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Communications

Catalytic Isomerization of Cyanoolefins Involved in the Adiponitrile Process. C−CN Bond Cleavage and Structure of the Nickel π-Allyl Cyanide Complex $Ni(\eta^3\text{-1-Me-}C_3H_4)(CN)(dppb)$

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Summary: Isomerization of 2-methyl-3-butenenitrile to 3-pentenenitrile is catalyzed by nickel π-allyl cyanide complexes. The mechanism is supported by in situ NMR monitoring and DFT studies.

The synthesis of adiponitrile (AdN) based on a nickel-catalyzed double hydrocyanation of butadiene is a major industrial success for homogeneous catalysis. In the first step, hydrocyanation leads to a mixture of the desired 3-pentenenitrile (3PN) and the undesired 2-methyl-3-butenenitrile (2M3BN). The branched isomer needs to be isomerized to the linear 3PN. The second hydrocyanation step produces AdN together with several byproducts. The reaction is assisted by Lewis acid cocatalysts. Extensive mechanistic investigations, in particular by the DuPont group, appeared almost 20 years ago, and the role of a π-allyl nickel cyanide complex has been outlined in the first hydrocyanation step.[1−3]

2M3BN production represents a major drawback of the first catalytic hydrocyanation step. For example, a typical batch experiment leads to a 1:1.5 ratio of 2M3BN and 3PN.[4] Herein we report an effective catalytic isomerization of 2M3BN into 3PN using the zerovalent $Ni(COD)_2$ precursor in the absence of any Lewis acid. The mechanism is established by in situ NMR catalytic monitoring and isolation of the key π-allyl nickel cyanide intermediate as well as by DFT theoretical studies.

The optimal catalytic experiment was carried out by adding $Ni(COD)_2$ (1 equiv, COD = 1,5-cyclooctadiene) to a mixture of 2M3BN (110 equiv) and PPh_3 (10 equiv). The mixture was stirred at 100 °C for 3 h. GC analysis shows a 96% conversion and the formation of 3PN in 81% yield (see Scheme 1).

A similar experiment was performed in an NMR tube, and the reaction was monitored directly in the NMR probe at 100 °C using C_7D_8 as solvent. Introduction of toluene reduces the conversion to 85% but allows a good

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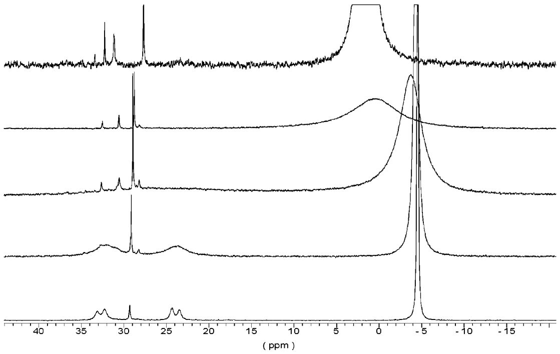


Figure 1. $^{31}P\{^1H\}$ NMR spectra of a $Ni(COD)_2$/2M3BN/PPh_3 mixture in a 1/16/8 ratio at various temperatures. From the top to the bottom T = 25, −60, −70, −80, and −90 °C. The sharp signals present in very small amounts in the region between 28 and 33 ppm are due to impurities.

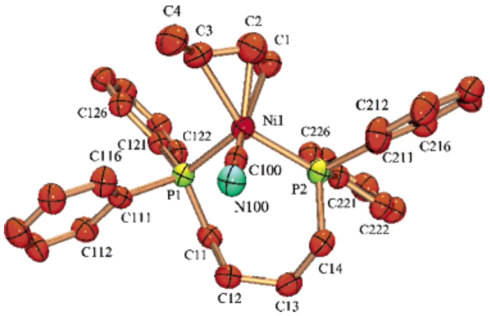
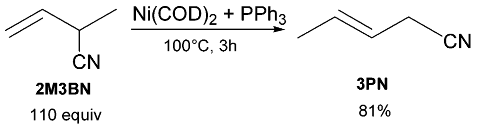
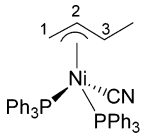


Figure 2. ORTEP drawing of compound **2**. Selected bond lengths (Å): Ni−C(100), 1.893(6); Ni−P(1), 2.2609(16); Ni−P(2), 2.1937(16); Ni−C(1), 2.064(6); Ni−C(2), 1.970(6); Ni−C(3), 2.130(6); C(1)−C(2), 1.374(8); C(2)−C(3), 1.359(9); C(3)−C(4), 1.495(8); C(100)−N(100), 1.173(6). Selected bond angles (deg): P(1)−Ni−P(2), 102.18(6); P(1)−Ni−C(100), 102.37(16); P(2)−Ni−C(100), 92.16(17).

Scheme 1

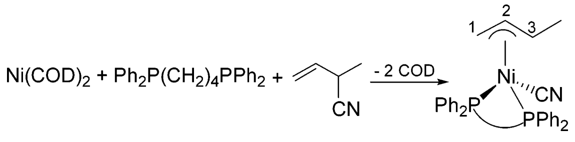


NMR analysis. The organic products are clearly identified by ^1H NMR, whereas the ^{31}P NMR spectrum shows at 100 °C a broad signal at 4.3 ppm indicative of an exchange. To better visualize the nickel species, we reduced the initial quantities of reactants. A C_7D_8 mixture of $Ni(COD)_2$/2M3BN/PPh_3 in a 1/16/8 ratio was heated for 30 min at 100 °C and then analyzed by NMR at various temperatures. The ^{31}P NMR spectrum shows at room temperature a very broad signal at 2 ppm (see Figure 1). Decoalescence leads at −90 °C to a sharp signal at −4.6 ppm, assigned to free PPh_3, and to an AB signal at 32.6 and 23.9 ppm with a J_{P-P} value of 103 Hz corresponding to the allyl cyanide complex $Ni(\eta^3\text{-}1\text{-}Me\text{-}C_3H_4)(CN)(PPh_3)_2$ (**1**) on the basis of several 1D and 2D NMR experiments.[5]



(**1**)

Scheme 2



(**2**)

All our attempts to isolate **1** have failed, but using a stabilizing diphosphine such as $Ph_2P(CH_2)_4PPh_2$ (dppb) allowed us to isolate the analogous complex $Ni(\eta^3\text{-}1\text{-}Me\text{-}C_3H_4)(CN)(dppb)$ (**2**) (see Scheme 2).[5]

The molecular structure is shown in Figure 2.[6] The structure can be described as a trigonal pyramid with a methylallyl unit in the apical position and confirms the C−CN bond breaking from the initial 2M3BN. The Ni−CN distance of 1.893(5) Å is analogous to that observed for other cyanide complexes[7] but shorter than in $Ni(\eta^3\text{-}C_3H_5)(CN)$(dippe) (1.994(3) Å, dippe = $^iPr_2P(CH_2)_2P^iPr_2$) very recently reported.[8] It is worth noting that a square-pyramidal geometry with a CN in an apical position is observed in this latter compound.[8]

A catalytic test was also performed by using a $Ni(COD)_2$/2M3BN/dppb mixture in a 1/110/1.3 ratio. GC analysis shows a 96% conversion and the formation of 3PN in 90% yield (2-methyl-2-butenenitrile, 3%; 4-pentenenitrile, 3%). A similar experiment was performed using **2** as catalyst precursor, in the absence of any added phosphine. Remarkably, a similar conversion (97%) was obtained after heating (3 h at 100 °C) a mixture of **2**/2M3BN in a 1/110 ratio, and GC analysis showed a 3PN selectivity of 83%.

On the basis of our DFT calculations (B3LYP) carried out using PH_3 as a model,[9] we propose the mechanism depicted in Scheme 3 for the isomerization of 2M3BN into 3PN, involving the following steps: (i) coordination of 2M3BN via the C=C bond; (ii) C−CN bond breaking and formation of a σ-allyl species; (iii) isomerization to the π-allyl species; (iv) σ-allyl formation; (v) C−CN bond coupling to 3PN coordination. The B3LYP calculated

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[5] Selected NMR data are as follows. For **1** (from TOCSY, COSY $^1H-^1H$, and HMQC $^1H-^{13}C$ experiments): ^1H NMR (400 MHz, C_7D_8, 273 K) δ 4.63 (m, H^2, 1H), 3.42 (qd, J_{H^3Me} = 6.2 Hz, $J_{H^3H^2}$ = 12.5 Hz, H^3, 1H), 2.25 (br, H^1, 1H), 1.65 (d, J_{H^3Me} = 6.2 Hz, Me, 3H), 1.45 (br, $H^{1'}$, 1H); ^{13}C NMR (100.6 MHz, C_7D_8, 273 K) δ 108.7 (C^2), 86.5 (C^3), 51.7 (C^1), 19.6 (Me). For **2**: ^1H NMR (400 MHz, C_7D_8, 293 K) δ 4.72 (m, H^2, 1H), 3.44 (br, H^3, 1H), 2.24 (br, H^1, 1H), 1.73 (brd, J_{H^3Me} = 6 Hz, Me, 3H), 1.25 (br, $H^{1'}$, 1H); ^{31}P NMR (161.97 MHz, C_7D_8, 293 K) δ 21 (br). extremely broad signals down to 183 K; $^{13}C\{^1H\}$ NMR (100.6 MHz, thf-d^8, 263 K) δ 152.2 (CN), 96.2 (C^2), 81.6 (C^3), 44.8 (C^1), 20.5 (Me). See Scheme 2 for atom labeling.

[6] Crystal data for **2**·C_7H_8: $C_{40}H_{43}NP_2Ni$, M_r = 658.40, triclinic, space group $P\bar{1}$, T = 160(2) K, a = 10.095(2) Å, b = 11.301(2) Å, c = 15.754(3) Å, α = 80.07(3)°, β = 86.08(3)°, γ = 74.07(3)°, V = 1701.9(6) Å^3, Z = 2, μ = 1.285 mm^{-1}, 14 884/5457 reflections collected/unique, R1 = 0.0536, wR2 = 0.1112, GOF = 0.938.

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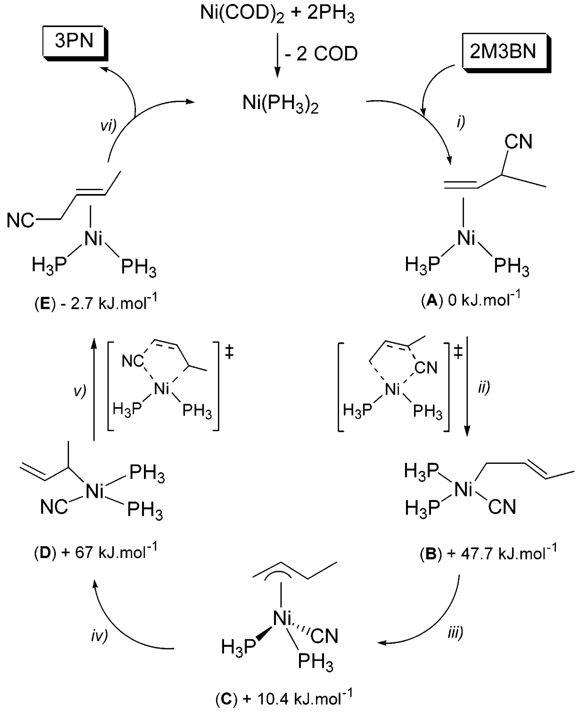
[8] Brunkan, N. M.; Jones, W. D. *J. Organomet. Chem.* **2003**, *683*, 77.

[9] For details of the calculations, see the Supporting Information. Geometrical data (Å) for **C**: Ni−CN = 1.892, Ni−C1 = 2.044, Ni−C2 = 2.045, Ni−C3 = 2.182, C1−C2 = 1.428, C2−C3 = 1.402, C3−C4 = 1.507. The anti isomer is found 15.5 kJ mol^{-1} above the syn isomer. We have ruled out a heterolytic C−CN cleavage, as this process leads to a cationic nickel species and CN^- would require a very high energy of 565 kJ mol^{-1}. As suggested by a reviewer, a concerted process involving C−CN bond cleavage and direct formation of **C** from **A** without the intermediacy of the σ-species **B** (and **D**) cannot be excluded. Further calculations are in progress.

Scheme 3. B3LYP-Optimized Structures and Energies of Isomers A−E Involved in the Isomerization of 2M3BN to 3PN



energy associated with the isomerization of 2M3BN to 3PN is -14.6 kJ mol^{-1}. Relative energies of the optimized geometries are indicated in Scheme 3. Isomers **A** and **E**, with 2M3BN and 3PN respectively coordinated through the double bond, are degenerate. The π-allyl species **C** corresponds to the syn isomer, and the geometrical data compare well with those obtained for the X-ray structure of compound **2**.[9] We propose that the key steps of C−CN bond cleavage and formation, through the π-allyl species, most probably involves $\sigma-\pi$ allyl conversion (species **B** and **D**). The importance of such a conversion has been very recently evidenced in related nickel species.[8,10,11] An alternative mechanism involving the intermediacy of a hydrido nickel cyanide complex and elimination of butadiene has been ruled out, being too high in energy. Such a mechanism has been proposed to operate on the basis of isotope exchange reactions in the presence of Lewis acid and with Ni[P(O-*p*-tolyl)$_3$]$_4$ as precursor.[3]

We have demonstrated here that the π-allyl nickel cyanide complexes **1** and **2** result from C−CN bond cleavage[12] from 2M3BN and that they are active precursors in the catalytic isomerization of 2M3BN into 3PN. **2** is the only complex so far reported which is active for the 2M3BN/3PN isomerization in the absence of any extra ligand and of any Lewis acid. Moreover, preliminary DFT studies show that a complex similar to **1** or **2** but replacing Ni by Pd cannot be optimized. All our attempts led to decoordination of one phosphine and formation of a square-planar palladium complex. This work highlights the unique properties of the nickel system. Full details will be reported in due course.

Acknowledgment. We acknowledge the support of the CNRS and Rhodia.

Supporting Information Available: Text and tables detailing the catalytic experiments and the synthesis of **2**, full details of the crystal structure analysis of **2** (CCDC Deposition No. 227317), and DFT calculation details. This material is available free of charge via the Internet at http://pubs.acs.org.

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