Table II. Extended Hückel Parameters

orbital	H_{ii}, eV	exponents[a] ζ_1	ζ_2
C 2s	-21.40	1.625	
2p	-11.40	1.625	
O 2s	-32.30	2.275	
2p	-14.80	2.275	
Fe 4s	-9.1	1.90	
4p	-5.32	1.90	
3d	-12.60	5.35 (0.5336)	1.8 (0.6678)
Co 4s	-9.21	2.00	
4p	-5.29	2.00	
3d	-13.18	5.55 (0.5550)	1.9 (0.6460)

[a] Two Slater exponents are listed for the 3d functions. Each is followed in parentheses by the coefficients in the double-ζ expansion.

of the product. Similar methods were employed for the ^{13}CO enrichment of $(Ph_3P)Co_3(CO)_8CCl$ and $CpMoCo_2(CO)_8CCO_2CHMe_2$.

Molecular Orbital Calculations. All calculations were carried out within the extended Hückel formalism[21] using the weighted H_{ij} formula.[22] The atomic parameters utilized are listed in Table II. The idealized experimental structure[6] of $Fe_3(CO)_9CCO^{2-}$ serves as the basic geometry for the iron and cobalt cluster models. Co–Co and Fe–Fe separations were 2.50 and 2.57 Å, respectively. The ketenylidene group was placed 1.30 and 1.25 Å, respectively, above the metallic core. In all cases M–C(carbonyl) = 1.80 Å, C–O = 1.15 Å, C–C(ketenylidene) = 1.30 Å, and C–O(ketenylidene) = 1.29 Å.

Acknowledgment. Financial support from the donors of the Petroleum Research Foundation, administered by the American Chemical Society, the Natural Sciences and Engineering Research Council of Canada, and the CNRS (France) is gratefully acknowledged. M.F.D. and M.M. are the recipients of NSERC summer and postgraduate scholarships, respectively.

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(21) (a) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397. (b) Hoffmann, R.; Lipscomb, W. N. *Ibid.* **1962**, *36*, 2179; 1962, 37, 2872.

(22) Ammeter, J. H.; Bürgi, H.-B.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 3686.

Stereochemistry and Mechanism of Nickel-Catalyzed Hydrocyanation of Olefins and Conjugated Dienes

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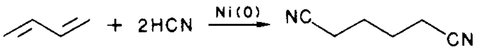
Received March 17, 1986

The mechanism of nickel-catalyzed hydrocyanation of 3,3-dimethyl-1-butene and 1,3-cyclohexadiene has been studied. Formation of *erythro*-2,3-dideuterio-4,4-dimethylpentanenitrile (**2**) from nickel-catalyzed addition of DCN to (*E*)-1-deuterio-3,3-dimethyl-1-butene (**1**) shows that the DCN adds cis across the double bond. Nickel-catalyzed addition of DCN to 1,3-cyclohexadiene occurs both 1,4 and 1,2 with cis stereochemistry as shown by the formation of a 1:1 mixture of *cis*-4-deuterio-2-cyclohexene-1-carbonitrile (**8a**) and *cis*-6-deuterio-2-cyclohexene-1-carbonitrile (**8b**). A competitive experiment using HCN/DCN in a 1:1 ratio gave an isotope effect of 3.6 ± 0.4 in the hydrocyanation of 1,3-cyclohexadiene. The mechanism for the hydrocyanation reactions involves cis addition of nickel hydride followed by migration of coordinated cyanide to the coordinated hydrocarbon ligand formed.

Introduction

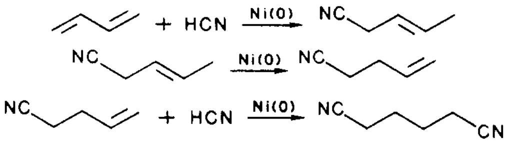
The nickel-catalyzed hydrocyanation of butadiene (eq 1), known as the adiponitrile process,[1] is today the most



(1)

important process for industrial manufacture of adiponitrile. Approximately 75% of the total world production of adiponitrile is based on this process. The hydrocyanation reaction, which is catalyzed by nickel(0) phosphite complexes[2] in combination with a Lewis acid,[3,4] proceeds in three discrete steps (Scheme I). All three steps, hydrocyanation of the diene, isomerization, and hydrocyanation of the terminal double bond, are catalyzed by nickel complexes.

Scheme I



Although nickel-catalyzed hydrocyanation has been known for some time, very little was reported in the literature concerning its mechanism until recently. In 1981 we reported in preliminary form on the stereochemistry of the nickel-catalyzed hydrocyanation of a monoolefin.[5] Since then several groups[4,6-8] have published mechanistic work on the hydrocyanation, and we[9] have communicated

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(1) Parshall, G. W. *Homogeneous Catalysis*; Wiley-Interscience: New York, 1980; *J. Mol. Catal.* **1978**, *4*, 256.

(2) Hubert, A. J.; Puentes, E. In *Catalysis in C_1 Chemistry*; Keim, W., Ed.; D. Reidel Publishing Co.: Dordrecht, 1983; pp 219–261.

(3) Brown, E. S. *Aspects Homogeneous Catal.* **1974**, *2*, 655.

(4) (a) Tolman, C. A.; Seidel, W. C.; Druliner, J. D.; Domaille, P. J. *Organometallics* **1984**, *3*, 33. (b) Tolman, C. A.; McKinney, R. J.; Seidel, W. C.; Druliner, J. D.; Stevens, W. R. *Adv. Catal.* **1985**, *33*, 1. (c) Seidel, W. C.; Tolman, C. A. *Ann. N.Y. Acad. Sci.* **1983**, *415*, 201.

(5) Bäckvall, J. E.; Andell, O. S. *J. Chem. Soc., Chem. Commun.* **1981**, 1098.

(6) (a) Druliner, J. D. *Organometallics* **1984**, *3*, 205. (b) McKinney, R. J.; Roe, C. *J. Am. Chem. Soc.* **1985**, *107*, 261.

(7) Keim, W.; Behr, A.; Luehr, H. O.; Weisser, J. *J. Catal.* **1982**, *78*, 209.

(8) Jackson, W. R.; Lovel, C. G. *Aust. J. Chem.* **1982**, *35*, 2053; *Tetrahedron Lett.* **1982**, *23*, 1621.

(9) Bäckvall, J. E.; Andell, O. S. *J. Chem. Soc., Chem. Commun.* **1984**, 260.

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Table I. Nickel-Catalyzed Deuteriocyanation of t-BuCH=CH$_2$[a]

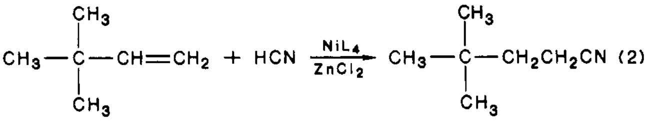
entry	equiv of t-BuCH=CH$_2$[b]	equiv of DCN[b]	equiv of ZnCl$_2$[b]	rel yield,[c] %			turnover no.
				5	6	7	
1	20	200	1	86	8	6	0.3
2	20	200	3	70	15	16	3.8
3	20	200	5	63	19	17	5.8
4	100	100	1	60.8	35.0	4.2	3.9

[a] Ni[P(OPh)$_3$]$_4$ was used as catalyst. In all cases 20 equiv of P(OPh)$_3$ per nickel atom were added. Reaction time, 40 min. [b] Equivalents relative to the nickel catalyst. [c] Estimated error ±1 in entries 1–3. In entry 4 the estimated errors are ±0.8 for 5 and 6 and ±0.2 for 7.

further results on the stereochemistry of the reaction. In this paper we give a full account of our preliminary reports[5,9] on the nickel-catalyzed hydrocyanation, discuss the mechanism, and also present additional results.

Results and Discussion

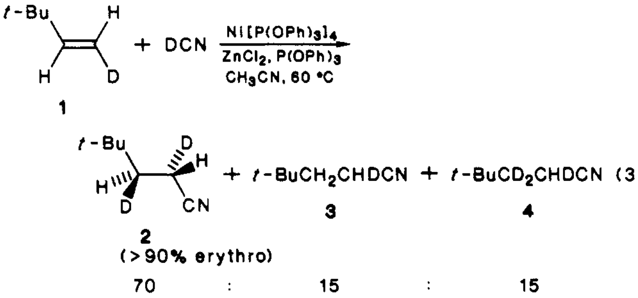
A. Hydrocyanation of 3,3-Dimethyl-1-butene. The nickel-catalyzed hydrocyanation of monoolefins in the presence of Lewis acid (e.g., ZnCl$_2$) was studied by Taylor and Swift.[10] They found that internal acyclic olefins underwent double-bond migration and terminal olefins afforded mixtures of 1- and 2-cyano adducts. One exception was 3,3-dimethyl-1-butene, which gave a highly regiospecific reaction to give exclusively the terminal cyano adduct (eq 2). The absence of allylic hydrogens eliminates the possibility of double-bond migration.



$$\text{CH}_3\text{—}\underset{\text{CH}_3}{\overset{\text{CH}_3}{\text{C}}}\text{—CH=CH}_2 + \text{HCN} \xrightarrow[\text{ZnCl}_2]{\text{NiL}_4} \text{CH}_3\text{—}\underset{\text{CH}_3}{\overset{\text{CH}_3}{\text{C}}}\text{—CH}_2\text{CH}_2\text{CN} \quad (2)$$

>99% regioselective

1. Stereochemistry. Because of the above-mentioned properties of 3,3-dimethyl-1-butene, its deuterated analogue 1 constitutes a suitable substrate for stereochemical studies of the nickel-catalyzed hydrocyanation. Reaction of 1 with a tenfold excess of DCN in the presence of nickel catalyst and ZnCl$_2$ afforded a 70:15:15 mixture of the deuterated nitriles 2, 3, and 4 as shown by ^{1}H NMR and mass spectroscopic analyses (eq 3). The stereochemistry



of the vicinally dideuterated 2 is readily determined by ^{1}H NMR spectroscopy since in the preferred conformation the t-Bu group and the nitrile group are anti to one another.[10] ^{1}H NMR analysis of the product mixture in eq 3 using deuterium decoupling revealed that product 2 was >90% erythro (J_{HH} = 10.5 Hz), showing that addition of DCN across the olefin has occurred cis.

The trideuterated product 4 is apparently formed by nickel-catalyzed DCN addition to t-BuCD=CHD, indicating that hydrogen–deuterium exchange occurs between the olefin and DCN. This is supported by the fact that the recovered olefin from this experiment was approximately a 70:30 mixture of t-BuCH=CHD ($E/Z \approx 90/10$) and t-BuCD=CHD ($E/Z \approx 10/90$). During this exchange HCN is formed (vide infra), which explains the formation of 3. Interestingly, no exchange of deuterium at the terminal carbon of the olefin was detected. Contrary to what we reported in our preliminary communication,[5] the slight loss of stereospecificty in the formation of 2 can thus be accounted for by E/Z isomerization of the olefin 1.

2. Hydrogen–Deuterium Exchange. It was of interest to see how the ratio between products 2, 3, and 4 varies with reaction conditions. Since there is no detectable exchange at the terminal carbon of 1, the same information can be obtained by using t-BuCH=CH$_2$ as the substrate. The results from DCN additions to t-BuCH=CH$_2$ are given in Table I. In all cases the reactions were run for 40 min. The relative amounts of 5, 6, and 7 (eq 4) were determined by mass spectroscopy. As can be seen

$$t\text{-BuCH=CH}_2 \xrightarrow[\text{Ni[P(OPh)}_3]_4,\ \text{ZnCl}_2]{\text{DCN}} \underset{5}{t\text{-BuCHDCH}_2\text{CN}} + \underset{6}{t\text{-BuCH}_2\text{CH}_2\text{CN}} + \underset{7}{t\text{-BuCD}_2\text{CH}_2\text{CN}} \quad (4)$$

from the table, the Lewis acid (ZnCl$_2$) increases the turnover number and the rate of exchange. The nickel-catalyzed hydrocyanation of monoolefins normally requires the presence of a Lewis acid,[3,10] and a study on the effects of Lewis acids has recently been published.[4a]

The results in Table I show that the hydrogen–deuterium exchange between olefin and DCN is rapid. In order to reduce the occurrence of HCN addition, it was necessary to use a large excess of DCN relative to the olefin. When a 1:1 ratio of the olefin and DCN was used, product 6 was formed in a relative yield of 35% (entry 4).

3. Isotope Effect. If hydrogen–deuterium exchange occurs only between the olefin and DCN, and unless DCN is contaminated with considerable amounts of HCN, the figures in Table I indicate a large isotope effect. With a negligible HCN contamination of the original DCN solution the isotope effect would approximately[12] be equal to the ratio of 6/7 in entry 4, since in this case a DCN/t-BuCH=CH$_2$ ratio of unity is maintained during the reaction and the HCN formed equals the t-BuCD=CH$_2$ formed. The ratio between 5 and 6 in entry 1 show that the highest possible concentration of HCN in the DCN must be <9%. Even with such a high contamination of HCN in the original DCN, entry 4 requires an isotope effect of >3. With an isotope effect of >3, it is evident from entry 1 that the contamination of HCN in DCN must be quite low. By combining the results of entries 1 and 4, provided the equilibrium HCN + NiL$_4$ $\rightleftarrows$ HNiL$_3$CN + L is maintained during the reaction (vide infra), the calculated deuterium isotope effect is 6.8 ± 1.0 and the original contamination of HCN in the DCN is 1.4% ± 0.4%.[13]

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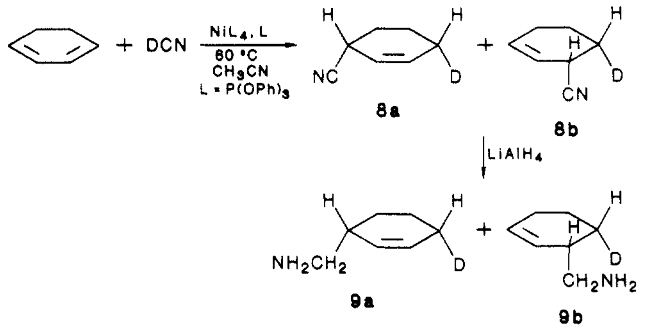
[10] Taylor, B. W.; Swift, H. E. *J. Catal.* **1972**, *26*, 254.

[11] The α- and β-protons in t-BuCH$_2$CH$_2$CN form an AA′BB′ system, and the two vicinal coupling constants J_{AB} and $J_{AB'}$ were determined to be 10.2 and 5.8 Hz, respectively: Whitesides, G. M.; Sevenair, J. P.; Goelz, R. W. *J. Am. Chem. Soc.* **1967**, *89*, 1135.

[12] The secondary isotope effect on addition to t-BuCD=CH$_2$ compared to t-BuCH=CH$_2$ has been neglected.

Scheme II

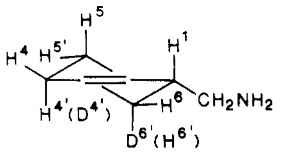


This large isotope effect in the hydrocyanation of 3,3-dimethyl-1-butene is remarkable and will be discussed below.

B. Hydrocyanation of 1,3-Cyclohexadiene. Reaction of 1,3-cyclohexadiene with HCN in the presence of Ni[P(OPh)$_3$]$_4$ resulted in a smooth hydrocyanation. Contrary to the hydrocyanation of monoolefins the hydrocyanation of 1,3-cyclohexadiene does not require the addition of Lewis acids.[14] The addition of a slight excess of P(OPh)$_3$ to the reaction without any Lewis acid afforded 2-cyclohexene-1-carbonitrile in high selectivity.

1. Stereochemistry. Addition on DCN to 1,3-cyclohexadiene in the presence of the nickel catalyst afforded monodeuterated nitriles according to mass spectrometry (Scheme II). The selectivity for monodeuterated product is high, and there was not detectable amount of dideuterated product. Furthermore, the recovered diene from this experiment did not contain any deuterium (<5%). This indicates that there is no hydrogen–deuterium exchange in the diene. The mass spectrum of the deuterated 2-cyclohexene-1-carbonitrile is consistent with a mixture of the deuterated nitriles **8a** and **8b**.

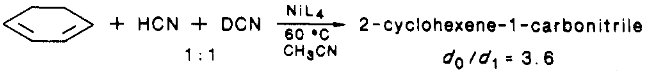
Since the high-field protons in the nitrile product were not resolved well enough in the ^{1}H NMR spectrum to allow a regio- and stereochemical analysis, the nitrile group was transformed into the primary amine **9** by LiAlH$_4$ reduction (Scheme II). The ^{1}H NMR of the amine **9** showed a good resolution of the high-field protons. The reason for this difference between the nitrile and the amine is that the CH_2NH_2 has approximately 10 times higher standard free energy of equatorial to axial equilibration than CN, and hence **9** is locked in conformation A.[15] From the ^{1}H NMR spectrum of the deuterated amine **9** it was found the deuterium is in the 4- and 6-positions relative to the CH_2NH_2 group in an approximate ratio of 1:1. Furthermore, from decoupling experiments of the undeuterated amine and the magnitude of the coupling constants it was possible to assign the resonance at 1.29 ppm to the axial homoallylic proton which is cis and vicinal to the CH_2NH_2 group ($H^{6'}$). The ^{1}H NMR analysis shows conclusively that in **9b** the deuterium and the CH_2NH_2 group are cis to one another (see Experimental Section). Although we cannot definitely assign deuterium to the 4′-position in **9a**, this is required by the mechanism depicted below. The fact that the splitting pattern of the olefinic protons in the ^{1}H NMR spectrum is unchanged in deuterated **9** compared to undeuterated **9** supports that deuterium is in the 4′-position.[16]



A

The fact that **9a** and **9b** have the configuration indicated shows that deuterium and cyanide must be cis to one another in **8a** and **8b**, and hence the nickel-catalyzed addition of DCN occurs cis across the diene.

2. Isotope Effect. The isotope effect of the nickel-catalyzed hydrocyanation of 1,3-cyclohexadiene was determined by a competitive experiment using HCN/DCN in a 1:1 ratio and in an excess to the olefin (eq 5). Since there is no exchange between DCN and double-bond hydrogens like that in 3,3-dimethyl-1-butene (vide supra), the HCN/DCN ratio will be essentially constant throughout the reaction. The 2-cyclohexene-1-carbonitrile formed from this experiment was analyzed by mass spectrometry, and it was found that the ratio d_0/d_1 in the product was 3.6. Thus, there is a deuterium isotope effect of 3.6 ± 0.4 in the nickel-catalyzed hydrocyanation of 1,3-cyclohexadiene, which is considerably smaller than the corresponding deuterium isotope effect for hydrocyanation of 3,3-dimethyl-1-butene. The isotope effect measured from this competitive experiment does not necessarily reflect the kinetic isotope effect of the overall reaction (vide infra).



(5)

C. Mechanism of the Hydrocyanation. The mechanisms for the nickel-catalyzed hydrocyanation of a monoolefin and a conjugated diene are shown in Scheme III. Dissociation of a ligand from NiL$_4$ followed by protonation of nickel(0) by D$^+$ would give the nickel deuteride species DNiL$_3$CN. This is formally an oxidative addition of DCN across nickel. The formation of nickel hydrides from nickel(0) and proton acids has been studied in detail.[17-19]

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(13) If we assume that the isotope effect $k_H/k_D = x$ and that the initial relative concentration of HCN in the DCN is y%, the initial relative formation of 5 and 6, before any H/D exchange occurs would be

5: 100 − xy%

6: xy%

The relative yield of undeuterated product 6 caused by the initial contamination of HCN in entry 4 (Table I) can approximately be expressed as

$$\frac{xy}{100 - xy}60.8$$

From entry 4 (Table I) we can express the isotope effect as

$$x = \frac{35 - \dfrac{xy}{100 - xy}60.8}{4.2}$$

and from entry 1 we have

$$\frac{xy}{100} = \frac{8}{86}$$

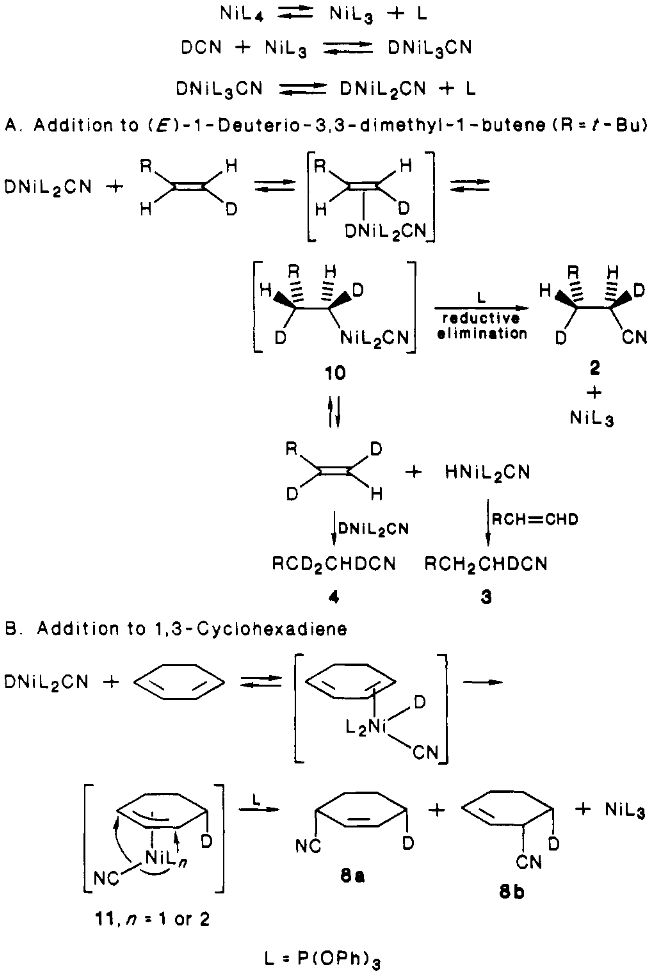
We have made the approximation that the product 5 in entries 1 and 4 (Table I) is derived only from DCN addition to t-BuCH=CH$_2$. By solving the equations above, we obtain x = 6.8 and y = 1.4. The estimated values are x = 6.8 ± 1.0 and y = 1.4 ± 0.4.

(14) This was also observed by Keim et al.[7] in their nickel-catalyzed hydrocyanation of acyclic conjugated dienes.

(15) The standard free energy change for the equatorial–axial equilibrium in cyclohexane is 0.71 kJ/mol for CN but 7.12 and 7.33 kJ/mol for CH$_3$ and CH$_2$CH$_3$, respectively: Hirsch, J. A. *Top. Stereochem.* **1967**, *1*, 199.

(16) The coupling constant between a pseudoaxial allylic proton and the vicinal olefin proton in cyclohexene systems is in the range of 0–1 Hz because of the dihedral angle being close to 90°. On the other hand the coupling constant between a pseudoequatorial allylic proton and the vicinal olefin proton is in the range of 4–5 Hz.

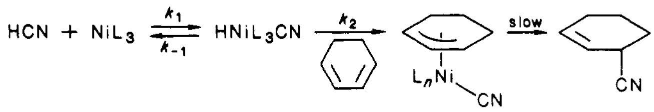
Scheme III[a]



It has been found that reaction of NiL_4 (L = phosphorus ligand) with strong acids produces the $HNiL_4^+$ species,[17,18] whereas the reaction of NiL_4 with HCN gives mainly $HNiL_3CN$ complexes.[19] The latter were found by spectroscopic methods to possess a trigonal-bipyramidal structure with the cyanide and the hydrogen in the apical positions.[18] Dissociation of a ligand produces the reactive 16-electron complex $DNiL_2CN$, which can coordinate a double bond. The deuteride then adds to the olefin, and it is known that nickel hydrides and other transition-metal hydrides add cis to double bonds.[18b,20]

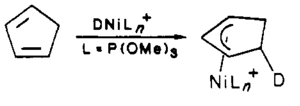
In the monoolefin case (A, Scheme III) cis migration of deuteride to the coordinated olefin would lead to stereospecific formation of the alkylnickel complex **10**. Reductive elimination, which should be favored by Lewis acids[21] and promoted by addition of a ligand,[22] gives the alkyl nitrile.

Scheme IV



Formation of the erythro nitrile **2** from complex **10** shows that the reductive elimination takes place with retention of configuration at the alkyl carbon. A β-hydride elimination in **10** may lead to reversible formation of (*E*)-RCH=CHD, or it may produce (*Z*)-RCD=CHD[23] and $HNiL_2CN$. The dideuterated olefin may then react with $DNiL_2CN$, which would account for the formation of the trideuterated nitrile **4** (cf. eq 3). In the same way monodeuterated nitrile **3** is explained by the reaction of $HNiL_2CN$ with the starting olefin. A similar hydrogen–deuterium exchange was observed by Tolman et al. in the nickel-catalyzed addition of DCN to ethene.[4a]

In the case of hydrocyanation of 1,3-cyclohexadiene, cis migration of deuteride to the coordinated diene would give the (π-allyl)nickel intermediate **11**. In fact Tolman has shown that cyclopentadiene reacts with $DNiL_4^+$ (generated from NiL_4 and D_2SO_4, L = $P(OMe)_3$) to give the deuterated (π-allyl)nickel complex **12** in which nickel and deuterium are cis to one another (eq 6).[18b] A cis migration of cyanide in the intermediate (π-allyl)nickel cyanide complex **11** would produce the observed nitriles **8a** and **8b** in equal amounts.



(6)

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The observation that there is no hydrogen–deuterium exchange in the diene shows that the nickel hydride addition step to give the π-allyl complex is irreversible under the reaction conditions. In accordance with this, Tolman and co-workers found that the stoichiometric reaction of $HNiL_3CN$ (L = $P(O\text{-}o\text{-tolyl})_3$) with butadiene is essentially irreversible at 25 °C.[4a] In the catalytic hydrocyanation reactions shown in Scheme III, the olefin substrate may take the site of one of the phosphite ligands L. This seems to be the case for less sterically demanding olefins, e.g., ethene.[6b]

A comparison between the hydrocyanation of an isolated double bond and a conjugated diene system show that in the former case there is a rapid nickel hydride addition–elimination equilibrium before the slow[4,6b] carbon–carbon bond-forming step, while in the latter case there is no such equilibrium. In both cases the slow step seems to be the carbon–carbon bond-forming step.[4a]

In the diene case the irreversible hydride addition occurring before the rate-limiting carbon–carbon bond-forming step would lead to an accumulation of the major catalytic species, the π-allyl complex **11** (Scheme IV). There are two limiting cases: (i) hydride addition is faster than elimination of HCN from $HNiL_3CN$, i.e., $k_2 >> k_{-1}$ or (ii) hydride addition is slower than elimination of HCN from $HNiL_3CN$, i.e., $k_2 << k_{-1}$. In the first case the isotope effect observed in the competitive experiment would reflect the isotope effect of the oxidative addition, k_{1H}/k_{1D}. An isotope effect of 3.6 is reasonable for this step. In the second case the isotope effect observed would reflect the isotope effect of the hydride addition step, k_{2H}/k_{2D}, multiplied by the equilibrium isotope effect K_{1H}/K_{1D},

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(17) (a) Drinkard, W. C.; Eaton, D. R.; Jesson, J. P.; Lindsey, R. W., Jr. *Inorg. Chem.* **1970**, *9*, 392. (b) Tolman, C. A. *Ibid.* **1972**, *11*, 3128. (c) Schunn, R. A. *Ibid.* **1970**, *9*, 394. (d) McEwen, G. K.; Rix, C. J.; Traynor, M. F.; Verkade, J. G. *Ibid.* **1974**, *13*, 2800.

(18) (a) Tolman, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 4217. (b) *Ibid.* **1970**, *92*, 6785.

(19) Druliner, J. D.; English, A. D.; Jesson, J. P.; Meakin, P.; Tolman, C. A. *J. Am. Chem. Soc.* **1976**, *98*, 2156.

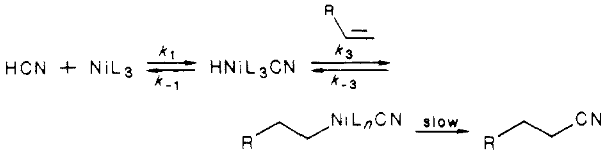
(20) Kochi, J. K. *Organometallic Mechanism and Catalysis*; Academic: New York, **1978**; p 312.

(21) (a) The reductive elimination in this case has similarities with the carbon–carbon bond formation between coordinated alkyl and coordinated carbon monoxide, which is known to be favored by Lewis acids.[21b] Also the increase in total rate on addition of Lewis acid is consistent with an increase of the rate-limiting reductive elimination. (b) Butts, S. B.; Holt, E. M.; Strauss, S. H.; Alcock, N. W.; Stinson, R. E.; Shriver, D. F. *J. Am. Chem. Soc.* **1979**, *101*, 5864.

(22) Tatsumi, K.; Nakamura, A.; Komiya, S.; Yamamoto, A.; Yamamoto, T. *J. Am. Chem. Soc.* **1984**, *106*, 8181.

(23) Note that the *Z* isomer is the one having the deuteriums trans to one another according to IUPAC nomenclature.

Scheme V



where $K_1 = k_1/k_{-1}$. The equilibrium isotope effect K_{1H}/K_{1D} should be significant since the stretching vibrations ν_{C-H} in HCN is 3225 cm^{-1} and the stretching vibrations ν_{Ni-H} in nickel hydride is ~1920 cm^{-1}.[24] A crude calculation of this isotope effect based only on stretching vibrations gives $K_{1H}/K_{1D} \approx 1.5$.[24a] Thus, for K_{1H}/K_{1D} to be 3.6 the deuterium isotope effect for the nickel hydride addition would have to be 2.4, which is a bit large but not unreasonable.[25] Although case (i) appears more probable, the present data do not exclude case (ii) or a mixture between the two cases (i.e., when k_2 and k_{-1} are of the same order of magnitude).

For the monoolefin the hydride addition is a reversible step (Scheme V). If $k_3 << k_{-1}$, the isotope effect would be the product of the two equilibrium isotope effects and correspond to $(K_{1H}/K_{1D})(K_{3H}/K_{3D})$, where $K_1 = k_1/k_{-1}$ and $K_3 = k_3/k_{-3}$. The observed isotope effect of 6.8 would seem too large for these equilibrium isotope effects. If $k_3 >> k_{-1}$, the isotope effect would be $(k_{1H}/k_{1D})(K_{3H}/K_{3D})$. However, in this case the $HNiL_3CN$ formed from exchange of NiL_3CN with the olefin would not equilibrate with DCN in solution. The ratio of $HNiL_3CN/DNiL_3CN$ would therefore be larger than the ratio of HCN/DCN in solution. This would contribute to the large value obtained for the competitive isotope effect. Now since there is approximately 1.5 equiv of dideuterated olefin (*Z*)-RCD=CDH produced per turnover in the reaction between DCN and **1**, there must be some exchange between $HNiL_3CN$ and DCN in solution, and k_3 can therefore only be moderately larger than k_{-1}.

After the publication of our preliminary report[5] on the stereochemistry of the nickel-catalyzed hydrocyanation of monoolefins, others[8] have shown that the analogous palladium-catalyzed hydrocyanation also proceeds with cis stereochemistry.

Conclusion

The nickel-catalyzed hydrocyanation of monoolefins and conjugated dienes involves a nickel hydride addition to a double bond followed by a migration of a coordinated cyanide to the coordinated hydrocarbon ligand formed (reductive elimination). In the former case the hydrocarbon ligand is a σ-alkyl group, and in the latter case it is a π-allyl group. The formal reductive elimination occurs with retention of configuration at the hydrocarbon ligand carbon. The same mechanism also seems to operate in the palladium system at least in the σ-alkyl case.[8,26] It thus seems that cyanide belongs to the group of nucleophiles that are able to undergo migration reactions in nickel and palladium chemistry. Recent ab initio ECP calculations on nucleophiles coordinated to palladium are in accordance with this and indicate that cyanide should be able to undergo migration reactions due to the high energy of the metal–cyanide bond.[27]

Experimental Section

All reactions were performed under a dry nitrogen atmosphere. Analytical grade ("pro analysi") acetonitrile was obtained from Merck, distilled from CaH_2, and stored over molecular sieves (3 Å). 1,3-Cyclohexadiene and triphenyl phosphite were commercially available and distilled before use. Analytical grade, dry $ZnCl_2$ and KCN were purchased from Merck. D_2O (99.8% deuterium) and D_2SO_4, 96–98% (99% deuterium), were obtained from Merck Sharp and Dohme.

(*E*)-1-Deuterio-3,3-dimethyl-1-butene[25d] and $Ni[P(OPh)_3]_4$[28] were synthesized according to literature procedures. A solution of DCN (4 M) in acetonitrile was obtained from the acidification with concentrated D_2SO_4 of a solution of dry KCN in D_2O.[29]

^1H NMR spectra were recorded in $CDCl_3$ with Me_4Si as an internal standard on a Bruker WP 200-FT spectrometer at 200 Mhz. Deuterium-decoupled ^1H NMR spectra were recorded on a Varian XL-100 spectrometer. Mass spectrometric analyses were performed on a LKB 9000 spectrometer or a Finnigan Model 4021 connected to an INCOS data system. Gas chromatographic analyses were carried out on a glass column of 5% SE 30 on Chromosorb W.

***erythro*-2,3-Dideuterio-4,4-dimethylpentanenitrile (2).** A solution of DCN (336 mg, 12.0 mmol) in acetonitrile (2.5 mL) was added in one portion to a stirred suspension of $Ni[P(OPh)_3]_4$ (78 mg, 0.06 mmol), $ZnCl_2$ (16 mg, 0.12 mmol), triphenyl phosphite (186 mg, 0.6 mmol), and (*E*)-1-deuterio-3,3-dimethyl-1-butene (102 mg, 1.2 mmol) in acetonitrile (4 mL) at 60 °C. After 1 h of stirring at 60 °C, the mixture was filtered through silica gel and the solvent evaporated via distillation using a vigreux column. The residue was bulb-to-bulb distilled (P = 30 mmHg), from a bulb precooled to −25 °C which was gradually allowed to reach room temperature. The distilled fractions were trapped at −78 °C; isolated yield 10.5 mg (8%) of **2**.

^1H NMR (deuterium decoupled): δ 1.076 (s, 9 H, CH_3), 1.595 (d, 1 H, J = 10.5 Hz, $CHDCMe_3$), 2.259 (d, 1 H, J = 10.5 Hz, $CHDCN$).

The recovered olefin from this experiment was analyzed by ^1H NMR and mass spectroscopy. It was found to be approximately a 70:30 mixture of t-BuCH=CHD ($E/Z \approx 90/10$) and t-BuCD=CDH ($E/Z \approx 10/90$). The ratios were determined from

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[24] (a) The equilibrium isotope effect for the oxidative addition of HCN to NiL_3 to give $HNiL_3CN$ was calculated by using a simplified version of the Wolfberg method[24b,c] in which only the stretching vibrations[24d,e] for each type of hydrogen (deuterium) bond were used. The calculated value of the equilibrium isotope effect $K_{1H}/K_{1D} \approx 1.5$. (b) Wolfsberg, M. *Acc. Chem. Res.* **1972**, *5*, 225. (c) Wolfsberg, M.; Stern, M. J. *Pure Appl. Chem.* **1964**, *8*, 225. (d) ν_{C-H} = 3225 cm^{-1} and ν_{C-D} = 2500 cm^{-1} for HCN was taken from ref 19. (e) $\nu_{Ni-H} \approx$ 1920 cm^{-1} and $\nu_{C-D} \approx 1.4\nu_{Ni-H}$ = 1371 cm^{-1}: Muetterties, E. L. *Transition Metal Hydrides*; Marcel Dekker: New York, 1971; Vol. 1, p 102.

[25] (a) The isotope effect in the hydroboration of styrene was found to be $k_H/k_D = 1.9$.[25b] No direct determinations of deuterium isotope effects for transition-metal hydride additions to olefins have been done. Recently, Doherty and Bercaw[25c] reported the kinetic deuterium isotope effect for niobium hydride addition to ethene defined as k_1/k_2 when $Cp^*_2Nb(H)C_2H_4 \xrightarrow{k_1} Cp^*_2NbC_2H_5$ and $Cp^*_2Nb(D)C_2D_4 \xrightarrow{k_2} Cp^*_2NbC_2D_5$ (Cp^* = pentamethylcyclopentadienyl). They found that k_1/k_2 = 1.1. To obtain an estimate of k_H/k_D for the hydride addition step, the value was corrected for the secondary deuterium isotope effect. The latter isotope effect was considered to be between 0.8 and 0.9 for each hydrogen in ethene, which gave k_H/k_D = 1.7–2.7 for the hydride addition. Now, since the hydrogens already are bent back in the olefin complex (carbons between sp^2 and sp^3, cf. bond length in the styrene complex of 1.43 Å: Bercaw et al.), a more reasonable value of the secondary isotope effect would be 0.90–0.95. This would give a deuterium isotope effect, k_H/k_D = 1.4–1.7, for the niobium hydride addition to coordinated ethene. The corresponding β-hydride elimination from alkylmetals are known and found to be ~1.8 for palladium (1.8,[25d] 1.86,[25e] 1.7[25f]), 2.28 for Ir,[25g] and 2.30 for Co.[25h] A slightly lower kinetic deuterium isotope effect, k_H/k_D = 1.4 ± 1, for β-elimination in $Pd(CH_2CD_3)(PMePh_2)_2$ was observed,[25i] but in this case the lower value is a result of that the elimination partly takes place via a three coordinated species. (b) Pasto, D. J.; Kang, S. Z. *J. Am. Chem. Soc.* **1968**, *90*, 3797. (c) Doherty, N. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1985**, *107*, 2670. (d) Andell, O. S.; Bäckvall, J. E. *J. Organomet. Chem.* **1983**, *244*, 401. (e) Kosaki, M.; Isemura, M.; Kitaura, Y.; Shinoda, S.; Saito, Y. *J. Mol. Catal.* **1977**, *2*, 351. (f) Henry, P. W. *J. Org. Chem.* **1973**, *38*, 2415. (g) Evans, J.; Schwartz, J.; Urguhart, P. W. *J. Organomet. Chem.* **1974**, *81*, C37. (h) Gikariga, T.; Yamamoto, A. *J. Organomet. Chem.* **1976**, *120*, 257. (i) Ozawa, F.; Ito, T.; Yamamoto, A. *J. Am. Chem. Soc.* **1980**, *102*, 6457.

[26] Larock, R. C.; Takagi, K.; Hershberger, S. S.; Mitchell, M. A. *Tetrahedron Lett.* **1981**, *22*, 5231.

[27] (a) Bäckvall, J. E.; Björkman, E. E.; Petterson, L.; Siegbahn, P. *J. Am. Chem. Soc.* **1985**, *107*, 7265. (b) *Ibid.* **1984**, *106*, 4369.

[28] Levisson, J. J.; Robinson, D. *J. Chem. Soc. A* **1967**, *89*, 1135.

[29] Brauer, G. *Handbook of Preparative Inorganic Chemistry*; Academic Press: New York, 1963; Vol. 1, p 658.

integration of the terminal protons which appear as distinct separate signals for the four isomers. ^1H NMR: (*Z*)-1,2-dideuterio-3,3-dimethyl-1-butene, δ 4.816 (t, 1 H, J = 1.6 Hz, =CDH); (*E*)-1,2-dideuterio-3,3-dimethyl-1-butene, δ 4.893 (t, 1 H, J = 2.5 Hz, =CDH); (*Z*)-1-deuterio-3,3-dimethyl-1-butene, δ 4.819 (d, 1 H, J = 10.7 Hz, =CDH); (*E*)-1-deuterio-3,3-dimethyl-1-butene, δ 4.903 (d, 1 H, J = 17.4 Hz, =CDH).

Dependence of Product Distribution on Reaction Conditions in the Nickel-Catalyzed Addition of DCN to 3,3-Dimethyl-1-butene. A solution of DCN in acetonitrile (4 M) was added in one portion to a slurry of $Ni[P(OPh)_3]_4$ (39 mg, 0.03 mmol), triphenyl phosphite (186 mg, 0.6 mmol), $ZnCl_2$, and 3,3-dimethyl-1-butene in 3 mL of acetonitrile at 60 °C. Analytical samples were taken after 40 min and analyzed by GC–MS. The analyses were performed with regard to the relative proportions between undeuterated and mono- and dideuterated 4,4-dimethylpentanenitrile. The results are listed in Table I.

Reference spectrum for 4,4-dimethylpentanenitrile: MS, m/z (relative intensity) 98 (22), 97 (73), 96 (7), 71 (7), 70 (27), 69 (14), 57 (100), 56 (22), 55 (35), 54 (10), 49 (12), 44 (21), 43 (18), 42 (23), 41 (49), 40 (67), 39 (15).

Ni(0)-Catalyzed Addition of DCN to 1,3-Cyclohexadiene. A solution of DCN (84 mg, 3.0 mmol) in acetonitrile (0.6 mL) was added to a stirred suspension of $Ni[P(OPh)_3]_4$ (78 mg, 0.06 mmol), triphenylphosphite (56 mg, 0.18 mmol), and 1,3-cyclohexadiene (240 mg, 3.0 mmol) in acetonitrile (2 mL) at 60 °C. The mixture was stirred at 60 °C for 2 h and then filtered through silica gel. Careful bulb-to-bulb distillation (0 °C, $P \approx 20$ mmHg) removed the solvent, and the residue was distilled (bulb-to-bulb, 20 °C, $P \approx 1$ mmHg). All distilled fractions were trapped at a temperature of −78 °C. Isolated yield was 107 mg (33%) of monodeuterated 2-cyclohexene-1-carbonitrile.[30]

^1H NMR: δ 1.67 (m, 1 H), 1.81 (m, 1 H), 1.95 (m, integrated for 1.5 H), 2.07 (m, integrated for 1.5 H, CH_2CH=), 3.22 (m, 1 H, CHCN), 5.63 (m, 1 H, =*C*HCHCN), 5.94 (m, 1 H, CH_2CH=). IR (neat): 2235 cm^{-1}. MS: m/z (relative intensity) 108 (10), 107 (7), 93 (11), 92 (8), 81 (62), 80 (80), 79 (31), 67 (8), 55 (48), 54 (58), 53 (16), 52 (37), 42 (69), 41 (100). Reference spectrum for 2-cyclohexene-1-carbonitrile:[29] MS, m/z (relative intensity) 107 (23), 106 (16), 92 (39), 81 (8), 80 (64), 79 (63), 78 (7), 77 (15), 67 (24), 66 (13), 65 (8), 54 (73), 53 (15), 52 (41), 51 (17), 50 (8), 41 (100).

Analysis of unreacted 1,3-cyclohexadiene: the reaction solution was analyzed by GC–MS with respect to 1,3-cyclohexadiene. The analysis showed that no incorporation of deuterium in the unreacted 1,3-cyclohexadiene had taken place. MS: m/z 80 (M^+).

Deuterated Amine 9 from $LiAlH_4$ Reaction of 8. A solution of **8** (46 mg, 0.42 mmol) in 2 mL of ether was added to a stirred slurry of $LiAlH_4$ (46 mg, 1.21 mmol) in 1 mL of ether at room temperature. The reaction mixture was stirred for 15 h and then quenched with 8 mL of wet ether. The resulting precipitate was filtered off after 24 h of stirring and the ether phase extracted with 2 M HCl (aqueous). The aqueous phase was washed with ether, made alkaline with NaOH, and extracted with ether. The organic phase was dried ($MgSO_4$) and concentrated to yield 44 mg (94%) of **9**.

^1H NMR (for denotions see conformation A of **9** in the text): δ 1.29 (m, 0.5 H, $J_{1,6'}$ = 8.9, $J_{5,6'}$ = 11.4, $J_{5',6'}$ = 3.0, $J_{6,6'}$ = −12.9 Hz, 6′-H), 1.54 (m, 1 H, 5-H), 1.73 (m, 1 H, 5′-H), 1.79 (m, 1 H, 6-H), 1.99 (m, 1.5 H, 4-H and 4′-H), 2.12 (m, 1 H, 1-H), 2.63 (dd, 2 H, J = 8.5, 2.1 Hz, CH_2NH_2), 5.63 (dd, 1 H, J = 10.3, 2.0 Hz, $=CHCH_2NH_2$), 5.77 (m, 1 H, J = 10.0 Hz, CH_2CH=). The coupling constants $J_{1,6'}$, $J_{5,6'}$, $J_{5',6'}$, and $J_{6,6'}$ were determined from the undeuterated parent compound by using a simulation and iteration procedure ("Panic", Bruker WP-200). From decoupling experiments it was evident that the proton at 1.29 ppm was either H_6 or $H_{6'}$. The vicinal coupling constants (11.4 and 8.9 Hz) require this proton to be axial, and hence it must be $H_{6'}$.

Integration of the signals of the deuterated product **9** indicates that half of the deuterium is in the $H_{6'}$ position and the other half in the 4-position. The remaining $H_{6'}$ signal (half intensity) had an identical pattern to that of the undeuterated parent compound. On the other hand, the patterns of protons H_6, H_5, H_5, and H_1 were much changed owing to deuterium couplings.

Investigation of the Hydrogen–Deuterium Isotope Effect in the Nickel(0)-Catalyzed Addition of Hydrogen Cyanide to 1,3-Cyclohexadiene. A solution of HCN/DCN, 50:50 (330 mg, 12.0 mmol) in acetonitrile (0.6 mL), was added in one portion to a stirred suspension of $Ni[P(OPh)_3]_4$ (78 mg, 0.06 mmol), triphenyl phosphite (56 mg, 0.18 mmol), and 1,3-cyclohexadiene (240 mg, 3.0 mmol) in acetonitrile (2.0 mL) at 60 °C. After 1 h of stirring at 60 °C the conversion was <10% according to GC. The slurry was filtered through silica gel and the solvent evaporated (bulb-to-bulb). The residue was bulb-to-bulb distilled at room temperature (P = 1 mmHg), and the fractions were trapped at −78 °C; isolated yield 26 mg (8%). The ratio between deuterio-2-cyclohexene-1-carbonitrile and 2-cyclohexene-]-carbonitrile was 1/3.6 according to mass spectroscopic analysis.

Acknowledgment. We thank the Swedish Natural Science Research Council and the Swedish Board for Technical Development for financial support, Dr. Toshiaki Nishida for recording the deuterium-decoupled ^1H NMR spectra, and Mr. Mikael Lindström for assistance in obtaining mass spectra. Discussions with C. P. Casey (Wisconsin) and J. R. Norton (Colorado State) are gratefully acknowledged.

Registry No. **1**, 57002-05-8; **2**, 81504-88-3; **5**, 104197-56-0; **6**, 15673-05-9; **7**, 104197-57-1; **8a**, 90522-79-5; **8b**, 90522-80-8; **9a**, 104197-54-8; **9b**, 104197-55-9; DCN, 3017-23-0; D_2, 7782-39-0; $Ni[P(OPh)_3]_4$, 14221-00-2; (*Z*)-*t*-BuCH=CHD, 6833-43-8; (*E*)-*t*-BuCD=CDH, 84784-40-7; (*Z*)-*t*-BuCD=CDH, 102369-35-7; 3,3-dimethyl-1-butene, 558-37-2; 1,3-cyclohexadiene, 592-57-4; 4,4-dimethylpentanenitrile, 15673-05-9.

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[30] A reference sample of 2-cyclohexene-1-carbonitrile was made according to a literature procedure. Broxton, T. J.; Butt, G.; Liu, R.; Teo, L. H.; Topsom, R. D.; Katritzky, A. R. *J. Chem. Soc., Perkin Trans.* **1974**, 463.