Organometallic Compounds

Organolithium Compounds

\[
\begin{align*}
\text{Br} & \quad \text{Li (2 equivalents)} \\
\text{Li} & \quad \text{Br} \quad + \quad \text{LiBr}
\end{align*}
\]

Organomagnesium Compounds (Grignard Reagents)

\[
\begin{align*}
\text{Br} & \quad \text{Mg} \quad \text{diethyl ether} \\
\text{MgBr} & \quad \text{Br}
\end{align*}
\]

Lithium dialkyl cuprates (Gilman Reagents)

\[
\begin{align*}
\text{Li} & \quad \text{CuI} \quad \text{diethyl ether} \\
\text{Cu} & \quad \text{Li} \quad + \quad \text{LiI}
\end{align*}
\]

Lithium dialkyl cyano cuprates

\[
\begin{align*}
\text{Li} & \quad \text{CuCN} \quad \text{diethyl ether} \\
\text{CuCN} & \quad \text{Li} \quad -2 \quad 2 \text{Li}^2+
\end{align*}
\]

These organometallic reagents are used to make carbon-carbon bonds, that is, lengthening hydrocarbon chains.

Organolithium and Grignard reagents are strong bases and strong nucleophiles. Therefore the reacting reagent with organometallics should not have acidic groups, i.e., -OH, -NH₂, etc.

Example:

\[
\begin{align*}
\text{HO} & \quad \text{Cl} \quad \text{MgBr} \quad \text{diethyl ether} \\
\text{BrMg}^+ & \quad \text{Cl} \quad + \quad \text{C}_3\text{H}_8(\text{g})
\end{align*}
\]
For these two reagents chains lengthening by $S_n2$ reaction mechanisms are the choice (see below). A second step, acid workup, which is a solution of a diluted acidic compound, is usually required to neutralize any un-protonated chemical species generated in the synthesis.

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This is especially important when the reagent being added is an epoxide*. Notice that in the example shown below an alkoxide was generated when a Grignard reagent was used. To generate the respective alcohol the alkoxide is “washed” with a solution of dilute acid.

Gilman reagents, on the other hand, are weaker bases. They can be used with $2^\circ$ alkyl halides.

* See Reaction of Epoxides with Organometallics.