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Design of Ionic Phosphites for Catalytic Hydrocyanation Reaction of 3-Pentenenitrile in Ionic Liquids†

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Abstract: The synthesis and characterization of a novel class of ionic phosphites bearing either a single cationic group obtained by quaternization of aminophosphites or three cationic groups prepared by reaction of phosphorus trichloride with imidazolium phenols are reported. The catalytic hydrocyanation reaction of 3-pentenenitrile (3PN) into adiponitrile has been performed in the presence of Ni(0) with ionic phosphite ligands, and a Lewis acid in biphasic ionic liquid/organic solvent system. The screening of several original cationic phosphites was performed and the experimental conditions were optimized for the tricationic phosphite tris-4-[(2,3-dimethylimidazol-1-yl) methyl]phenyl phosphite tris[bis(trifluoromethylsulfonyl)amide]. It is possible to obtain performance similar to molecular systems and the catalyst and the Lewis acid were immobilized in the ionic phase.

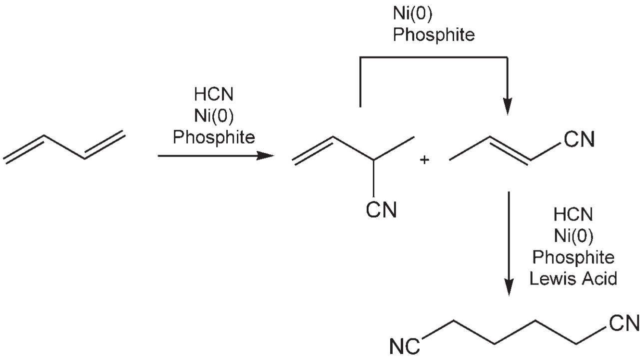
Keywords: adiponitrile; hydrocyanation; ionic liquids; ionic phosphite; nickel; P ligands

Introduction

Adiponitrile [AdN], a nylon 6,6 intermediate is industrially prepared by the hydrocyanation of butadiene[1] which 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 industrial hydrocyanation of butadiene into adiponitrile is catalyzed by homogeneous zero-valent triaryl phosphate-nickel complexes. Triaryl phosphites are also the subject of constant research for hydrocyanation: new structures are regularly claimed, in particular by DuPont[3–5] and BASF.[6,7] Other ligands containing P–O bonds were used for this reaction, like phosphinites,[8] phosphonites[9,10] and bidentate phosphorus amide ligands.[11,12]

We have recently reported the first example of the catalytic isomerization of 2-methyl-3-butenenitrile (2M3BN) into 3-pentenenitrile (3PN) (the second step in the adiponitrile preparation) under biphasic conditions {1-butyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide [BMMI][NTF$_2$]/heptane} in the presence of Ni(cod)$_2$ and (*m*-sulfophenyl)-diphenylphosphine sodium salt, [TPPMSNa], with a conversion of 2M3BN of 96% and selectivity to 3PN of 93%. Partition experiments proved that the catalyst was immobilized in the ionic phase. TON (1020) and turn-over frequency (TOF) (103 h^{-1}) of the catalyst were measured.



Scheme 1. Industrial preparation of AdN by hydrocyanation of butadiene catalyzed by homogeneous nickel(0)-phosphite complexes.[2]

Recycling of the catalyst was 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. Such an exchange was recently proved by ^{23}Na solid state NMR.[13]

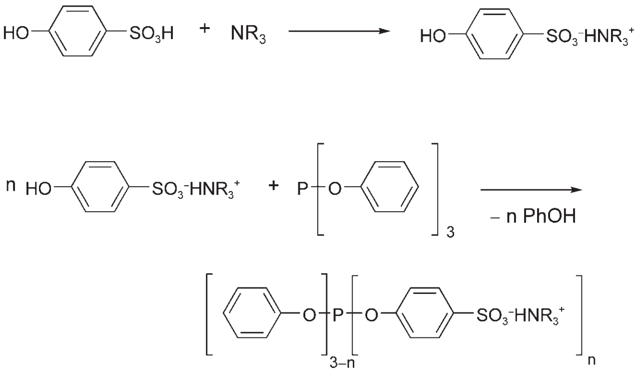
Although phosphite ligands are considered to be easier to synthesize and less prone to oxidation than phosphines, they are more sensitive to hydrolysis. They are much cheaper than most phosphines and a wide variety can be obtained. However, their use in ionic liquids was rarely reported and limited to the hydroformylation of methyl 3-pentenoate[14] and 1-hexene.[15,16] In order to immobilize the catalyst in the ionic phase, ionic phosphites were prepared and characterized. Applications of the catalytic systems involving these ligands to the hydrocyanation of 3PN are described herein.†

Results

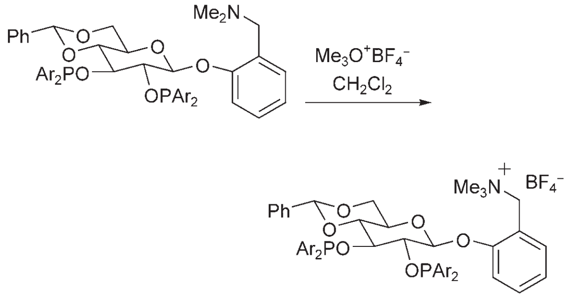
Ionic phosphines have largely been described and this field has been supported by the successes of aqueous catalysis.[18] Publications related to ionic phosphites are much more limited. Indeed these ligands can be used very rarely in water as the P–O single bond is likely to be easily hydrolyzed. However non-aqueous ionic liquids could enhance the attractiveness of such ligands. Recently, we have demonstrated that the presence of an ionic group on the aromatic ring of a phosphine improved the immobilization of the catalyst in the ionic liquid phase.[17] As a consequence, the synthesis of triaryl phosphites containing at least one ionic group has been developed to reach the same goal.

Synthesis of Ionic Aryl Phosphites

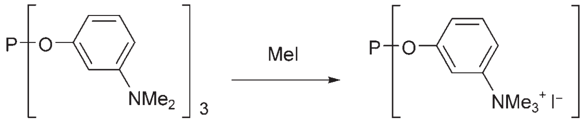
The ***anionic aryl phosphites*** reported in the literature[19–23] were generally a mixture of ammonium or sodium salts of the mono-, di-, and tri-sulfonated triphenyl phosphite and which were used as ligand for the rhodium-catalyzed hydroformylation of 1-hexene in the ionic liquid [BMI][PF_6].[16]



Scheme 2. Synthesis of a mixture of sulfonated phosphites.[23,24]



Scheme 3. Synthesis of a cationic phosphinite.[21]



Scheme 4. Synthesis of a cationic phosphite.[25]

A ***cationic phosphinite*** obtained by reaction of trimethyloxonium tetrafluoroborate with an aminophosphinite (Scheme 3) was prepared *in situ* and directly reacted with rhodium in a reaction of catalytic asymmetric hydrogenation.[21]

The only ***cationic phosphite*** described in the literature was obtained by reaction of methyl iodide with the tris-[3-(*N,N*-dimethylamino)-phenyl] phosphite to form the ammonium compound (Scheme 4).[25] This compound was not characterized further than the determination of its melting point.

To conclude, the field of ionic ligands containing P–O single bonds has received very little attention. While a few examples of anionic phosphites have been reported only a single example of a cationic phosphinite was found. To our knowledge, cationic phosphites have never been mentioned in the literature as ligands for organometallic catalysis. The development of non-aqueous ionic liquids could enhance the attractiveness of such ligands. Special efforts were therefore devoted to their synthesis.

Note that all our attempts for the synthesis in large quantities of pure anionic phosphite and cationic phosphinite failed. In contrast, several original tricationic aryl phosphites were efficiently prepared.

Two different routes were considered for the synthesis of ***cationic phosphites***. The first one required the synthesis of an aminoaryl phosphite and subsequent quaternization of the amino group with an appropriate reagent. The second possibility begun with the preparation of a phenol with an ammonium group and was pursued by reaction of this compound with a P–Cl bond. Tetraalkylammonium and imidazolium were chosen as cationic groups, and our work was limited to triaryl phosphites.

Quaternization of an Aminoaryl Phosphite

The biphenyl chlorophosphite **1** prepared in good yields from 2,2′-biphenol and phosphorus trichloride reacted with 3-*N,N*-dimethylaminophenol in the presence of triethylamine. After filtration of triethylamine hydrochloride salt, the pure aminoaryl phosphite **2** was isolated (Scheme 5). A suspension of trimethyloxonium tetrafluoroborate in dichloromethane was added to this compound. After solvent concentration, the ammonium phosphite **3** was obtained quantitatively. The product was fully characterized by NMR spectroscopy (^{1}H, ^{13}C and ^{31}P) and elemental analysis.

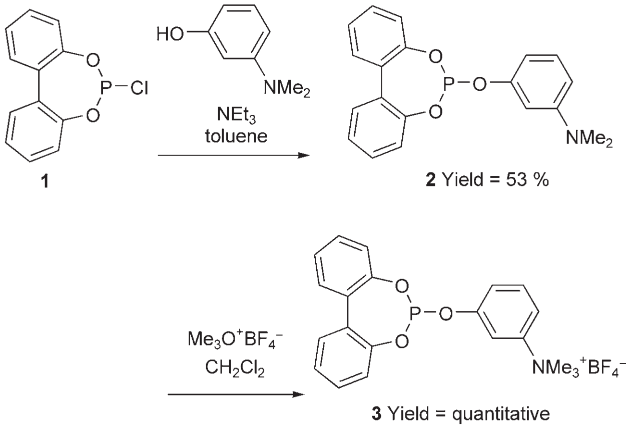
The versatility of this new synthetic route was assessed by the preparation of several ligands having various electronic and steric properties.

A sterically hindered 2,2′-(3,3′,4,4′-tetramethyl-6-6′-di-*tert*-butyl)-biphenyl chlorophosphite **5** was prepared from the corresponding substituted biphenol **4** and phosphorus trichloride (Scheme 6). Bis-*m*-tolyl chlorophosphite **6** was furnished by Rhodia.

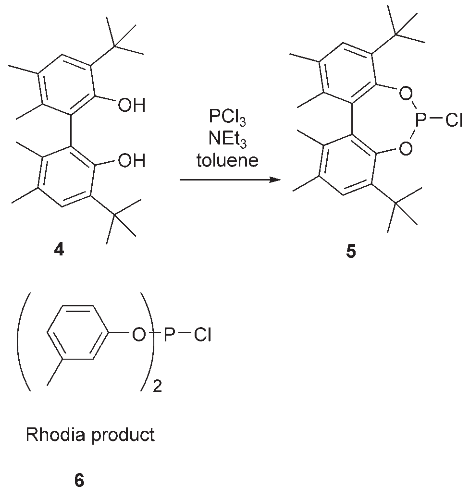
The third aryl oxide group of the phosphite was derived from 4-imidazol-1-yl-phenol **7** and from either 3- or 4-(*N,N*-dimethylaminomethyl)-phenol (**8** or **9**), which were prepared from 3-or 4-hydroxybenzaldehyde by a reductive amination with dimethylamine and sodium triacetoxyborohydride in THF[26] (Scheme 7).

Several aminoaryl phosphites were prepared by combination of these chlorophosphites and aminophenols and were obtained in modest to good yields (Scheme 8). Compounds **10**, **11** and **12** were purified through a thin silica column (eluent dichloromethane) and the phosphite **13** was purified through a thin Florisil® column (eluent dichloromethane). Crude phosphites **14** and **15** were sufficiently pure to be used directly for the subsequent step. The amino groups in these compounds were then transformed into ammonium groups by reaction with trimethyloxonium tetrafluoroborate. The cationic phosphites were obtained in high yields (Scheme 8).

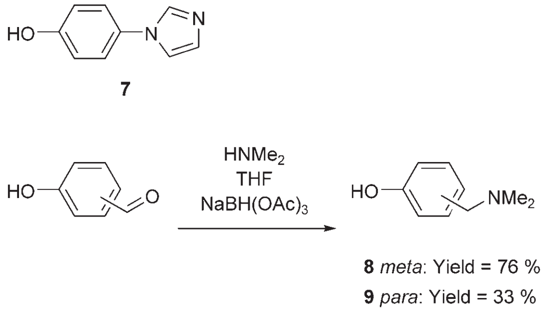
The ligands **16** to **21** were obtained as oils containing small amounts of hydrolysis products [$(RO)_2P(O)H$], phosphonium salts [$(RO)_3PMe^+BF_4^-$] and compounds resulting from redistribution of the phenols around phosphorus. All attempts at purification were unsuccessful and mainly led to degradation products. As a consequence, crude products were engaged in catalytic tests and the purity of the compounds was estimated by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy. For all of these phosphites, the anion was tetrafluoroborate.



Scheme 5. Synthesis of a cationic phosphite.



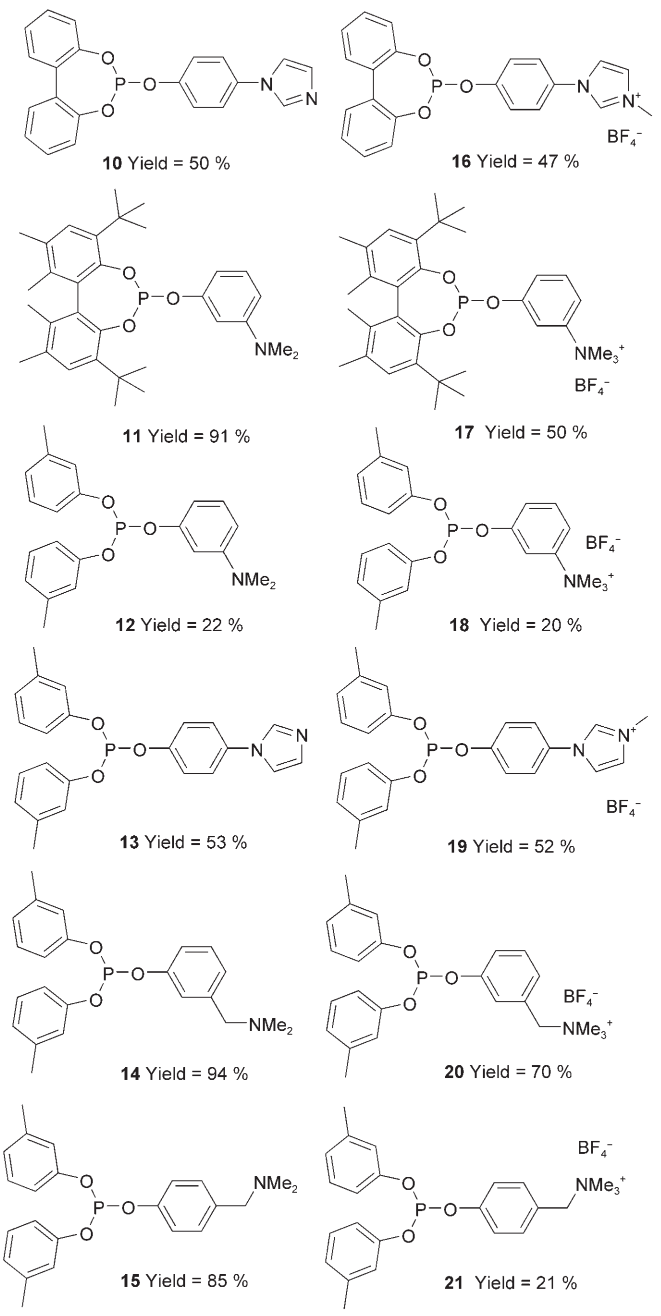
Scheme 6. Chlorophosphites.



Scheme 7. Aminophenols.[26]

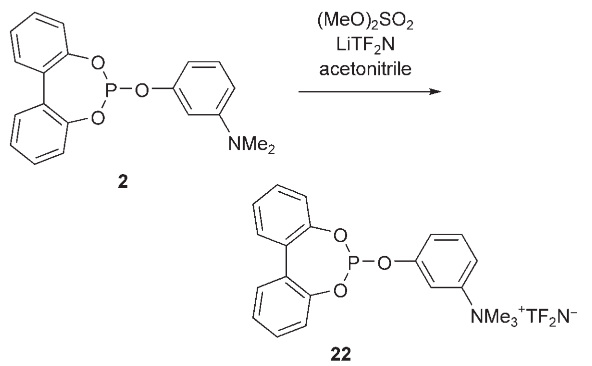
As [BMMI][TF$_2$N] was the best ionic liquid for the studied catalytic reaction, we developed ligands bearing the anionic TF_2N^- moiety. The ammonioaryl phosphite **22** was obtained as a TF_2N^- salt by reaction of aminoaryl phosphite **2** with LiTF$_2$N in acetonitrile in the presence of dimethyl sulfate (Scheme 9).

A family of phosphites with three amino groups was synthesized by reacting phosphorus trichloride with 3-*N,N*-dimethylaminophenol in the presence of triethylamine (Scheme 10). The phosphite **23** was purified by filtration on silica and then submitted to various alkylat-

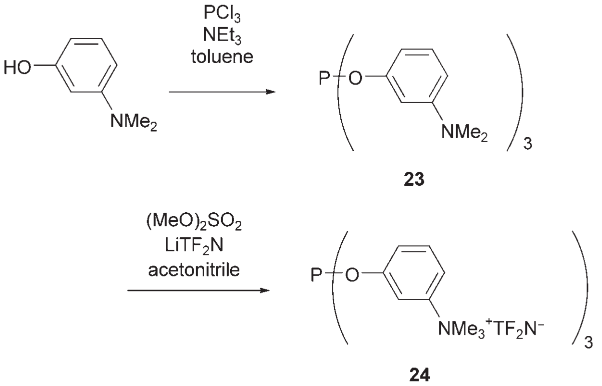


Scheme 8. Aminoaryl phosphates and cationic phosphates.

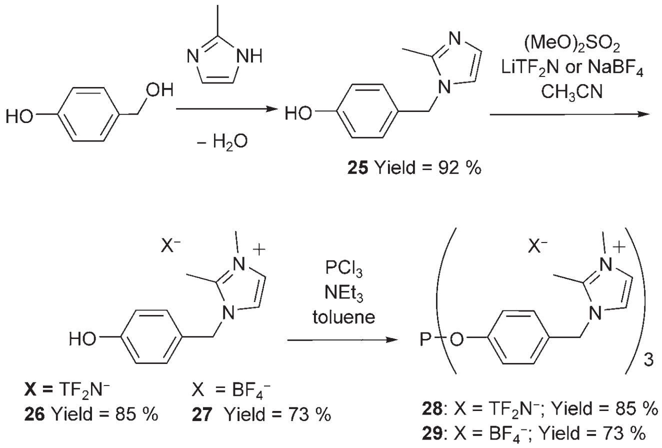
ing reagents. Trimethyloxonium tetrafluoroborate, triethyloxonium hexafluorophosphate and methyl trifluoromethanesulfonate led to complex mixtures containing partially quaternized phosphites and several phosphonium derivatives. An equimolar dimethyl sulfate/LiTF$_2$N mixture gave the expected products **24**.



Scheme 9. Cationic phosphite with a TF$_2$N$^-$ anion.



Scheme 10. Synthesis of tri-ammonioaryl phosphites.

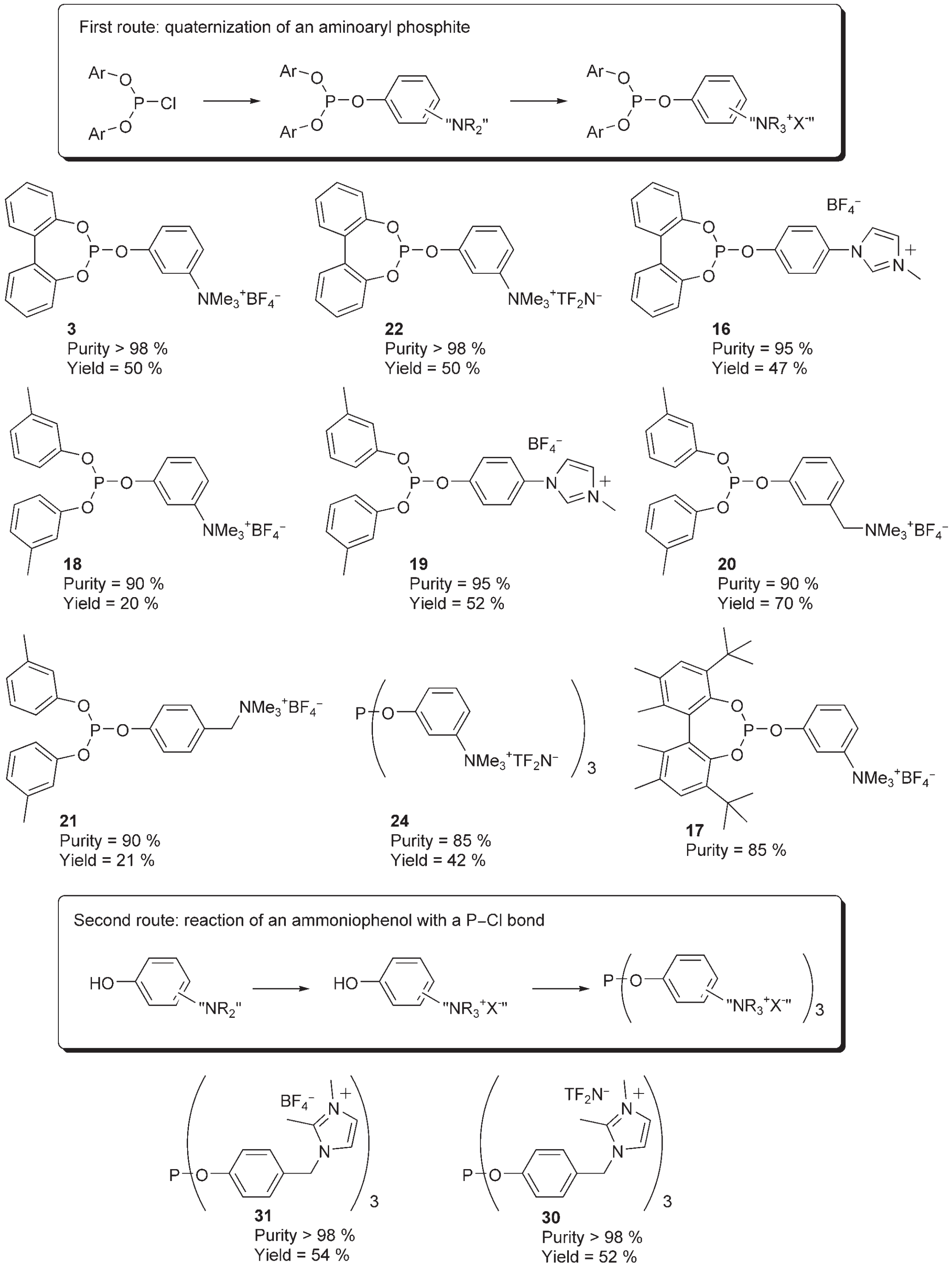


Scheme 11. Synthesis of tricationic phosphites.

During this work, we were able to synthesize several cationic phosphites bearing a single cationic group with good to excellent purity. On the other hand, attempts at the synthesis of tri-cationic ligands led to only one ligand of moderate purity. To avoid this problem, the quaternization of the starting phenol was performed before reaction with phosphorus derivatives.

Reaction of a Cationic Phenol with a P–Cl Bond

Suitable phenols were prepared in two steps: 2-methylimidazole was heated with 4-hydroxybenzyl alcohol to



Scheme 12. Summary of the two routes of synthesis and list of synthesized phoshites (with purity and overall yield).

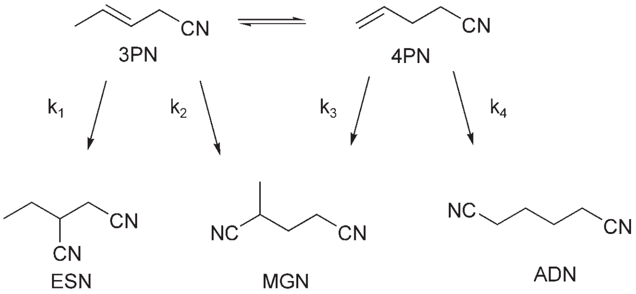
yield product **25** (Scheme 11)[27] which was then quaternised by reaction with $LiTF_2N$ (**26**) or $NaBF_4$ (**27**)in the presence of dimethyl sulfate. Reaction of phosphorus trichloride with these imidazolium phenols yielded tricationic phosphites and triethylamine hydrochloride salts (Scheme 12). Chloride salts were eliminated by successive washings with dichloromethane as the phosphites were not soluble in this solvent. Phosphites with TF_2N^- anions (**28**) or BF_4^- anions (**29**) were obtained in good yields and characterized by NMR spectroscopy (^1H, ^{13}C and ^{31}P in acetonitrile-d_3) and elemental analysis. It was possible to prepare **28** on a 20-g scale.

To conclude, two routes of synthesis of cationic phosphites were successfully developed. In the first one, an aminoaryl phosphite was synthesized and the amino group was transformed into ammonium by reaction with an alkylation reagent: this method was particularly suitable for the synthesis of a monocationic phosphite. The second strategy began with preparation of phenols bearing an imidazolium group. The reaction with phosphorus trichloride led to tricationic phosphites in high yield and purity. These results are summarized on Scheme 12.

Catalytic Studies

The hydocyanation of 3PN was realized in the presence of catalytic precursor Ni(0)-triphenyl phosphite and Lewis acid promoter which affect the double bond isomerization of 3PN to 4-pentenenitrile (4PN) concurrently with the selective addition of HCN to 4PN. Byproducts include 2-methylglutaronitrile (MGN), ethylsuccinonitrile (ESN) arising, respectively, from Markovnikov addition to 4PN, and direct addition of HCN to 3PN.[2]

The catalytic results were given in conversion of 3PN, yield and linearity in dinitriles, data determined as depicted in Equations (1) and (2):



Scheme 13. Formation of dinitrile derivatives during the hydrocyanation reaction of 3PN.[2]

$$\text{Yield dinitriles} = \frac{\text{moles of (ADN + MGN + ESN) final}}{\text{moles of 3PN introduced}} \quad (1)$$

$$\text{Linearity} = \frac{\text{moles of ADN final}}{\text{moles of (ADN + MGN + ESN) final}} \quad (2)$$

Cationic Biphenyl Phosphites

Phosphites **3**, **16**, **17** and **22** which have the same structure, were tested both for isomerization of 2M3BN into 3PN and for the hydrocyanation of 3PN in adiponitrile, but, in both reactions, no activity was observed.

A ^{31}P NMR spectrum of the reaction mixture containing Ni(cod)$_2$/phosphite **3**/2M3BN/[BMMI][TF$_2$N] after reaction and work-up was recorded at room temperature. Two peaks were observed at $\delta = 141.6$ and 157.5 ppm (Figure 1: spectrum III). The peak at $\delta = 141.6$ ppm could be attributed to **3** ($\delta = 138.8$ ppm in CDCl$_3$) (Figure 1: spectrum I). On the other hand, when a mixture of Ni(cod)$_2$ and 4 equivalents of ligand **3** was stirred at room temperature in THF, a white precipitate was formed whose ^{31}P NMR spectrum (Figure 1: spectrum II) exhibited a single peak at $\delta = 157.5$ ppm attributed to an NiL$_4$ complex. Thus the spectrum of the catalytic solution after reaction could be interpreted as containing mainly an NiL$_4$ complex and free ligand. This result supported the fact that the complex was stable in the presence of pentenenitriles and ionic liquid preventing any coordination of an olefin to the nickel and preventing any catalytic reaction.

Cationic Tolyl Phosphites

In a typical run, acetone cyanohydrin (24 equivalents) was slowly added at 70 °C in 3 h to a solution of Ni(cod)$_2$

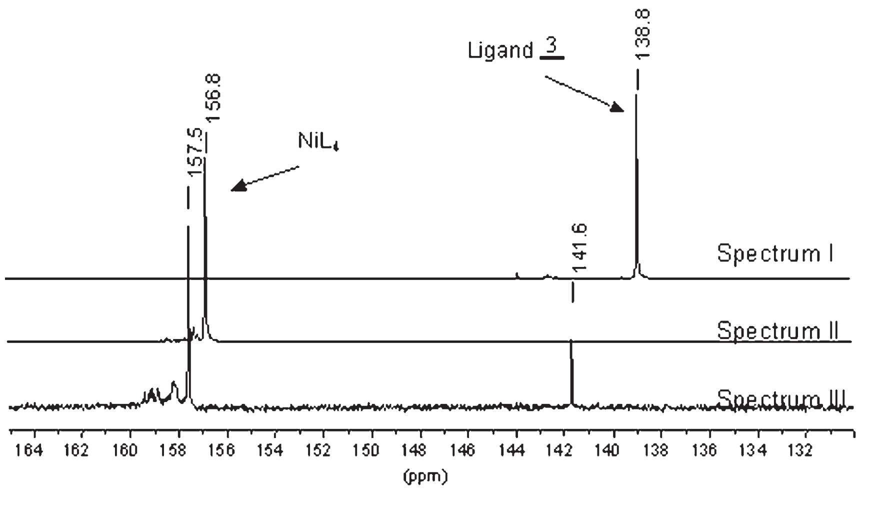
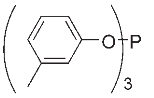
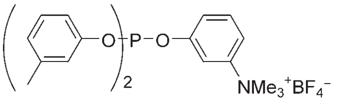
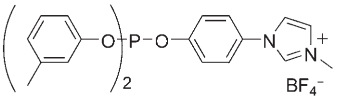
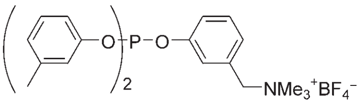
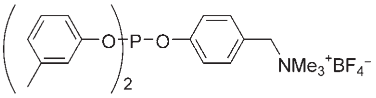


Figure 1. ^{31}P NMR spectra registered at room temperature. (I): **3** in CDCl$_3$; (II): Ni(cod)$_2$ + 4 equivs. of **3** in CD$_3$CN; (III): Ni(cod)$_2$ + 5 equivs. of **3** + 3PN + [BMMI][TF$_2$N] after 3 h at 100 °C.

Table 1. Hydrocyanation of 3PN with cationic phosphites in [BMMI][TF_2N].

Ligand		Conv. 3PN	Yield of dinitriles [%]	Linearity
	TPP	49	46	84
	**18**	28	24	70
	**19**	21	15	75
	**20**	11	7	76
		35[a]	30	77
	**21**	44	38	77

[a] The mixture of nickel, phosphite, substrate and ionic liquids was stirred overnight at room temperature in order to form the nickel-phosphite complex.

(40 mg), cationic phosphites **18**–**21** (5 equivalents), 3PN (30 equivalents) and zinc chloride (1 equivalent) in [BMMI][TF_2N]. After 3 h of reaction, products were analyzed by gas chromatography. Results obtained with the molecular ligand tris(*meta*-tolyl) phosphite (*m*-TTP) are included as a base for comparison (Table 1). Note that the performance of the catalytic system including the cationic phosphite **21** was the closest to that of the molecular *m*-TTP based system.

With one ligand (Table 1), the hydrocyanation reaction was performed after a different time of reaction between **20** and $Ni(COD)_2$ (20 min and 12 h); it appeared that when the ligand/nickel system was allowed to react for a longer time before reaction, superior performance was observed. It thus appeared that disparities due to experimental conditions were much more important that those due to the structure of the phosphites.

The cationic phosphite **21** yielded very promising results for the hydrocyanation of 3PN in ADN. However, the possibility of the redistribution of phenol around the phosphorus atom could not be excluded. Such a redistribution might have a dramatic importance, as it was likely to generate *in situ* molecular *m*-TTP ligand which might be responsible for the catalytic activity. In order to eliminate this alternative, a tricationic ligand was tested in catalysis.

*Tricationic Phosphite **28***

The importance of experimental parameters such as the ligand to metal ratio, the presence of Lewis acid and the temperature of the catalytic reaction in the isomerization of 2M3BN has been already mentioned.[17] The hydrocyanation reaction is also sensitive to experimental parameters, i.e., the preparation of the catalytic mixture had a strong effect on catalytic performances in the brief study of the monocationic ligands. As the phosphite **28** was synthesized on a 20-g scale, it was decided to further explore this parameter space using an established design of experiments technique (DOE).[28]

For this study, the influence of two different factors at different levels were retained, in first the ratio of ligand per nickel: a value of 2, which corresponds to a minimum number of ligands necessary to stabilize nickel(0), and one of 5 (an excess of ligand). The second factor was the ratio of zinc chloride per nickel: one to three equivalents of Lewis acid per nickel were used. The factors which were studied and the level which were chosen are depicted in Table 2. The responses of the DOE were the yield in dinitriles and the linearity.

A full factorial design with a center point ($L/Ni = 3.5$ and $ZnCl_2/Ni = 2$) was chosen. Two reproductions of the DOE were performed, with a blocking on the preparation of the catalyst.

Table 2. Parameters of the experimental design.

	Level −1	Level +1
Ratio L/Ni	2	5
Ratio $ZnCl_2/Ni$	1	3

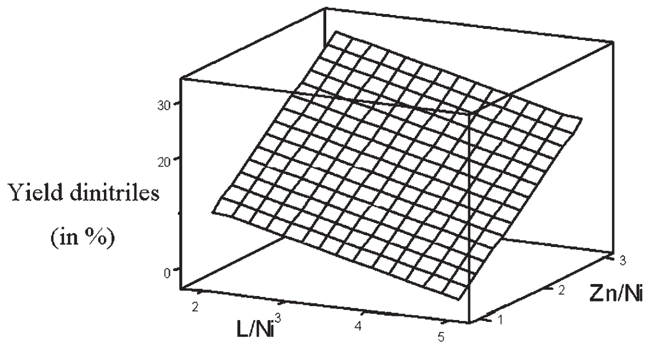


Figure 2. Yield in dinitriles as a function of L/Ni and Zn/Ni.

Each reproduction was divided in two blocks depending on the catalyst preparation procedure. In the first block the trials were run after *in situ* catalyst preparation whereas those of the second block were run with a preformed catalyst (see Table 1). If the variability between the two blocks is significant, the preparation of the catalyst will be identified as a potential factor. Otherwise the reproduction of the tests will provide information about the reproducibility of the tests.

Concerning the first response, dinitriles yields, neither the interactions between L/Ni and $ZnCl_2$/Ni nor the block (the preparation of the nickel complex) had significant effects. The situation was therefore clearly different of that with the monocationic ligand **20**, as the preparation of the catalyst had a strong impact on the catalytic performance in the latter case. However, the origin of this difference was not understood and would require further investigation.

Concerning the principal effects, the first factor, ($ZnCl_2$/Ni ratio) had a significant consequence on the yield which increased when an excess of Lewis acid was used, and 65% of the yield variations could be attributed to this factor effect (more precisely, the factor variance was 65% of total variance).

The second factor, (ligand/nickel ratio) had a significant but less important effect. An excess of ligand had a detrimental impact on the yield and this factor effect could explain 16% of the variations.

Globally, the two main factors ($ZnCl_2$/Ni ratio and ligand/nickel ratio) were responsible for more than 80% of yield variations and the resting part could be attributed to background noise. It was an indication that the critical factors of the reaction had been identified. The yield can be represented as a function of the two significant factors in a three-dimensional graph (Figure 2).

The analysis of the DOE in terms of the second response, the linearity, was also performed although the variations of this response were limited. The ratio of zinc chloride per nickel was the only statistically significant factor and it explained only a small part (31%) of the variation of linearity. As a consequence, it was not possible to establish a robust predictive model for the linearity.

To conclude, the DOE allowed the optimization of the reaction conditions with respect to two factors previously identified as having an important effect. A low ratio of ligand per nickel and a large excess of Lewis acid are necessary to obtain high yields. Furthermore, it has been proved that there was no significant interaction between the two factors. Further reduction of the number of ligands per nickel seemed useless, as it would certainly lead to unstable catalysts. In contrast, it was possible to increase the proportion of zinc chloride. A few tests were then performed with 5 or 10 equivalents of Lewis acid per nickel (Table 4).

When 5 equivalents of zinc chloride per nickel were used (entry 401), the results were very similar to the one with 3 equivalents (entry 398). When a further excess of Lewis acid was employed (entries 402 and 403), lower activity resulted. The large excess of Lewis acid might be negative for the stability of the nickel complex.

By optimization of experimental conditions with zinc chloride, it has been possible to obtain high yields of dinitriles with phosphite **28**. The highest linearity obtained was 73% and thus further improvements were required. To this end, different Lewis acids were tested as co-catalysts (Table 5).

Table 3. Hydrocyanation of 3PN with phosphite 30 in [BMMI][TF_2N].

Experiments order	L/Ni	Lewis acid/Ni	Blocks[a]	Yield of dinitriles*	Linearity*
1	5	1	a	4	65
2	3.5	2	a	4	61
3	5	3	a	17	71
4	2	3	a	36	71
5	2	1	a	6	65
6	2	3	b	34	72
7	2	1	b	8	71
8	5	3	b	19	71
9	3.5	2	b	22	73
10	5	1	b	2	50

[a] Block a means in *situ* formation of the catalyst while block b means reaction with preformed catalyst (see Table 1).

Table 4. Hydrocyanation of 3PN with phosphite 28 in [BMMI][TF$_2$N].

Entry	L/Ni	ZnCl$_2$/Ni	Conv. 3PN	Yield of dinitriles	Linearity
398	2	3	40	36	71
401	2	5	39	34	70
402	2	10	12	7	67
403	5	10	17	13	71

Table 5. Hydrocyanation of 3PN with phosphite 28 and different Lewis acids.

Lewis acid	Entry	Conv. 3PN	Yield of dinitriles	Linearity	Yield of other products
ZnCl$_2$	398	40	36	71	4
BPh$_3$	404	11	5	74	3
CoCl$_2$	407	21	15	65	3
In(CF$_3$CO$_2$)$_3$	405	24	19	59	3
In(CF$_3$SO$_3$)$_3$	409	7	2	53	3
ErCl$_3$	406	32	29	80	4
YCl$_3$	408	19	15	81	3

Triphenylborane led to a low activity and no significant improvement of the linearity was observed (entry 404). With cobalt chloride (entry 407), both yield and linearity were inferior to those obtained with zinc chloride. Indium-based Lewis acids gave different results in terms of activity, but the linearity was systematically inferior to 60% (entries 405 and 409). Rare earth chlorides yielded the best results, with linearities exceeding 80% (entries 406 and 408).

It was difficult to further interpret these results. Indeed, it is worth remembering that a variety of parameters have been shown to be important in a complex manner. They were optimized for zinc chloride but these conditions were not necessarily optimal for other Lewis acids. Furthermore, the solubility of the Lewis acids in [BMMI][TF$_2$N] has not been studied, and the exact nature of the Lewis acid promoter in the reaction medium is unknown.

For all these reasons, it was not possible to interpret these data from a mechanistic point of view. It is, however, important to note that high activity and linearity have been obtained with lanthanides chlorides. Even if these co-catalysts are somewhat more expensive than zinc chloride, the recycling of the co-catalyst thanks to ionic liquids might improve the economic attractiveness of the use of such compounds in an industrial context.

Conclusion

By quaternization of aminoaryl phosphites, it was possible to isolate in good yields ligands bearing a single cationic group. Tricationic aryl phosphites were efficiently prepared by reaction of phosphorus trichloride with imidazolium phenols. All these compounds, obtained in high quantity with excellent purity, were original ones, and they are likely to offer new opportunities for catalysis in ionic liquids.

The hydrocyanation of 3PN in AdN was considered in this work. The dramatic importance of experimental conditions has been highlighted. The importance of the experimental conditions is such that the comparison of data which are not obtained in rigorously identical conditions might be misleading for the choice of the nature of the ligand. The screening of several original cationic phosphites was performed and the experimental conditions were optimized for tris-4-[(2,3-dimethylimidazol-1-yl)methyl]phenyl phosphite tris[bis(trifluoromethylsulfonyl)amide]. It was possible to obtain performance similar to molecular systems for the hydrocyanation reactions [conversion of 3PN $\approx$ 40% ;yield of dinitriles $\approx$ 40% and linearity $>$ 70%]. The cationic phosphite-based system might afford the supplementary advantage of the immobilization of the catalyst and the Lewis acid in the ionic phase when the reaction is run under these biphasic conditions.

Experimental Section

Syntheses and Characterization of Cationic Ligands

All the synthesis were carried out under dry argon using standard Schlenk techniques. Solvents were distilled using the appropriate drying agents: CaH$_2$ for acetonitrile and dichloromethane, sodium/benzophenone for diethyl ether and tetrahydrofuran, K$_2$CO$_3$ for chloroform, sodium for toluene and sodium/potassium for pentane.

Phosphorus trichloride and diphenylchlorophosphine were purchased from Aldrich and distilled before use. Bis-*m*-tolyl chlorophosphite was supplied by Rhodia and used as is. Triethylamine was purchased from Aldrich and distilled over calcium hydride.

Classical neutral alumina for chromatography (Fluka), silica gel 60 (Merck) or Florisil® were used for purification of the ligands. All other reagents were obtained from commercial sources and used as received.

^{1}H, ^{13}C and ^{31}P NMR were obtained on a Bruker AC 300 MHz spectrometer. Chemical shifts were measured relative to $SiMe_4$ as internal standard for ^{1}H and ^{13}C. Positive ^{31}P chemical shifts are downfield from external 85% H_3PO_4. The solvents used ($CDCl_3$, CD_3CN, DMSO-d_6) were purchased from SDS and distilled using the appropriate drying agent.

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

General Procedure A: 2,2′-Biphenyl Chlorophosphite (1)

2,2′-Biphenol (2.00 g, 10.7 mmol) was dissolved in toluene (25 mL) and the solution was cooled to 0 °C. A solution of phosphorus trichloride (2.21 g, 16.0 mmol) and triethylamine (4.5 mL, 32.0 mmol) in toluene (10 mL) was slowly added. The mixture was allowed to warm to room temperature and stirred for 36 h. It was filtered and concentrated to afford a slightly yellow oil; yield: 2.55 g (95%). ^{31}P{^{1}H} NMR ($CDCl_3$): $\delta = 178.9$.

General Procedure B : 2,2′-Biphenyl-3-(*N,N*-dimethylamino)-phenyl Phosphite (2)

2,2′-Biphenyl chlorophosphite (**1**; 2.55 g, 10.2 mmol) and triethylamine (4.3 mL, 31 mmol) were dissolved in toluene (10 mL) and the solution was cooled to 0 °C. A solution of 3-(*N,N*-dimethylamino)-phenol (1.40 g, 10.2 mmol) in toluene (10 mL) was slowly added. The mixture was allowed to warm to room temperature and stirred for 12 h. The product was purified through a short silica column (eluent: dichloromethane) to afford a purple solid; yield: 1.89 g (53%). ^{1}H NMR ($CDCl_3$): $\delta = 2.95$ (s, 6H, CH_3), 6.47–6.63 (m, 2H), 7.14–7.53 (m, 10H); ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta = 40.6$ (CH_3), 104.7 (d, $J_{CP} =$ 7.7 Hz), 107.1 (d, $J_{CP} = 9.2$ Hz), 108.7, 122.3, 125.5, 129.3, 130.1, 130.1, 131.4 (d, $J_{CP} = 3.2$ Hz), 149.1 (d, $J_{CP} = 5.1$ Hz), 152.1, 152.7 (d, $J_{CP} = 8.3$ Hz); ^{31}P{^{1}H} NMR ($CDCl_3$): $\delta =$ 143.6. HRMS (CI): *m/z* = 352.1129; calcd. for $C_{20}H_{19}NO_3P^+$: 352.1125.

General Procedure C: 2,2′-Biphenyl-3-(*N,N,N*-trimethylammonio)-phenyl Phosphite Tetrafluoroborate (3)

A solution of 2,2′-biphenyl-3-(*N,N*-dimethylamino)-phenyl phosphite (**2**; 500 mg, 1.42 mmol) in dichloromethane (5 mL) was quickly added to a suspension of trimethyloxonium tetrafluoroborate (210 mg, 1.42 mmol) in dichloromethane. The mixture was stirred for 1 h and solvent was removed under vacuum to afford a purple foam; yield: 640 mg (99%). ^{1}H NMR ($CDCl_3$): $\delta = 3.49$ (s, 9H, CH_3), 7.04–7.63 (m, 12 H, CH); ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta = 57.2$ (CH_3), 112.6 (d, $J_{CP} =$ 5.1 Hz), 115.8, 122.3, 122.5 (d, $J_{CP} = 9.2$ Hz), 126.0, 129.8, 130.2, 130.8 (d, $J_{CP} = 2.8$ Hz), 132.2, 147.9, 148.7 (d, $J_{CP} =$ 5.1 Hz), 153.8 (d, $J_{CP} = 4.1$ Hz); ^{31}P{^{1}H} NMR ($CDCl_3$): $\delta =$ 138.8; anal. calcd. for $C_{21}H_{21}BF_4NO_3P$: C 55.66, H 4.67, N 3.09; found: C 56.02, H 4.57, N 2.97; MS (ESI): *m/z* = 366 ($C_{21}H_{21}NO_3P^+$).

2,2′-(3,3′,4,4′-Tetramethyl-6,6′-di-*tert*-butyl)biphenyl Chlorophosphite (5) by Procedure A: From phosphorus trichloride (0.75 mL, 8.5 mmol), triethylamine (2.35 mL, 16.9 mmol) , 2,2′-(3,3′,4,4′-tetramethyl-6-6′-di-*tert*-butyl)-biphenol (2.0 g, 5.64 mmol); slightly yellow solid; yield: 2.33 g (99%); ^{31}P{^{1}H} NMR (CD_3Cl): $\delta = 165.7$.

3-[(*N,N*-Dimethylamino)-methyl]-phenol (8)

3-Hydroxybenzaldehyde (0.977 g, 8.00 mmol) and dimethylamine (2.0 M solution in THF, 6 mL, 12.00 mmol) were dissolved in THF (10 mL). Sodium triacetoxyborohydride (2.544 g, 12.00 mmol) was added and the mixture was stirred at room temperature for 18 h. A saturated aqueous $NaHCO_3$ solution was added and solvents were removed under vacuum to yield a white solid. The solid was extracted with dichloromethane and the solution acidified with hydrogen chloride (1.0 M in diethyl ether, 8 mL, 8 mmol). A white precipitate appeared and was washed with dichloromethane. The solid was then dissolved in saturated aqueous $NaHCO_3$ solution and the basic phase (pH = 9) obtained was extracted with dichloromethane. Organic phases were dried on magnesium sulfate and solvent was removed under vacuum to give a slightly yellow solid; yield: 0.92 g (76%). ^{1}H NMR ($CDCl_3$): $\delta = 2.27$ (s, 6H, CH_3), 3.42 (s, 2H, CH_2), 6.70–6.80 (m, 3H, CH), 7.14 (t, 1H, $^3J_{HH} =$ 7.8 Hz, CH); ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta = 44.8$ (CH_3), 63.9 (CH_2), 115.4, 117.1, 121.3, 129.4, 138.5 (CCH_2), 157.0 (CO).

4-[(*N,N*-Dimethylamino)-methyl]-phenol (9): Using the same procedure as for **8**: from 4-hydroxybenzaldehyde (0.977 g, 8.00 mmol), dimethylamine (2.0 M solution in THF, 6 mL, 12.00 mmol), THF (10 mL), sodium triacetoxyborohydride (2.544 g, 12.00 mmol) to afford a slightly yellow solid which was recrystallized in a toluene-hexane mixture (1/1) to give a white solid; yield: 400 mg (33%). ^{1}H NMR ($CDCl_3$): $\delta = 2.29$ (s, 6H, CH_3), 3.42 (s, 2H, CH_2), 6.0 (br s, 1H, OH), 6.60–6.70 (m, 2H, CH), 7.05–7.15 (m, 2H, CH); ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta = 44.7$ (CH_3), 63.5 (CH_2), 115.6, 128.3 (CCH_2), 130.9, 156.2 (CO).

2,2′-Biphenyl-4-(imidazol-1-yl)-phenyl Phosphite (10) by Procedure B: From 4-(imidazol-1-yl)-phenol (1.07 g, 6.66 mmol), triethylamine (2.8 mL, 20 mmol), toluene (5 mL), 2,2′-biphenyl chlorophosphite (**1**; 2.01 g, 7.00 mmol) solution in toluene (10 mL); white solid; yield: 1.25 g (50%). ^{1}H NMR ($CDCl_3$): $\delta = 7.15$–7.81 (m, 15H); ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta = 118.7$, 122.0 (d, $J_{CP} = 7.4$ Hz), 122.1, 123.2, 125.8, 129.5, 130.3, 130.5, 131.1 (d, $J_{CP} = 3.4$ Hz), 133.9, 135.8, 148.9 (d, $J_{CP} = 5.5$ Hz), 151.1 (d, $J_{CP} = 7.1$ Hz); ^{31}P{^{1}H} NMR ($CDCl_3$): $\delta = 141.6$.

2,2′-(3,3′,4,4′-Tetramethyl-6,6′-di-*tert*-butyl)-biphenyl-3-(*N,N*-dimethylamino)-phenyl Phosphite (11) by Procedure B: From 3-(*N,N*-dimethylamino)-phenol (751 mg, 5.45 mmol), triethylamine (2.27 mL, 16.35 mmol), toluene (5 mL), 2,2′-

(3,3′,4,4′-tetramethyl-6,6′-di-*tert*-butyl)-biphenyl chlorophosphite (**5**; 2.36 g, 5.64 mmol) solution in toluene (10 mL); purple oil; yield: 2.59 g (91%). ^{1}H NMR ($CDCl_3$): δ = 1.48, 1.49 [2 s, 18H, $C(CH_3)_3$], 1.84, 185, 2.25, 2.26 (4 s, 12H, CCH_3), 2.91 (s, 6H, NCH_3), 6.40–6.55 (m, 2H), 7.05–7.30 (m, 4H); ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 16.8, 17.1, 31.4, 31.9, 34.8, 35.0, 40.6, 104.6 (d, J_{CP} = 8.4 Hz), 108.0 (d, J_{CP} = 9.7 Hz), 108.2, 127.9, 128.4, 129.9, 130.6, 132.2, 132.1, 132.9, 134.4, 135.3, 138.2, 138.2, 144.9, 144.6, 151.9, 153.6 (d, J_{CP} = 10.2 Hz); ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 133.5.

Bis-(*m*-tolyl)-3-(*N,N*-dimethylamino)-phenyl Phosphite (12) by Procedure B: From 3-(*N,N*-dimethyamino)-phenol (930 mg, 6.78 mmol), triethylamine (2.83 mL, 20.3 mmol), toluene , bis-(*m*-tolyl) chlorophosphite (2.00 g, 7.12 mmol) solution in toluene (10 mL); viscous purple oil; yield: 580 mg (22%); ^{1}H NMR ($CDCl_3$): δ = 2.32 (s, 6H, CCH_3), 2.89 (s, 6H, NCH_3), 6.40–7.25 (m, 12H, CH); ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 21.5, 40.5, 104.9 (d, J_{CP} = 6.5 Hz), 108.3 (d, J_{CP} = 7.3 Hz), 108.5, 117.9 (d, J_{CP} = 7.8 Hz), 121.6 (d, J_{CP} = 6.9 Hz), 125.0, 129.4, 130.0, 139.9, 151.7 (d, J_{CP} = 3.2 Hz), 152.0, 152.8 (d, J_{CP} = 5.1 Hz); ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 128.9.

Bis-(*m*-tolyl)-4-(imidazol-1-yl)-phenyl Phosphite (13) by Procedure B: From 4-(imidazol-1-yl)-phenol (1.01 g, 6.32 mmol), triethylamine (2.63 mL, 18.96 mmol), toluene (5 mL), bis-(*m*-tolyl) chlorophosphite (1.86 g, 6.64 mmol) solution in toluene (10 mL); colorless oil; yield: 1.35 g (53%); ^{1}H NMR ($CDCl_3$): δ = 2.33 (s, 6H, CH_3), 6.85–7.80 (m, 15H, C*H*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 21.5, 117.6 (d, J_{CP} = 7.4 Hz), 118.7, 121.3 (d, J_{CP} = 6.9 Hz), 122.3 (d, J_{CP} = 6.4 Hz), 123.1, 125.4, 129.6, 130.4, 133.7, 135.8, 140.2, 150.9, 151.5 (d, J_{CP} = 4.2 Hz); ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 126.6.

Bis-(*m*-tolyl)-3-[(*N,N*-dimethylamino)-methyl]-phenyl Phosphite (14) by Procedure B: From 3-[(*N,N*-dimethylamino)-methyl]-phenol (0.616 g, 4.08 mmol), triethylamine (1.7 mL, 12.2 mmol), toluene (10 mL), bis-(*m*-tolyl) chlorophosphite (1.203 g, 4.28 mmol) solution in toluene (5 mL); colorless oil; yield: 1.526 g (94%). ^{1}H NMR ($CDCl_3$): δ = 2.28 (s, 6H, NCH_3), 2.37 (s, 6H, CCH_3), 3.45 (s, 2H, CH_2), 6.95–7.35 (m, 12H, C*H*); ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 21.4, 45.3, 63.9, 117.7 (d, J_{CP} = 6.1 Hz), 119.4 (d, J_{CP} = 7.1 Hz), 121.4 (d, J_{CP} = 7.1 Hz), 121.5 (d, J_{CP} = 7.1 Hz), 124.8, 125.0, 129.4, 129.5, 139.9, 140.8, 151.6 (d, J_{CP} = 3.3 Hz), 151.7 (d, J_{CP} = 3.3 Hz); ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 129.0.

Bis-(*m*-tolyl)-4-[(*N,N*-dimethylamino)-methyl]-phenyl Phosphite (15) by Procedure B: From 4-[(*N,N*-dimethylamino)-methyl]-phenol (0.438 g, 2.90 mmol), triethylamine (1.2 mL, 8.70 mmol), toluene (10 mL), bis-(*m*-tolyl) chlorophosphite (0.856 g, 3.05 mmol) solution in toluene (5 mL); colorless oil; yield: 0.977 g (85%); ^{1}H NMR ($CDCl_3$): δ = 2.27 (s, 6H, NCH_3), 2.36 (s, 6H, CCH_3), 3.43 (s, 2H, CH_2), 6.95–7.35 (m, 12H, C*H*); ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 21.4 (CCH_3), 45.2 (NCH_3), 63.6 (CH_2), 117.6 (d, J_{CP} = 7.2 Hz, C*H*), 120.6 (d, J_{CP} = 6.6 Hz, C*H*), 121.4 (d, J_{CP} = 7.1 Hz, C*H*), 125.0 (C*H*), 129.4 (C*H*), 130.4 (C*H*), 134.6, 139.8, 150.7 (d, J_{CP} = 2.7 Hz), 151.6 (d, J_{CP} = 3.9 Hz); ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 128.7.

2,2′-Biphenyl-4-(3-methylimidazol-1-yl)-phenyl Phosphite Tetrafluoroborate (16) by Procedure C: From 2,2′-biphenyl-4-(imidazol-1-yl)-phenyl phosphite (**10**; 398 mg, 1.06 mmol), trimethyloxonium tetrafluoroborate (157 mg, 1.06 mmol), dichloromethane (5 mL); white paste; yield: 499 mg (99%). ^{1}H NMR ($CDCl_3$): δ = 3.99 (s, 3H, CH_3), 7.15–7.57 (m, 15H); ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 36.9 (CH_3), 121.4, 122.2, 122.4 (d, J_{CP} = 7.9 Hz), 124.1, 124.6, 126.0, 129.6, 130.3, 130.6, 131.0 (d, J_{CP} = 2.8 Hz), 135.4, 148.7 (d, J_{CP} = 5.1 Hz); ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 141.3; HR-MS (LSI): *m/z* = 419.1526; calcd. for $C_{24}H_{24}N_2O_3P^+$: 419.1525.

2,2′-(3,3′,4,4′-Tetramethyl-6,6′-di-*tert*-butyl)-biphenyl-3-(*N,N,N*-trimethylammonio)-phenyl Phosphite Tetrafluoroborate (17) by Procedure C: From 2,2′-(3,3′,4,4′-tetramethyl-6,6′-di-*tert*-butyl)-biphenyl-3-(*N,N*-dimethylamino)-phenyl phosphite (**11**; 520 mg, 1.00 mmol), trimethyloxonium tetrafluoroborate (148 mg, 1.00 mmol), dichloromethane (10 mL), brown solid. ^{1}H NMR ($CDCl_3$): δ = 1.38, 1.40 [2 s, 18H, $C(CH_3)_3$], 1.81, 1.83, 2.25, 2.27 (4 s, 12H, CCH_3), 3.54 (s, 9H, NCH_3), 6.90–7.55 (m, 6H); ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 134.4.

Bis-(*m*-tolyl)-3-(*N,N,N*-trimethylammonio)-phenyl Phosphite Tetrafluoroborate (18) by Procedure C: From bis-(*m*-tolyl)-3-(*N,N*-dimethylamino)-phenyl phosphite (**12**; 290 mg, 0.76 mmol), trimethyloxonium tetrafluoroborate (112 mg, 0.76 mmol), dichloromethane (10 mL); purple product; yield: 329 mg (89%). ^{1}H NMR ($CDCl_3$): δ = 2.31 (s, 6H, CCH_3), 3.58 (s, 9H, NCH_3), 6.85–7.65 (m, 12H, C*H*); ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 21.5 (CCH_3), 57.3 (NCH_3), 112.5 (d, J_{CP} = 5.1 Hz), 115.6, 117.4 (d, J_{CP} = 7.4 Hz), 121.2 (d, J_{CP} = 6.9 Hz), 125.6, 129.5, 129.8, 132.2, 140.4, 147.8, 151.2 (d, J_{CP} = 4.1 Hz), 152.8; ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 134.4; HR-MS (LSI): *m/z* = 410.1877; calcd. for $C_{24}H_{29}NO_3P^+$: 410.1885.

Bis-(*m*-tolyl)-4-(3-methylimidazol-1-yl)-phenyl Phosphite Tetrafluoroborate (19) by Procedure C: From bis-(*m*-tolyl)-4-(imidazol-1-yl)-phenyl phosphite (**13**; 1.305 g, 3.23 mmol), trimethyloxonium tetrafluoroborate (430 mg, 2.90 mmol), dichloromethane (10 mL); colorless oil; yield: 1.47 g (99%). ^{1}H NMR ($CDCl_3$): δ = 2.32 (s, 6H, CCH_3), 4.03 (s, 3H, NCH_3), 6.85–7.55 (m, 15H, C*H*); ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 21.5, 36.7, 117.5 (d, J_{CP} = 6.9 Hz), 121.3 (d, J_{CP} = 7.0 Hz), 122.7 (d, J_{CP} = 6.4 Hz), 121.4, 123.9, 124.7, 125.5, 129.7, 130.6, 135.1, 140.3, 151.3 (d, J_{CP} = 4.6 Hz), 153.1; ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 126.3; HR-MS (LSI): *m/z* = 410.1887; calcd. for $C_{24}H_{29}NO_3P^+$: 410.1885.

Bis-(*m*-tolyl)-3-[(*N,N,N*-trimethylammonio)-methyl]-phenyl Phosphite Tetrafluoroborate (20) by Procedure C: From bis-(*m*-tolyl)-3-((*N,N*-dimethylamino)-methyl)-phenyl phosphite (**14**; 1.526 g, 3.86 mmol), dichloromethane (10 mL), a suspension of trimethyloxonium tetrafluoroborate (243 mg, 3.67 mmol) in dichloromethane (10 mL); colorless oil; yield: 1.83 g (99%). ^{1}H NMR ($CDCl_3$): δ = 2.32 (s, 6H, CCH_3), 3.04 (s, 9H, NCH_3), 4.44 (s, 2H, CH_2), 6.90–7.40 (m, 12H, C*H*); ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 127.7.

Bis-(*m*-tolyl)-4-[(*N,N,N*-trimethylammonio)-methyl]-phenyl Phosphite Tetrafluoroborate (21) by Procedure C: From bis-(*m*-tolyl)-4-[(*N,N*-dimethylamino)-methyl]-phenyl phosphite (**15**; 756 mg, 1.93 mmol), dichloromethane (5 mL), a suspension of trimethyloxonium tetrafluoroborate (272 mg, 1.84 mmol) in dichloromethane (5 mL); colorless oil; yield: 690 mg (75%). ^{1}H NMR ($CDCl_3$): δ = 2.32 (s, 6H, CCH_3), 3.06 (s, 9H, NCH_3), 4.44 (s, 2H, CH_2), 6.90–7.50 (m, 12H, C*H*); ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 127.5.

General Procedure D: 2,2′-Biphenyl-3-(*N,N,N*-trimethylammonio)-phenyl phosphite Bis(trifluoromethylsufonyl)amide (22)

A solution of dimethyl sulfate (220 mg, 1.74 mmol) and lithium bis(trifluoromethylsulfonyl)amide (500 mg, 1.74 mmol) in acetonitrile (5 mL) was slowly added to a solution of 2,2′-biphényl-3-(*N,N*-dimethylamino)-phenyl phosphite (**3**; 611 mg, 1.74 mmol) in acetonitrile (5 mL). The mixture was stirred for 72 h at room temperature and filtered. The solvent was removed under reduced pressure and a purple oil was obtained; yield: 1.11 g (99%). ^{1}H NMR (CDCl$_3$): δ = 3.47 (s, 9H, C*H*$_3$), 7.15–7.55 (m, 12H, C*H*). ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 57.4 (*C*H$_3$), 112.4 (d, J_{CP} = 5.5 Hz), 115.3, 119.9 (q, J_{CF} = 320 Hz), 122.0, 122.7 (d, J_{CP} = 8.7 Hz), 126.0, 129.6, 130.1, 130.6 (d, J_{CP} = 3.3 Hz), 132.2, 147.2, 148.6 (d, J_{CP} = 5.2 Hz), 153.1 (d, J_{CP} = 3.3 Hz); ^{31}P{^{1}H} NMR (CDCl$_3$): δ = 138.2.

Tris-[3-(*N,N,N*-dimethylamino)-phenyl] Phosphite (23) by Procedure A: From 3-(*N,N*-dimethylamino)-phenol (6.57 g, 48.00 mmol), phosphorus trichloride (2.20 g, 16.00 mmol), triethylamine (6.46 g, 64 mmol), toluene (20 mL); viscous dark oil; yield: 2.96 g (43%). ^{1}H NMR (CDCl$_3$): δ = 2.90 (s, 18H, NC*H*$_3$), 6.45–6.60 (m, 9H), 7.15 (m, 3H); ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 40.6, 105.1 (d, J_{CP} = 6.9 Hz), 108.4, 108.6 (d, J_{CP} = 7.9 Hz), 129.9, 152.0, 152.9 (d, J_{CP} = 4.6 Hz); ^{31}P{^{1}H} NMR (CDCl$_3$): δ = 129.7.

Tris-[3-(*N,N,N*-trimethylammonio)-phenyl] Phosphite Tris[bis(trifluoromethylsufonyl)amide] (24) by Procedure D: From dimethyl sulfate (231 mg, 1.83 mmol) ,tris[3-(*N,N*-dimethylamino)-phenyl] phosphite (**23**; 268 mg, 0.61 mmol), acetonitrile (10 mL) [Li][TF$_2$N] (525 mg, 1.83 mmol) in acetonitrile (10 mL); brown oil; yield: 791 mg (98%). ^{1}H NMR (CD$_3$CN): δ = 3.56 (s, 27H, NC*H*$_3$), 7.40–7.70 (m, 12H, C*H*); ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 57.0, 113.4 (d, J_{CP} = 5.5 Hz), 116.5, 119.9 (q, J_{CF} = 320 Hz), 122.5 (d, J_{CP} = 8.2 Hz), 131.9, 147.9, 151.9 (d, J_{CP} = 3.3 Hz); ^{31}P{^{1}H} NMR (CDCl$_3$): δ = 128.7.

N-(4-Hydroxybenzyl)-2-methylimidazole (25)

4-Hydroxybenzyl alcohol (5.0 g, 40.3 mmol) and 2-methylimidazole (3.31 g, 40.3 mmol) were heated at 160 °C for 1 h. The resulting solid was washed with dichloromethane to afford *N*-(4-hydroxybenzyl)-2-methylimidazole as a yellow powder; yield: 6.9 g (92%). ^{1}H NMR (DMSO-d_6): δ = 2.22 (s, 3H, C*H*$_3$), 4.97 (s, 2H, C*H*$_2$), 6.70–7.10 (m, 6H, C*H*); ^{13}C{^{1}H} NMR (DMSO-d_6): δ = 13.2 (*C*H$_3$), 48.7 (*C*H$_2$), 115.8 (*C*H), 120.5 (*C*H Im-4), 126.6 (*C*H Im-5), 128.0 (*C*CH$_2$), 129.0 (*C*H), 144.1 (*C*H Im-2), 157.3 (*C*O); anal. calcd. for $C_{11}H_{12}N_2O$: C 70.19, H 6.43, N 14.88; found: C 70.37, H 6.92, N 14.11.

***N*-(4-Hydroxybenzyl)-2,3-dimethylimidazolium Bis(trifluoromethylsufonyl)amide (26) by Procedure C:** From *N*-(4-hydroxybenzyl)-2-methylimidazole (**25**; 3.514 g, 18.7 mmol) and [Li][TF$_2$N] (5.366 g, 18.7 mmol) dissolved in acetonitrile (15 mL). Dimethyl sulfate (2.35 g, 18.7 mmol) was added rapidly and the solution stirred at room temperature for 24 h. It was filtered, concentrated and washed repeatedly with diethyl ether (8 × 20 mL). Purification through a short alumina column afforded **22** as a yellow oil; yield: 7.72 g (85%). ^{1}H NMR (CD$_3$CN): δ = 2.53 (s, 3H, CC*H*$_3$), 3.71 (s, 3H, NC*H*$_3$), 5.15 (s, 2H, C*H*$_2$), 6.85–6.90 (m, 2H, C*H*), 7.15–7.25 (m, 4H, C*H*); ^{13}C{^{1}H} NMR (CD$_3$CN): δ = 9.4 (CC*H*$_3$), 34.8 (NC*H*$_3$), 51.1 (*C*H$_2$), 115.8 (*C*H), 120.5 (q, J_{CF} = 321 Hz, *C*F$_3$), 120.7, 122.4 (*C*H Im-4,5), 124.7 (*C*CH$_2$), 129.8 (*C*H), 144.6 (*C*H Im-2), 157.5 (*C*O); anal. calcd. for $C_{14}H_{15}F_6N_3O_5S_2$: C 34.78, H 3.13, N 8.69; found: C 34.80, H 3.51, N 8.38.

N-(4-Hydroxybenzyl)-2,3-dimethylimidazolium Tetrafluoroborate (27)

N-(4-Hydroxybenzyl)-2-methylimidazole (**25**; 2.50 g, 13.3 mmol) and [Na][BF$_4$] (1.46 g, 13.3 mmol) were dissolved in acetonitrile (12 mL). Dimethyl sulfate (1.68 g, 13.3 mmol) was rapidly added and the solution stirred at room temperature for 24 h. It was filtered, concentrated and washed repeatedly with diethyl ether (8 × 20 mL). It was purified through a short alumina column to afford *N*-(4-hydroxybenzyl)-2,3-dimethylimidazolium tetrafluoroborate as a yellow oil; yield: 2.82 g (73%). ^{1}H NMR (CD$_3$CN): δ = 2.53 (s, 3H, CC*H*$_3$), 3.71 (s, 3H, NC*H*$_3$), 5.16 (s, 2H, C*H*$_2$), 6.85–6.90 (m, 2H, C*H*), 7.15–7.30 (m, 4H, C*H*); ^{13}C{^{1}H} NMR (CD$_3$CN): δ = 9.4 (CC*H*$_3$), 34.8 (NC*H*$_3$), 51.1 (*C*H$_2$), 115.8 (*C*H), 120.8, 122.4 (*C*H Im-4,5), 124.7 (*C*CH$_2$), 129.8 (*C*H), 144.6 (*C*H Im-2), 157.6 (*C*OH); anal. calcd. for $C_{12}H_{15}BF_4N_2O$: C 49.69, H 5.21, N 9.66; found: C 49.40, H 7.11, N 9.71.

Tris-4-[(2,3-dimethylimidazol-1yl)methyl]phenyl Phosphite Tris[bis(trifluoromethylsulfonyl)amide] (28) by Procedure A: From *N*-(4-hydroxybenzyl)-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)amide (6.521 g, 13.50 mmol), triethylamine (1.82 g, 18 mmol), PCl$_3$ (618 mg, 4.50 mmol), acetonitrile; yellow oil; yield: 4.37 g (66%). ^{1}H NMR (CD$_3$CN): δ = 2.54 (s, 9H, CC*H*$_3$), 3.75 (s, 9H, NC*H*$_3$), 5.27 (s, 6H, C*H*$_2$), 7.15–7.35 (m, 18H, C*H*); ^{13}C{^{1}H} NMR (CD$_3$CN): δ = 9.4 (CC*H*$_3$), 34.9 (NC*H*$_3$), 50.8 (*C*H$_2$), 120.5 (q, J_{CF} = 321 Hz, *C*F$_3$), 121.0, 121.2 (d, *J* = 7.2 Hz, *o*-*C*H), 122.7 (*C*H), 129.9 (*m*-*C*H), 130.2 (*C*CH$_2$), 144.9 (*C*H Im-2), 151.5 (d, *J* = 2.7 Hz, *C*O); ^{31}P{^{1}H} NMR (CD$_3$CN): δ = 128.00; anal. calcd. for $C_{42}H_{42}F_{18}N_9O_{15}PS_6$: C 34.13, H 2.86, N 8.53, P 2.10; found: C 34.52, H 2.74, N 8.19, P 2.43; MS (ESI): *m/z* = 1197 ($C_{40}H_{42}F_{12}N_8O_{11}PS_4^{+}$), 458 ($C_{38}H_{42}F_6N_7O_7PS_2^{2+}$), 212 ($C_{36}H_{42}N_6O_3P^{3+}$).

Tris-4-[(2,3-dimethylimidazol-1-yl)methyl]phenyl Phosphite Tetrafluoroborate (29) by Procedure A: From *N*-(4-hydroxybenzyl)-2,3-dimethylimidazolium tetrafluoroborate (1.749 g, 6.03 mmol), triethylamine (0.812 g, 8.04 mmol), PCl$_3$ (276 mg, 2.01 mmol); white powder; yield: 1.46 g (80%); ^{1}H NMR (CD$_3$CN): δ = 2.54 (s, 9H, CC*H*$_3$), 3.74 (s, 9H, NC*H*$_3$), 5.28 (s, 6H, C*H*$_2$), 7.15–7.35 (m, 18H, C*H*); ^{13}C{^{1}H} NMR (CD$_3$CN): δ = 9.4 (CC*H*$_3$), 34.9 (NC*H*$_3$), 50.7 (*C*H$_2$), 121.0 (*C*H), 121.2 (d, *J* = 6.6 Hz, *o*-*C*H), 122.6 (*C*H), 129.9 (*m*-*C*H), 130.3 (*C*CH$_2$), 144.9 (*C*H Im-2), 151.5 (d, *J* = 2.7 Hz, *C*O); ^{31}P{^{1}H} NMR (CD$_3$CN): δ = 128.15; MS (ESI): *m/z* = 362 ($C_{36}H_{42}BF_4N_6O_3P^{2+}$), 212 ($C_{36}H_{42}N_6O_3P^{3+}$).

Catalysis, Hydrocyanation Experiments and Analysis

Ni(cod)$_2$ was purchased from Strem Chemicals, stored under argon and used without further purification. Triphenyl phosphite was obtained from Aldrich and tri-*m*-tolyl phosphite was furnished by Rhodia. They were stored under argon and used as is. Anhydrous zinc chloride (99.999%, H$_2$O < 100 ppm) was purchased from Aldrich.

Catalysis Runs: In a typical reaction, 40 mg of Ni(cod)$_2$, 5 equivalents of ligand, 400 mg of 3PN (30 equivalents), 20 mg of zinc chloride (1 equivalent) and 2.0 g of ionic liquid were weighed in a Schott tube under argon. The tube was then heated up for 3 h at 70 °C with slow continuous addition of acetone cyanohydrin (24 equivalents).

Work-up: At the end of the run, tubes were cooled to room temperature and acetone (20 mL) was added. The solutions were stirred for 30 minutes, and the tubes were opened (***beware: hydrogen cyanide concentration level has to be monitored***). The reaction mixture was diluted with 10 mL of THF and butylbenzene was added as an internal standard. The solution was filtered through a Millipore filter and analyzed by gas chromatography.

Analyses: The products were quantitatively analyzed by gas chromatography on an HP 6890 chromatograph equipped with TCD detector and a Stabilwax®-DA [(poly(ethylene glycol)] column ($L = 30$ m, $\phi_{int} = 0.53$ mm, film thickness $= 1$ μm). Injector and detector temperatures were 250 °C. The temperature program was from 50 °C (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.

Statistical analysis of the DOE was performed with Minitab V13.0.[28]

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