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Nickel Complexes Involved in the Isomerization of 2-Methyl-3-butenenitrile

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The nickel(0) fragment [(P−P)Ni], where (P−P) = dcype (1,2-bis(dicyclohexylphosphino)ethane) or dtbpe (1,2-bis(di-*tert*-butylphosphino)ethane), reacts with the cyano-olefins involved in the isomerization process of 2-methyl-3-butenenitrile (2M3BN), producing the corresponding complex [(P−P)Ni(η^2-*C,C*-cyano-olefin)]. In the case of 2M3BN and 3-pentenenitrile (3PN), the π-methylallyl metal complex was observed in solution. All of the intermediates in the catalytic cycle were detected and characterized by heteronuclear NMR spectroscopy; some of these were also characterized by single-crystal X-ray diffraction studies. The initial catalytic behavior of this system for the isomerization of 2M3BN was studied also.

Introduction

Ever since the discovery of Nylon-66 (poly(hexamethylene adipamide)),[1] the large-scale production of adiponitrile (AdN)—a precursor of 1,6-hexanediamine—has been a very important industrial process.[2] The catalytic industrial process requires the double hydrocyanation of butadiene, with Ni(0)-phosphite complexes typically being added as catalysts to drive this process. The first HCN addition produces a kinetic mixture of isomers, composed of the desirable linear isomer 3-pentenenitrile (3PN) and the undesirable branched isomer 2-methyl-3-butenenitrile (2M3BN); the latter is converted *in situ* into 3PN by means of a catalytic C−CN bond breaking/forming reaction, driven by a Ni(II) allyl cyanide complex. Once formed, 3PN is catalytically isomerized further to the terminal olefin derivative 4-pentenenitrile (4PN). The process is carried out in the presence of a Ni(0) complex and Lewis acids (LA), which are used as cocatalysts. The addition of a second HCN to the olefin in this linear nitrile ultimately takes place, producing AdN.[3]

2M3BN and 3PN may also undergo a rearrangement of the C═C bond through a C−H bond activation reaction to produce other stable products, such as *Z*- or *E*-2-methyl-2-butenenitrile (2M2BN) and the linear 2-pentenenitrile (2PN) isomer, the stability of these isomers being associated with the conjugation of the C═C bond in these compounds with the C≡N moiety. All eight possible isomers are shown in Figure 1.

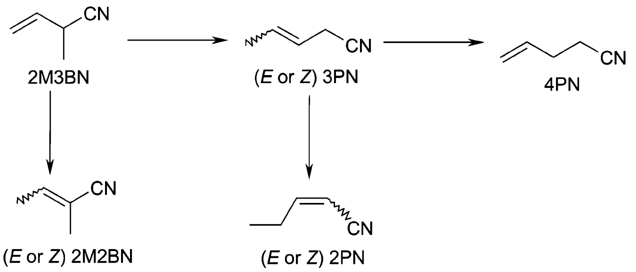

Figure 1. Isomerization of 2-methyl-3-butenenitrile catalyzed by Ni(0).

Several mechanistic studies have been made using [(phosphite)Ni(0)] complexes, cyano-olefins, and HCN, to yield additions to C═C bonds, including the use of Lewis acids in such processes.[4−6] More recently, the use of [Ni(COD)$_2$] as catalytic precursor, in combination with P-donor-bidentate ligands such as phosphines,[7−11] phosphonites,[8] and phosphites,[12] has been reported to achieve the transformation from the

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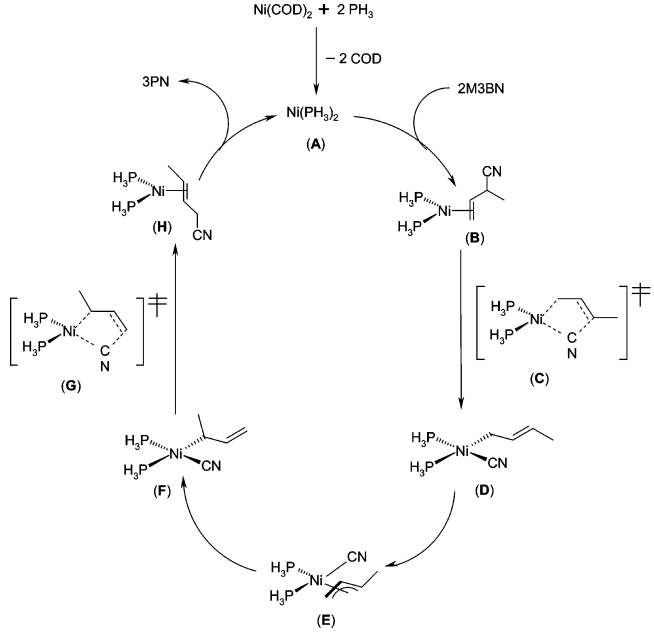

Figure 2. Catalytic cycle proposed for the isomerization of 2M3BN to 3PN.[7]

branched nitrile (2M3BN) to the linear nitrile (3PN). Although some mechanistic details are still unknown, Sabo-Etienne recently disclosed a proposal for the catalytic isomerization of 2M3BN to 3PN on the basis of DFT calculations (see Figure 2),[7] in which the substitution of COD ligands by phosphines in [Ni(COD)$_2$] produces the reactive intermediate [Ni(PH$_3$)$_2$] (**A**). The latter was proposed to react with a molecule of 2M3BN to give an η^2-*C,C* bound olefin complex of the formula [(PH$_3$)$_2$Ni(η^2-*C,C*-2M3BN)] (**B**), in which the C−CN bond oxidative cleavage by nickel(0) occurs producing a σ-allyl nickel(II) complex of the type [(PH$_3$)$_2$Ni(η^1-allyl)(CN)] (**D**). A transition state metallacycle of the type [(PH$_3$)$_2$Ni(η^1-*C*-allyl,η^1-*C*-CN)] (**C**), resulting from the rearrangement of the nitrile ligand, was proposed to exist prior to the oxidative addition of the C−CN bond to form complex **D**. This species was then proposed to isomerize into a π-allyl complex, [(PH$_3$)$_2$Ni(η^3-1-methylallyl)(CN)] (**E**), which evolved into a second σ-allyl complex, [(PH$_3$)$_2$Ni(η^1-allyl)(CN)] (**F**), with the inner skeleton of the allyl now bound to the nickel(II) center, proximal to the −CN ligand. From this intermediate, re-formation of the C−CN bond through another metallacycle transition state (**G**) leads to the η^2-*C,C* linear bound 3PN nickel(0) complex (**H**), from which 3PN could be obtained along with the original catalyst species **A**, thereby continuing the catalytic cycle.

For a number of years, our group has been interested in the activation of C−CN bonds of aryl-, heteroaryl-, and alkyl-nitriles using nickel(0) complexes of the general formula [(P−P)Ni(μ-H)]$_2$, in which (P−P) is a chelating diphosphine ligand such as dcype (1,2-bis(dicyclohexylphosphino)ethane), dtbpe (1,2-bis(di-*tert*-butylphosphino)ethane), or dippe (1,2-bis(diisopropylphosphino)ethane).[13,14] The reactions that occur result in the immediate formation of nickel(0) complexes of the type [(P−P)Ni(η^2-*C,N*-R)] (R = aryl, heteroaryl,[14] alkyl[13]), in which the nitrile is *side-on* coordinated to the [(P−P)Ni] moiety. Under certain conditions (thermal[14] or photochemical[13]) and depending on the substituent that is present (except for adamantyl-nitrile, which is stable to further reaction[13]), these η^2-nitrile complexes undergo oxidative addition of the C−CN bond to the nickel(0) center, producing the nickel(II) derivatives of the type [(P−P)Ni(CN)(R)]. The latter results have prompted us to study the reactivity of nickel complexes containing the moiety [(P−P)Ni] in reactions using unsaturated nitriles. In particular, the catalytic isomerization of 2M3BN to 3PN using the [(dppf)Ni] species (dppf = 1,2-bis(diphenylphosphino)ferrocene) has recently been reported.[11] The catalytic isomerization of 2M3BN was achieved with 100% conversion using [(dppf)Ni], and the yield of 3PN was found to be 83% by both GC-MS and ^{1}H NMR spectroscopy.[11] In this study, the methodology for the characterization and quantification of products was rigorously demonstrated, the available literature addressing the mechanistic details of such process being very limited,[7−10] and a lack of hard analytical data being cited to permit reproduction of the reported results (see ref 11). Recently, Jones and co-workers have extended the chemistry of the [(dippe)Ni] moiety to the C−CN activation of allylnitrile in order to investigate the C−H and C−CN cleavage reaction in this substrate. The reaction of [(dippe)NiH)]$_2$ with allyl cyanide at low temperature quantitatively generated the η^2-olefin complex [(dippe)Ni(η^2-*C,C*-CH$_2$=CHCH$_2$CN)], which at ambient temperature or above was converted to a mixture of the C−CN cleavage product [(dippe)Ni(η^3-allyl)(CN)] and the olefin-isomerization products *cis*- and *trans*-[(dippe)Ni(η^2-*C,C*-crotononitrile)], formed via C−H activation.[15] Ultimately, only the latter products were observed, as they represent the thermodynamic sink for the reaction. Herein, we report the isolation of the key intermediates involved in the isomerization of 2M3BN to the linear 3- and 4-PN products using nickel(0) complexes, the [(dcype)Ni] moiety being particularly useful for such ends. Spectroscopic characterization of Ni(0) complexes of all eight isomers of 2M3BN is provided, as well as characterization of σ- and π-allyl cyanide intermediates in the isomerizations.

Results and Discussion

Reactions of 2M3BN and 3PN. The *in situ* reaction of [(dcype)Ni(COD)][16] with a 2-fold excess of 2M3BN in toluene-*d*$_8$ solution produces an instantaneous color change from brown-red to brown-yellow. After 15 min of stirring, the ^{31}P{^{1}H} NMR spectrum showed two doublets centered at δ 58.3 and 61.9 ($^2J_{P-P}$ = 52 Hz), the magnitude of the coupling constant being indicative of a nickel(0) complex with two distinct phosphorus environments.[13,14] This initial complex was assigned as [(dcype)Ni(η^2-*C,C*-2M3BN)], **1** (Figure 3a). After 6 h at room temperature, four new species were observed to form gradually, the evolution of reaction intermediates being determined by the corresponding ^{31}P{^{1}H} NMR spectrum at different reaction times (15 min, 6 h, and 12 h, see Figure 3). The new species can be described in these spectra as follows: (1) two doublets at δ 63.5 and 59.1, with $^2J_{P-P}$ = 52.2 Hz, attributed to [(dcype)Ni(η^2-*C,C-trans*-3PN)], **3**, (2) a broad signal centered at δ 66.0 indicative of an exchange process, assigned as a fluxional η^3-1-methylallyl complex, **2**, (3) a singlet at δ 85.8 ppm due to

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[16] The reaction of [Ni(COD)$_2$] with 1 equiv of dcype in a toluene solution produced an instantaneous color change from yellow to brown-red. The ^{31}P{^{1}H} NMR spectrum in toluene-*d*$_8$ revealed the presence of a singlet at 67.3 ppm, assigned to the complex [(dcype)Ni(COD)].

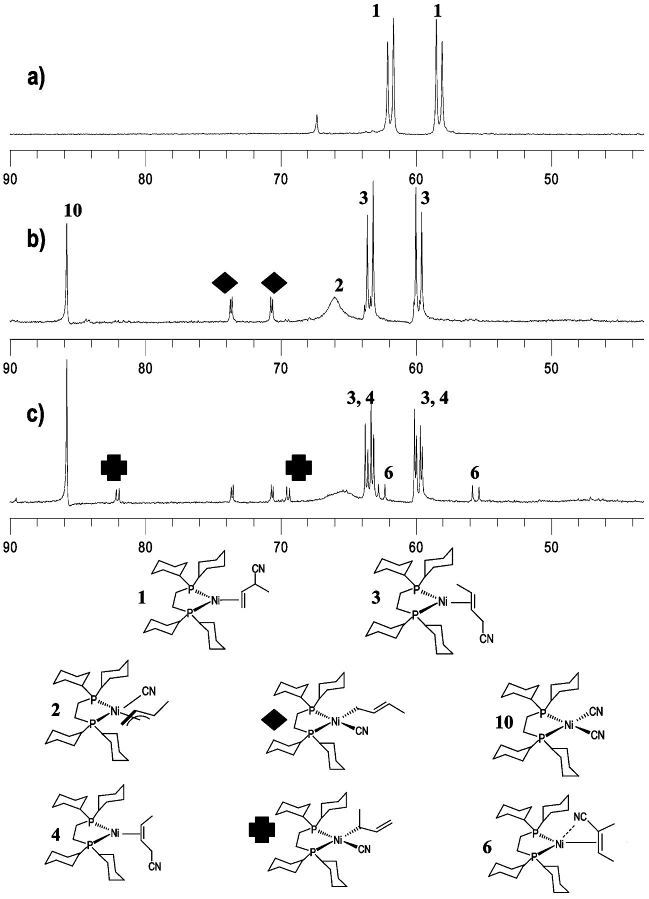


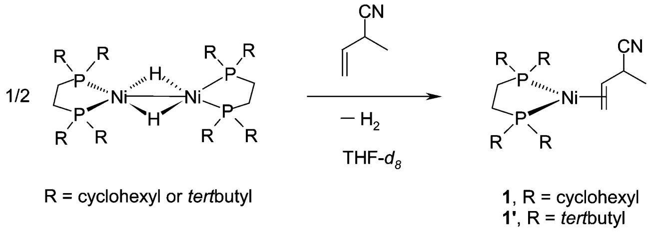
Figure 3. ^{31}P{^{1}H} NMR spectra in toluene-d_8 at different times, for the isomerization of 2M3BN using nickel complexes: (a) 15 min, (b) 6 h, (c) starting from *trans*-3PN, 12 h.

the nickel(II) complex [(dcype)Ni(CN)$_2$], **10** (confirmed further by X-ray structure analysis, *vide infra*; the latter being analogous with the complex [(dippe)Ni(CN)$_2$]),[13] and (4) two small doublets centered at δ 73.6 and 71.3 with $^{2}J_{P-P}$ = 16.3 Hz characteristic of a nickel(II) complex.

Confirmation of the new nickel(0) and nickel(II) intermediates was obtained by using pure *trans*-3PN. (These intermediates are labeled in Figure 3b as **3** and ◆, respectively.) The reaction of [(dcype)Ni(COD)] with a 2-fold excess of *trans*-3PN at ambient temperature in toluene-d_8 gave rise after 15 min to signals in the ^{31}P{^{1}H} NMR spectrum at δ 63.5 and 59.1 with $^{2}J_{P-P}$ = 52.2 Hz, the same as observed in the reaction using 2M3BN after 6 h of reaction and thereby assigned to [(dcype)Ni(η^2-*C,C-trans*-3PN)]. The same reaction with pure *trans*-3PN was also examined after 12 h at room temperature (Figure 3c). The ^{31}P{^{1}H} NMR spectrum displayed some of the signals observed in the reaction starting with 2M3BN after 6 h, as well as some additional signals that were assigned as follows: (a) two small doublets centered at δ 82.2 and 69.5 with $^{2}J_{P-P}$ = 25.9 Hz, assigned to a nickel(II) complex, (b) two small doublets at δ 62.5 and 55.8 with $^{2}J_{P-P}$ = 57.9 Hz, attributed to the nickel(0) complex [(dcype)Ni(η^2-*C,C-E*-2M2BN)], **6** (*vide infra*), and (c) two signals at δ 63.3 and 58.9 with $^{2}J_{P-P}$ = 52.1 Hz, which were assigned to [(dcype)Ni(η^2-*C,C-cis*-3PN)], **4** (*vide infra*).

The above nickel(II) complexes were tentatively assigned to Ni-σ-allyl species depicted in Figure 2 as **D** and **F**, respectively, the small coupling constants of 16.3 and 25.9 Hz being consistent with this formulation. The compound labeled as ◆ in Figure 3 was observed on using 2M3BN or starting from *trans*-3PN, whereas the complex labeled as + was formed only on using *trans*-3PN. Consequently complex ◆ may be the analogue of complex **D** in Figure 2 and complex + may be the analogue of complex **F** in Figure 2. Similar reactions were performed using [(dcype)Ni(μ-H)]$_2$ as nickel source, giving similar behavior, ruling out the involvement of COD in these species. The above assignment requires that the broadness of π-allyl cyanide **2** be attributed to hindered rotation of the allyl group, not $\pi \rightarrow \sigma$ interconversion.

Scheme 1



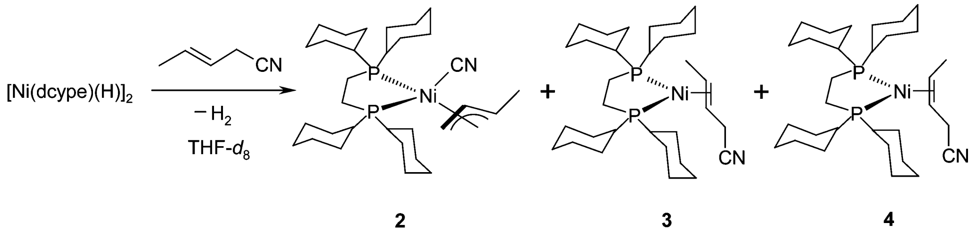
Characterization of the Complexes [(dcype)Ni(η^2-*C,C*-2M3BN)] (1) and [(dtbpe)Ni(η^2-*C,C*-2M3BN)] (1′). The reaction of the nickel(I) dimer [(dcype)Ni(μ-H)]$_2$ in toluene-d_8 with 2M3BN immediately yielded the olefinic complex **1** with evolution of H$_2$ gas (color change of the solution from dark red to yellow). The ^{31}P{^{1}H} NMR spectrum displayed the signals mentioned above for this complex, located at δ 58.3 and 61.9 ($^{2}J_{P-P}$ = 52 Hz). In the ^{1}H NMR spectrum the resonances assigned to the coordinated olefinic protons were shifted upfield from those in free 2M3BN (δ 5.80 and 5.28) and overlapped with the signals rising from the alkylphosphine ligand, consistent with the *side-on* coordination of the C═C bond to the nickel center (Scheme 1). No ^{13}C{^{1}H} is available for **1** due to the reactivity of the sample at room temperature during the acquisition process. The presence of two ^{31}P resonances indicates that the olefin lies in the NiP$_2$ plane and is not rotating rapidly.

On using a bulkier diphosphine as dtbpe, the analogous complex **1′** was obtained. The ^{31}P{H} NMR spectrum displayed two sharp doublets at 89.5 and 91.7 ppm, with $^{2}J_{P-P}$ = 64.7 Hz. The ^{1}H NMR spectrum depicted no signals for the free olefin, and only slightly broad multiplets between δ 2.4 and 0.8 were observed. The ^{13}C{^{1}H} NMR spectrum was more informative, the olefinic carbons appearing as doublets of doublets at δ 47.7 (J_1 = 25.7 Hz, J_2 = 2.7 Hz) and δ 32.9 ppm (J_1 = 20.8 Hz, J_2 = 2.6 Hz), the two chemical shifts for these carbons shifted substantially upfield from those of the free ligand (δ 135.2 for *C*HR═ and δ 117.4 ppm for *C*H$_2$═), which appear as singlets. The −CN signal was located at δ 123.8, close to the resonance of this moiety in the free ligand in the same solvent (121.4 ppm), thereby indicating no η^2-CN coordination to the nickel(0) center. In both cases (**1** and **1′**) only one isomer was detected at room temperature in the NMR spectra for ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H}, despite the fact that the double bond in 2M3BN has two distinct faces. This may be due to small NMR differences between the diastereomers not resolved or to the nickel preferentially binding to one particular face of the olefin.

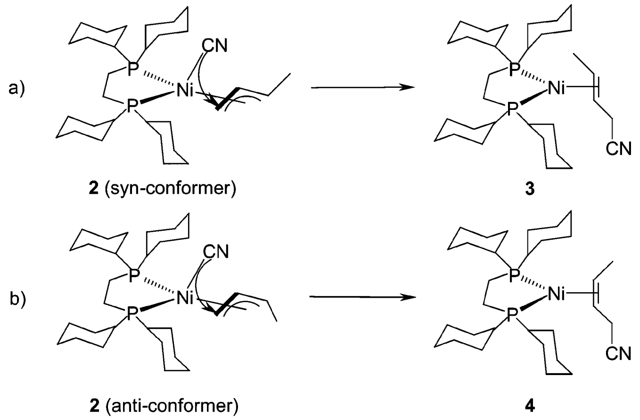
Characterization of Complexes [(dcype)Ni(η^3-1-methylallyl)(CN)] (2), [(dcype)Ni(η^2-*C,C-trans*-3PN) (3), and [Ni(dcype)(η^2-*C,C-cis*-3PN)] (4). The reaction of [(dcype)Ni(μ-H)]$_2$ with *trans*-3PN produces a mixture of the complexes **2**, **3**, and **4** (Scheme 2); complex **3** forms first and isomerizes into complexes **2** and **4** after 12 h.

Complex **2** was separated from the other two by column chromatography over silica gel and was characterized separately; separation of complexes **3** and **4** was not possible, and the two complexes were characterized in the mixture. In the case of **2**,

Scheme 2



Scheme 3



the $^{31}P\{^{1}H\}$ NMR spectrum of this complex showed only a broad signal centered at δ 66.0 ppm, indicative of an exchange process consistent with the hindered rotation of the π-allyl ligand (*syn*- and *anti*-conformers illustrated in Scheme 3, *vide infra*).[17] The same kind of spectrum has been observed in closely related compounds such as [(dppb)Ni(η^3-1-methylallyl)(CN)][7] and [(dppf)Ni(η^3-1-methylallyl)(CN−BEt_3)].[11] The ^1H NMR spectrum displayed one resonance for each allylic proton in the complex, the latter being located at δ 4.93 (s, br, C*H* central), 4.41 (q, $^3J_{H-H} = 9.6$ Hz, C*H*Me), and 3.35 (d, $^3J_{H-H} = 9.6$ Hz, CH_2). The resonance for the methyl group was obscured by the resonances of the cyclohexyl groups from the phosphine. The $^{13}C\{^{1}H\}$ spectrum of complex **2** displayed the expected signals for the allylic ligand at δ 107.8 (br, *C*H central), 83.7 (pt, *C*HMe), and 51.2 (pt, *C*H_2). The signal for the −CN moiety in the same spectrum appeared as a broad signal centered at 146.5 ppm.

The $^{31}P\{^{1}H\}$ spectrum of the mixture of **3** and **4** showed two slightly asymmetric doublets with coupling constants of 52 Hz, consistent with the presence of nickel(0): in the case of **3**, at δ 63.5 ($^2J_{P-P} = 52.2$ Hz) and 59.1 ($^2J_{P-P} = 52.2$ Hz), and in the case of **4**, at δ 63.3 ($^2J_{P-P} = 52.1$ Hz) and 58.9 ($^2J_{P-P} = 52.1$ Hz). The $^{13}C\{^{1}H\}$ spectrum of this mixture displayed signals for the olefinic carbons in both complexes shifted upfield from those in the free ligand (δ 130.6, =*C*HCH_2CN and δ 120.7, =*C*HMe): at δ 52.6 ($^2J_{C-P} = 26.8$ Hz) and 35.3 ($^2J_{C-P} = 15.5$ Hz) for **3**, and at δ 50.1 ($^2J_{C-P} = 26.9$ Hz) and 35.1 ppm ($^2J_{C-P} = 15.5$ Hz) for **4**. The uncoordinated −CN moieties were located at δ 125.9 and 124.6 for **3** and **4**, respectively. In both cases, the chemical shifts appear slightly downfield from that of free *trans*-3PN (δ 118.5, s), due to coordination through the double bond to the metal center. The ^1H NMR spectrum of the mixture was also obtained, showing two slightly broad multiplets at δ 3.37 and 2.55, attributed to olefinic proton resonances. The two resonances overlap partially with those of the phosphine ligand and are shifted upfield from those of the free 3PN ligand (δ 5.78 (=*H*CH_2CN) and δ 5.38 (=*H*Me)).

The formation of the *cis*- and *trans*-3PN isomers can be explained on the basis of the coexistence of *syn*- and *anti*-conformers within the 1-methylallyl complex, arising from $\pi-\sigma-\pi$ isomerization.[17] Reductive elimination of the −CN moiety in the *syn*-isomer will produce the *trans*-3PN isomer **3**, while reductive elimination in the *anti*-allyl conformer will produce the corresponding nickel(0) *cis*-3PN complex **4**. Alternatively, these reductive eliminations might proceed through a transition state similar to that in **G**. This type of reactivity has already been established for closely related allyl-palladium complexes.[18]

Reactions of [(dcype)Ni(μ-H)]$_2$ with 4PN, *E*-2M2BN, *Z*-2M2BN, and *cis*-2PN. Given that 2M3BN not only isomerizes to 3PN and 4PN but also produces *E*- and *Z*-2M2BN and 2PN, the reactions of the nickel(I) hydride dimer [(dcype)Ni(μ-H)]$_2$ were also studied with these nitriles under stoichiometric conditions (Scheme 4). In all cases, the reactions occurred instantaneously upon addition of the corresponding nitrile (two per nickel center), resulting in the immediate change of color from the solution from dark red to yellow and the sudden evolution of H_2 gas. After 15 min, complexes **5**−**7** and **9** were obtained. These compounds were characterized by heteronuclear NMR and in the case of **6′** and **7′** by single-crystal X-ray diffraction studies (*vide infra*). None of the complexes derive from C−CN bond cleavage. On using a 2-fold excess of *cis*-2PN, the isomerization from *cis*- to *trans*-isomer on the olefin was observed, giving rise to complex **8**, a feature that can be explained by a reversible C−H breaking/forming reaction (*vide infra*).

Characterization of [(dcype)Ni(η^2-*C,C*-4PN)] (9). As in all other nickel complexes containing the [(dcype)Ni] moiety, the $^{31}P\{^{1}H\}$ NMR spectrum of complex **9** displayed two sharp doublets at δ 62.0 ($^2J_{P-P} = 65.5$ Hz) and 57.5 ($^2J_{P-P} = 65.5$ Hz), characteristic of nickel(0). The ^1H NMR spectrum of **9** was indicative of η^2-coordination of the C=C bond in 4PN, showing two multiplets at δ 2.57 and 2.35 (overlapping with the resonances for the dcype ligand). Both sets of signals are shifted upfield from those in the free ligand (δ 6.0 and 5.22). The $^{13}C\{^{1}H\}$ NMR spectrum is consistent with η^2-*C,C* coordination of the C=C bond, with signals being observed at δ 47.7 (d, $^2J_{C-P} = 21.2$ Hz, *C*H) and δ 35.1 (d, $^2J_{C-P} = 18.5$ Hz, *C*H_2). The signal for the uncoordinated −CN moiety in **9** was located at δ 120.9. For comparison, the signals for the free ligand appear as singlets at δ 135.5 (*C*H), 117.3 (*C*H_2), and 121.2 (*C*N).

Characterization of Complexes [(dcype)Ni(η^2-*C,C*-*Z*-2M2BN)] (5), [(dcype)Ni(η^2-*C,C*-*E*-2M2BN)] (6), and [(dtbpe)Ni(η^2-*C,C*-*E*-2M2BN)] (6′). Complexes **5** and **6** exhibit similar spectroscopic features in THF-d_8 solution. Complex **5** has ^{31}P resonances at 61.0 and 54.1 ppm ($^2J_{P-P} = 58.3$ Hz), while complex **6** has resonances at 62.5 and 55.8 ppm ($^2J_{P-P} = 57.9$ Hz). The ^1H NMR spectra for both compounds reveal

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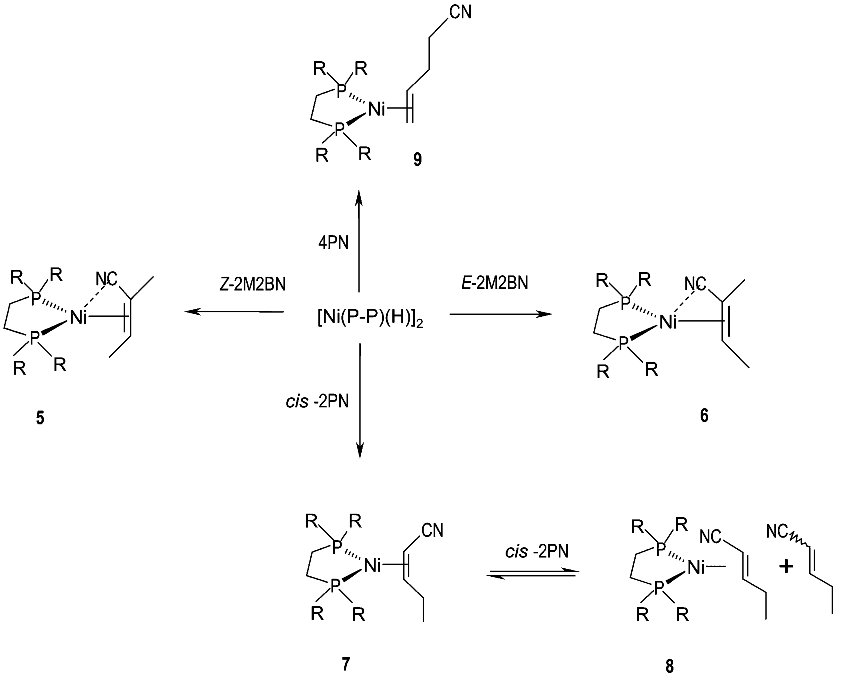
Scheme 4



R= Cy; t-Bu

that the signal for the single olefinic proton was shifted from its free ligand position (δ 6.3 for *Z*-2M2BN and 6.4 for *E*-2M2BN) to overlap with the phosphine signals. The $^{13}C\{^{1}H\}$ NMR spectra provided better evidence for the η^2-coordination of the olefin moiety. The signal for the *C*H olefinic carbon shifted significantly upfield from δ 143.24 (free *Z*-2M2BN) to δ 47.9 ppm (d, $^{2}J_{C-P} = 26.4$ Hz) in **5**. The same effect was observed in the case of **6** with the resonance shifting from δ 143.27 (*E*-2M2BN) to δ 47.9 (d, $^{2}J_{C-P} = 26.5$ Hz) for complex **6**. The methyl groups in **5** give resonances at δ 17.9 ppm (d, $^{2}J_{C-P} = 3$ Hz, Me− *cis* to CN) and δ 16.3 ppm (bs, Me *gem* to CN). The corresponding resonances in **6** appear at δ 17.9 (s, br, Me *trans* to CN) and δ 16.3 (s, br, Me *gem* to CN). An interesting feature in complexes **5** and **6** is that the signal for the −CN moiety is shifted downfield to δ 128.6 in both complexes (from δ 120.9 in *Z*-2M2BN and δ 118.2 in *E*-2M2BN). This observation may be due to a weak interaction between the Ni center and the C≡N moiety.[15a]

On using a bulkier diphosphine such as dtbpe, the analogous complex **6′**, [(dtbpe)Ni(η^2-*C*,*C*-*E*-2M2BN)],[19] was isolated and characterized by single-crystal X-ray diffraction. A summary of crystallographic results and the molecular structure for **6′** are shown in Table 1 and Figure 4, respectively. The Ni center in **6′** adopts a pseudo-square-planar geometry, as observed in other related Ni-cyano-olefin complexes.[15a] The bond distances in complex **6′** are in agreement with those found in closely related structures where *cis*- and *trans*-crotonitrile were used. No significant differences in the C═C bond distance in the three complexes were detected, the latter being 1.442(3) Å in complex **6′**, 1.441(4) Å in [(dippe)Ni(η^2-*C*,*C*-*trans*-crotonitrile)], and 1.442(5) Å in [(dippe)Ni(η^2-*C*,*C*-*cis*-crotonitrile-BPh$_3$)]. As mentioned above, the interaction between the nickel center and the −CN moiety was also corroborated in the solid state. The Ni1−C21 distance is 2.885 Å, where the sum of the van der Waals radii is 3.33 Å, indicative of this interaction.[14a,15a]

Characterization of Complexes [(dcype)Ni(η^2-*C*,*C*-*cis*-2PN)] (7), [(dtbpe)Ni(η^2-*C*,*C*-*cis*-2PN)] (7′), and [(dcype)Ni-(η^2-*C*,*C*-*trans*-2PN)] (8). Complex **7** was formed by the reaction of [(dcype)Ni(μ-H)]$_2$ and *cis*-2PN. The $^{31}P\{^{1}H\}$ NMR spectum of this complex depicts two large doublets at δ 61.8 and 65.4, with coupling constants of 52.8 Hz, confirming the formation of a Ni(0) complex. Two additional small doublets were observed at δ 65.6 ($^{2}J_{P-P} = 52$ Hz) and δ 62.0 ($^{2}J_{P-P} = 52$ Hz). The $^{13}C\{^{1}H\}$ NMR spectrum of **7** permitted further characterization of the η^2-*C*,*C*-coordinated C═C bond to the nickel(0) center. The signals for the olefinic carbons appear at δ 49.8 (d, $^{2}J_{C-P} = 27.3$ Hz, Et*C*H═) and δ 18.7 (d, $^{2}J_{C-P} = 19.7$ Hz, ═*C*HCN), downfield from the free ligand (δ 157.8 and 101.2). The −CN resonance was located at δ 124.5 as a slightly broad singlet, again indicating an interaction of the nickel(0) center with the −CN moiety (cf. the free ligand at δ 117.6).

Addition of a 2-fold excess of *cis*-2PN to the THF-d_8 solution of **7** resulted in the increase of the two small signals in the $^{31}P\{^{1}H\}$ NMR spectum after 30 min at room temperature. The ^{1}H NMR spectrum permitted confirmation of the presence of free *trans*-2PN, therefore suggesting that this second species corresponds to the nickel(0) complex [(dcype)Ni(η^2-*C*,*C*-*trans*-2PN)] (**8**). After 12 h at room temperature, the **7**/**8** ratio had increased to 2:1, as indicated by ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopy. The key signals establishing the presence of a bound olefin in **8** in the ^{13}C NMR spectrum were at δ 52.4 (d, $^{2}J_{C-P} = 27.3$ Hz, *C*HCN) and 19.0 (d, $^{2}J_{C-P} = 15.2$ Hz, *C*HEt), with the uncoordinated −CN moiety appearing at δ 125.8.

The *cis*−*trans* isomerization reaction can be described as occurring via a C−H activation reaction to form a π-allyl hydride species, although no hydride species was detected by ^{1}H NMR spectroscopy (see Scheme 5).

X-ray Structure of [(dtbpe)Ni(η^2-*C*,*C*-*cis*-2PN)] (7′). Complex **7′** was prepared following the same methodology used for **7**,[20] providing crystals suitable for X-ray diffraction. A summary

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[19] Complex **6′** displays in the $^{31}P\{^{1}H\}$ NMR two sharp doublets at δ 83.5 and 80.9 with $^{2}J_{P-P} = 61.4$ Hz.

[20] Complex **7′** displays in the $^{31}P\{^{1}H\}$ NMR two sharp doublets at δ 90.2 and 86.6 with $^{2}J_{P-P} = 57.3$ Hz.

Table 1. Summary of Crystallographic Data for 6′, 7′, and 10

	6′	7′	10
empirical formula	$C_{23}H_{47}NNiP_2$	$C_{23}H_{46}NNiP_2$	$C_{28}H_{48}N_2NiP_2$
fw	458.27	457.23	533.33
temperature	100 (2) K	100(2) K	100(2) K
wavelength	0.71073 Å	0.71073 Å	0.71073 Å
cryst syst	monoclinic	monoclinic	triclinic
space group	*P*2(1)/*n*	*C*2/*c*	$P\bar{1}$
unit cell dimens	$a = 11.1322(15)$ Å $b = 14.1435(19)$ Å $c = 16.532(2)$ Å $\alpha = 90°$ β=102.732(2)° $\gamma = 90°$	$a = 18.886(4)$ Å $b = 10.536(2)$ Å $c = 12.667(3)$ Å $\alpha = 90°$ $\beta = 91.843(4)°$ $\gamma = 90°$	$a = 7.4217(18)$ Å $b = 9.326(2)$ Å $c = 10.718(3)$ Å $\alpha = 93.263(4)°$ $\beta = 108.721(4)°$ $\gamma = 101.016(4)°$
volume	2539.0(6) Å^3	2519.2(10) Å^3	1.295(3) Å^3
Z	4	4	1
density (calcd)	1.199 Mg/m^3	1.206 Mg/m^3	1.295 Mg/m^3
absorp coeff	0.899 mm^{-1}	0.906 mm^{-1}	0.845 mm^{-1}
F(000)	1000	996	288
cryst size	0.31 × 0.23 × 0.17 mm^3	0.2 × 0.14 × 0.1 mm^3	0.08 × 0.14 × 0.17 mm^3
θ range for data collection	1.92 to 24.99	2.16 to 28.27°.	2.02 to 28.28°.
index ranges	$-5 \le h \le 12$, $-11 \le k \le 16$, $-19 \le l \le 19$	$-25 \le h \le 24$, $-13 \le k \le 13$, $-16 \le l \le 16$	$-9 \le h \le 9$, $-12 \le k \le 12$, $-12 \le l \le 13$
no. of reflns collected	6320	11 295	4747
no. of indep reflns	4050 [*R*(int) = 0.0198]	2993 [*R*(int) = 0.0604]	4180 [*R*(int) = 0.0220]
completeness to θ_{max}	90.6%	95.7%	83.1%
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
no. of data/restraints/params	4050/0/258	2993/0/154	4180/3/298
goodness-of-fit on F^2	0.679	1.000	1.062
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0311, wR2 = 0.0856	R1 = 0.0562, wR2 = 0.1322	R1 = 0.0346, wR2 = 0.0833
R indices (all data)	R1 = 0.0349, wR2 = 0.0896	R1 = 0.0808, wR2 = 0.1430	R1 = 0.0353, wR2 = 0.0837
largest diff peak and hole	0.563 and −0.252 e·Å^{-3}	0.466 and −0.304 e·Å^{-3}	0.826 and −0.548 e·Å^{-3}

Table 2. Isomerization of 2M3BN Using Ni(0) Complexes[a]

entry	precursor	*t* (h)	conversion (%)	yield of 3-PN (%)	yield of 4-PN (%)	yield of E-2M2BN (%)	other nitriles (%)
1	$[(dcype)Ni(H)]_2$	1	68	0	0	57	11
2	$[(dtbpe)Ni(H)]_2$	1	100	0	0	85	15
3	complex **9**[b]	192	100	39	22	36	3
4	complex **9**	24	77	66	2	2	7

[a] Neat substrate:precursor = 110:1. *T* = 25 °C. 2M3BN conversion % and yields were obtained by GC-MS and confirmed by ^{1}H NMR spectroscopy. [b]This reaction was evaluated using a substrate:precursor ratio of 2:1 and THF as solvent (1 mL).

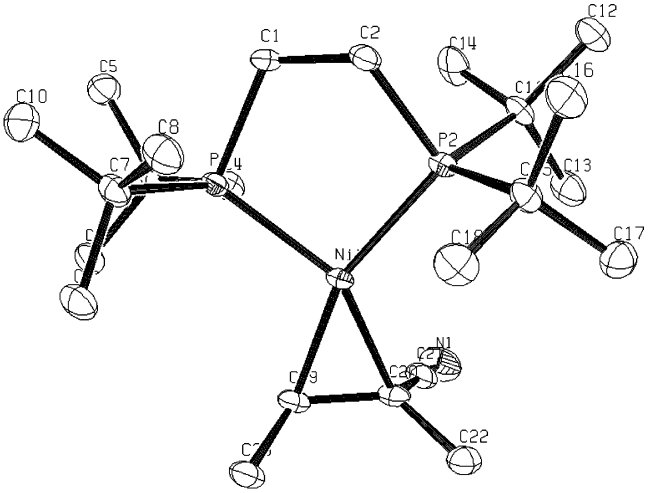


Figure 4. Molecular structure of complex **6′** at 50% probability. Selected bond distances (Å): Ni1−P1(2.1930(6)), Ni1−P2 (2.2072-(6)), C19−C20 (1.442(3)), C21−N1 (1.150(3)), Ni1−C19 (1.9590-(19)), Ni1−C20 (1.9936(18)), Ni1−C21 (2.885). Selected angles (deg): P1−Ni1−P1A (92.49(4)), C11−Ni1−C12 (43.1(3)).

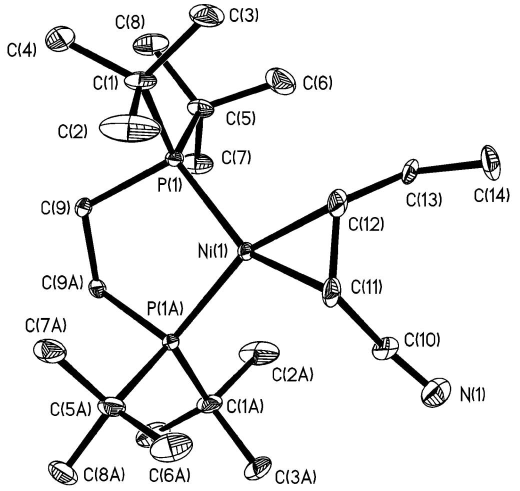


Figure 5. Molecular structure of complex **7′** at 50% probability. Selected bond distances (Å): Ni−P1 (2.1792(18)), Ni1−P1A (2.1945(18)), C11−C12 (1.441(9)), C10−N1 (1.17(3)), Ni1−C11 (1.968(6)), Ni1−C12 (1.954(6)). Selected angles (deg): P1−Ni1−P1A (92.49(4)), C11−Ni1−C12 (43.1(3)).

of crystallographic results and the molecular structure for **7′** are shown in Table 1 and Figure 5, respectively. The ethyl group and the nitrile ligand are disordered. In the crystallographic model, the nickel lies slightly off of the crystallographic 2-fold axis, which generates a second nickel (population 50%) and a second orientation of the nitrile and ethyl groups (population 50%).

The structure is rather similar to that reported for [(dippe)-Ni(η^2-*C*,*C*,-*trans*-crotylnitrile)] and [(dippe)Ni(η^2-*C*,*C*,-*cis*-cro-

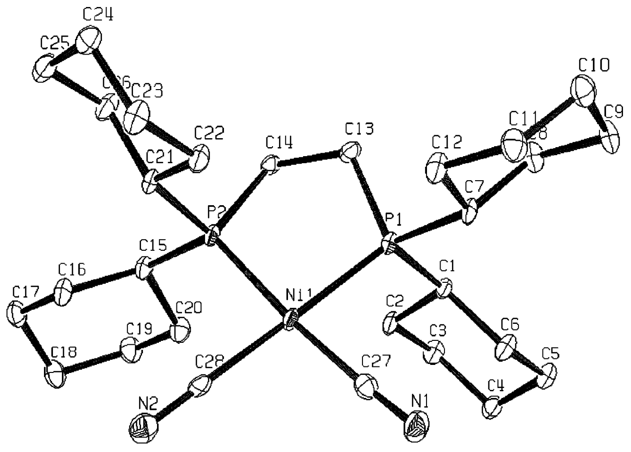
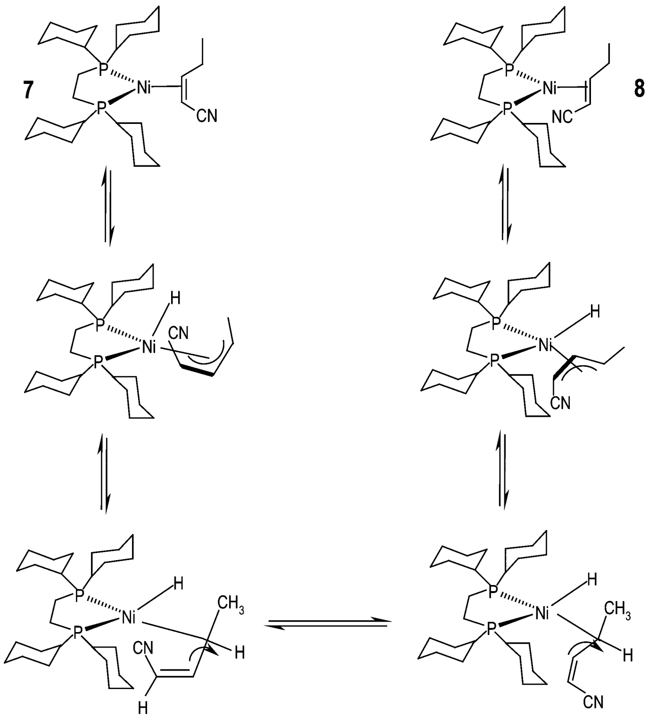


Figure 6. Molecular structure of complex **10** at 50% probability. Selected bond distances (Å): Ni1−C27 (1.871(4)), Ni1−C28 (1.879(4), Ni−P1 (2.1693(10)), Ni−P2 (2.1657(11)), C27−N1 (1.151(5)), C28−N2 (1.144(4)). Selected angles (deg): C27−Ni1−C28 (93.30(16)), C28−Ni1−P2 (89.72(12)), C27−Ni1−P1 (88.72(11)), P1−Ni−P2 (88.38(4)).

Scheme 5



tylnitrile-B(Ph)$_3$].[15a] All of these complexes present a pseudo-square-planar geometry around the nickel(0) center. Bond distances are in agreement with these related structures, the C═C bond distance being the same in the three cases: 1.441(9) Å, complex **7′**; 1.441(4) and 1.442(5) Å in the complexes with *trans*- and *cis*-crotonitrile, respectively. The Ni−C bond distances are also very similar between complex **7′** (1.959(2) Å) and [(dippe)Ni(η^2-*C,C,-trans*-crotylnitrile) (1.949(2) Å).

X-ray Structure of [(dcype)Ni(CN)$_2$] (10). Yellow crystalline cubes of complex **10**, suitable for X-ray determination, were obtained during the isomerization reaction of 2M3BN with [(dcype)Ni(μ-H)]$_2$ (the product of this reaction confirmed by an independent reaction of [(dcype)NiCl$_2$] with NaCN). The molecular structure is depicted in Figure 6, and crystallographic data are summarized in Table 1. The structure shows a square planar geometry around the nickel(II) center, the distances and angles within the structure being in agreement with the analogous structure of [(dippe)Ni(CN)$_2$] reported previously.[13] **10** is believed to form in these reactions when butadiene is lost to produce small amounts of (dcype)Ni(CN)$_2$ and (dcype)NiH$_2$. The latter loses H$_2$ and continues in the reaction with 2M3BN.

Isomerization of 2M3BN. Since the [(dcype)Ni] moiety can isomerize 2M3BN to 3PN under stoichiometric conditions, such isomerization using catalytic amounts of [(dcype)Ni(μ-H)]$_2$ or [(dtbpe)Ni(μ-H)]$_2$ as catalyst precursors was also examined. The results using a 110-fold excess of the 2M3BN substrate are summarized in Table 2.

In sharp contrast with the results observed in the stochiometric reaction with the [(dcype)Ni] moiety, the reaction under catalytic conditions using neat substrate showed that the selectivity for linear 3PN decreased significantly, producing *E*-2M2BN instead, the latter being obtained as the major product. The use of the bulkier dtbpe ligand resulted in a more active catalytic system, producing mainly *E*-2M2BN. In the case of **9** as a convenient precursor to [(dcype)Ni], the use of catalytic conditions resulted in increased catalyst activity, with equilibrium being been reached after 24 h (entry 4), giving 77% conversion with a modest selectivity for 3PN (66%) and a small amount of 4PN, implying a better performance of complex **9** under the catalytic conditions than those observed in the stoichiometric situation (entry 3).

Conclusions

The use of σ-donor P-ligands as dcype and dtbpe has allowed the detection and in some cases isolation of the nickel complexes involved in the isomerization of 2M3BN to 3PN. The two nickel(0) moieties [(dcype)Ni] and [(dtbpe)Ni] convert 2M3BN under catalytic conditions in high efficiency, although the selectivity for the branched *E*-2M2BN isomeric product was preferred, in a sharp contrast to the stochiometric reaction in which the opposite occurs. The use of [(dcype)Ni(η^2-*C,C*-4PN)] (**9**) resulted in a different outcome, a moderate yield of the linear 3PN isomer been obtained under both stochiometric and catalytic conditions.

Comparison of the current report with previous results from our group[11] allowed us to conclude that the use of bulky, electron-rich ligands (σ-donor ligands) in the isomerization reaction of 2M3BN yields much more 2M2BN and therefore favors net H$^-$ transfer rather than CN$^-$ transfer, relative to dppf (σ-donor, π-aceptor ligand), a general statement that is probably appliable to other similar ligands. Further studies are currently underway to extend the scope of this research to other closely related bis(phosphino)ferrocenes.

Experimental Section

All manipulations were carried out using standard Schlenk and glovebox techniques under argon (Praxair 99.998). THF (J. T. Baker) was dried and distilled from dark purple solutions of sodium/benzophenone ketyl. Deuterated solvents were purchased from Cambridge Isotope Laboratories and stored over 3 Å molecular sieves in an MBraun glovebox (<1 ppm H$_2$O and O$_2$). [Ni(COD)$_2$] was purchased from Strem and purified from a THF solution, filtered through Celite, and vacuum-dried to yield yellow, crystalline [Ni(COD)$_2$], which was further dried for 3 h *in vacuo*. dcype was purchased from Strem and was used as received. dtbpe was prepared according to the previously reported procedure.[21] The synthesis of [(dcype)Ni(μ-H)]$_2$ and [(dtbpe)Ni(μ-H)]$_2$ was carried out using the

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(21) Pörschke, K. R.; Pluta, C.; Prof., B.; Lutz, F.; Krüger, C. *Naturforsch. B. Anorg. Chem. Org. Chem.* **1993**, *48*, 608.

previously reported procedure.[22] 2M3BN and *E*- and *Z*-2M2BN were purchased from TCI America, purged, and stored in the glovebox. *trans*-3PN, *cis*-2PN, and 4PN were purchased from Aldrich, purged, and stored in the glovebox. ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra were recorded at room temperature on a 300 MHz Varian Unity spectrometer in THF-d_8, toluene-d_8, or $CDCl_3$. ^{1}H and ^{13}C{^{1}H} chemical shifts (δ) are reported relative to the residual proton resonances in the deuterated solvent. All ^{31}P{^{1}H} NMR spectra were recorded relative to external 85% H_3PO_4. All NMR spectra and catalytic reactions were carried out using thin-wall (0.38 mm) WILMAD NMR tubes with J. Young valves. Elemental analyses were carried out by USAI-UNAM using an EA 1108 FISONS Instruments analyzer; reproducible elemental analyses could not be obtained due to the samples' high instability. A Bruker APEX CCD diffractometer with monochromatized Mo Kα radiation (λ = 0.71073 Å) was used for the X-ray structure determinations. Crystals of **6′**, **7′**, and **10** were mounted under Paratone 8277 on a glass fiber and immediately placed under a cold stream of nitrogen.

Isomerization of 2M3BN to 3PN. A solution of dcype (46 mg, 0.109 mmol) in toluene-d_8 was added to the yellow, crystalline [Ni(COD)$_2$] (30 mg, 0.109 mmol), producing a brown-red solution. The mixture was transferred to an NMR tube with a J. Young valve, and 2M3BN was added (10 μL, 0.109 mmol). The reaction was followed by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy.

Preparation of [(dcype)Ni(η^2-*C*,*C*-2M3BN)] (1) and [(dtbpe)Ni(η^2-*C*,*C*-2M3BN)] (1′). To a stirred solution of [(dcype)Ni(μ-H)]$_2$ or [(dtbpe)Ni(μ-H)]$_2$ (0.08 mmol) in 10 mL of THF was added 16 μL (0.16 mmol) of 2M3BN. On using [(dcype)Ni(μ-H)]$_2$ an instantaneous color change from dark red to brown was observed, while on using [(dtbpe)Ni(μ-H)]$_2$ the solution turned orange-yellow but only after overnight reaction at room temperature. In both cases, the solvent was removed *in vacuo* and the residue was dried for 3 h to give red solids (**1**, 80.9 mg, 90% and **1′**, 62.5 mg, 89%). **1:** ^{1}H NMR (299.7 MHz, THF-d_8): δ 0.8−2.5 (br, m). ^{31}P{H} (121.3 MHz, toluene-d_8): δ 58.3 (d, $^{2}J_{P-P}$ = 52 Hz), 61.9 (d, $^{2}J_{P-P}$ = 52 Hz). **1′**: ^{1}H NMR (299.7 MHz, THF-d_8): δ 0.8−2.1 (br, m), 2.3 (m, 1H, C*H*=), 2.06 (m, 2H, C*H*$_2$=). ^{31}P{^{1}H} NMR (121.3 MHz, THF-d_8): δ 89.5 (d, $^{2}J_{P-P}$ = 64.7 Hz), 91.7 (d, $^{2}J_{P-P}$ = 64.7 Hz). ^{13}C{^{1}H} NMR (THF-d_8): δ 47.7 (dd, $^{1}J_{C-P}$ = 25.7 Hz and 2.7 Hz, *C*H=), 32.9 (dd, $^{1}J_{C-P}$ = 20.8 and 2.6 Hz, *C*H$_2$=), 123.8 (s, *C*N). Crystallization of [(dcype)Ni(CN)$_2$] (**10**) was achieved from the above reaction mixture after 2 days at room temperature. ^{31}P{^{1}H} NMR (toluene-d_8) at 85.8 ppm (s).

Preparation of [(dcype)Ni(η^3-1-methylallyl)(CN)] (2), [(dcype)Ni(η^2-*C*,*C*-*trans*-3PN) (3), and [(dcype)Ni(η^2-*C*,*C*-*cis*-3PN)] (4). To a stirred solution of [(dcype)Ni(μ-H)]$_2$ (110 mg 0.114 mmol) in 10 mL of THF was added 22 μL (0.224 mmol) of *trans*-3PN. An instantaneous color change from red-wine to brown-yellow and a strong effervescence were observed, and all the gas vented into the box. After 15 min, the solvent was removed *in vacuo* and the residue was dried for 3 h to give a red solid. Complexes **3** and **4** were separated as a mixture from complex **2** by column chromatography on silica gel (complexes **3** and **4** with hexane/THF = 10:1 and complex **2** with THF). **2**: ^{1}H NMR (299.7 MHz, THF-d_8): δ 4.93 (pq, 1H, C*H* central), 4.41 (m, 1H, C*H*Me), 3.35(m, 1H, C*H*H). ^{13}C{^{1}H} NMR (75.4 MHz, THF-d_8): δ 146.5 (s, CN), 107.8 (pt, *C*H central), 83.7 (pt, *C*HMe), 51.2 (*C*H$_2$). ^{31}P{^{1}H} NMR (toluene-d_8): δ 66.0 (br). **3**: ^{1}H NMR (299.7 MHz, THF-d_8): δ 0.8−2.5 (br, m), 3.37 (m, 1H, CNCH$_2$C*H*=), 2.55 (m, 2H, MeC*H*=). ^{31}P{^{1}H} NMR (121.3 MHz, toluene-d_8): δ 63.5 (d, $^{2}J_{P-P}$ = 52.2 Hz), 59.1 (d, $^{2}J_{P-P}$ = 52.2 Hz). ^{13}C{^{1}H} NMR (THF-d_8): δ 52.5 (d, $^{2}J_{C-P}$ = 26.8 Hz, CNCH$_2$*C*H=), 35.3 (d, $^{2}J_{C-P}$ = 15.5 Hz, Me*C*H=), 125.9 (s, *C*N). **4**: ^{31}P{^{1}H} NMR (121.3 MHz, toluene-d_8): δ 63.3 (d, $^{2}J_{P-P}$ = 52.1 Hz), 58.9 (d, $^{2}J_{P-P}$ = 52.1 Hz). ^{13}C{^{1}H} NMR (THF-d_8): δ 50.1 (d, $^{2}J_{C-P}$ = 26.9 Hz, CNCH$_2$*C*H=), 35.1 (d, $^{2}J_{C-P}$ = 15.5 Hz, Me*C*H=), 124.6 (s, *C*N).

Preparation of [(dcype)Ni(η^2-*C*,*C*-4PN) (9). To a stirred solution of [(dcype)Ni(μ-H)]$_2$ (100 mg 0.104 mmol) in 10 mL of THF was added 20.5 μL (0.208) of 4PN to give an instantaneous color change from dark wine to brown-yellow along with a strong effervescence; all the gas vented into the box. After 15 min the solvent was removed *in vacuo* and the residue was dried for 3 h to give a red solid (111 mg, 95%). ^{1}H NMR (299.7 MHz, THF-d_8): δ 0.8−2.2 (br, m), 2.57 (m, 1H, CH*H*=), 2.35 (m, 1H, C*H*H=). ^{31}P{H} NMR (121.3 MHz, THF-d_8): δ 62.0 (d, $^{2}J_{P-P}$ = 65.5 Hz), 57.5 (d, $^{2}J_{P-P}$ = 65.5 Hz). ^{13}C{H} NMR (THF-d_8): δ 47.7 (d, $^{2}J_{C-P}$ = 21.2,*C*H=), 35.1 (d, $^{2}J_{C-P}$ = 18.5 Hz, *C*H$_2$=), 120.9 (s, *C*N).

Preparation of Complexes [(dcype)Ni(η^2-*C*,*C*-*Z*-2M2BN)] (5), [(dcype)Ni(η^2-*C*,*C*-*E*-2M2BN)] (6), and [(dtbpe)Ni(η^2-*C*,*C*-*E*-2M2BN)] (6′). Complexes **5** and **6** were prepared using the same procedure as described above for complex **4**, using 25 mg of [(dcype)Ni(μ-H)]$_2$ (0.026 mmol) and 5.1 μL of *Z*-2M2BN or *E*-2M2BN (0.052 mmol), obtaining in both cases yellow-brown solutions and after evaporation brown solids (**5** 25.7 mg, 88% and **6** 26.8 mg, 92%). Complex **6′** was prepared using the same procedure as used for complex **1′**, using 30 mg of [(dtbpe)Ni(μ-H)]$_2$ (0.04 mmol) and 8 μL of *E*-2M2BN (0.08 mmol), obtaining a red-brown solution and dark red solid after solvent evaporation (31.8 mg, 87%). Suitable crystals for X-ray diffraction of **6′** were obtained by slow diffusion of hexane in a THF solution of the complex. **5**: ^{1}H NMR (299.7 MHz, THF-d_8): δ 0.8−2.5 (br, m), 2.58 (m, 1H, MeC*H*=). ^{31}P{^{1}H} NMR (121.3 MHz, THF-d_8): δ 61.0 (d, $^{2}J_{P-P}$ = 58.3 Hz), 54.1 (d, $^{2}J_{P-P}$ = 58.3 Hz). ^{13}C{^{1}H} NMR (THF-d_8): δ 47.9 (d, $^{2}J_{C-P}$ = 26.4, Me*C*H=), 17.9 (d, $^{2}J_{C-P}$ = 3 Hz, Me *cis* to CN), 16.3 (bs, Me *gem* to CN), 128.6 (*C*N). **6**: ^{1}H NMR (299.7 MHz, THF-d_8): δ 0.8−2.5 (br, m), 2.59 (m, 1H, MeC*H*=). ^{31}P{H} NMR (121.3 MHz, toluene-d_8): δ 62.5 (d, $^{2}J_{P-P}$ = 57.9 Hz), 55.8 (d, ^{2}JP−P = 57.9 Hz). ^{13}C{H} NMR (THF-d_8): δ 47.9 (d, $^{2}J_{C-P}$ = 26.5, Me*C*H=), 17.9 (bs, Me *trans* to CN), 16.3 (bs, Me *gem* to CN), 128.6 (s, *C*N). **6′**: ^{1}H NMR (299.7 MHz, THF-d_8): δ 0.8−2.0 (br signals) and 2.65 (br). ^{13}C{^{1}H} NMR (THF-d_8): 17.2 (Me, gem CN), 19.3 (Me *trans* to CN), 28.4 (dd, $^{2}J_{C-P}$ = 22.8 Hz C), 47.2 (dd, $^{2}J_{C-P}$ = 26.5 Hz, =CHMe), 128.6 (CN). ^{31}P{^{1}H} NMR (121.3 MHz, THF-d_8): δ 84.7 (d, $^{2}J_{P-P}$ = 61.4 Hz), 87.4 (d, $^{2}J_{P-P}$ = 61.4 Hz).

Preparation of Complexes [(dcype)Ni(η^2-*C*,*C*-*cis*-2PN)] (7) and [(dtbpe)Ni(η^2-*C*,*C*-*cis*-2PN)] (7′), and [(dcype)Ni(η^2-*C*,*C*-*trans*-2PN)] (8). Complex **7** was prepared using the same procedure used for complex **4**, using 30 mg of [(dcype)Ni(μ-H)]$_2$ (0.031 mmol) and 6 μL of *cis*-2PN (0.062 mmol), obtaining a yellow-brown solution and brown solid after solvent removal (**7** 31.1 mg, 95%). Complex **7′** was prepared using the same procedure as used for complex **1′**, using 30 mg of [(dtbpe)Ni(μ-H)]$_2$ (0.04 mmol) and 8 μL of *cis*-2PN (0.08 mmol), to yield a red-brown solution and dark red solid (**7′** 34.4 mg, 94%). Complex **8** was prepared by adding a 2-fold excess of *cis*-2PN to a solution of **7** in THF-d_8 solution. After 12 h at room temperature complex **8** was obtained. On cooling to −35 °C in the drybox, crystals of **7′** suitable for X-ray diffraction were obtained. **7**: ^{1}H NMR (299.7 MHz, THF-d_8): δ 0.8−2.35 (br, m), (m, 1H, CNC*H*=), 2.10 (m, 1H, EtC*H*=). ^{31}P{^{1}H} NMR (121.3 MHz, THF-d_8): δ 61.8 (d, $^{2}J_{P-P}$ = 52.8 Hz), 65.4 (d, $^{2}J_{P-P}$ = 52.8 Hz). ^{13}C{^{1}H} NMR (THF-d_8): δ 49.8 (d, $^{2}J_{C-P}$ = 27.3 Hz, CN*C*H=), 18.7 (d, $^{2}J_{C-P}$ = 19.7 Hz, Et*C*H=), 124.5 (*C*N). **7′**: ^{1}H NMR (299.7 MHz, THF-d_8): δ 0.8−2.4 (br signals). ^{13}C{^{1}H} NMR (THF-d_8): 14.6 (CH3), 18.0 (CH2), 20.7 (dd, $^{2}J_{C-P}$ = 19.8 Hz, CH$_2$Et), 50.6 (dd, $^{2}J_{C-P}$ = 27.8 Hz, CHCN), 125.1(CN). ^{31}P{^{1}H} NMR (121.3 MHz, THF-d_8): δ 90.2 (d, $^{2}J_{P-P}$ = 57.3 Hz), 86.6 (d, $^{2}J_{P-P}$ = 57.3 Hz). **8**: ^{31}P{H} NMR (121.3 MHz, THF-d_8): δ 65.6 (d, $^{2}J_{P-P}$ = 52 Hz), 62.0 (d, $^{2}J_{P-P}$ = 52 Hz). ^{13}C{^{1}H} NMR (THF-d_8): δ 52.4 (d, $^{2}J_{C-P}$ = 27.3 Hz, CN*C*H=), 19 (d, $^{2}J_{C-P}$ = 15.2 Hz, Et*C*H=), 125.9 (*C*N).

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[22] Vicic, D. A.; Jones, W. D. *J. Am. Chem. Soc.* **1997**, *119*,10855.

Catalytic Isomerization of 2M3BN. 2M3BN (0.4 mL, 4.00 mmol) was added to the precursor [(dcype)Ni(μ-H)]$_2$, [(dtbpe)Ni(μ-H)]$_2$, or complex **4** (0.036mmol), producing red-colored solutions. The mixture was stirred at room temperature and was analyzed by GC-MS taking a sample from the reaction mixture and dissolved in THF inside the drybox. Simultaneously, a second sample was taken and dissolved in toluene-d_8 and analyzed by ^{1}H NMR spectroscopy.

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Supporting Information Available: Detailed GC-MS determinations and tables of complete crystallographic data for **6′**, **7′**, and **10**. NMR spectra are included for the compounds lacking elemental analyses. This material is available free of charge via the Internet at http://pubs.acs.org.

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