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Lanthanide Bis[(trifluoromethyl)sulfonyl]imides as Reusable Catalysts for Mononitration of Substituted Benzenes in Ionic Liquids

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Abstract: Lanthanide bis[(trifluoromethyl)sulfonyl]imides as a kind of effective catalyst were used in quaternary ammonium ionic liquids to afford a useful new method for the nitration of substituted benzenes with concentrated nitric acid (95%) as nitrating agent. The less expensive lanthanum bis[(trifluoromethyl)sulfonyl]imide was found to be the most effective catalyst employed in the ionic liquid tributylammonium bis[(trifluoromethyl)sulfonyl]imide. The lanthanum bis[(trifluoromethyl)sulfonyl]imide/tributylammonium bis[(trifluoromethyl)sulfonyl]imide system demonstrated high catalytic activity for the nitration of halobenzenes and rendered good to excellent yields. This catalyst/ionic liquid system could be recovered by simple procedures and recycled for at least 5 times.

Keywords: catalyst recycling; electrophilic substitution; ionic liquids; lanthanides; Lewis acids

Introduction

Nitration of aromatic compounds is one of the most important fundamental and unit reactions in the chemical industry, providing very important intermediates for the preparation of various compounds.[1] Traditionally in industry and academic laboratories, nitration of aromatic compounds requires the use of mixtures of concentrated nitric acid with sulfuric acid leading to an excessive acid waste stream that was environmentally unfriendly. Therefore, various clean approaches have been developed to improve this traditional mixed-acid method.[1,2]

As an important alternative approach, the nitration of aromatic compounds in ionic liquids (ILs) has been documented in the past few years.[3–5] Among various nitrating agents, acetyl nitrate has proved to be very efficient for the nitration of halobenzenes[4]. However, from the environmental or industrial point of view, nitric acid should be the ideal nitrating reagent because it is inexpensive and only generates water as waste. Until now, only a few catalyst systems that involved the use of nitric acid as nitrating agent in ionic liquids have been reported. Handy et al.[5a] reported the ytterbium(III) triflate [Yb(OTf)$_3$] catalyzed nitration of activated aromatic compounds with 1 equiv. of nitric acid (70%) in [bmpy][NTf$_2$]. Quite recently, Qiao et al.[5b] and Fang et al.[5c] investigated the nitration of aromatic compounds with 2 or 3 equiv. of aqueous nitric acid using SO$_3$H-functional Brønsted acidic ILs as a recoverable catalyst. In their study, good yields were obtained for activated aromatic compounds, whereas the yields for halobenzenes were only moderate.

In our previous work, lanthanide bis[(trifluoromethyl)sulfonyl]imides {Ln[N(CF$_3$SO$_2$)$_2$]$_3$ or Ln(NTf$_2$)$_3$] have been developed for catalyzing diverse organic reactions in organic solvents and exhibited high catalytic activity.[6] Therefore, we envisioned that the combination of these excellent Lewis acid catalysts and environmentally benign ILs could render a clean and efficient catalyst/solvent system for the nitration of substituted benzenes with nitric acid as nitrating agent. In this research, the catalytic performance of Ln(NTf$_2$)$_3$ in ILs with quaternary ammonium cations paired with the [Tf$_2$N]$^-$ anion (Figure 1) are investigated for the nitration of toluene and halobenzenes with 95% HNO$_3$ (Scheme 1).

Results and Discussion

1,3-Dialkylimidazolium and quaternary ammonium are both common cations in ILs, but the 1,3-dialkylimidazolium cations were reported to be less stable towards the nitrating reagents[4a,4b]. Consequently, the

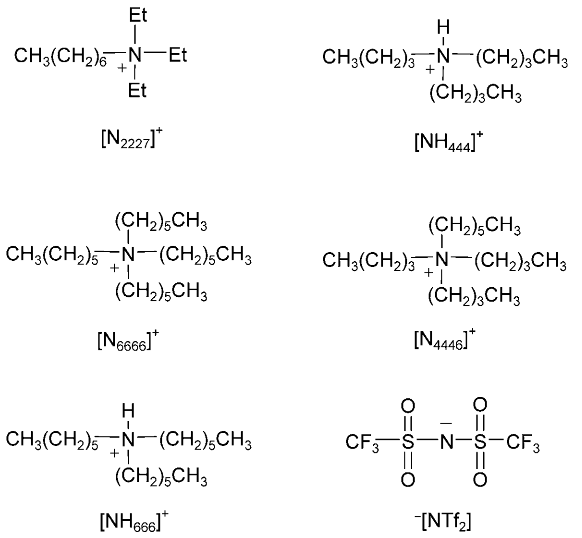
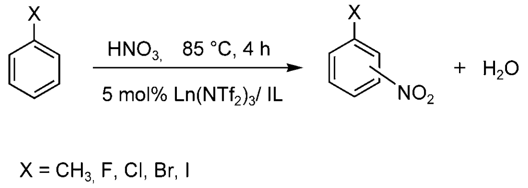


Figure 1. Cations and anion used to prepare the ILs.



Scheme 1. Nitration of substituted benzenes.

quaternary ammonium cations were selected in the present work (Figure 1).

For comparison, five structurally different ILs, such as $[N_{2227}][NTf_2]$, $[N_{4446}][NTf_2]$, $[N_{6666}][NTf_2]$, $[NH_{444}][NTf_2]$, and $[NH_{666}][NTf_2]$, were used in this work. As the Kamlet–Taft three-parameter equation[7] is a rigorous approach for the treatment of multiple interacting solvent effects, we tried first to measure the three parameters to probe the fundamental properties of five structurally different ILs. But as the Reichardt dye was confirmed not to be applicable to the polarity measurement of protic ILs,[8] only the β and π^* values were measured by using 4-nitroaniline and *N*,*N*-diethyl-4-nitroaniline in this work, and the Kamlet–Taft parameter β ,which provides a measure of a solvent's hydrogen bond-accepting basicity (HBA), was found to have a good correlation with the results of the nitration of toluene. As shown in Table 1, the values of β varied with the structural transformation of quaternary ammonium cations and in an order of $[NH_{444}][NTf_2] < [NH_{666}][NTf_2] < [N_{2227}][NTf_2] < [N_{4446}][NTf_2] < [N_{6666}][NTf_2]$. This result implies that the protic ionic liquid has a lower tendency for accepting hydrogen bonds than the aprotic ones. Consequently, the active proton could be less restrained in protic ILs and might exhibit a higher catalytic activity in reaction.

Table 1. Kamlet–Taft parameter β for ILs at 55 °C.

Ionic liquid	β
$[NH_{444}][NTf_2]$	0.200
$[NH_{666}][NTf_2]$	0.254
$[N_{2227}][NTf_2]$	0.299
$[N_{4446}][NTf_2]$	0.321
$[N_{6666}][NTf_2]$	0.390

On the other hand, it has been reported that the halochromism of azo dyes could be used in the measurement of acid strength of Lewis catalysts in organic solvents:[9] Unfortunately, the attempt to investigate the Lewis acidity of $Ln(NTf_2)_3$ in ILs also failed. For example, in the case of $[NH_{444}][NTf_2]$ it was difficult to evaluate the difference of Lewis acidity of the metal cations (Yb^{3+}, Sm^{3+}, La^{3+}) because the protic ionic liquid $[NH_{444}][NTf_2]$ itself had a strong interaction with the azo dye, 2,4,4′,6-tetramethoxyazobenzene.[9c]

The nitration of toluene was selected as the model reaction to optimize the reaction conditions. Our initial effort aimed to use aqueous nitric acid (68%) as the nitrating reagent in ILs, but the results obtained were not satisfying. In an attempt to improve the reaction, concentrated nitric acid (95%) was found to be a suitable nitrating agent.

Parallel experiments of the nitration of toluene were carried out with the foresaid five structurally different ionic liquids. The reactions were conducted at 85 °C for certain times (Table 2), and a stoichiometric amount of 95% HNO_3 was employed. The products were analyzed by gas chromatography.

As can be seen from Table 2, the nitration of toluene is a somewhat self-catalyzing reaction in neutral ILs when nitric acid was used as nitrating agent in the absence of any catalyst. However, the yields of nitrotoluenes obtained were in the range 35.7 to 63.9%, manifesting that the structure of the cation of ILs has a great effect on the nitration of aromatic compounds.[4a] The tendency for increases in the yield of nitrotoluenes was approximately coincident with the decrease of the β value of the ILs (Table 1). The highest product yield was observed in the protic quaternary ammonium ionic liquid $[NH_{444}][NTf_2]$ and after 24 h a 75.9% of yield of nitrotoluenes could be achieved. We inferred that it might be attributable to the higher Brønsted acidity and polarity of $[NH_{444}][NTf_2]$.

Different metal cations (La^{3+}, Sm^{3+}, Yb^{3+}, In^{3+}, Cu^{2+}) paired with the $[Tf_2N]^-$ anion were investigated as Lewis catalysts for the nitration of toluene. All these metal bis[(trifluoromethyl)sulfonyl]imides could catalyze the nitration and achieve nearly the same level of equilibrium in different ILs. When using 2 mol% of catalyst, nitrotoluenes were obtained in the yields ranging from 70.6 to 81.7% with a *para/*

Table 2. Nitration of toluene in different ILs.[a]

Entry	Ionic liquid	Time [h]	Yield [%][b]	Product distribution [%][b]			*para/ortho*[b]
				ortho	*meta*	*para*	
1	$[N_{6666}][NTf_2]$	4	35.7	54.0	3.7	4.23	0.8
2	$[N_{4446}][NTf_2]$	4	39.6	56.0	2.9	41.1	0.7
3	$[N_{2227}][NTf_2]$	4	54.1	54.0	3.1	42.9	0.8
4	$[NH_{666}][NTf_2]$	4	52.0	52.9	4.2	42.8	0.8
5	$[NH_{444}][NTf_2]$	4	63.9	53.6	2.9	43.5	0.8
6	$[NH_{444}][NTf_2]$	24	75.9	53.8	3.1	43.2	0.8

[a] *Reaction conditions:* 3 mmol toluene, 3 mmol 95% nitric acid, ILs 5 mmol, 85 °C.

[b] By quantitative GC analysis.

Table 3. Nitration of toluene in different ILs catalyzed by various catalyst.[a]

Entry	Ionic liquid	Catalyst	Yield [%][b]	Product distribution [%][b]			*para/ortho*[b]
				ortho	*meta*	*para*	
1	$[NH_{444}][NTf_2]$	$La(NTf_2)_3$	81.7	54.0	3.1	42.9	0.8
2			89.8[c]	52.8	3.0	42.2	0.8
3	$[NH_{444}][NTf_2]$	$Sm(NTf_2)_3$	78.8	53.2	3.5	43.3	0.8
4	$[NH_{444}][NTf_2]$	$Yb(NTf_2)_3$	75.7	53.7	3.1	43.2	0.8
5	$[N_{4446}][NTf_2]$	$La(NTf_2)_3$	72.0	53.2	2.8	44.0	0.8
6	$[N_{4446}][NTf_2]$	$Sm(NTf_2)_3$	76.2	52.9	2.8	44.4	0.8
7	$[N_{4446}][NTf_2]$	$Yb(NTf_2)_3$	76.6	53.0	2.8	44.2	0.8
8	$[N_{4446}][NTf_2]$	$In(NTf_2)_3$	71.3	53.1	2.9	44.0	0.8
9	$[N_{4446}][NTf_2]$	$Cu(NTf_2)_2$	70.6	53.3	2.9	43.8	0.8
10	$[N_{2227}][NTf_2]$	$La(NTf_2)_3$	78.8	53.4	3.0	43.7	0.8
11	$[N_{6666}][NTf_2]$	$La(NTf_2)_3$	76.9	53.7	2.9	43.4	0.8
12	$[NH_{666}][NTf_2]$	$La(NTf_2)_3$	76.9	52.9	3.0	44.1	0.8

[a] *Reaction conditions:* 3 mmol toluene, 3 mmol 95% nitric acid, ILs 5 mmol, 2 mol% catalyst, 85 °C, reaction time 4 h.

[b] By quantitative GC analysis.

[c] Result of 24 h.

ortho ratio of 0.8. The *para/ortho* ratios of the products were almost the same in the different ILs, regardless of whether the reactions were carried out with or without catalysts (Table 2) and the ratios were consistent with obtained those using HNO_3/Ac_2O as nitrating agent in ILs.[4] The results of Table 3 demonstrate that $La(NTf_2)_3$ was the most effective catalyst for accelerating the nitration of toluene, especially in $[NH_{444}][NTf_2]$ with 1 equiv. of 95% nitric acid. Further extending the reaction time to 24 h only led to a limited increase of yield in the $La(NTf_2)_3/[NH_{444}][NTf_2]$ system (entry 2 in Table 3) and this suggests that the nitration reactions approximately reach the equilibrium after 4 h under the experimental conditions. On the other hand, as $[Tf_2N]^-$ is a weakly coordinating organic anion, the catalytic activity order of the Lewis catalysts with the $[Tf_2N]^-$ anion normally is $Yb^{3+} > Sm^{3+} > La^{3+}$ in organic solvents, but in ILs (Table 3) this trend is not followed and further investigation is underway.

The temperature effect on the nitration of toluene was also studied. The reaction was carried out in the presence of 2 mol% catalyst, using 1 equiv. of nitric acid and the reaction temperatures were varied from 60 °C to 100 °C. The results are presented in Figure 2. It was observed that yield of nitrotoluenes jumped rapidly from 60.4 to 81.7% while increasing the reaction temperature from 60 °C to 85 °C. However, when the temperature exceeded 85 °C the yield gradually decreased. From both the results and the red-brown nitrogen dioxide that observed in the experiment, we concluded that the nitric acid probably decomposed at the higher temperature.

The results of the nitration of toluene using nitric acid with different dosages of catalyst $La(NTf_2)_3$ in $[NH_{444}][NTf_2]$ are given in Table 4. We found that increasing the catalyst loading brought about a marginal increase of the yield. Even when using only 1 mol% catalyst with 1 equiv. of 95% HNO_3 the reaction equilibrium was almost attained after 4 h. However, considering that halobenzes were much more deactivated than toluene, 5 mol% of catalyst was used for further study.

The effect of the molar ratio of nitric acid to toluene on the nitration reaction at 85 °C over 5 mol% catalyst was investigated and the result are shown in

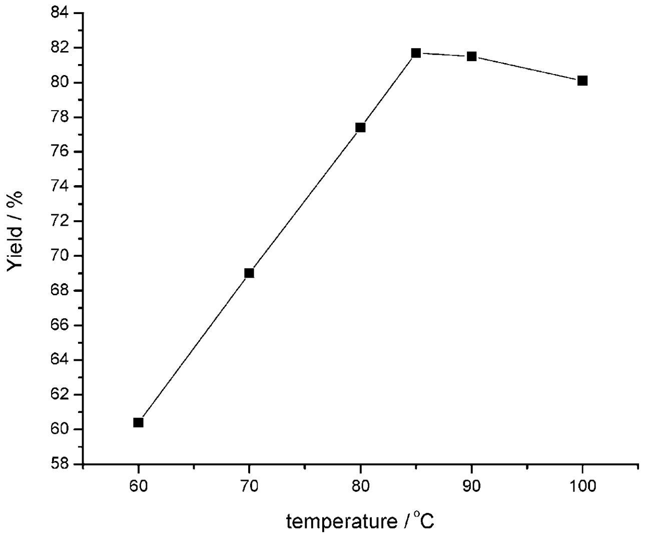


Figure 2. The effect of temperature on the nitration of toluene. Toluene and HNO_3 (95%) = 3 mmol; reaction time 4 h; 2 mol% $La(NTf_2)_3$ as catalyst; yields were determined by quantitative GC analysis.

Table 4. Nitration of toluene catalyzed by $La(NTf_2)_3$ in $[NH_{444}][NTf_2]$ system with different dosages of catalyst.[a]

Entry	HNO_3:toluene molar ratio	Amount of catalyst [mol%]	Yield [%][b]
1	1:1	0	63.9
2	1:1	1	80.6
3	1:1	2	81.7
4	1:1	3	82.4
5	1:1	5	83.3

[a] *Reaction conditions:* 3 mmol toluene, 3 mmol 95% nitric acid, ILs 5 mmol, 85 °C.

[b] By quantitative GC analysis.

Table 5. Nitration of toluene catalyzed by $La(NTf_2)_3$ in $[NH_{444}][NTf_2]$ system with different dosages of nitric acid.[a]

Entry	HNO_3:toluene molar ratio	Yield [%][b]
1	1:1	83.3
2	1.1:1	84.9
3	1.2:1	91.3
4	1.3:1	96.7

[a] *Reaction conditions:* 3 mmol toluene, IL 5 mmol, 85 °C, 5 mol% $La(NTf_2)_3$ as catalyst, reaction time 4 h.

[b] By quantitative GC analysis.

Table 5. Clearly, the molar ratio of the nitric acid to toluene has a conspicuous positive effect on the nitration of toluene in $[NH_{444}][NTf_2]$. With the increase of molar ratio of 95% nitric acid, the yield of nitrotoluenes was gradually enhanced and an excellent yield (96.7%) of mononitrotoluenes was obtained by using only 1.3 equiv. of HNO_3 (entry 4 in Table 5).

The nitration of halobenzenes was further studied and the results are shown in Table 6. We can see that the $La(NTf_2)_3/[NH_{444}][NTf_2]$ system demonstrated very good catalytic activity for deactivated benzenes at 5 mol% catalyst loading with 1.3 equiv. of 95% HNO_3. Extending the reaction time from 8 to 24 h, greatly increased the yield of nitrohalobenzenes. $La(NTf_2)_3$ could catalyze the nitration of halobenzenes affording good to excellent yield (78.4–94.3%) after 24 h. Furthermore, it can be seen that the *para*-selectivity of the nitration of halobenzenes gradually decreased from fluorobenzene to iodobenzene along with the decrease of electron affinity of the halogen atoms. This indicated that a correlation exists between the degree of *para*-selectivity and the ability of electron-withdrawing halogen atoms to induce an electrostatic attraction between substrate and $[NH_{444}][NTf_2]$.[5b] For the nitration of fluorobenzene a 94.3% of yield could be achieved and the reaction was highly *para*-selective. Notably, the $La(NTf_2)_3/[NH_{444}][NTf_2]$ system was very effective even for the nitration of iodobenzene,[4b] an 87.6% of yield of nitroiodobenzenes could be attained by using 5 mol% of catalyst and 1.3 equiv. of 95% HNO_3.

The reusability is one of the important properties of catalytic systems. The recycling performance of $La(NTf_2)_3/[NH_{444}][NTf_2]$ system was investigated by the nitration of toluene under identical experimental conditions. The recovered catalyst with IL was then directly used for the next catalytic reaction, and no further purification was done. As revealed in Table 7, the $La(NTf_2)_3/[NH_{444}][NTf_2]$ catalyst system could be recovered in high yields during each cycle and reused for at least five times, still providing very good yield and the similar selectivity as at the beginning. So this means that the ionic liquid $[NH_{444}][NTf_2]$ might be an effective solvent for lanthanide-mediated organic reactions[10].

It is well known that aromatic nitration is a classical electrophilic substitution involving the attack by a nitronium ion (NO_2^+), a nitrate species generally produced with a proton. Waller et al. assumed a mode producing nitronium ion in the presence of lanthanide triflate: hydrated trivalent lanthanide can bind nitric acid to its center and then promote the release of an active proton to produce the requisite active nitronium ion by protonation of nitric acid.[2b] Similarly, here we present a mechanism for the formation of nitronium ion in the presence of $Ln(NTf_2)_3$ in quaternary ammonium ILs (Scheme 2).

The differences of catalytic activity among metal bis[(trifluoromethyl)sulfonyl]imides may mainly depend on the differences of solvation of metal cations in ILs.[10b] It is obvious that the protic ionic liquid

Table 6. Nitration of halobenzenes catalyzed by $La(NTf_2)_3$ in $[NH_{444}][NTf_2]$ system.[a]

Entry	Arene	Time [h]	Yield [%][b]	Product distribution [%][b] *ortho*	*meta*	*para*	*para/ortho*[b]
1	C_6H_5F	8	81.4	10.9	–	89.1	8.2
2		24	94.3 (91.0)[c]	10.4	–	89.6	8.6
3	C_6H_5Cl	8	67.9	26.5	–	73.5	2.8
4		24	82.5	25.8	–	74.2	2.9
5	C_6H_5Br	8	66.2	31.1	–	68.9	2.2
6		24	78.4	31.7	–	68.3	2.2
7	C_6H_5I	8	77.4 (76.7)[c]	38.8	–	61.7	1.6
8		24	87.6	37.9	–	62.1	1.6
9	C_6H_5 CH_3	4	96.7 (91.0)[c]	53.3	2.0	44.1	0.8

[a] *Reaction conditions:* 3 mmol halobenzene, 3.9 mmol 95% nitric acid, 5 mol% catalyst, IL 5 mmol, 85 °C.
[b] By quantitative GC analysis
[c] Isolated yields in parenthesis.

Table 7. Recycled $La(NTf_2)_3/[NH_{444}][NTf_2]$ for nitration of toluene.[a]

Entry	Yield [%][b]	Product distribution [%][b] *ortho*	*meta*	*para*	Recovery ratio [%][c]
1	96.7	53.3	2.0	44.1	–
2	96.8	53.4	2.9	43.7	0.99
3	95.0	53.5	2.8	43.7	0.99
4	94.6	53.8	2.9	43.3	0.99
5	93.1	53.5	3.0	43.5	0.98

[a] *Reaction conditions:* 3 mmol toluene, 3.9 mmol nitric acid (95%), 5 mol% catalyst, IL 5 mmol, 85 °C, 4 h.
[b] By quantitative GC analysis.
[c] The weight ratio of recovered and intial IL.

$$\text{IL-Ln(NTf}_2)_3 \xrightleftharpoons{+x\,H_2O} \text{IL-Ln[(H}_2\text{O)}_x\text{(NTf}_2)_3]$$

$$\text{IL-Ln[(H}_2\text{O)}_x\text{(NTf}_2)_3] \rightleftharpoons [\text{IL-Ln(H}_2\text{O)}_x]^{3+} + \text{IL-3NTf}_2^-$$

$$\text{IL} \xrightarrow{HNO_3} \text{IL-HNO}_3$$

$$[\text{IL-Ln(H}_2\text{O)}_x]^{3+} + \text{IL-HNO}_3 \rightleftharpoons [\text{IL-Ln(H}_2\text{O)}_x\text{(HNO}_3)]^{3+}$$

$$[\text{IL-Ln(H}_2\text{O)}_x\text{(HNO}_3)]^{3+} \rightleftharpoons [\text{IL-Ln((H}_2\text{O)}_x\text{(NO}_3)]^{2+} + \text{IL-H}^+$$

$$\text{IL-HNO}_3 + \text{IL-H}^+ \rightleftharpoons [\text{IL-NO}_2]^+ + \text{IL-H}_2\text{O}$$

Scheme 2. Proposed mechanism for the formation of NO_2^+.

will favor the liberation of a proton to form the electrophilic nitronium ion. At the same time, this mechanism mode can also illustrate the unchangeable distribution of nitrated products, since free NO_2^+ is not regioselective while attacking aromatic rings.

Conclusions

In conclusion, we have developed a novel Lewis acid catalyst/solvent system that afforded a useful new method for the nitration of aromatic compounds with 95% nitric acid as nitrating agent. The less expensive $La(NTf_2)_3$ was found to be the most effective catalyst employed in $[NH_{444}][NTf_2]$ for the nitration of halobenzenes and good to excellent yield*s* could be obtained. The catalyst/solvent system could be recovered by simple procedures and recycled at least 5 times.

Experimental Section

General

All chemicals (AR grade) were commercially available and pretreated before used. ^{1}H NMR and ^{19}F NMR spectra were recorded on a Bruker AV400 spectrometer. UV- vis spectra were obtained using a Shimadzu UV-2550 spectrometer. The compositions of the nitration products were analyzed by using a GC 9790 gas chromatograph (FULI Company) equipped with a 30QC3/AC225 capillary column (SGE Company) and a flame ionization detector using temperature programmed from 60 to 220 °C.

Preparation of Metal Bis[(trifluoromethyl)sulfonyl]-imides

The syntheses of metal bis[(trifluoromethyl)sulfonyl]imides followed procedures reported by Nie et al.[6a,d] Lanthanide bis[(trifluoromethyl)sulfonyl]imides were prepared almost quantitatively by the reactions of $HNTf_2$ with stoichiometric amounts of corresponding metal oxide in aqueous solution. Colorless solids were obtained after filtration, evaporation of the aqueous solution and drying under vacuum at 100 °C overnight.

Preparations of Tetraalkylammonium (R_4N^+) Based ILs

The used tetraalkylammonium (R_4N^+) Based ILs were synthesized by two-step reactions according to the literature[11] (Figure 1).

Preparations of Trialkylammonium (R_3NH^+) Based ILs

The trialkylammonium based ILs were synthesized through neutralization of trialkylamine with stoichiometric amounts of $HNTf_2$ in distilled water. The structures of ILs were characterized by ^1H NMR and ^{19}F NMR (Figure 1). All of the ILs were dried under vacuum in 90 °C overnight before use.

Tributylammonium bis[(trifluoromethyl)sulfonyl]imide $[NH_{444}][NTf_2]$: ^1H NMR ($CDCl_3$, TMS): $\delta = 6.86$ (broad peak, 1 H, -NH), 3.09 (m, 6 H, -*N*-CH_2-), 1.67 (m, 6 H, -CH_2-CH_2CH_3), 1.39 (m, 6 H, -CH_2-CH_3), 0.99 (m, 9 H, -CH_3); ^{19}F NMR ($CDCl_3$, CCl_3F): $\delta = -78.89$ (s).

Trihexylammonium bis[(trifluoromethyl)sulfonyl]imide $[NH_{666}][NTf_2]$: ^1H NMR ($CDCl_3$, TMS): $\delta = 6.60$ (s, 1 H, -NH), 3.03 (m, 6 H, -*N*-CH_2-), 1.66 (s, 6 H, -CH_2-$C_3H_6CH_3$), 1.33 (s,18 H, -C_3H_6-CH_3), 0.90 (t, $J = 5.8$ Hz, 9 H, -CH_3); ^{19}F NMR ($CDCl_3$, CCl_3F): $\delta = -78.85$ (s).

Measurement of Kamlet–Taft Parameter β of ILs

4-Nitroaniline and *N,N*-diethyl-4-nitroaniline were dissolved respectively in ILs in a concentration range 10^{-5} to 10^{-4} mol/L and the ILs were dried under vacuum at 80 °C for 12 h before use. The sample was loaded into a dry cuvette in a glove box and the cuvette was then capped and sealed. The UV-vis absorbance was measured and fitted with a Gaussian profile according to literature procedures.[12] The temperature was controlled with an SYC temperature controller (±0.1 °C).

Measurements of the Lewis Acidity

Typically, 1.0 mL of IL, 1.0 mL of nitromethane solutions of the $Ln(NTf_2)_3$ (0.15 $\mu mol\,mL^{-1}$) and 0.1 mL of nitromethane solutions of the 2,4,4′,6-tetramethoxyazobenzene[9b] (0.3 $\mu mol\,mL^{-1}$) were mixed. The resultant ILs were dried under vacuum at 80 °C for 12 h before use. A sample was loaded into a dry cuvette in a glove box and the cuvette was then capped and sealed. The UV-vis determination was carried out in the range of 350–700 nm.

Catalytic Reactions

Typically, 5 mmol of IL with catalyst were dried under vacuum for 1 h before the reaction. 0.32 mL of toluene (3.0 mmol) were added into the IL, followed by dropwise addition of 0.13 mL of 95% nitric acid (3.0 mmol). The reaction mixture was stirred at 85 °C for several hours. After stopped the reaction, the product was extracted with a mixture of hexane and ether. The combined organic extracts was washed with saturated $NaHCO_3$ solution, dried over $MgSO_4$, and analyzed by gas chromatography using the internal standard method (*n*-decane, 1.54 mmol).

In order to determine the isolated yields of nitration products, we removed the solvent under reduced pressure; the residue was purified with silica gel (200–300 mesh) column chromatography (eluent: petroleum ether/EtOAc = 10/1). All products were identified by comparing their melting points and ^1H NMR spectra with those of standard samples.

The catalyst/ionic liquid layer was directly reused for the next run if necessary after it was heated to 100 °C for 4 h under vacuum (0.1 Torr).

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References

[1] a) G. A. Olah, R. Malhotra, S. C. Narang, *Nitration, Methods and Mechanisms*, Wiley-VCH, New York, **1989**; b) K. Schofield, *Aromatic Nitration*, Cambridge University Press, Cambridge, **1980**; c) R. Taylor, *Electrophilic Aromatic Substitution*, John Wiley & Sons, Chichester, **1990**.

[2] a) F. J. Waller, A. G. M. Barrett, D. C. Braddock, D. Ramparsad, *Chem. Commun.* **1997**, *6*, 613–614; b) F. J. Waller, A. G. M. Barrett, D. C. Braddock, D. Ramparsad, *Tetrahedron Lett.* **1998**, *39*, 641–1642; c) F. J. Waller, A. G. M. Barrett, D. C. Braddock, R. M. McKinnell, D. Ramparsad, *J. Chem. Soc. Perkin Trans. 1* **1999**, 867–872; d) S. Kobayashi, M. Sugiura, H. Kitagawa, W. L. W. Lam, *Chem. Rev.* **2002**, *102*, 2227–2302; e) M. Shi, S. C. Cui, *Chem. Commun.* **2002**, *9*, 994–995.

[3] a) T. Welton, *Chem. Rev.* **1999**, *99*, 2071–2083; b) P. Wasserscheid, T. Welton, *Ionic Liquids in Synthesis* Wiley-VCH, Weiheim, **2002**, pp 191–192; c) K. K. Laali, V. J. Gettwert, *J. Org. Chem.* **2001**, *66*, 35–40; d) R. Rajagopal, K. V. Srinivasan, *Synth. Commun.* **2003**, *33*, 961–966; e) G. B. Cheng, X. L. Duan, X. F. Qi, C. Lu, *Catal. Commun.* **2008**, *10*, 201–204.

[4] a) N. L. Lancaster, V. Llopis-Mestre, *Chem. Commun.* **2003**, *22*, 2812–2813; b) K. Smith, S. F. Liu, A. G. El-Hiti, *Ind. Eng. Chem. Res.* **2005**, *44*, 8611–8615; c) B. D. Powell, G. L. Powell C. P. Reeves, *Lett. Org. Chem.* **2005**, 550–553; d) S. J. Wang, Z. Y. Sun, J. Nie, *Chin. J. Chem.* **2008**, *26*, 2256–2260.

[5] a) S. T. Handy, C. R. Egrie, *ACS Symp. Ser.* **2002**, *818*, 134–146; b) K. Qiao, C. Yokoyama. *Chem. Lett.* **2004**, *33*, 808–809; c) D. Fang, Q. R. Shi, J. Cheng, K. Gong, Z. L. Liu, *Appl. Catal. A: Gen.* **2008**, *345*, 158–163.

[6] a) J. Nie, H. Kobayashi, T. Sonoda, *Catal. Today* **1997**, *36*, 81–84; b) J. Nie, J. Xu, G. Y. Zhou, *J. Chem. Res. Syn.* **1999**, *7*, 446–447; c) Y. B. Yuan, J. Nie, Z. B. Zhang, S. J. Wang, *Appl. Catal. A: Gen.* **2005**, *295*, 170–176; d) Y. B. Yuan, J. Nie, S. J. Wang, Z. B. Zhang, *Chin. J. Org. Chem.* **2005**, *25*, 394–398.

[7] a) M. J. Kamlet, R. W. Taft, *J. Am. Chem. Soc.* **1976**, *98*, 377–383; b) R. W. Taft, M. J. Kamlet, *J. Am. Chem. Soc.* **1976**, *98*, 2886–2894; c) M. J. Kamlet, J. L. Abboud, M. H. Abraham, R. W. Taft, *J. Org. Chem.* **1983**, *48*, 2877–2887.

[8] W. Ogihara, T. Aoyama, H. Ohno, *Chem. Lett.* **2004**, *33*, 1414–1415.

[9] a) C. Reichardt, *Chem. Soc. Rev.* **1992**, *21*, 147–153; b) H. Iwamoto, H. Kobayashi, P. Murer, T. Sonoda, H. Zollinger, *Bull. Chem. Soc. Jpn.* **1993**, *66*, 2590–2602; c) H. Kobayashi, K. Fujiki, A. Nagira, J. Nie, A. Sonoda, T. Sonoda, *Rep. Inst. Adv. Mater. Study* **1993**, *7*, 103–113.

[10] a) K. Mikami, Y. Mikami, H. Matsuzawa, Y. Matsumoto, J. Nishikido, F. Yamamoto, N. Nakajima, *Tetrahedron* **2002**, *58*, 4015–4021; b) K. Binnemans, *Chem. Rev.* **2007**, *107*, 2592–2614.

[11] J. Z. Sun, D. R. MacFarlane, *Ionics* **1997**, *3*, 356–362.

[12] J. M. Lee, S. Ruckes, J. M. Prausnitz, *J. Phys. Chem. B* **2008**, *112*, 1473–1476.