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Isomerization of 2-methyl-3-butenenitrile with (bis-diphenylphosphinoferrocene)nickel compounds: Catalytic and structural studies

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Abstract

The catalytic isomerization of 2-metyl-3-butenenitrile to 3-pentenenitrile was carried out by (dppf)Ni species (dppf = bis-diphenylphosphinoferrocene) in the absence and the presence of Lewis acids. Studies in solution reveal the intermediacy of Ni(II) allyl complexes. Addition of Lewis acids such as BEt_3 allow the crystallization and full characterization of the latter by X-ray diffraction studies.

Keywords: Nitrile; Isomerization; Catalytic; Nickel; X-ray structure

1. Introduction

The production of adiponitrile (AdN) is among the most important industrial processes in existence. AdN is a precursor of 1,6-hexanediamine, which is used for the preparation of Nylon 66 [1]. AdN is prepared by the double catalytic hydrocyanation of butadiene using Ni(0)-phosphite complexes (Scheme 1). The first addition of HCN leads both to the desirable linear isomer 3-pentenenitrile (3PN) and to the undesirable branched isomer 2-methyl-3-butenenitrile (2M3BN) in a variable ratio, some times quoted as a 2:1 ratio, respectively [2]. Thermodynamics favours 3PN (about 9:1) and 2M3BN may be isomerized to 3PN in the presence of a nickel catalyst, through a C—CN bond breaking/forming reaction involving a Ni(II) allyl cyanide complex. The selective anti-Markovnikov addition of the second HCN to yield AdN requires the concurrent isomerization of 3PN to 4-pentenenitrile (4PN) and HCN addition to 4PN, in presence of a Ni(0) complex and Lewis acids (LA) as co-catalysts [3,4].

Since 1984, 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 [5–7]. More recently, the use of $[Ni(COD)_2]$ as catalytic precursor, in combination with P-donor-bidentate ligands such as phosphines, [8–11] phosphonites [9] and phosphites, [12] has been reported to achieve the transformation of the branched nitrile (2M3BN) to the linear nitrile (3PN). Additionally, this reaction has been studied in aqueous media [13] and ionic liquids [14].

Due to the continued interest of our group in the activation of C—CN bonds in alkyl, aryl, and heterocyclic nitriles with the use of nickel complexes, [15,16] we have expanded the scope of these investigations to study the related reactions involving allyl nitriles and the isomerization of cyano-olefins [17]. We report here the study of the catalytic isomerization of 2M3BN using nickel(0) compounds with bis-diphenylphosphinoferrocene (dppf).

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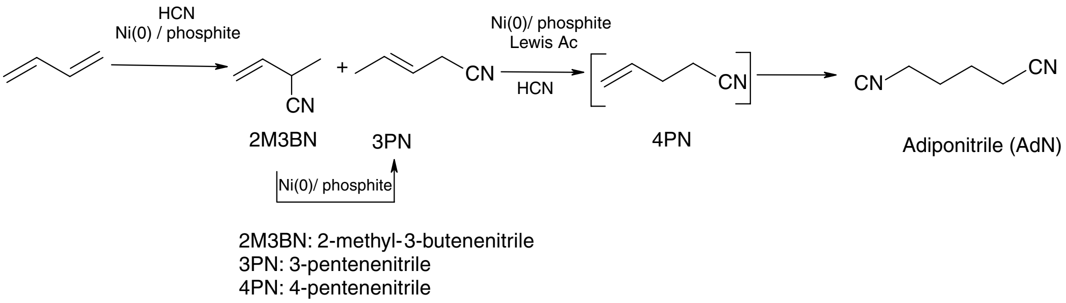


Scheme 1.

2. Results and discussion

2.1. Isomerization of 2M3BN using Ni(0) compounds

The isomerization of neat 2M3BN using [Ni(COD)$_2$] as catalyst precursor and dppf, both in the presence and the absence of LA, was explored at 100 °C. The corresponding catalytic results using a 110-fold excess of substrate are summarized in Table 1.

The most active catalytic system found was that of [Ni(COD)$_2$] and dppf without the use of Lewis acids (entries 1–3), producing 79% conversion and 67% yield of 3PN in 1 h. After 2.5 h, all the substrate was converted, with a yield of 83% for 3PN. This result is slightly better than the one reported by Sabo–Etienne's group using PPh$_3$ under similar reaction conditions (96% conversion, 3 h, 81% 3PN), [8] which in our hands and reaction apparatus, systematically gave 58% yield. The system reported herein also outperformed in terms of activity and selectivity the bis(2-diphenylphosphinophenyl)ether (DPEphos) catalytic system reported by Vogt and co-workers [10]. The reaction was followed up to a 75% conversion, but the precise yield of 3PN was not reported, and the formation of additional by products was not mentioned. In our hands and in our apparatus, the same experiment was followed up to 90% conversion at 16 h, with a yield of 82% of 3PN and 8% other nitriles (3:1, *cis*-2-pentenenitrile: *Z*-2-methyl-butenenitrile).

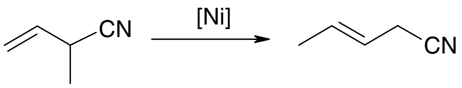
The use of Lewis acids with the Ni(COD)$_2$/dppf catalytic system resulted in a dramatic drop in catalytic activity, giving no conversion at all after 1 h of reaction. On using ZnCl$_2$, 5 h at 100 °C were necessary to obtain total conversion with a moderate yield of 3PN (54%). The reaction using BEt$_3$ gave just 10% conversion after 120 h. In all the cases where activity was observed (entries 1–3, 5 and 7), the other nitriles produced were mainly *Z*-2-methyl-2-butenenitrile, with small amounts of *cis*-2-pentenenitrile and *E*-2-methyl-2-butenenitrile.

2.2. Synthesis and characterization of Ni(II)-allyl cyanide complex (*1*)

The reaction of [Ni(COD)$_2$] with one equivalent of dppf in a THF solution produced an instantaneous color change from yellow to orange. The $^{31}P\{^1H\}$ NMR spectrum in toluene-d_8 revealed the presence of a singlet at 33.0 ppm, assigned to the complex [Ni(COD)(dppf)]. Addition of 1 equivalent of 2M3BN to [Ni(COD)(dppf)] produced a color change to red to yield complex **1** (Scheme 2).

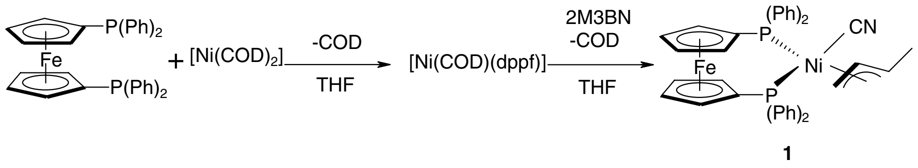
The $^{31}P\{^1H\}$ NMR spectrum of **1** in toluene-d_8 at room temperature showed several broad signals in the range of δ 20.6–13.3, which did not change on cooling to −60 °C, i.e., a low-temperature limit was not observed. Similar behavior was observed by ^{1}H NMR at room temperature. A COSY spectrum allowed us to propose the existence of two species or conformers for the allyl cyanide complex in a 1:1 ratio.

Table 1
Catalytic isomerization of 2M3BN

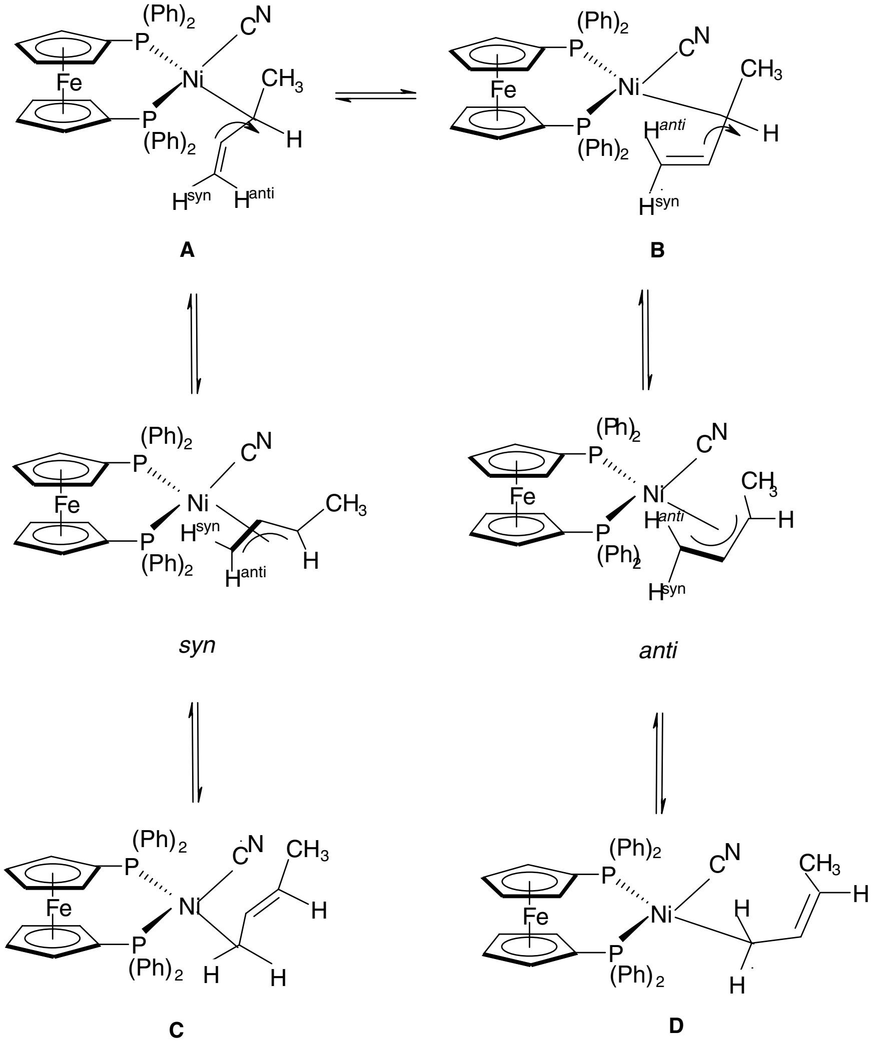


Entry	System	*t* (h)	Conversion (%)	Yield of 3-PN (%)	Other nitriles (%)
1	[Ni(COD)$_2$]/dppf	1	79	67	12
2	[Ni(COD)$_2$]/dppf	2	93	76	17
3	[Ni(COD)$_2$]/dppf	2.5	100	83	16
4	[Ni(COD)$_2$]/dppf/ZnCl$_2$	1	0	–	–
5	[Ni(COD)$_2$]/dppf/ZnCl$_2$	5	100	54	46
6	[Ni(COD)$_2$]/dppf/BEt$_3$	1	0	–	–
7	[Ni(COD)$_2$]/dppf/BEt$_3$	120	10	7	3

Neat substrate:ligand:[Ni(COD)$_2$]:Lewis acid = 110:1:1:1, $T = 100$ °C. 2M3BN conversion % and yield were obtained by GC–MS and confirmed by ^{1}H NMR spectroscopy. GC error ±1%.



Scheme 2.



Scheme 3. π–σ–π isomerization.

Both species may be assigned to the *syn* and *anti* conformers of the allyl moiety, formed via a π–σ–π isomerization (Scheme 3), but by analogy to complex **3**, vide infra, therefore at least one is likely to be the *syn* isomer [18]. However, we cannot discard the co-formation of species A, B, C or D in the same isomerization process.

In agreement with the existence of at least two species in solution, two broad resonances for each type of allyl proton environment were observed at: δ 4.82 and 4.71 (C*H* central), 4.19 and 4.15 (C*H*Me), 2.77 and 2.66 (C*H*H), 1.77 and 1.68 (CH_3), and 1.55 and 1.44 (CH*H*). This was also corroborated by $^{13}C\{^1H\}$ NMR spectroscopy, where two signals for each carbon of the allyl ligand were detected (δ 112.7 and 111.7 (*C*H central), 85.3 and 82.7 (*C*HMe), 48.9 and 47.3 ($\mathit{C}H_2$), and 18.7 and 17.8 ($\mathit{C}H_3$)). The CN ligand gives one broad signal only at 145.6.

Most of the signals in the ^1H and $^{13}C\{^1H\}$ NMR spectra are in the range reported for closely related allyl compounds with diphenylphosphinobutane (dppb), [8] with the exception of the resonance for the central *CH* of the allyl moiety, located at δ 112.7 and 111.7 for both isomers containing dppf and reported at 96.2 for dppb. NMR assignments were in most cases corroborated by a series of 2D NMR experiments.

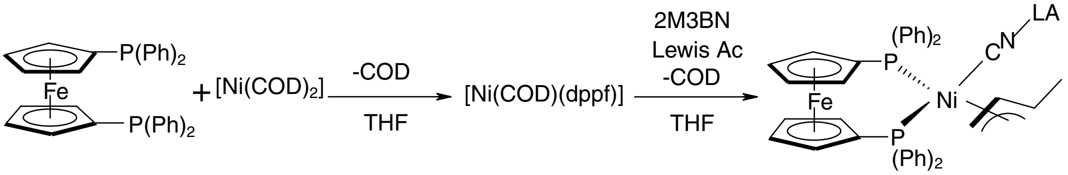
*2.3. Synthesis and characterization of Ni(II) allyl cyanide–Lewis acid complexes (**2**) and (**3**)*

The *in situ* reaction of [Ni(COD)(dppf)] in THF with an equimolar ratio of 2M3BN/$ZnCl_2$ or 2M3BN/BEt_3 in THF solution produced a red–orange solution in either case. After evaporation of the solvent an orange solid for complex **2** and a red–orange solid for complex **3** were obtained (Scheme 4).

The $^{31}P\{^1H\}$ NMR spectrum in CD_2Cl_2 at room temperature for complex **2** displayed two overlapping very broad signals roughly centered at 24.6 and 23 ppm, indicative of an interchange, and also two sharp doublets at 24.5 and 23.1 ppm ($^2J_{P-P} = 19.5$ Hz) (see Fig. 1a). On cooling the sample to 0 °C, the broad overlapping signals begin to sharpen into two signals at δ 25.4 and 22.5. Total decoalescence is reached at -60 °C, resulting in two doublets at δ 25.7 and 22.3 ($^2J_{P-P} = 20.1$ Hz, 70%), along with the two doublets originally observed at room temperature (δ 24.5 and 23.1, $^2J_{P-P} = 19.5$ Hz, 30%) that remain unchanged. The two doublets involved in coalescence are for one isomer, probably the *syn* isomer, based on the X-ray structure determined for **3**, vide infra, that undergoes rotation upon warming. The unchanging doublets can be assigned again with the related species C or D, depicted in Scheme 3, but with a coordinated LA to the CN moiety or alternatively to the cation $[Ni(dppf)(\pi\text{-allylMe})]^+$ which can be static because it is a d^8 square planar, having the cyanide out of the coordination sphere due to removal by the LA [17]. Alternatively, the unchanged doublets can also be associated with a 4-coordinate Zn species, in different coordination environments, as represented in Scheme 4. Closely related species have been structurally characterized by Vogt and co-workers [10].

In agreement with the above description, the ^1H NMR spectrum for complex **2** at room temperature displays two sets of signals for each allyl group proton, with signals located at: δ 5.81 and 5.55 (m, C*H* central), 3.35 and 3.05 (m, C*H*Me), 2.63 and 2.55 (d, $^3J_{H-H} = 14.1$ Hz, C*H*H), 1.63 and 1.61 (d, $^3J_{H-H} = 13.3$ Hz, CH*H*), and 1.72 (d, $^3J_{H-H} = 6.6$ Hz, C*H*$_3$) and 1.4 (d, $^3J_{H-H} = 7.2$ Hz, C*H*$_3$). In sharp contrast, the $^{13}C\{^1H\}$ spectrum at room temperature displayed only one resonance for each carbon of the allylic moiety at δ 88.4 (*C*H central), 69.6 (*C*HMe), 51.5 (*C*H_2) and 20.5 (*C*H_3), the resonance for CN appearing at 144 ppm. All the above quoted chemical shifts are similar to the ones reported in closely related allylic systems [10].

Complex **3** presents a fluxional behavior in the $^{31}P\{^1H\}$ NMR spectrum, i.e., a very broad signal at room tempera-



2 LA= $ZnCl_2$
3 LA= BEt_3

Scheme 4.

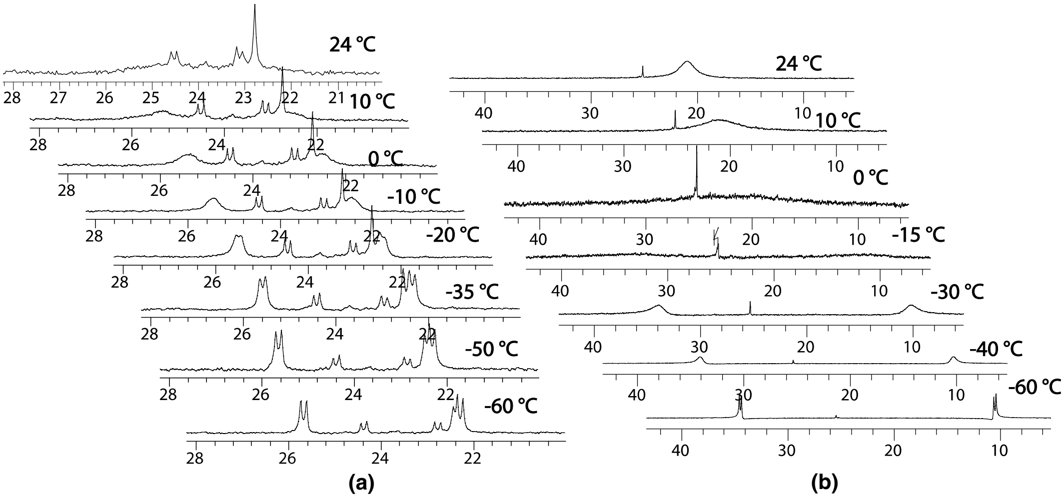


Fig. 1. Variable temperature $^{31}P\{^1H\}$ NMR for complexes **2** (a) and **3** (b). Signals at δ 22.8 in (a) and 25.1 ppm in (b) are impurities.

ture located at δ 20.9, indicative of exchange, that on cooling to −60°C decoaleses to give two sharp doublets located at δ 34.4 and 10.5 ppm ($^2J_{P-P} = 32.9$ Hz) (see Fig. 1b). The activation energy for this process, again assigned as allyl group rotation, was determined to be $11.0\ \mathrm{kcal \cdot mol^{-1}}$, which is almost half of the one reported in the case of cationic d^8 square planar nickel-allylic systems [19].

The ^1H NMR spectrum for complex **3** displays only one signal for each allyl group proton, at room temperature: δ 4.83 (pq, C*H* central), 2.90 (m, C*H*Me), 2.98(m, C*H*H), 1.51 (m, CH*H*), and 1.44 (d, $^3J_{H-H} = 5.1$ Hz, C*H*$_3$). The bonding of BEt_3 to the CN moiety was confirmed by the upfield shift to δ 0.63 (BC*H*$_2$) and 0.09 (C*H*$_3$) [20]. The $^{13}C\{^1H\}$ spectrum for complex **3** displays the relevant signals assigned as follows: the allyl ligand at δ 98.4 (*C*H central), 86.6 (*C*HMe), 52.2 (*C*H$_2$) and 15.7 (*C*H$_3$) ppm; the CN ligand at 142.2. The carbons of the ethyl groups for BEt_3 produce resonances at δ 20.8 (*C*H$_2$) and 11.2 (*C*H$_3$).

Crystals suitable for X-ray diffraction studies of complex **3**, isolated from the catalytic reaction mixture using BEt_3, were obtained upon cooling the mixture to −35 °C in the dry box. A summary of crystallographic results and the molecular structure of complex **3** are shown in Table 2 and Fig. 2, respectively. The geometry around the Ni center is pseudotetrahedral, as observed for the structure of [Ni(DPEphos)(η^3-1-Me–C_3H_4)(CN–$ZnCl_2 \cdot$EtOH)], [10] in contrast to the reported [Ni(dppb)(η^3-1-Me–C_3H_4)(CN)], [8] [Ni(dippe)(η^3-allyl)(CN–BPh_3)], [17a] and [Ni(dippe)-(η^3-allyl)(CN)], [17b] which are described as square-pyramidal at the metal center, with the CN ligand in the apical position.

Table 2
Summary of crystallographic results for **3**

Empirical formula	$C_{45}H_{50}BFeNNiP_2$
Formula weight	792.17
Temperature (K)	273(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	11.664(2)
b (Å)	12.070(2)
c (Å)	15.918(3)
α (°)	105.857(3)
β (°)	94.501(4)
γ (°)	107.635(3)
Volume (Å^3)	2022.4(7)
Z	2
Density (calculated) (Mg m^{-3})	1.301
Absorption coefficient (mm^{-1})	0.935
F(000)	832
Crystal size (mm^{-3})	0.18 × 0.14 × 0.11
Theta range for data collection (°)	1.35–25.00
Index ranges	$-13 \leqslant h \leqslant 13$, $-14 \leqslant k \leqslant 14$, $-18 \leqslant l \leqslant 18$
Reflections collected	19284
Independent reflections [R_{int}]	7086 [0.0581]
Completeness to $\theta = 25.00°$ (%)	99.4
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	7086/0/464
Goodness-of-fit on F^2	1.256
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0742$, $wR_2 = 0.1627$
R indices (all data)	$R_1 = 0.0887$, $wR_2 = 0.1695$
Largest difference peak and hole (e Å^{-3})	0.826 and −0.467

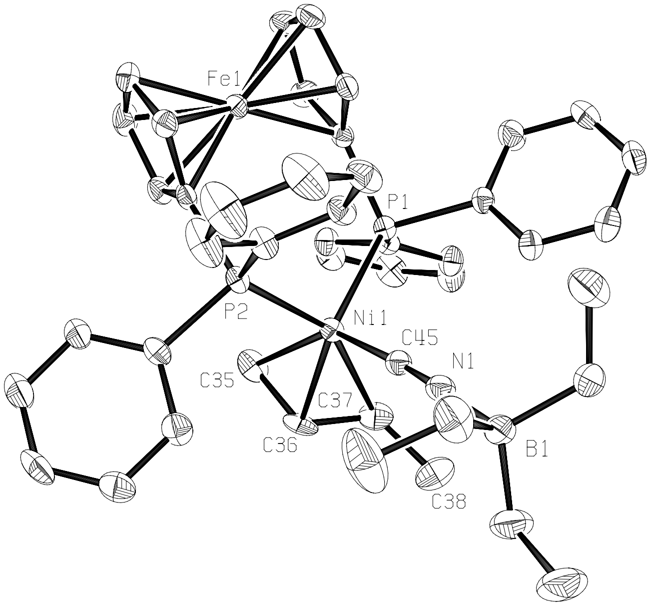


Fig. 2. Molecular structure of complex **3** at the 30% probability. Selected bond distances in Å: Ni–P1(2.3305(14)), Ni–P2 (2.2143(14)), Ni–C45(1.898(5)), Ni–C35(2.075(4)), Ni–C36(2.007(5)), Ni–C37(2.150(5)), C35–C36(1.409(7)), C36–C37(1.387(8)), C37–C38(1.512(8)). Selected angles in °: P1–Ni–P2(105.18(5)), P1–Ni–C45(109.51(14)), P2–Ni–C45(96.04(14)).

The bond distances in complex **3** are in agreement with those found in closely related structures. A noteworthy feature of the structure is that no substantial effect is observed due to the LA coordination to the CN moiety. The C–N distance without LA being 1.173(6) Å in [Ni(dppb)(η^3-1Me–C_3H_4)(CN)], [8] and 1.146(4) Å in [Ni(dippe)(η^3-allyl)(CN)], [17b] while in the case of complex **3** it is 1.144(6) Å. This distance is also very similar to those reported for [Ni(DPEphos)(η^3-1-Me–C_3H_4)(CN–$ZnCl_2 \cdot$EtOH)] (1.150(3) Å), [10] and [Ni(dippe)(η^3-allyl)(CN–BPh_3)] (1.1517(19) Å) [17a]. None of the Ni—CN bond distances showed dramatic differences, these being 1.894 ± 0.001 Å in complex **3** and those with DPEphos [10] and dppb [8] ligands.

The lack of catalytic activity of compounds **2** and **3** for isomerization of 2M3BN, is consistent with the ability of BEt_3 and $ZnCl_2$ to stabilize the corresponding allyl complex upon coordination to the cyanide moiety. This coordination inhibits return of the cyanide to the allyl fragment for the formation of 3PN.

3. Conclusions

The use of both bis-diphenylphosphinoferrocene and [Ni(COD)$_2$] as catalytic precursors gave improved yields and reaction times for the catalytic isomerization of

2M3BN to 3PN. Allyl species are involved as intermediates in the C—CN bond cleavage and formation. The use of Lewis acids decreases the activity of the complexes due to coordination to the nitrogen in the Ni—CN moiety, but allows full X-ray characterization. Further work is underway to expand the scope of this reaction with the use of closely related bis-diphosphinoferrocene ligands.

4. Experimental

All manipulations were carried out using standard Schlenk and glove box techniques under argon (Praxair 99.998). THF (J.T. Baker) was dried and distillated 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 glove box (<1 ppm H_2O 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. BEt_3 and dppf were purchased from Aldrich and were used as received. 2M3BN (86.5% by GC–MS, see Fig. S-1) was purchased from TCI America, purged and stored in the glove box. $ZnCl_2$ was purchased from J.T. Baker and dried in vacuo. ^{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 CD_2Cl_2. ^{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. Variable temperature ^{31}P{^{1}H} NMR spectra were recorded on a 400 MHz Varian Unity. All NMR spectra and catalytic reactions were carried out using thin wall (internal diameter 0.38 mm) WILMAD NMR tubes with J. Young valves. A Bruker APEX CCD diffractometer with monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) was used for the X-ray structure determinations. A crystal of **3** was mounted under Paratone 8277 on a glass fiber and immediately placed under a cold stream of nitrogen. Mass determinations (FAB$^+$) on a JEOL SX-102 A, using nitrobenzilic alcohol matrix and GC–MS determinations on a Varian Saturn 3, on a 30 m DB-5MS capillary column.

4.1. Catalytic isomerization of 2M3BN in the absence of LA

A solution of 2M3BN (0.4 mL, 4.00 mmol) and dppf (19.9 mg, 0.036 mmol) was added to the yellow crystalline [Ni(COD)$_2$] (10 mg, 0.036 mmol), producing a red solution. The mixture was transferred to an NMR tube with a J. Youngs valve, and the tube was heated at 100 °C in an oil bath with stirring. After cooling to room temperature, a sample of the reaction mixture was dissolved in THF inside the dry box and analyzed by GC–MS. A second sample was dissolved in toluene-d_8 and analyzed by ^{1}H NMR spectroscopy, showing resonances identical to those of *trans*-3PN.

4.2. Catalytic isomerization of 2M3BN in the presence of LA

A solution of 2M3BN (0.4 mL, 4.00 mmol), BEt_3 or $ZnCl_2$ (0.036 mmol), and dppf (19.9 mg, 0.036 mmol) was added to yellow crystalline [Ni(COD)$_2$] (10 mg, 0.036 mmol), producing a red solution. The mixture was transferred to an NMR tube with a J. Youngs valve, and the tube was heated at 100 °C in an oil bath with stirring. After cooling to room temperature, a sample was dissolved in THF inside the dry box, and analyzed by GC–MS. Also a second sample was dissolved in toluene-d_8 and analyzed by ^{1}H NMR spectroscopy as described in the text.

4.3. Preparation of [Ni(dppf)(η^3-1Me–C_3H_4)(CN)] (1)

A solution of dppf (50 mg, 0.09 mmol) in 2 mL of THF was added dropwise to a stirred solution of [Ni(COD)$_2$] (25 mg, 0.09 mmol) in 3 mL of THF, giving an orange solution of [Ni(COD)(dppf)] which was further stirred for 15 min. Nine microliters of 2M3BN (0.09 mmol) were then added, and after 30 min of stirring a red solution was obtained. The solvent was then removed in vacuo and the residue was dried for 3 h to give a red solid (57.3 mg, 92%). ^{1}H NMR (299.7 MHz): δ 4.82 (m, 1H, C*H* central) and 4.71 (m, 1H, C*H* central), 4.19 (m, 1H, C*H*Me) and 4.15 (m, 1H, C*H*Me), 2.77(m, 2H, C*H*H) and 2.66 (m, 2H, C*H*H), 1.77 (m, 3H, CH_3) and 1.68 (m, 3H, CH_3), and 1.55 (m, 2H, CH*H*) and 1.44 (m, 2H, CH*H*). ^{13}C{^{1}H} NMR (75.4 MHz): δ 145.6 (CN), 112.7 and 111.7 (*C*H central), 85.3 and 82.7 (*C*HMe), 48.9 and 47.3 (*C*H$_2$), and 18.7 and 17.8 (*C*H$_3$). ^{31}P{^{1}H} NMR (100 MHz): δ 20.6–13.3. FAB+: 667 (M$^+$–CN).

4.4. Preparation of [Ni(dppf)(η^3-1Me–C_3H_4)(CN–Lewis acid)]: LA=$ZnCl_2$ (2) and LA=BEt_3 (3)

To a stirred solution of **1**, prepared as above, 0.09 mmol of the corresponding LA in 1 mL of THF was added. After 30 min of stirring, an orange solution was obtained. The solvent was then removed *in vacuo* and the residue was further dried for 3 h, producing **2** as an orange solid (66.4 mg, 89%) or **3** as a red–orange solid (63.5 mg, 89.1%). ^{1}H NMR for **2** (299.7 MHz): δ 5.81 (m, 1H, C*H* central) and 5.55 (m, 1H, C*H* central), 3.35 (m, 1H, C*H*Me) and 3.05 (m, 1H, C*H*Me), 2.63 and 2.55 (d, 2H $^3J_{H–H} = 14.1$ Hz, C*H*H), 1.63 and 1.61 (d, 2H, $^3J_{H–H} = 13.3$ Hz, CH*H*), and 1.72 (d, 3H, $^3J_{H–H} = 6.6$ Hz, C*H*$_3$) and 1.4 (d, 3H, $^3J_{H–H} = 7.2$ Hz, C*H*$_3$). ^{13}C{^{1}H} NMR (75.4 MHz) for **2**: δ 144 ppm (CN), 88.4 (*C*H central), 69.6 (*C*HMe), 51.5 (*C*H$_2$), and 20.5 (*C*H$_3$). ^{31}P{^{1}H} for **2** (100 MHz, 25 °C): δ 24.5, 23 (bs), 24.5(d) and 23.1(d) ($^2J_{P–P} = 19.5$ Hz). FAB+: 667 (M$^+$–CN–$ZnCl_2$). ^{1}H NMR for **3** (299.7 MHz): δ 4.83 (pq, 1H, C*H* central), 2.90 (m, 1H, C*H*Me), 2.98(m, 1H, C*H*H), 1.51 (m, 1H, CH*H*), and 1.44 (d, 3H, $^3J_{H–H} = 5.1$Hz, C*H*$_3$), 0.63 (m, 6H, BC*H*$_2$) and 0.09 (m, 9H, C*H*$_3$). ^{13}C{^{1}H} NMR (75.4 MHz) for **3**: δ 142.2(CN), 98.4 (*C*H central), 86.6 (*C*HMe), 52.2 (*C*H$_2$), and 15.7 (CH_3), 20.8 (BCH_2) and 11.2 (CH_3). $^{31}P\{^1H\}$ NMR for **3**: δ 20.9 (br). FAB+: 667 (M^+–CN–BEt_3).

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Appendix A. Supporting information

Tables of complete crystallographic data for **3**. Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 605934 for compound **3**. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.05.042.

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[20] Free BEt_3 in THF-d_8 gives resonances at 1.02 ppm (CH_2) and 0.95 (CH_3) ppm, respectively.