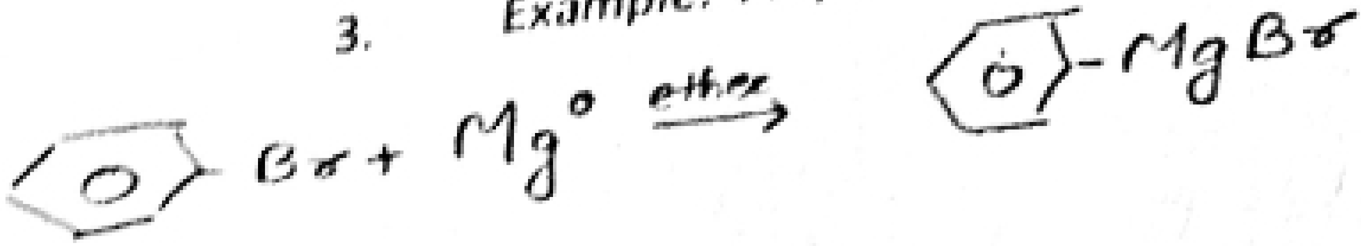
0 - Elemental state.

3. Example: Preparation of phenylmagnesium bromide

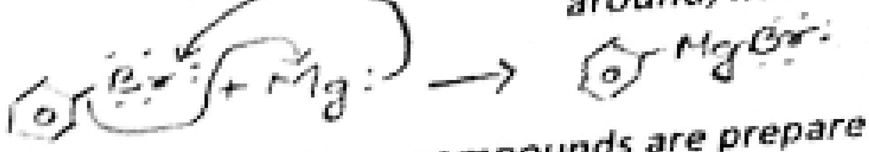


a. In this reaction, we oxidize Mg from standard state (Mg^0) to Mg^{2+}

b. Grignard reagents form coordination complexes that are solvated by ether – this adds to the stability of the Grignard reagent.

4. There's some argument as to the mechanism by which this reaction occurs, but there is a consensus that radicals are involved at some point.

a. The way I was taught was that it was a pair of electrons moving around, not radicals.



C. Organolithium compounds are prepared by treating an alkyl, aryl, or alkenyl halide with two equivalents of lithium metal

1. Example: synthesis of butyllithium

2. Organolithium compounds are very reactive as nucleophiles in carbonyl addition reactions – even at low temperatures

a. They also react very rapidly with atmospheric oxygen and moisture and have to be used under an inert atmosphere of N_2 or Ar

D. The carbon-metal bond is described as being polar covalent, where the C will have a partially -ve charge. Metal partially +ve charge.

1. In this aspect, Grignard and organolithium compounds behave as **carbanions** (ions in which carbon has an unshared pair of electrons and bears a negative charge)

Akshay Altekar.

Chapter 15 – An Introduction to Organometallic Compounds

Lecture Outline

Introduction

Metals IA, IIA, IIIA, Transition M.

A. **Organometallic compounds** are comp. that contain a carbon metal bond.

- Huge area of research.
- Mg, Li, Cu.
- Ch-24

I. Organomagnesium and Organolithium Compounds

A. Organomagnesium compounds are the most readily available, easily prepared, and easily handled compounds. (normal air)

- Grinyard reagents (Victor Grignard) (Not much heat is needed

1. Nobel prize (1912)

B. They are typically prepared by... the slow addn of an alkyl, aryl or alkenyl (vinylic) halide to a stirred suspension of a slight Excess of Mg Metal in ether solvent

diethyL ↙ ↘ THF

1. Bromides and ~~chlorides~~ Iodide. work well for these reactions

Br is best.

< reactive halide a. diethyL ether.

Less reactive halide ⇒ THF

b.

2. There's generally an "induction period" in which you're waiting for the reaction to start.

a. You know it starts when you see the magnesium oxidize (there will be a greyish tint or film to the magnesium).

b. Once the reaction starts, it's exothermic

c. Then add the rest of organohalide while gently refluxing.

Table 16.1 Percent Ionic Character of Some C—M Bonds

$\delta-$ $\delta+$ C—M Bond	Difference in Electronegativity	Percent Ionic Character*
C—Li	2.5 − 1.0 = 1.5	60
C—Mg	2.5 − 1.2 = 1.3	52
C—Al	2.5 − 1.5 = 1.0	40
C—Zn	2.5 − 1.6 = 0.9	36
C—Sn	2.5 − 1.8 = 0.7	28
C—Cu	2.5 − 1.9 = 0.6	24
C—Hg	2.5 − 1.9 = 0.6	24

*Percent ionic character = $\frac{E_C - E_M}{E_C} \times 100$

% ↑ = C becomes a great nucleophile.

ionic - 1.7
NP - cov = 0 - 0.4
P - cov = 0.5 - 1.7

3. Because the carbon takes on the appearance of a carbanion, that means that these compounds will react with the elctrophilic carbon atom of carbonyl groups – this means that we can form new carbon-carbon bonds!

E. Both Grignard and organolithium compounds are very strong bases and react readily with any acid stronger than the alkane that they were originally derived from.

1. Example: reaction of ethylmagnesium bromide with water

(lies to product formation.

$$CH_3\text{-}CH_2\text{-}MgBr + H\text{-}OH \rightarrow CH_3\text{-}CH_2\text{-}H + Mg^{2+} + OH^- + Br^-$$

pKa = 15.7   pKa = 51

$\boxed{K_{eq} = 10^{35}}$ $pK_{eq} = -35$

F. The following are several classes of proton donors that can react readily with Grignard and organolithium compounds

(learn the value & order)

	R_2NH	$RC\equiv CH$	ROH	HOH	ArOH	RSH	RCOOH
	less reactive						v. reactive
pKa	38-40	~25	16-18	15.7	9-10	8-9	4-5