Nickel-Catalyzed Isomerization of 2-Methyl-3-butenenitrile[†]

Jos Wilting,[‡] Christian Müller,[‡] Alison C. Hewat,[‡] Dianne D. Ellis,[§]
Duncan M. Tooke,[§] Anthony L. Spek,[§] and Dieter Vogt*,[‡]

Laboratory of Homogeneous Catalysis, Eindhoven University of Technology,
Eindhoven, The Netherlands, and Department for Crystal and Structural Chemistry,
Utrecht University, Utrecht, The Netherlands

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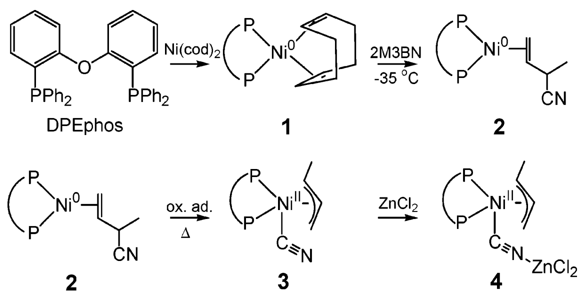
Summary: The isomerization of the branched 2M3BN to the linear 3PN by a DPEphosNi species has been investigated by means of variable-temperature NMR spectroscopy, and activation parameters have been determined. An intermediate in this reaction, which is formed via C–C bond activation, could be trapped by addition of $ZnCl_2$, and the molecular structure of the corresponding Ni(II) complex has been determined by X-ray crystallography.

Among C–C bond formation reactions, the hydrocyanation of alkenes is an attractive, yet challenging, route for the functionalization of carbon–carbon double bonds.[1,2] The isomerization of 2-methyl-3-butenenitrile (2M3BN) to 3-pentenenitrile (3PN), for example, is closely related to hydrocyanation and is at the same time an important step in the industrial adiponitrile process.[3] In combination with $Ni(cod)_2$, all classes of bidentate phosphorus ligands (phosphines,[4,5] phosphinites,[6] phosphonites,[4,7] and phosphites[8]) catalyze the isomerization, without the addition of Lewis acids. However, the influence of ligand parameters on this conversion still remains unknown. The isomerization is, in fact, a suitable reaction to study reductive elimination to the final product 3PN without the deactivation of the catalyst usually caused by HCN during hydrocyanations.[9,10] We started a spectroscopic investigation of the isomerization of 2M3BN to 3PN catalyzed by DPEphos/$Ni(cod)_2$ to study the reductive elimination of nitriles, which is the crucial step in catalytic hydrocyanation reactions. In fact, we were moved to report on our results because of recent contributions in this field by Santini et al.[11] and Chaudret et al.[5]

Scheme 1



Upon addition of 1 equiv of DPEphos to $Ni(cod)_2$ in toluene-d_8 the ^{31}P NMR spectrum displays a singlet at δ 33.1 ppm for the species (DPEphos)Ni^0(cod) (**1**) (Scheme 1). This signal disappears on addition of approximately 3 equiv of 2M3BN at −35 °C, and two doublets appear at δ 21.3 and 24.2 ppm, with $^2J_{PP} = 38$ Hz. These resonances correspond to (DPEphos)Ni^0(2M3BN) (**2**), with 2M3BN coordinating most likely through its alkene bond; the η^2-alkene complex (DPEphos)Ni^0(styrene) gives a very similar ^{31}P NMR spectrum, which shows two doublets at δ 20.2 and 22.9 ppm with $^2J_{PP} = 44$ Hz. When the temperature is raised to +25 °C, the two doublets of **2** disappear and a signal could no longer be detected in the ^{31}P NMR spectrum. The ^1H NMR spectrum shows broad signals at δ 4.5 ($CHCH_2$), 3.4 ($CHCH_3$), 2.4 (1H, $CH^{syn}H^{anti}$), 1.6 (CH_3), and 1.2 (1H, $CH^{syn}H^{anti}$) ppm. Increasing the temperature to +35 °C causes slow isomerization of 2M3BN to 3PN, indicated by the methyl signals in the ^1H NMR spectrum. The 3PN analogue (DPEphos)Ni^0(3PN) (**5**) could not be detected with VT NMR spectroscopy when approximately 5 equiv of 3PN was added to **1**. However, **1** disappears and the same broad signals in the ^1H NMR spectrum occur which were detected upon warming of **2**. We ascribe this spectrum to (DPEphos)$Ni^{II}(C_4H_7)(CN)$ (**3**), which is formed by oxidative addition of 2M3BN or

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* To whom correspondence should be addressed. E-mail: d.vogt@tue.nl.

[†] Dedicated to Professor Wilhelm Keim on the occasion of his 70th birthday.

[‡] Eindhoven University of Technology.

[§] Utrecht University.

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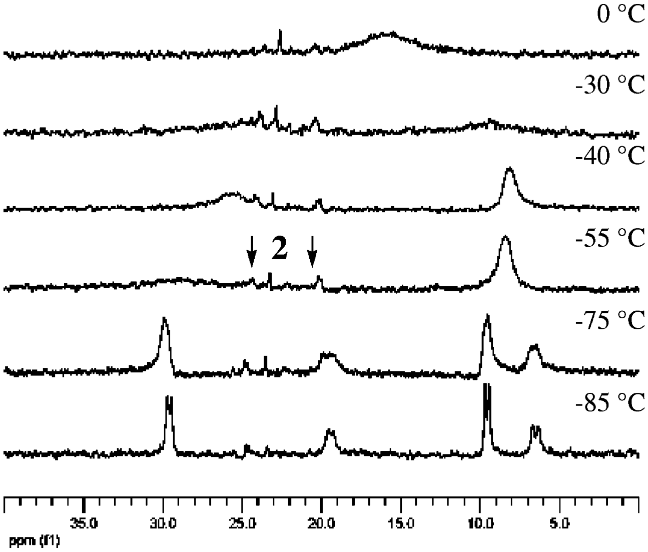


Figure 1. $^{31}P\{^1H\}$ VT NMR spectra on a sample of 1 equiv of DPEphos and $Ni(cod)_2$ in toluene-d_8 to which 3 equiv of 2M3BN was added at −78 °C.

3PN to the Ni center (Scheme 1). Chaudret et al. reported similar ^1H NMR data for (dppb)$Ni^{II}(C_4H_7)$(CN).[5] Both complexes display distinct signals for the syn and anti protons. The substitution of 1,5-cyclooctadiene by 2M3BN occurs more quickly compared to the substitution by 3PN, as is expected for a terminal versus an internal alkene.[12]

Cooling the NMR tube from +35 to −85 °C results in three sets of signals, as displayed in Figure 1.[13] One set of very low intensity is similar to the signals for **2**. The other two sets most likely correspond to the syn and anti isomers of **3** (Scheme 2), with $^2J_{PP} = 49$ and 64 Hz. Isomerization between syn and anti is indeed possible via the η^1-methylallyl species **I** and **II**, which can undergo rotation of the C2−C3 bond without exchange of the syn and anti protons of the CH_2 group.[14] The other η^1-methylallyl species **III** and **IV** would give interconversion of the syn and anti protons upon rotation of the C1−C2 bond. Although this interconversion is not observed, we strongly believe that formation of 3PN proceeds via **III** and **IV**. Slowly warming the NMR tube shows the dynamic behavior: first the two sets of doublets become one set of broad signals (−40 °C), indicating fast exchange between the syn and anti isomers without rotation of the allyl group. Only one position seems to be favored, as only two species were detected at low temperature. Rotation of the allyl group, indicated by one broad signal, is observed at 0 °C. This signal disappears after warming the NMR tube to temperatures above 20 °C. At these temperatures the complex becomes catalytically active: i.e., reductive elimination to form the isomerized product occurs.

The addition of $ZnCl_2$ to **3** caused precipitation of complex **4**. The ^1H NMR spectrum is similar to the spectrum of **3**. An alternative route to complex **4** is addition of either 2M3BN or 3PN to DPEphos$NiCl_2$ in the presence of zinc dust. However, from a mixture of 2M3BN and 3PN (1:1) only 2M3BN gave oxidative addition to Ni(0) at 20 °C; no isomerization is observed, due to precipitation of complex **4**. This demonstrates the large difference in reaction rates for coordination of 2M3BN over 3PN to the Ni center (vide infra).

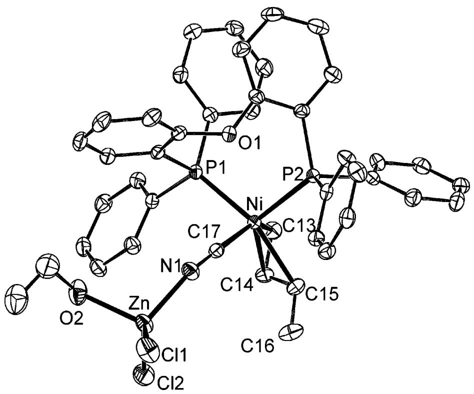
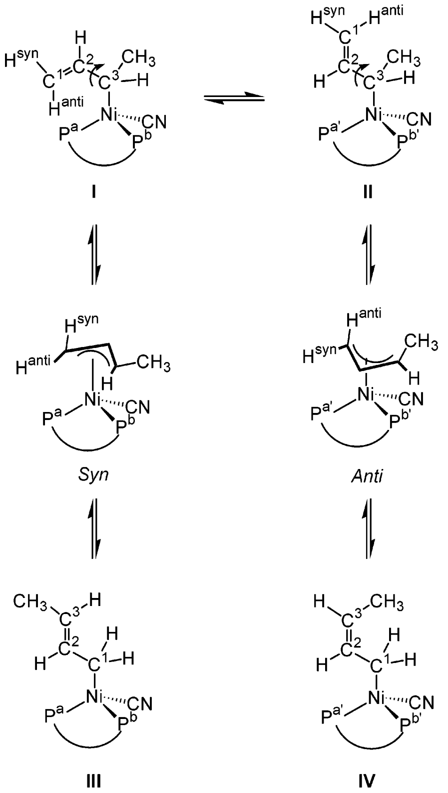


Figure 2. Crystal structure of **4**. Hydrogen atoms and a solvent molecule have been omitted for clarity. Bond lengths (Å) and angles (deg): Ni(1)−P(1) = 2.3080(6), Ni(1)−P(2) = 2.2031(6), P(1)−Ni(1)−P(2) = 105.89(2), Ni(1)−C(17) = 1.893(2), C(17)−N(1) = 1.150(3), Ni(1)−C(13) = 2.067(3), Ni(1)−C(14) = 2.000(3), Ni(1)−C(15) = 2.148(3), N(1)−Zn(1) = 1.985(2).

Scheme 2



Single crystals of **4** suitable for X-ray diffraction could be obtained.[15] The molecular structure of **4** is shown in Figure 2 and is best described as pseudo-tetrahedral around the nickel center. This has also been observed in the recently reported structure for (dppb)$Ni^{II}(C_4H_7)$-

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[12] Tolman, C. A. *Organometallics* **1983**, *2*(5), 614−621.

[13] The small sharp singlet at δ 23 ppm is an impurity.

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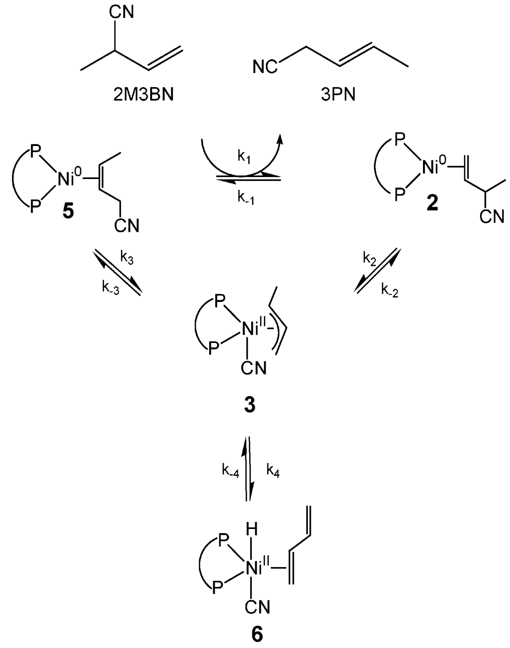
[15] Crystal data for **4**: $(C_{43}H_{41}Cl_2NNiO_2P_2Zn)\cdot{}^1/_2C_6H_6$, $M_r = 899.74$, monoclinic, space group $C2/c$, $a = 24.9627(4)$ Å, $b = 12.0804(2)$ Å, $c = 28.9802(5)$ Å, $\beta = 106.7861(7)$, $V = 8366.9(2)$ Å^3, $Z = 8$, $D_{calcd} = 1.429$ Mg m^{-3}, $F(000) = 3720$, λ(Mo Kα) = 0.710 73 Å, $\mu = 1.267$ mm^{-1}, $T = 150(2)$ K, crystal dimensions 0.18 × 0.12 × 0.08 mm. Of 36 646 reflections measured, 9590 unique reflections were used in the refinement. Final $R = 0.0379$ ($R_w = 0.0881$); $S = 1.03$.

Scheme 3



(CN).[5] Both molecular structures are very similar, i.e. the Ni−CN bond length is 1.893 Å in both structures, and thus the Lewis acid $ZnCl_2$ has little influence. This is also observed during catalysis, which shows similar rates for 0, 1, and 2 equiv of $ZnCl_2$ in DMSO. However, the molecular structure reported for (dippe)$Ni^{II}(C_3H_5)$(CN)[16] has a square-pyramidal geometry, with the CN in the apical position.

The structural difference originates from the short bridge between the phosphorus atoms, resulting in different P−Ni−P angles (105.0° in **4** vs 88.7° in (dippe)$Ni^{II}(C_3H_5)$(CN)).

Upon analysis by GC, the isomerization of 2M3BN to 3PN (with and without $ZnCl_2$) was determined to be zero order in substrate (eq 1 and Scheme 3), which has been observed in the hydrocyanation of 6-methoxy-2-vinylarene as well.[9]

$$d[3PN]/dt = k[\text{catalyst}] \qquad (1)$$

This result is in contradiction to the report by Santini et al. They concluded the system to have first-order kinetics in substrate for the isomerization of 2M3BN to 3PN in ionic liquids with monodentate phosphines in combination with $Ni(cod)_2$.[11] However, their results could equally well point to zero-order kinetics.[17] First-order kinetics in substrate would suggest an associative mechanism for the reductive elimination, as observed in the hydrocyanation of ethylene.[18]

The activation parameters of the isomerization reaction were determined to be $\Delta H^{\ddagger} = 60.5 \pm 5.2$ kJ mol^{-1} and $\Delta S^{\ddagger} = -112 \pm 15$ J mol^{-1} K^{-1}. An investigation on ligand differentiations on the isomerization reaction, by measurement of the activation parameters, is currently being carried out in our laboratories, and the results will be published elsewhere.

However, the data indicate that the reductive elimination is the rate-determining step in the isomerization of 2M3BN. It has been proposed that the allyl species **3** is in equilibrium with its hydrido cyano butadiene species **6** with $k_{-4} \gg k_4$ (Scheme 3), which explains the labeling experiments described by Druliner[19] and RajanBabu.[9] This hypothesis was rejected by Chaudret et al. on the basis of DFT calculations for a Ni−PH_3 model system without Lewis acids. The substitution reaction (**5** to **2**) most likely follows an associative mechanism, avoiding the unstable 14-electron complex.

The isomerization of 2M3BN to 3PN can be used to study the influence of different ligand parameters on the reductive elimination, which is currently being performed in our group. It should be mentioned here that the formation of 2M3BN is not included in the rate of isomerization. The activation parameters were determined for the DPEphos/$Ni(cod)_2$ catalyst system, and the individual reaction steps were studied by NMR. The reversibility of the reductive elimination reaction was demonstrated. Furthermore, the C−C activation product **4**, which was synthesized independently and characterized by single-crystal X-ray diffraction, is an intermediate in the isomerization of 2M3BN to 3PN.

Supporting Information Available: Text and figures giving details of kinetic measurements and a CIF file giving full characterization of **4** including crystal structure analysis. This material is available free of charge via the Internet at http://pubs.acs.org. The crystallographic data have also been deposited with the Cambridge Crystallographic Database (CCDC No. 252435).

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