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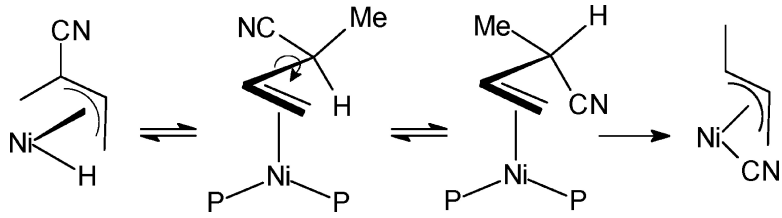

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Solvent Effects and Activation Parameters in the Competitive Cleavage of C−CN and C−H Bonds in 2-Methyl-3-Butenenitrile Using [(dippe)NiH]$_2$

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Abstract: The reaction of [(dippe)NiH]$_2$ with 2-methyl-3-butenenitrile (2M3BN) in solvents spanning a wide range of polarities shows significant differences in the ratio of C−H and C−CN activated products. C−H cleavage is favored in polar solvents, whereas C−C cleavage is favored in nonpolar solvents. This variation is attributed to the differential solvation of the transition states, which was further supported through the use of sterically bulky solvents and weakly coordinating solvents. Variation of the temperature of reaction of [(dippe)NiH]$_2$ with 2M3BN in decane and *N*,*N*-dimethylformamide (DMF) allowed for the calculation of Eyring activation parameters for the C−CN activation and C−H activation mechanisms. The activation parameters for the C−H activation pathway were $\Delta H^{\ddagger} = 11.4 \pm 5.3$ kcal/mol and $\Delta S^{\ddagger} = -45 \pm 15$ e.u., compared with $\Delta H^{\ddagger} = 17.3 \pm 2.6$ kcal/mol and $\Delta S^{\ddagger} = -29 \pm 7$ e.u. for the C−CN activation pathway. These parameters indicate that C−H activation is favored enthalpically, but not entropically, over C−C activation, implying a more ordered transition state for the former.

Introduction

The cleavage of C−C σ-bonds has many potentially important applications in synthesis and industry, leading to increased exploration of this area of organometallic chemistry. Many studies have shown that C−C cleavage can be accomplished through the insertion of a transition metal center into certain types of C−C bonds.[1] One notable industrial process employing a C−C cleavage application is the 3-step adiponitrile (AdN) process developed by DuPont (Figure 1),[2] in which C−CN cleavage by a homogeneous nickel catalyst plays a critical role.

The AdN process starts with the reaction of HCN, butadiene, and a Ni(0) phosphite catalyst producing a 2:1 mixture of 3-pentenenitrile (3PN) and 2-methyl-3-butenenitrile (2M3BN).[1] The desirable, linear 3PN is simultaneously isomerized to the terminal olefin 4-pentenenitrile (4PN) under the reaction conditions and a second HCN addition then gives AdN using a Ni(0) catalyst and a Lewis acid cocatalyst.[2−4] The branched isomer 2M3BN is capable of being catalytically isomerized to the desirable linear isomer 3PN beginning with η^2-coordination of nickel to 2M3BN (**1**) followed by the formation of a π-allylic intermediate (**2**) formed by cleavage of the C−CN bond (Figure 2), permitting rearrangement to 3PN.[2−7] There has been much recent work investigating the mechanistic aspects of the conversion of 2M3BN to 3PN using Ni(0) catalysts via activation and rearrangement of the C−CN bond. [8−11]

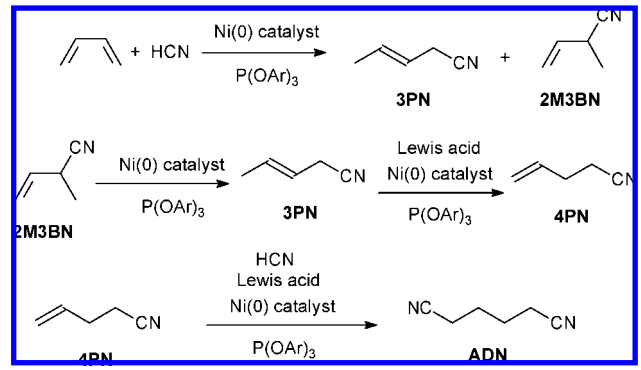

Figure 1. General sequence of the DuPont adiponitrile (AdN) process.

Vogt and others performed studies using a variety of chelating Xantphos ligands (Figure 3) with rigid backbones that showed

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(1) For a recent review of these topics, see: *Topics in Organometallic Chemistry. Activation of Unreactive Bonds and Organic Synthesis*; Murai, S., Ed.; Springer-Verlag: Berlin, 1999.
(2) McKinney, R. J. In *Homogeneous Catalysis*; Parshall, G. W., Ed.; Wiley: New York, 1992; pp 42−50. Abbreviations used: 2-methyl-3-butenenitrile (2M3BN); 2-methyl-2-butenenitrile (2M2BN); 2-pentenenitrile (2PN); 3-pentenenitrile (3PN); 4-pentenenitrile (4PN).
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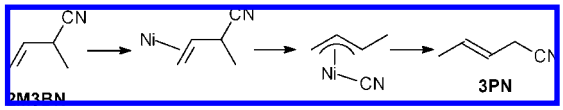


Figure 2. Conversion of 2M3BN to 3PN via π-allyl intermediate.

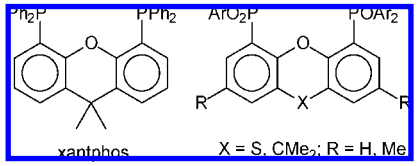


Figure 3. Structures of xantphos catalysts and derivatives used for 2M3BN isomerization.

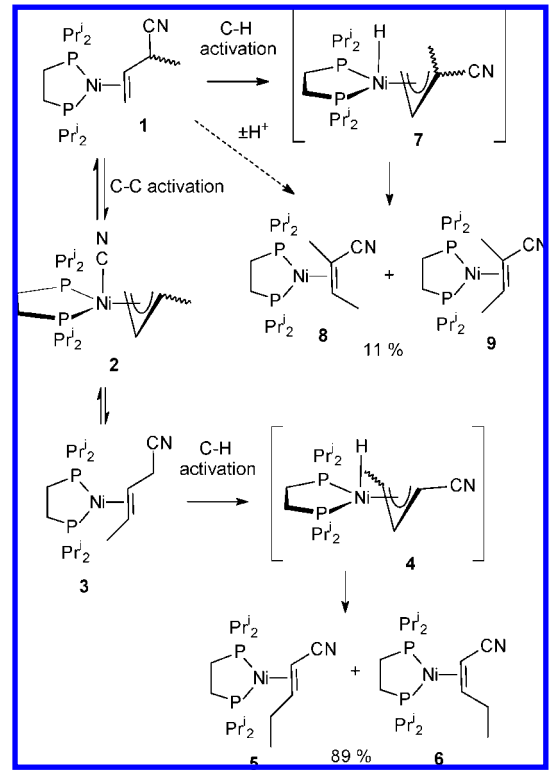
a good selectivity toward the isomerization of 2M3BN to 3PN.[8] The POP-Xantphos ligand, while not showing the highest conversion of the ligands examined, did show the best selectivity possibly due to its large natural bite angle which increases the driving force for reductive elimination. During a spectroscopic study of the reductive elimination step associated with this reaction the addition of $ZnCl_2$ to the reaction enabled the observation and isolation of the C−CN cleavage intermediate [(xantphos)(η^3-allylmethyl)Ni(CN-$ZnCl_2$)].[9]

Sabo-Etienne et al. presented a mechanism for the isomerization of 2M3BN to 3PN using a Ni(PMe_3)$_2$ catalyst that was supported by DFT calculations.[10] According to these calculations, there are five steps involved in the mechanism beginning with the coordination of the Ni-catalyst to the C=C bond of 2M3BN. The C−CN bond was shown to be cleaved, forming a σ-allylic species that was further isomerized into a π-allylic species. This intermediate then rearranged further into another σ-allylic species and finally, the C−CN bond was reformed giving the Ni−3PN complex.

Reactions of [(dippe)NiH]$_2$ with a variety of aryl, heteroaryl, and alkyl cyanides have demonstrated the formation of an η^2-nitrile complex of nickel(0), which undergoes oxidative addition via either C−CN or C−H cleavage to form a nickel(II) complex.[5−7] More recently, the reaction of [(dippe)NiH]$_2$ with allyl cyanide showed the quantitative generation of the η^2-coordinated olefin complex, which was later converted to a mixture of the C−CN cleavage product [(dippe)Ni(η^3-allyl)(CN)] and the C−H cleavage products cis- and trans-[(dippe)Ni(η^2-C,C-crotononitrile)].[6,7]

The use of [(dippe)NiH]$_2$ as a catalyst has provided mechanistic insight into a number of C−CN cleavage reactions including those in aryl-[5] and alkyl-[12] nitriles. The experiments reported here describe the stoichiometric and catalytic isomerization of 2M3BN with [(dippe)NiH]$_2$ under changing solvent and temperature conditions as a means of further investigating the mechanistic details of this system, and show a remarkable

Scheme 1. Proposed Mechanism Including C−C vs. C−H Activation Intermediates



tool for controlling linear/branched ratios in the isomerization that has not been reported previously.

Results and Discussion

Stoichiometric Reaction of [(dippe)NiH]$_2$ with 2M3BN. A solution of [(dippe)NiH]$_2$ was treated with 2 equiv of 2M3BN in THF-d_8 at −20 °C, turning the deep red solution to yellow-brown with the evolution of H_2 gas. The reaction was monitored primarily through ^{31}P {^{1}H} NMR spectroscopy and initially showed two pairs of doublets at δ 72.0 and 66.1 with $^2J_{P-P}$ = 59 Hz and δ 71.2 and 66.3 with $^2J_{P-P}$ = 61 Hz associated with the η^2-coordination of the Ni(0) complex to either face of the prochiral olefin 2M3BN (**1a**, **1b**). After four hours at room temperature, a very broad singlet was observed at δ54 for complex **2** as the original doublets became smaller. This singlet converted over 1 day to two new pairs of doublets at δ 70.9 and 67.6 with $^2J_{P-P}$ = 53 Hz (**5**) and δ 70.5 and 67.0 with $^2J_{P-P}$ = 53 Hz (**6**). Two additional pairs of doublets at δ 70.1 and 62.9 with $^2J_{P-P}$ = 58 Hz (**8**) and δ 69.7 and 62.8 with $^2J_{P-P}$ = 58 Hz (**9**) were also observed, giving a total of four products in all. Based on this data, ^{1}H NMR spectroscopy, X-ray crystallography, independent synthesis, GC analysis, and by analogy to previous studies showing the π-allylic intermediate of the allyl cyanide system,[7] the mechanism illustrated in Scheme 1 is proposed. It is interesting that with [Ni(dippe)] both isomers **1a** and **1b** are observed, whereas earlier studies of binding of 2M3BN to L_2Ni^0 have shown only one set of signals in the ^{31}P NMR spectra.

The mechanism shown in Scheme 1 presents two possible pathways for bond activation resulting in the formation of π-allylic intermediates based on C−CN activation (**2**, observed) or C−H activation (**7**, not observed). These intermediates undergo further rearrangement to form either η^2-coordinated, nonconjugated 3PN (**3**) or η^2-coordinated, conjugated 2-methyl-

(11) (a) Acosta-Ramírez, A; Muñoz-Hernández, M.; Jones, W. D.; García, J. J. *J. Organomet. Chem.* **2006**, *691*, 3895. (b) Acosta-Ramírez, A.; Flores-Gaspar, A.; Muñoz-Hernández, M.; Arévalo, A.; Jones, W. D.; García, J. J. *Organometallics* **2007**, *26*, 1712. (c) Ateşin, T. A.; Li, T.; Brennessel, W. W.; Lachaize, S.; García, J. J.; Jones, W. D. *J. Am. Chem. Soc.* **2007**, *129*, 7562. (d) Acosta-Ramírez, A.; Muñoz-Hernández, M.; Jones, W. D.; García, J. J. *Organometallics* **2007**, *26*, 5766.

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2-butenenitrile (2M2BN) (**8** and **9**). **3** undergoes irreversible C−H cleavage to produce the more stable, conjugated 2-pentenenitrile (2PN) (**5** and **6**). The final ratio of this reaction showed 89% linear isomers (**5** and **6**) and 11% branched isomers (**8** and **9**). Neither π-allyl hydride (**4** or **7**) nor olefin complex **3** were observed directly over the course of the reaction.

Characterization of 2. The first species observed in the C−CN pathway is the π-allylic intermediate **2**. Independent synthesis of **2** was accomplished through the reaction of bis-cyclooctadienyl nickel ($(cod)_2Ni$) with methyl-allyl bromide followed by the addition of dippe and then NEt_4CN. $^{31}P\{^1H\}$ NMR spectroscopy indicated the presence of a very broad singlet at δ54, the same as observed in the reaction of 2M3BN with $[(dippe)NiH]_2$.

The ^1H NMR spectrum is consistent with η^3-coordination of the allylic unit to nickel.[6] Three allylic resonances for **2** were observed as a quartet at δ 5.1, a multiplet at δ 3.9 and a multiplet at δ 2.2. The latter multiplet overlaps with the isopropyl C−H from the dippe ligand. As **2** was consumed, all of these resonances were converted into those of the other isomers.

Characterization of 3−6. During the stoichiometric reaction of $[(dippe)NiH]_2$ with 2M3BN, neither **3** nor **4** were observed via NMR spectroscopy. **3** was independently synthesized, however, by the reaction of $[(dippe)NiH]_2$ with trans-3PN. $^{31}P\{^1H\}$ NMR spectroscopy of **3** shows a pair of doublets at δ 67.5 and 66.7 with $^2J_{P-P} = 65$ Hz that were observed to disappear within ~1 h at room temperature, forming primarily **2**. **5** and **6** were also observed in small quantities, identified by their characteristic doublets at δ 70.9 and 67.6 with $^2J_{P-P} = 53$ Hz and δ 70.5 and 67.0 with $^2J_{P-P} = 53$ Hz, respectively. The ^1H NMR spectrum of **3** showed two olefinic resonances as a quartet of doublets at δ 5.6 and a triplet of doublets at δ 4.9. The CH_2 resonance was identified as part of an overlapping multiplet from δ 1.5−2.1 and the CH_3 resonance was observed to overlap with the isopropyl CH_3 groups of dippe at δ 0.8−1.1. The presence of trans-3PN was also confirmed through GC analysis after quenching with $CHCl_3$.

After one day at room temperature in THF-d_8, **2** was mostly converted into **5** and **6** (89%) and **8** and **9** (11%). Independent synthesis of **5** and **6** from the corresponding nitrile and $[(dippe)NiH]_2$ confirmed these assignments. A yellow crystal of **6** suitable for X-ray diffraction was obtained. Selected bond lengths and angles for the complex are given in Figure 4. The olefinic carbons lay approximately in the P_2Ni square plane with similar Ni−C bond lengths. The olefin bond length is similar to those in the allyl-cyanide and acrylonitrile systems and the C−N bond length is similar to that in the allyl-cyanide system.[7] The ^1H NMR spectrum of **6** showed two olefinic resonances as a doublet of triplets at δ 5.5 and a doublet at δ 4.5. The CH_2 resonance was identified as part of a multiplet at δ 1.5−2.3 and the CH_3 resonance was observed as a triplet at δ 0.6. The presence of the free olefin trans-2PN or cis-2PN was confirmed by GC analysis following treatment of **5** or **6**, respectively, with $CHCl_3$.

Reactions of *cis*- and *trans*-2PN with $[(dippe)NiH]_2$ indicated that there is no reverse equilibrium once **5** or **6** are formed. Complex **4** was not observed in intermediate NMR spectra but is implied as a potential intermediate based on the prior reactant and subsequent products formed during the reaction.

Characterization of 7−9. The $^{31}P\{^1H\}$ NMR spectrum of **8** and **9** showed two sets of doublets at δ 70.1 and 62.9 with $^2J_{P-P} = 58$ Hz and δ 69.7 and 62.8 with $^2J_{P-P} = 58$. Independent synthesis of **8** or **9** from $[(dippe)NiH]_2$ and pure *Z*- or *E*-2M2BN

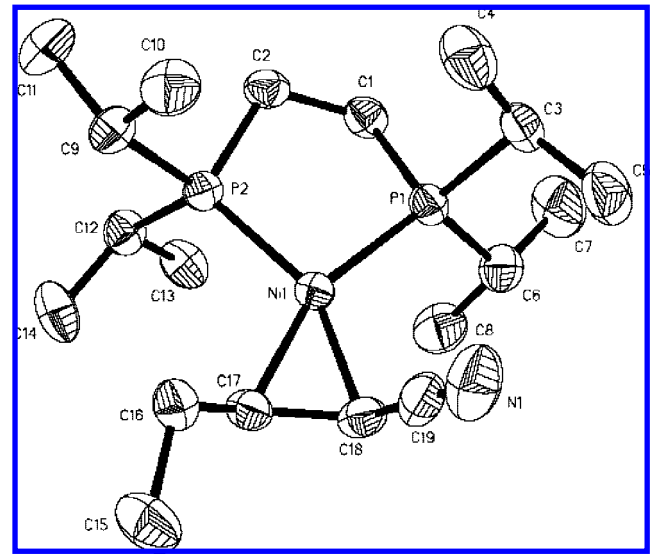


Figure 4. ORTEP drawing of **6** showing 30% probability ellipsoids. Selected bond distances (Å): N1−C19 (1.148(3)), C17−C18 (1.446(3)), Ni1−C17 (1.940(2)), Ni1−C18 (1.962(2)). Selected angles in degrees: P1−Ni1−P2 (92.21(2)), C17−Ni1−C18 (43.49(9)).

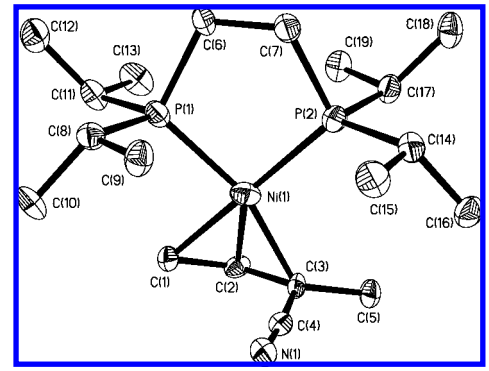


Figure 5. ORTEP drawing of **10** showing 30% probability ellipsoids. Selected bond distances (A): Ni1−C1 (2.089(7)), Ni1−C2 (2.036 (7)), Ni1−C3 (2.032(7)), C1−C2 (1.410(9)), C2−C3(1.424(8)). Selected angles in degrees: P1−Ni1−P2 (90.44(6)), C3−Ni1−C1 (72.8(3)). BPh_4^- is left out for clarity.

confirmed these assignments and showed no evidence for a reversible equilibrium once **8** or **9** was formed (i.e., **8** and **9** do not interconvert). The ^1H NMR spectrum of **8** showed one olefinic resonance as a doublet of doublets at δ 4.9. The two CH_3 groups were observed as a doublet at δ 1.5 and a multiplet overlapping with CH_3 groups from dippe at δ 0.8−1.3. The presence of the corresponding free olefin *Z*- or *E*-2M2BN was also confirmed by GC analysis following treatment of **8** or **9**, respectively, with $CHCl_3$.

The independent synthesis of **7** started with the formation of $(dippe)Ni(\eta^3\text{-}CH_2CHC(Me)(CN))^+BPh_4^-$ (**10**) from the reaction of $[(dippe)NiH]_2$, $NaBPh_4$, and 1-bromo-3-cyano-2-butene. A yellow, needle-like crystal suitable for X-ray diffraction was obtained and selected bond lengths and angles are given in Figure 5. The allylic bond lengths are similar to those in the allyl-cyanide and acrylonitrile systems and the C−N bond length is similar to the allyl-cyanide system.[7] Although a crystal structure could be obtained for complex **10**, it proved to be unstable in solution, preventing the characterization via NMR spectroscopy.

Table 1. Solvent Study Data for the Catalytic Isomerization of 2M3BN to Other Isomers by $[Ni(dippe)H]_2$[a]

				% products					
entry	solvent	dielectric constant (ϵ)	% conv	*Z*-2M2BN	*E*-2M2BN	*cis*-2PN	*trans*-2PN	*trans*-3PN[b]	linear:branched[c]
1	decane	2	96.9	2.6	4.9	4	6.1	82.5	12.4:1
2	benzene	2.3	95.9	3.8	9.2	6.3	9.9	66.8	6.7:1
3	2,2,5,5-tetramethyl THF	5	96.9	3.1	9	3.7	5.5	78.7	7.3:1
4	THF	7.5	87.2	5.7	14.7	5.5	8.6	65.5	3.9:1
5	trifluoro-toluene	9.2	67.4	8.3	30.5	4.5	6	49[d]	1.6:1
6	di-*t*-butyl ketone	10	99.6	9	50.6	5.7	9.3	22.5[d]	1:1.5
7	acetone	21	99.6	22.3	70	1.1	1.6	5	1:12
8	pivalonitrile	21.1	98.6	8.9	31	4.8	6.8	47.1[d]	1.5:1
9	CH_3CN	36.6	100	24.3	73.9	0.6	0.8	2.2	1:27.3
10	DMF	38.3	95.8	16.4	73.4	0	0.7	5.4	1:14.9

[a] Reaction conditions: [2M3BN] = 1 mM; [Ni] = 0.105 mM; equiv 2M3BN = 10; T = 100 °C; t = 180 min. [b] A total of 1−2% of *cis*-3PN was seen in all samples. [c] Linear: branched ratio calculated with linear products cis-2PN, trans-2PN, cis-3PN, trans-3PN, and 4PN vs branched products Z-2M2BN and *E*-2M2BN. [d] About 2% 4-PN was also observed.

This precursor was then treated with $LiBEt_3H$ in THF to form **7**. Although **7** was not directly observed, the organic products of this reaction were observed via GC following reaction of the organometallic products with $CHCl_3$ (which produces $(dippe)NiCl_2$ and the corresponding free olefin), indicating that the reaction forms primarily **8** and **9** (80%), but also **1** (20%). Therefore, the step **1** → **7** must be at least partially reversible, but the following step (**7** → **8** + **9**) is not. This reaction further supports the characterization of **7** and **10** in conjunction with the crystal structure.

Catalytic Reaction of $[(dippe)NiH]_2$ and 2M3BN in Different Solvents. Catalytic isomerization of 2M3BN was examined by injection of 2M3BN into a preheated, septum-capped reaction tube containing $[(dippe)NiH]_2$ and solvent under a positive pressure of dinitrogen (see Supporting Information for picture). This procedure provided reproducible results by ensuring that oxygen would not contact the reaction solution, which was independently demonstrated to cause erratic behavior in reaction times and product distributions.

The reaction of $[(dippe)NiH]_2$ with a 10-fold excess of 2M3BN in THF at 100 °C produced an instantaneous color change from deep-red to red-orange. After three hours under an atmosphere of N_2, the color was observed to change from red-orange to yellow-brown with a yellow precipitate. Analysis of the resultant solutions by GC indicate a reaction preference toward the linear C−CN activation products 3PN and 2PN versus the branched C−H activation products *E*- and *Z*-2M2BN. A similar trend was observed in the additional nonpolar solvents studied. In sharp contrast, a preference toward the branched C−H products was observed in any other polar solvent studied (Table 1). Confirmation of GC peaks was determined using authentic samples of each nitrile.

Decane showed the highest linear to branched ratio (12.4:1), whereas polar solvents such as acetonitrile gave the lowest linear to branched ratio (1:27). In decane, the dominant isomer formed was trans-3-pentenenitrile (82%), although some trans-2-pentenenitrile (6%) and cis-2-pentenenitrile (4%) were formed via olefin isomerization. In acetonitrile, the branched isomers *E*-2M2BN (74%) and *Z*-2M2BN (24%) constituted the majority of the products. All of the other solvents produced results within the range mentioned above. In some instances, small amounts of 4PN were observed, likely resulting from the isomerization of 3PN.

The observed selectivity data appear to be strongly governed by solvent effects. The initial trials included solvents lacking sterically bulky groups (entries 1, 2, 4, 7, and 9) and appear to follow a trend of linear to branched product ratio based on dielectric constant. One possible explanation for this trend is that the distribution of charge in intermediate π-allyl hydride **7** (Scheme 1) is such that it can interact with solvent to a greater extent than intermediate π-allyl cyanide **2**. A more polar solvent might then be capable of stabilizing the transition state leading to **8** or **9** more than that to **3**, which would result in preferential C−H activation. The high polarity associated with the nickel-cyanide bond, however implies that C−C cleavage should be expected to be favored in polar solvents, and argues against this explanation. A second consideration is the effect of possible solvent coordination to the 16-electron nickel(0) complex. Although some of these solvents have been shown to coordinate to metal complexes,[12,13] this is likely not a significant factor in this reaction based on the use of trifluorotoluene as a noncoordinating solvent (entry 5), which follows the trend based on dielectric constant. Further evidence for a general solvation model is provided by entries 3, 6, and 8 where solvents with sterically bulky, electron-donating substituents were used. Tetramethyl THF and di-*t*-butyl ketone fit the trend based on dielectric constant fairly well (entries 3 and 6), whereas pivalonitrile (entry 8) seems to be somewhat different in its solvation abilities than its neighbors of similar dielectric effect. A possible explanation is that as the bulk of the solvent increases, it leads to weakened solvation of **7** relative to **2**, thereby resulting in the more favorable formation of products derived from C−CN cleavage.

An alternative consideration that would be consistent with the greater amount of C−H activation seen in polar solvent would be a deprotonation mechanism for the conversion of **1** into **8** and **9**. In an attempt to look for such a pathway, 0.75 equiv piperidine ($pK_b = 2.8$) or pyridine ($pK_b = 8.8$) was added to several of the catalytic reactions. As shown in Table 2, added base has little effect on the linear to branched ratio in decane or THF. A slight change in ratio is seen in di-t-butylketone, producing twice as much branched product as without piperidine. The effect of added base was greatest in pivalonitrile, which shifted the product ratio by a factor of 6 toward C−H activation products when piperidine was present. Consequently, it can be concluded that a deprotonation pathway may constitute a reasonable pathway leading to branched products in polar solvents. In nonpolar solvents an ionic pathway is still disfavored even with base present.

Determination of Molecularity. Previous experiments involving the isomerization of 2M3BN into 3PN have shown this reaction

(13) Mindiola, D. J.; Waterman, R.; Jenkins, D. M.; Hillhouse, G. L. *Inorg. Chim. Acta* **2003**, *345*, 299.

Table 2. Isomerization of 2M3BN by [Ni(dippe)H]$_2$ in the Presence of Base[a]

solvent/additive	dielectric constant	linear: branched ratio with added base	linear:branched ratio without added base
decane/pyridine	2	12:1	12:1
decane/piperidine	2	9:1	12:1
THF/piperidine	7.5	4:1	4:1
di-t-butyl ketone/piperidine	10	1:3	1:1.5
pivalonitrile/piperidine	21.1	1:4	1.5:1

[a] Reaction conditions: [2M3BN] = 1 mM; [Ni] = 0.105 mM; equiv 2M3BN = 10; T = 100 °C; t = 180 min; 0.75 equiv base.

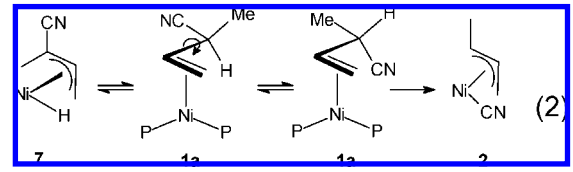
to be both zero order and first order with regards to substrate.[9,14] A series of reactions were run with 2M3BN (1−9.5 mM) to determine the molecularity of the system. The method of initial rates was used as a result of catalyst deactivation by conversion to (dippe)Ni(CN)$_2$ over the course of the reaction. The resulting data show a first order dependence on [2M3BN] (see Supporting Information). Additionally, variation of nickel concentration (0.0105 mM−0.105 mm) also showed a first order dependence of the initial rate indicating that the reaction is overall second order (eq 1).

$$\text{rate} = k[\text{2M3BN}][\text{catalyst}] \quad (1)$$

Temperature Dependence of C−CN and C−H Activation in 2M3BN Reaction. It was previously reported in the π-allylic cyanide system that C−C cleavage becomes more competitive kinetically with C−H cleavage with an increase of temperature.[7] The temperature dependence of the isomerization of 2M3BN was also investigated. Two series of reactions were run at various temperatures using either decane or *N*,*N*-dimethylformamide (DMF) as solvents, these solvents being chosen to examine regimes in which the dominant reaction pathway is either C−CN (93%) or C−H (90%) cleavage (Table 3). In general, the linear to branched product ratio increases by about a factor of 3 with increasing temperature in both nonpolar decane and polar DMF.

Rate constants (Table 4) were determined for each reaction temperature and the activation parameters for C−CN and C−H bond cleavage were obtained from Eyring plots (Figure 6, Table 5). While the enthalpic difference between C−CN and C−H activation shows the latter to be more favorable by about 6 kcal mol^{-1}, the unfavorable entropy of activation for C−H activation results in comparable $\Delta G^{\ddagger}$ values for these reactions under typical catalytic conditions. These values for $\Delta S^{\ddagger}$ suggest a more ordered transition state in the C−H mechanism, as seen in the earlier study of C−H vs C−CN activation of allyl cyanide by [(dippe)NiH]$_2$.[7] Perhaps this order is associated with the deprotonation of **1** by an external base or solvent molecule.

The reaction of [(dippe)NiH]$_2$ with 2M3BN begins with the η^2-coordination of the reactive (dippe)Ni(0) fragment to one of two faces of the olefin in 2M3BN (**1a, 1b**) as observed by ^{31}P{^{1}H} NMR spectroscopy. The C−C bond then rotates so CN is able to interact with the nickel center (eq 2, **1a** shown). Alternatively, if the rotation places the allylic hydrogen endo to the nickel then C−H activation can occur giving 2M2BN products (**8**, **9**).



A similar type of mechanism has been proposed for the isomerization of 2M3BN into 3PN by Chaumonnot et al.[10] beginning with η^2-coordination of the Ni(0) fragment to 2M3BN followed by C−CN activation to a σ-allyl species and isomerization to the π-allylic species. A C−H activation pathway was not calculated in these studies. The pathway was supported by DFT calculations and these sequences are consistent with the activation parameters determined both in this study and in the study with allyl cyanide.[7] DFT calculations are underway on the current system to try to determine the origin of the differences in these thermodynamic parameters.

It is also worth noting that under typical industrial conditions, neat 2M3BN (a polar solvent) is used during catalysis. Could use of a nonpolar solvent lead to improvements in selectivity, thereby avoiding the second branched-to-linear isomerization in the DuPont Adiponitrile process?[15] In an attempt to evaluate this possibility, the catalyst Ni[P(O-p-tolyl)$_3$]$_3$ was synthesized[16] and reacted with 2M3BN in decane under the same reaction conditions as used in Table 1. Surprisingly, only 36% conversion was seen and the products were exclusively branched. Consequently, verification of this hypothesis seems unlikely, although it would be preferable to test under true industrial conditions.

Summary and Conclusions

Reactions of [(dippe)NiH]$_2$ with 2M3BN in different solvents and at different temperatures gives different linear to branched product ratios in the isomerization. As the solvent polarity increases, the ratio of C−H activated branched products to C−CN activated linear products increases, apparently as a result of better solvation of the C−H activation transition state vs the C−CN transition state, or because of the appearance of a deprotonation pathway, since the ground-state is the same for both reactions. The activation parameters indicate a smaller $\Delta H^{\ddagger}$ for the C−H oxidative cleavage by ~6 kcal/mol, while the $\Delta S^{\ddagger}$ value was ~15 eu more negative, suggesting a more tightly bound and more ordered transition state in the C−H activation step.

Experimental Section

General Considerations. All manipulations were performed under a nitrogen atmosphere, either on a high-vacuum line using modified Schlenk techniques or in a Vacuum Atmospheres Corporation glovebox. Decane, octane, benzene, and tetrahydrofuran were distilled from dark purple solutions of sodium/benzophenone ketyl. Acetone and acetonitrile were dried over calcium hydride and 4A molecular sieves and distilled before use. All other solvents were dried using 4A molecular sieves and distilled before use. [(dippe)NiH]$_2$ was synthesized according to the previously reported procedure.[17] *trans*-3-Pentenenitrile, *cis*-2-pentenenitrile, and 4-pentenenitrile were purchased from Aldrich Chemical Co. 2-Methyl-3-butenenitrile, *Z*-2-methyl-2-butenenitrile, and *E*-2-methyl-2-butenenitrile were supplied by DuPont. *trans*-2-Pentenenitrile was

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(15) For an example of direct hydrocyanation of butadiene to 3PN, see: Bini, L; Mueller, C.; Wilting, J.; von Chrzanowski, L.; Spek, A. L.; Vogt, D *J. Am. Chem. Soc.* **2007**, *129*, 12622.
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Table 3. Temperature Dependence Data for the Catalytic Isomerization of 2M3BN to Other Isomers by $[Ni(dippe)H]_2$[a]

					% products					
entry	solvent	*T* (°C)	*t* (min)	% conv	*Z*-2M2BN	*cis*-2PN	*E*-2M2BN	*trans*-3PN	*trans*-2PN	linear:branched[b]
1	decane	100	7	94	2.1	2.4	3.9	87.7	3.8	15.7:1
2	decane	90	16	94.1	2.7	2.1	6.2	85.6	3.4	10.4:1
3	decane	80	17	86.2	1.7	1.4	4.2	90.5	2.2	15.9:1
4	decane	70	30	71.1	3	1	7.6	86.9	1.5	8.4:1
5	decane	60	60	71.3	3.9	0.8	11.1	82.9	1.3	5.7:1
6	DMF	100	16	95.8	17.1	0	76.5	5.6	0.7	1:14.9
7	DMF	90	16	91.8	17.7	0.7	73.1	7.4	1	1:10.1
8	DMF	80	30	97.2	17.5	0.4	75.2	6.3	0.6	1:12.5
9	DMF	70	60	99	18.3	0.2	78.8	2.5	0.2	1:33.5
10	DMF	60	60	99	16.8	0.2	80.3	2.5	0.2	1:34

[a] Reaction conditions: [2M3BN] = 1 mM; [Ni] = 0.105 mM; %*v* 2M3BN = 10; equiv 2M3BN = 10. [b] Linear:branched ratio calculated with linear products *cis*-2PN, *trans*-2PN, *cis*-3PN, *trans*-3PN, and 4PN vs. branched products *Z*-2M2BN and *E*-2M2BN.

Table 4. Initial Rates for C−CN and C−H Activation of 2M3BN by $[Ni(dippe)H]_2$ in Decane and DMF

T (°C)	k_{init}(C−CN), decane, s^{-1}	k_{init}(C−H), DMF, s^{-1}
100	0.233	0.202
90	0.142	0.170
80	0.0575	0.0699
70	0.0296	0.0558
60	0.0167	0.0346

synthesized by modification of a previously reported method.[18] $[(dippe)Ni(\eta^3\text{-}CH_2CHCHMe)]^+BPh_4^-$ was prepared by modification of a previously reported method,[19] substituting methyl-allyl bromide for allyl-bromide. *cis*-3-Pentenenitrile was unable to be synthesized and no commercial samples were available, but its GC retention time was estimated based upon relative retention time patterns of the other cis/trans isomers of the products (Z isomers elute before E, but in the same order). All other chemicals, filter aids, and chromatographic materials were used as received.

All reactions were run in modified Schlenk flasks (see Supporting Information) under a positive pressure of nitrogen in an aluminum heating block at temperatures ranging from 25 to 100 °C ± 0.2°. The temperature was controlled with an Omega CSC32 benchtop controller. Samples were collected in 10 μL aliquots and chemically quenched with chloroform to destroy any remaining catalyst and stored at −20 °C until analysis. NMR data (^1H and $^{31}P\{^1H\}$) were recorded on a Bruker Avance 400 instrument. Chemical shifts are given in δ and referenced to residual solvent peaks.

Stoichiometric Isomerization of 2M3BN. $[(dippe)NiH]_2$ (0.015 g, 0.023 mmol) was dissolved in THF-d_8 in a septum-capped NMR tube and cooled to −50 °C. 2M3BN (4.8 μL, 0.047 mmol) was added via syringe. The reaction was monitored via variable temperature ^{31}P NMR spectroscopy at 10° increments from −50 to 30 °C. Observations are described in the text.

Preparation of 2. $[(dippe)Ni(\eta^3\text{-}CH_2CHCHMe)]^+BPh_4^-$ (0.199 g, 0.286 mmol) and NEt_4CN (0.055 g, 0.352 mmol) were dissolved in 30 mL THF and stirred for 3 h producing a dark-red solution with white precipitate. The solution was filtered through celite and the solvent was removed under vacuum leaving 0.053 g of an orange residue (37% yield). ^1H NMR (400 MHz, THF-d_8): δ 5.07 (q, 1 H, allylic $CH_2CHCHMe$), 3.91 (m, 1 H, allylic $CH_2CHCHMe$), 2.2 (m, 6H, ^{i}pr CH and allylic $CH_2CHCHMe$), 1.72 (dd, 4 H, PCH_2CH_2P), 1.26 (dd, 12 H, ^{i}pr CH_3), 1.17 (dd, 12 H, ^{i}pr CH_3). The allylic methyl group was obscured by the phosphine resonances. $^{31}P\{^1H\}$ NMR (400 MHz, THF-d_8): δ 54 (v br s).

Preparation of 3, 5, 6, 8, and 9. $[(dippe)NiH]_2$ (0.0125 g, 0.0194 mmol) was dissolved in THF and placed in a septum-capped NMR tube at −30 °C. *trans*-3PN, *trans*- or *cis*-2PN, or *E*- or *Z*-2M2BN (3.7 μL, 0.038 mmol) was added to the reaction changing the color from dark-red to yellow-brown as **3**, **5**, **6**, **8**, or **9** formed respectively. The reaction was monitored while warming at intervals of 10 °C up to 55 °C via $^{31}P\{^1H\}$ and ^1H NMR spectroscopy. Aliquots (5 μL) were collected, quenched with $CHCl_3$ (25 μL) and analyzed via GC. ^1H NMR of **3** (400 MHz, THF-d_8): δ 5.1 (dq, 1 H, $CH_3CHCHCH_2CN$), 4.9 (q, 1 H, $CH_3CHCHCH_2CN$), 1.5−2.1 (m, 10 H, ^{i}pr CH, $CH_3CHCHCH_2CN$ and PCH_2CH_2P), 0.8−1.1 (m, 27 H, ^{i}pr CH_3 and $CH_3CHCHCH_2CN$). $^{31}P\{^1H\}$ NMR of **3** (400 MHz, THF-d_8): δ 67.5 and 66.7 (d). ^1H NMR of **6** (400 MHz, THF-d_8): δ 5.5 (dt, 1 H, $CH_3CH_2CHCHCN$), 4.5 (d, 1 H, $CH_3CH_2CHCHCN$), 1.5−2.3 (m, 10 H, ^{i}pr CH, $CH_3CH_2CHCHCN$ and PCH_2CH_2P), 0.8−1.3 (m, 24 H, ^{i}pr CH_3), 0.6 (t, 3 H, $CH_3CH_2CHCHCN$. $^{31}P\{^1H\}$ NMR of **6** (400 MHz, THF-d_8): δ 70.5 and 67.0 (d). ^1H NMR of **8** (400 MHz, THF-d_8): δ 5.3 (q, 1 H, $CH_3CHC(CH_3)(CN)$), 2.1 (septet, 4 H, ^{i}pr CH), 0.8−1.7 (m, 34 H, ^{i}pr CH_3, $CH_3CHC(CH_3)(CN)$, $CH_3CHC(CH_3)(CN)$ and PCH_2CH_2P. $^{31}P\{^1H\}$ NMR of **8** (400 MHz, THF-d_8): δ 70.1 and 62.9 (d).

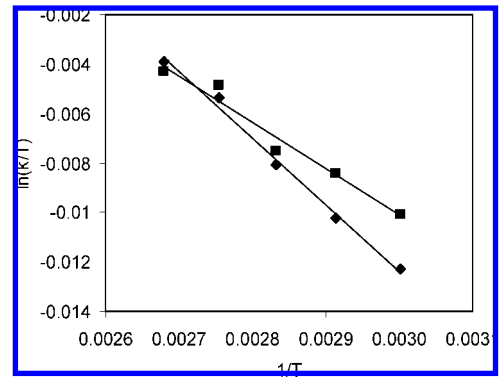

Figure 6. Eyring Plot of C−CN(♦) and C−H(■) activation.

Table 5. Thermodynamic Parameters for C−CN and C−H Activation of 2M3BN by $[Ni(dippe)H]_2$[a]

	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (e.u.)	$\Delta G^{\ddagger}$ at 100 °C (kcal/mol)
C−CN	17.3 ± 2.6	−29 ± 7	28.2
C−H	11.4 ± 5.3	−45.3 ± 15	28.3

[a] Errors calculated based on 95% confidence limits.

Preparation of 10. $[(dippe)NiH]_2$ (0.02 g, 0.031 mmol) and $NaBPh_4$ (0.015 g, 0.044 mmol) were dissolved in THF at 25 °C. 1-Bromo-3-cyano-2-butene (0.015 g, 0.094 mmol) was added, and the solution was stirred for 3 h and allowed to sit overnight forming a yellow-orange solid. The solution was decanted and the remaining solid extracted with diethyl ether. The ether solution was dried leaving 0.02 g of yellow crystals (29% yield). This complex was too unstable to allow for spectroscopic characterization other than through low temperature X-ray crystallography.

Reaction of 10 with $LiBEt_3H$. 10 (0.01 g, 0.139 mmol) was dissolved in 1 mL THF yielding a yellow solution. An excess of

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$LiBEt_3H$ (0.2 mL, 1.68 mmol) was added and the solution was stirred for 30 min. A white precipitate was observed to form. The solution was filtered through alumina, chemically quenched with chloroform, and analyzed via GC. The results are described in the text.

Catalytic Isomerization of 2M3BN in Different Solvents. $[(dippe)NiH]_2$ (0.068 g, 0.105 mmol) was dissolved in 1.5 mL decane (or selected solvent) and 0.300 mL octane (GC internal standard) and added to a modified Schlenk flask under N_2 (see Supporting Information). The reaction mixture was sealed and placed in an aluminum heating block at 100 °C for 3 h. Once the reaction reached 100 °C, 2M3BN (0.205 mL, 2.5 mmol) was added via syringe. After 3 h, the reaction was chemically quenched with 2 mL $CHCl_3$ to destroy any remaining catalyst and a sample was extracted and stored at −20 °C until analysis by GC.

Catalytic Isomerization of 2M3BN at Different Temperatures. $[(dippe)NiH]_2$ (0.068 g, 0.105 mmol) was dissolved in 1.5 mL decane (or DMF) and 0.3 mL octane in a modified Schlenk flask under N_2 (see Supporting Information). The reaction mixture was placed in an aluminum heating block, subjected to positive nitrogen pressure via a needle, and heated to the required temperature (25−100 °C). 2M3BN (0.205 mL, 2.5 mmol) was added and samples were collected at specific intervals via syringe. The samples were quenched with 20 μL $CHCl_3$ and stored at −20 °C until analysis. This reaction was followed and quantified by GC. See Supporting Information for additional details regarding the kinetic determinations. Reactions run with added base (piperidine or pyridine) were performed under identical conditions; 0.79 mmol piperidine (7.8 μL) or pyridine (6.4 μL) were added prior to addition of 2M3BN. The reaction was analyzed as described above.

Catalytic Isomerization of 2M3BN using $Ni[P(O\text{-}p\text{-}tolyl)_3]_3$. This reaction was run using 0.226 g (0.203 mmol) $Ni[P(O\text{-}p\text{-}tolyl)_3]_3$ and 0.205 mL (2.02 mmol) 2M3BN in 1.5 mL solvent with 0.3 mL octane added as internal standard. The reaction was carried out and analyzed as described above.

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Supporting Information Available: GC traces for reaction products, pictures of reaction apparatus, and X-ray data collection parameters for **6** and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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