Organometallics **2007,** *26,* 5766−5769

Communications

Catalytic Isomerization of 2-Methyl-3-butenenitrile by Nickel Systems Using Bis-diphosphinoferrocene Ligands: Evidence for Hemilability

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Received September 18, 2007

Summary: The use of catalytic amounts of [Ni(COD)$_2$] and a series of bis-diphosphinoferrocene ligands allows the catalytic isomerization of 2-methyl-3-butenenitrile to the linear 3-pentenenitrile, via allyl intermediates that display hemilability.

The catalytic isomerization of the branched nitrile 2-methyl-3-butenenitrile (2M3BN) to the linear isomer 3-pentenenitrile (3PN) is a key step in the hydrocyanation of butadiene, from which adiponitrile, a precursor of the building blocks for Nylon 6,6, is produced.[1] Despite the importance of this topic, there are a relatively small number of papers concerning this reaction. By using [Ni(COD)$_2$] as a metal precursor, different P-donor ligands (phosphines and phosphites) have been used in the catalytic rearrangement of 2M3BN to the linear 3PN isomer, giving selectivities from 70 to 95%.[2−6] The reaction has been studied in aqueous media[7] and in ionic liquids.[8] Some recent mechanistic proposals have been made using DFT calculations;[2] other proposals include the addition of HCN to the C=C bond of cyano-olefins in the presence of Lewis acids (LA), the latter compounds apparently playing a critical role within the actual catalytic cycle.[9−11]

Our group has been interested in the activation of C−CN bonds of a variety of nitriles.[12,13] We reported the use of Ni(dppf) compounds (dppf = bis-diphenylphosphinoferrocene) in the catalytic isomerization of 2M3BN to 3PN. The catalytic system reached 100% conversion within 2.5 h, to yield 83% 3PN.[14] Recently, we extended such studies to the use of nickel and σ-donor alkyl-diphosphine systems and fully characterized all the intermediates involved in the catalytic cycle.[15] In the current work, we have now expanded the scope of such reactions to the use of closely related bis-diphosphinoferrocene ligands in which the σ-donor/π-acceptor character of the diphosphines has been modified, and their resulting influence in lowering the catalytic activity in order to trap key intermediates has also been studied.

The isomerization of 2M3BN using [Ni(COD)$_2$] as catalytic precursor and bis-diphosphinoferrocene ligands (Figure 1), both in the presence and in the absence of LA, has been explored. Relevant catalytic results are presented in Tables 1 and 2.The catalytic results of the isomerization experiments in the absence of LA are summarized in Table 1. The results showed a decrease in the catalytic activity of the systems when the electronic properties of the phosphorus atom were varied from dppf, a σ-donor/π-acceptor ligand that already displayed a moderate activity (entry 1), to a stronger σ-donor such as tBuppf (entries 2 and 3). The effect was found to be even more dramatic in the case of dipf, in which two alkyl substituents are present on each P-donor atom (entries 4 and 5). In a general way, the selectivities of the systems were also driven to give poor yields of 3PN when a σ-donor substituent on the ligand was present. It is noteworthy,

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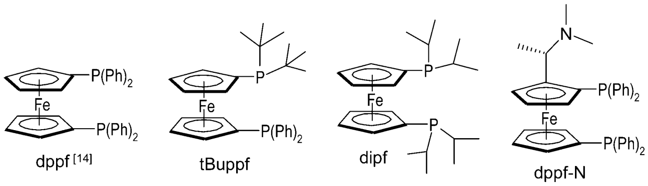
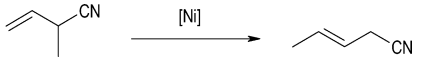


Figure 1. Bis-diphosphinoferrocene ligands used in the catalytic isomerization of 2M3BN.

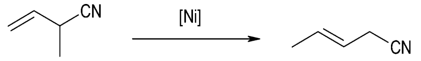
Table 1. Catalytic Isomerization of 2M3BN[a]



entry	system	*t* (h)	conversion (%)	yield of 3-PN (%)	other nitriles (%)[b]
1	$[Ni(COD)_2]$/dppf[14]	2.5	100	83	16
2	$[Ni(COD)_2]$/tBuppf	2.5	7	6	1
3	$[Ni(COD)_2]$/tBuppf	15	98	76	22
4	$[Ni(COD)_2]$/dipf	2.5	0		
5	$[Ni(COD)_2]$/dipf	120	39	8	31
6	$[Ni(COD)_2]$/dppf-N	2.5	0		
7	$[Ni(COD)_2]$/dppf-N	36	95	70	25

[a] Neat substrate:ligand:$[Ni(COD)_2]$ = 110:1:1. T = 100 °C. 2M3BN conversion % and yields were determined by GC-MS and confirmed by ^1H NMR spectroscopy. [b] Mainly *E*-2M2BN and small amounts of *Z*-2M2BN and *cis*-2PN.

Table 2. Catalytic Isomerization of 2M3BN Using $ZnCl_2$ as Cocatalyst[a]



entry	system	*t* (h)	conversion (%)	yield of 3-PN (%)	other nitriles (%)[b]
1	$[Ni(COD)_2]$/dppf[14]	5	100	54	46
2	$[Ni(COD)_2]$/tBuppf	15	8	3	5
3	$[Ni(COD)_2]$/tBuppf	144	100	70	30
4	$[Ni(COD)_2]$/dipf	15	18	0	100
5	$[Ni(COD)_2]$/dipf	144	100	14	86
6	$[Ni(COD)_2]$/dppf-N	15	100	9	91
7	complex **1**	144	100	71	29

[a] Neat substrate:ligand:$[Ni(COD)_2]$: $ZnCl_2$ = 110:1:1:1. T = 100 °C. 2M3BN conversion % and yield were determined by GC-MS and confirmed by ^1H NMR spectroscopy. [b] Mainly *E*-2M2BN and small amounts of *Z*-2M2BN and *cis*-2PN.

however, that in the case of the tBuppf ligand, which contains alkyl and aryl substituents on the phosphorus, the yield and selectivity to the linear product was affected very little compared to dppf.

When $ZnCl_2$ was used as cocatalyst, the activity of these catalytic systems was affected, as indicated in Table 2. Again, as mentioned above, the ligands bearing alkyl substituents on the phosphorus atoms gave low performances (reaching total conversion at 144 h), the dppf-N system being the least affected, yet producing mainly undesirable isomers (100% conv 15 h, entry 6, Table 2). On reaching equilibrium, the selectivity of the Ni-tBuppf/$ZnCl_2$ system for 3PN was superior to that of the Ni-dppf/$ZnCl_2$ system, with 70% 3PN being attained with the use of tBuppf (entry 3, Table 2), while only 54% yield was obtained with dppf (entry 1, Table 2). Similarly, the use of Ni-dipf/$ZnCl_2$ and Ni-dppf-N/$ZnCl_2$ produced mainly the *E*-2M2BN isomer (entries 5 and 6).

In contrast with the Lewis acid $ZnCl_2$, the results using BEt_3 as cocatalyst produced in general slightly more active catalytic systems (see Supporting Information Table S-1). The most active of these series was the Ni-dppf-N system/BEt_3 (entries 7 and 8), which is very similar to the Ni-dppf-N/$ZnCl_2$ system. An interesting feature was the increase in selectivity to 3PN with the tBuppf ligand and BEt_3, which contains both types of electronic properties on the P-donor atoms (σ-donor and σ-donor/π-acceptor ligand) (entry 4), giving an 80% yield of 3PN. Again, when only alkyl substituents on the phosphorus atoms are present, the selectivity favors the formation of *E*-2M2BN and only 5% of the linear product was obtained (entry 6).

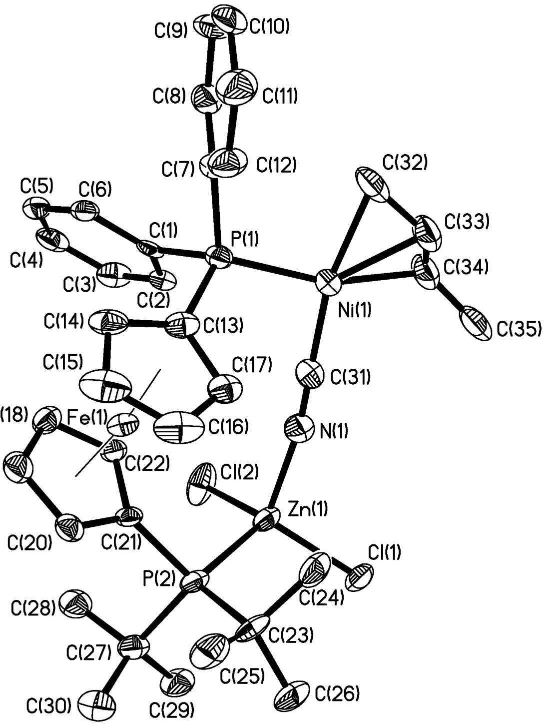


Figure 2. Structure of complex **1** at the 50% probability level. Crystallization solvent and hydrogen atoms are omitted for clarity. Selected bond distances [Å]: Ni−P1 (2.1789(19)), Zn−P2 (2.452(2)), Ni−C32 (2.012(8)), Ni−C33 (2.013(9)), Ni−C34 (2.073(9)), Ni−C31 (1.859(8)), C32−C33 (1.36(2)), C33−C34 (1.418(14)), C34−C35 (1.419(14)), N−C31 (1.157(8)). Selected angles [deg]: P1−Ni−C32 (93.6(3)), P1−Ni−C31 (99.5(2)), C31−Ni−C34 (94.5(4)), P2−Zn−N (105.07(17)), N−Zn−Cl1 (108.24(17)), N−Zn−Cl2 (104.01(18)).

The reaction of [Ni(COD)(P−P)] (P−P = tBuppf) with an equimolar ratio of 2M3BN/$ZnCl_2$ produced an orange solution. After reaction (30 min), the solvent was evaporated and an orange solid was isolated for complex **1**, Ni-tbuppf-$ZnCl_2$, in very high yield (89% isolated) (Scheme 1).

Crystals of complex **1** suitable for single-crystal X-ray diffraction studies[16] were obtained by vapor diffusion of a hexane/toluene system. The molecular structure of complex **1** is depicted in Figure 2. The structure shows that for the tBuppf ligand only the phosphorus bearing the phenyl substituents is coordinated to the nickel center, while the phosphorus bearing the alkyl substituents is coordinated to the zinc atom. The latter is also bonded to the nitrogen of the −CN ligand, bridging

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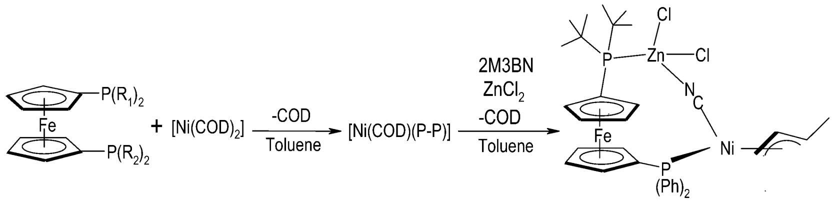
(16) Crystallographic data deposited at the Cambridge Crystallographic Data Center, CCDC 644364. $C_{38.50}H_{47}Cl_2FeNNiP_2Zn$; fw 836.54; 0.21 × 0.17 × 0.13 mm; monoclinic; $P2(1)/c$; a = 19.301(3) Å, b = 9.7826(18) Å, c = 20.697(4) Å, $\alpha = 90°$, $\beta = 103.064(4)°$, $\gamma = 90°$; V = 3806.7(12) Å^3; Z = 4; R_{calcd} = 1.460 Mg m^{-3}; abs coeff 1.743 mm^{-1}; wavelength 0.71073 Å; temp 100(2) K; θ range 1.08 to 25.01°; reflns collected 17 795, independent 6670 [R(int) = 0.0684]; data/restraints/parameters 6670/8/443; final R indices [$I > 2\sigma(I)$] R1 = 0.0740, wR2 = 0.1501; R indices (all data) R1 = 0.1016, wR2 = 0.1627; largest diff peak and hole 1.463 and −0.636 e Å^{-3}; full-matrix least-squares on F^2.

Scheme 1



1, Ni-tBuppf-ZnCl$_2$

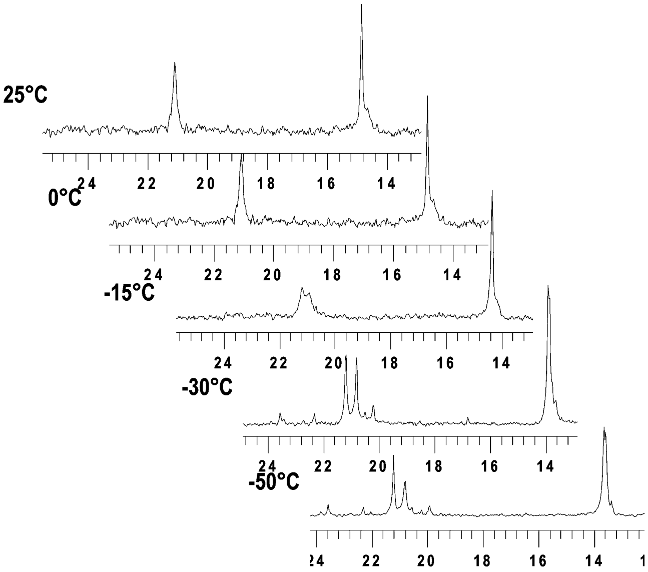


Figure 3. VT ^{31}P{H} NMR for complex **1**.

through the carbon atom to the nickel center, forming a heterotrimetallic macrocycle. To the best of our knowledge, this is the first structure in which a Lewis acid used in the isomerization reaction of 2M3BN appears simultaneously bonded to the −CN moiety and to the P-donor ligand in a bridging fashion, despite the fact that several LA/nickel-cyano X-ray structures have been reported;[4,14,17] particularly in our group we had previously structurally characterized related nickel compounds where both phosphorus atoms of the phosphinoferrocene ligand coordinate to nickel.[14] Consequently, the current structure provides evidence for hemilability at the phosphine ligand, presumably switching from a dicoordinated phosphine at the nickel center to a monocoordinated one during the actual catalytic isomerization process in solution. The geometry around the Ni center in **1** is square-planar, while being tetrahedral around the Zn atom. Full comparisons with other structures cannot be established due to the disorder displayed by the allyl moiety. The bond distances and angles are in general similar to those observed in the closely related square-planar Ni allyl complex [Ni(dippe)(η^3-C_3H_5)],[17] although most of the nickel−carbon distances in the allyl fragment in complex **1** (Ni−C32 (2.012(8)), Ni−C33 (2.013(9)), Ni−C34 (2.073(9) Å) are slightly shorter than those in [Ni(dppb)(η^3-1Me-C_3H_4)(CN)] (2.064(6), 1.970(6), 2.130(6) Å),[2] [Ni(DPEphos)(η^3-1-Me-C_3H_4)(CN-$ZnCl_2$·EtOH)] (2.067(3), 2.000(3), 2.148(3) Å),[4] and [Ni(dppf)(η^3-1Me-C_3H_4)(CN-BEt_3)] (2.075(4), 2.007(5), 2.150(5) Å).[14]

The structure depicted for complex **1** corresponds to the *syn* allyl isomer. This complex showed a high selectivity for formation of 3PN during the isomerization of 2M3BN in solution, and consequently, the hemilability of the coordinated ligand may play an important role around the Ni coordination sphere during the catalytic isomerization reaction. The role of the hemilabile ligand might be to allow substrates, products, and solvents to go in and out of the coordination sphere of the nickel center.

The ^{31}P{^{1}H} NMR spectrum for complex **1** in CD_2Cl_2 at room temperature showed two broad singlets at 21.1 and 14.8 ppm, assigned to two different phosphine groups present. VT-NMR experiments showed that at −30 °C the downfield singlet decoalesed, producing two sharp singlets at δ 21.2 and 20.8 and four small singlets nearby, at δ 23.6, 22.3, 20.5, and 20.2. The activation energy for this process was determined to be 14.3 kcal mol^{-1}, which is 1.6 kcal mol^{-1} smaller than those found in other closely related square-planar allyl complexes.[17] At −50 °C, the upfield resonance displayed two major resonances at δ 13.7 and 13.6. No further changes in the multiplicity for this signal were observed at −80 °C (Figure 3).

According to this evidence, the resonance at 21.1 ppm (at room temperature) was assigned to the aromatic phosphine moiety coordinated to the nickel center in **1**, the signals at 21.2 and 20.8 ppm (at −30 °C) being associated with the *syn* and *anti* allyl isomers and the small additional signals attributed to other species involved in the isomerization process. The signal at 14.8 ppm (also at room temperature) was assigned to the dialkyl phosphine moiety bonded to the zinc center; that at low temperature hardly provided a distinctive difference between the *syn* and *anti* allyl isomers. The ^{1}H NMR spectrum for **1** at room temperature displayed one broad signal for each proton in the allyl moiety: δ 5.38 (CH central), 3.19 (CHMe), 2.0 (CH_2), and 1.22 (CH_3). The ^{13}C{^{1}H} NMR spectrum in CD_2Cl_2 confirmed the identity of the allyl ligand in **1**; NMR signals were found at δ 116.7 (CH central), 91.1 (CHMe), 61.6 (CH_2), and 18.8 (CH_3) and the CN ligand at δ 151, all of them broad.

The catalytic isomerization of 2M3BN in the presence of [Ni(COD)$_2$] and bis-phosphinoferrocene ligands containing aromatic substituents on the phosphorus donor atom (σ-donor/π-acceptor substituents) was found to yield linear 3PN as the major product of the reaction. The use of alkyl substituents on the phosphorus atom (σ-donor substituents) was found to dramatically decrease the selectivity to this product.

The use of Lewis acids such as $ZnCl_2$ as cocatalyst, combined with the presence of phenyl-phosphine donor atoms, highly decreases the activity and causes a significant drop in the selectivity to 3PN. The same decrease in selectivity was observed on having only σ-donor substituents on the phosphine. The use of phosphines combining both types of substituents (i.e., σ-donor and σ-donor/π-acceptor) increases the selectivity to 3PN with only slight variations in the overall activity of the catalytic system. Allyl species were found to be

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involved as active intermediates in the C−CN bond cleavage and formation and have thereby demonstrated their participation in the isomerization process. The ferrocenyl phosphines have been shown to exhibit hemilabile behavior. The presence of these intermediates potentially plays a key role in the final outcome of catalysis and has a crucial effect on the overall yield and selectivity that may be achieved in the production of linear 3PN.

Acknowledgment. We thank CONACyT (42467-Q) and DGAPA-UNAM (IN202907-3) for the financial support to this work. We also thank Dr. A. Arévalo, R. I. del Villar, and Dr. W. W. Brennessel for technical assistance. A.A.-R. also thanks CONACyT for a Ph.D. grant. W.D.J. thanks the NSF (INT-0102217) for travel support.

Supporting Information Available: Includes detailed experimental procedures, preparation of **1**, GC-MS determinations, NMR spectra, and a CIF file for complex **1**. This material is available free of charge via Internet at http://pubs.acs.org.

OM700928Y