14.11
Alkane Synthesis Using Organocopper Reagents

Lithium Dialkylcuprates

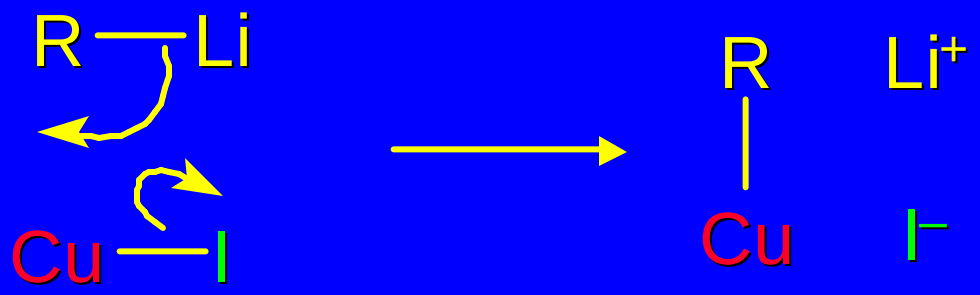
Lithium dialkylcuprates are useful synthetic reagents.

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

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

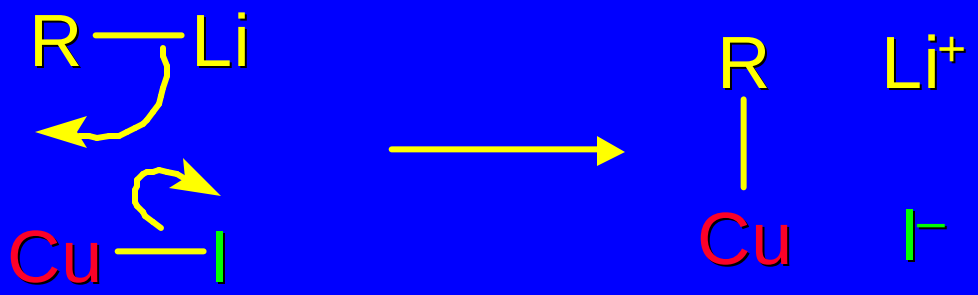
How?

the alkyllithium first reacts with the copper(I) halide

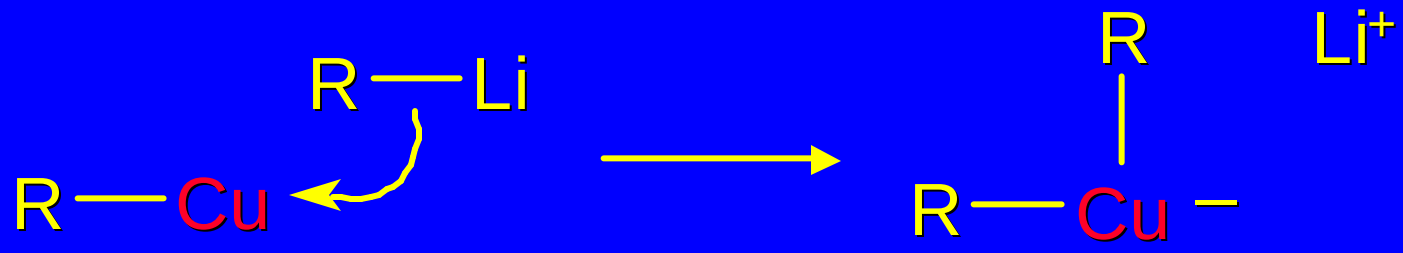


How?

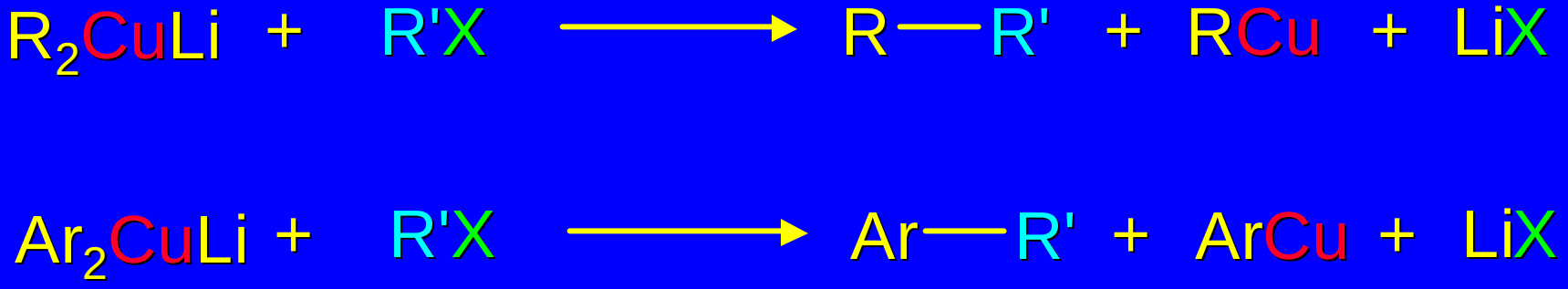
the alkyllithium first reacts with the copper(I) halide



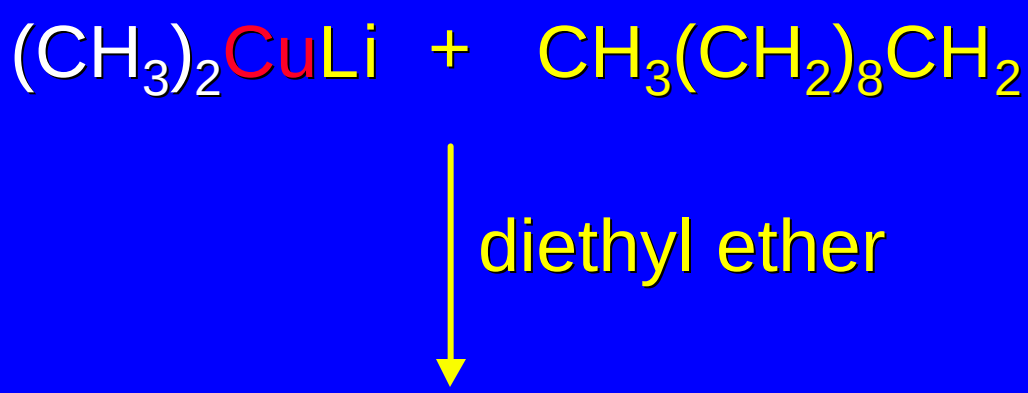
then a second molecule of the alkyllithium reacts with the alkylcopper species formed in the first step



Lithium diorganocuprates are used to form C—C bonds

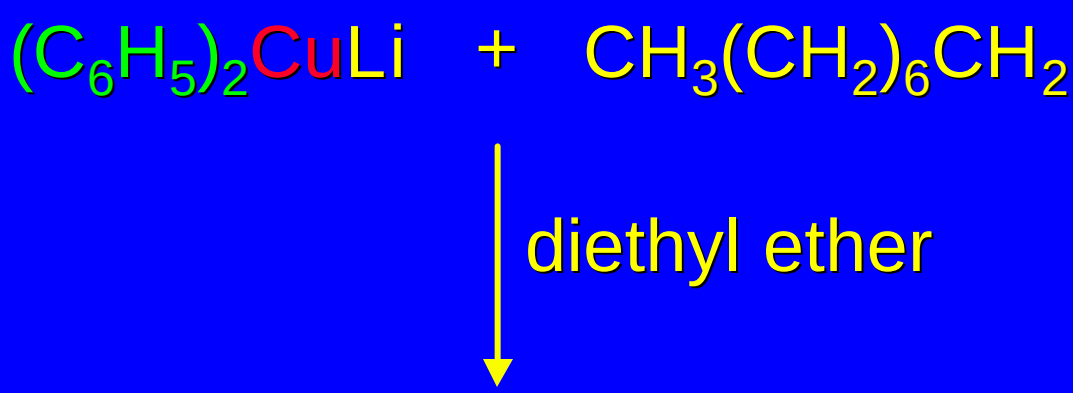


Example: Lithium dimethylcuprate

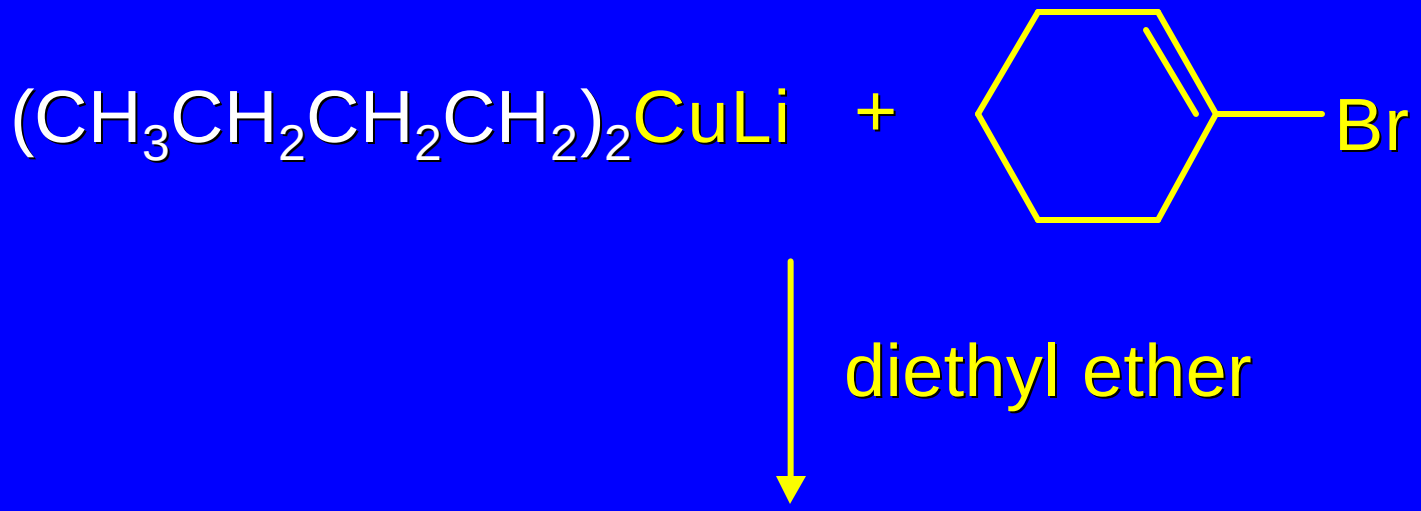


primary alkyl halides work best (secondary and tertiary alkyl halides undergo elimination)

Example: Lithium diphenylcuprate

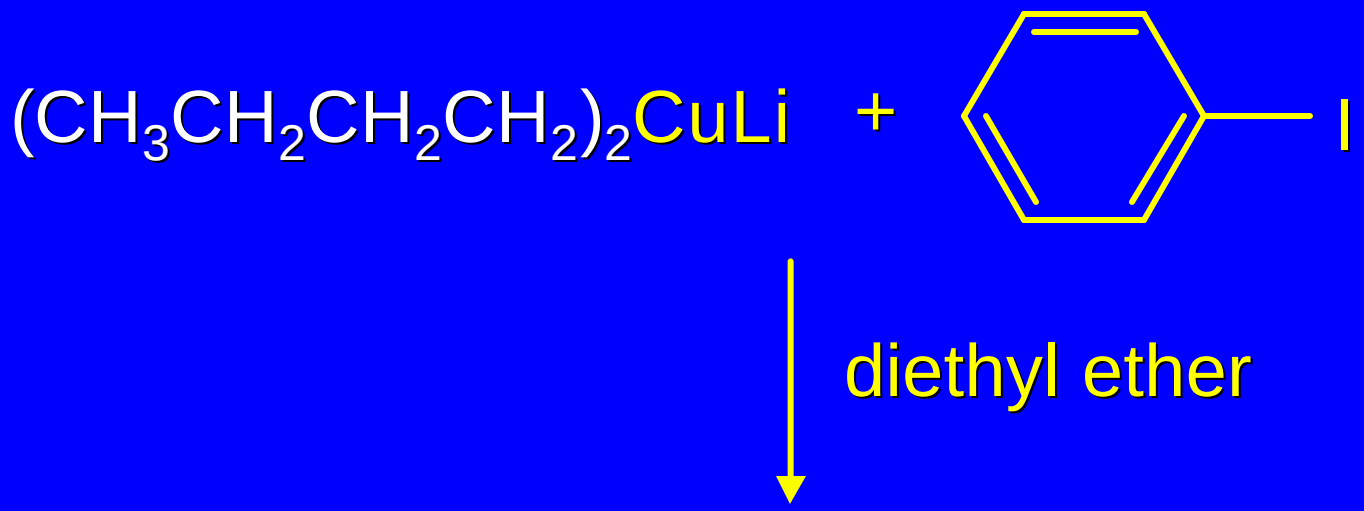


Vinylic halides can be used



(80%)

Aryl halides can be used

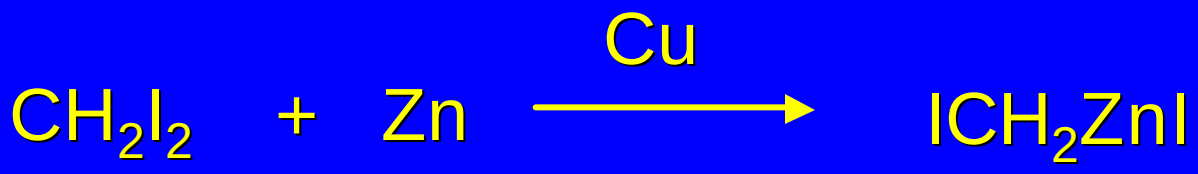


(75%)

14.12
An Organozinc Reagent
for
Cyclopropane Synthesis

Iodomethylzinc iodide

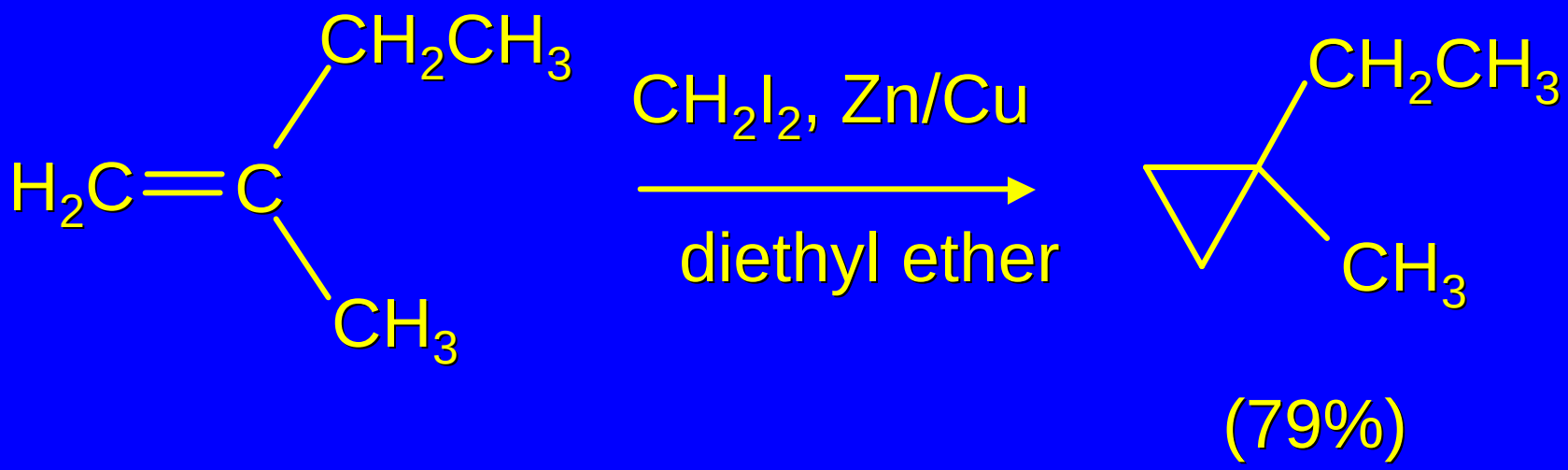
formed by reaction of diiodomethane with zinc that has been coated with copper (called zinc-copper couple)



reacts with alkenes to form cyclopropanes

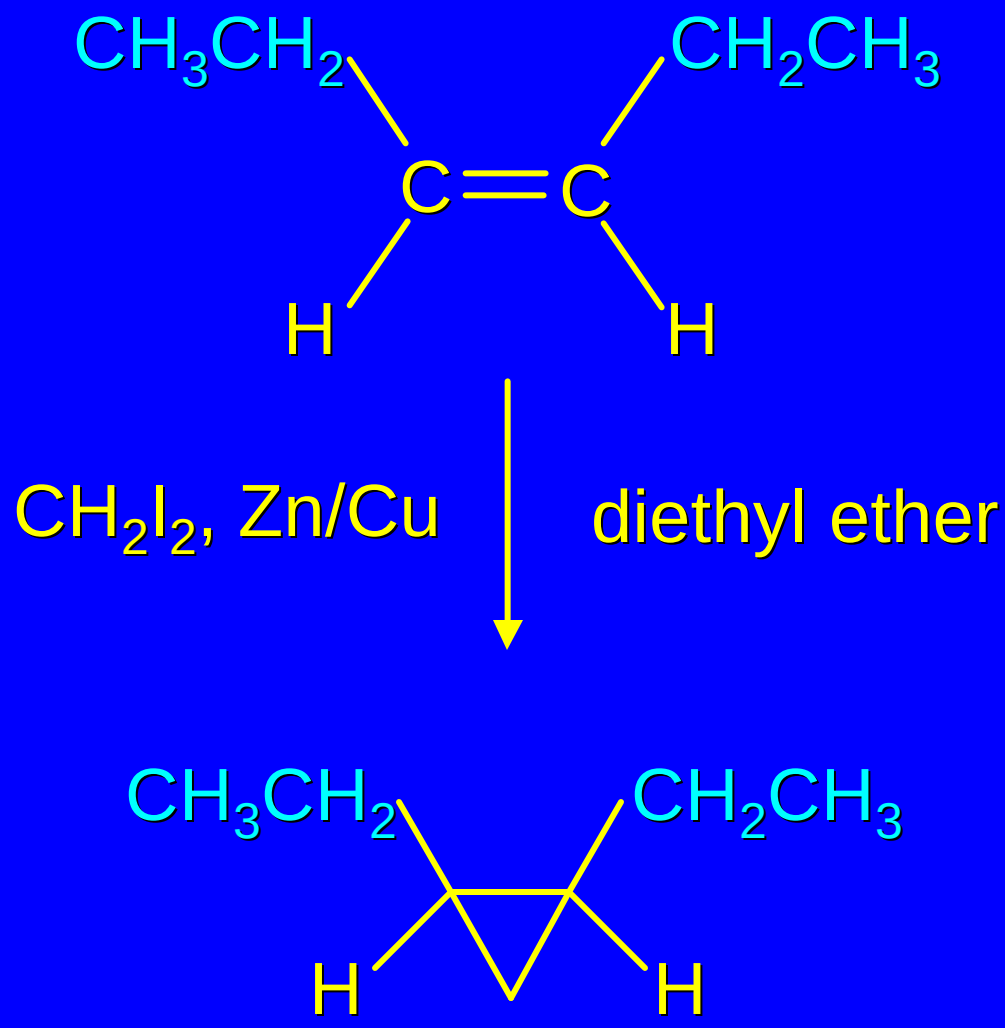
reaction with alkenes is called the Simmons-Smith reaction

Example

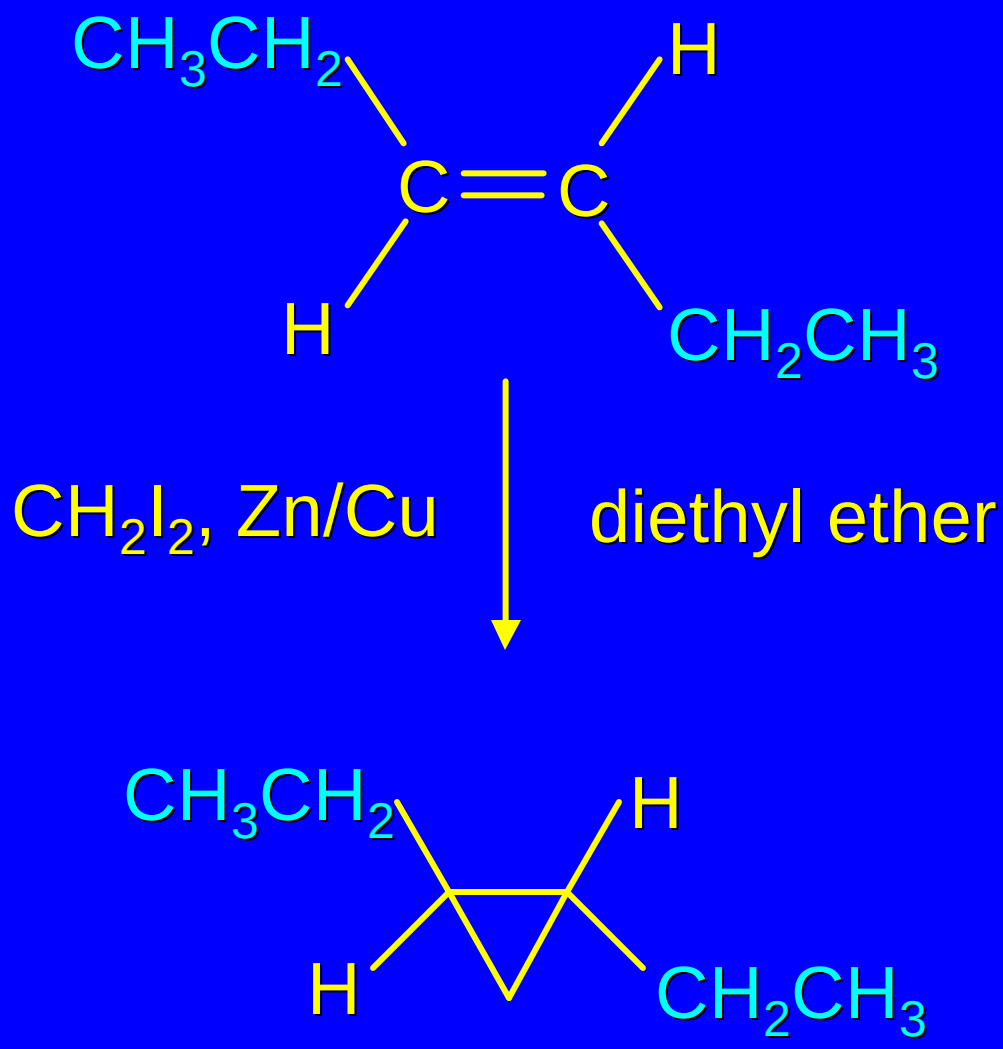


(79%)

Stereospecific syn-addition



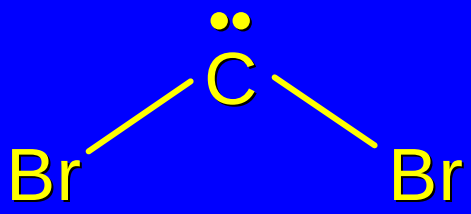
Stereospecific syn-addition



14.13
Carbenes and Carbenoids

Carbene

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

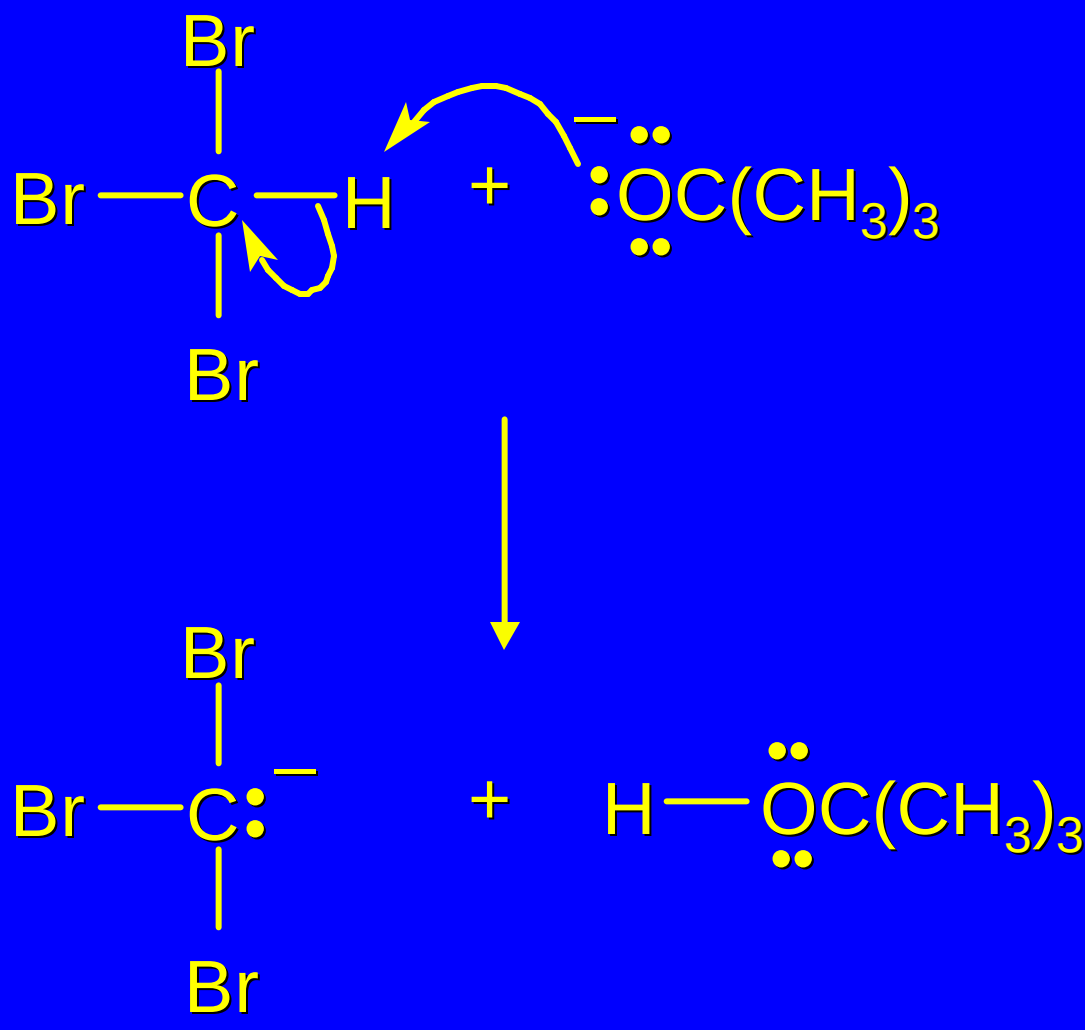


dibromocarbene

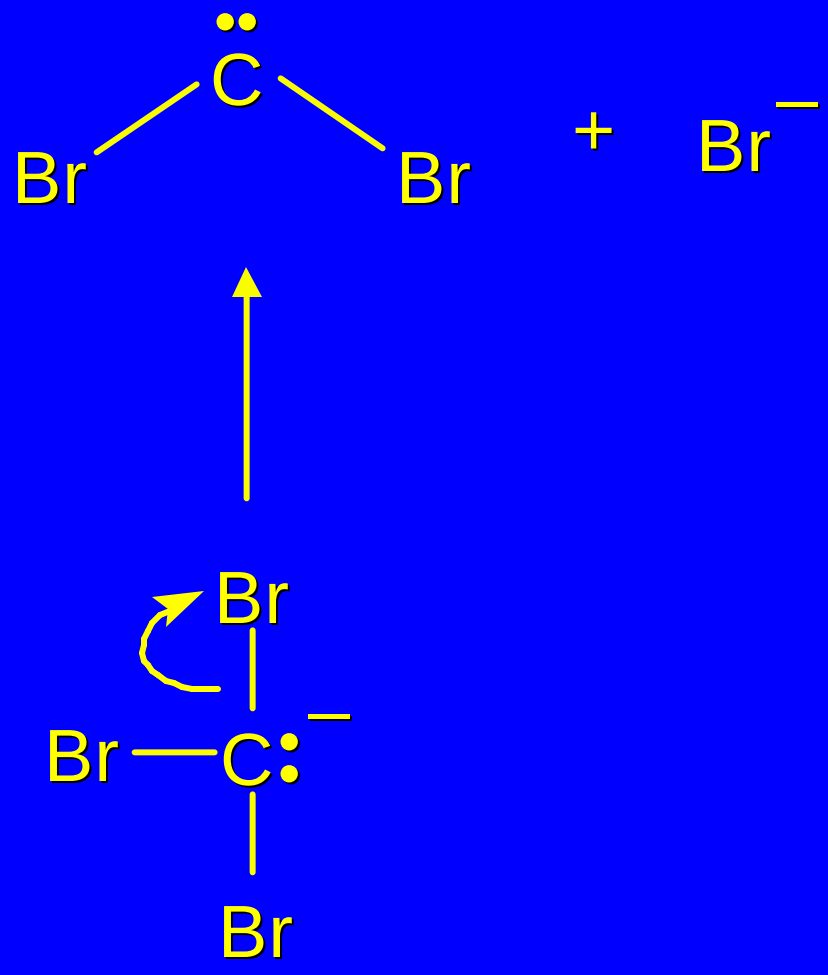
Carbenes are very reactive; normally cannot be isolated and stored.

Are intermediates in certain reactions.

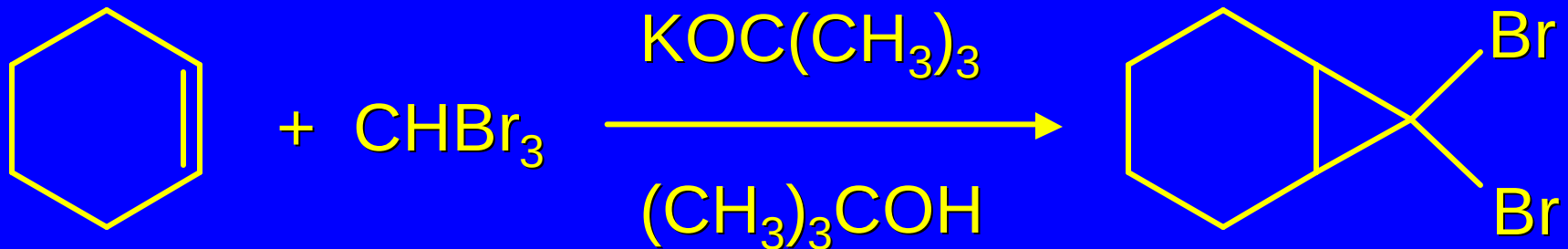
Generation of Dibromocarbene



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.

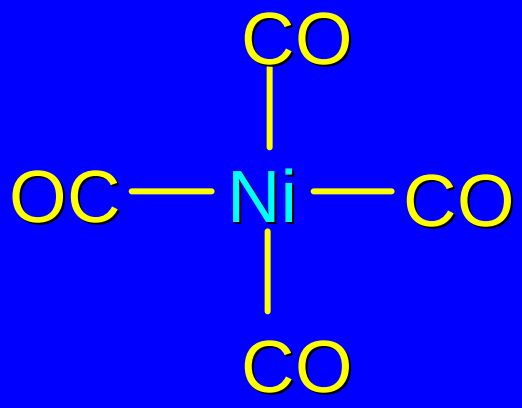
18-Electron Rule

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]$4s^2 3d^8$

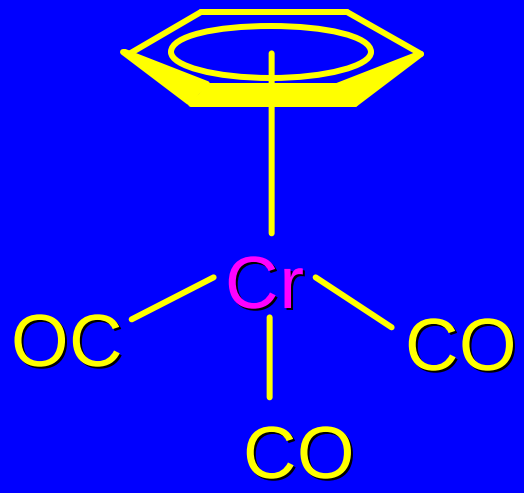
Ni has 10 valence electrons

Each CO uses 2 electrons to bond to Ni

4 CO contribute 8 valence electrons

10 + 8 = 18

Example



(Benzene)tricarbonylchromium

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

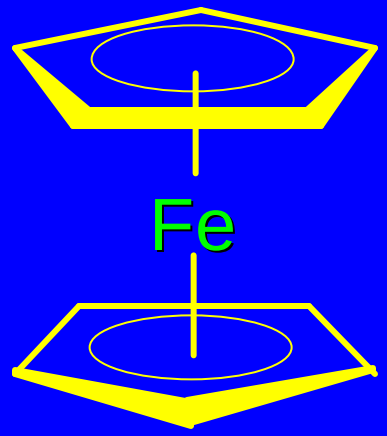
Cr has 6 valence electrons

Each CO uses 2 electrons to bond to Cr

3 CO contribute 6 valence electrons

benzene uses its 6 p electrons to bind to Cr.

Example



Ferrocene

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

Each cyclopentadienide anion contributes 6 p electrons

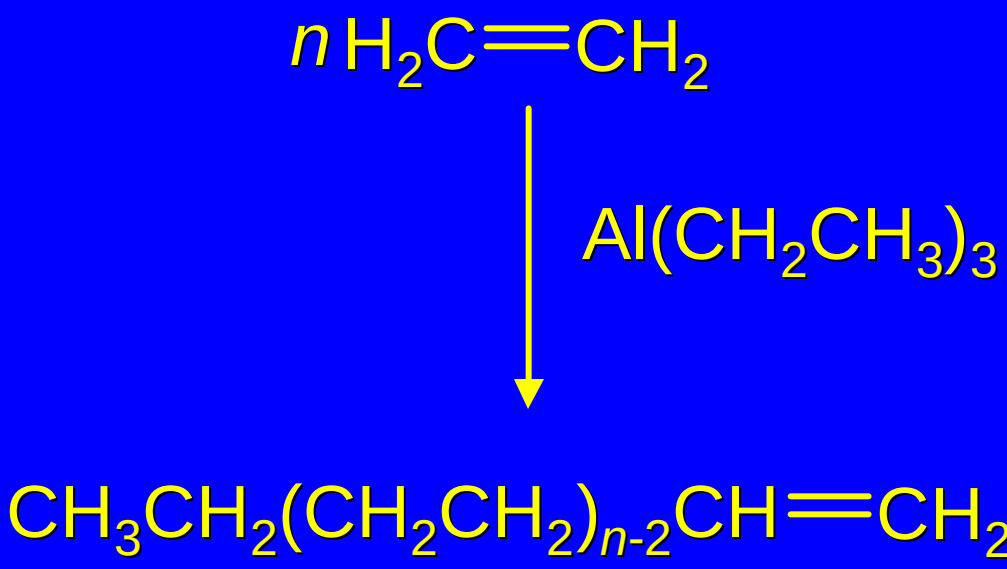
Total 6 + 6 + 6 = 18

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.

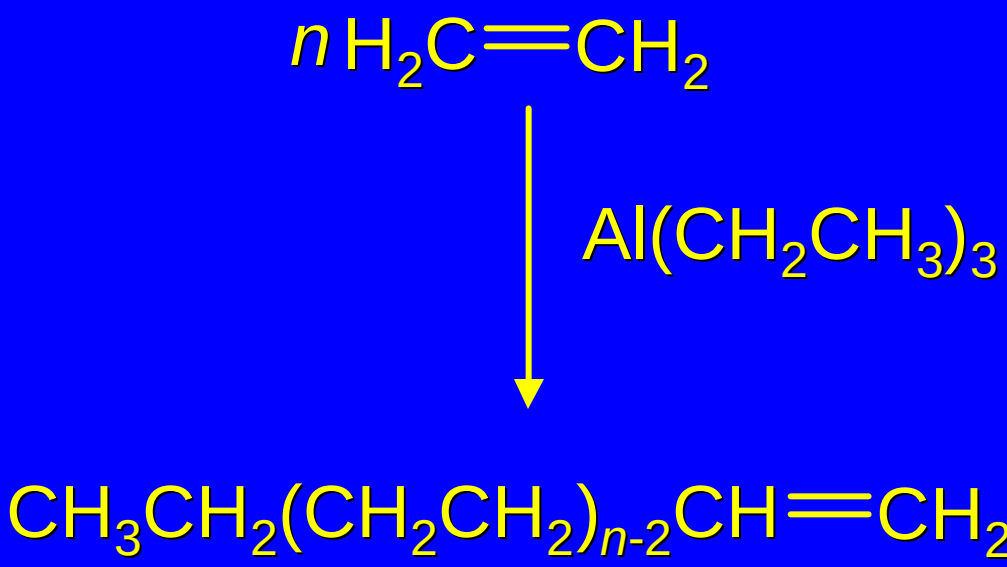
Ethylene oligomerization



Triethylaluminum catalyzes the formation of alkenes from ethylene.

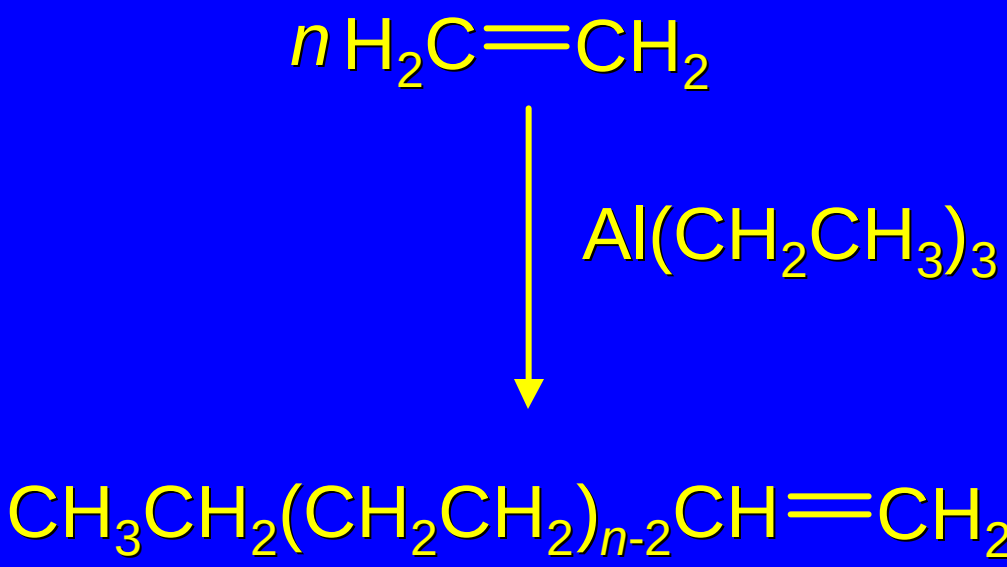
These compounds are called *ethylene oligomers* and the process is called *oligomerization*.

Karl Ziegler (1950)



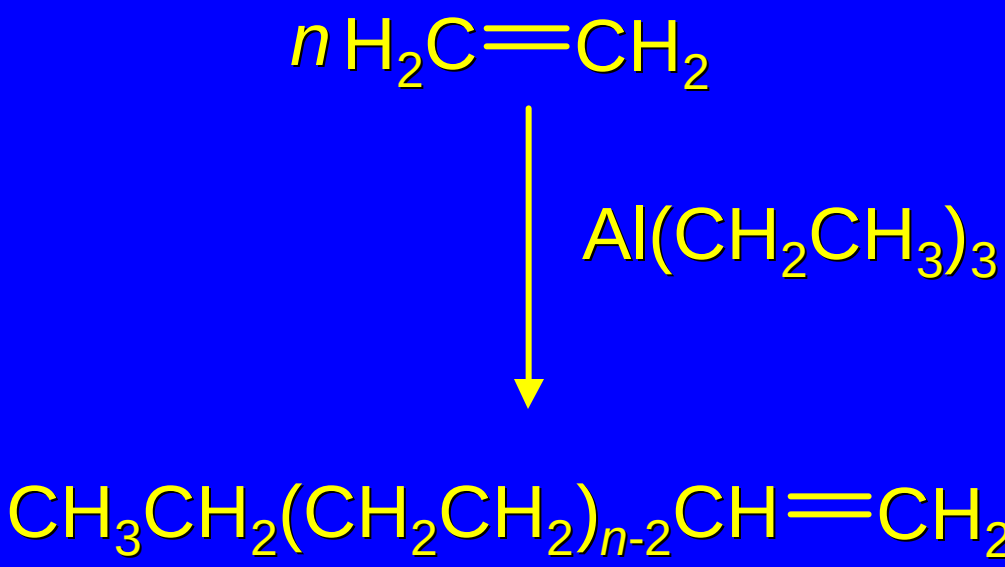
Ziegler found that oligomerization was affected differently by different transition metals. Some gave oligomers with 6-18 carbons, others gave polyethylene.

Karl Ziegler (1950)



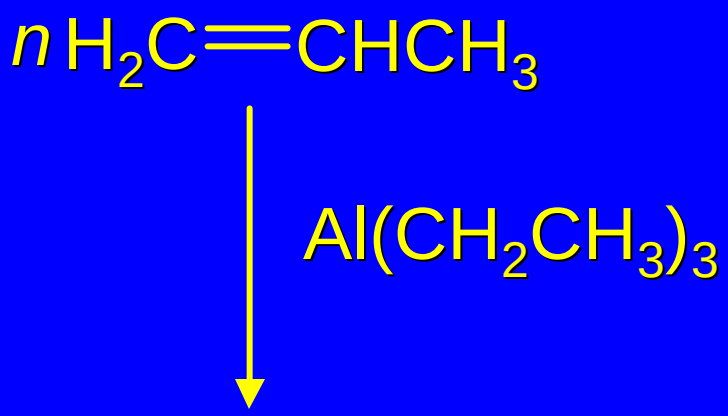
The ethylene oligomers formed under Ziegler's conditions are called *linear α-olefins* and have become important industrial chemicals.

Karl Ziegler (1950)



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



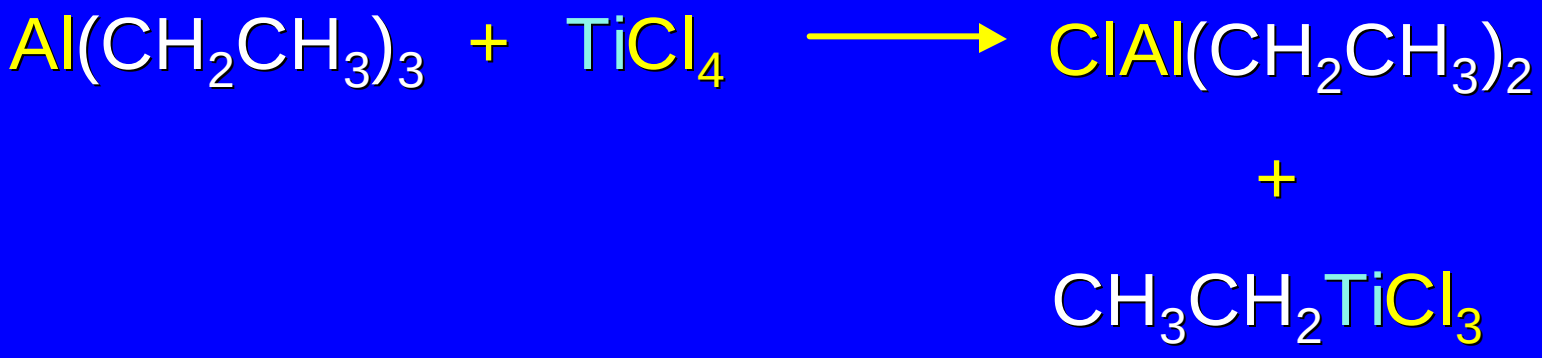
Natta found that polymerization of propene under Ziegler's conditions gave mainly isotactic polypropylene. This discovery made it possible to produce polypropylene having useful properties.

Ziegler-Natta Catalysts

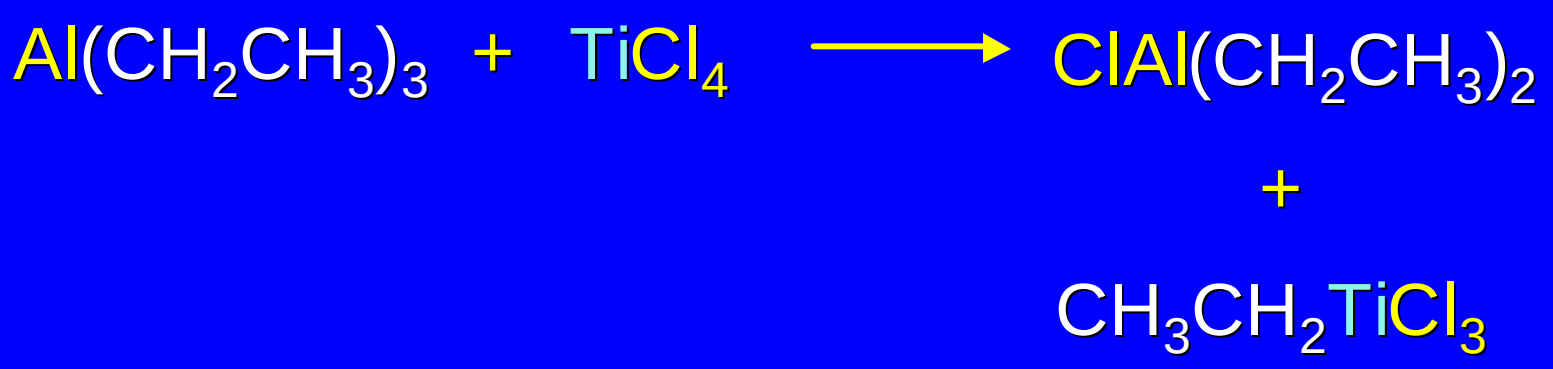
A typical Ziegler-Natta catalyst is a combination of $TiCl_4$ and $(CH_3CH_2)_2AlCl$, or $TiCl_3$ and $(CH_3CH_2)_3Al$.

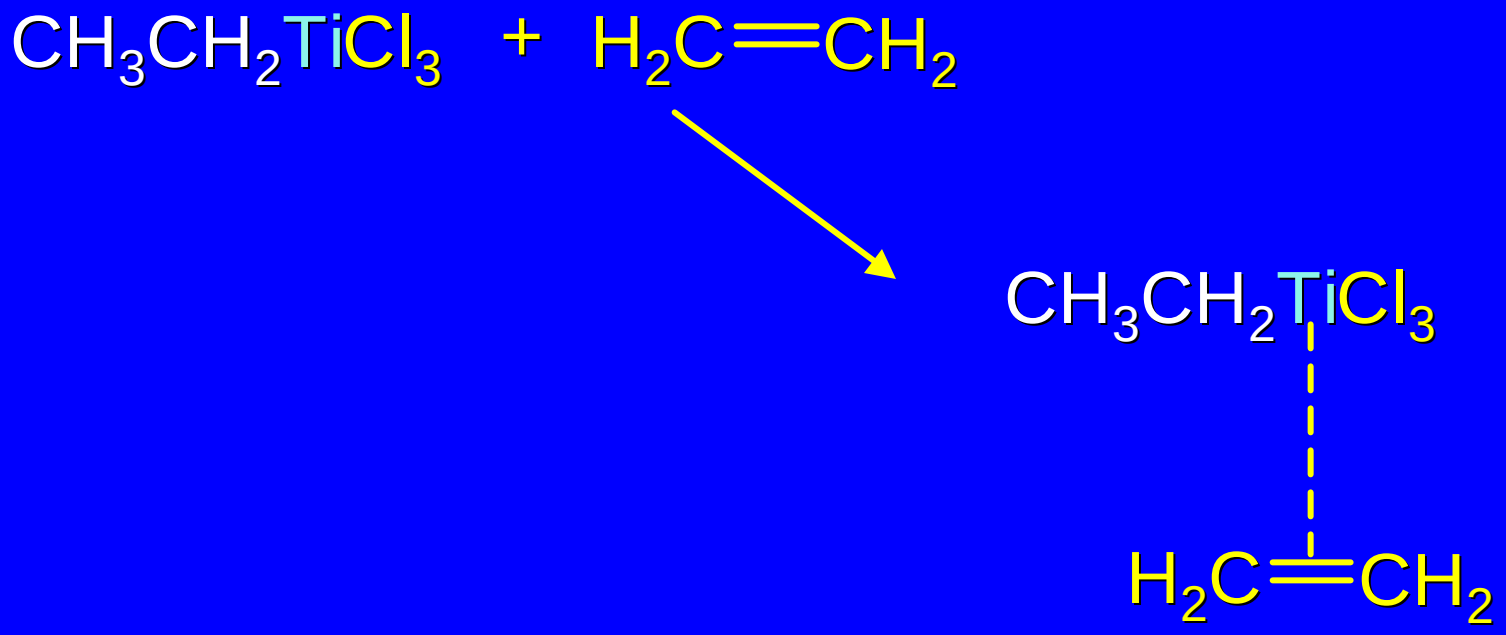
Many Ziegler-Natta catalyst combinations include a metallocene.

Mechanism of Coordination Polymerization

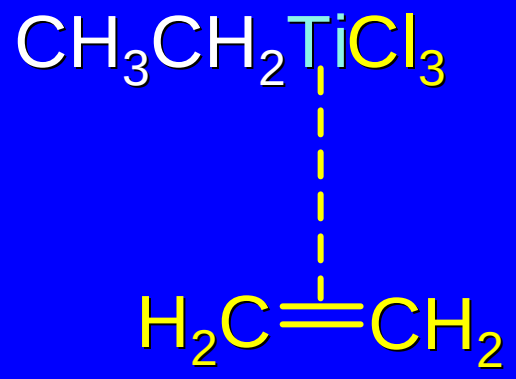


Mechanism of Coordination Polymerization

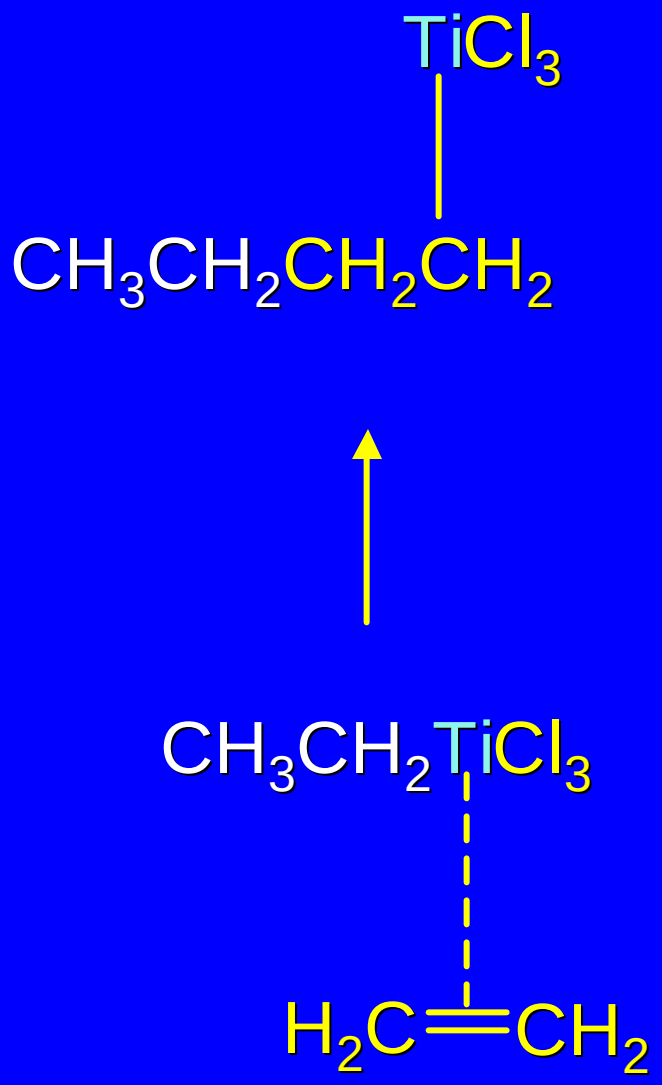




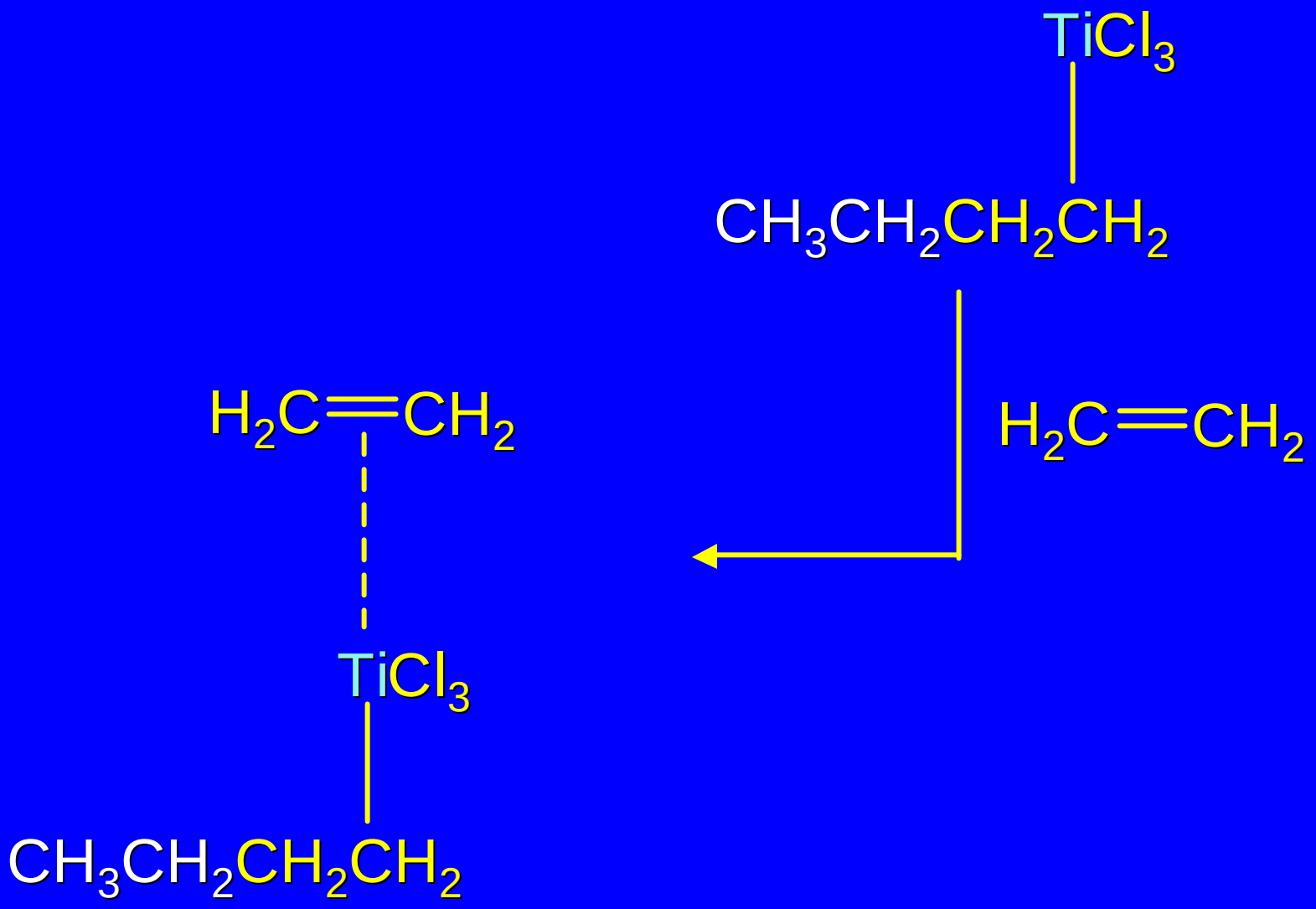
Mechanism of Coordination Polymerization



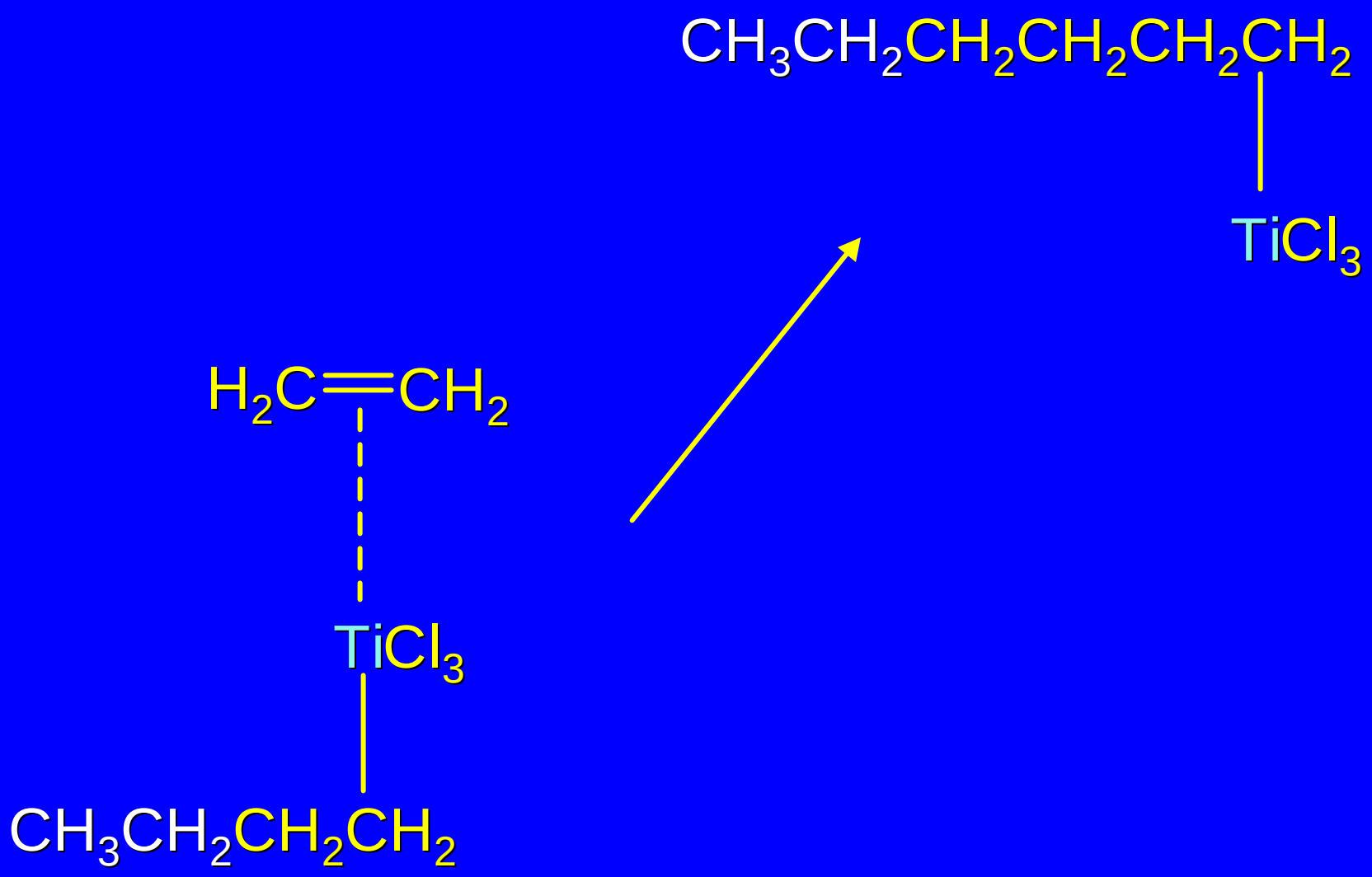
Mechanism of Coordination Polymerization



Mechanism of Coordination Polymerization



Mechanism of Coordination Polymerization



Mechanism of Coordination Polymerization