

Before coordination polymerization was discovered by Ziegler and applied to propene by Natta, there was no polypropylene industry. Now, more than  $10^{10}$  pounds of it are prepared each year in the United States. Ziegler and Natta shared the 1963 Nobel Prize in chemistry: Ziegler for discovering novel catalytic systems for alkene polymerization and Natta for stereoregular polymerization.

## 14.16 SUMMARY

Section 14.1 Organometallic compounds contain a carbon–metal bond. They are named as alkyl (or aryl) derivatives of metals.

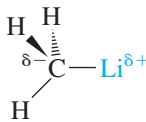


Butyllithium



Phenylmagnesium bromide

Section 14.2 Carbon is more electronegative than metals and carbon–metal bonds are polarized so that carbon bears a partial to complete negative charge and the metal bears a partial to complete positive charge.



Methyl lithium has a polar covalent carbon–lithium bond.

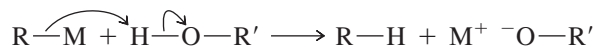


Sodium acetylide has an ionic bond between carbon and sodium.

Section 14.3 See Table 14.5

Section 14.4 See Table 14.5

Section 14.5 Organolithium compounds and Grignard reagents are strong bases and react instantly with compounds that have —OH groups.



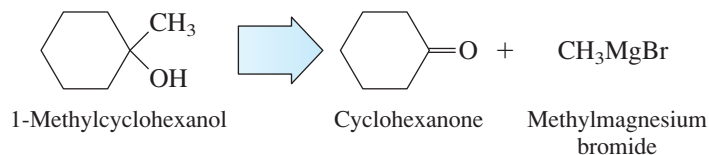
These organometallic compounds cannot therefore be formed or used in solvents such as water and ethanol. The most commonly employed solvents are diethyl ether and tetrahydrofuran.

Section 14.6 See Tables 14.3 and 14.6

Section 14.7 See Table 14.6

Section 14.8 See Table 14.6

Section 14.9 When planning the synthesis of a compound using an organometallic reagent, or indeed any synthesis, the best approach is to reason backward from the product. This method is called **retrosynthetic analysis**. Retrosynthetic analysis of 1-methylcyclohexanol suggests it can be prepared by the reaction of methylmagnesium bromide and cyclohexanone.



**TABLE 14.5** Preparation of Organometallic Reagents Used in Synthesis

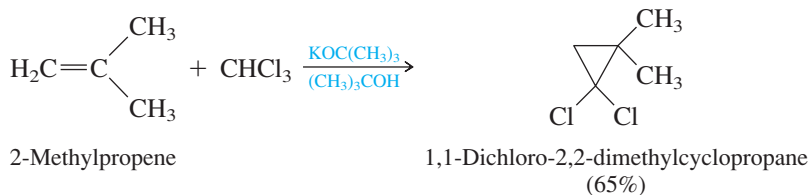
Type of organometallic reagent (section) and comments	General equation for preparation and specific example
<b>Organolithium reagents (Section 14.3)</b> Lithium metal reacts with organic halides to produce organolithium compounds. The organic halide may be alkyl, alkenyl, or aryl. Iodides react most and fluorides least readily; bromides are used most often. Suitable solvents include hexane, diethyl ether, and tetrahydrofuran.	$\text{RX} + 2\text{Li} \longrightarrow \text{RLi} + \text{LiX}$ <p>Alkyl halide      Lithium      Alkyl lithium      Lithium halide</p>
	$\text{CH}_3\text{CH}_2\text{CH}_2\text{Br} \xrightarrow[\text{diethyl ether}]{\text{Li}} \text{CH}_3\text{CH}_2\text{CH}_2\text{Li}$ <p>Propyl bromide      Propyllithium (78%)</p>
<b>Grignard reagents (Section 14.4)</b> Grignard reagents are prepared in a manner similar to that used for organolithium compounds. Diethyl ether and tetrahydrofuran are appropriate solvents.	$\text{RX} + \text{Mg} \longrightarrow \text{RMgX}$ <p>Alkyl halide      Magnesium      Alkylmagnesium halide (Grignard reagent)</p>
	$\text{C}_6\text{H}_5\text{CH}_2\text{Cl} \xrightarrow[\text{diethyl ether}]{\text{Mg}} \text{C}_6\text{H}_5\text{CH}_2\text{MgCl}$ <p>Benzyl chloride      Benzylmagnesium chloride (93%)</p>
<b>Lithium dialkylcuprates (Section 14.11)</b> These reagents contain a negatively charged copper atom and are formed by the reaction of a copper(I) salt with two equivalents of an organolithium reagent.	$2\text{RLi} + \text{CuX} \longrightarrow \text{R}_2\text{CuLi} + \text{LiX}$ <p>Alkyl lithium      Copper(I) halide      Lithium dialkylcuprate      Lithium halide</p>
	$2\text{CH}_3\text{Li} + \text{CuI} \xrightarrow[\text{diethyl ether}]{\text{diethyl ether}} (\text{CH}_3)_2\text{CuLi} + \text{LiI}$ <p>Methyl lithium      Copper(I) iodide      Lithium dimethylcuprate      Lithium iodide</p>
<b>Iodomethylzinc iodide (Section 14.12)</b> This is the Simmons–Smith reagent. It is prepared by the reaction of zinc (usually in the presence of copper) with diiodomethane.	$\text{CH}_2\text{I}_2 + \text{Zn} \xrightarrow[\text{Cu}]{\text{diethyl ether}} \text{ICH}_2\text{ZnI}$ <p>Diiodomethane      Zinc      Iodomethylzinc iodide</p>

Section 14.10 See Table 14.6

Section 14.11 See Tables 14.5 and 14.6

Section 14.12 See Tables 14.5 and 14.6

Section 14.13 Carbenes are species that contain a *divalent carbon*; that is, a carbon with only two bonds. One of the characteristic reactions of carbenes is with alkenes to give cyclopropane derivatives.



Certain organometallic compounds resemble carbenes in their reactions and are referred to as **carbenoids**. Iodomethylzinc iodide (Section 14.12) is an example.



**TABLE 14.6** Carbon–Carbon Bond-Forming Reactions of Organometallic Reagents (*Continued*)

Reaction (section) and comments	General equation and specific example
<b>Synthesis of acetylenic alcohols (Section 14.8)</b> Sodium acetylide and acetylenic Grignard reagents react with aldehydes and ketones to give alcohols of the type $\text{C}\equiv\text{C}-\underset{\text{OH}}{\text{C}}$	$\text{NaC}\equiv\text{CH} + \begin{array}{c} \text{O} \\ \parallel \\ \text{RCR}' \end{array} \xrightarrow[2. \text{H}_3\text{O}^+]{1. \text{NH}_3, -33^\circ\text{C}} \begin{array}{c} \text{OH} \\   \\ \text{HC}\equiv\text{CCR}' \\   \\ \text{R} \end{array}$ <p>Sodium acetylide      Aldehyde or ketone      Alcohol</p>
	$\text{NaC}\equiv\text{CH} + \begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{CCH}_2\text{CH}_3 \end{array} \xrightarrow[2. \text{H}_3\text{O}^+]{1. \text{NH}_3, -33^\circ\text{C}} \begin{array}{c} \text{OH} \\   \\ \text{HC}\equiv\text{CCCH}_2\text{CH}_3 \\   \\ \text{CH}_3 \end{array}$ <p>Sodium acetylide      2-Butanone      3-Methyl-1-pentyn-3-ol (72%)</p>
<b>Preparation of alkanes using lithium dialkylcuprates (Section 14.11)</b> Two alkyl groups may be coupled together to form an alkane by the reaction of an alkyl halide with a lithium dialkylcuprate. Both alkyl groups must be primary (or methyl). Aryl and vinyl halides may be used in place of alkyl halides.	$\text{R}_2\text{CuLi} + \text{R}'\text{CH}_2\text{X} \longrightarrow \text{RCH}_2\text{R}'$ <p>Lithium dialkylcuprate      Primary alkyl halide      Alkane</p>
	$(\text{CH}_3)_2\text{CuLi} + \text{C}_6\text{H}_5\text{CH}_2\text{Cl} \xrightarrow{\text{diethyl ether}} \text{C}_6\text{H}_5\text{CH}_2\text{CH}_3$ <p>Lithium dimethylcuprate      Benzyl chloride      Ethylbenzene (80%)</p>
<b>The Simmons–Smith reaction (Section 14.12)</b> Methylene transfer from iodomethylzinc iodide converts alkenes to cyclopropanes. The reaction is a stereospecific syn addition of a CH <sub>2</sub> group to the double bond.	$\text{R}_2\text{C}=\text{CR}_2 + \text{ICH}_2\text{ZnI} \xrightarrow{\text{diethyl ether}} \begin{array}{c} \text{R} \quad \text{R} \\ \diagdown \quad \diagup \\ \text{C} \\ \diagup \quad \diagdown \\ \text{R} \quad \text{R} \end{array} + \text{ZnI}_2$ <p>Alkene      Iodomethylzinc iodide      Cyclopropane derivative      Zinc iodide</p>
	$\text{Cyclopentene} \xrightarrow[\text{diethyl ether}]{\text{CH}_2\text{I}_2, \text{Zn}(\text{Cu})} \text{Bicyclo}[3.1.0]\text{hexane}$ <p>Cyclopentene      Bicyclo[3.1.0]hexane (53%)</p>

Section 14.15 Coordination polymerization of ethylene and propene has the biggest economic impact of any organic chemical process. Ziegler–Natta polymerization is carried out using catalysts derived from transition metals such as titanium and zirconium.  $\pi$ -Bonded and  $\sigma$ -bonded organometallic compounds are intermediates in coordination polymerization.

## PROBLEMS

14.14 Write structural formulas for each of the following compounds. Specify which compounds qualify as organometallic compounds.

- |                                   |                            |
|-----------------------------------|----------------------------|
| (a) Cyclopentyllithium            | (d) Lithium divinylcuprate |
| (b) Ethoxymagnesium chloride      | (e) Sodium carbonate       |
| (c) 2-Phenylethylmagnesium iodide | (f) Benzylpotassium        |