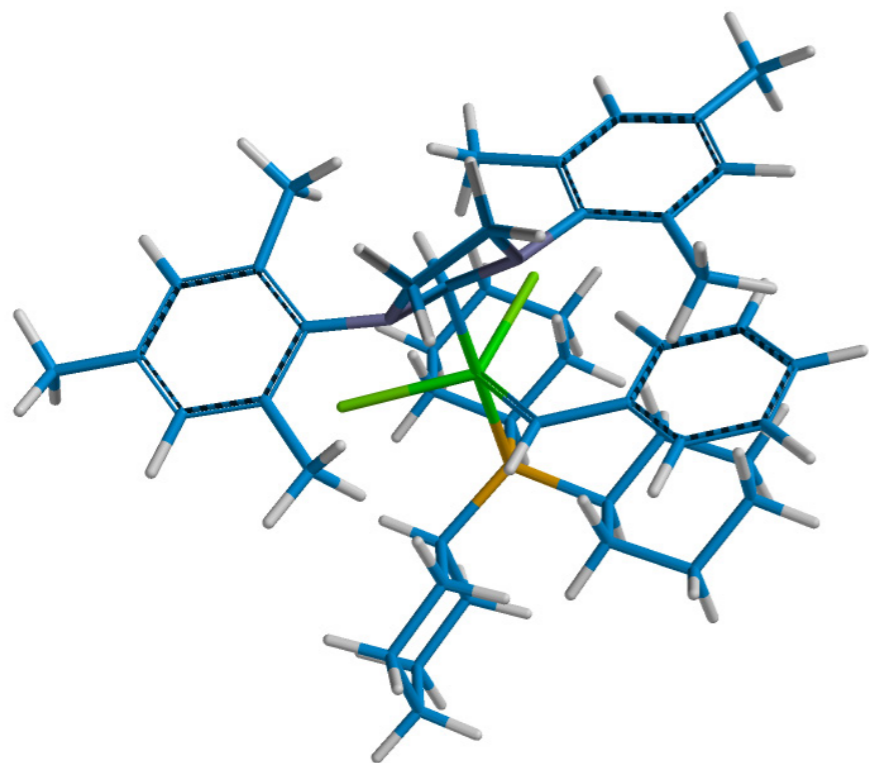


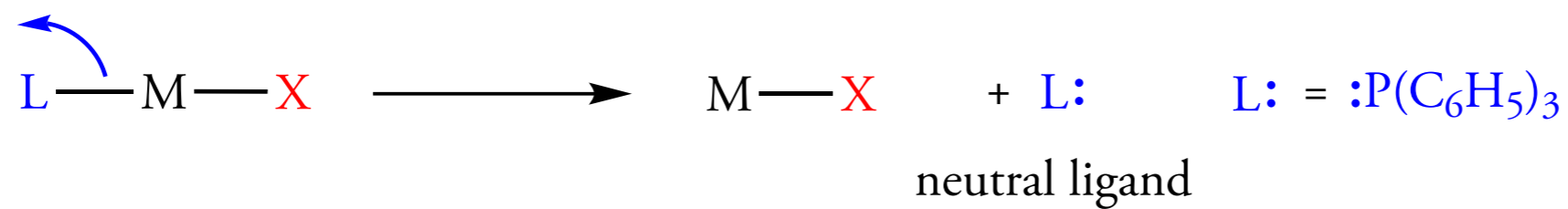
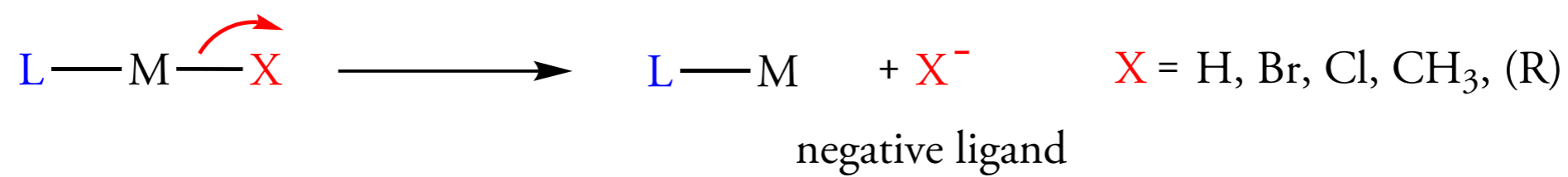
17

ORGANOMETALLIC
CHEMISTRY OF TRANSITION
METAL ELEMENTS
AND
INTRODUCTION TO
RETROSYNTHESIS



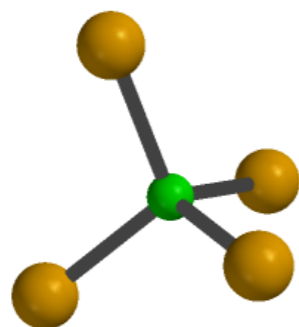
17.1 BRIEF OVERVIEW OF TRANSITION METAL COMPLEXES

Transition Metal Complexes



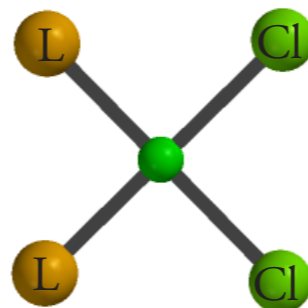
17.1 BRIEF OVERVIEW OF TRANSITION METAL COMPLEXES

Geometry of Transition Metal Complexes

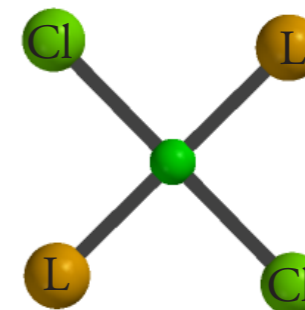


Pd(0) bound to four ligands. The geometry of the complex is tetrahedral, and the metal atom is sp^3 hybridized.

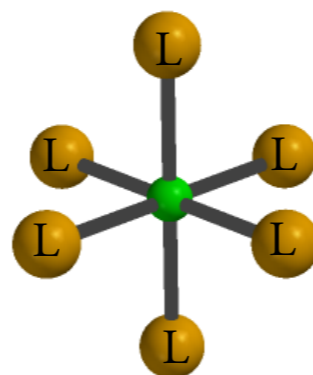
Square planar complexes of $Pd(II)L_2Cl_2$, Pd(II) is dsp^2 hybridized.



$Pd(II)L_2Cl_2$
cis isomer



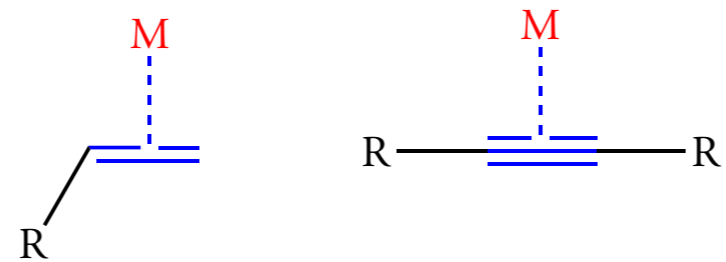
$Pd(II)L_2Cl_2$
trans isomer



Octahedral PdL_6 complex
Pd is d^2sp^3 hybridized.

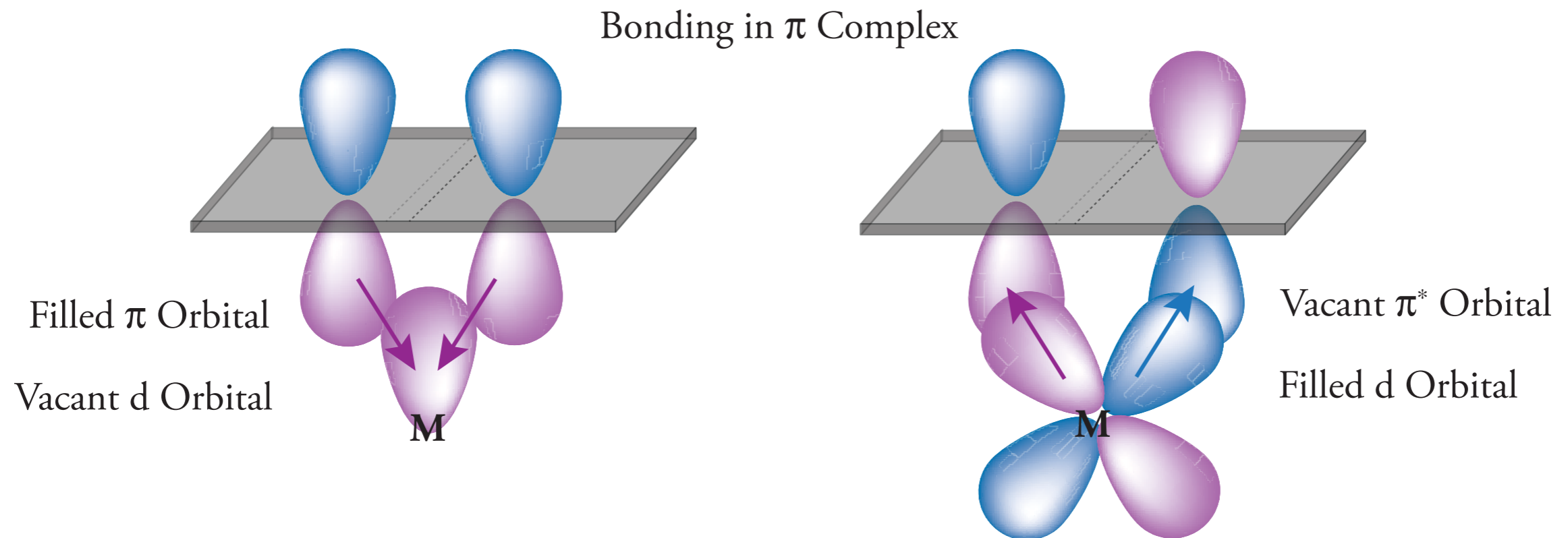
17.1 BRIEF OVERVIEW OF TRANSITION METAL COMPLEXES

Formation of π Complexes



π Complexes with neutral ligands.
The transition metal has a vacant d orbital,
the π bond is the electron donor.

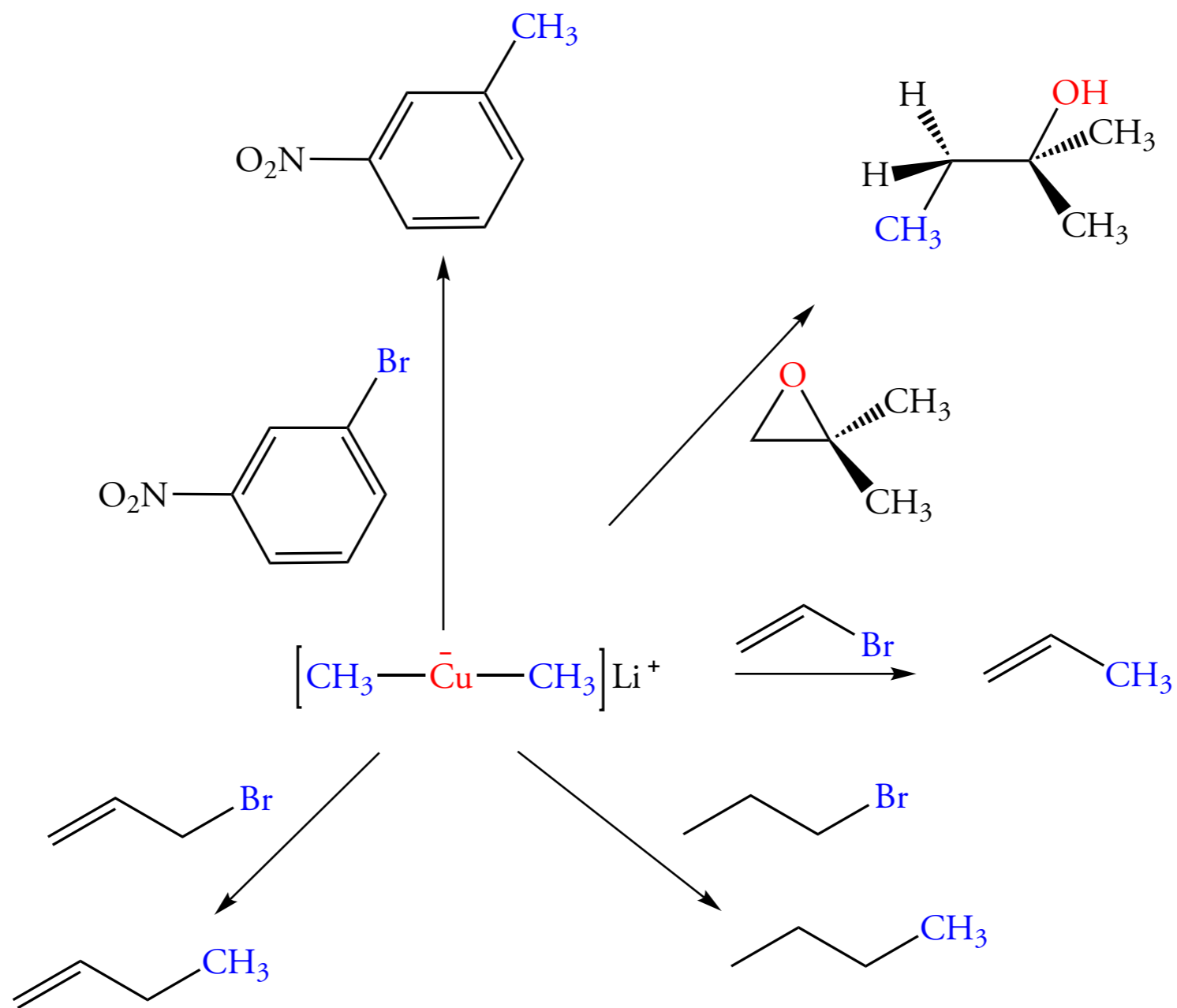
Figure 17.1 Schematic View of Bonding In a π Complex of an Alkene With a Transition Metal



17.2 THE GILMAN REAGENT

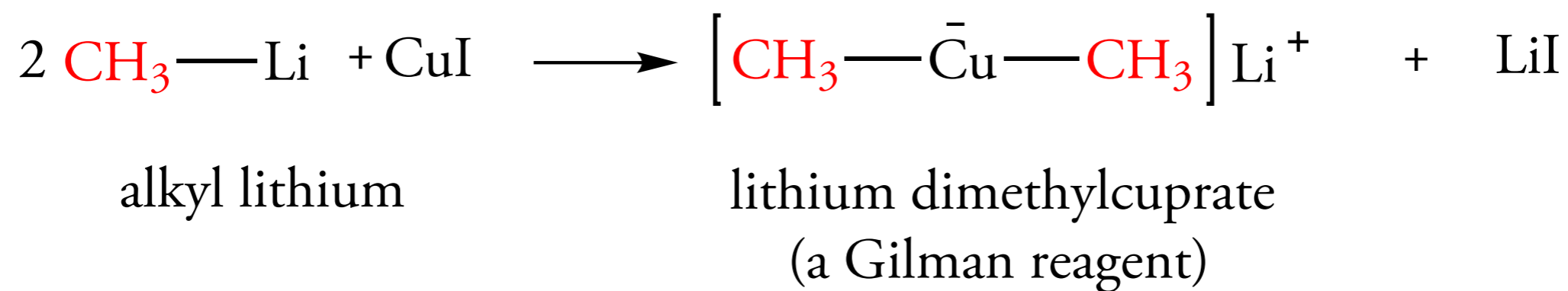
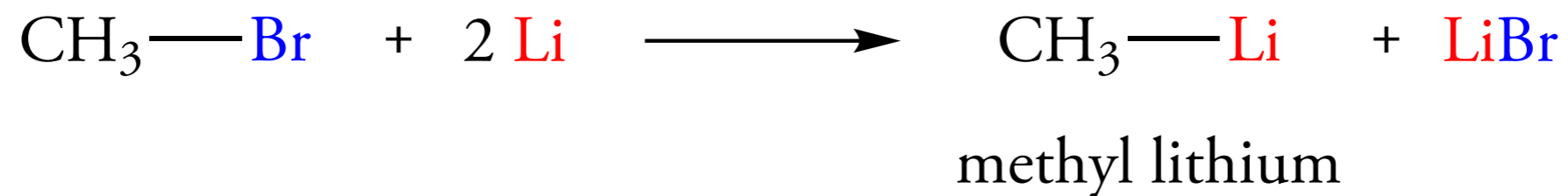
Overview of Gilman Reagents

Figure 17.2 Coupling Reactions of the Gilman Reagent



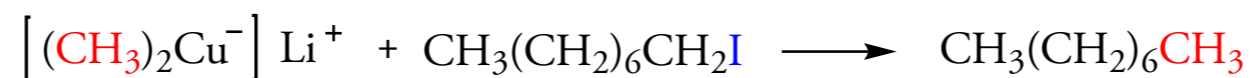
17.2 THE GILMAN REAGENT

Preparation of Gilman Reagents



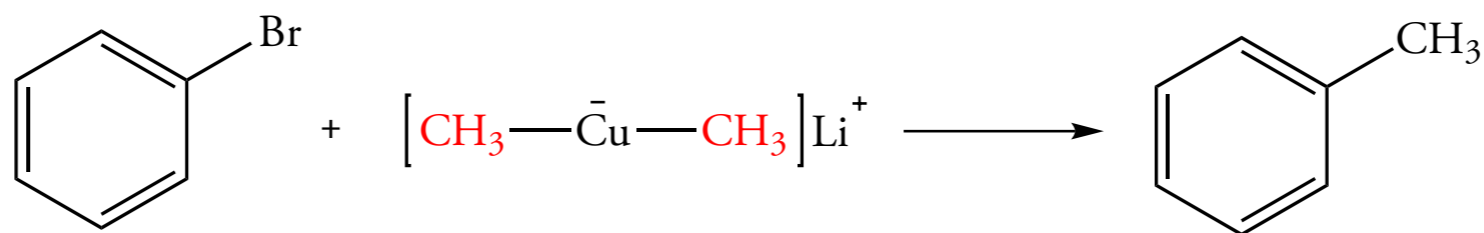
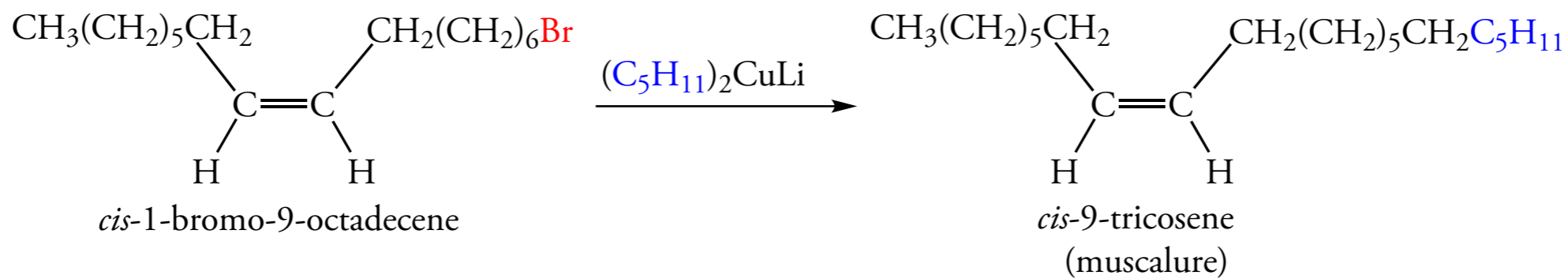
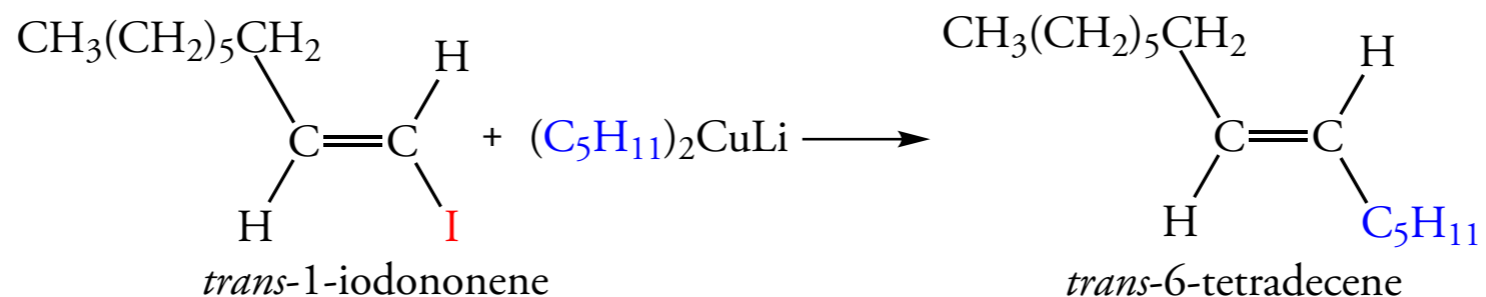
17.2 THE GILMAN REAGENT

Reactions of Gilman Reagents



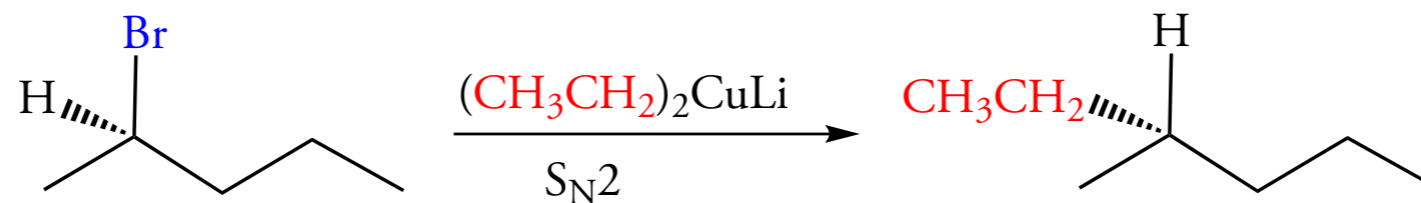
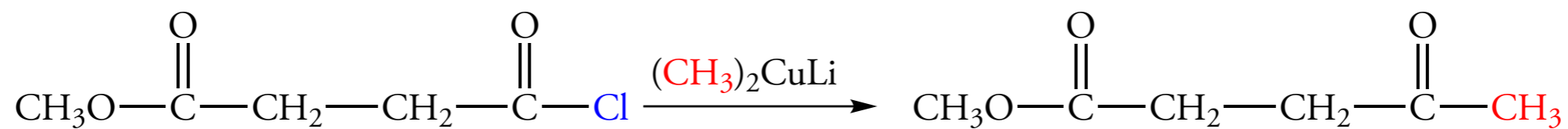
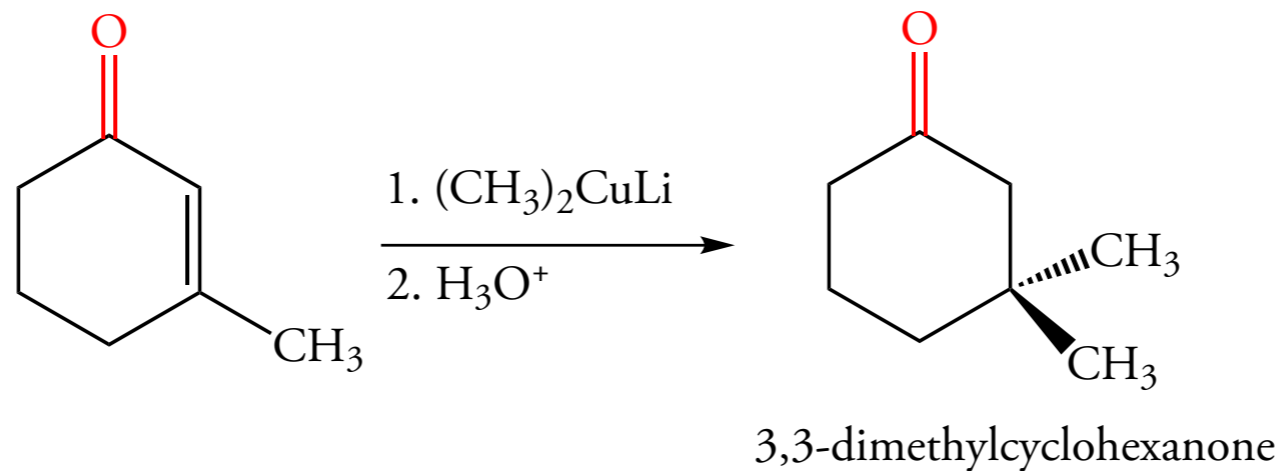
1-iodooctane

nonane



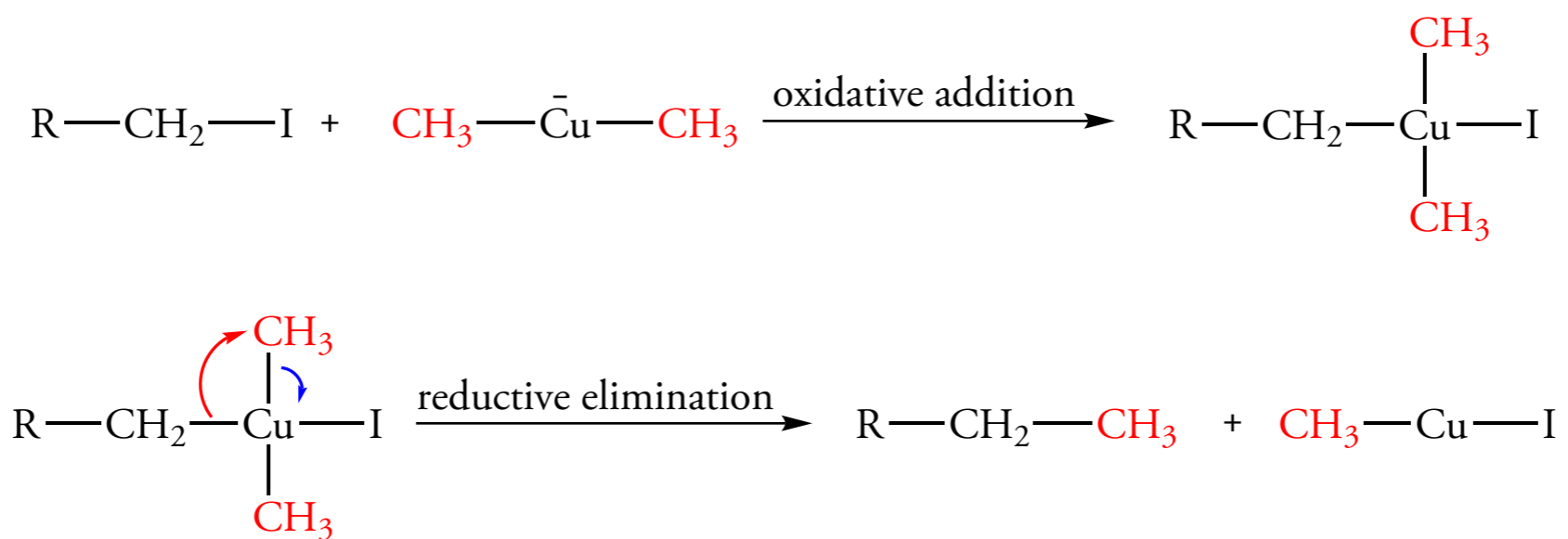
17.2 THE GILMAN REAGENT

Reactions of Gilman Reagents



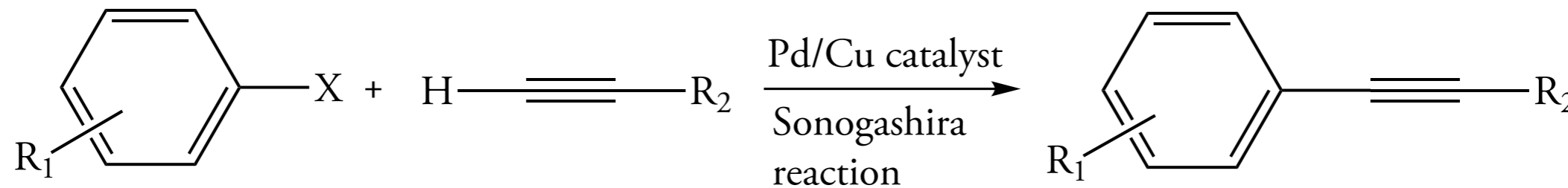
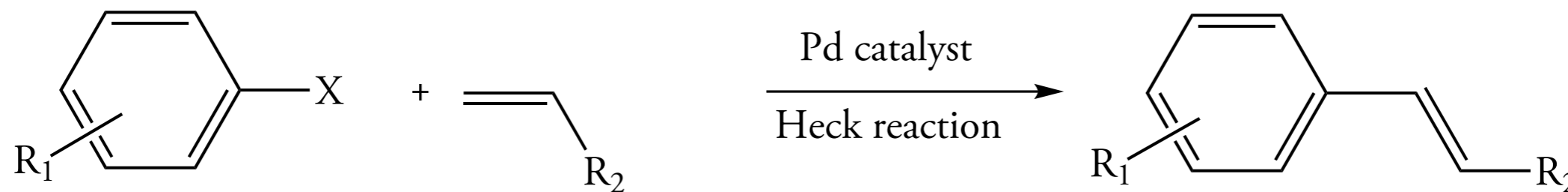
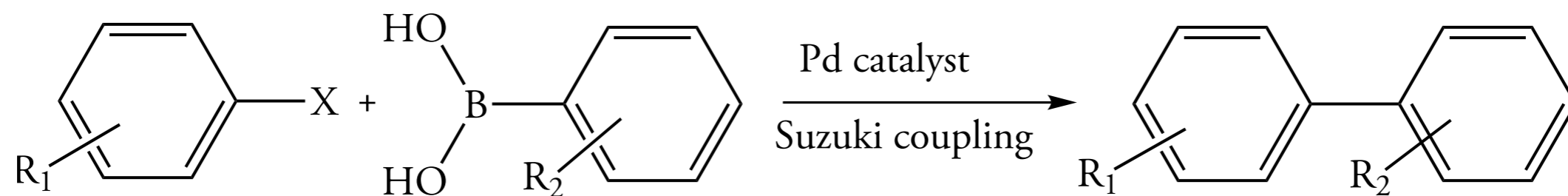
17.2 THE GILMAN REAGENT

Oxidative Addition and Reductive Elimination in the Gilman Reaction



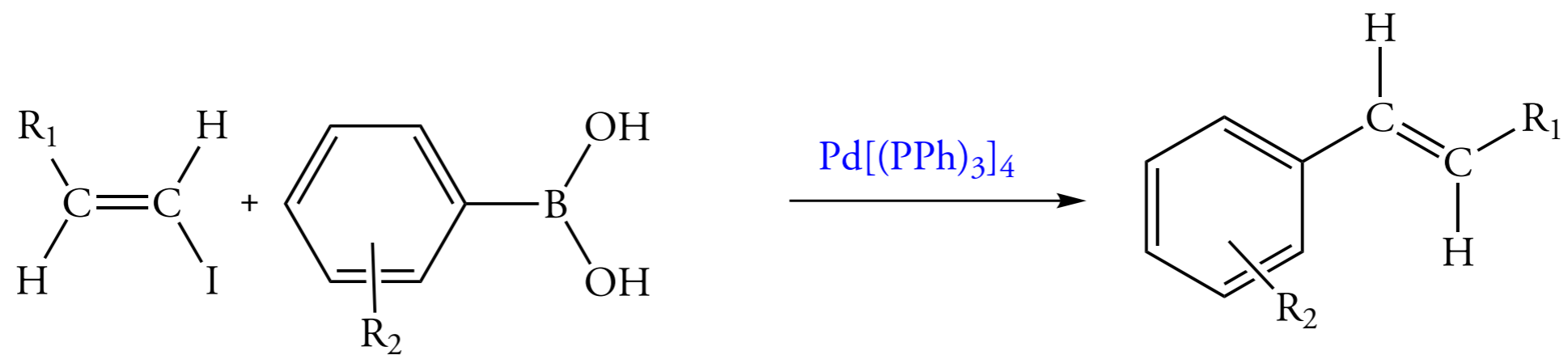
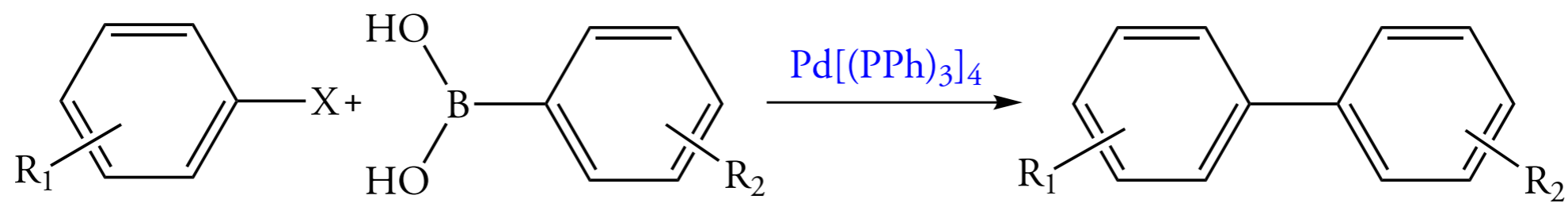
17.3 OVERVIEW OF PALLADIUM-CATALYZED CROSS-COUPLING REACTIONS

Figure 17.3 Cross-Coupling Reactions of Organopalladium Complexes



17.4 THE SUZUKI COUPLING REACTION

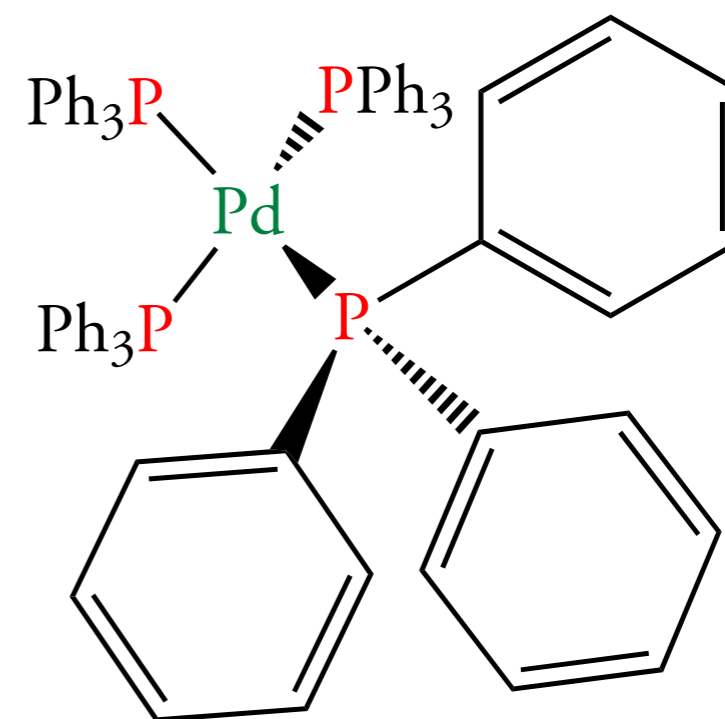
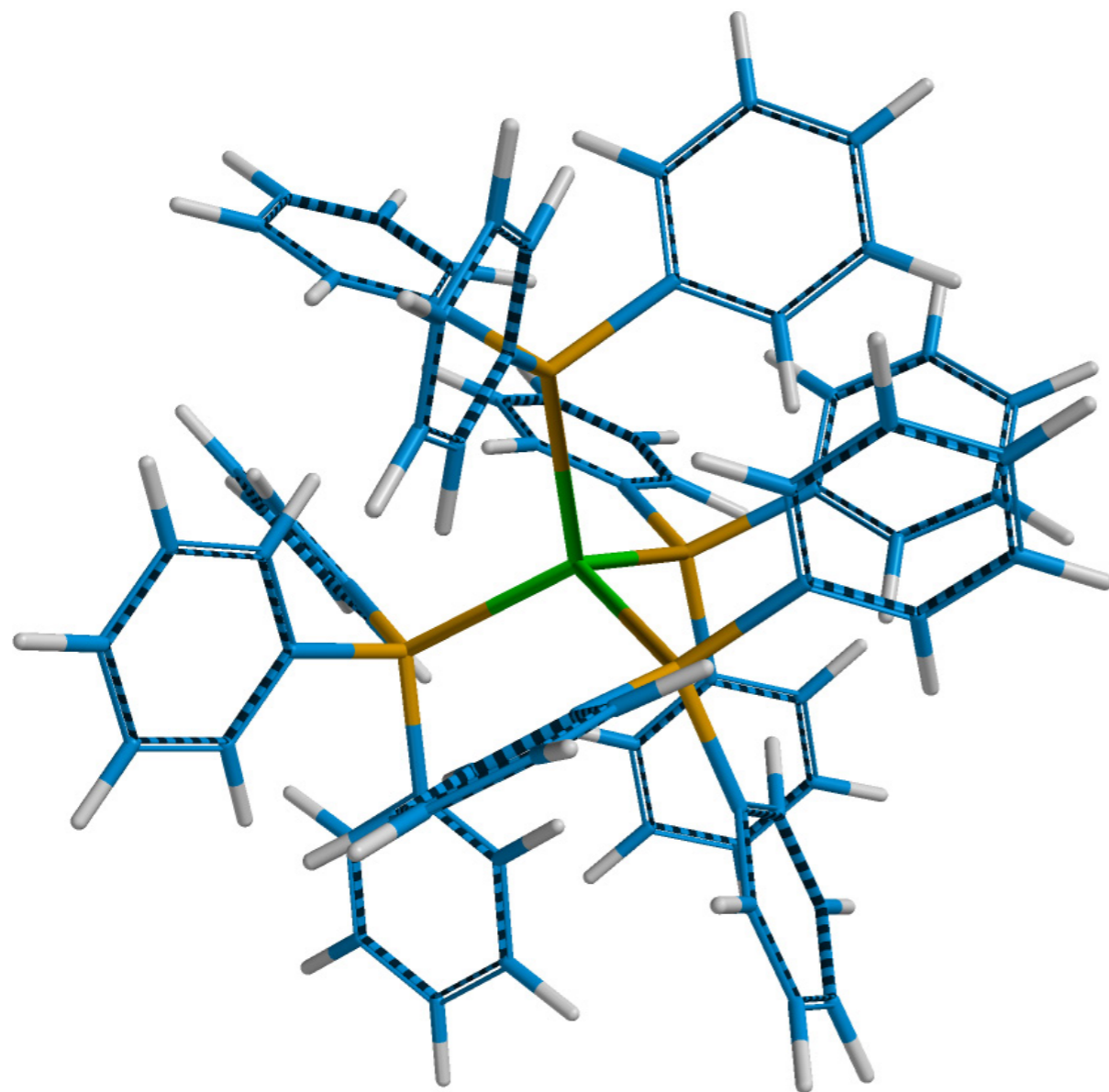
Suzuki coupling reactions



17.4 THE SUZUKI COUPLING REACTION

Figure 17.4 Structure of the Suzuki Catalyst

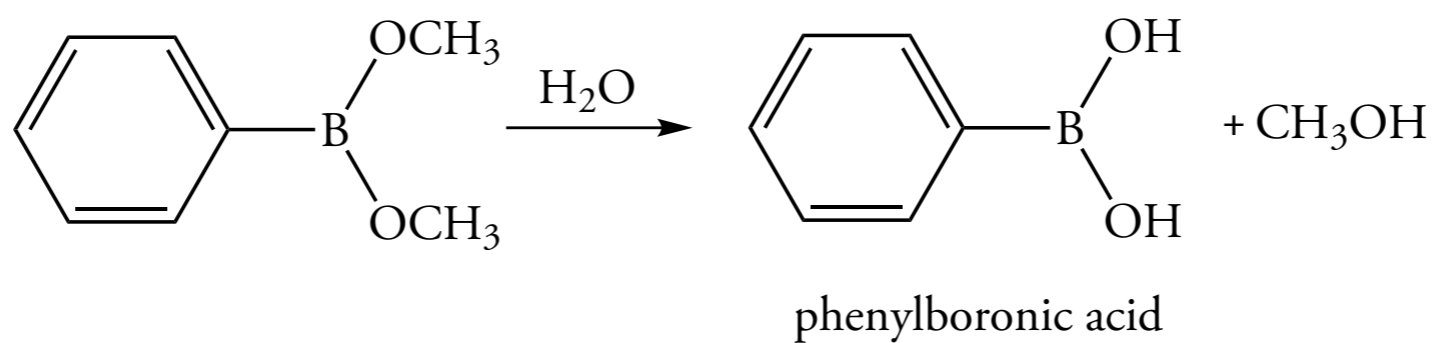
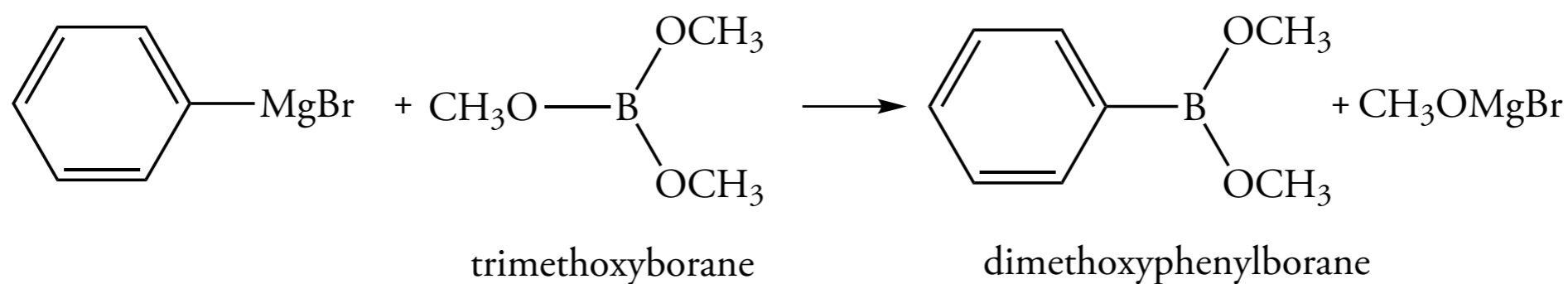
The palladium, Pd(0), atom of the catalyst is at the center of a tetrahedron. A triphenylphosphine group (PPh₃) is at each corner of the tetrahedron.



Suzuki catalyst
(Ph = C₆H₅)

17.4 THE SUZUKI COUPLING REACTION

Preparation of Aryl Boronic Acids



17.4 THE SUZUKI COUPLING REACTION

The Catalytic Cycle in the Suzuki Coupling Reaction

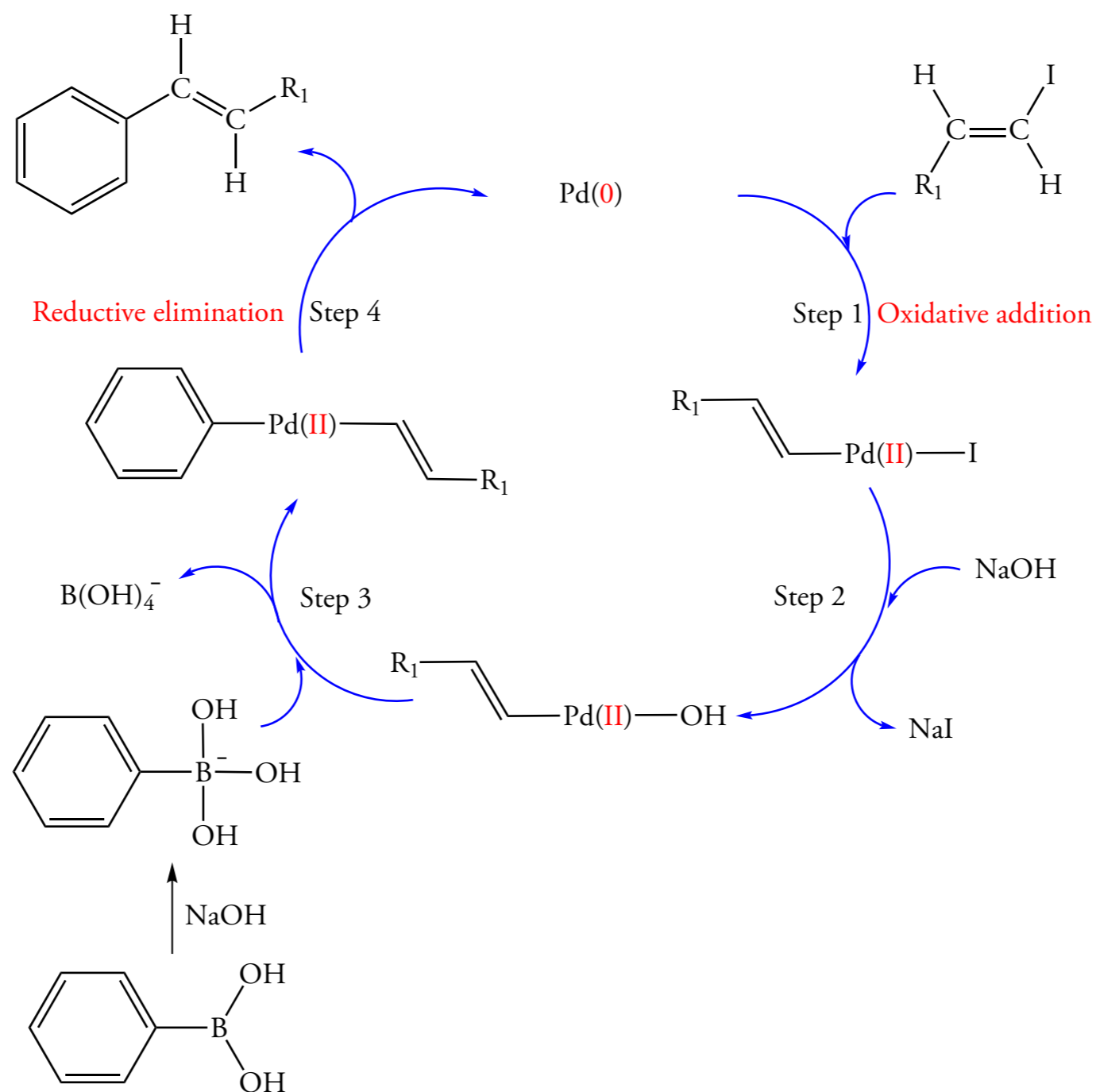
Figure 17.5 Catalytic Cycle of the Suzuki Coupling Reaction

Step 1. The vinyl halide adds to the catalyst in an oxidative addition step.

Step 2. Hydroxide displaces iodide.

Step 3. The base that is present in the reaction medium activates the boronic acid. The aryl group of the borate anion then adds to the catalyst.

Step 4. Cross-coupling of the aryl and vinyl groups occurs in a reductive elimination step. The palladium atom of the catalyst returns to its original oxidation state, Pd(0), and the cycle continues. The ligands have been eliminated from the diagram for clarity.



17.5 THE HECK REACTION

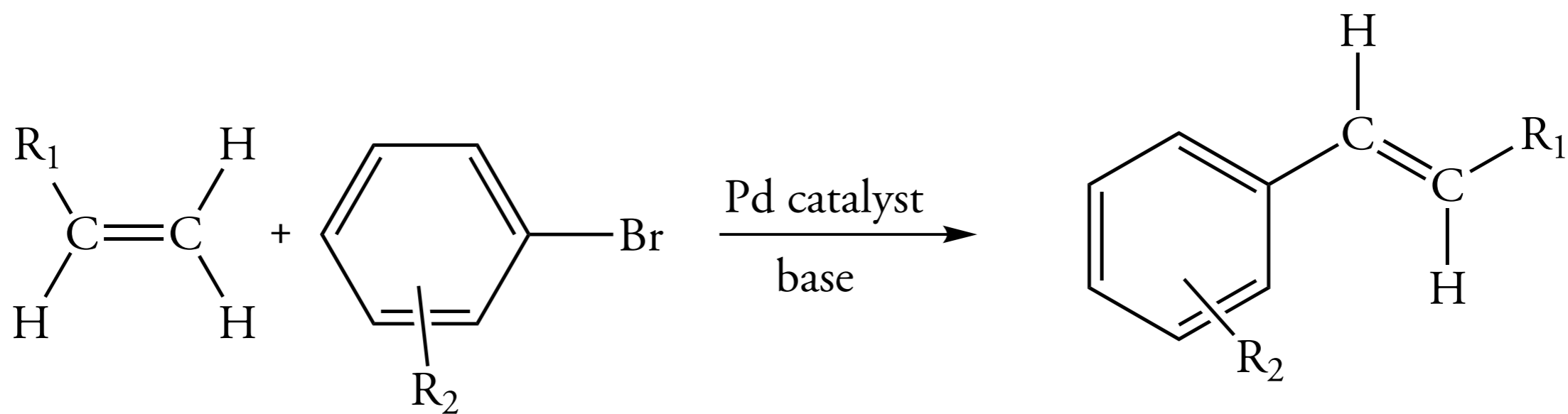
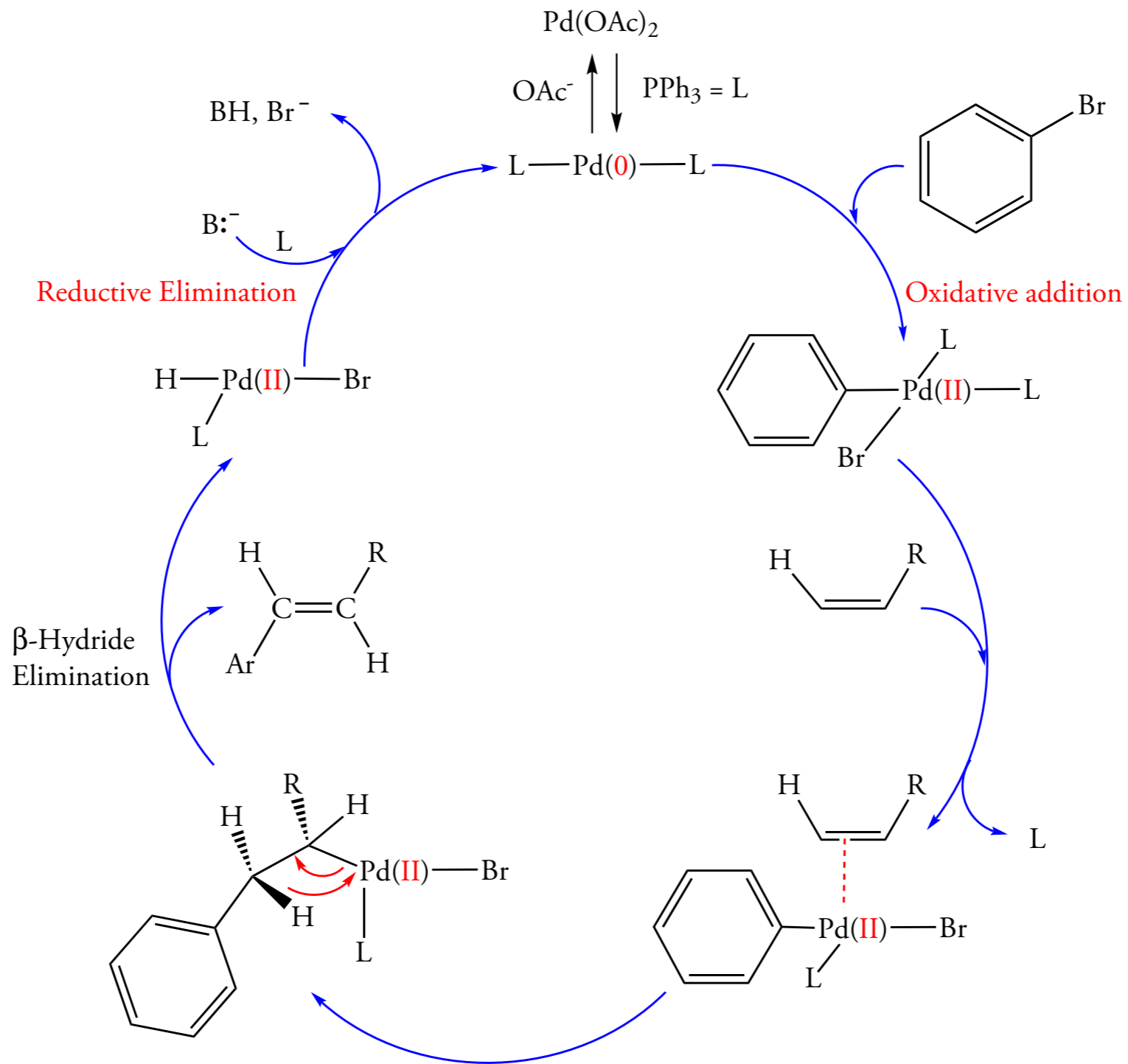
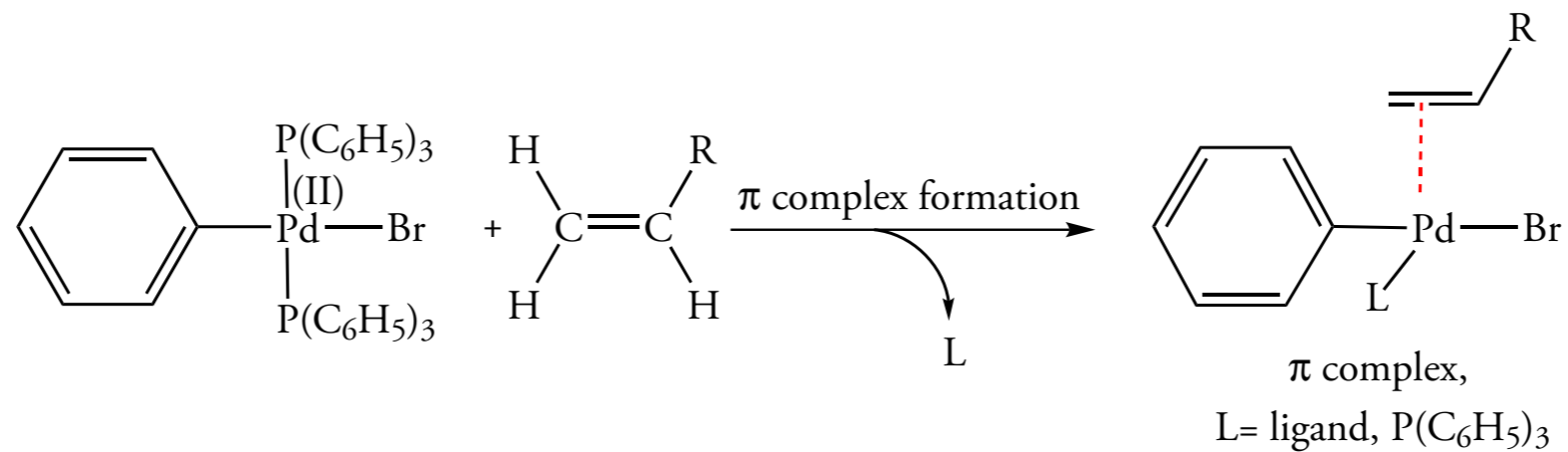
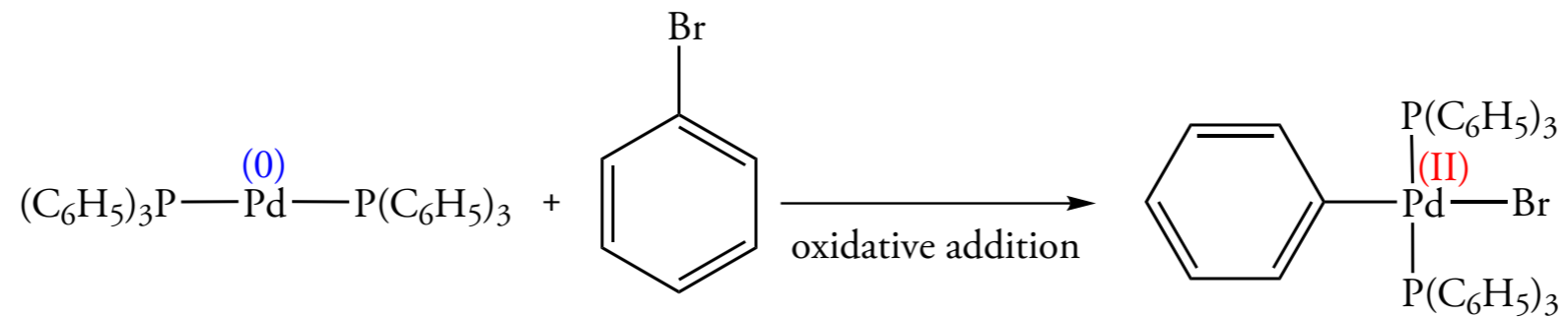
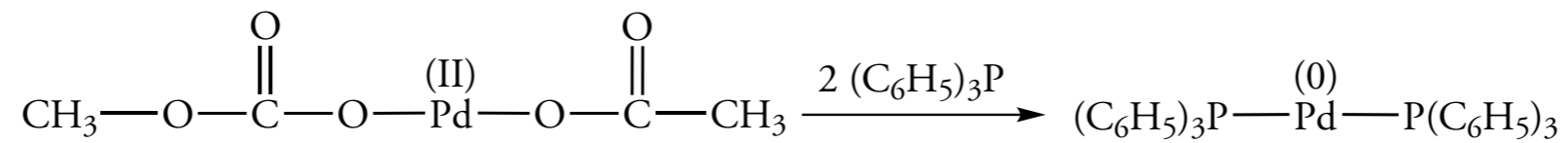


Figure 17.6 Catalytic Cycle of the Heck Reaction



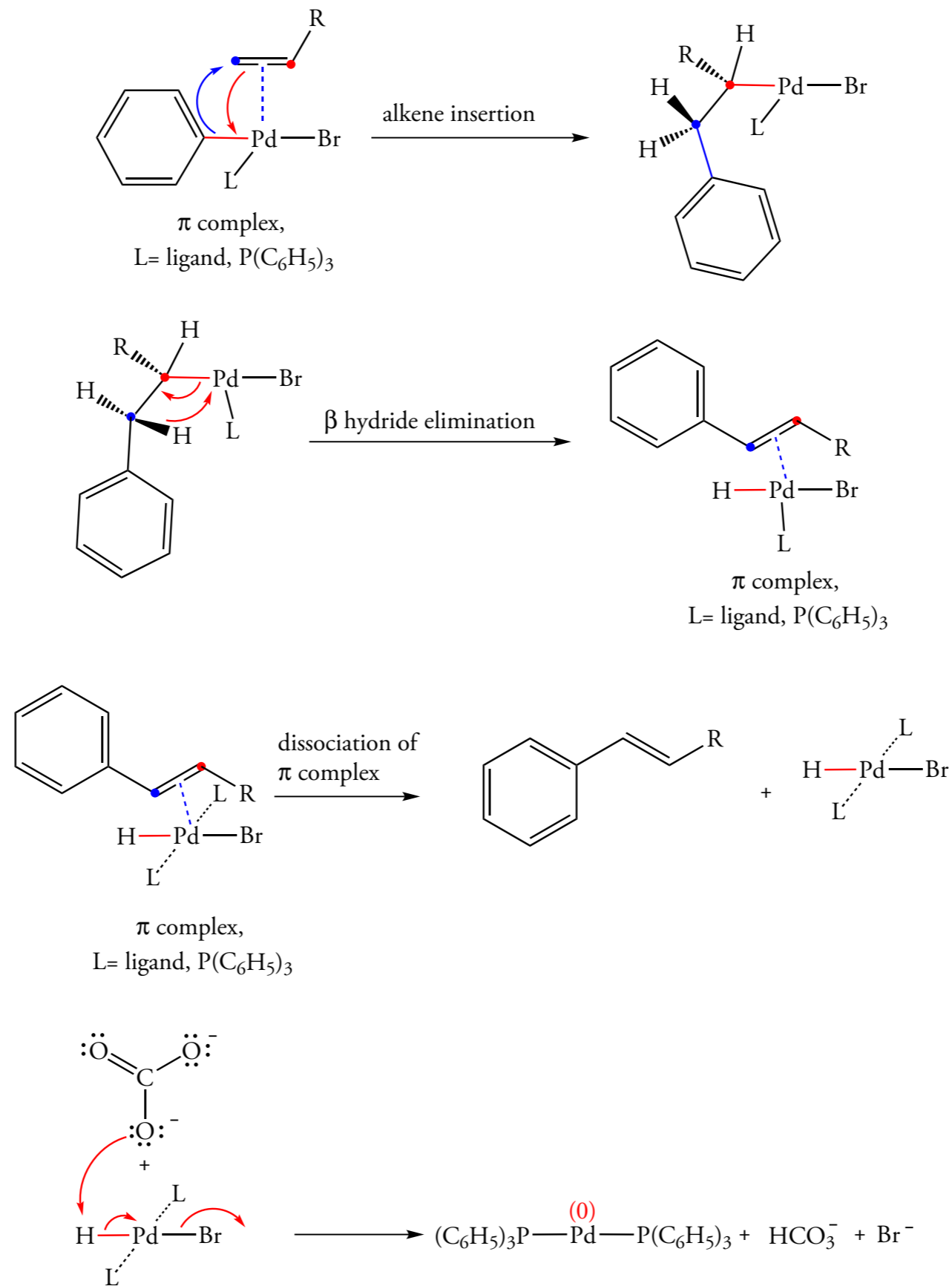
17.5 THE HECK REACTION

The Catalytic Steps 1-3 in the Heck Reaction



17.5 THE HECK REACTION

The Catalytic Steps 4-6 in the Heck Reaction



17.6 THE SONOGASHIRA REACTION

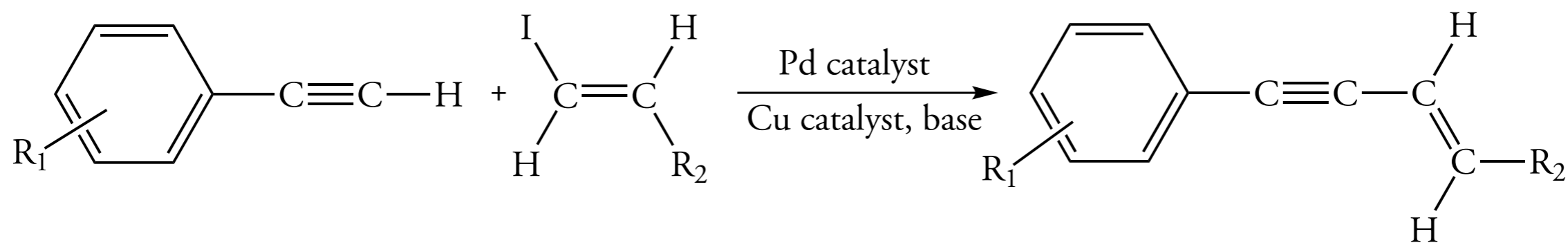
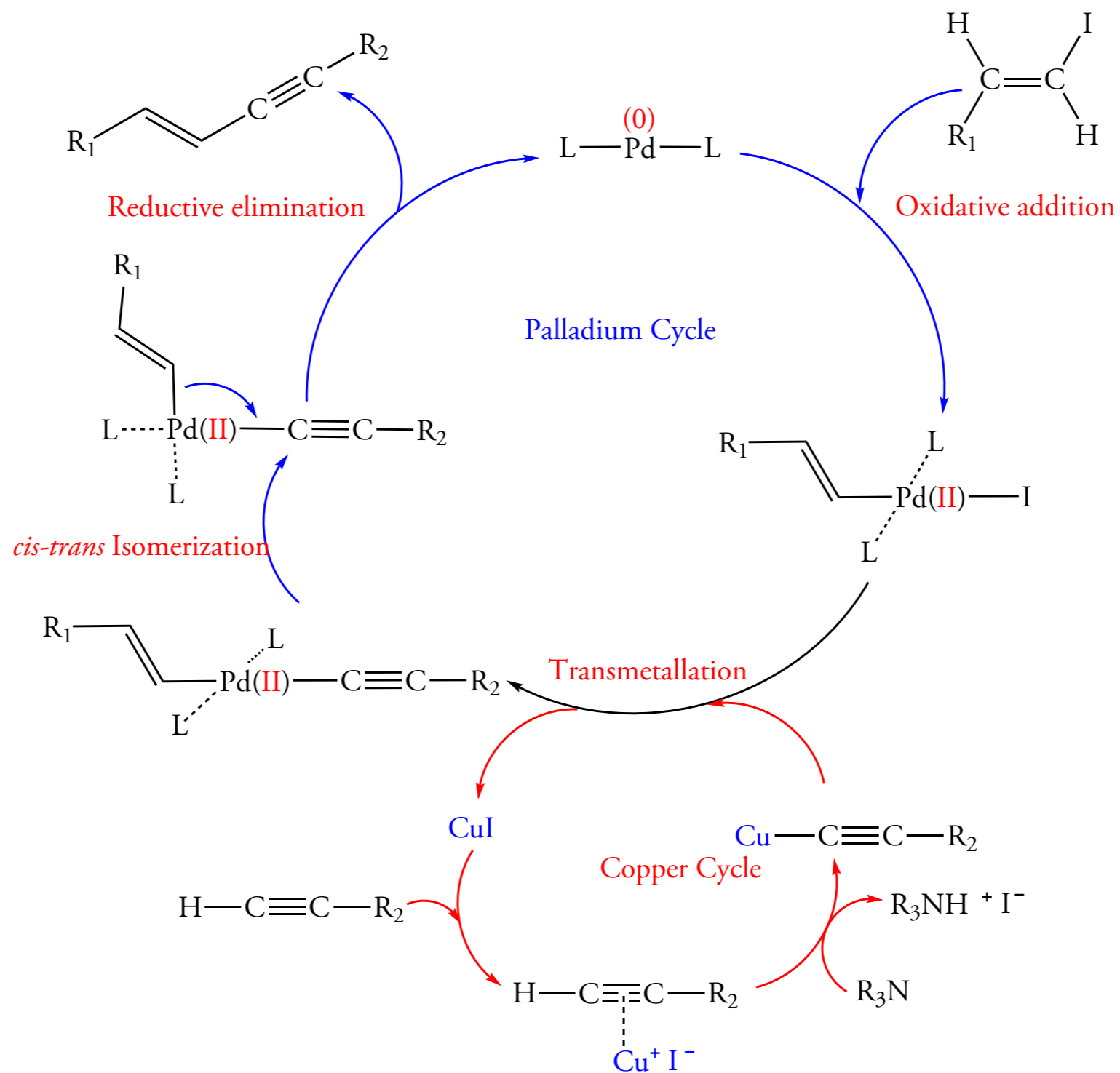


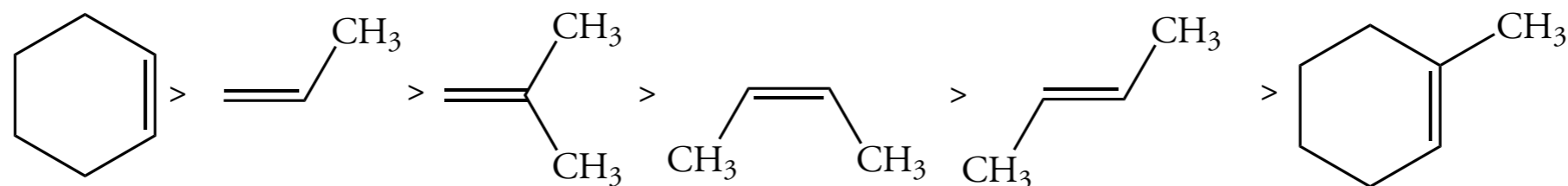
Figure 17.6 Catalytic Cycle of the Sonogashira Reaction

The Sonogashira reaction couples aryl and alkenyl halides with terminal alkynes. A Pd(0) catalyst, a copper(I) catalyst, and an amine base, which is the solvent, are required for the reaction.



17.7 THE WILKINSON CATALYST: HOMOGENEOUS CATALYTIC HYDROGENATION

Relative Reactivities of Alkenes in Wilkinson Homogenous Hydrogenation



Relative rates of hydrogenation by Wilkinson's catalyst

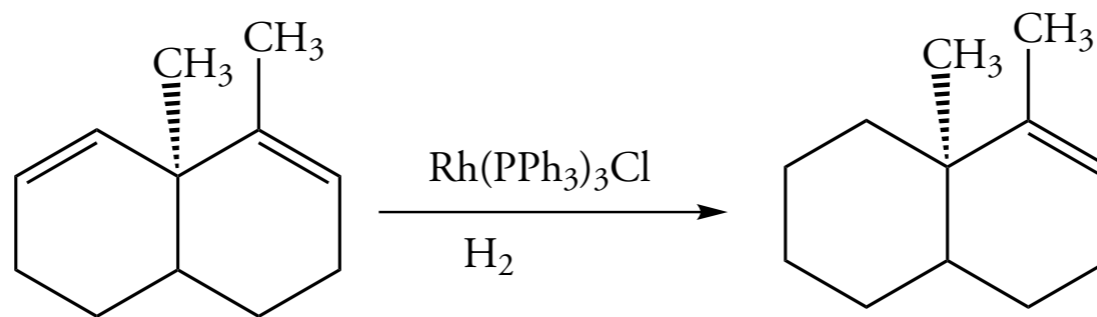
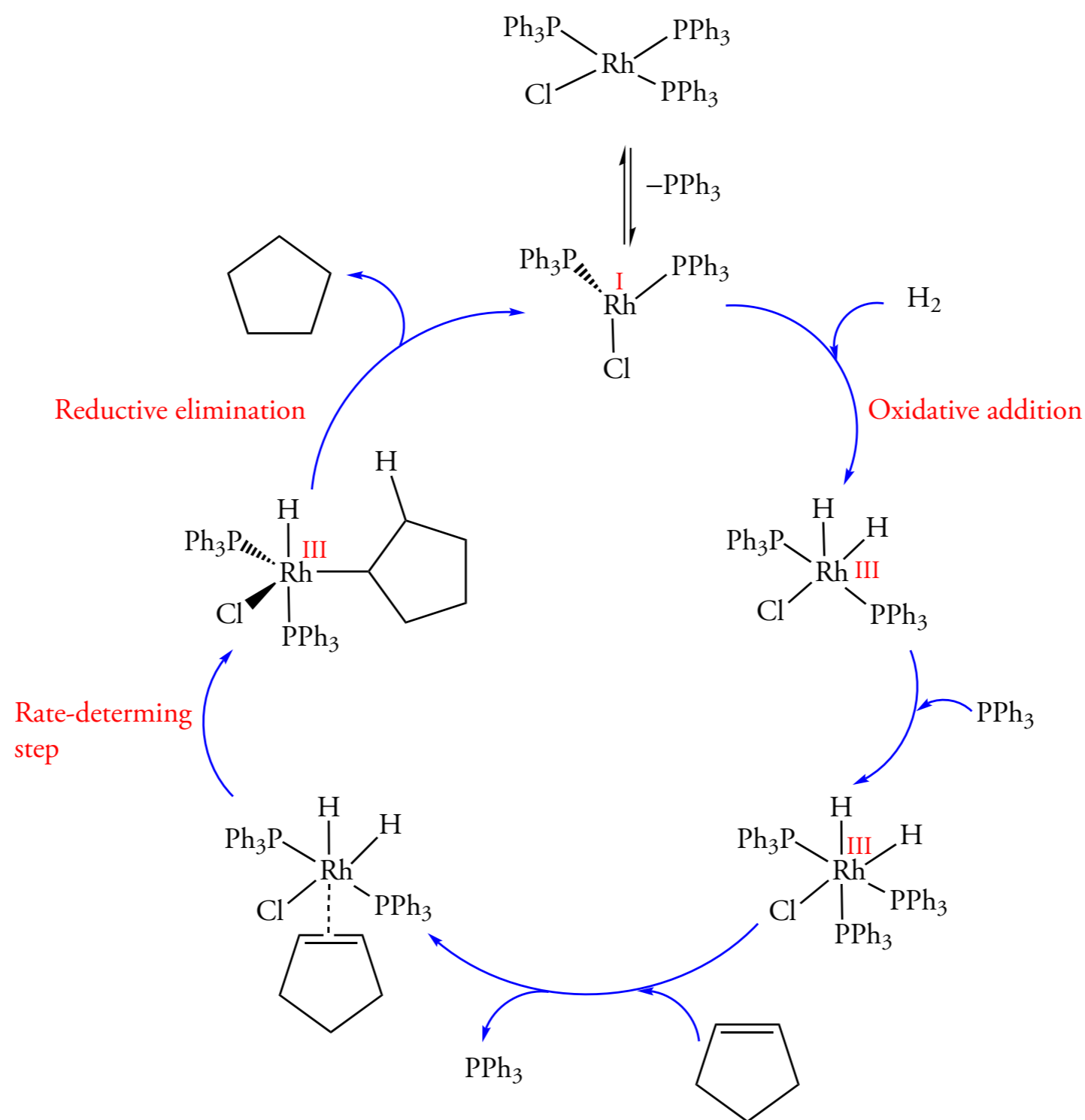


Figure 17.8 Catalytic Cycle of the Wilkinson Catalyst

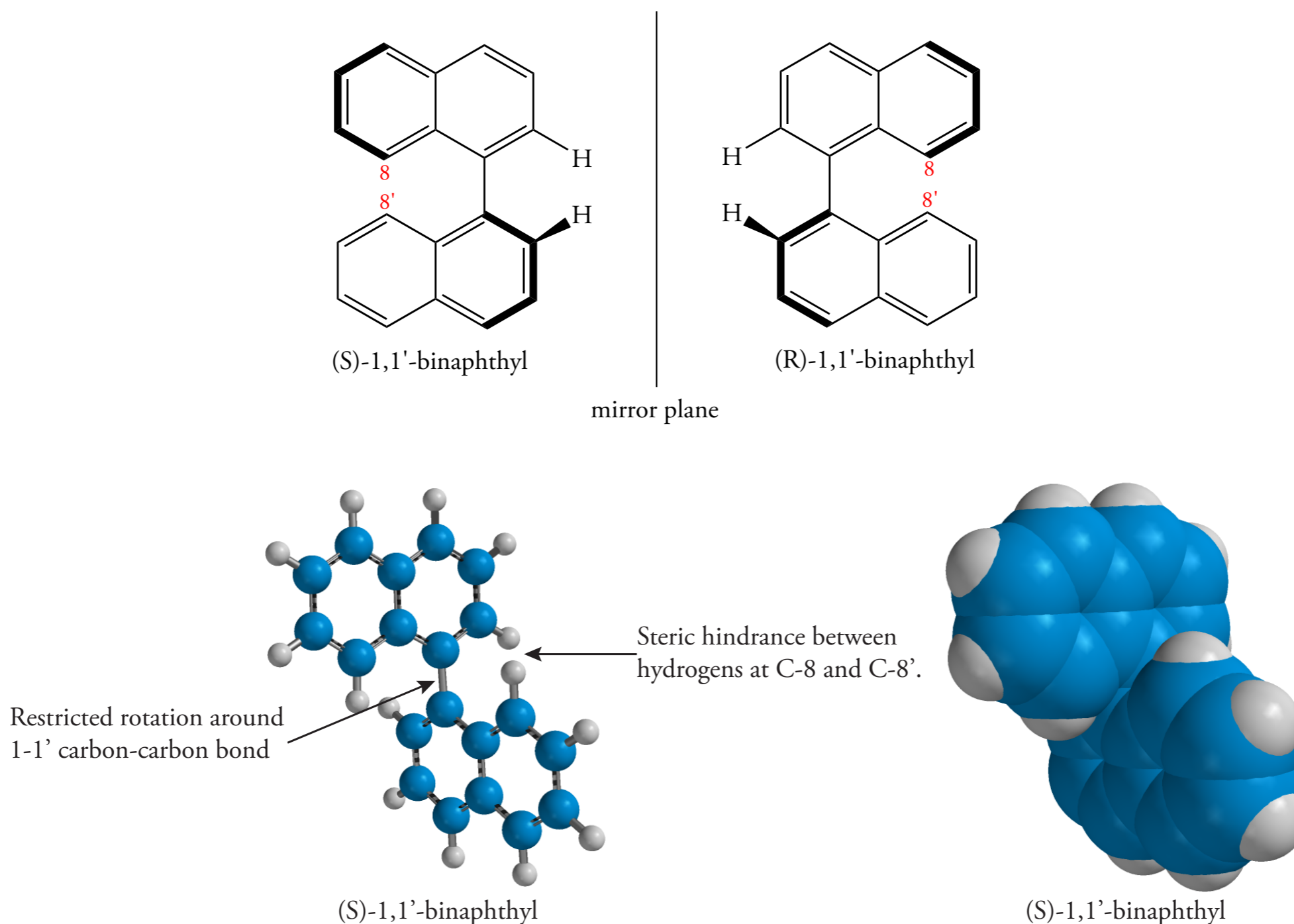
Wilkinson's catalyst carries out homogenous hydrogenation of alkenes. The initial rhodium(I) complex undergoes oxidative addition of hydrogen to give a rhodium(III) species. After a ligand exchange step, the alkene forms a π complex with the catalyst. The slow, rate-determining step of the reaction is addition of the first hydrogen atom to the double bond of the substrate. Reductive elimination releases the product and regenerates the catalyst in its +1 oxidation state.



17.8 ASYMMETRIC HYDROGENATION WITH CHIRAL RUTHENIUM CATALYSTS

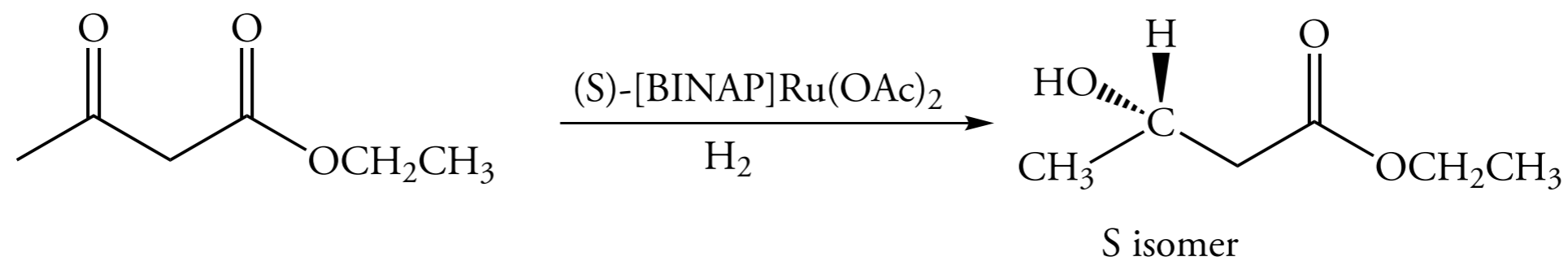
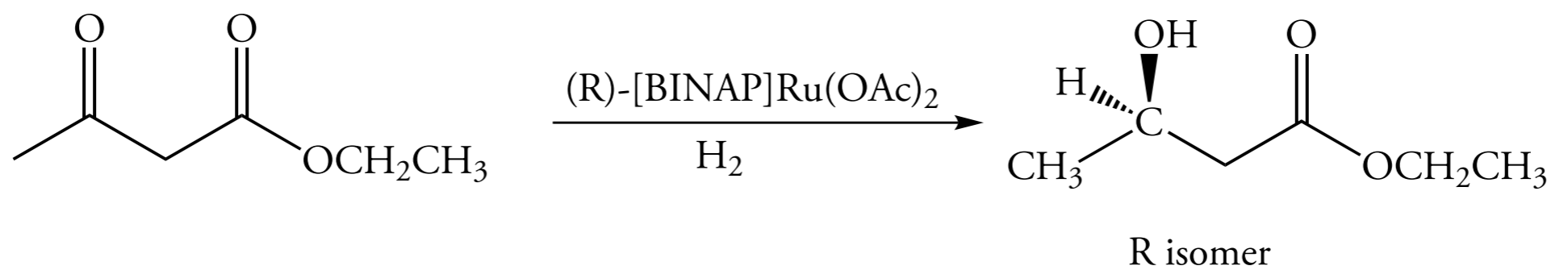
Figure 17.9 1,1'-Binaphthyl, a Chiral Ligand

Stereoisomers that result from restricted rotation around single bonds are atropisomers. (S)-1,1'-binaphthyl is an example of an atropisomer. The space-filling model is identical to the ball-and-stick model, but it shows the three-dimensional structure more clearly. The naphthyl groups cannot rotate around each other. Therefore, two nonsuperimposable, mirror-image isomers exist.

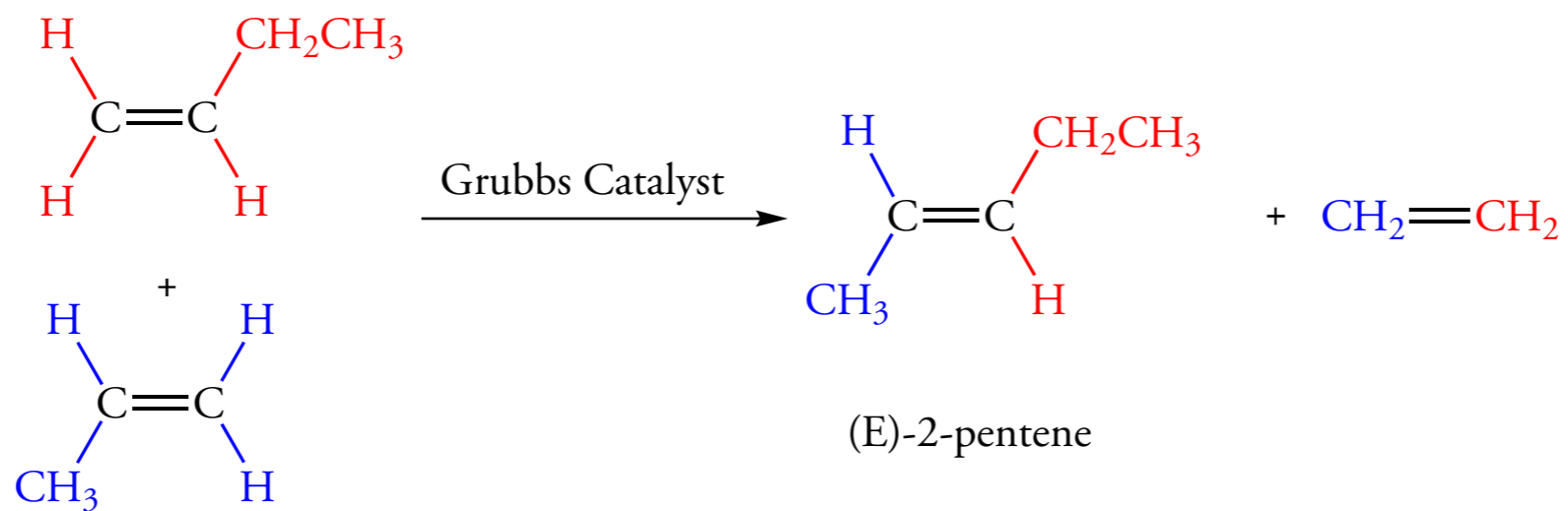
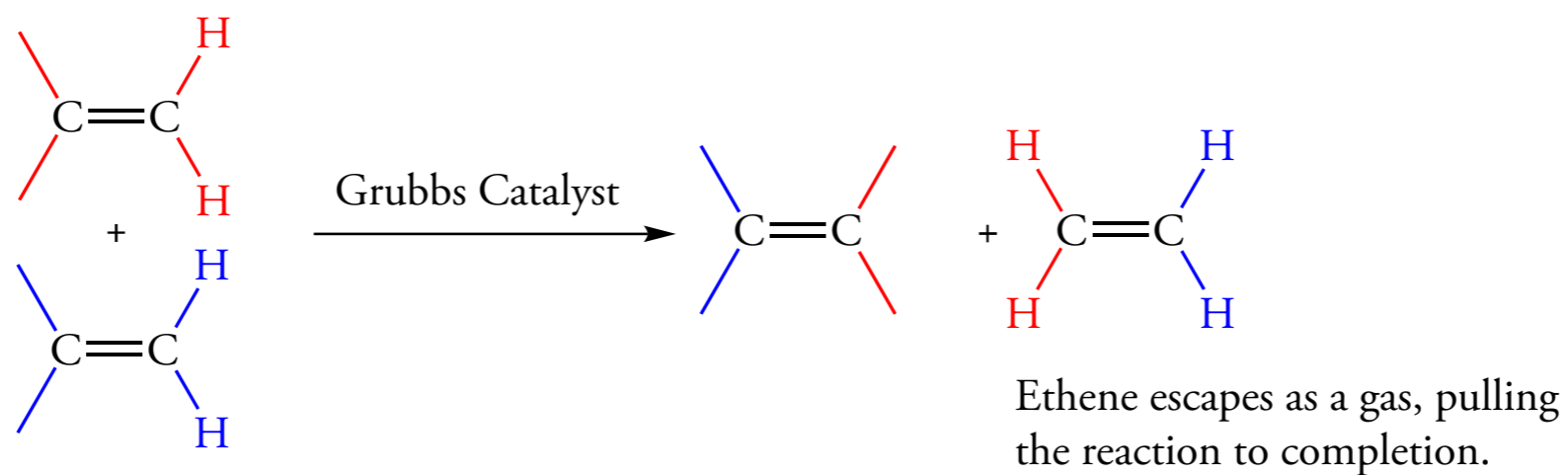
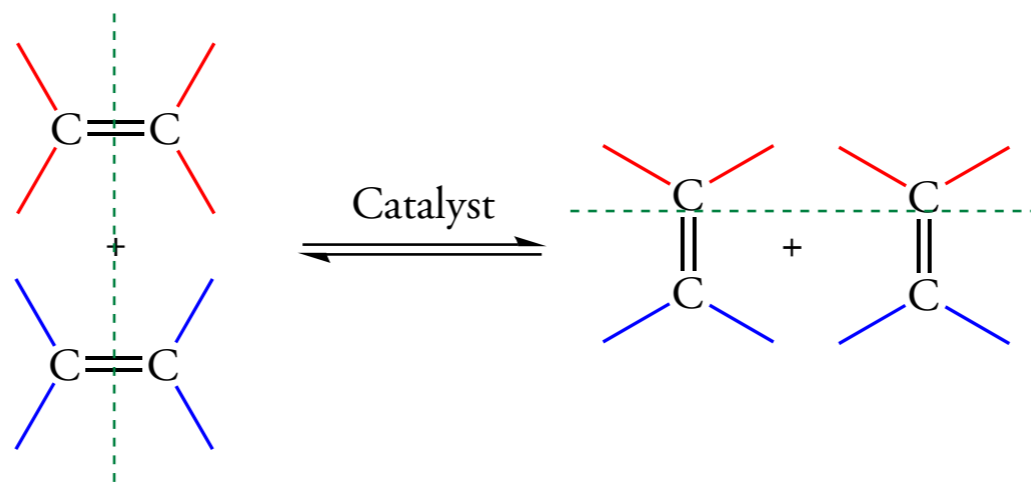


17.8 ASYMMETRIC HYDROGENATION WITH CHIRAL RUTHENIUM CATALYSTS

Noyori Asymmetric Reduction of Ketones



17.9 THE GRUBBS REACTION: A METATHESIS REACTION FOR ALKENE SYNTHESIS

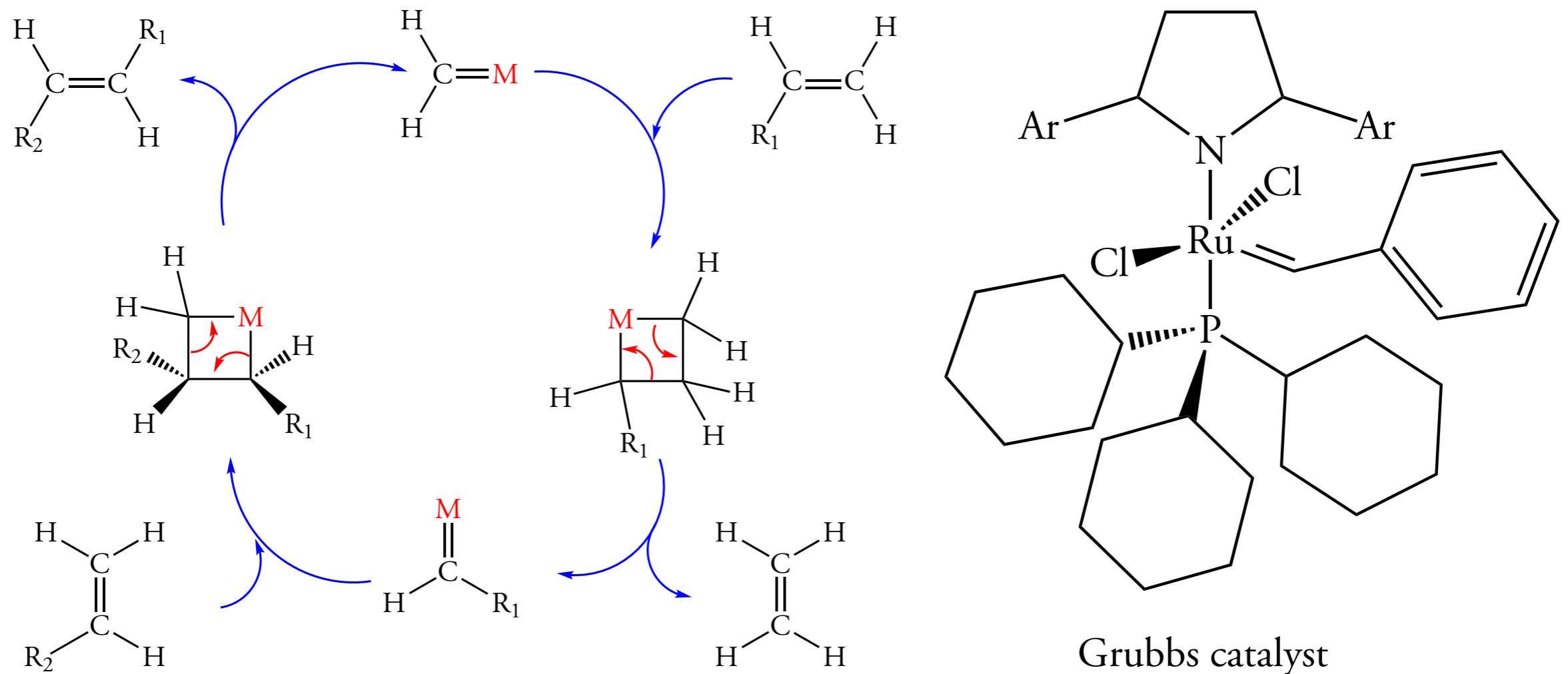


17.9 THE GRUBBS REACTION: A METATHESIS REACTION FOR ALKENE SYNTHESIS

The Grubbs Catalyst

Figure 17.10 The Grubbs Catalyst

The Grubbs catalyst is an organoruthenium complex. The π bond between carbon and ruthenium is the center at which the catalytic reaction occurs.

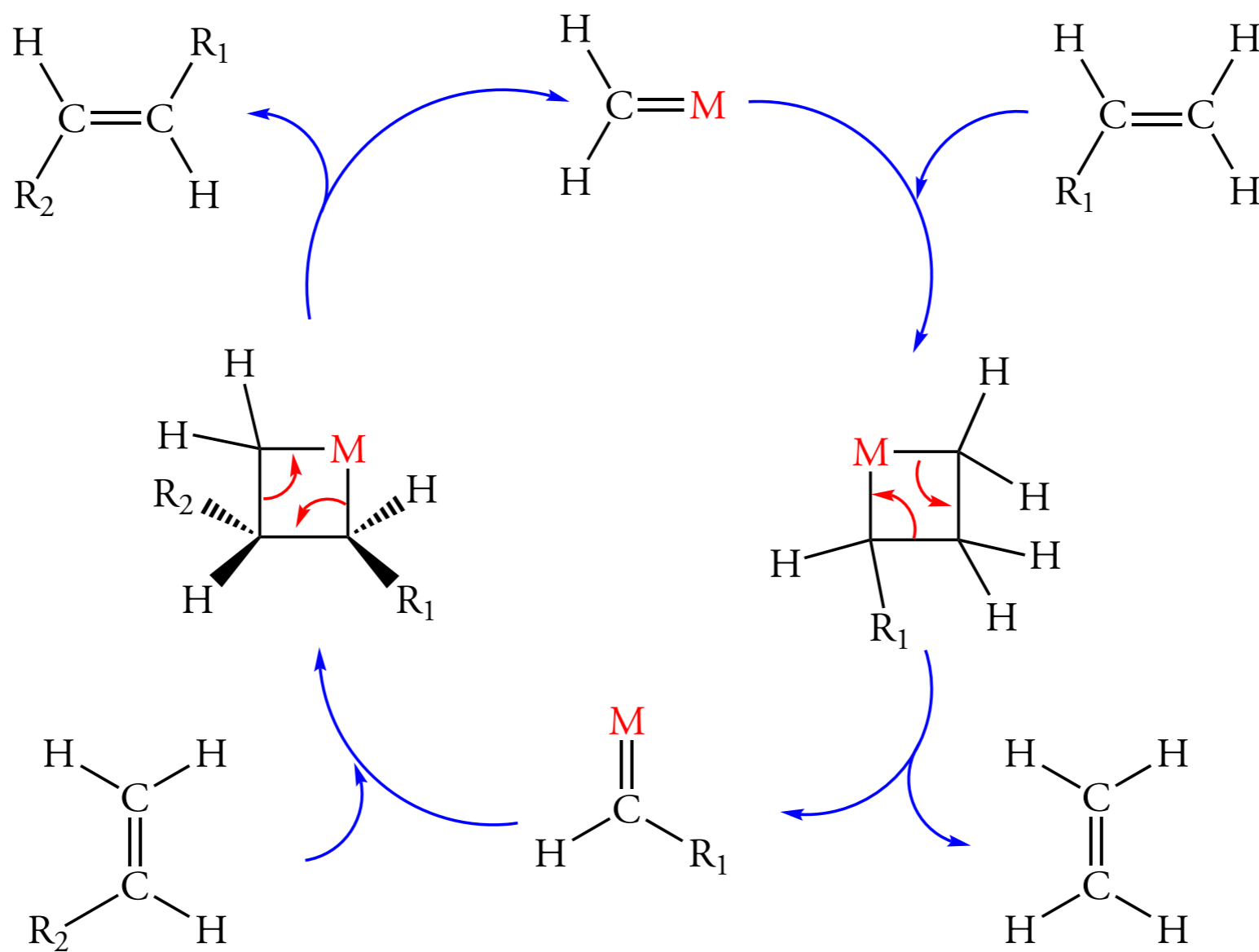


17.9 THE GRUBBS REACTION: A METATHESIS REACTION FOR ALKENE SYNTHESIS

The Chauvin Mechanism for the Grubbs Reaction

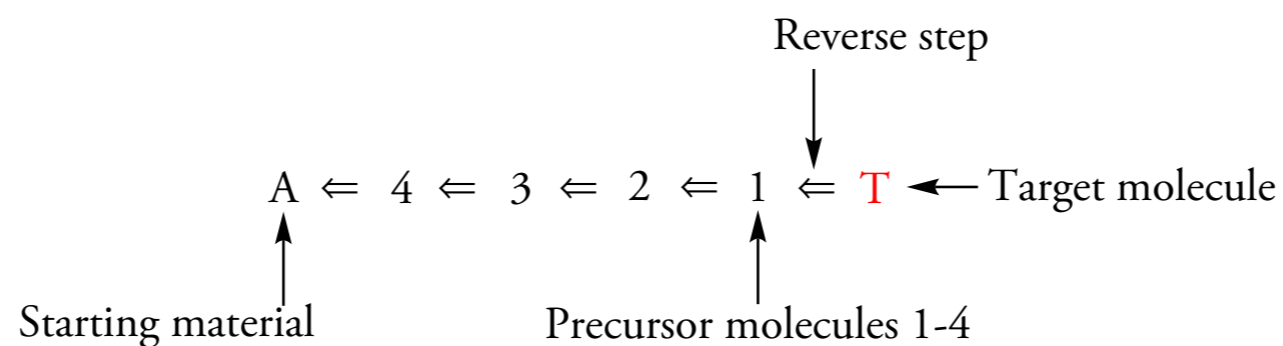
Figure 17.11 The Chauvin Grubbs Mechanism for the Grubbs Metathesis Reaction

The ligands of the Grubbs catalyst are omitted from the mechanism for clarity, and the ruthenium atom has been replaced with a generic transition metal, M. The catalytic cycle for the Grubbs reaction with two terminal alkenes generates ethene in each catalytic cycle. Ethene escapes as a gas, pulling the reaction to completion.

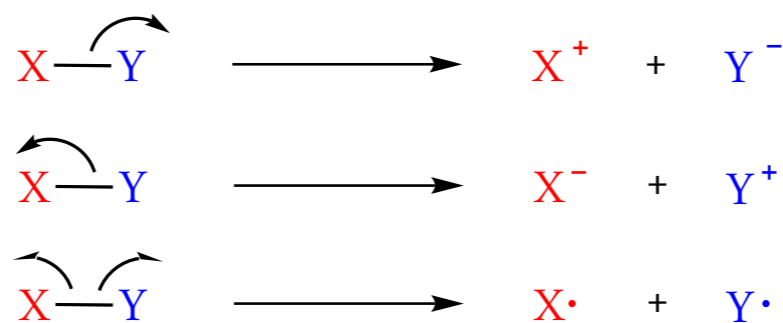


17.9 INTRODUCTION TO RETROSYNTHESIS: THINKING BACKWARDS

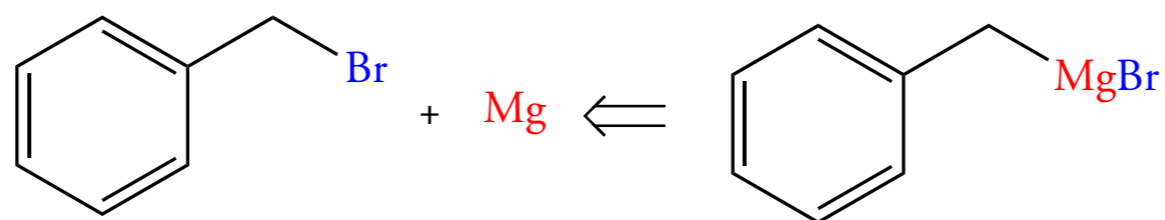
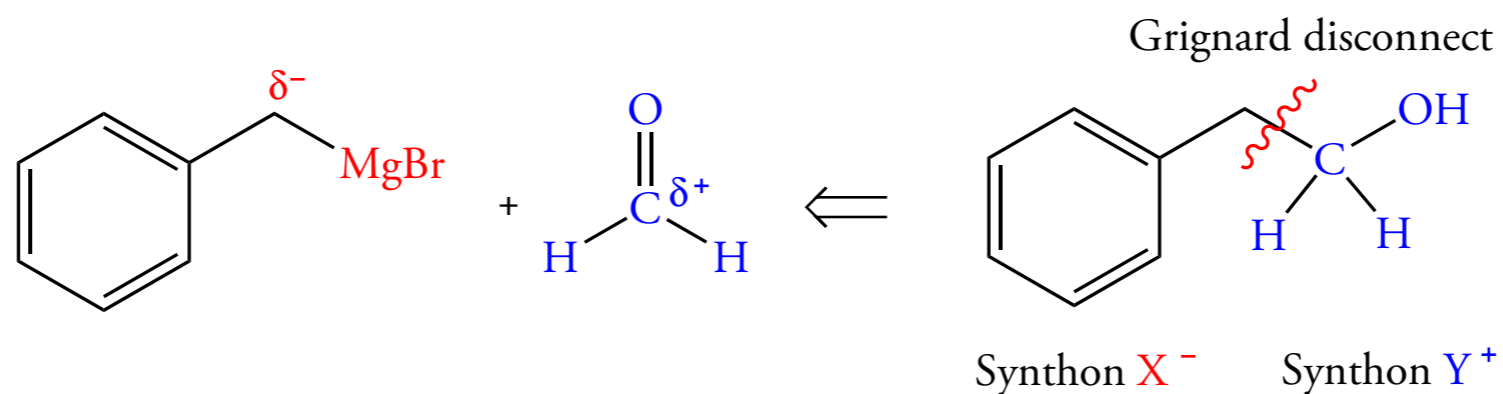
The Terminology of Retrosynthesis



Retrosynthetic Scheme I

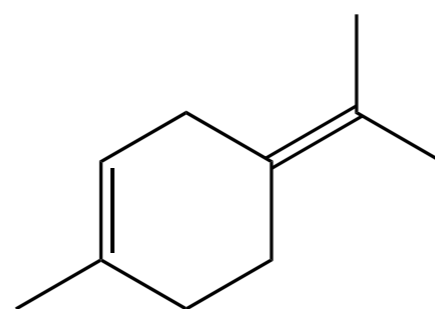


Types of Bond Disconnection

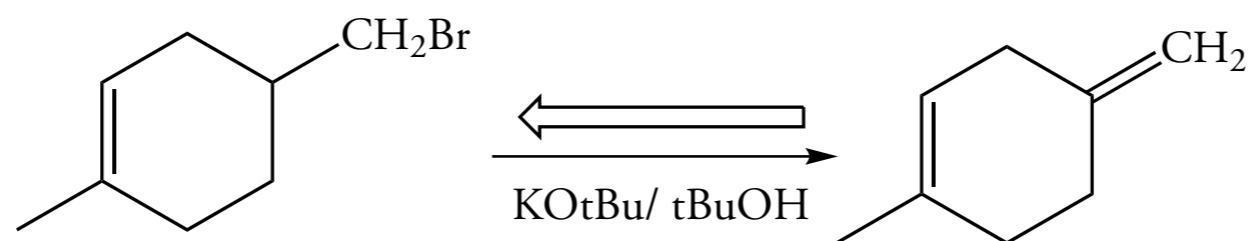
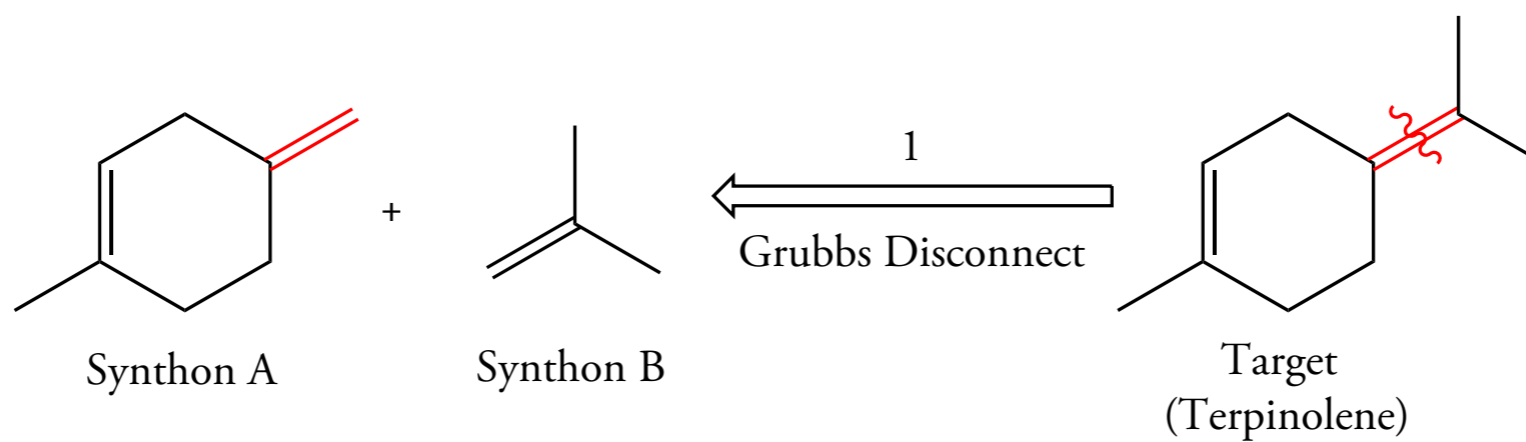


17.9 INTRODUCTION TO RETROSYNTHESIS: THINKING BACKWARDS

Synthesis of Terpinolene: A Retrosynthetic Analysis- Steps 4-6



Terpinolene
(1-methyl-4-isopropylidene-cyclohexene)



17.9 INTRODUCTION TO RETROSYNTHESIS: THINKING BACKWARDS

Synthesis of Terpinolene: A Retrosynthetic Analysis- Steps 1-3

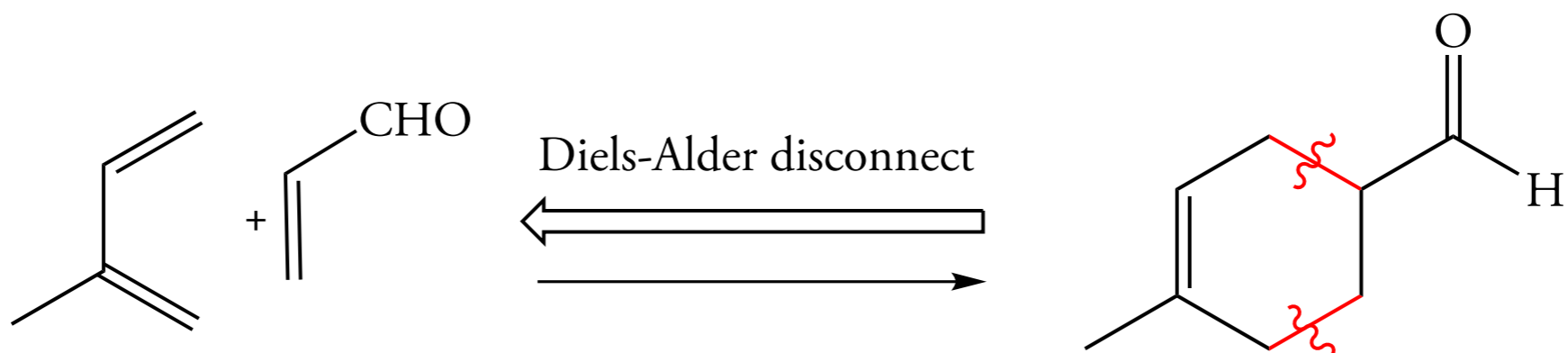
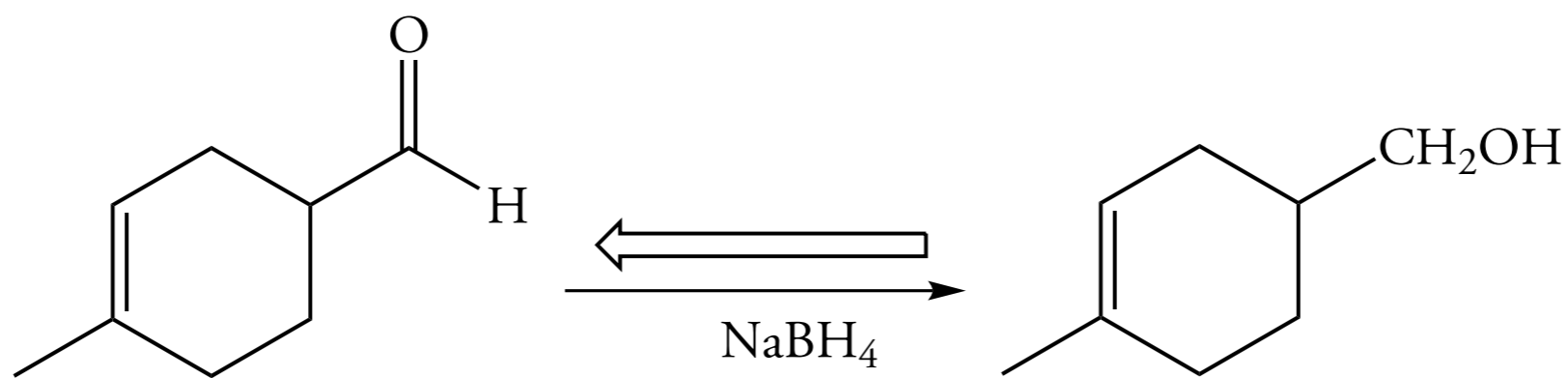
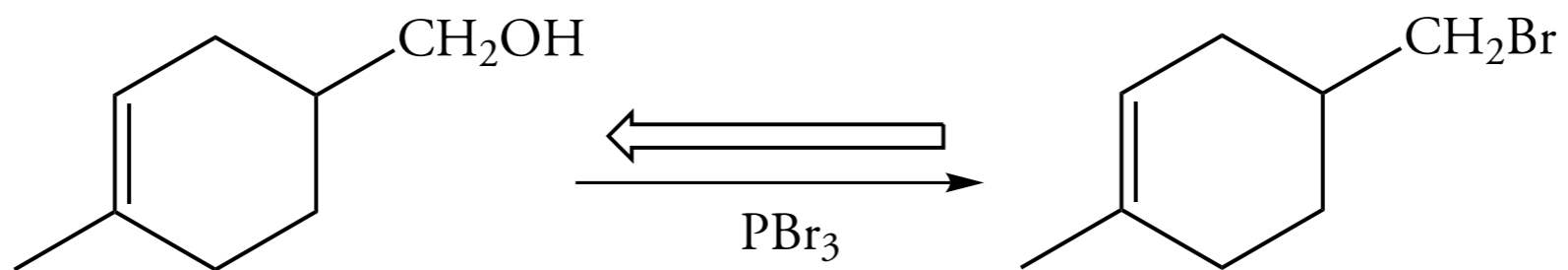


Figure 17.11 Retrosynthetic Scheme for the Synthesis of Terpinolene

The synthesis would proceed in reverse order; that is, from retrosynthetic step 5 to retrosynthetic step 1. First, a Diels-Alder reaction yields the six-membered ring with the methyl group and the aldehyde side chain in the correct positions to give terpinolene. We see in the Grubbs disconnect how to convert 1-methyl-4-methylidene-cyclohexene into terpinolene. We need a methylidene group at C-4 of the six membered ring to have the reactants we need for the Grubbs metathesis reaction. We can convert the aldehyde group to a methylidene group by a series of functional group conversions.

