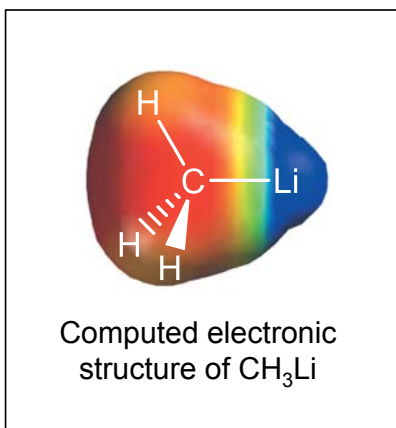


# Organometallic Reagents are Synthetically Equivalent to Carbanions



R—Li                    alkyllithium  
                              (organolithium)

R—Mg—Br                Grignard reagent  
                              (organomagnesium halide)

R—C≡C—Na             alkynylsodium

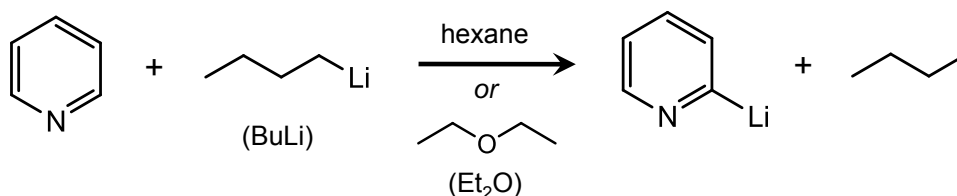
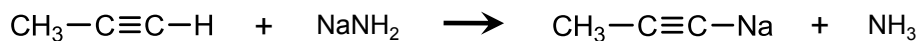
*All of these react as "R<sup>⊖</sup>"*

## Generating Organometallic Reagents

### 1. Deprotonation.

Not common. *Works for alkynyl, some sp<sup>2</sup> anions, but not for sp<sup>3</sup> (because alkanes are not acidic enough).*

*Examples:*

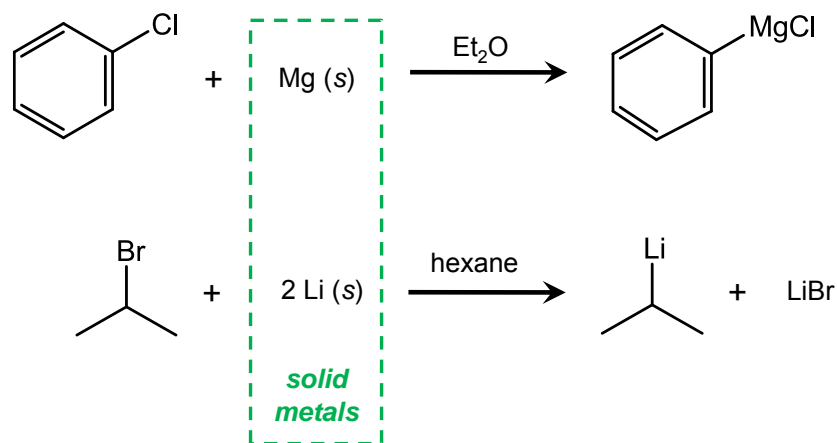


# Generating Organometallic Reagents

## 2. Metalation of an alkyl halide.

Common for Grignard reagents,  $sp^3$  alkyllithiums.

Examples:

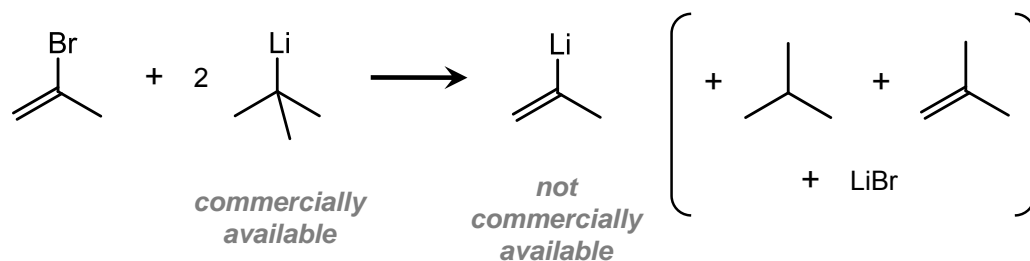


# Generating Organometallic Reagents

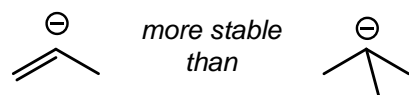
## 3. Lithium-halogen exchange.

Common for  $sp^2$  alkyllithiums. Not useful for  $sp^3$  alkyllithiums.

Example:

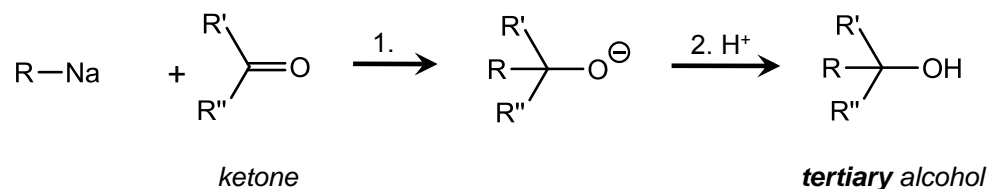
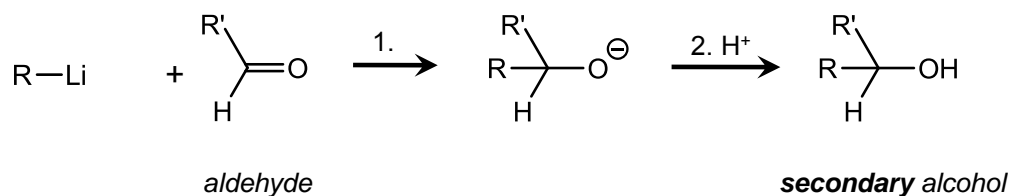
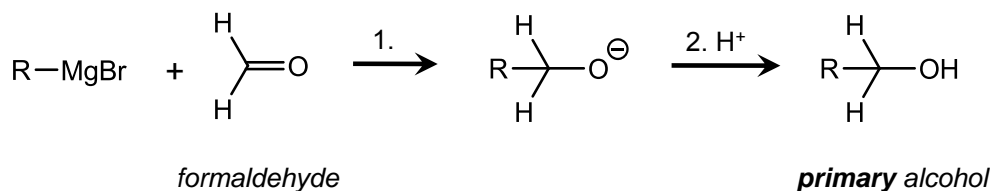


Reaction is driven by formation of more stable carbanion:

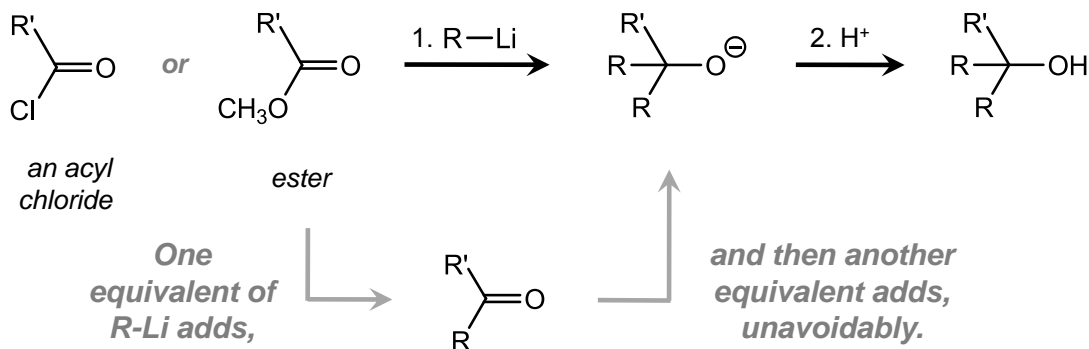


# Reaction of Alkylmetals With C=O Bonds

For any alkylmetal reagent,

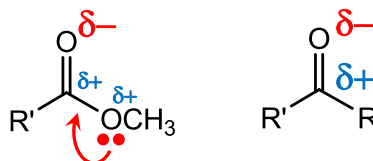


## Double Addition of Alkylmetals to Esters and Acyl Halides



*Why?*

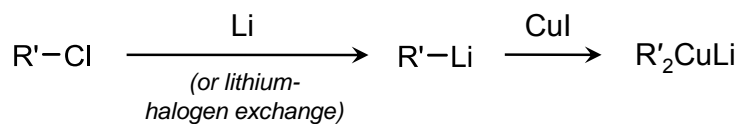
Ketones and aldehydes are more electrophilic than esters and acyl halides.



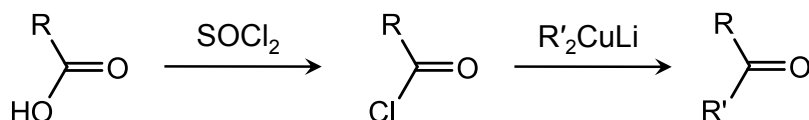
**Lone pair donation by oxygen reduces partial positive charge on C=O carbon.**

# Ketones from Lithium Dialkylcuprates

Synthesis of dialkylcuprates:

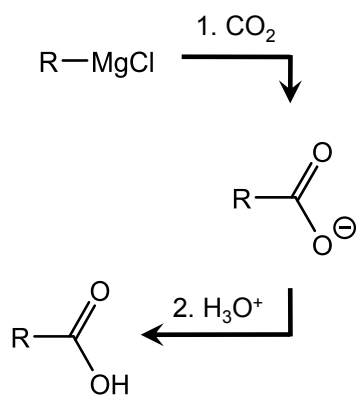


Addition of dialkylcuprates to acyl chlorides:

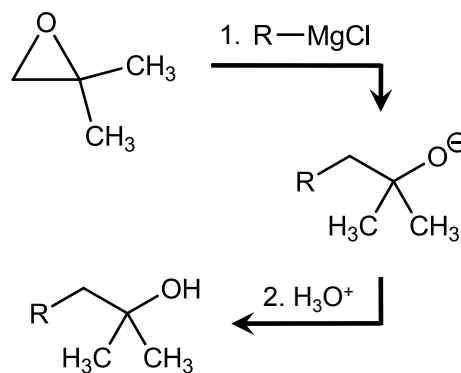


Unlike other alkylmetals, cuprate adds only once.

## Carboxylic Acids from Grignards and CO<sub>2</sub>



## Alkylmetals Open Epoxides



- Another way of making new C-C bonds with alkylmetals.