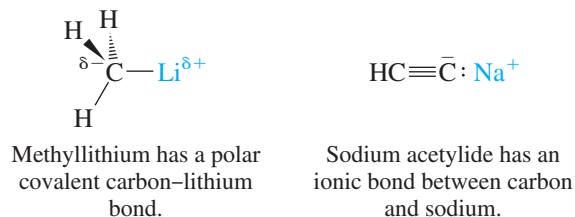


14.18 SUMMARY

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



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.



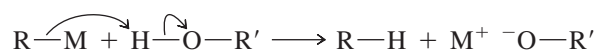
Section 14.3 See Table 14.4

Section 14.4 See Table 14.4

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

TABLE 14.4 Preparation of Organometallic Reagents Used in Synthesis

| Type of organometallic reagent (section) and comments | General equation for preparation and specific example |
|---|---|
| Organolithium reagents (Section 14.3) 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> |
| Grignard reagents (Section 14.4) 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> |
| Lithium dialkylcuprates (Section 14.11) 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> |
| Iodomethylzinc iodide (Section 14.12) 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> |



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 14.2 and 14.5

Section 14.7 See Table 14.5

Section 14.8 See Table 14.5

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**.

TABLE 14.5 Carbon–Carbon Bond-Forming Reactions of Organometallic Reagents

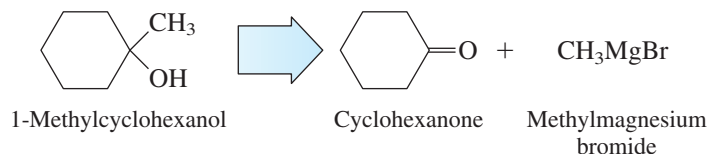
| Reaction (section) and comments | General equation and specific example |
|---|--|
| <p>Alcohol synthesis via the reaction of Grignard reagents with carbonyl compounds (Section 14.6) This is one of the most useful reactions in synthetic organic chemistry. Grignard reagents react with formaldehyde to yield primary alcohols, with aldehydes to give secondary alcohols, and with ketones to form tertiary alcohols.</p> | $\text{RMgX} + \text{R}'\overset{\text{O}}{\parallel}\text{CR}'' \xrightarrow[2. \text{H}_3\text{O}^+]{1. \text{diethyl ether}} \begin{array}{c} \text{R}' \\ \\ \text{RCOH} \\ \\ \text{R}'' \end{array}$ <p>Grignard reagent Aldehyde or ketone Alcohol</p> $\text{CH}_3\text{MgI} + \text{CH}_3\text{CH}_2\text{CH}_2\overset{\text{O}}{\parallel}\text{CH} \xrightarrow[2. \text{H}_3\text{O}^+]{1. \text{diethyl ether}} \text{CH}_3\text{CH}_2\text{CH}_2\underset{\text{OH}}{\text{CH}}\text{CH}_3$ <p>Methylmagnesium iodide Butanal 2-Pentanol (82%)</p> |
| <p>Reaction of Grignard reagents with esters (Section 14.10) Tertiary alcohols in which two of the substituents on the hydroxyl carbon are the same may be prepared by the reaction of an ester with two equivalents of a Grignard reagent.</p> | $2\text{RMgX} + \text{R}'\overset{\text{O}}{\parallel}\text{COR}'' \xrightarrow[2. \text{H}_3\text{O}^+]{1. \text{diethyl ether}} \begin{array}{c} \text{R}' \\ \\ \text{RCOH} \\ \\ \text{R} \end{array}$ <p>Grignard reagent Ester Tertiary alcohol</p> $2\text{C}_6\text{H}_5\text{MgBr} + \text{C}_6\text{H}_5\overset{\text{O}}{\parallel}\text{COCH}_2\text{CH}_3 \xrightarrow[2. \text{H}_3\text{O}^+]{1. \text{diethyl ether}} (\text{C}_6\text{H}_5)_3\text{COH}$ <p>Phenylmagnesium bromide Ethyl benzoate Triphenylmethanol (89–93%)</p> |
| <p>Synthesis of alcohols using organolithium reagents (Section 14.7) Organolithium reagents react with aldehydes, ketones, and esters in a manner similar to that of Grignard reagents to produce alcohols.</p> | $\text{RLi} + \text{R}'\overset{\text{O}}{\parallel}\text{CR}'' \xrightarrow[2. \text{H}_3\text{O}^+]{1. \text{diethyl ether}} \begin{array}{c} \text{R}' \\ \\ \text{RCOH} \\ \\ \text{R}'' \end{array}$ <p>Alkyl lithium Aldehyde or ketone Alcohol</p> $\text{Cyclopropyl-Li} + \text{CH}_3\overset{\text{O}}{\parallel}\text{CC}(\text{CH}_3)_2 \xrightarrow[2. \text{H}_3\text{O}^+]{1. \text{diethyl ether}} \begin{array}{c} \text{OH} \\ \\ \text{Cyclopropyl-CC}(\text{CH}_3)_2 \\ \\ \text{CH}_3 \end{array}$ <p>Cyclopropyl lithium 3,3-Dimethyl-2-butanone 2-Cyclopropyl-3,3-dimethyl-2-butanol (71%)</p> |

—Continued

TABLE 14.5 Carbon–Carbon Bond-Forming Reactions of Organometallic Reagents (*Continued*)

| Reaction (section) and comments | General equation and specific example |
|--|--|
| <p>Synthesis of acetylenic alcohols (Section 14.8) Sodium acetylide and acetylenic Grignard reagents react with aldehydes and ketones to give alcohols of the type</p> $\text{C}\equiv\text{C}-\text{C}-\text{OH}$ | $\text{NaC}\equiv\text{CH} + \begin{array}{c} \text{O} \\ \parallel \\ \text{RCR}' \end{array} \xrightarrow[2. \text{H}_3\text{O}^+]{1. \text{NH}_3, -33^\circ\text{C}} \begin{array}{c} \text{OH} \\ \\ \text{HC}\equiv\text{CCR}' \\ \\ \text{R} \end{array}$ <p>Sodium acetylide Aldehyde or ketone Acetylenic 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> |
| <p>Preparation of alkanes using lithium dialkylcuprates (Section 14.11) 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.</p> | $\text{R}_2\text{CuLi} + \text{R}'\text{CH}_2\text{X} \longrightarrow \text{RCH}_2\text{R}'$ <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> |
| <p>The Simmons–Smith reaction (Section 14.12) Methylene transfer from iodomethylzinc iodide converts alkenes to cyclopropanes. The reaction is a stereospecific syn addition of a CH_2 group to the double bond.</p> | $\text{R}_2\text{C}=\text{CR}_2 + \text{ICH}_2\text{ZnI} \xrightarrow{\text{diethyl ether}} \begin{array}{c} \text{R} \quad \text{R} \\ \diagdown \quad / \\ \text{C} \\ / \quad \diagdown \\ \text{R} \quad \text{R} \end{array} + \text{ZnI}_2$ <p>Alkene Iodomethylzinc iodide Cyclopropane derivative Zinc iodide</p> |
| | $\text{Cyclopentene} \xrightarrow[\text{diethyl ether}]{\text{CH}_2\text{I}_2, \text{Zn}(\text{Cu})} \text{Bicyclo[3.1.0]hexane (53\%)}$ |

Retrosynthetic analysis of 1-methylcyclohexanol suggests it can be prepared by the reaction of methylmagnesium bromide and cyclohexanone.

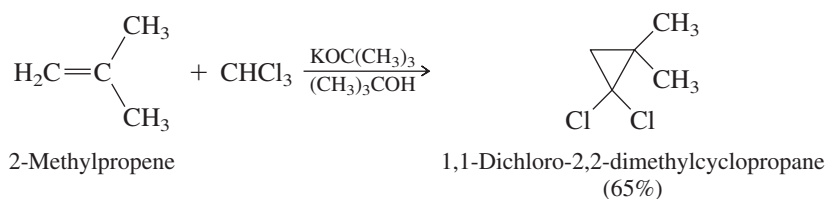


Section 14.10 See Table 14.5

Section 14.11 See Tables 14.4 and 14.5

Section 14.12 See Tables 14.4 and 14.5

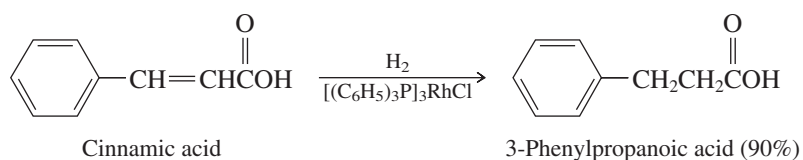
Section 14.13 Carbenes are species that contain a *divalent carbon*; that is, a carbon with only two bonds. One of the characteristic reactions of carbenes is with alkenes to give cyclopropane derivatives.



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

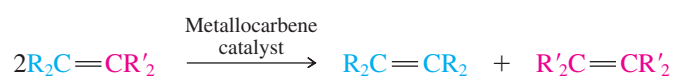
Section 14.14 Transition-metal complexes that contain one or more organic ligands offer a rich variety of structural types and reactivity. Organic ligands can be bonded to a metal by a σ bond or through its π system. **Metallocenes** are transition-metal complexes in which one or more of the ligands is a cyclopentadienyl ring. Ferrocene was the first metallocene synthesized; its electrostatic potential map opens this chapter.

Section 14.15 Organometallic compounds based on transition metals, especially rhodium and ruthenium, can catalyze the hydrogenation of alkenes under homogeneous conditions.



When a single enantiomer of a chiral catalyst is used, hydrogenations can be carried out with high enantioselectivity.

Section 14.16 The doubly bonded carbons of two alkenes exchange partners on treatment with transition-metal carbene complexes, especially those derived from ruthenium and tungsten.



Among other applications olefin metathesis is useful in the synthesis of cyclic alkenes, the industrial preparation of propene, and in polymerization.

Section 14.17 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. π -Bonded and σ -bonded organometallic compounds are intermediates in coordination polymerization.

PROBLEMS

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

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

14.18 *Dibal* is an informal name given to the organometallic compound $[(\text{CH}_3)_2\text{CHCH}_2]_2\text{AlH}$, used as a reducing agent in certain reactions. Can you figure out the systematic name from which “dibal” is derived?

14.19 Suggest appropriate methods for preparing each of the following compounds from the starting material of your choice.

- | | |
|---|--|
| (a) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{MgI}$ | (c) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Li}$ |
| (b) $\text{CH}_3\text{CH}_2\text{C}\equiv\text{CMgI}$ | (d) $(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)_2\text{CuLi}$ |

14.20 Which compound in each of the following pairs would you expect to have the more polar carbon–metal bond?

- | | |
|--|--|
| (a) $\text{CH}_3\text{CH}_2\text{Li}$ or $(\text{CH}_3\text{CH}_2)_3\text{Al}$ | (c) $\text{CH}_3\text{CH}_2\text{MgBr}$ or $\text{HC}\equiv\text{CMgBr}$ |
| (b) $(\text{CH}_3)_2\text{Zn}$ or $(\text{CH}_3)_2\text{Mg}$ | |