Module 2: Organometallic chemistry of s- and p-block elements
Lecture 3: Organometallic compounds of alkaline earth metals (beryllium and magnesium)

Objectives
In this lecture you will learn the following

- Organometallic compounds of beryllium and magnesium.
- Structural features of alkyl lithium and beryllium sandwich compounds.

Organometallic compounds of alkaline earth metals

Beryllium

In vapor phase, $\text{Me}_2\text{Be}$ is monomeric with a linear $\text{C—Be—C}$ (Be-C = 170 pm).
The solid state structure is polymeric and resembles that of $\text{BeCl}_2$.

The X-ray diffraction at 128 K suggested $([\eta^1-\text{Cp})(\eta^5-\text{Cp})\text{Be}]$.
However, $^1\text{H}$ NMR spectrum shows that all protons environments are equivalent even at 163 K.
Also, solid state structure shows the Be atom is disordered over two equivalent sites and NMR data can
be interpreted in terms of fluxional process in which the Be atom moves between these two sites.
However, $\text{Cp}^*\text{Be}$ possesses a sandwich structure with both the rings are coplanar.

![Image of Beryllium compound](image)

$$\text{HgMe}_2 + \text{Be} \rightarrow \text{Me}_2\text{Be} + \text{Hg} \text{ (at 383 K)}$$

$$2\text{PhLi} + \text{BeCl}_2 \rightarrow \text{Ph}_2\text{Be} + 2\text{LiCl} \text{ (in diethyl ether)}$$
In vapor phase, $\text{Me}_2\text{Be}$ is monomeric with a linear $\text{C—Be—C}$ (Be-C = 170 pm).
The solid state structure is polymeric and resembles that of $\text{BeCl}_2$.

$$2\text{NaCp} + \text{BeCl}_2 \rightarrow \text{Cp}_2\text{Be} + 2\text{NaCl}$$

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Also, solid state structure shows the Be atom is disordered over two equivalent sites and NMR data can
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![Image of Beryllium compound](image)

Magnesium

Alkyl and aryl magnesium halides (Grignard reagents, RMgX) are extremely well-known on account of their uses in synthetic chemistry.

$$\text{Mg} + \text{RX} \rightarrow \text{RMgX} \text{ (in diethyl ether)}$$
Transmetallation is useful means of preparing pure Grignard reagents

$$\text{Mg} + \text{R}\text{HgBr} \rightarrow \text{Hg} + \text{RMgBr}$$
$$\text{Mg} + \text{R}_2\text{Hg} \rightarrow \text{Hg} + \text{R}_2\text{Mg}$$

Two-coordination at Mg in $\text{R}_2\text{Mg}$ is observed only when the R groups are sufficiently bulky, e.g. $\text{Mg}\{\text{C(SiMe}_3\}_3\}_2$.
RMgX are generally solvated and Mg centre is typically tetrahedral.
e.g. $\text{EtMgBr}.2\text{Et}_2\text{O}; \text{PhMgBr}.2\text{Et}_2\text{O}$.

$\text{Cp}_2\text{Mg}$ has a staggered sandwich structure.

Solutions of Grignard reagent may contain several species, e.g. RMgX, $\text{R}_2\text{Mg}$, $\text{MgX}_2$, $\text{RMg(\mu-X)}_2\text{MgR}$, which are further complicated by solvation. The position of equilibrium between these species is markedly dependent on concentration, temperature and solvent; strongly donating solvents favour monomeric species in which they coordinate to the metal centre.
Treatment with dioxane results in the precipitation of \( \text{MgCl}_2(\text{dioxane}) \) leaving behind pure \( \text{R}_2\text{Mg} \) in the solution.

**Problems:**

1. The compound \((\text{Me}_3\text{Si})_2\text{C} (\text{MgBr})_2.n\text{THF}\) is monomeric. Suggest a value of ‘\( n \)’ and propose a structure for this Grignard reagent.

   **Solution:**

   The coordination number of Mg is likely to be 4; and the shape and the geometry would be tetrahedral. THF is a monodentate ligand, and O-donor. The part of the formula shows that the Mg is two coordinated and and each Mg requires two THF molecules. The structure is shown (\( n = 4 \)).

2. If a typical Grignard reagent exists as an equilibrium mixture of dialkylmagnesium and magnesium halide, give a method of isolating pure dialkyl magnesium. Your answer should be in the form of balanced chemical equations only.

   **Solution:**

   \[
   2\text{RMgX} \rightleftharpoons \text{R}_2\text{Mg} + \text{MgX}_2
   \]

   Treatment of equilibrium mixture with dioxane results in the precipitation of, say, \( \text{MgCl}_2(\text{dioxane}) \) (if, \( X = \text{Cl} \)), leaving behind pure \( \text{R}_2\text{Mg} \) in the solution.

   \[
   \text{R}_2\text{Mg} + \text{MgX}_2 \rightarrow \text{Adduct precipitates leaving behind R}_2\text{Mg in solution}
   \]