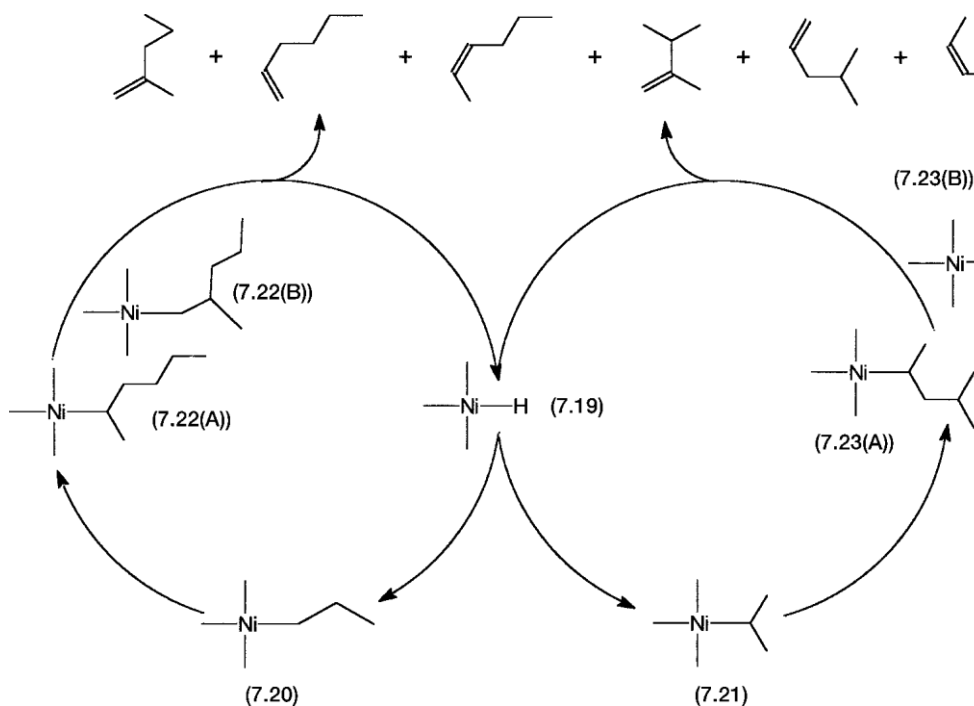


## Dimerization of Propylene

The dimerization of propylene carried out by IFP is called the DIMEROSOL process and involves the use of nickel catalysts. This is shown in Fig. 7.7. Complexes 7.20 and 7.21 are the anti-Markovnikov and Markovnikov insertion products into the Ni–H bond. Structures 7.23(A) and (B) are intermediates derived from 7.21 by inserting the *second* propylene molecule in a Markovnikov and anti-Markovnikov manner, respectively. Similarly 7.22(A) and (B) are intermediates from 7.20 by the insertion of the second propylene molecule. These four nickel–alkyl intermediates by *p*-elimination give six alkenes. Under the process conditions these alkenes may undergo further isomerization.

## Di- and Trimerization of Butadiene

Both di- and trimerization of butadiene with soluble nickel catalysts are well-established homogeneous catalytic reactions. The precatalyst having nickel in the zero oxidation state may be generated in many ways. Reduction of a Ni<sup>2+</sup> salt or a coordination complex such as Ni(acac)<sub>2</sub> (acac = acetylacetonate) with alkyl aluminum reagent in the presence of butadiene and a suitable tertiary phosphine is the preferred method. The nature of the phosphine ligand plays an important role in determining both the activity and selectivity of the catalytic

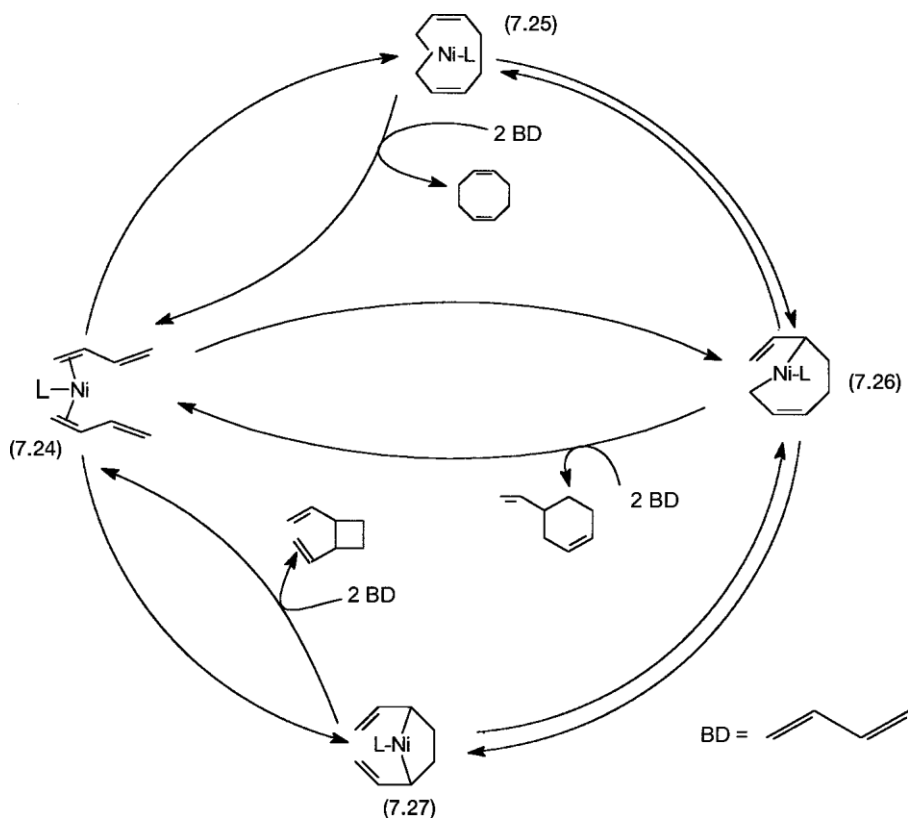


**Figure 7.7** Catalytic cycles for propylene dimerization. For the first propylene molecule the left and right cycles represent the anti-Markovnikov and Markovnikov pathways, respectively. Note that for 7.22(A) and 7.23(A) there are two *b*-hydride positions.

system. The other products that may be formed in this reaction are vinylcyclohexene and divinylcyclobutane. By an optimal choice of ligand and reaction conditions, formation of these by-products may be avoided to a large extent, and 1,5-cyclooctadiene may be obtained with >96% selectivity.

The catalytic cycle proposed for the dimerization of butadiene is shown in Fig. 7.8. As shown by 7.24, two molecules of butadiene coordinate to NiL. A formal oxidative addition, as shown by Eq. 7.8, produces two nickel-carbon bonds and the carbon-carbon bond required for ring formation. The structure of 7.25 with

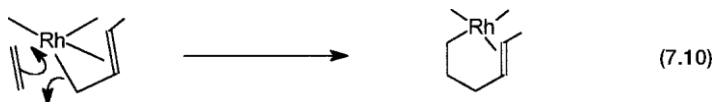
two nickel– carbon bonds (see Fig. 7.8), is a hypothetical one that helps us to understand the carbon–carbon bond formation process. The actual catalytic intermediates that have been observed by spectroscopy have an  $\mu^3$ - allyl type of bonding. As shown by reaction 7.9, species 7.25 can reductively eliminate 1,5-cyclooctadiene and the zerovalent nickel complex Ni–L.

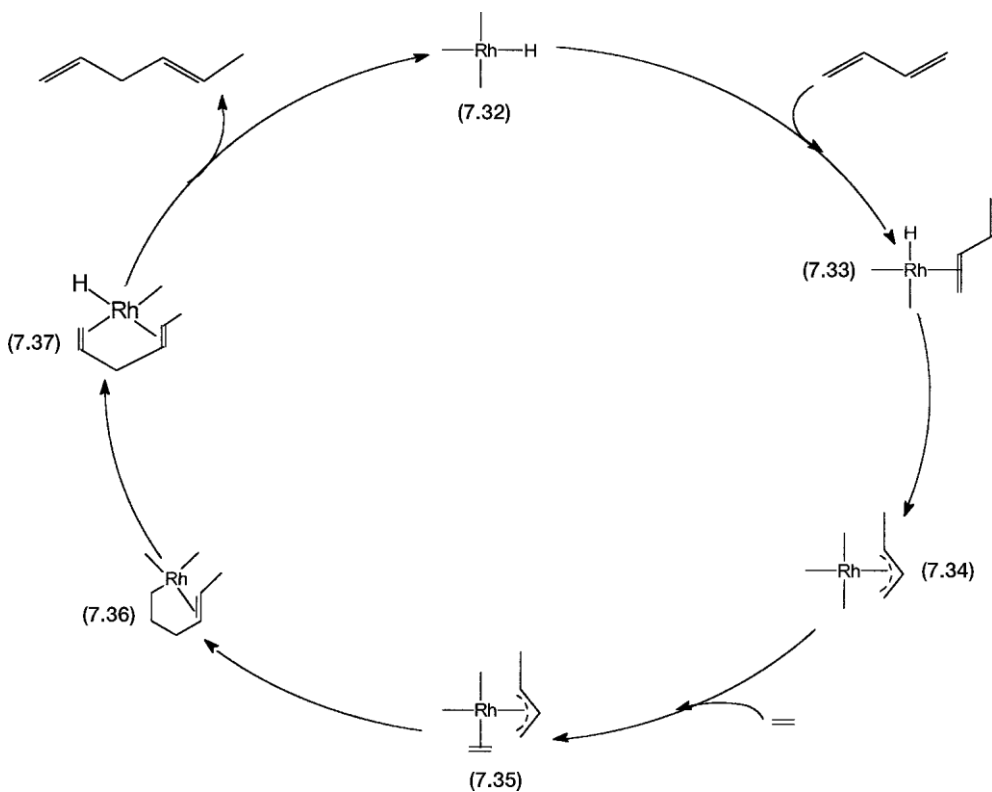


**Figure 7.8** Dimerization of butadiene. L is a phosphine or phosphite (see Problem 11). 7.26 and 7.27 can be formed from butadiene (BD) and L–Ni

### Dimerization of Butadiene with Ethylene

Butadiene and ethylene are codimerized with a soluble rhodium– phosphine complex as the catalyst. Very little has been reported on the mechanistic evidence for this reaction. However, a catalytic cycle as shown in Fig. 7.9 involving a rhodium hydride seems likely. Reducing rhodium trichloride with ethanol in the presence of a tertiary phosphine generates the hydride complex 7.32. The 1,4-hydride attack on the coordinated butadiene gives an  $\mu^3$ -allyl complex. This is shown by the conversion of 7.33 to 7.34. Ethylene coordination to 7.34 produces 7.35. The latter undergoes insertion of ethylene into the rhodium– carbon  $\sigma$  bond to give 7.36. The formal mechanism for the formation of 7.36 is shown by reaction 7.10. Complex 7.36 undergoes  $\beta$ -elimination to generate 7.37, which liberates 1,4-hexadiene and completes the catalytic cycle.





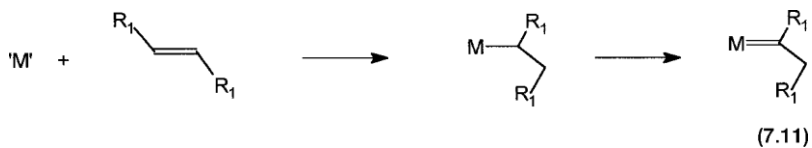
**Figure 7.9** Dimerization of butadiene and ethylene by a rhodium–hydride catalyst. Note the allyl bonding proposed in 7.34 and 7.35.

shown in Fig. 7.11 consists of these three basic steps. The alkylidene species

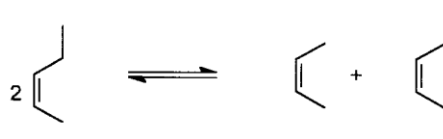
7.38 or 7.40 is formed by the reactions of the precatalyst M, with the two hypothetical alkenes.

The most likely way that this can happen is through the formation of metal–alkyls followed by  $\alpha$ -elimination, as shown by reaction 7.11. The primary alkylidene species thus generated can undergo reactions 7.12 and 7.13. The alkenes that are generated in reaction 7.12 and 7.13 are obviously not the products of the catalytic cycle; they are generated only initially when the pre-catalyst is converted into the active catalytic

intermediates. Note that similar pathways involving the other alkene also exist. These are not shown.



EXCHANGE / DISPROPORTIONATION  
METATHESIS



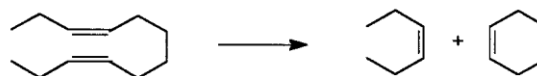
RING-OPEN METATHESIS  
POLYMERIZATION (ROMP)



RING CLOSURE  
POLYMERIZATION



DEGRADATIVE  
METATHESIS



**Figure 7.10** Different types of metathesis reaction. The first two have found significant use in industry.