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Dual-functionalised ionic liquids: synthesis and characterisation of imidazolium salts with a nitrile-functionalised anion†

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A series of 'dual-functionalised' ionic liquids, comprising imidazolium cations with various functionalities and the nitrile functionalised anion $[CH_3CH(BF_3)CH_2CN]^-$ have been prepared; some exhibit very low viscosities—a highly valuable property in many applications.

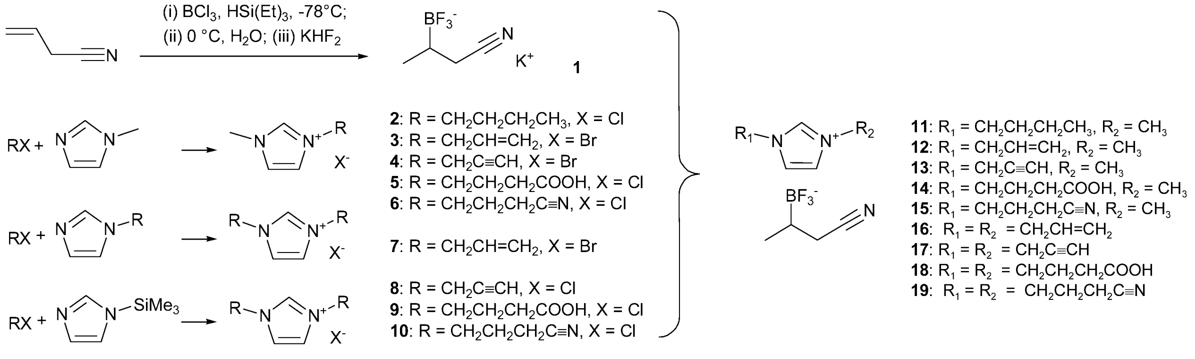
Room temperature ionic liquids (ILs), often referred to as 'designer solvents' since they can be tuned for specific applications, are attracting considerable attention as solvents for multiphasic catalysis as well as other applications.[1] Of the various types of ILs available, those based on imidazolium cations are without doubt the most intensively investigated, with structural modifications leading to (predictable) changes in the physical and chemical properties of the liquid.[2] Attention has mostly focused on cation modification, and, for example, ILs incorporating alkyne,[3] nitrile,[4] hydroxyl and carboxylic acid[5] functionalities have recently been reported. Although the synthesis of functionalised ILs *via* imidazolium cation modification is relatively straightforward, the main problem with such ILs is that their melting points and viscosities tend to be much higher than closely related alkyl-substituted imidazolium salts; some are in fact solids at ambient temperature.[6] Increased melting points and viscosities are not conducive to the application of ILs as solvents.

Much less attention has been directed towards the preparation of ILs functionalised through anion design. There are, however, examples of ILs with transition metal carbonyl,[7] perfluoroalkyltrifluoroborate[8] and chiral[9] anions. While the nature of the anion exerts a major influence on physical and chemical properties of ILs we are not aware of any report describing the modification of ILs' properties through the design of a functionalised anion. Herein, we describe the synthesis of several 'dual-functionalised' ILs (DF-ILs) containing various functionalised imidazolium cations combined with the $[CH_3CH(BF_3)CH_2CN]^-$ anion. This anion was selected for the study as a continuation of our work on nitrile-functionalised imidazolium cations, which show considerable promise in catalysis.[4]

The synthetic strategy involves the preparation of the functionalised anion initially as a potassium salt, followed by anion metathesis with various imidazolium halides (see Scheme 1), which represents the most widely used method to prepare ILs.[2] The first step of the anion synthesis involves hydroboration of allyl cyanide using boron trichloride and triethylsilane, then addition of water to afford the boronic acid which is subsequently stirred with KHF_2 in ether/H_2O at ambient temperature, in accord with a published protocol.[10,11] The product, $K[CH_3CH(BF_3)CH_2CN]$ **1**, was recrystallised from acetone on addition of diethyl ether as colourless needles in 74% yield. The formation of **1** is somewhat surprising, since α-alkene hydroboration affords boronic esters or acids at the α-position (Markovnikov addition).[11] Such regioselectivity may be due to the nitrile group, which tethers the boron to the β-position. In the ^1H NMR spectrum of **1**, the CH group exhibits a broad multiplet at 0.59 ppm; the CH_3 group a doublet at 0.91 ppm ($^3J(HH)$ of 7.3 Hz); the CH_2 group two sets of doublets of doublets at 1.93 ppm and 2.36 ppm, the two H atoms are magnetically non-equivalent as indicated by two very different $^3J(HH)$ of 4.3 Hz and 10.7 Hz; the $^2J(HH)$ for the H–H coupling of CH_2 is -17.1 Hz. The signals in the ^{19}F and ^{11}B NMR spectra are very broad even at low temperature in methanol or acetone, indicating strong interactions between F and H atoms with the solvent. However, the $^1J(BF)$ can be roughly resolved as 60 Hz, this value is in accordance with structurally similar compounds.[8] The structure of the anion was confirmed by single crystal X-ray diffraction analysis for the bistriphenylphosphinoimine salt, and will be reported in due course.

Commencing with 1-methylimidazole or 1-trimethylsilylimidazole[12] a series of imidazolium halides **2–10** were prepared using standard methods. Subsequent metathesis with **1** in acetone gave the DF-ILs **11–19** in high yield (typically 80–90%).‡ The residual halide in the ionic liquids was determined by ionic chromatography[13–15] indicating *ca.* 0.8 mol kg^{-1} in the product, which is within the range typical of tetrafluoroborate ionic liquids.[16]

All the new salts were characterised by IR and NMR spectroscopy, electrospray ionisation mass spectrometry (ESI-MS) and elemental analysis. The IR spectra of the DF-ILs reveal that the absorption at 2500–2800 cm^{-1}, indicative of the halide, has disappeared, to be replaced by the characteristic absorption of the nitrile functionality on the anion at 2236–2240 cm^{-1}. The ^1H and



Scheme 1 Synthesis of 'dual-functionalised' ionic liquids with the $[CH_3CH(BF_3)CH_2CN]^-$ anion.

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† Electronic supplementary information (ESI) available: synthetic details, IR, ^1H, ^{11}B, ^{13}C and ^{19}F NMR spectroscopic data, electrospray ionisation mass spectrometry and elemental analysis of all new compounds. See http://www.rsc.org/suppdata/cc/b4/b408938c/

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Table 1 Comparison of the melting point and viscosity data of the DF-ILs with tetrafluoroborate counterparts

Ionic liquids[a]	Melting point/°C	Viscosity/cP, 20 °C
11	−84.5	101
$[C_4mim][BF_4]$[2]	−81.0	115
12	−89.2	25
$[CC{=}Cmim][BF_4]$	−81.1	6110
13	−80.4	175
14	−58.6	3047
$[C_3COOHmim][BF_4]$[5b]	−58.0	4415
15	−76.6	107
$[C_3CNmim][BF_4]$[4]	−71.9	230
16	−87.3	56
17	−55.1	1797
$[DiCC{\equiv}Cim][BF_4]$[3b]	67.0	—
18	38.0	—
19	−69.8	402

[a] $[C_4mim][BF_4]$: 1-methyl-3-butylimidazolium tetrafluoroborate; $[CC{=}Cmim][BF_4]$: 1-methyl-3-allylimidazolium tetrafluoroborate; $[DiCC{\equiv}Cim][BF_4]$: 1,3-propargylimidazolium tetrafluoroborate; $[C_3COOHmim][BF_4]$: 1-methyl-3-propylcarboxylimidazolium tetrafluoroborate.

^{13}C NMR spectra of the DF-ILs are not too dissimilar from their corresponding halide salts, except with additional peaks present corresponding to the anion (see above and ESI†). The electrospray ionisation mass spectra of **11–19** exhibit the parent peaks for the cations (positive ion mode) and a strong molecular ion signal at *m*/*z* 136 for **1** in negative ion mode.

The melting points and viscosities of the DF-ILs are compared with the analogous tetrafluoroborate salts in Table 1. Significantly, despite the presence of a functional group on the anion, making it bulkier than BF_4^-, and also potentially taking part in intermolecular interactions, the DF-ILs exhibit lower melting points and viscosities. For example, the melting point of $[CC{=}Cmim][CH_3CH(BF_3)CH_2CN]$ (**12**) is 8 °C lower than that of $[CC{=}Cmim][BF_4]$; however, the viscosity is considerably reduced (25 *vs.* 6110 cP at 20 °C). As far as we are aware, this is one of the lowest viscosities that has ever been measured for an IL.[17] It is not unreasonable to attribute the reduced melting points and viscosities of these ILs to the asymmetry of the anion, the related effect for asymmetric cations has been known for many years.[18] It is also possible that the BF_3 group may interact with the imidazolium ring, delocalising the positive and negative charges over the entire system, and reducing the salt property of the molecule. Preliminary results in the hydrogenation of 1,3-cyclohexadiene in **15** using $PdCl_2$ show improved turnover frequency and selectivity towards cyclohexene compared to $[C_3CNmim][BF_4]$.[4] The anion itself is stable towards catalytic hydrogenation, as evidenced by high pressure NMR spectroscopy.

To conclude, we report what we believe is the first example of an anti-Markovnikov hydroboration product of an α-alkene, *viz.* $[CH_3CH(BF_3)CH_2CN]^-$. We have also shown that combining the anion with various functionalised imidazolium cations not only endows ILs with additional functionality, but reduces melting point and viscosity. The functionality on the anion is not confined to the nitrile group, and other functional groups can also be introduced using a similar strategy. Such combinations of both functionalised cations and anions will enrich the field of ILs by adding another dimension to their design. The DF-ILs reported herein are composed of potential donor groups for transition metals, they dissolve a wide range of transition metal oxides and halide salts, and further results will be reported in due course.

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Notes and references

‡ Preparation of **1**. To a flask containing a mixture of allyl cyanide (5.37 g, 80 mmol) and $HSiEt_3$ (10.0 g, 85 mmol), a solution of BCl_3 (1.0 M in dichloromethane, 90 ml, 90 mmol) was added at −78 °C under an inert atmosphere. The resulting solution was stirred at −78 °C for 1 h and then allowed to warm to room temperature. The mixture was cooled to 0 °C, and water (100 ml), followed by diethyl ether (100 ml), was added slowly. The resulting suspension was stirred for 10 h and then extracted with ether (3 × 50 ml), dried over $MgSO_4$ and filtered. After removal of solvent a colourless liquid was obtained. This liquid was transferred to a PFA beaker and redissolved in diethylether followed by addition of KHF_2 (22.1 g, 284 mmol). The mixture was then stirred for 1 h and extracted with acetone (3 × 50 ml). The acetone extracts were collected and the acetone removed under reduced pressure leaving a white solid. The solid was recrystallised from acetone–diethylether yielding colourless needles (10.4 g, 74%). Preparation of **11–19**. **1** (1.0 g, 5.71 mmol) and the appropriate imidazolium halide (**2–10**, 5.71 mmol) were stirred in acetone at room temperature for 24 h. The resulting suspension was filtered and the filtrate dried in vacuum affording DF-ILs **11–19**. The resulting ILs were purified by washing with diethyl ether. Spectroscopic and analytical data for the new compounds are provided in the ESI.†

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