JOC Article
pubs.acs.org/joc

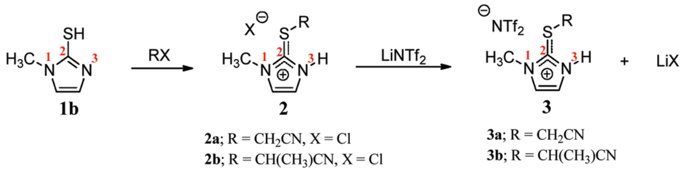
Nitrile Functionalized Methimazole-Based Ionic Liquids

Amal I. Siriwardana,[*,†,‡] Angel A. J. Torriero,[†,‡] Juan M. Reyna-González,[†]
Iko M. Burgar,[§] Noel F. Dunlop,[⊥] Alan M. Bond,[*,†,‡] Glen B. Deacon,[†] and
Douglas R. MacFarlane[†,‡]

[†]*School of Chemistry, Monash University, Clayton, 3800, VIC, Australia,* [‡]*ARC Special Research Centre for Green Chemistry, Monash University, Clayton, 3800, VIC, Australia,* [§]*CMSE Division, CSIRO, Clayton, 3800, VIC, Australia, and* [⊥]*Orica Ltd, 1 Nicholson St., Melbourne, VIC 3000, Australia*

amal.siriwardana@monash.edu; alan.bond@monash.edu

Received July 24, 2010



The alkylation reaction of 2-mercapto-1-methylimidazole **1b** with 2-chloroacetonitrile and 2-chloropropionitrile produced *S*-alkyl methimazole chlorides **2a** and **2b** which were subjected to anion metathesis with lithium bis(trifluoromethanesulfonyl)amide, $LiNTf_2$, to afford nitrile functionalized methimazole-based room temperature ionic liquids **3a** and **3b** in 94% and 89% yields, respectively. Ionic liquids **3a** and **3b** have reasonably wide electrochemical windows. The efficient extraction of Ag^+ from aqueous media into **3a** and **3b** is also reported.

1. Introduction

In recent years, ionic liquids (ILs) have attracted a great deal of interest as potential replacements for volatile organic solvents in synthetic and especially in catalytic applications[1] due, in some cases, to their very low vapor pressure, wide liquid temperature range, good ionic conductivity, excellent electrochemical properties, and potential as solvents for liquid−liquid extraction.[2,3] While all of these properties are not necessarily always present, a number of well-characterized ionic liquids exhibiting many of them are now available. The salts are defined as functionalized ionic liquids when the functional group is covalently tethered to (a) the cation, (b) the anion, or (c) a zwitterionic form of the salt. It is typically the cation that bears the reactive moiety. In fact, instances in which the anion comprises the active constituent are few.[4] Recently, a number of low-melting salts of imidazolium cation with functional groups, such as amine[5,6] and amide,[7] sulfonic acid,[8] ether and alcohol,[9] carboxylic[10] and thiourea,[5] and phosphine functionalities,[11] as well as fluoro chains[12] attached to the alkyl side chains of imidazolium cation, have been developed (Figure 1).

One of the attractive features of functionalized ILs is that both the cationic and anionic components can be varied and modified, so that a liquid can be tailored to a specific application such as catalysis, organic synthesis, extraction, construction of nanostructure materials, and ion conductive materials.[13] The incorporation of functional groups can impart a particular capability to the ionic liquids, enhancing catalytic stability and reducing catalytic leaching.[14]

---

(1) Davis, J. H.; Fox, P. A. *Chem. Commun.* **2003**, 1209–1212.

(2) Welton, T. *Chem. Rev.* **1999**, *99*, 2071–2083.

(3) Wasserscheid, P.; Keim, W. *Angew. Chem., Int. Ed.* **2000**, *39*, 3773–3789.

(4) Lee, S. G. *Chem. Commun.* **2006**, 1049–1063.

(5) Visser, A. E.; Swatloski, R. P.; Reichert, W. M.; Mayton, R.; Sheff, S.; Wierzbicki, A.; Davis, J. H.; Rogers, R. D. *Chem. Commun.* **2001**, 135–136.

(6) Visser, A. E.; Swatloski, R. P.; Reichert, W. M.; Mayton, R.; Sheff, S.; Wierzbicki, A.; Davis, J. H.; Rogers, R. D. *Environ. Sci. Technol.* **2002**, *36*, 2523–2529.

(7) Lee, K. M.; Lee, Y. T.; Lin, I. J. B. *J. Mater. Chem.* **2003**, *13*, 1079–1084.

(8) Cole, A. C.; Jensen, J. L.; Ntai, I.; Tran, K. L. T.; Weaver, K. J.; Forbes, D. C.; Davis, J. H. *J. Am. Chem. Soc.* **2002**, *124*, 5962–5963.

(9) Branco, L. C.; Rosa, J. N.; Ramos, J. J. M.; Afonso, C. A. M. *Chem.—Eur. J.* **2002**, *8*, 3671–3677.

(10) Holbrey, J. D.; Reichert, W. M.; Tkatchenko, I.; Bouajila, E.; Walter, O.; Tommasi, I.; Rogers, R. D. *Chem. Commun.* **2003**, 28–29.

(11) Bronger, R. P. J.; Silva, S. M.; Kamer, P. C. J.; van Leeuwen, P. *Chem. Commun.* **2002**, 3044–3045.

(12) Merrigan, T. L.; Bates, E. D.; Dorman, S. C.; Davis, J. H. *Chem. Commun.* **2000**, 2051–2052.

(13) Davis, J. H. *Chem. Lett.* **2004**, *33*, 1072–1077.

(14) Zhao, D. B.; Fei, Z. F.; Geldbach, T. J.; Scopelliti, R.; Dyson, P. J. *J. Am. Chem. Soc.* **2004**, *126*, 15876–15882.

DOI: 10.1021/jo101449q

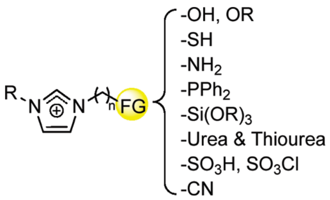


FIGURE 1. Examples of functional groups covalently tethered to the imidazolium cation.

Development of multiphasic systems for immobilizing homogeneous catalysts to facilitate the separation and subsequent reuse of catalysts has become very important in organometallic chemistry.[15] In this context, the use of ionic liquids to immobilize homogeneous metallic catalysts[16,17] based on Rh, Co, Fe, Cu, Ni, Pd, and lithium and potassium ions has been one of the most fruitful areas of ionic liquid research. To minimize catalytic leaching, functionalized heterocyclic cations are incorporated into the catalysts via ligands, catalyst precursors, and support materials, resulting in enhancement of the catalytic reusability, as well as in some cases enhanced activity in conventional ionic liquids.[4]

Ligands containing donor atoms such as N or S have been explored for the extraction of heavy metals through the use of thioether,[18] thiourea,[5] and urea[19] functional groups. These tunable ILs or designer solvents exhibit high extraction efficiencies when used as an extracting phase alone or when doped into nonspecific 1-alkyl-3-methylimidazolium-based ILs.[6] These biphasic extractions mainly focused on the removal of metal ions from the water phase into an ionic liquid phase. Functional groups which are covalently tethered to the imidazolium cation, such as SH, COOH, NH_2, OH, and alkoxysilyl groups, have been used for many catalytic reactions as immobilization solvents, but their ability to coordinate to the catalytic intermediate is somewhat limited.[15]

The nitrile group represents a potential donor to main group metals and transition metals. An attractive feature of nitrile functionalized ionic liquids is the possibility that the nitrile group might stabilize catalytic species, as CH_3CN is known to do.[20] However, very few ILs having nitrile functionality are known. Highly efficient and convenient syntheses of new nitrile functionalized ionic liquids are required to assess their usefulness and therefore broaden their applications.

Methimazole **1b** (2-mercapto-1-methylimidazole) is a molecule of considerable current interest in the fields of inorganic and organometallic chemistry, in which the sulfur atom acts as a soft donor toward a variety of transition metals.[21] In the context of ionic liquids, the importance of methimazole lies with its direct analogy to the ubiquitous 1-methylimidazole **1a**, with the distinction that the somewhat acidic C2 proton is replaced by a thiol linkage.

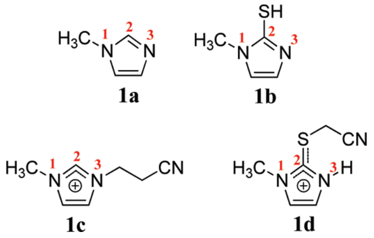


FIGURE 2. Nitrile functional group covalently tethered to the imidazolium (**1c**) and methimazolium (**1d**) cations.

So far, most nitrile functionalized ILs incorporate functionality into a branch appended to the cation, especially the imidazolium cation, **1c**.[15] Introducing nitrile functionality onto the sulfur leaves a free proton on one of the ring nitrogen atoms. This type of ILs is expected to be highly useful in metal extraction processes of biphasic systems. In particular, the acidic proton may be displaced and hence allow a supporting interaction through the nitrile group. Direct coordination with **1d** also may make extraction efficient (Figure 2). Recently, we reported the synthesis of methimazole-based ILs[21,22] and showed they could be used for extraction of Cu^{2+} ions from aqueous media (see section 3.4 below). However, no functionalized methimazolium-based ionic liquids have yet been reported. In this paper, we describe the synthesis and characterization of two nitrile functionalized ionic liquids together with the precursors. Since structurally related **1b** has been investigated electrochemically, a study of the potential windows is provided for comparative purposes. The extraction of Ag^+ from aqueous media into ionic liquids **3a** and **3b** (Scheme 1) is also demonstrated.

2. Experimental Section

2.1. Chemicals and Instrumentation. ILs were synthesized using the following chemicals: 2-chloroacetonitrile, 2-chloropropionitrile, methimazole, lithium bis(trifluoromethanesulfonyl)amide, HPLC grade acetonitrile, and acetone. Ferrocene and cobaltocenium hexafluorophosphate were used in electrochemical studies to provide internal reference potential scale standards. All of these chemicals were used as received from the manufacturer.

2.2. Instrumentation. ^{1}H NMR, ^{13}C NMR, IR. ^{1}H NMR and ^{13}C NMR spectra were recorded on 400 and 200 MHz spectrometers and chemical shifts (ppm) are calibrated relative to those derived from the DMSO-d_6 standard. IR spectra of two neat liquids and two neat salts were obtained using ATIR facilities.

Electrochemical Instrumentation. Voltammetric studies were undertaken at 20 ± 2 °C using an electrochemical workstation. The working disk electrodes were glassy carbon (GC), gold (Au), and platinum (Pt). Prior to each experiment, the working electrodes were polished with 0.30 μm alumina on a clean polishing cloth, sequentially rinsed with distilled water and acetone, and then dried with lint-free tissue paper. Effective electrode areas of 7.24×10^{-3} cm^2 for the GC electrode, 7.78×10^{-3} cm^2 for the Au electrode, and 7.34×10^{-3} cm^2 for the Pt electrode were determined from the peak current for the oxidation of a 1.00 mM Fc solution in CH_3CN (0.10 M Bu_4NPF_6) degassed with N_2 and use of the Randles-Sevcik relationship. A diffusion coefficient of 2.30×10^{-5} cm^2 s^{-1} for Fc

---

(15) Zhao, D. B.; Fei, Z. F.; Scopelliti, R.; Dyson, P. J. *Inorg. Chem.* **2004**, *43*, 2197–2205.

(16) Brauer, D. J.; Kottsieper, K. W.; Liek, C.; Stelzer, O.; Waffenschmidt, H.; Wasserscheid, P. *J. Organomet. Chem.* **2001**, *630*, 177–184.

(17) Sasaki, T.; Zhong, C. M.; Tada, M.; Iwasawa, Y. *Chem. Commun.* **2005**, 2506–2508.

(18) Zuo, G. J.; Muhammed, M. *React. Polym.* **1995**, *24*, 165–181.

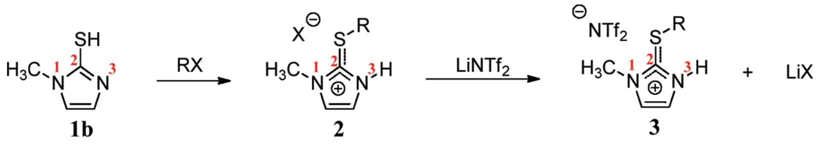
(19) Baumann, T. F.; Reynolds, J. G.; Fox, G. A. *Chem. Commun.* **1998**, 1637–1638.

(20) Lombardo, M.; Pasi, F.; Trombini, C.; Seddon, K. R.; Pitner, W. R. *Green Chem.* **2007**, *9*, 321–322.

(21) Siriwardana, A. I.; Crossley, I. R.; Torriero, A. A. J.; Burgar, I. M.; Dunlop, N. F.; Bond, A. M.; Deacon, G. B.; MacFarlane, D. R. *J. Org. Chem.* **2008**, *73*, 4676–4679.

(22) Torriero, A. A.; Siriwardana, A. I.; Bond, A. M.; Burgar, I. M.; Dunlop, N. F.; Deacon, G. B.; MacFarlane, D. R. *J. Phys. Chem. B* **2009**, *113*, 11222–31.

SCHEME 1. **Metathesis Reactions of Methimazole Halides 2 with $\mathrm{LiNTf_2}$**



2a; R = $\mathrm{CH_2CN}$, X = Cl
2b; R = $\mathrm{CH(CH_3)CN}$, X = Cl

3a; R = $\mathrm{CH_2CN}$
3b; R = $\mathrm{CH(CH_3)CN}$

was used in these calibrations. A standard three-electrode arrangement was used in voltammetric studies with a Pt wire counter electrode and a silver (Ag) wire, separated from the test solution with a frit, was employed as the quasi-reference electrode (QRE). However, the oxidation of 5 mM ferrocene (Fc) or reduction of 5 mM cobaltocenium (Cc^{+}) hexafluorophosphate was used to provide an internal reference standard against which potential data are reported. The ionic liquids were dried under vacuum at 70 °C for 2 days prior to measurement, and the electrochemical experiments were conducted inside a homemade nitrogen-filled glovebox.

2.3. Analysis. Water Content. The water content of the ionic liquids was determined coulometrically using the Karl Fischer method. Duplicate measurements agreed to within 5%.

Melting Point and Glass Transition Temperatures. Temperature dependent phase behavior over the range of −150 to 180 °C was obtained by differential scanning calorimetry using 10−20 mg masses of sample. Thermal scans below room temperature were calibrated using the cyclohexane solid−solid transition and melting point of −87.0 and 6.5 °C, respectively. Higher than room temperature data were calibrated against the melting point of indium (156.6 °C). Transition temperatures are reported as the peak maximum of the thermal transition.

Decomposition Temperatures. Thermogravimetric analysis was conducted in a flowing dry nitrogen atmosphere (50 mL $\mathrm{min^{-1}}$) using a temperature range of 25−500 °C at a heating rate of 10 deg $\mathrm{min^{-1}}$. Calibration was achieved using the Curie points of four reference materials: Alumel, Perkin-alloy, iron, and nickel. Platinum pans were used in all experiments with sample masses between 5 and 10 mg.

Viscosity. Viscosity was determined from the time for a fixed volume to flow through a narrow orifice in a calibrated glass viscometer. Duplicate measurements were undertaken inside a homemade nitrogen-filled glovebox.

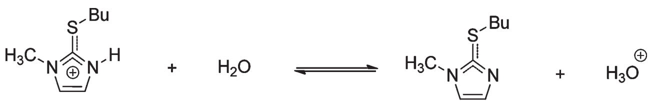
2.4. Synthesis. Synthesis of 2-(Cyanomethyl)thiolonium Chloride [mimSCH$_2$CN][Cl] (2a). Under dinitrogen, an excess of freshly distilled 2-chloroacetonitrile (0.6 mL, 10 mmol) was added to solid methimazole (0.571 g, 5 mmol) and the mixture was stirred for 72 h. After 72 h the excess 2-chloroacetonitrile was removed under reduced pressure to afford an off-white solid, which was recrystallized from acetonitrile/ether to yield the pure title compound as an off-white solid that was dried under vacuum. Yield 94%. Melting point 140 °C. IR (neat) 3478*w* (br), 3219, 3184, 3050, 2963, 2779, 2734, 2703, 2679, 2553, 2239, 1695, 1630, 1542, 1529, 1487, 1429, 1414, 1283; ^{1}H NMR (DMSO-d_6, 200 MHz) δ_H 5.00−7.00 concentration dependent[21] [$^{+}\mathrm{N\underline{H}{-}CH{=}CH}$ (im)], 7.87 [s, 1H, $\mathrm{NCH_3{-}C\underline{H}{=}CH}$ (im)], 7.76 [s, 1H, $^{+}\mathrm{NH{-}C\underline{H}{=}CH}$ (im)], 4.40 (s, 2H, $\mathrm{SC\underline{H}_2CN}$), 3.85 [s, 3H, $\mathrm{NC\underline{H}_3{-}CH{=}CH}$ (im)]; ^{13}C NMR (DMSO-d_6, 50 MHz) δ_C 137.3 [$\mathrm{N{-}\underline{C}(S){-}N}$ (im)], 126.9 [$\mathrm{NCH_3{-}\underline{C}H{=}CH}$ (im)], 122.8 [$^{+}\mathrm{NH{-}\underline{C}H{=}CH}$ (im)], 117.6 ($\mathrm{SCH_2\underline{C}N}$), 35.9 [$\mathrm{N\underline{C}H_3{-}CH{=}CH}$ (im)], 21.2 ($\mathrm{S\underline{C}H_2CN}$). Anal. Calcd for $\mathrm{C_6H_8ClN_3S}$: C, 38.00; H, 4.25; N, 22.15; S, 16.91; Cl, 18.69. Found: C, 37.74; H, 4.20; N, 22.35; S, 16.79; Cl, 18.95. MS (ESI) calcd for $\mathrm{C_6H_8N_3S^{+}}$ m/z 154.0, found m/z 154.0; calcd for $\mathrm{Cl^{-}}$ m/z 35.0, found m/z 34.9

Synthesis of 2-(1-Cyanoethyl)thiolonium Chloride [mimSCH(CH$_3$)CN][Cl] (2b). Under dinitrogen, an excess of freshly distilled 2-chloropropionitrile (0.9 mL, 10 mmol) was added to solid methimazole (0.571 g, 5 mmol) and the mixture was stirred for 72 h. After 72 h the excess 2-chloropropionitrile was removed under reduced pressure to afford an off-white solid, which was recrystallized from acetonitrile/ether to yield the pure title compound as an off-white solid that was dried under vacuum. Yield 89%. Melting point 151 °C. IR (neat) 3380*w* (br), 3214, 3164, 3080, 2940, 2886, 2764, 2713, 2666, 2543, 2239, 1683, 1640, 1557, 1519, 1486, 1427, 1404, 1292 $\mathrm{cm^{-1}}$; ^{1}H NMR (DMSO-d_6, 200 MHz) δ_H 5.75 {broad, 1H, [$^{+}\mathrm{N\underline{H}{-}CH{=}CH}$ (im)]}, 7.97 [s, 1H, $\mathrm{NCH_3{-}C\underline{H}{=}CH}$ (im)], 7.82 [s, 1H, $^{+}\mathrm{NH{-}C\underline{H}{=}CH}$ (im)], 4.84 (q, J = 7.2 Hz, 1H, $\mathrm{SC\underline{H}(CH_3)CN}$), 3.89 [s, 3H, $\mathrm{NC\underline{H}_3{-}CH{=}CH}$ (im)], 1.59 (d, J = 2.4 Hz, 3H, $\mathrm{SCH(C\underline{H}_3)CN}$); ^{13}C NMR (DMSO-$d_6$, 50 MHz) δ_C 135.4 [$\mathrm{N{-}\underline{C}(S){-}N}$ (im)], 127.4 [$\mathrm{NCH_3{-}\underline{C}H{=}CH}$ (im)], 123.6 [$^{+}\mathrm{NH{-}\underline{C}H{=}CH}$ (im)], 120.1 [$\mathrm{SCH(CH_3)\underline{C}N}$], 36.0 [$\mathrm{N\underline{C}H_3{-}CH{=}CH}$ (im)], 32.0 [$\mathrm{S\underline{C}H(CH_3)CN}$], 19.3 [$\mathrm{SCH(\underline{C}H_3)CN}$]. Anal. Calcd for $\mathrm{C_7H_{10}ClN_3S}$: C, 41.21; H, 4.95; N, 20.63; S, 15.74; Cl, 17.41. Found: C, 40.89; H, 4.90; N, 20.32; S, 15.79; Cl, 17.99. MS (ESI) calcd for $\mathrm{C_7H_{10}N_3S^{+}}$ m/z 168.1, found m/z 168.1; calcd for $\mathrm{Cl^{-}}$ m/z 35.0, found m/z 34.9

Synthesis of 2-(Cyanomethyl)thiolonium Bis(trifluoromethanesulfonyl)amide [mimSCH$_2$CN][NTf$_2$] (3a). The salt **2a** [mimSCH$_2$CN][Cl] (0.759 g, 4 mmol) was dissolved in water (10 mL). With vigorous stirring, an aqueous solution (15 mL) of $\mathrm{LiNTf_2}$ (2.009 g, 7 mmol) was added, resulting in immediate formation of a colloidal suspension. The mixture was screened from light and stirred overnight. After 15 h, the mixture was transferred to a separating funnel and allowed to settle. The ionic liquid (IL) layer (bottom) was separated and washed several times with 30-mL aliquots of hot water. The IL was then taken into acetone and stirred over activated carbon at 50 °C for 12 h. After filtration through Celite, followed by a plug of basic alumina, the solvent was removed at reduced pressure. Finally the liquid was passed through a 0.45 μm syringe filter and dried under vacuum at 120 °C. Yield 92%. IR (neat) 3548*w* (br), 3249, 3123, 3082, 2962, 2835, 2779, 2729, 2683, 2254, 1651, 1589, 1490, 1454, 1333, 1247, 1257, 1180, 1167, 1049 $\mathrm{cm^{-1}}$; ^{1}H NMR (DMSO-d_6, 400 MHz) δ_H 7.88 [s, 1H, $\mathrm{NCH_3{-}C\underline{H}{=}CH}$ (im)], 7.79 [s, 1H, $^{+}\mathrm{NH{-}C\underline{H}{=}CH}$ (im)], 6.38 {broad, 1H, [$^{+}\mathrm{N\underline{H}{-}CH{=}CH}$ (im)]}, 4.21 (s, 2H, $\mathrm{SC\underline{H}_2CN}$), 3.87 [s, 3H, $\mathrm{NC\underline{H}_3{-}CH{=}CH}$ (im)]; ^{13}C NMR (DMSO-d_6, 100 MHz) δ_C 136.7 [$\mathrm{N{-}\underline{C}(S){-}N}$(im)], 126.9 [$\mathrm{NCH_3{-}\underline{C}H{=}CH}$ (im)], 122.8 [$^{+}\mathrm{NH{-}\underline{C}H{=}CH}$ (im)], 120.2 (q, J = 319.7 Hz, 2 × $\mathrm{\underline{C}F_3}$), 117.2 [$\mathrm{SCH_2\underline{C}N}$], 35.7 [$\mathrm{N\underline{C}H_3{-}CH{=}CH}$ (im)], 20.8 [$\mathrm{S\underline{C}H_2CN}$]; Anal. Calcd for $\mathrm{C_8H_8F_6N_4O_4S_3}$: C, 22.12; H, 1.86; N, 12.90; S, 22.15; F, 26.24. Found: C, 22.49; H, 1.90; N, 12.54; S, 22.49; F, 26.83. The Li content of **3a** was 1.8 ppm. MS (ESI) calcd for $\mathrm{C_6H_8N_3S^{+}}$ m/z 154.0, found m/z 154.0; calcd for $\mathrm{NTf_2^{-}}$ m/z 279.9, found m/z 279.9

Synthesis of 2-(2-Cyanoethyl)thiolonium Bis(trifluoromethanesulfonyl)amide [mimSCH(CH$_3$)CN][NTf$_2$] (3b). The salt **2b** [mimSCH(CH$_3$)CN][Cl] (0.815 g, 4 mmol) was dissolved in water (10 mL). With vigorous stirring, an aqueous solution (15 mL) of $\mathrm{LiNTf_2}$ (2.009 g, 7 mmol) was added, resulting in immediate formation of a colloidal suspension. The mixture was screened from light and stirred overnight. After 15 h, the mixture was transferred to a separating funnel and allowed to settle. The ionic liquid (IL) layer (bottom) was separated and washed several times with 25-mL aliquots of hot water. The IL was then

SCHEME 2. Acidity of 3d in Aqueous Solution



3d **3d'**

taken into acetone and stirred over activated carbon at 50 °C for 14 h. After filtration through Celite, followed by a plug of basic alumina, the solvent was removed at reduced pressure. Finally the liquid was passed through a 0.45 μm syringe filter and dried under vacuum at 120 °C. Yield 95%. IR (neat) 3558*w* (br), 3239, 3148, 3089, 2962, 2841, 2783, 2739, 2683, 1652, 1579, 1490, 1454, 1345, 1180, 1133, 1051 cm^{-1}; ^{1}H NMR (DMSO-d_6, 200 MHz) δ_{H} not detected, but 5.00−7.00 concentration dependent for **3d** (Scheme 2)[21] [$^{+}$N$\underline{\mathrm{H}}$—CH=CH (im)], 7.93 [s, 1H, NCH$_3$—C$\underline{\mathrm{H}}$=CH (im)], 7.82 [s, 1H, $^{+}$NH—C$\underline{\mathrm{H}}$=CH (im)], 4.61 (q, J = 7.2 Hz, 1H, SC$\underline{\mathrm{H}}$(CH$_3$)CN), 3.90 [s, 3H, NC$\underline{\mathrm{H}}_3$—CH=CH (im)], 1.59 (d, J = 7.2 Hz, 3H, SCH(C$\underline{\mathrm{H}}_3$)CN); ^{13}C NMR (DMSO-d_6, 50 MHz) δ_{C} 135.4 [N—$\underline{\mathrm{C}}$(S)—N (im)], 127.6 [NCH$_3$—$\underline{\mathrm{C}}$H=CH (im)], 124.0 [$^{+}$NH—$\underline{\mathrm{C}}$H=CH (im)], 120.1 [SCH(CH$_3$)$\underline{\mathrm{C}}$N], 120.1 (q, J = 319.7 Hz, 2 × $\underline{\mathrm{C}}$F$_3$), 36.0 [N$\underline{\mathrm{C}}$H$_3$—CH=CH (im)], 31.9 [S$\underline{\mathrm{C}}$H(CH$_3$)CN], 19.3 [SCH-($\underline{\mathrm{C}}$H$_3$)CN]. Anal. Calcd for $C_9H_{10}F_6N_4O_4S_3$: C, 24.11; H, 2.25; N, 12.50; S, 21.45; F, 25.42. Found: C, 24.39; H, 2.47; N, 12.39; S, 21.49; F, 25.89. The Li content of **3b** was 2.1 ppm. MS (ESI) calcd for $C_7H_{10}N_3S^+$ *m*/*z* 168.1, found *m*/*z* 168.1; calcd for NTf_2^- *m*/*z* 279.9, found *m*/*z* 279.9

2.5. Extraction of Ag^+ from Aqueous Media into the Ionic Liquids, 3a and 3b. A 0.2 mL sample of ionic liquid (**3a** or **3b**) was used to extract silver ions from 0.2 mL of aqueous solution. In these studies, 0.46 mmol of silver trifluoromethanesulfonate (AgOTf) present in 0.2 mL of aqueous solution was mixed with 0.46 mmol (0.2 mL) of ionic liquid (**3a** or **3b**). The phases were separated and residual silver in the aqueous layer was determined electrochemically to be less than 10%. ^{1}H NMR, ^{13}C NMR, and IR spectra of the ionic liquid (**3a**) layer are given in Results and Discussion. Likewise, ^{1}H NMR and ^{13}C NMR spectra of the ionic liquid (**3b**) layer are given in Supporting Information (SI), whereas the IR spectrum of the ionic liquid (**3b**) layer is given in Results and Discussion.

3. Results and Discussion

3.1. Synthesis. The reaction of **1b** with 2-chloroacetonitrile gave methimazolium chloride **2a** in 94% yield. Likewise, the reaction of methimazole with 2-chloropropionitrile afforded **2b** in 89% yield (Scheme 1). The metathesis reaction of the methimazolium halide **2a** with lithium bis(trifluoromethanesulfonyl)amide, $LiNTf_2$ (also known as LiTFSA), proceeded smoothly at room temperature (20 ± 2 °C) in water to give the corresponding ionic liquid [mimSCH$_2$CN][NTf$_2$] **3a**. Likewise, the reaction of **2b** afforded [mimSCH(CH$_3$)CN][NTf$_2$] **3b**. All the ionic liquids were dried at 70 °C under high vacuum for 2 days, then characterized by NMR spectroscopy, microanalysis, IR, ESI mass spectrometry (Experimental Section), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and viscosity.

3.2. Physicochemical Characterization of Nitrile Functionalized Ionic Liquids. Spectroscopic and analytical data showed that the isolated materials were pure, free from methimazole and metal salt starting materials. The Li^+ contents of **3a** and **3b** were < 2.1 ppm. The water content of dried samples of **3a** and **3b**, determined with a Karl Fischer Coulometer, was < 150 ppm. [mimCH$_2$CN][Cl] **2a** and [mimSCH(CH$_3$)CN][Cl] **2b** salts are solids at room temperature. The DSC traces showed that **2a** and **2b** melt at temperatures of 140 and 151 °C, respectively, above the ionic liquid range. Also, glass transition temperatures (T_g) of these ionic salts **2a** and **2b** were found at −39 and −42 °C, respectively. DSC measurements on the room temperature ionic liquids (RTILs) **3a** and **3b** provided no evidence of melting point (T_m), but glass transition temperatures were detected at −89 and −92 °C, respectively. The viscosities of ionic liquids **3a** and **3b** were 166 and 169 mPa s at 40 °C, respectively.

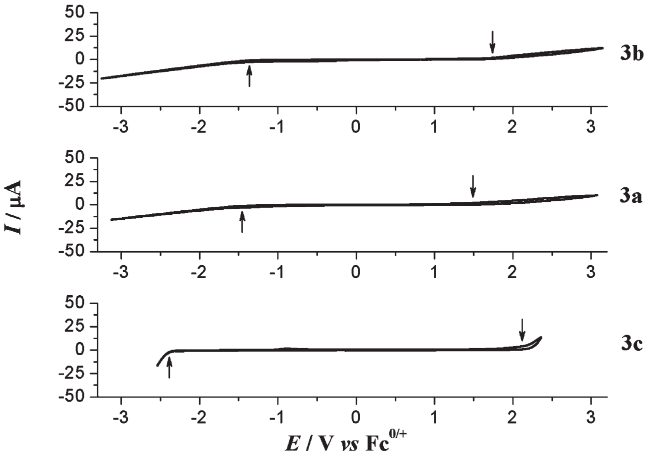


FIGURE 3. Cyclic voltammograms at a glassy carbon electrode (1 mm diameter) for **3a**, **3b**, and **3c** (1-ethyl-3-methylimidazolium NTf$_2$). Scan rate: 0.1 V s^{-1}; *T*: 20 ± 1 °C.

TABLE 1. Potential Window Data Obtained from Cyclic Voltammetry for 3a, 3b, and 3c

ionic liquid	electrode material	E_w (V)[a]	cathodic limit (V)	anodic limit (V)
3c	GC	4.51	−2.40	2.11
	Pt	4.21	−1.94	2.27
	Au	4.33	−2.17	2.16
3a	GC	2.94	−1.45	1.49
	Pt	2.50	−0.87	1.63
	Au	2.72	−1.10	1.62
3b	GC	3.09	−1.36	1.73
	Pt	2.45	−0.90	1.55
	Au	2.68	−1.00	1.68

[a] Potential window data obtained from cyclic voltammetry using a scan rate of 0.1 V s^{-1}. E_W: Potential window as determined using procedures described in ref 2121; T = 20 ± 1 °C. Potentials are vs the Fc$^{0/+}$ reference scale.

The thermogravimetric analyses for thoroughly dried [mimSCH$_2$CN][NTf$_2$] and [mimSCH(CH$_3$)CN][NTf$_2$] compounds showed no weight loss at temperatures up to at least 360 °C and hence they can be classified as highly thermally stable ILs, providing a large, stable liquid range. This contrasts with, for example, methimazolium chloride **2a** and **2b** that decompose at much lower temperatures (~250 °C).

3.3. Electrochemical Characterization. Potential Windows. The potential windows for **3a** and **3b** as neat ionic liquids and commercially available 1-ethyl-3-methylimidazolium NTf$_2$ (**3c**, used as reference) have been measured by cyclic voltammetry at glassy carbon (GC), Pt, or Au working electrodes using a scan rate of 0.1 V s^{-1} (Figure 3 and Table 1). The drawn out nature of the solvent oxidation and reduction process for **3a** and **3b**, in comparison with the sharper rise in the current for **3c**, implies that the resistance of **3a** and **3b** is significantly larger than that for **3c**. The magnitude of the potential windows lies in

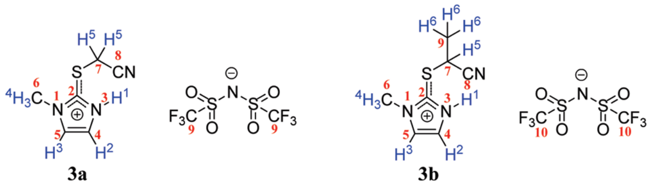


FIGURE 4. Ionic Liquids **3a** and **3b**.

the order **3c** > **3a** = **3b**. The positive potential limit of **3a** and **3b**, attributed to oxidation of the thioether, was less positive than found with the 1-ethyl-3-methylimidazolium NTf_2[4,21,23] ionic liquid.

The negative potential limit for **3c** is attributed to the reduction of the $mimNCH_2CH_3$ cation,[22] although small processes, which are related to trace impurities, are also present at around −1.5 V and have been noted by Endres et al.[24] The relatively smaller negative potential limit for **3a** and probably **3b** are tentatively attributed to the reduction of the proton present at the N(3) position, as proposed for nonfunctionalized methimazole ILs.[22]

3.4. Extraction of Ag^+ from Aqueous Media into the Ionic Liquid, 3a and 3b. Recently, we reported the synthesis of methimazole-based ILs[21,22] and showed Cu^{2+} ions can be readily extracted from aqueous media into the new ionic liquid [mimSBu][NTf_2] **3d**.[25] We also observed that the acidity of the aqueous solution increased when **3d** is added, an effect that is associated with the hydrogen attached to the nitrogen atom (N3) of the cation of the ionic liquid (Scheme 2).

Introducing nitrile functionality onto the sulfur of the cation of a IL as in **3a** and **3b** (Figure 4) may be expected to enhance the efficiency of the extraction process. Therefore, **3a** and **3b** have been used to assess if silver(I) ions, that are known to bind strongly to the nitrile group, can be extracted from aqueous solution into these ionic liquids.

Ag^+ is electroactive in the aqueous phase and gives rise to a well-defined $Ag^+ + e \rightarrow Ag$ process with a current that is proportional to the concentration of silver ion. Voltammetric studies showed that the extraction of Ag^+ ions from aqueous solution into **3a** and **3b** was extremely high (≥90%) and fast (≤5 min). The bottom ionic liquid phase was separated and examined for evidence of Ag^+ extraction by IR and NMR measurements.

Panels A and B in Figure 5 show the IR spectra of **3a** and **3b** over the wavenumber range from 2200 to 2300 cm^{-1} before and after being in contact with an aqueous solution contains Ag^+. IR bands in this region are characteristic of the C≡N stretching vibration. In neat ionic liquids {**3a** [Figure 5A, (a)], **3b** [Figure 5B, (a)]}, the bands at 2254 and 2246 cm^{-1} are assigned to the $\nu_{(C\equiv N)}$ band for the C≡N group of $-SCH_2CN$ and $-SCH(CH)_3CN$ of the neat ionic liquids, respectively. This band is slightly shifted to 2255 cm^{-1} in water saturated ionic liquid, **3a** [Figure 5A, (b)]. Two bands at 2249 and 2241 cm^{-1} are detected after interaction of Ag^+ with **3a** after silver ions are extracted from aqueous media [Figure 5A, (c)]. Likewise, one band at 2244 cm^{-1} is detected after interaction of Ag^+ with **3b** [Figure 5B, (b)]. Shifting of C≡N vibration from 2254 to 2249 and 2241 cm^{-1} implies that the coordination is through the C≡N π system to Ag^+.[26] The IR spectrum of **3a** shows $\nu_{(C\equiv N)}$ (ca. 2241 cm^{-1}) and the characteristic combination band [$\delta_{(CH)} + \nu_{(C\equiv N)}$] (ca. 2249 cm^{-1}).[27] For **3b**, this feature is not resolved.

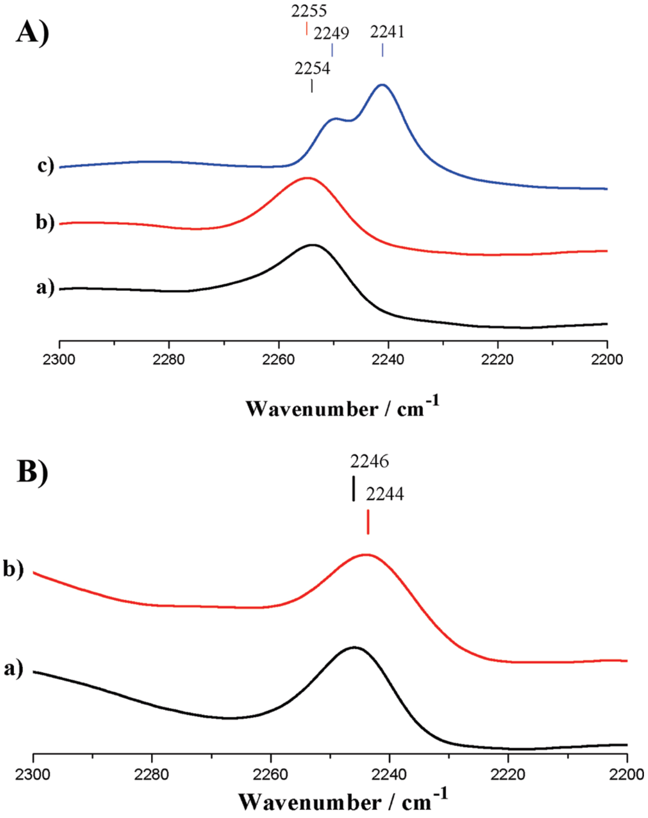


FIGURE 5. (A) IR spectra (range 2300 to 2200 cm^{-1}) of (a) neat ionic liquid **3a**, (b) water saturated ionic liquid phase, and (c) ionic liquid phase, after extraction of Ag^+ from the water phase. (B). IR spectra (range 2300 to 2200 cm^{-1}) of (a) neat ionic liquid **3b** and (b) ionic liquid phase, after extraction of Ag^+ from the water phase.

Evidence for Ag^+ complexation also is supported by ^1H (Figure 6) and ^{13}C (Figure 7) NMR data (Tables 2 and 3), obtained after the ionic liquid phase used for extraction of Ag^+ was dissolved in DMSO-d_6. Thus, the presence of silver ions produces a significant chemical ^{13}C shift change in C2 [1.2 ppm (**3a**), 0.8 ppm (**3b**)], C4 [4.2 ppm (**3a**), 3.0 ppm (**3b**)], and C5 [1.3 ppm (**3a**), 0.2 ppm (**3b**)]. This is expected if the silver ion coordinates to the imidazolium N3. A smaller ^{13}C chemical shift change [0.7 ppm (**3a**), 0.1 ppm (**3b**)] in the carbon (C8) of the CN group confirms that CN coordination also contributes to efficient extraction of Ag^+ from aqueous media. Thus N3 and the CN functional group chelate to Ag^+ (Figure 8). In contrast, the CF_3 carbon [C9 (**3a**), C10 (**3b**)] resonances of the IL anion (NTf_2^-) are not affected by the presence of Ag^+ [**3a** (Figure 7, a and b), **3b** (SI, S13)] suggesting Ag^+ interaction is confined to the cation of ionic liquids **3a** and **3b**. The broad ^1H NMR resonances associated with the ^+NH of the ionic liquid (**3a**) is detected at δ_H 6.38 ppm (SI, S4) but not detected for **3b**. After the Ag^+ is extracted into the IL phase from aqueous media, the ^1H resonance associated with ^+NH was not observed (Tables 2

---

[23] Zhang, J.; Bond, A. M. *Analyst* **2005**, *130*, 1132–1147.

[24] Borisenko, N.; El Abedin, S. Z.; Endres, F. *J. Phys. Chem. B* **2006**, *110*, 6250–6256.

[25] Reyna-Gonzalez, J. M.; Torriero, A. A. J.; Siriwardana, A. I.; Burgar, I. M.; Bond, A. M. *Anal. Chem.*, **2010**, *82*, 7691−7698.

[26] Son, D. H.; Ahn, S. J.; Lee, Y. J.; Kim, K. *J. Phys. Chem.* **1994**, *98*, 8488–8493.

[27] Deacon, G. B.; Forsyth, C. M.; Newnham, R. H.; Tuong, T. D. *Aust. J. Chem.* **1987**, *40*, 895–906. and references cited therein.

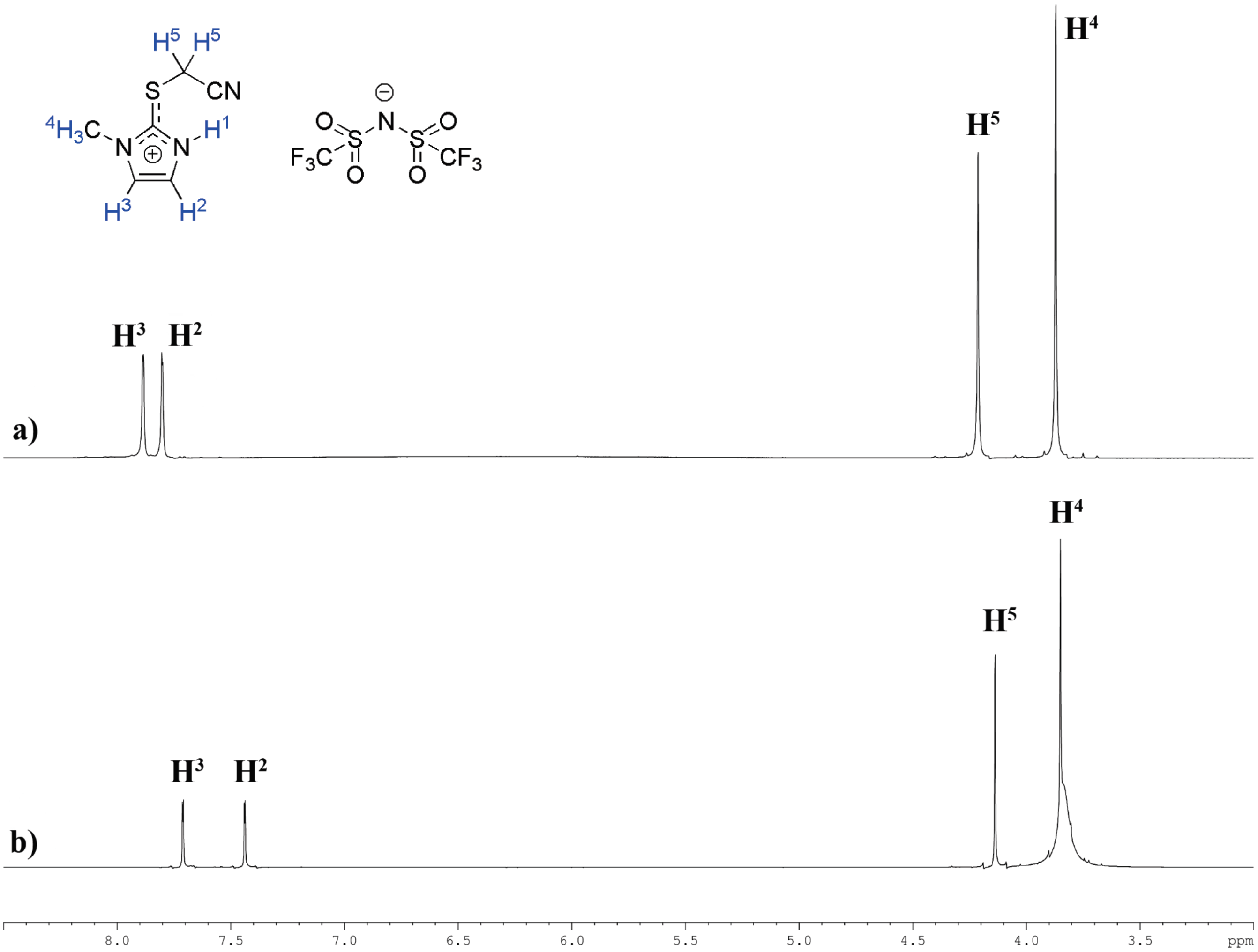


FIGURE 6. ^{1}H NMR spectra (DMSO-d_6 as solvent) for (a) **3a** and (b) **3a** with Ag$^+$.

TABLE 2. NMR Data[a] Obtained for 3a before and after Extraction of Ag$^+$

nuclei	molecular position	**3a** (ppm)	**3a** with Ag$^+$ (ppm)
^{1}H	**H^{1}**; $^{+}$NH—CH=CH (im)	6.38 (SI, S4)[b]	not observed
	H^{2}; $^{+}$NH—CH=CH (im)	7.79	7.43
	H^{3}; NCH$_3$−CH=CH (im)	7.88	7.70
	H^{5}; S−CH$_2$CN	4.21	4.13
	H^{4}; NCH$_3$—CH=CH (im)	3.87	3.85
^{13}C	**C2**; N—C(S)—N (im)	136.70	137.94
	C5; NCH$_3$—CH=CH (im)	126.94	128.24
	C4; $^{+}$NH—CH=CH (im)	122.77	126.97
	C8; S—CH$_2$CN	117.17	117.86
	C7; S—CH$_2$CN	20.79	21.10
	C6; NCH$_3$—CH=CH (im)	35.66	35.57
	C9; CF$_3$	120.20	120.20

[a] NMR data obtained in DMSO-d_6 and calibrated with respect to residual protons of the DMSO-d_6 solvent. [b] Very broad signal not seen in Figure 6 (a) but provided in SI, S4.

TABLE 3. NMR Data[a] Obtained for 3b before and after Extraction of Ag$^+$

nuclei	molecular position	**3b** (ppm)	**3b** with Ag$^+$ (ppm)
^{1}H	**H^{1}**; $^{+}$NH—CH=CH (im)	not observed	not observed
	H^{2}; $^{+}$NH—CH=CH (im)	7.82	7.58
	H^{3}; NCH$_3$—CH=CH (im)	7.93	7.81
	H^{4}; NCH$_3$—CH=CH (im)	3.90	3.89
	H^{5}; S—CH(CH$_3$)CN	4.61	4.56
	H^{6}; S—CH(CH$_3$)CN	1.59	1.55
^{13}C	**C2**; N—C(S)—N (im)	135.44	136.21
	C5; NCH$_3$—CH=CH (im)	127.61	127.45
	C4; $^{+}$NH—CH=CH (im)	123.97	126.95
	C7; S—CH(CH$_3$)CN	31.96	31.82
	C8; S—CH(CH$_3$)CN	120.05	120.16
	C9; S—CH(CH$_3$)CN	19.35	18.95
	C6; NCH$_3$—CH=CH (im)	36.05	35.83
	C10; CF$_3$	120.10	119.97

[a] NMR data obtained in DMSO-d_6 and calibrated with respect to residual protons of the DMSO-d_6 solvent.

and 3; Figure 6a and 6b; SI, S12). Ionic liquid **3d** has been shown to be a source of H$^+$ when mixed with the aqueous phase (Scheme 2).[25] This implies that hydrogen ions are released by the **3a** and **3b** cation molecules ($^{+}$NH) to form H$_3$O$^+$, explaining the absence of $^{+}$NH proton in ^{1}H NMR spectra when the $^{+}$NH group in **3a** and **3b** interacts dynamically with Ag$^+$ ions. Significant proton chemical shifts change in H^{2} [0.4 ppm (**3a**), 0.2 ppm (**3b**)], H^{3} [0.2 ppm (**3a**), 0.1 ppm (**3b**)], and H^{5} [0.1 ppm (**3a**), 0.1 ppm (**3b**)] confirms that Ag$^+$ coordinates to the ring and C≡N π system (Figure 6; Tables 2 and 3; SI, S6 and S12). In contrast, the H^{4} (**3a** and **3b**) and H^{6} (**3b**) resonances of the IL cations are less affected.

Thus, NMR spectra provide evidence for coordination between silver ions and N3 nitrogen of the ionic liquid. In

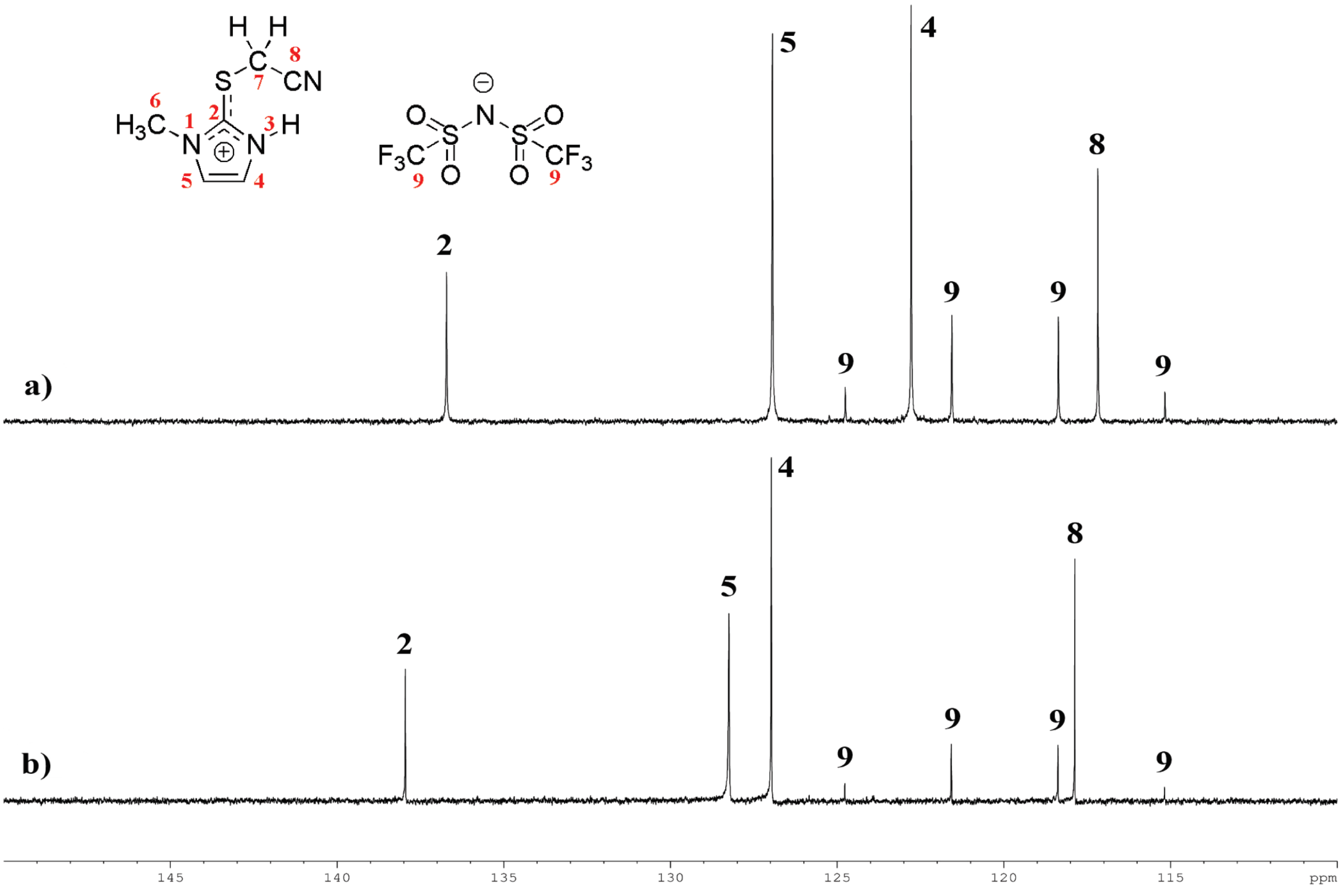


FIGURE 7. ^{13}C NMR spectra (DMSO-d_6 as solvent) for (a) **3a** and (b) **3a** with Ag$^+$.

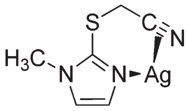


FIGURE 8. Interaction between silver ions and the nitrile functionalized ionic liquid.

conjunction with IR data that imply coordination of Ag$^+$ through the C≡N π system, a ring structure (Figure 8) is proposed as the basis of Ag$^+$ extraction from **3a**. However, full details of the structure of the extracted complex are unknown.

4. Conclusions

We have disclosed a new, highly efficient way to synthesize two new cyanoalkyl salts **2a** and **2b**, and two new room temperature ionic liquids (**3a** and **3b**) based on the methimazole cation and chloride (**2a**, **2b**) or the NTf$_2$ (ILs) anions in good to high yield. The structures of the four materials have been confirmed via microanalysis, IR and NMR spectroscopy, and mass spectrometry. The two compounds that are liquids (**3a** and **3b**) at room temperature have reasonably wide electrochemical windows. Silver ion extraction from aqueous media into ionic liquids **3a** and **3b**, which is efficient and fast, is reported, and deduced to occur via replacement of the acidic proton at the N3 position of the imidazolium ring together with an interaction with the nitrile group. The full characterization of an extensive series of new nitrile functionalized methimazole-based ionic liquids as well as electrochemical and metal extraction studies in these potentially coordinating environments are now under active investigation in our laboratories.

Acknowledgment. This research was financially supported by the Australian Research Council-Orica Linkage grant LP0668123. Francess Separovic from Melbourne University is gratefully acknowledged for valuable discussions.

Supporting Information Available: Spectral data for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.