow [Cp(OC)_2RuMe] + LiBr$
- $[Cp_2TiCl_2] + 2 LiMe \rightarrow [Cp_2TiMe_2] + 2 LiCl$
- $[Cp_2TiCl_2] + AlMe_3 \rightarrow [Cp_2TiCl(Me)] + AlClMe_2$
- $WCl_6 + 6 AlMe_3 \rightarrow [WMe_6] + 6 AlClMe_2$

AlR₃ usually transfer only **one alkyl** group.

The nucleophilicity of the R⁻ varies as given below.



3. via Oxidative addition

Alkyl and aryl halides add to coordinatively unsaturated transition metal centres to form metal-carbon bonds. Some examples are given below.

- $[IrCl(PPh_3)_3] + MeI \rightarrow [IrCl(I)(Me)(PPh_3)_3]$
- $[Fe(CO)_5] + MeC(=O)CH_2Br \rightarrow [(MeCOCH_2)FeBr(CO)_4]$
- $[Pd(PPh_3)_4] + CH_2=CHBr \rightarrow trans-[PdCl(CH=CH_2)(PPh_3)_2]$

Oxidative addition of a C-H bond of a coordinated ligand generates a metallacycle with a M-C bond.

4. via Reacting with an electrophile

Some complexes have *nucleophilic* (π -basic) metal

centers: particularly, in complex anions. These metal centers readily react with organic *electrophiles* (R^+) to give M-C bonds. This process can be considered as a *nucleophilic substitution* on carbon. Some examples are given below.

- (i) $\text{Na}[\text{Mn}(\text{CO})_5] + \text{MeI} \longrightarrow [\text{MeMn}(\text{CO})_5] + \text{NaI}$
- (ii) $\text{Na}[\text{CpW}(\text{CO})_3] + \text{MeI} \longrightarrow [\text{CpW}(\text{CO})_3\text{Me}] + \text{NaI}$
- (iii) $\text{Na}[\text{CpFe}(\text{CO})_2] + \text{EtI} \longrightarrow [\text{CpFe}(\text{CO})_2\text{Et}] + \text{NaI}$
- (iv) $[\text{CpFe}(\text{CO})_2]^- + \text{Ph}_3\text{S}^+ \longrightarrow [\text{CpFe}(\text{CO})_2\text{Ph}] + \text{Ph}_2\text{S}$

5. Deinsertion reactions

By the action of heat or light, new M-R, bonds can be formed via the elimination of a small molecule such as $\text{C}\equiv\text{O}$, CO_2 , SO_2 or N_2 from complexes containing M-COR, M-CO₂R, M-SO₂R and M-N₂R fragments, respectively.

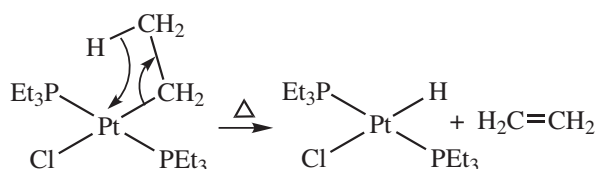
- (i) $[(\text{OC})_5\text{Mn}(\text{C}=\text{OMe})] \longrightarrow [(\text{OC})_5\text{MnMe}] + \text{CO}$
- (ii) $[\text{Cp}(\text{OC})_2\text{FeSO}_2\text{R}] \longrightarrow [\text{Cp}(\text{OC})_2\text{FeR}] + \text{SO}_2$
- (iii) $[(\text{bipy})\text{NiCO}_2\text{Me}]_2 \longrightarrow [(\text{bipy})\text{NiMe}_2] + 2 \text{CO}$
- (iv) $[(\text{Et}_3\text{P})_2\text{Pt}(\text{N}=\text{NPh})\text{Cl}] \longrightarrow [(\text{Et}_3\text{P})_2\text{PtPh}(\text{Cl})] + \text{N}_2$

Reactions of alkyl metal complexes

Most metal alkyls are reactive. They can undergo (i) β hydride abstraction, (ii) reductive elimination, and (iii) insertion and deinsertion reactions. Metal alkyls are prone to be attacked by electrophiles.

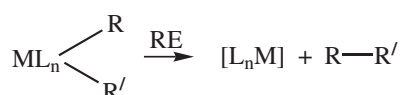
a) β -Hydride abstraction

The major decomposition path of metal alkyls is *via* the β -H abstraction. When it is not possible, other hydrogen transfer reaction (e.g., α - or γ -H abstraction) may take place.



b) Reductive elimination reactions

cis-Dialkyl complexes $[\text{L}_n\text{M}(\text{R})\text{R}']$ can decompose via reductive elimination (RE) of $\text{R}-\text{R}'$.



c) Insertion reactions

Unsaturated molecules such as CO, alkenes and alkynes insert into M-R bonds forming M-COR, M-CH₂CH₂R and M-CH=CHR fragments.

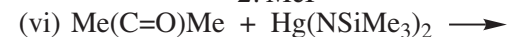
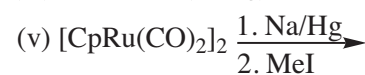
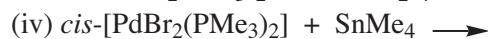
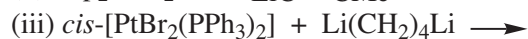
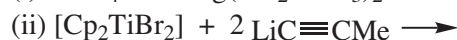
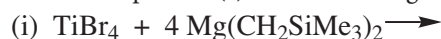
d) Electrophilic attack on M-R

The reaction of alkyl metal complexes with electrophiles such as H^+ , halogens, cleaves the M-C bond or substitutes the R group.



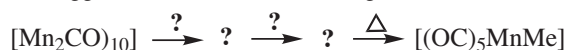
Problems

- Predict the product(s) of the following reactions.



- How would you prepare MeTiCl_3 , Me_2TiCl_2 and TiMe_4 from TiCl_4 .

- Suggest a route to the following reaction.



- Calculate the valence electron count of $[\text{Ti}(\text{CH}_2\text{SiMe}_3)_4]$ and $[\text{Ti}\{\text{CH}(\text{SiMe}_3)_2\}_3]$. Comment on the stability of them.