14.11
Alkane Synthesis Using Organocopper Reagents

Lithium Dialkylcuprates

Lithium dialkylcuprates are useful synthetic reagents.

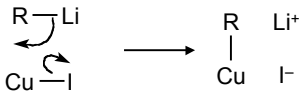
They are prepared from alkyllithiums and a copper(I) halide.

$$2RLi + CuX \longrightarrow R_2CuLi + LiX$$

[customary solvents are diethyl ether and tetrahydrofuran (THF)]

How?

the alkyllithium first reacts with the copper(I) halide



then a second molecule of the alkyllithium reacts with the alkylcopper species formed in the first step

Lithium diorganocuprates are used to form C—C bonds

$$R_2CuLi + R'X \longrightarrow R—R' + RCu + LiX$$

$$Ar_2CuLi + R'X \longrightarrow Ar—R' + ArCu + LiX$$

Example: Lithium dimethylcuprate

$(CH_3)_2CuLi + CH_3(CH_2)_8CH_2I$

↓ diethyl ether

$CH_3(CH_2)_8CH_2CH_3$

(90%)

primary alkyl halides work best (secondary and tertiary alkyl halides undergo elimination)

Example: Lithium diphenylcuprate

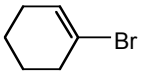
$(C_6H_5)_2CuLi + CH_3(CH_2)_6CH_2I$

↓ diethyl ether

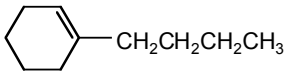
$CH_3(CH_2)_6CH_2C_6H_5$

(99%)

Vinylic halides can be used

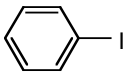
$(CH_3CH_2CH_2CH_2)_2CuLi$ + 

↓ diethyl ether

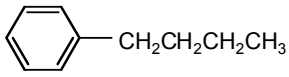


(80%)

Aryl halides can be used

$(CH_3CH_2CH_2CH_2)_2CuLi$ + 

↓ diethyl ether

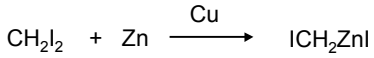


(75%)

14.12
An Organozinc Reagent
for
Cyclopropane Synthesis

Iodomethylzinc iodide

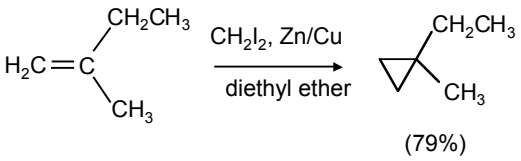
formed by reaction of diiodomethane with zinc that has been coated with copper (called zinc-copper couple)



reacts with alkenes to form cyclopropanes

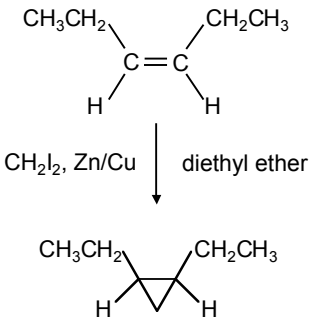
reaction with alkenes is called the Simmons-Smith reaction

Example

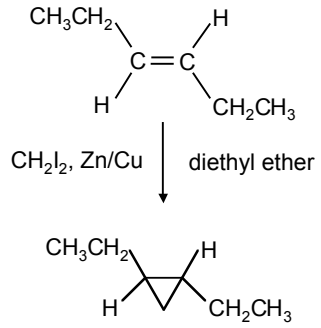


(79%)

Stereospecific syn-addition



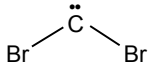
Stereospecific syn-addition



14.13
Carbenes and Carbenoids

Carbene

name to give to species that contains a divalent carbon (carbon with two bonds and six electrons)

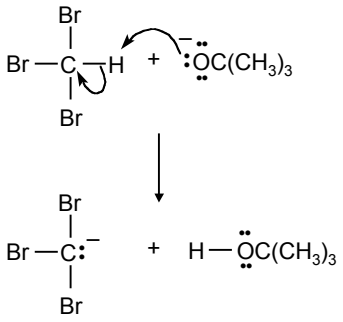


dibromocarbene

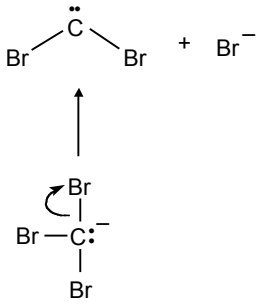
Carbenes are very reactive; normally cannot be isolated and stored.

Are intermediates in certain reactions.

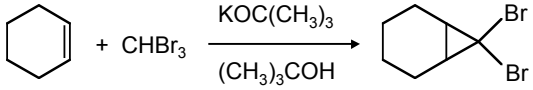
Generation of Dibromocarbene



Generation of Dibromocarbene



Carbenes react with alkenes to give cyclopropanes



(75%)

CBr_2 is an intermediate
stereospecific syn addition

14.14
Transition-Metal Organic Compounds

Introduction

Many organometallic compounds derived from transition metals have useful properties. Typical transition metals are iron, nickel, chromium, platinum, and rhodium.

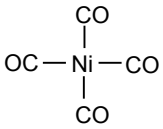
18-Electron Rule

The number of ligands attached to a metal will be such that the sum of the electrons brought by the ligands plus the valence electrons of the metal equals 18.

When the electron-count is less than 18, metal is said to be *coordinatively unsaturated* and can take on additional ligands.

18-Electron rule is to transition metals as the octet rule is to second-row elements.

Example



Nickel carbonyl

Ni has the electron configuration [Ar]4$s^2$3d^8

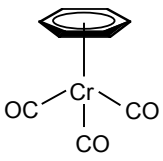
Ni has 10 valence electrons

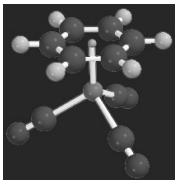
Each CO uses 2 electrons to bond to Ni

4 CO contribute 8 valence electrons

10 + 8 = 18

(Benzene)tricarbonylchromium





Cr has the electron configuration [Ar]4$s^2$3d^4

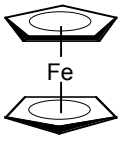
Cr has 6 valence electrons

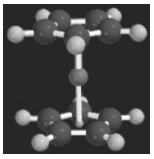
Each CO uses 2 electrons to bond to Cr

3 CO contribute 6 valence electrons

benzene uses its 6 π electrons to bind to Cr.

Ferrocene





Fe^{2+} has the electron configuration [Ar]3d^6

Each cyclopentadienide anion contributes 6 π electrons

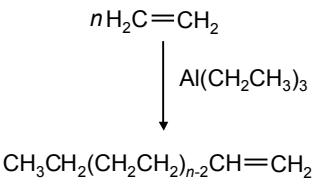
Total 6 + 6 + 6 = 18

Organometallic compounds with cyclopentadienide ligands are called *metallocenes.*

14.15
Ziegler-Natta Catalysis of Alkene Polymerization

The catalysts used in coordination polymerization are transition-metal organic compounds.

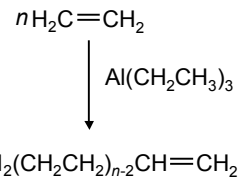
Ethylene oligomerization



Triethylaluminum catalyzes the formation of alkenes from ethylene.

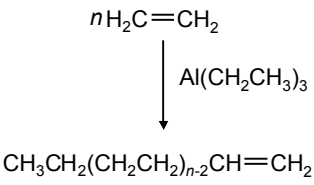
These compounds are called *ethylene oligomers* and the process is called *oligomerization*.

Karl Ziegler (1950)



Ziegler found that oligomerization was affected differently by different transition metals. Some gave oligomers with 6-18 carbons, others gave polyethylene.

Karl Ziegler (1950)



The ethylene oligomers formed under Ziegler's conditions are called *linear □-olefins* and have become important industrial chemicals.

Karl Ziegler (1950)

$$n\,H_2C{=}CH_2 \xrightarrow{Al(CH_2CH_3)_3} CH_3CH_2(CH_2CH_2)_{n\text{-}2}CH{=}CH_2$$

The polyethylene formed under Ziegler's conditions is called *high-density polyethylene* and has, in many ways, more desirable properties than the polyethylene formed by free-radical polymerization.

Giulio Natta

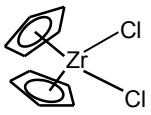
$$n\,H_2C{=}CHCH_3 \xrightarrow{Al(CH_2CH_3)_3} \text{polypropylene}$$

Natta found that polymerization of propene under Ziegler's conditions gave mainly isotactic polypropylene. This discovery made it possible to produce polypropylene having useful properties.

Ziegler-Natta Catalysts

Early Ziegler-Natta catalyst were a combination of $TiCl_4$ and $(CH_3CH_2)_2AlCl$, or $TiCl_3$ and $(CH_3CH_2)_3Al$.

Currently used Ziegler-Natta catalyst combinations include a metallocene such as bis(cyclopentadienyl)zirconium dichloride.



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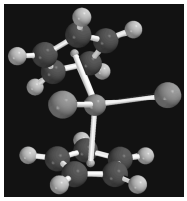
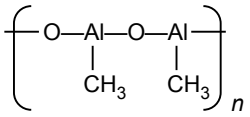
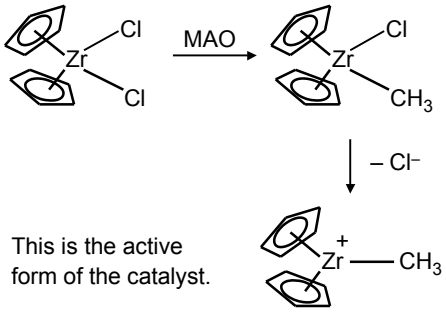


Ziegler-Natta Catalysts

The metallocene is used in combination with a promoter such as methyl alumoxane (MAO)

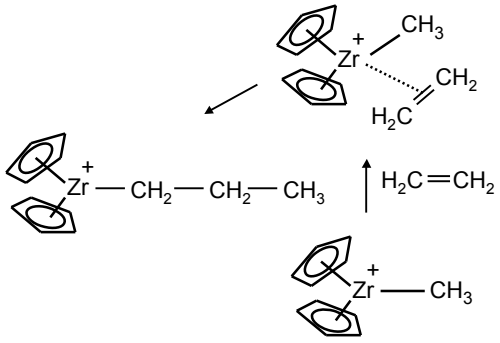


Mechanism of Coordination Polymerization

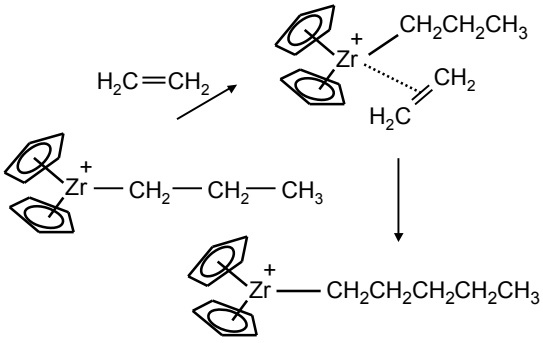


This is the active form of the catalyst.

Mechanism of Coordination Polymerization



Mechanism of Coordination Polymerization



Mechanism of Coordination Polymerization