

The catalytic isomerization reactions of 2-methyl-3-butenitrile into 3-pentenitrile in ionic liquids

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Abstract

The catalytic isomerization reaction of 2-methyl-3-butenitrile (2M3BN) into 3-pentenitrile (3PN) has been performed in the presence of Ni(0) and phosphine complexes and in biphasic ionic liquid/organic solvent. Several neutral and ionic phosphines and ionic liquids have been tested, the best results for the reaction of isomerization in conversion, selectivity, and immobilization of the catalyst in the ionic liquid phase have been obtained with the (*m*-sulfophenyl)-diphenylphosphine sodium salt, [TPPMSNa] as ligand and 1-butyl-2,3-dimethylimidazolium-bis(trifluoromethylsulfonyl)imide [BMMI][TFSI], as the ionic liquid.

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1. Introduction

Adiponitrile [AdN], a nylon 6,6 and nylon 6 intermediate is industrially prepared by the hydrocyanation of butadiene [1]. The reaction is catalyzed by homogeneous nickel(0)-phosphite complexes and it can be described in three steps [2]. A first hydrogen cyanide molecule is added to butadiene to yield a mixture of branched and linear pentenenitriles. The branched isomer is then isomerized into the linear one: this is the second step. Then the addition of a second hydrogen cyanide molecule leads to AdN (Scheme 1). The current industrial research objectives are the enhancement of the selectivity in AdN with the development of new ligand structures [3] or the recycling of the catalyst, by using heterogeneous catalysts [4] or biphasic catalysis such as water/organic solvent system [5].

Application of ionic liquids in biphasic catalysis has blossomed within the last decade and has been driven by the need for environmental-friendly solvents. Comprehensive information about later developments may be found in re-

cent reviews [6,7]. A wide range of organic, inorganic, and organometallic compounds can be dissolved in ionic liquids, while some organic solvents (especially alkanes) remain immiscible at moderate to high temperatures. Most importantly, it is possible to tune their physical and chemical properties by varying the nature of the cations and the anions [6a,8a]. However, ionic liquids are very complex media and may interact with some products [8b]. So, in the preparation of AdN we chose the isomerization of 2-methyl-3-butenitrile (2M3BN) into 3-pentenitrile (3PN) as a model reaction in order to determine the stability of major reactants (2M3BN, 3PN) and if this catalytic reaction could be performed in ionic liquids.

Herein, we report the first example of the catalytic isomerization of 2M3BN into 3PN under biphasic conditions in ionic liquids/organic solvent system, in the presence of bis(1,5-cyclooctadiene)nickel(0), [Ni(cod)₂] and neutral or ionic phosphine as ligand [9].

2. Experimental

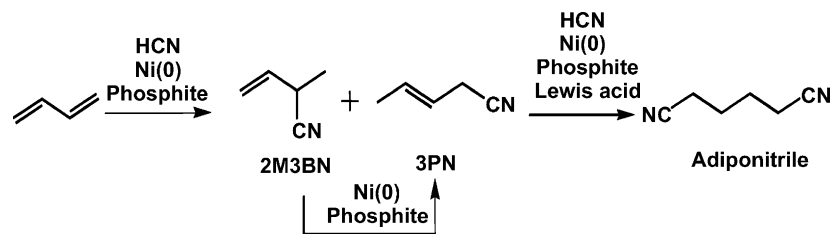
All of the syntheses were carried out under dry argon using standard Schlenk techniques. Solvents were distilled before use. [Ni(cod)₂] was obtained from Strem Chemicals.

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Scheme 1. Industrial preparation of AdN by hydrocyanation of butadiene catalyzed by homogeneous nickel(0)-phosphite complexes.

[TPPMSNa] was obtained from Fluka or prepared along published procedures [10] in both cases it was dried several hours at 60 °C under vacuum before use. The triphenylphosphine [TPP], which was obtained from Aldrich, and all other phosphorus ligands, which were provided by Rhodia, were stored under argon and used without further purification. Tetrabutylammonium salts were obtained from Aldrich and were used as-received. 2M3BN was obtained from Fluka, and was dried over 3 Å molecular sieves and distilled and stored under argon prior to use. The molecular sieves used in these procedures were pre-treated by washing continuously with distilled water for 12 h, and then activating them at 250 °C for 12 h under vacuum, a treatment found to be necessary to prevent the isomerization of the 2M3BN to 2-methyl-2-butenitrile (2M2BN).

^1H , ^{13}C , and ^{31}P NMR were recorded on a BRUKER AC 300 MHz spectrometer. Chemical shifts were measured relative to SiMe_4 as internal standard for ^1H and ^{13}C . Positive ^{31}P chemical shifts are downfield from external 85% H_3PO_4 . The solvents used (CD_2Cl_2 , D_2O , CDCl_3) were purchased from SDS and used as-received.

Elemental analyses for carbon, hydrogen, and nitrogen were performed by the ‘Laboratoire de Synthèse et Electrochimie Organométallique’ at Dijon. All other elemental analyses were performed by the ‘Service Central d’Analyse’ of the CNRS at Solaize.

The melting points of solid salts were measured on a digital Electrothermal melting point apparatus.

2.1. Ionic liquids

Cations were tetrabutylammonium [NBu_4], 1-butyl-3-methylimidazolium [BMI] or 1-butyl-2,3-dimethylimidazolium [BMMI], and the anions, halide [Cl, Br, I], tetrafluoroborate (BF_4^-), hexafluorophosphate (PF_6^-), bis(trifluoromethylsulfonyl)imide [TFSI], or trifluoromethane-sulfonate [CF_3SO_3] and have been prepared as described in the literature [6a], purified by chromatography on classical neutral alumina (Fluka) and characterized by elemental analysis and NMR spectroscopy.

2.2. Compatibility runs

Reactions were performed either in a closed Schlenk tube or in a Carousel tube (‘Radleys’ parallel reactor equipped

with an external cooler). In a typical reaction, 0.50 g of ionic liquids and 0.50 mg of 2M3BN were weighed in a Schlenk under argon. It was then heated for 3 h at 100 or 150 °C, and then cooled in liquid nitrogen.

2.3. Catalysis runs for isomerization reaction

Reactions were performed in a Schlenk or in a Carousel tube (‘Radleys’ parallel reactor). In a typical reaction, 0.030 g of $\text{Ni}(\text{cod})_2$ (1 equivalent), 0.286 g of triphenylphosphine (10 equivalents), 0.972 g of 2M3BN (110 equivalents), and 0.320 g of ionic liquid are weighed in a Schlenk under argon. The reaction medium is then heated for 3 h at 100 °C, and then cooled in liquid nitrogen.

2.3.1. Work-up

Three different work-ups were performed according to the experiment.

- Work-up A = Butylbenzene (0.100 g) was added to the reaction mixture as an internal standard and the organic products were extracted with 5 ml of pentane and 5 ml of THF, or (work-up A’) with 5 ml of pentane and 10 ml of THF. The ionic liquid remained in the lower phase, and the upper phase was separated and analyzed by gas chromatography.
- Work-up B = Butylbenzene (0.1 g) was added to the reaction mixture as an internal standard, the reaction medium was then diluted with 10 ml of THF and a portion was directly injected into a gas chromatograph.
- Work-up C = The volatile products were distilled between 60 and 100 °C under dynamic vacuum. Butylbenzene (0.1 g) was then added to the volatile products as an internal standard, and the solution was analyzed by gas chromatography.

2.3.2. Analyses

The products were quantitatively analyzed by gas chromatography on a HP 6890 chromatograph equipped with TCD detector and a Stabilwax[®]-DA (polyethyleneglycol) column (length = 30 m, ϕ_{int} = 0.53 mm, film thickness = 1 μm). Injector and detector temperature was 250 °C. The temperature program was from 50 (3 min) to 200 °C at a heating rate of 4 °C/min and then to 220 °C (25 min) at a heating rate of 2 °C/min. The relative response factors of the reaction products were determined from pure samples.

ICP analyses were performed at Rhodia Research Center, Lyon.

2.4. Partition of the catalyst

Ligand = TPP: (A) Ni(cod)₂ (0.010 g), TPP (0.046 g), [BMMI][TFSI] (1.928 g), 2M3BN (0.436 g), and heptane (0.801 g) were stirred for 2 h at room temperature. Ionic phase (2.433 g) and organic phase (0.730 g) were allowed to separate and the upper organic layer was syringed-off.

(B) Ni(cod)₂ (0.010 g), TPP (0.052 g), [BMMI][TFSI] (1.924 g), 2M3BN (0.437 g), and heptane (0.81 g) were stirred for 2 h at room temperature and 3 h at 100 °C. Ionic phase (2.454 g) and organic phase (0.605 g) were allowed to separate at 100 °C and the upper organic layer was syringed-off. Then the samples were treated with sulfonitric mixture and analyzed by ICP.

	Conditions			
	Room temperature		100 °C	
	Ionic	Organic	Ionic	Organic
Nickel content (ppm)	750	665	800	3110
Phosphorus content (ppm)	1590	21500	1825	34400

Ionic and organic are the various phases.

L = [TPPMSNa]: (1) In[BMMI][TFSI]: (A) Ni(cod)₂ (0.010 g), [TPPMSNa] (0.064 g), [BMMI][TFSI] (1.925 g), 2M3BN (0.422 g), and heptane (0.826 g) were stirred for 1 h at room temperature. Ionic phase (2.425 g) and organic phase (0.722 g) were allowed to separate and the upper organic layer was syringed-off.

(B) Ni(cod)₂ (0.010 g), [TPPMSNa] (0.063 g), [BMMI][TFSI] (1.945 g), 2M3BN (0.415 g), and heptane (0.836 g) were stirred for 1.5 h at 100 °C. Ionic phase (2.395 g) and organic phase (0.850 g) were allowed to separate at 100 °C and the upper organic layer was syringed-off.

(C) Ni(cod)₂ (0.010 g), [TPPMSNa] (0.063 g), [BMMI][TFSI] (1.952 g), 2M3BN (0.419 g), and heptane (0.836 g) were stirred for 4 h at 100 °C. Ionic phase (2.387 g) and organic phase (0.782 g) were allowed to separate at 100 °C and the upper organic layer was syringed-off. Then the samples were treated with sulfonitric mixture and analyzed by ICP.

	Conditions					
	Room temperature		100 °C, 1.5 h		100 °C, 4 h	
	Ionic	Organic	Ionic	Organic	Ionic	Organic
Nickel content (ppm)	870	<5	760	<5	690	<5
Mass balance: nickel		98		85		77
Phosphorus content (ppm)	2000	<5	2040	<5	1980	10
Mass balance: phosphorus		89		96		87

Ionic and organic are the various phases.

3. Results and discussion

The Ni(0)-phosphine catalyzed isomerization of 2M3BN into 3PN was chosen as a model reaction in order to determine in the first instance, if this catalytic reaction can be performed in ionic liquids. Secondly, to improve the catalytic performance of the Ni(0)-phosphine system, different ionic liquids and phosphines have been tested (Scheme 2).

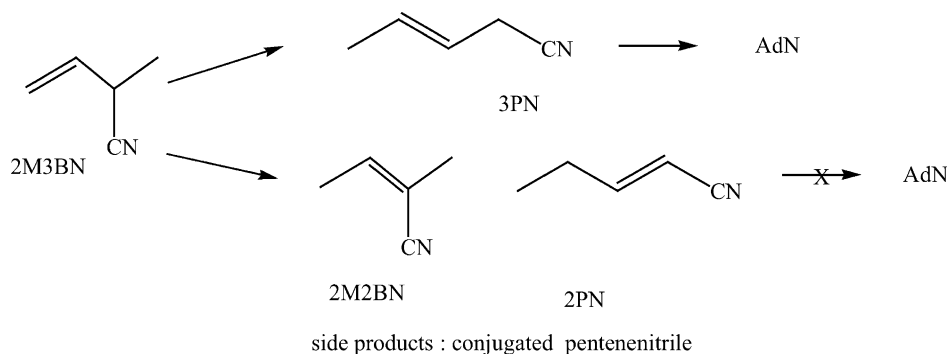
3.1. Isomerization of 2-methyl-3-butenitrile (2M3BN) into 3-pentenitrile (3PN)

3.1.1. Stability of 2-methyl-3-butenitrile in ionic liquids

During this reaction, besides 3PN, the formation of thermodynamically-favored conjugated pentenenitriles, 2M2BN and 2PN can be observed. These conjugated pentenenitriles cannot be converted to AdN. As pentenenitrile can be transformed into these undesired products by thermal treatment [12], as well as by basic [13] or acidic catalytic routes [14], it was necessary to investigate the compatibility of ionic liquids with the substrate (2M3BN) of the reaction at 100 and 150 °C. This study was performed in several ionic liquids in which the cation was [NBu₄], [BMI] or [BMMI] and the anion, (Cl⁻, Br⁻, I⁻), (BF₄⁻), (PF₆⁻), (TFSI⁻) or (CF₃SO₃⁻).

A mixture of 50 wt.% of substrate and 50 wt.% of an ionic liquid was introduced into a stirred reaction vessel or in Carousel tubes (equipped with an external cooler to avoid incorrect mass balance) for 3 h at 100 or 150 °C. The reactor was cooled down to room temperature and the products analyzed by gas chromatography. To avoid the presence of water, 2M3BN was distilled over activated molecular sieves (3 Å) before use. Different protocols for work-up analysis were tested (extraction of the molecular organic compounds from the ionic liquid phase with a mixture of pentane and tetrahydrofuran, distillation of volatile organic products under dynamic vacuum and dilution of reaction medium with tetrahydrofuran and direct injection into a gas chromatograph. This last procedure was therefore adopted and afforded good results in terms of analysis.

In all cases, at 100 °C as well as at 150 °C, no other organic compounds were detected in the gas chromatogram. However the value for the conversion of 2M3BN was often above 10%, probably because of the work-up and due to a chemical reaction (Table 1). Note that with [NBu₄][Cl] as



Scheme 2. Products which can be formed during the isomerization reaction of 2M3BN in the presence of Ni(0)-phosphane catalysts [11].

with $[\text{NBu}_4][\text{CN}]$ [2], a significant amount of conjugated isomer 2M2BN was formed. In consequence, ionic liquids with [BMI] or [BMMI] as cation were inert towards the substrate even at high temperature.

3.1.2. Effect of the nature of ionic liquids on the isomerization reaction of 2M3BN to 3PN in the presence of $\text{Ni}(\text{cod})_2$ and triphenylphosphine as a catalyst

Zero-valent nickel stabilized by triphenylphosphine has been used to catalyse 2M3BN isomerization into 3PN. The effect of ionic liquids on the reaction with such a catalyst was thus investigated.

A protocol was developed wherein a mixture of $\text{Ni}(\text{cod})_2$, TPP, 2M3BN and a mass of ionic liquid amounting to 25% of total weight were introduced into a stirred reaction vessel for 3 h at 100 °C. A homogeneous solution was obtained and the products of the reaction were analyzed by gas chromatography with internal standard (butylbenzene) without any other characterization of the reaction media. The color of the final solution, which could reflect a possible nickel oxidation, was nevertheless noted.

A test without ionic liquids was first performed as a reference trial, Table 2. Note that, when the reaction was run without phosphine, $\text{Ni}(\text{cod})_2$ was degraded to nickel metal

Table 1
Compatibility of ionic liquids with 2M3BN

Ionic liquids	Conversion 2M3BN	Yield 3PN + 4PN	Yield 2M2BN	Yield 2PN	Mass balance
Study at 100 °C					
None	4	0	-1	0	95
$[\text{Bu}_4\text{N}][\text{Cl}]$	52	-1	17	-3	70
$[\text{BMI}][\text{Cl}]$	10	0	-1	0	90
$[\text{BMMI}][\text{Cl}]$	7	0	-1	0	93
$[\text{BMI}][\text{Br}]$	18	0	-2	0	82
$[\text{Bu}_4\text{N}][\text{I}]$	6	0	-1	0	94
$[\text{BMI}][\text{I}]$	22	0	-3	-1	77
$[\text{MMI}][\text{I}]$	7	0	-2	0	93
$[\text{MMMI}][\text{I}]$	6	0	-2	0	93
$[\text{BMI}][\text{BF}_4]$	21	0	-3	-1	80
$[\text{BMMI}][\text{BF}_4]$	4	0	-1	0	95
$[\text{BMI}][\text{CF}_3\text{SO}_3]$	21	0	-3	-1	79
$[\text{BMMI}][\text{CF}_3\text{SO}_3]$	18	0	-3	-1	82
$[\text{Bu}_4\text{N}][\text{PF}_6]$	7	0	0	1	93
$[\text{BMI}][\text{PF}_6]$	1	0	0	0	99
$[\text{BMMI}][\text{PF}_6]$	-1	0	0	0	101
$[\text{MMI}][\text{PF}_6]$	0	0	-1	0	99
$[\text{MMMI}][\text{PF}_6]$	7	0	-2	-1	92
$[\text{BMI}][\text{TFSI}]$	1	0	0	0	99
$[\text{BMMI}][\text{TFSI}]$	0	0	0	0	101
Study at 150 °C					
None	11	0	-2	-1	88
$[\text{BMI}][\text{PF}_6]$	2	0	0	0	98
$[\text{BMMI}][\text{PF}_6]$	-2	0	0	0	102
$[\text{BMI}][\text{TFSI}]$	-1	0	0	0	101
$[\text{BMMI}][\text{TFSI}]$	1	0	0	0	99

A mixture of 50 wt.% of substrate and 50 wt.% of an ionic liquid were introduced into a stirred reaction vessel or in Carousel tubes for 3 h at 100 or 150 °C.

Table 2
Isomerization of 2M3BN into 3PN in the presence of TPP and halide ionic liquids

Ionic liquids	Conversion 2M3Bn ^a	Selectivity ^c 3PN + 4PN	Selectivity ^c 2M2BN	Selectivity ^c 2PN ^b	Mass balance	Aspect
No	98	80	5	0	88	Red
No and no ligand	23	−1	79	−2	96	Black
[Bu ₄ N][Cl]	98	23	39	−1	71	Green
[BMI][Cl]	50	44	14	5	85	Green
[BMMI][Cl]	96	37	49	2	92	Green
[BMI][Br]	63	65	8	4	89	Brown
[Bu ₄ N][I]	96	74	11	2	94	Red
[BMI][I]	60	51	15	2	85	Red
[MMI][I]	58	67	17	4	96	Orange
[MMMI][I]	96	79	6	1	90	Red

Conditions: Ni(cod)₂ (0.072 mmol) + TPP (0.72 mmol) + 2M3BN (8.64 mmol) + ionic liquids (320 mg) were stirred for 3 h at 100 °C. After work-up the products of the reaction were analyzed by gas chromatography.

^a Commercial 2M3BN contains (79% 2M3BN, 12% *trans*-2M2BN, 6% *cis*-2PN, and 2% *trans*-3PN).

^b Note that the presence of both the desired and undesired products in the commercially available substrate can produce negative yields for conjugated nitriles (for example, if no reaction other than the degradation of *cis*-2PN were observed, a 0% conversion and a negative yield of *cis*-2PN would be observed.)

^c Selectivity in product A: Select A = Yield A/Conversion 2M3BN mass balance ≠ 100% due to the effect of the work-up, no others organic compounds have been detected.

and black precipitates appeared. The metal was able to promote the isomerization of 2M3BN into 2M2BN.

For all ionic liquids with halide anion the conversions were high and a significant part of the 2M3BN was transformed into the conjugated isomer 2M2BN. With chloride ion the media turned green indicating that in the presence of chloride ionic liquids a part of the nickel was oxidized to Ni(II).

With all the ionic liquids containing neutral weakly coordinating anions, reaction media were orange or red solutions. Conversions obtained in the different ionic liquids are represented in Fig. 1. A clear correlation between the nature of the cation of the ionic liquids and the conversion can be seen. Indeed a complete transformation was attained with [BMMI] while the conversion was limited to 60–70% with [BMI]. A possible explanation is the formation of metal–carbene complex by deprotonation of the imidazolium cation or by oxidative addition of the imidazolium cation to the metal center [15]. However, when the reaction mixture in the ionic liquid [BMI][TFSI] was monitored by ¹³C NMR spectroscopy (small amount of CD₃CN as internal references), no peaks corresponding to a carbene could be detected at room temperature or after heating 5 h at 85 °C. In addition, the conversion reached 83% in [BMI][TFSI] when the isomerization of 2M3BN was run for 8 h.

While the rate of reaction seems to be governed by the nature of the cations, the relation between the nature of the anions and the selectivity is less straightforward, Fig. 2. However the selectivity in 3PN was slightly inferior with the anions BF₄[−] and CF₃SO₃[−] than with the anions PF₆[−] and TFSI[−].

To conclude, the ionic liquids [BMMI][PF₆] and [BMMI][TFSI] yielded activities and selectivities identical to reference experiments without ionic liquids. The possibility per-

forming the isomerization of 2M3BN to 3PN in ionic liquids was thus demonstrated.

However, the study of the partition of the complexes prepared from Ni(cod)₂ and triphenylphosphine between an ionic liquid phase (containing [BMMI][TFSI]) and a part of the 2M3BN and an organic phase (containing heptane and the rest of the 2M3BN) showed that only 55–57% of phosphorous and 62–71% of nickel were recovered in the ionic phase. The nickel complexes were not efficiently

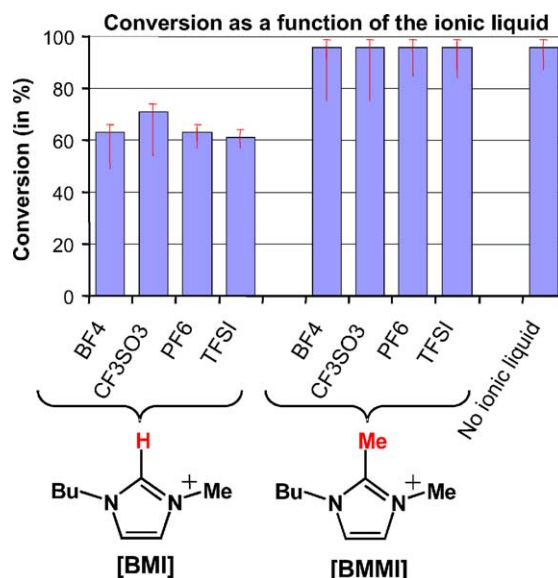


Fig. 1. Conversion of 2M3BN into 3PN in different ionic liquids containing neutral, weakly coordinating anions. Conditions: Ni(cod)₂ (0.072 mmol) + TPP (0.72 mmol) + 2M3BN (8.64 mmol) + ionic liquids (320 mg) were stirred for 3 h at 100 °C. After work-up the products of the reaction were analyzed by gas chromatography.

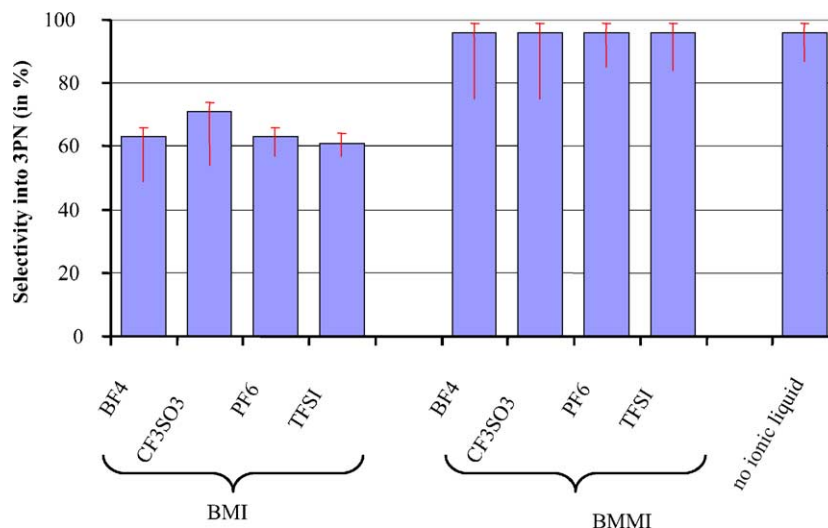


Fig. 2. Selectivity to 3PN in different ionic liquids containing neutral, weakly coordinating anions. Conditions: Ni(cod)₂ (0.072 mmol) + TPP (0.72 mmol) + 2M3BN (8.64 mmol) + ionic liquids (320 mg) were stirred for 3 h at 100 °C. After work-up the products of the reaction were analyzed by gas chromatography.

immobilized in the ionic liquid phase. During the development of biphasic Rh-catalyzed hydroformylation in ionic liquid, several research groups have clearly demonstrated that ionic ligands were especially suitable to avoid catalyst leaching from the ionic liquid phase [8,16]. A variety of ionic phosphines have thus been tested.

3.1.3. Effect of the ionic phosphine structure on the isomerization of 2M3BN into 3PN in the presence of the catalyst Ni(cod)₂ and [BMMI][TFSI]/heptane system

3.1.3.1. Cationic phosphines. The use of cationic phosphines as ligands in ionic liquids has been reported [8,16] as well as the solubilities of some of them in [BMI][PF₆] [17]. Six cationic phosphines were tested for the isomerization

of 2M3BN into 3PN under two-phase conditions, with the ionic phase being [BMMI][TFSI]. Biphasic conditions with heptane as the organic phase were used in order to model an extraction (heptane also had a beneficial effect on the mass balance).

Under the reaction conditions, the concentration of the ligand in the ionic liquid was 0.12 mol l⁻¹ and complete dissolution was observed at room temperature. For all ligands an orange solution was obtained at 100 °C, with little or no visual evidence for the deposition of metallic nickel.

With most cationic phosphines no isomerization of 2M3BN was observed. With the guanidinium phosphine, the 2M3BN conversion was high (57%) with a poor selectivity into 3PN, (Fig. 3).

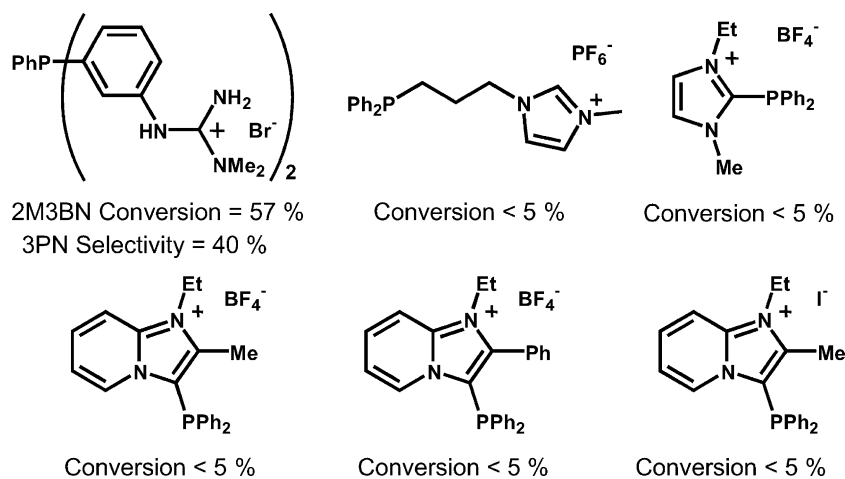


Fig. 3. Results of the reaction of isomerization of 2M3BN in the presence of cationic phosphines in [BMMI][TFSI]. Conditions: Ni(cod)₂ (0.036 mmol) + cationic phosphines (0.18 mmol) + 2M3BN (4.94 mmol) + [BMMI][TFSI] (2.0 g) were stirred for 3 h at 100 °C. The products of the reaction were analyzed by gas chromatography.

3.1.3.2. Anionic phosphines. In 1976, a biphasic aqueous/organic system for AdN synthesis was proposed and enabled the easy recovery of the catalytic solution by decantation [18]. The best ligand was tris(*m*-sulfophenyl)phosphine trisodium salt (TPPTS, Na₃). Important efforts were devoted to the improvement of the selectivity of the reaction for linear products and the preparation, the lifetime and the regeneration of the catalyst. Despite these efforts, no industrial application of the aqueous/organic biphasic system was achieved but research are still in progress [3c].

We first considered sulfonated phosphines derived from triphenylphosphine. However, several anionic phosphines in which the phosphorus atom is linked to phenyl or furyl moieties substituted by one, two or three ionic groups (phosphonates, sulfonates, sulfates or carboxylates...) per phosphorus atom were also used (Fig. 4).

With this range of ligands, it was first possible to investigate the effect of the number of ionic groups per phosphorus atom on the isomerization of 2M3BN, (Fig. 5, M = Na, Li).

With all phosphines bearing two or three anionic groups per phosphorus atom, conversions were low (<40%), yields into 3PN never exceeded 5%, and the reaction medium

turned rapidly black (at room temperature or after heating at 100 °C). This color indicates the formation of metallic nickel. A plausible explanation was the low solubility of these phosphines in ionic liquids, inducing a low concentration of phosphine in the media to maintain the nickel(0) as a ligated monometallic complex, leading to formation of metallic nickel. The steric or electronic properties of the phosphines cannot be held responsible for the low stability of the nickel-complex. Indeed an aqueous solution of 2,2'-phenylphosphino-bis(furyl-5-phosphate disodium salt) with Ni(cod)₂ (with a ratio ligand/metal equal to 4.5) yielded high conversions and selectivities for the isomerization of 2M3BN at 90 °C [19]. However, with the phosphines with a single anionic group per phosphorus atom, high conversions were systematically obtained. As a consequence, further studies were limited to this class of ligands. The detailed catalytic results for these phosphines and TPP are summarized in Table 3. Both [TPPMSNa] and (*m*-sulfino phenyl)-diphenyl phosphine sodium salt which have similar steric and electronically properties gave similar results for conversion and selectivity. The discrepancy in the results and the contrasting aspects of the reaction mixtures

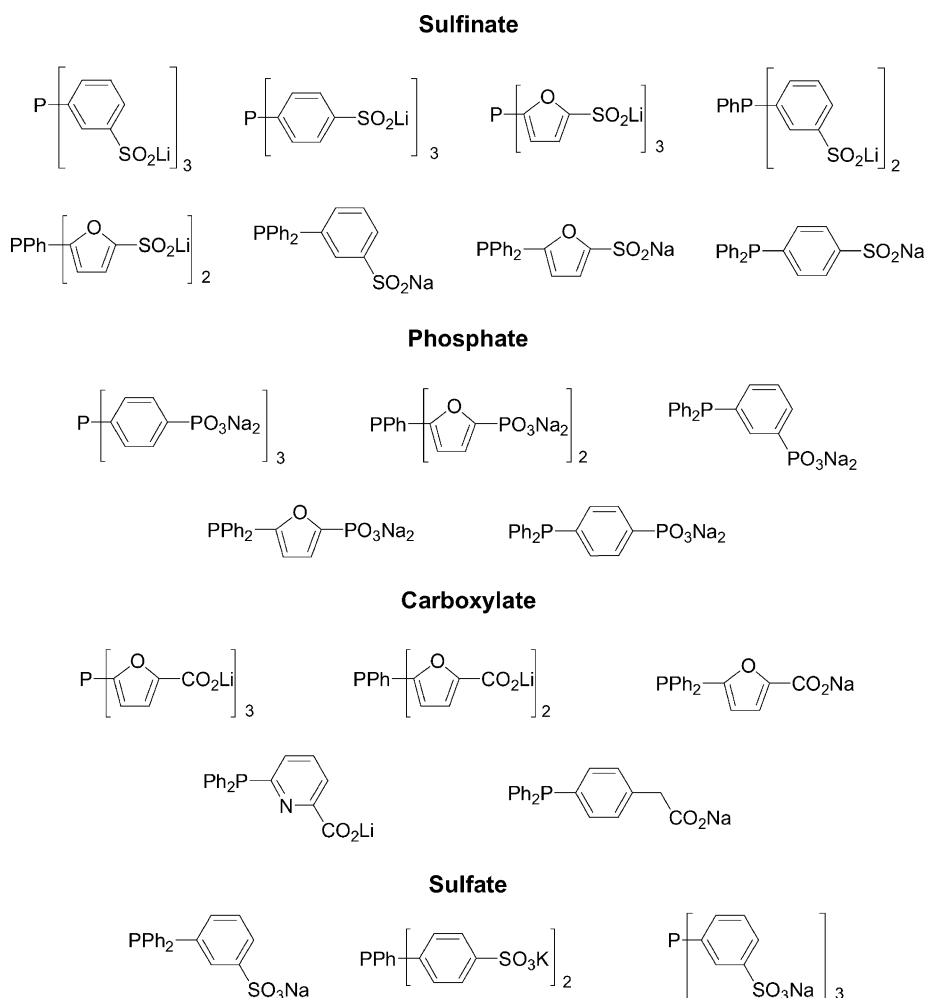


Fig. 4. List of ionic phosphines tested in the isomerization reaction of 2M3BN in the presence of cationic phosphines in [BMMI][TFSI].

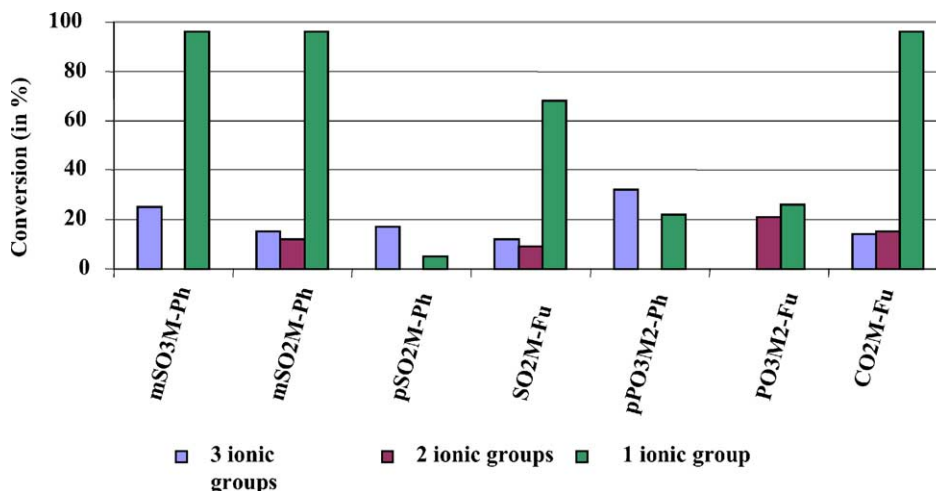


Fig. 5. Isomerization of 2M3BN in the presence of ionic phosphines in [BMMI][TFSI]. Conditions: Ni(cod)₂ (0.036 mmol) + ionic phosphines (0.18 mmol) + 2M3BN (4.94 mmol) + [BMMI][TFSI] (2.0 g) + heptane (1.2 ml) were stirred for 3 h at 100 °C. The products of the reaction were analyzed by gas chromatography.

observed when the catalytic reaction was performed with the sodium (5-sulfinofuryl)diphenyl phosphine or with the sodium (5-carboxylatefuryl)diphenyl phosphine indicate that the electronic properties of the ligand are crucial in this reaction (Table 3).

3.1.4. Effect of the nature of the ionic liquid in the isomerization reaction of 2M3BN into 3PN in the presence of the catalyst precursor Ni(cod)₂ [TPPMSNa]

From the above results, the ligand [TPPMSNa] was selected for further studies due to the fact that the catalytic results are among the best and also that it is readily available. With catalyst precursor Ni(cod)₂, [TPPMSNa], nine ionic liquids were tested under biphasic conditions. Generally, at room temperature the upper phase was colorless while the

lower phase was an orange suspension. When tubes were heated to 100 °C there were still two phases: the upper one was colorless while the lower one was an orange or red solution. The results (Table 4), indicated that both conversion and selectivity were highly sensitive to the nature of the anions. [BF₄] or [CF₃SO₃] gave low conversions and selectivities into 3PN while ionic liquids with [PF₆] and [TFSI] anions yielded high conversions and selectivities into 3PN. [BMI][PF₆] was an exception, with only a 42% conversion and 57% selectivity after 3 h. However high conversions and selectivities were reached when the reaction time was extended. Contrary to TPP, with [TPPMSNa] there was an effect of the ionic liquids anions on the catalyst activity which could be due to a modification of the anions of the ligand.

Table 3
Isomerization of 2M3BN in the presence anionic phosphines with a single anionic group per phosphorus atom in [BMMI][TFSI]

Ligand	Conversion 2M3BN	Selectivity 3 + 4PN	Selectivity 2M2BN + 2PN	Mass balance	Aspect
	68	2	95	98	Black
	96	91	3	94	Red solution
	96	89	3	93	Red solution
 [TPPMSNa]	96	93	2	97	Red solution
Ph ₃ P	96	82	5	93	Red

Conditions: Ni(cod)₂ (0.036 mmol) + ionic phosphines (0.18 mmol) + 2M3BN (4.94 mmol) + [BMMI][TFSI] (2.0 g) + heptane (1.2 ml) were stirred for 3 h at 100 °C and analyzed by gas chromatography.

Table 4

Isomerization of 2M3BN in the presence of [TPPMSNa] in neutral, weakly coordinating ionic liquids

Ionic liquids	Conversion 2M3BN	Selectivity 3PN + 4PN	Selectivity 2M2BN	Selectivity 2PN	Mass balance
None	96	86	2	-1	92
[BMMI][BF ₄]	27	25	-4	8	84
[BMI][BF ₄]	22	39	-1	10	91
[BMMI][CF ₃ SO ₃]	25	36	-3	11	88
[BMI][CF ₃ SO ₃]	27	35	-3	8	86
[BMMI][TFSI]	96	93	1	1	97
[BMI][TFSI]	88	92	2	1	98
[BMMI][PF ₆]	93	90	0	2	94
[BMI][PF ₆]	42	57	-3	6	86
[BMMI][PF ₆]	78 ^a	86	3	2	96
[BMMI][PF ₆]	96 ^b	86	2	-1	93

Conditions: Ni(cod)₂ (0.036 mmol) + [TPPMSNa] (0.18 mmol) + 2M3BN (4.94 mmol) + ionic liquids (2.0 g) + heptane (1.2 ml) were stirred for 3 h at 100 °C. The products of the reaction were analyzed by gas chromatography.

^a Reaction time 19 h.

^b Reaction time 42 h.

The best results were obtained with three ionic liquids: [BMMI][PF₆], [BMI][TFSI], and [BMMI][TFSI]. However, the ionic liquid [BMMI][PF₆] was solid at room temperature (m.p. = 35 °C) and the anion is sensitive to hydrolysis [6] and [BMI][TFSI] was rejected because the formation of a carbene could not be excluded. All subsequent studies were therefore pursued with [BMMI][TFSI].

3.1.5. Partition of the catalyst Ni(cod)₂ [TPPMSNa] in the ionic liquid

The partitioning of the catalyst between an ionic lower phase (composed of [BMMI][TFSI] and a fraction of the pentenenitriles) and an organic upper phase (heptane and the remainder of the pentenenitriles) was studied at room temperature and 100 °C (details are given in the experimental section). The organic phase was colorless while the ionic phase was red. The level of nickel in the organic phase was systematically below the detection level (5 ppm), while a very small quantity of phosphorus (10 ppm) was only detected after 4 h at 100 °C. In conclusion, the ligand [TPPMSNa] generates with Ni(cod)₂ an active and selective catalyst, which is totally immobilized in the ionic phase.

3.1.6. Kinetics of the isomerization reaction of 2M3BN into 3PN in the presence of the catalyst Ni(cod)₂ [TPPMSNa] in biphasic [BMMI][TFSI]/heptane system

All catalytic tests had been previously performed for 3 h at 100 °C. With [TPPMSNa] in [BMMI][TFSI] complete conversion was obtained under these conditions. In order to determine how fast the equilibrium was reached, the reactions were performed from 10 to 180 min. Conversions were plotted as a function of reaction time (Fig. 6).

The shape of the curve was modeled by considering a kinetic law with a first order in 2M3BN: $d[2M3BN]/dt = -k[2M3BN]$ ($k = 0.015 \text{ s}^{-1}$). The consistency between the model and the experimental data was satisfactory (Fig. 6) which indicates that the reaction rate was not under diffu-

sion control. It also means that the concentration of the active species was roughly constant over the time period of the experiment. The turn-over frequency (TOF) was determined using experimental points at 10 and 15 min; the medium value was 103 h^{-1} . Using the first order model, it was possible to estimate the TOF when time tends towards zero (the value was 126 h^{-1}).

Selectivity versus conversion is represented in Fig. 7. Product selectivity was constant over the entire conversion range. It indicates that 3PN is probably a primary product of reaction. The high 3PN selectivity suggests that the nickel mainly reacts via a π -allyl intermediate [11]. The nickel hydride or nickel metal species, which would isomerize the 2M3BN into 2M2BN, were not preponderant.

A similar Ni(cod)₂/[TPPMSNa] catalyzed reaction was performed under more dilute conditions (1450 equivalents of 2M3BN) in order to evaluate the maximal turn-over number. After 20 h at 100 °C, 70% conversion of 2M3BN was obtained and therefore the catalyst TON was equal or superior to 1020.

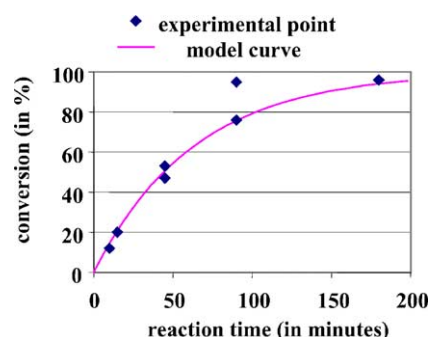


Fig. 6. Conversion of 2M3BN to 3PN as a function of reaction time. Conditions: Ni(cod)₂ (0.036 mmol) + [TPPMSNa] (0.18 mmol) + 2M3BN (4.94 mmol) + [BMMI][TFSI] (2.0 g) + heptane (1.2 ml) were stirred at 100 °C. The products of the reaction were analyzed by gas chromatography.

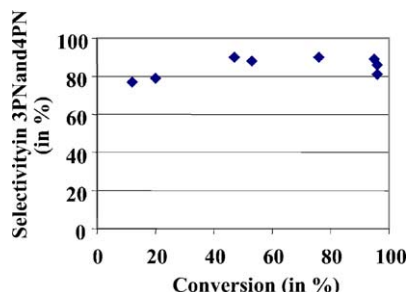


Fig. 7. Selectivity to 3PN as a function of conversion. Conditions: $\text{Ni}(\text{cod})_2$ (0.036 mmol) + [TPPMSNa] (0.18 mmol) + 2M3BN (4.94 mmol) + [BMMI][TFSI] (2.0 g) + heptane (1.2 ml) were stirred at 100 °C. The reactions were stopped after different reaction times and the products were analyzed by gas chromatography.

3.1.7. Recycling of the catalyst $\text{Ni}(\text{cod})_2$, [TPPMSNa] in the biphasic [BMMI][TFSI] / heptane system

One of the most important potential advantages of ionic liquids lies in the possibility to recycle the catalyst simply by extracting the products with an organic solvent from a catalytically active ionic phase at the end of the reaction. In this study, the catalytic reaction was run under the two-phase conditions as described above. At the end of a cycle, pentenenitriles were distilled off. Fresh substrate 2M3BN and heptane were then added under inert atmosphere and the reactor was sealed and reheated to 100 °C for 180 min.

The recycling experiments were performed in [BMMI][TFSI] and distillations were run for 10 min at 100 °C under dynamic vacuum. Visually, it was noted that the ionic liquid phase changes from orange/red at the end of the first run to orange at the end of the second run and finally to brown at the end of the third. Chromatographic analysis showed that the activity of the catalyst decreased rapidly. The total turn-over (TTO) was plotted as a function of time (Fig. 8). Each point of the graph corresponds to the distillation of the organic products from the reaction medium followed by recycling of the ionic phase. TTO for these tests was at the maximum 280, which was well below the TON previously determined (1020). The work-up at the end of each run (dis-

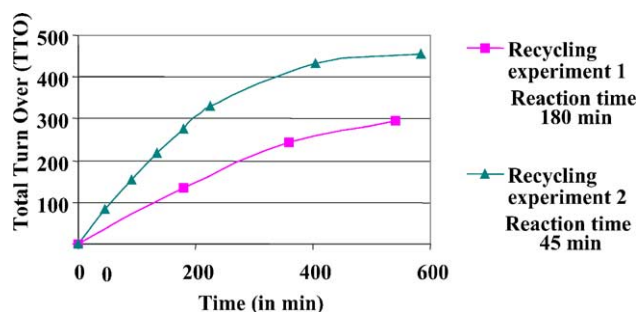


Fig. 8. Recycling of the catalyst $\text{Ni}(\text{cod})_2$ + [TPPMSNa] in [BMMI][PF₆] and [BMMI][TFSI]. Conditions: $\text{Ni}(\text{cod})_2$ (0.036 mmol) + [TPPMSNa] (0.18 mmol) + 2M3BN (4.94 mmol) + [BMMI][TFSI] (2.0 g) + heptane (1.2 ml) were stirred at 100 °C. Organic products were distilled for 10 min at 100 °C under dynamic vacuum and analyzed by gas chromatography. The ionic phase was recycled.

tillation at high temperature and addition of 2M3BN) could possibly be responsible for deactivation. Recycling was thus undertaken in [BMMI][TFSI] with shorter reaction times, (45 min instead of 180 min). Under this protocol, it was possible to improve the productivity of the catalyst (TTO went from 300 to 450). The degradation of the catalyst caused by the work-up could then be excluded, as well as poisoning by impurities in the substrate (water, conjugated nitrile, ...). The deactivation of the catalyst was nevertheless related to the total duration of reaction: indeed the slopes of the curves after 500 min of reaction were identical whatever the frequency of recycling.

4. Conclusion

The isomerization of 2M3BN into 3PN was performed under biphasic conditions (ionic liquid/organic solvent) in the presence of $\text{Ni}(\text{cod})_2$ and [TPPMSNa]. This reaction is sensitive to the nature of the anions and cations of the ionic liquids. The difference in the catalytic results between the cations BMI and BMMI could be due to the formation of carbene in the case of BMI. From this study, [BMMI][TFSI] was selected.

Several cationic and anionic phosphines and also TPP were screened. With TPP, conversion of 2M3BN (96%) and selectivity to 3PN (82%) were high but a detrimental leaching of the catalyst into the organic phase was observed. Cationic and anionic phosphines with two or three ionic groups per phosphorus atom showed very low catalyst activity probably due to a poor solubility in ionic liquids. From this ligand screening, [TPPMSNa] was found to be the most convenient ligand for further studies of the reaction of isomerization of 2M3BN into 3PN.

The best results in the conversion of 2M3BN (96%) and selectivity to 3PN (93%) was obtained with the catalytic system associating $\text{Ni}(\text{cod})_2$, [TPPMSNa] and a [BMMI][TFSI]/heptane solvent system which was therefore the more thoroughly studied. Partition experiments proved that the catalyst was immobilized in ionic phase. TON (1020) and TOF (103 h⁻¹) of the catalyst were measured. Recycling of the catalyst is possible but led to an important deactivation which could be related to a possible evolution of the nature of the ligand by ion exchange between the cation (Na) of the ligand and the cation [BMMI] of the ionic liquid. This hypothesis is under investigation.

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