HYDROCYANATION

DuPont manufactures adiponitrile (ADN), a raw material for nylon 6,6, by the hydrocyanation of butadiene using homogeneous nickel catalysts. As shown

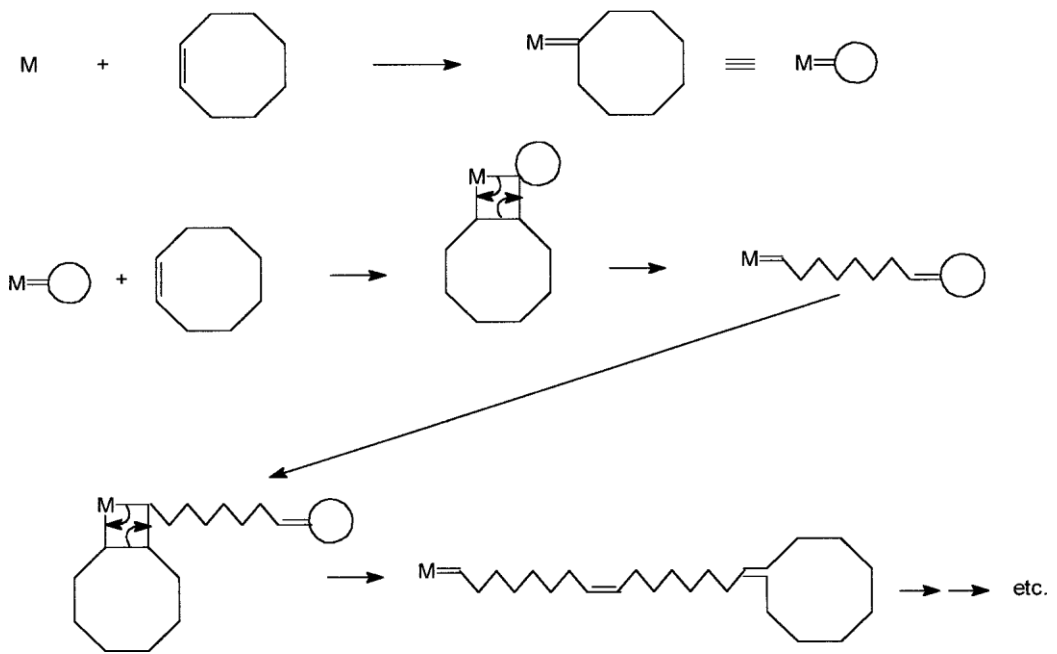
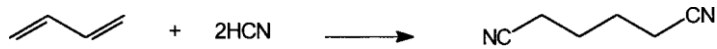


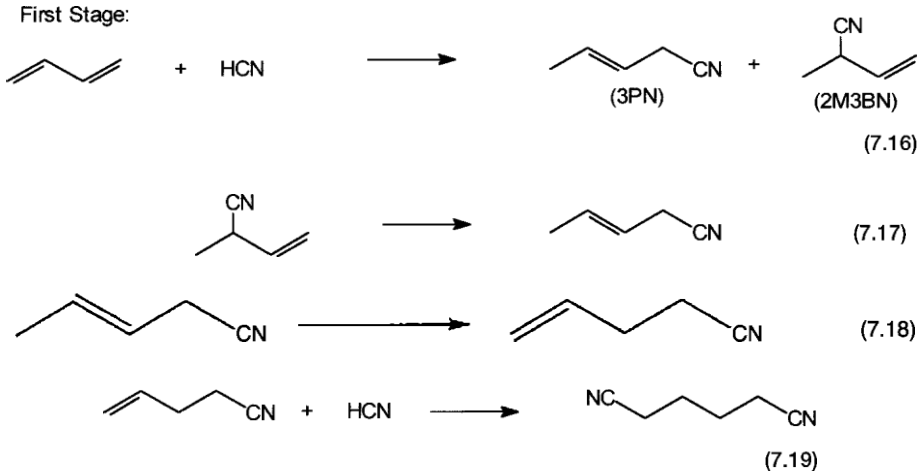
Figure 7.12 Ring-opened metathesis polymerization (ROMP) of cyclooctene. Note that ROMP could be initiated with any M—CR_2, and for a living polymer the end group will be CH—CR_2.

by reaction 7.15, this involves the addition of two molecules of HCN to buta- diene.



(7.15)

The reaction is carried out in two stages. In the first stage one molecule of HCN is added to butadiene to give 3-pentenenitrile (3PN) and 2-methyl 3- butenenitrile (2M3BN) by anti-Markovnikov and Markovnikov addition of the CN^- group, respectively. Under the reaction conditions, as shown by reaction 7.17, 2M3BN is isomerized to 3PN. So the first stage involves reactions 7.16 and 7.17. In the second stage 3PN is isomerized to 4-pentenenitrile and the second molecule of HCN is added to 4-pentenenitrile to give ADN, the desired product. Reactions 7.18 and 7.19 show these steps.



The hydrocyanation reaction is important not only because it is practiced industrially on a large scale, but also because it clearly illustrates some of the fundamental postulates of homogeneous catalysis. The potential of the hydro- cyanation reaction in asymmetric catalysis has also been explored and appears to be promising (see Chapter 9).

Catalysts for Hydrocyanation

All the reactions of the hydrocyanation process are catalyzed by zero-valent nickel phosphine or phosphite complexes. These are used in combination with Lewis acid promoters such as zinc chloride, trialkyl boron compounds, or tri- alkyl borate ester. The ability of the precatalyst to undergo ligand dissociation

followed by oxidative addition of HCN plays a crucial role in the hydrocya- nation reaction. The Lewis acid is very important for the facile and selective formation of 3PN and ADN in the first and the second stage, respectively.

The energetics of the ligand dissociation process, reaction 7.20, depends on the electronic and steric characteristics of the ligand. The equilibrium constants for different Ls are found to be correlated to the cone angles of the phosphorus ligand: The larger the cone angle, the bigger the equilibrium constant. However, the rate at which this equilibrium is established (i.e., the kinetics of the process) does not appear to depend on the steric bulk.

$$NiL_4 \rightleftharpoons NiL_3 + L \qquad (7.20)$$

The essential role of the Lewis acid is to act as an electron acceptor of the nitrogen lone pair of the coordinated cyano group. Such an interaction increases the steric crowding in catalytic intermediates, weakens the Ni– CN bond, and stabilizes the catalytic intermediates with respect to degradation. The net effect is an enhancement in the rates of formation of the desired products in both stages of the hydrocyanation process. The Lewis acid interacts with the coor- dinated cyano group rather than the nitrile functionality of the free nitrile. This is because of the higher Lewis basicity of the coordinated cyano group.

Catalytic Cycle for the First Stage

The catalytic cycle for the formation of 3PN and 2M3BN is shown in Fig.

The following points deserve attention. First, interactions of Lewis acid with the coordinated cyano groups are not shown. The evidence for such in- teractions comes from full characterization of $HNiL_3CN–BPh_3$ (L = *o*-tolylphosphite) as well as detailed IR and multinuclear NMR studies of a num- ber of analogous nickel complexes. Second, the intermediates NiL_3 and 7.45–
7.47 are well characterized by IR and multinuclear NMR techniques. Single crystal X-ray structures of NiL_2 (alkene), where the alkene is ethylene or ac- rylonitrile and L is *o*-tolyl phosphite, have been determined. These are obvious models for

the proposed intermediates 7.48 and 7.50. As both these intermediates are 16-electron species, addition of L to give 7.49 or 7.51 prior to the elimination of 3PN or 2M3BN are reasonable mechanistic steps.

Although for clarity the reactions of Fig. 7.13 are shown to be unidirectional, all the reactions of the catalytic cycle are in fact reversible. This is an important aspect of the first stage of the hydrocyanation process. It provides for a mech- anism for the isomerization of the unwanted 2M3BN to the desired 3PN. The isomerization reaction of 2M3BN to 3PN has been studied by deuterium- labeling experiments. The results are consistent with a mechanism where bu- tadiene is formed in one of the intermediate steps. This means that the revers- ibility of all the steps allows isomerization to follow the path: 7.51 □ 7.50 □ 7.47 □ 7.46 □ 7.47 □ 7.48 □ 7.49.

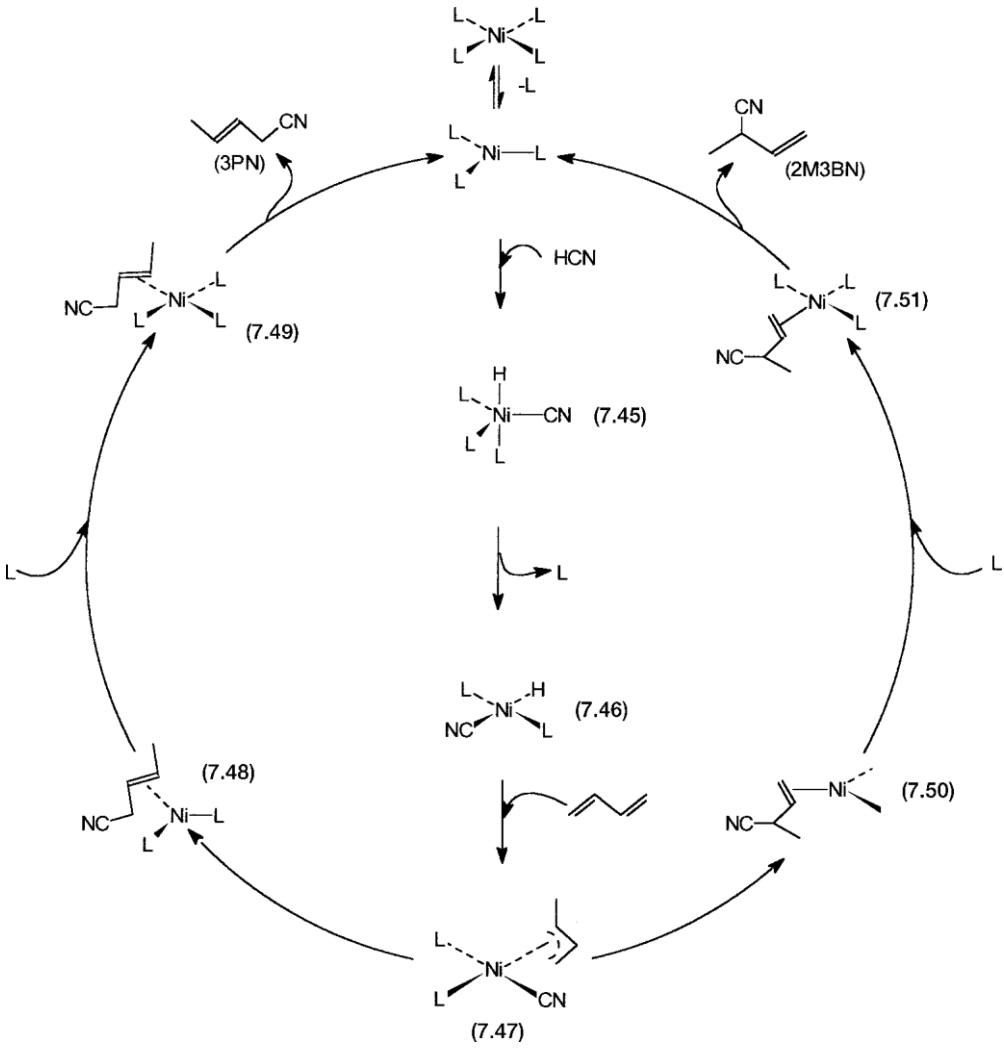
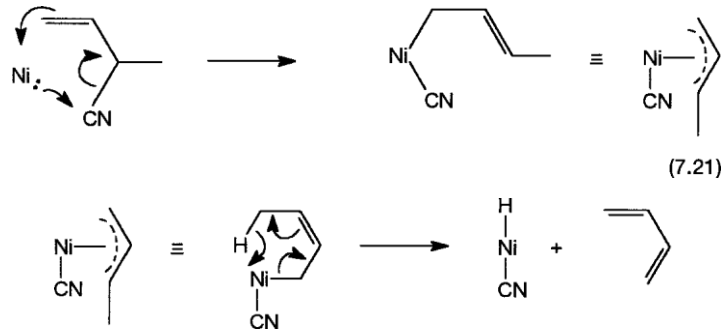


Figure 7.13 First stage of hydrocyanation. Conversion of butadiene to 3PN. Under the reaction conditions 2M3BN is isomerized to 3PN. Interaction of Lewis acid with coordinated nitrile is not shown for clarity. The left and right side involve CN^{-} addition in an anti-Markovnikov and Markovnikov manner. L = $P(OEt)_3$ or P(O-*o*-tolyl)3.

Note that dehydrocyanation of 2M3BN (i.e., 7.50 to 7.47) is nothing but a simple oxidative addition reaction. This is shown

formally by reaction 7.21. Reaction 7.22 shows the formal mechanism of butadiene formation and con- version of 7.47 to 7.46. Between the two isomers, 3PN is thermodynamically more stable than 2M3BN. A mixture of these two nitriles, if allowed to reach

a thermodynamic equilibrium over a catalyst, would have the concentration ratio of approximately 9:1.



(7.21)

(7.22)

Catalytic Cycle for the Second Stage

As mentioned earlier, the first reaction in the second stage is the isomerization of 3PN to 4PN, reaction 7.18. The mechanism of this reaction is very similar to the mechanism of alkene isomerization discussed in Section 7.2.1, and shown by Fig. 7.14. The following points need attention.

The nickel– hydride complex that acts as a precatalyst for this isomerization reaction is thought to be the cationic part of 7.52. The evidence for the exis- tence and participation of a cationic species such as 7.52 comes from multi- nuclear NMR and IR data. An equilibrium as shown by 7.23 exists, and the cation $[HNiL_4]^+$ is the dominant precatalyst for the isomerization reaction. The cation is an 18-electron complex. It undergoes ligand dissociation to give 7.53 before alkene coordination takes place. A ligand dissociated species such as
7.53 with L = *p*-tolylphosphite has been observed spectroscopically at low temperatures.

$$HNiL_3(CN\text{-}A) + L \rightleftharpoons [HNiL_4]^+ [CN\text{-}A]^- \qquad (7.23)$$

The isomerization of 3PN can lead to two possible products, 2-pentenenitrile (2PN), the unwanted isomer, and 4PN, the desired isomer. The former does *not* undergo hydrocyanation and thermodynamically is the most stable isomer. If the isomerization

of 3PN were allowed to reach thermodynamic equilibrium, the concentrations of the three isomers 2PN, 3PN, and 4PN would be approx- imately 78:20:2. Fortunately the isomerization of 3PN to 4PN is about 70 times as fast as that of 3PN to 2PN. In other words, although 4PN is thermodynam- ically the less stable isomer, the favorable kinetics allows its preferential for- mation.

The catalytic cycle for the hydrocyanation of 4PN to desired adiponitrile and undesired 2-methyl glutaronitrile (MGN) is shown by Fig. 7.15. The in- termediates that lead to the formation of 7.56 or 7.57 from NiL_3 are not shown

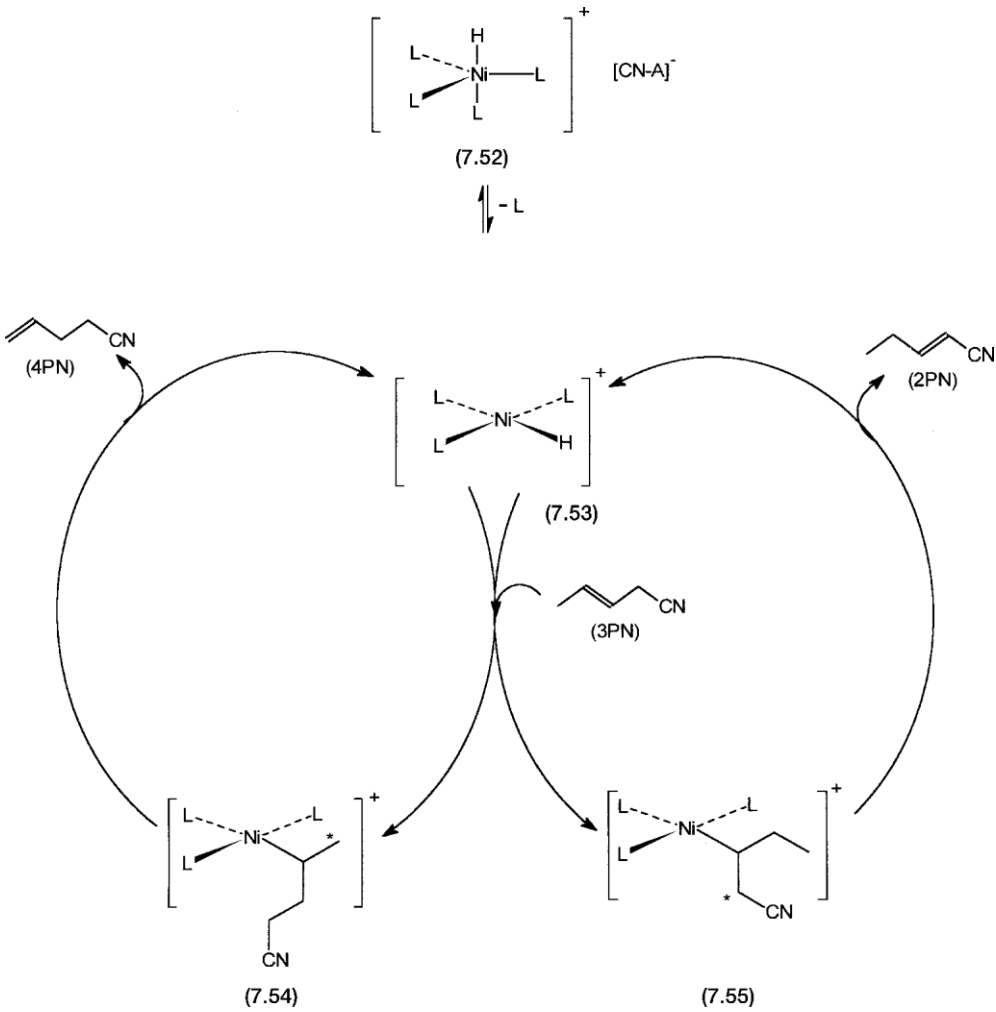


Figure 7.14 Second stage of hydrocyanation. Isomerization of 3PN to 4PN, the de- sired isomer, and 2PN, the unwanted isomer. The C atoms marked by asterisks are the ones from which the *b*-hydride abstraction takes place.

but are considered to be 7.45 and 7.46, with the Lewis acid A attached to the coordinated cyano group.

The left- and right-hand loops of the catalytic cycle involves anti-Markov- nikov and Markovnikov additions, giving 7.56 and 7.57, respectively. The pres- ence of the Lewis acid ensures that

the former pathway is favored. Spectro- scopic evidence for species 7.56 or 7.57 have so far not been reported. However, dissociation of two moles of ligand and involvement of the Lewis

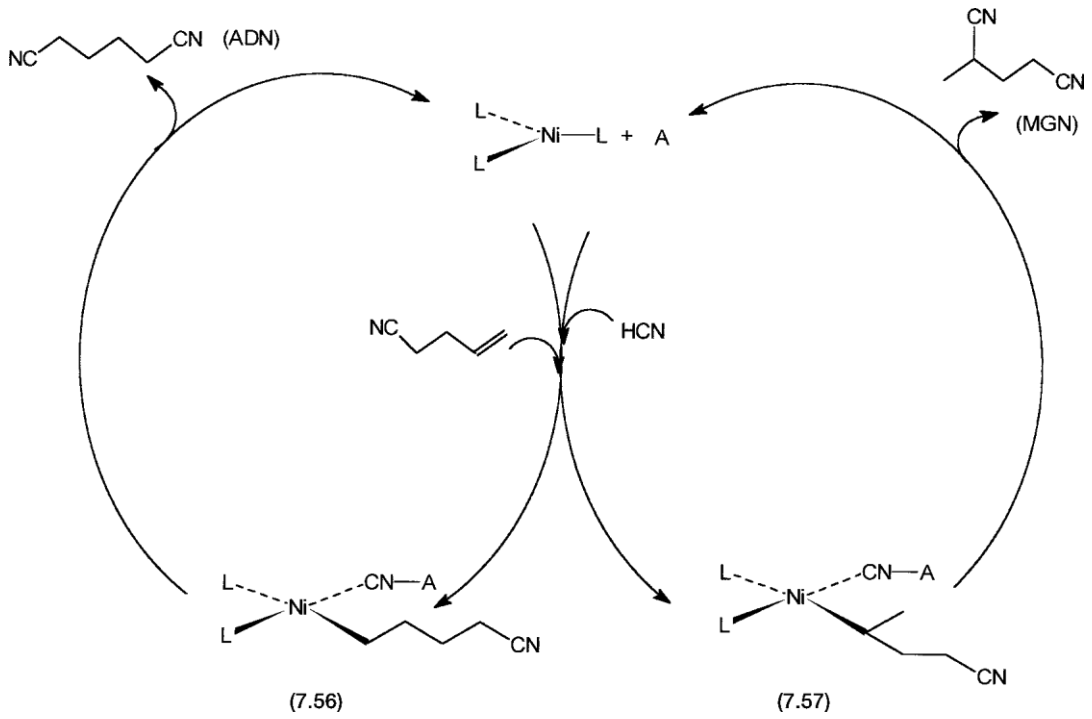


Figure 7.15 Second stage of hydrocyanation. Conversion of 4PN to adiponitrile (ADN) and MGN. A is the Lewis acid. The left loop dominates, giving ADN as the main product. Analogues of 7.45 and 7.46 with Lewis acid are not shown for clarity but are definitely involved.