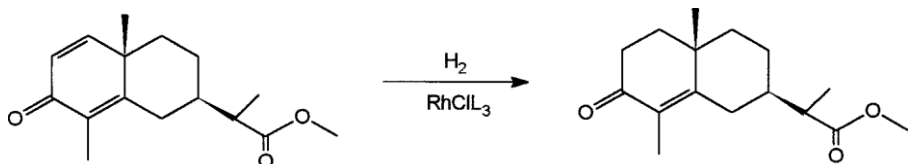


HYDROGENATION OF ALKENES

The industrial importance of homogeneous hydrogenation lies mainly in the fact that by using a chiral catalyst hydrogenated chiral products could be obtained from prochiral alkenes (see Table 9.1). With achiral catalysts also, a very high degree of chemo- and regioselectivity could be obtained. An example of this is shown by reaction (7.2). As could be seen, the disubstituted



(7.2)

rather than the trisubstituted alkene functionality is preferentially hydrogenated. Hydrogenation of alkenes is one of the most well-studied homogeneous catalytic reactions.

In the following section, we discuss the basic mechanism of homogeneous hydrogenation by Wilkinson's catalyst, $\text{RhCl}(\text{PPh}_3)_3$. Many other complexes of rhodium as well as complexes of other metals such as ruthenium, platinum, lutetium, etc. have also been used as homogeneous, laboratory-scale, hydro- genation catalysts. The mechanisms in all these cases may differ substantially.

Catalytic Cycle

The basic mechanism of hydrogenation is shown by the catalytic cycle in Fig.

7.3. This cycle is simplified, and some reactions are not shown. Intermediate

7.9 is a 14-electron complex (see Section 2.1). Phosphine dissociation of Wil- kinson's complex leads to its formation. Conversion of 7.9 to 7.10 is a simple oxidative addition of H_2 to the former. Coordination by the alkene, for example, 1-butene, generates 7.11. Subsequent insertion of the alkene into the metal–hydrogen bond gives the metal alkyl species 7.12. The latter undergoes reduc- tive elimination of butane and regenerates 7.9.

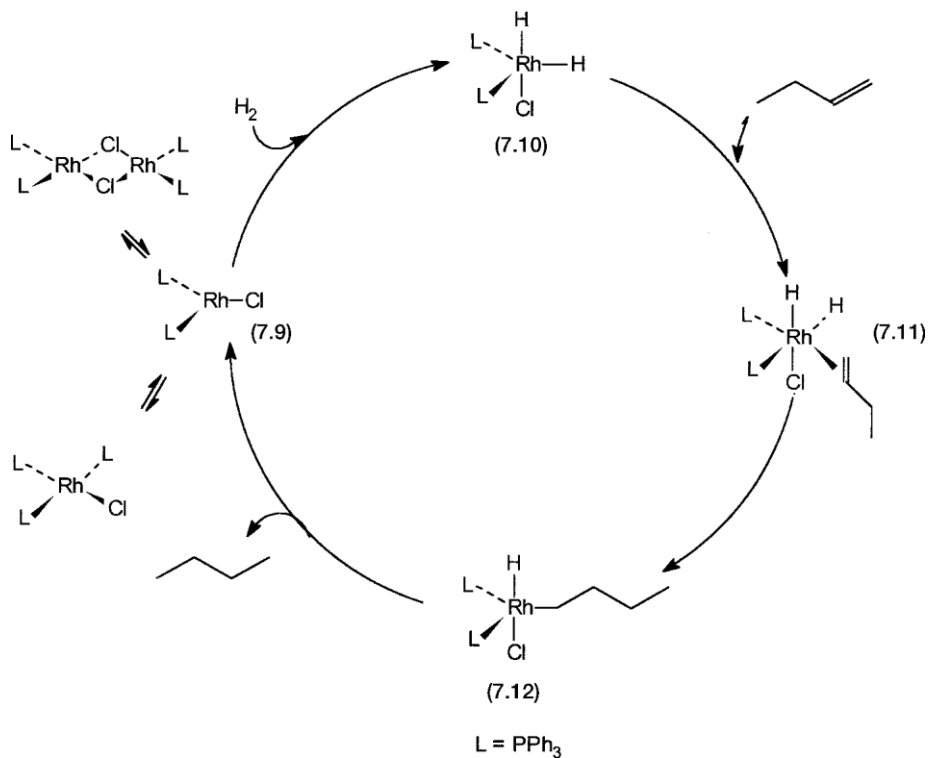


Figure 7.3 Hydrogenation by Wilkinson's catalyst. For butene, oxidative addition of H₂ precedes alkene coordination but not necessarily for all other alkenes.

Note that although the conversion of 7.11 to 7.12 assumes anti-Markovnikov addition, the Markovnikov product also gives butane. Conversion of 7.9 to 7.11 could also take place by prior coordination of alkene followed by the oxidative addition of dihydrogen. Indeed this parallel pathway for the formation of 7.11 does operate. Like the equilibrium shown between RhClL_3 , 7.9, and the dimer $[\text{RhClL}_2]_2$, there is an equilibrium between 7.9 and the alkene coordinated complex $\text{RhCl}(\text{alkene})\text{L}_2$.

OLIGOMERIZATION OF ETHYLENE

Oligomerization of ethylene to give linear terminal alkenes or the so-called *a*-olefins is a very important industrial reaction. The linear *a*-olefins with 10 to

18 carbon atoms are important feed stock for a variety of detergents. Oligomers with 4– 10 carbon atoms find uses as co-monomers in the manufacture of poly- ethylene and also as starting materials for the manufacture of plasticizer alco- hols by the hydroformylation reaction.

Industrial processes utilize aluminum or nickel complexes as catalysts for oligomerization. Both Gulf Oil and Ethyl Corporation use aluminum alkyls, while the Shell higher olefin process (SHOP) involves the use of a nickel catalyst. Both these basic reactions (i.e., oligomerization of ethylene by alu- minum alkyl, “Aufbaurektion,” and the fact that in the presence of nickel such an oligomerization reaction yields mainly butene (the “nickel effect”), were discovered by Ziegler in the early 1950s. The mechanism of oligomerization is basically the same as that of ethylene polymerization (see Section 6.4.1). However, in this case chain termination by *p*-elimination has to occur far more frequently to keep the chain length down.

Stoichiometric reaction of the type shown by 7.4 also leads to the formation of ethylene oligomers. In the Ethyl Corporation process one step involves stoi- chiometric reaction of this type. Another variant of this is the Conco process, where such stoichiometric reactions are followed by oxidation and hydrolysis of the aluminum alkyls. This gives linear *a*-alcohols that are used in biode- gradable detergents. The co-product is highly pure alumina, which has a variety of uses, including that of an acidic heterogeneous catalyst.



Shell Higher Olefin Process

SHOP involves essentially four sequential operations. First ethylene is oligo- merized with a soluble nickel catalyst to give linear *a*-alkenes. In the second step, over a heterogeneous catalyst these are isomerized to internal alkenes. In the third step internal alkenes containing four to eight carbon atoms are mixed with internal alkenes of 20 and more carbon atoms and the mixture is subjected to the metathesis reaction (see Section 7.6). In the

fourth step three reactions

— isomerization, hydroformylation, and hydrogenation— are simultaneously carried out with a homogeneous cobalt catalyst to give long-chain α -alcohols. The reactions of the fourth step were discussed in Chapter 5 (see Table 5.1 and Section 5.3). The sequence of reactions is schematically shown in Fig. 7.5. In this section, we discuss only the first step, the oligomerization of ethylene to give linear α -olefins by soluble nickel catalysts.

As already mentioned, the mechanism of oligomerization is the same as discussed for polymerization, and a catalytic cycle similar to the one shown in Fig. 6.3 operates. Many nickel– phosphine complexes have been successfully used as the precatalysts; 7.17 is one such example. As shown by 7.5, reaction of a phosphorous ylide with a suitable nickel-containing precursor makes this

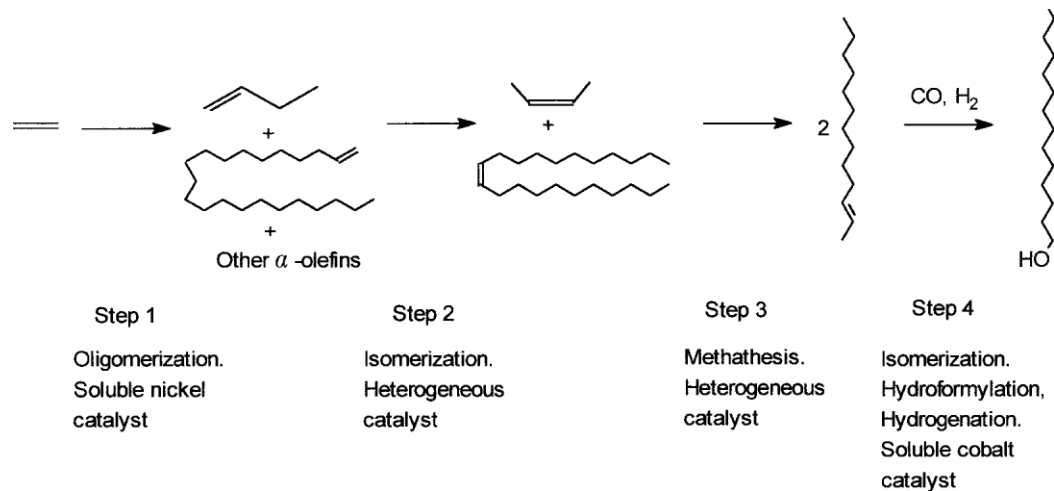
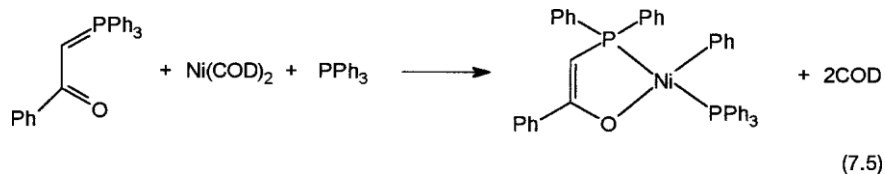
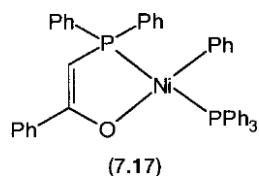


Figure 7.5 The four steps of Shell's higher olefin process (SHOP). Four- and 22-carbon-atom alkenes are taken as representative examples.

complex. The selectivity of the oligomerization reaction is largely controlled by the chelating ligand.



Under the reaction conditions the precursor complex probably generates a nickel–hydride species, which then initiates the oligomerization reaction. Evidence for this comes from the studies on the reactions of 7.17. As shown by 7.6, on reaction with ethylene 7.17 eliminates styrene and produces a nickel–hydride complex. A model catalytic intermediate 7.18 has been characterized by single-crystal X-ray studies. Complex 7.18 reacts with ethylene to give a nickel–ethyl species in a reversible manner. This is shown by reaction 7.7. Reactions 7.6 and 7.7 are strong evidence for the involvement of a nickel–hydride catalytic intermediate.

