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Synthesis, characterisation and properties of ferrocenylalkylimidazolium salts

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ABSTRACT

New ferrocenylalkylimidazolium salts $[Fc(CH_2)_n(C_3H_3N_2)\mathbf{R}]\mathbf{X}^-$ were synthesised through the incorporation of green chemistry principles of atom economy and when feasible under solvent-free conditions. The products comprise a series of salts all characterised by the ferrocenyl moiety with variations in the length of the linker alkyl chain (n), the size of the imidazolium alkyl substituent (**R**) or the electronic nature of the counter-ion ($\mathbf{X}^-$). The dependence of the physical and electronic properties of the salts on the three main structural variants was studied. It was found that variation in the steric size of the **R** group has the most profound influence on the melting points of the ionic liquids. The compounds were fully characterised by IR, ^{1}H and ^{13}C NMR, MS and melting point determinations.

1. Introduction

The study of substituted imidazolium-based salts has been an active area of research due to the wide variety of applications that utilizes their unique physical and chemical properties [1]. Specifically, they have been used as ionic liquids [2] and as ancillary ligands in catalysis [3]. Relevant to the current study is the tethering of ferrocene to an imidazolium ion which extends the chemical diversity of intrinsically electroactive ionic liquid phases to redox molten salts [4]. This also diversifies the class of stable *N*-heterocyclic carbene (NHC) ligands especially as sources of carbenes containing redox-active ferrocenyl substituents [5].

The ferrocenyl moiety represents a quite bulky group with unique spatial requirements due to its sandwich shape, and electronically, the powerful donor capacity of ferrocene is important in the stabilization of highly reactive metal centres and other electroactive species. Some of the important properties that ferrocenyl containing imidazolium salts exhibit that makes their study significant include electronic stabilisation of adjacent electron-deficient centres due to participation of the iron atom in the dispersal of the positive charge; the unique steric bulk, chemical stability and reversibility of the ferrocene/ferrocenium redox couple [6]. In recent years, aryl and alkyl imidazolium compounds have been the subject of intense scientific study including the topical work by Arduengo et al. [7] who demonstrated the stabilisation of carbenes with a variety of substituents that allows not only for the *in situ* synthesis and study of the reactivity, but also the isolation and full characterisation of the first nucleophilic NHC (Fig. 1). It is, however, noteworthy that the ferrocenyl moiety containing analogues of the NHCs has received less attention, with the exception of the work by Snegur et al. [8] with a series of *N*-heterocyclic groups linked to ferrocenyl compounds such as ferrocenylmethylbenzimidazole which were found to exhibit anticancer activity. The importance of related compounds is again highlighted by Howarth and Hanlon [9] through the synthesis of *N*-ferrocenylmethyl-*N*′-methyl-2-substituted benzimidazolium iodide salts which are active against the malaria parasite, *P. falciparum*. Later, Bildstein [10] highlighted the stereoelectronic influence of the ferrocenyl group on carbenes in terms of steric protection, electron-donation and reversible redox chemistry that makes them interesting compounds for a variety of applications. However, in his findings, he suggests that the ferrocenyl group has no capability of electronically stabilising NHCs.

Another important aspect of this study is the application of green chemistry principles to synthesis. Especially relevant is the exclusion of solvents whenever possible by applying solvent-free synthetic techniques which have been shown to give higher yields and selectivities as compared to the same reaction carried out in the presence of organic solvents [11]. Hence, the methods of Ranu et al. [12] has been adopted and modified in this study. Therefore, in this report we present work on the synthesis and characterisation of new ferrocenylalkylimidazoles and ferrocenylalkylimidazolium salts with the aim of studying the effects of structural variations on the physical and electronic properties of the salts, since the ability to tune their structural and electronic properties has implications on their applications in catalysis [13] and as environmentally green ionic liquid solvents.

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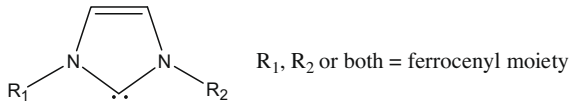


Fig. 1. General structure of ferrocenylalkylimidazolium carbenes.

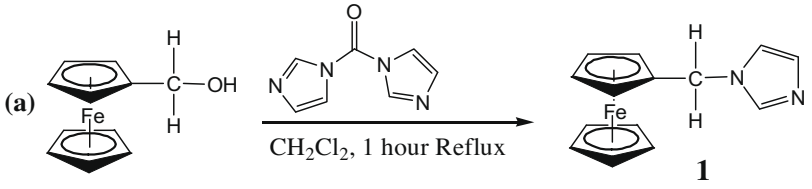
2. Results and discussion

All the series of ferrocenylalkylimidazolium salts reported here were synthesised by using ferrocenylalkylimidazoles as precursors, which were synthesised via two routes. In the first method, ferrocenylcarbinols were first synthesised from the reduction of ferrocene monocarboxyaldehyde. The second step involved synthesis of ferrocenylalkylimidazoles (Scheme 1) from a reaction of equimolar amounts of ferrocenylcarbinols and *N,N′*-carbonyldiimidazole in anhydrous dichloromethane. Attempts to perform this reaction under solvent-free conditions were unsuccessful even though a similar reaction with the sulfur analogue, *N,N′*-thiocarbonyldiimidazole, has been reported [14]. The reaction mixture was refluxed for 1 h followed by a work-up procedure and then chromatographic isolation of the products as reported by Simenel et al. [15] was performed.

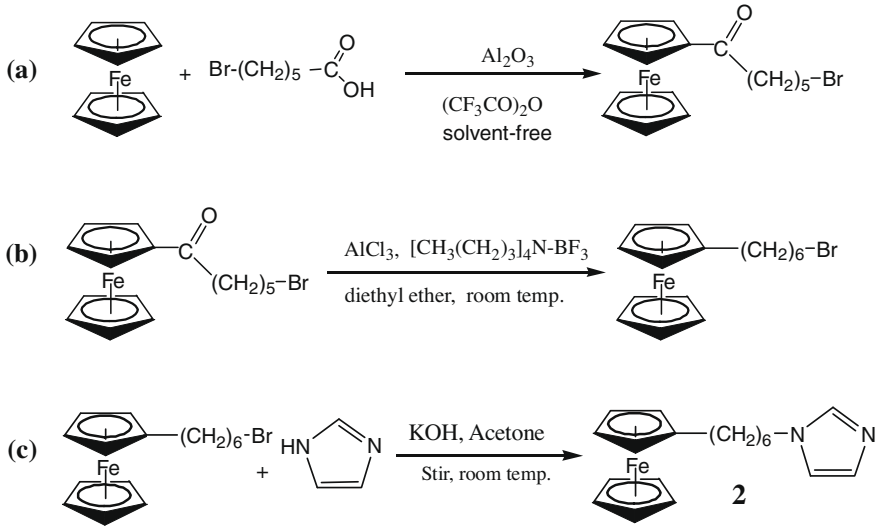
In the second method, ferrocenylalkyl bromides were first synthesised as precursors for the synthesis of ferrocenylalkylimidazoles through selective monoacylation of ferrocene. This was achieved by using a *greener approach* (as opposed to the common conditions and reagents for a Friedel–Crafts acylation reaction) involving the reaction between bromoalkylcarboxylic acid and trifluoroacetic anhydride with ferrocene on activated alumina under solvent-free conditions (Scheme 2a). A similar reaction has been described by Ranu et al. [12], however, attempts to follow the suggested method led to lower yields and significant amount of decomposition. Hence, we slightly modified the described procedure by cooling the reaction mixture (~15 °C). This was achieved by having the reaction flask with the exothermic mixture initially kept in a temperature controlled cool water bath with occasional shaking and cooling in an ice bath for about 30 min to obtain a pink coloured solid mass. This was then placed on a shaker at room temperature under vacuum and vigorously shaken for 36 h to ensure maximum homogeneity of the mixture and minimal decomposition of the product. The above method for the acylation of ferrocene has a significant advantage over existing methods in that it avoids the synthesis of acyl chlorides as a separate step and the handling of aluminium trichloride, a corrosive and sensitive reagent was also avoided. Moreover, the methodology provides a direct use of carboxylic acids, operational simplicity and excellent selectivity (only monoacylation occurs), and thus it offers significant improvements over other procedures involving Friedel–Crafts acylation of ferrocenes [16].

The second step involved the reduction of the ferrocenylalkyl ketone (Scheme 2b) by using equimolar quantities of aluminium trichloride and *tert*-butylamine-borane in dry diethyl ether under a nitrogen atmosphere at room temperature. This reaction proved to be very efficient, providing yields in excess of 92%. The third step (Scheme 2c) also occurred under mild conditions with the use of equimolar amounts of the ferrocenylalkyl bromide and the imidazole in the presence of a base, KOH powder. The ferrocenylalkylimidazole product was isolated fairly easily and yields were good.

The synthesis of ferrocenylalkylimidazolium salts was achieved firstly by quaternization of the ferrocenylalkylimidazoles **1** and **2** to form the corresponding desired cations and anions (Scheme 3). This was achieved by using an alkyl iodide or bromide compound



Scheme 1. Synthesis of ferrocenylalkylimidazole *via* a ferrocenylmethanol route.



Scheme 2. Synthesis of ferrocenylalkylimidazole *via* a ferrocenylalkyl bromide route.

as the alkylating reagent. This yielded the primary halide salts (compounds **3–8**, Table 1). Secondly, a metathesis reaction was carried out that involved anion exchange using compounds such as sodium tetrafluoroborate, sodium hexafluorophosphate and sodium hexafluoroantimonate with the aim of introducing a variety of counter anions.

The ferrocenylalkylimidazolium halide salts **3–7** were found to be solids at room temperature while **8** was a liquid oil. If the alkyl linker chain length is kept constant (i.e. $n = 1$ or 6), then the trend observed for a series of salts is that the melting points decrease with an increase in the molecular size of the imidazolium alkyl side chain **R** on the imidazole moiety in the order *methyl* > *n-butyl* > *n-octyl*. Compound **8** was a liquid oil due to a combination of a long alkyl linker (hexyl) and an equally long octyl imidazole side chain. The two long alkyl derivatives combine to exert strain on the molecular chain of **8** and affect its ability to pack in any ordered fashion that will result in solidification. This poor crystal packing causes a lowering of the melting point and is a general observation for all the series studied. The melting points of the salts studies are affected by a combination of the properties of the constituent anions and cations. It is interesting to note that the results correlate with what is known for ionic liquid anion–cation combinations [17]. In addition, the oily compound **8** is expected to have the weakest inter-ion Coulombic attraction due to a larger ionic separation, since the size of its cation is unusually larger than its anion as compared with those of the halide salts **3–7.** The change in the length of the alkyl ferrocenyl-imidazolium linker from $n = 1$ to $n = 6$ whilst keeping the other variables constant, also had a similar but less drastic effect on the melting point in that the longer chain ($n = 6$) salts have lower meting points. This may be observed by comparing salts **3** vs. **6**, **4** vs. **7**, **5** vs. **8**, **9** vs. **12**, **10** vs. **13** and **11** vs. **14** with the larger anions being anomalies (i.e. salts **15** vs. **18** and **19** vs. **22**).

As indicated earlier the halide salts were further investigated by carrying out anion exchange reactions to provide other ferrocenylalkylimidazolium salts which are used to further probe the effect of the counter anion. This was achieved by the metathesis reactions shown in Scheme 4.

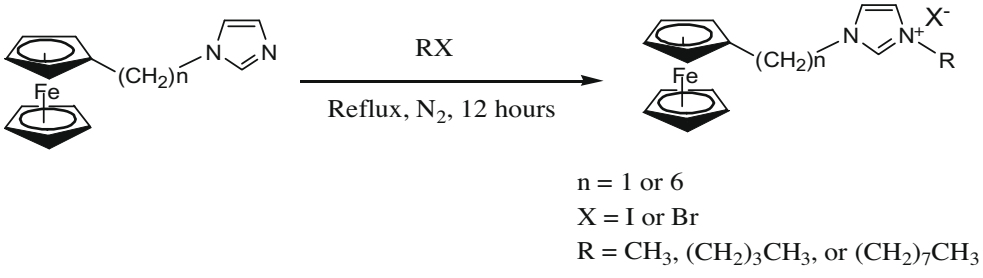
It is interesting to note again the effect of changing the counter-ion on the physical properties of the salts. An example is the change from the solid-state in compound **5**, to pastes in compounds **11** and **17** and subsequently to a liquid oil in compound **21**. This phenomenon correlates with previous observation whereby an increase in the size of the counter-ion introduces increased asymmetry which usually leads to a decrease in the melting points of salts [17]. A larger counter anion will also cause a reduction in the melting point of a salt as a result of the disruption in the crystal packing and a reduction of the crystal lattice energy. Moreover, a gradual increase in the size of the anion while keeping the same cation reduces the Coulombic attraction between the two ions in addition to the fact that larger ions enable charge delocalization, further reducing the overall charge density and hence causing a decrease in melting point.

In addition to the observation of changes in melting point, the effect of varying the structural features of the salts was also monitored on the electronic environment around the imidazolium ion. To understand this, in Table 1 we tracked the chemical shifts of the imidazolium C-1 protons of the primary halide salts and the derivatives that were obtained via metathesis. The ^{1}H NMR analysis of the ferrocenylalkylimidazolium salts show that there is a considerable deshielding effect by the various anions on the imidazolium protons. This is evident from the significant shift to a lower resonance experienced by the imidazolium salts protons relative to those of the neutral ferrocenylalkylimidazole compounds **1** (7.50 ppm) and **2** (7.47 ppm). For instance, this is illustrated by comparing the ^{1}H NMR spectrum of compound **2** with that of its derivative salt compound **6** (see also Fig. 2.1 and Tables 2.1–2.5 of the Supplementary material). Generally, the deshielding effect is more pronounced by the halide salts compared to other anions. The size of the anion and its effective charge influence the electrostatic interaction on the imidazolium protons, hence different chemical shifts are observed. The size of the anions increases in the order $Br^- < I^- < BF_4^- < PF_6^- < SbF_6^-$, however, the effective charge is highest on Br^-. Hence, the NMR chemical shift on the imidazolium protons of salts **3** to **8** are relatively shifted down field compared to all the analogues derived from them through anion

Table 1
The effects of molecular structural variations on the properties of ferrocenylalkylimidazolium salts.

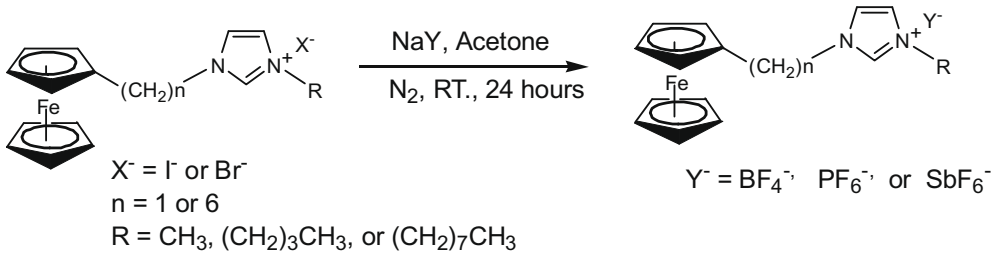
Compound[a]	*n*	–**R**	**X**$^-$	mp (°C)[b]	^{1}H NMR (ppm)[c]
1	1	None	None	66–67	7.50
2	6	None	None	68–70	7.47
3	1	$-CH_3$	I	130–135	10.13
4	1	$-(CH_2)_3CH_3$	Br	85	10.58
5	1	$-(CH_2)_7CH_3$	Br	71	10.69
6	6	$-CH_3$	I	95	10.08
7	6	$-(CH_2)_3CH_3$	Br	75	10.79
8	6	$-(CH_2)_7CH_3$	Br	Oil	10.76
9	1	$-CH_3$	BF_4^-	145	8.91
10	1	$-(CH_2)_3CH_3$	BF_4^-	73	9.19
11	1	$-(CH_2)_7CH_3$	BF_4^-	Paste	9.17
12	6	$-CH_3$	BF_4^-	91	9.94
13	6	$-(CH_2)_3CH_3$	BF_4^-	Oil	8.96
14	6	$-(CH_2)_7CH_3$	BF_4^-	Oil	9.17
15	1	$-CH_3$	PF_6^-	66–68	9.05
16	1	$-(CH_2)_3CH_3$	PF_6^-	70	8.62
17	1	$-(CH_2)_7CH_3$	PF_6^-	Paste	8.61
18	6	$-CH_3$	PF_6^-	93	9.18
19	1	$-CH_3$	SbF_6^-	66	9.94
20	1	$-(CH_2)_3CH_3$	SbF_6^-	52	8.44
21	1	$-(CH_2)_7CH_3$	SbF_6^-	Oil	8.44
22	6	$-CH_3$	SbF_6^-	68	9.58

[a] See Section 4.
[b] Some compounds are oils or pastes at RT.
[c] Chemical shifts of imidazole H_1 Proton ($CDCl_3$).



n = 1 or 6
X = I or Br
R = CH_3, $(CH_2)_3CH_3$, or $(CH_2)_7CH_3$

Scheme 3. Synthesis of ferrocenylalkylimidazolium halide salts.



Scheme 4. Anion exchange reaction on ferrocenylalkylimidazolium halide salts

metathesis. The relatively higher charge density seen on the halide anions also contributes to their relatively higher melting points compared with their salt analogues. Solid-state X-ray crystallography and ^{1}H NMR evidence suggests that the halides can enter into hydrogen bonding with cationic centres [18]. This bonding has been postulated to be between the electron-deficient C-2 carbon atom of the imidazolium ring and the halides.

3. Conclusions

The synthesis of a series of ferrocenylalkylimidazolium salts has been achieved. In some steps the green chemistry concept of solventless reactions and atom economy was applied by the use of equimolar amounts of neat reagents without the use of potentially harmful organic solvents. Generally, the salts generated via the solventless technique were obtained in higher yields as compared to procedures utilizing solvents. The key structure-dependent property of the salts was investigated by determining their melting temperatures. Salts that structurally contain bulkier cations or anions have relatively lower melting points compared with those consisting of sterically smaller ionic components. This is postulated to be due to weaker intermolecular forces of interaction and a poorer ability for ordered crystal packing. The electronic nature of the various anions has been shown to influence the chemical shifts of the imidazolium protons with the halide anions showing the largest influence.

4. Experimental

4.1. General

All reactions involving air and moisture sensitive compounds were carried out under a nitrogen atmosphere using standard Schlenk techniques. Solvents were dried by using standard methods under a nitrogen atmosphere. Melting points were recorded with a Stuart Scientific Melting Point apparatus SMP3 in duplicate and the readings were averaged. Infrared spectra were recorded with a Perkin Elmer Universal ATR (Spectrum 100) FT-IR spectrometer. All NMR experiments were conducted in deuterated chloroform with a 400 MHz Bruker Advance 3 spectrometer. Mass spectra were recorded on a VG70-SEQ/MSSMS2 spectrometer at the Cape Technikon or the Waters LCT Premier TOF (time of flight) MS using direct infusion at the University of KwaZulu-Natal.

All chemicals used for synthesis were commercially available and were used as received. Ferrocenylalkylimidazole precursors were synthesised by adaptation of literature procedures. The first precursor 1-(ferrocenylmethyl)-1H-imidazole **1** was obtained from ferrocenylmethanol by the method of Simenel et al. [15]. The second precursor 1-(6-ferrocenylhexyl)-1H-imidazole **2** was obtained through a three-step synthetic procedure. The first step (Scheme 2a) was an adaptation from Ranu et al. [12], while the second step (Scheme 2b) was adapted from Lau et al. [19]. In the final step (Scheme 2c), imidazole (148 mg, 2.17 mmol) was added to acetone (2.0 cm^3) and the solution was stirred. Potassium hydroxide powder (128 mg, 2.27 mmol) was then introduced and allowed to dissolve, forming a homogenous solution. The solution was stirred for about 30 min and then 6-bromohexylferrocene (834 mg, 2.39 mmol) in acetone (1.0 cm^3) was introduced to the solution dropwise and allowed to stir for about 1 h at room temperature. The solution was then filtered and concentrated. The crude product was passed through a column of silica gel. Diethyl ether recovered unreacted 6-bromohexylferrocene (150 mg) while ethyl acetate/methanol (10:1) afforded the product **2** as yellow crystals (591 mg, 81%); mp 68–70 °C; IR (KBr cm^{-1}) 3090, 2932, 2859, 1655, 1508, 1466, 1439, 1234, 1107, 1076, 999, 829, 802, 745, 671, 509, 486; ^{1}H NMR ($CDCl_3$) 7.47 (1H, s, NCH), 7.07 (1H, s, NCH), 6.91 (1H, s, NCH), 4.09 (5H, s, C_5H_5), 4.04 (4H, m, C_5H_4), 3.91 (2H, t, *J* 7.1, CH_2), 2.31 (2H, t, *J* 7.3, CH_2), 1.77 (2H, m, CH_2), 1.48 (2H, m, CH_2), 1.31 (4H, m, 2 × CH_2); ^{13}C NMR ($CDCl_3$) 137.48, 129.76, 119.22, 89.45, 68.87, 68.45, 67.48, 47.42, 31.44, 31.37, 29.89, 29.35, 26.83; *m*/*z* (EI) 337 (M^++1, 14%), 336 (M^+, 61%), 272 (19), 271 (100), 269 (10), 199 (9), 121 (26); Anal. Calc. for $C_{19}H_{24}N_2Fe$: C, 67.8; H, 7.2; N, 8.3; [M^+], 336.128888. Found: C, 67.5; H, 7.3; N, 8.0%; [M^+], 336.128905.

4.2. Synthesis of ferrocenylalkylimidazolium halide salts

The ferrocenylalkyl imidazolium halide (Br and I) salts were all synthesised following a similar procedure. A typical method is described for 1-(ferrocenylmethyl)-3-methylimidazolium iodide **3**.

4.2.1. 1-(Ferrocenylmethyl)-3-methylimidazolium iodide *3*

In a two-neck round-bottom flask, methyl iodide (4 mL, 9.12 g, 64.26 mmol) was added to ferrocenylmethyl imidazole (1.0098 g, 3.7944 mmol) and allowed to reflux gently for ~15 h at 50 °C under an atmosphere of nitrogen. The solution was then allowed to cool to room temperature before it was washed with anhydrous diethyl ether several times to yield a yellow solid. The crude product was dissolved in dichloromethane and recrystallized in hexane to yield yellow crystals of **3** (1.07 g, 70%), mp 130–135 °C; IR (cm^{-1}) 3434, 3042, 1567, 1549, 1428, 1150, 1040, 837, 821, 755, 620, 502, 482; ^{1}H NMR ($CDCl_3$) 10.13 (1H, s, NCH), 7.09 (2H, m, 2 × NCH), 5.33 (2H, s, CH_2), 4.43 (2H, t, *J* 1.8, C_5H_4), 4.26 (2H, t, *J* 1.8, C_5H_4), 4.25 (5H, s, C_5H_5), 4.01 (3H, s, CH_3); *m*/*z* (ESI) 197.1 (3%), 198.5 (100%), 199.2 (15%), 280.6 (M^+ - I^-, 7.4%); Anal. Calc. for $C_{15}H_{17}N_2Fe^+$; [M^+]–I, 281.07411.

4.2.2. 1-(Ferrocenylmethyl)-3-butylimidazolium bromide *4*

This salt was synthesised following a similar method to **3** using butyl bromide (10 mL) to yield 1.48 g, 97% of **4**; mp 85 °C; IR (ATR cm^{-1}) 3404, 3065, 2958, 1625, 1558, 1464, 1238, 1150, 1105, 1000, 816, 773, 624, 480; ^{1}H NMR ($CDCl_3$) 10.58 (1H, s, NCH), 7.06 (2H, m, 2 × NCH), 5.31 (2H, s, NCH_2), 4.42 (2H, s, CH_2), 4.26 (7H, s, C_5H_5, C_5H_4), 4.24 (2H, m, C_5H_4), 1.87 (2H, m, CH_2), 1.36 (4H, m, 2 × CH_2), 0.95 (3H, m, CH_3); *m*/*z* (ESI) 124.9 (0.9%), 181.1 (22%),

196.9 (3%), 198.6 (100%), 199.4 (15%), 322.8 (M^+-Br^-), 323.7 (7%), 378.9 (4%), 464.7 (6%), 724.8 (1%); Anal. Calc. for $C_{18}H_{23}N_2Fe^+$; $[M^+]-Br$, 323.12051.

4.2.3. 1-(Ferrocenylmethyl)-3-octylimidazolium bromide **5**

This salt was synthesised following a similar method to **3** using octyl bromide (12 mL) to yield 1.54 g, 94% of **5**; mp 71 °C; IR (ATR cm^1) 3476, 3409, 3090, 2924, 2854, 1621, 1438, 1157, 1105, 999, 835, 814, 770, 734, 558, 481; ^1H NMR ($CDCl_3$) 10.69 (1H, s, NCH), 7.07 (2H, d, 2 × NCH), 5.36 (2H, s, CH_2), 4.42 (2H, s, CH_2), 4.24 (9H, m, C_5H_5, C_5H_4), 1.24 (14H, m, 7 × CH_2), 0.84 (3H, m, CH_3); *m/z* (ESI) 181 (0.6%), 197 (3.4%), 198.7 (100%), 199.5 (14%), 265.8 (0.5%), 293.1 (4%), 377.2 (5%), 378.9 (M^+–Br, 100%), 379.5 (23%); Anal. Calc. for $C_{22}H_{29}N_2Fe^+$; $[M^+]$–Br, 377.16801.

4.2.4. 1-(6-Ferrocenylhexyl)-3-methylimidazolium iodide **6**

This salt was synthesised following a similar method to **3** using methyl iodide (3.0 cm^3, 6.84 g, 48.2 mmol) and compound **2** (5.00 g, 13.7 mmol) to yield yellow solid crystals of **6** (6.16 g, 94%), mp 95 °C; IR (KBr cm^{-1}) 3083, 2927, 2858, 1584, 1564, 1471, 1433, 1374, 1257, 1174, 1103, 1040, 1000, 920, 808, 729, 653, 616, 512, 491, 419; ^1H NMR ($CDCl_3$), 10.08 (1H, s, NCH), 7.43 (1H, s, NCH), 7.34 (1H, s, NCH,), 4.31 (2H, t, *J* 7.3, CH_2), 4.11 (3H, s, NCH_3), 4.09 (5H, s, C_5H_5), 4.04 (4H, m, C_5H_4), 2.33 (2H, t, *J* 7.5, CH_2), 1.92 (2H, m, CH_2), 1.47 (2H, m, CH_2), 1.38 (4H, m, 2 × CH_2); ^{13}C NMR ($CDCl_3$), 137.44, 123.86, 122.29, 89.37, 68.91, 68.51, 67.49, 50.66, 37.53, 31.33, 30.58, 29.88, 29.20, 26.54; *m/z* (FAB) 351 (M^+–I, 100%), 199 (7), 154 (21), 136 (20), 83 (12), Anal. Calc. for $C_{20}H_{27}N_2FeI$: C, 50.2; H, 5.7; N, 5.9; $[M^+]$–I, 351.152363. Found: C, 50.1; H, 5.8; N, 5.8%; $[M^+]$–I, 351.152426.

4.2.5. 1-(6-Ferrocenylhexyl)-3-butylimidazolium bromide **7**

This salt was synthesised following a similar method to **3** using *n*-bromobutane (5.0 cm^3, 6.38 g, 46.6 mmol) and compound **2** (5.00 g, 13.7 mmol) to yield 5.77 g, 89%, of brown powder of **7** (mp 75 °C; IR (KBr cm^{-1}) 3047, 2954, 2935, 2856, 1691, 1559, 1465, 1377, 1329, 1167, 1105, 1021, 999, 922, 820, 754, 732, 658, 635, 614; ^1H NMR ($CDCl_3$), 10.79 (1H, s, NCH), 7.25 (2H, s, 2 × NCH), 4.37 (4H, m, 2 × CH_2), 4.18 (5H, s, C_5H_5), 4.14 (4H, m, C_5H_4), 2.27 (2H, t, *J* 7.2, CH_2), 1.38 (8H, m, 4 × CH_2), 0.99 (3H, t, *J* 6.5, CH_3); ^{13}C NMR ($CDCl_3$), 137.63, 122.33, 122.25, 89.36, 68.88, 68.47, 67.47, 50.44, 50.24, 32.58, 31.35, 30.70, 29.86, 29.25, 26.54, 19.88, 13.90; *m/z* (FAB) 393 (M^+–Br, 100%), 271 (10), 199 (12), 179 (7), 165 (5), 151 (10), 138 12), 121 (11); (Found: $[M^+]$–Br, 393.199288. $C_{23}H_{33}N_2FeBr$ requires $[M^+]$–Br, 393.199314).

4.2.6. 1-(6-Ferrocenylhexyl)-3-octylimidazolium bromide **8**

This salt was synthesised following a similar method to **3** using *n*-bromooctane (5.0 cm^3, 5.59 g, 29.0 mmol) and compound **2** (5.00 g, 13.7 mmol) to yield 6.24 g, 86% of brown oil **8**; IR ($CHCl_3$ cm^{-1}) 3022, 2935, 2860, 1584, 1559, 1468, 1238, 1223, 1162, 1104, 1001, 821, 693, 485; ^1H NMR ($CDCl_3$), 10.76 (1H, s, NCH), 7.28 (2H, m, 2 × NCH), 4.37 (5H, s, C_5H_5), 4.17 (8H, m, 2 × CH_2, C_5H_4), 2.29 (2H, m, CH_2), 1.97 (4H, m, 2 × CH_2), 1.70 (4H, m, 2 × CH_2), 1.33 (12H, m, 6 × CH_2), 0.89 (3H, t, *J* 7.2, CH_3); ^{13}C NMR ($CDCl_3$), 137.63, 122.33, 122.25, 89.36, 68.88, 68.47, 67.47, 50.24, 32.58, 31.35, 30.70, 29.86, 29.25, 26.54, 19.88, 13.90; *m/z* (FAB) 449 (M^+–Br, 100%), 403 (7), 328 (8), 293 (5), 271 (20), 249 (11), 235 (11), 221 (11), 199 (28), 181 (9), 151 (7), 135 (10), 121 (40), 108 (18); (Found: $[M^+]$–Br, 449.261993. $C_{27}H_{41}N_2FeBF_4$ requires $[M^+]$–Br, 449.261914).

4.3. Anion exchange on ferrocenylalkylimidazolium halide salts

All the ion exchange reactions were conducted following a similar procedure. A typical method is described for the tetrafluoroborate ion.

4.3.1. 1-(Ferrocenylmethyl)-3-methylimidazolium tetrafluoroborate **9**

In a two-neck round-bottom flask was added sodium tetrafluoroborate (0.08 g, 0.77 mmol) to a solution of 1-(ferrocenylmethyl)-3-methylimidazolium iodide (0.31 g, 0.75 mmol) in acetone (20 mL). The mixture was stirred under a nitrogen atmosphere for 24 h at room temperature. The reaction mixture was filtered through a plug of celite and the filtrate was then concentrated in *vacuo* to give 0.21 g, 76% of an orange powder **9** (mp 145 °C; IR (ATR cm^{-1}) 3436, 3069, 1559, 1323, 1152, 1104, 1039, 1000, 819, 772, 748, 618, 480; ^1H NMR ($CDCl_3$) 8.91 (1H, s, NCH), 7.08 (1H, s, NCH), 7.07 (1H, s, NCH), 5.18 (2H, s, CH_2), 4.37 (2H, t, *J* 1.8, C_5H_4), 4.27 (2H, t, *J* 1.8, C_5H_4), 4.27 (5H, s, C_5H_5), 3.91 (3H, s, CH_3); ^{13}C NMR ($CDCl_3$) 136.18, 123.08, 121.40, 78.35, 77.26, 69.89, 69.68, 69.26, 50.11; *m/z* (ESI) 197.1 (3%), 198.6 (100%), 199.2 (14%), 280.6 ($M^+-BF_4^-$, 7.5%), 281.6 (1.1%). Anal. Calc. for $C_{15}H_{17}N_2Fe^+$; $[M^+]-BF_4$, 281.07411.

4.3.2. 1-(Ferrocenylmethyl)-3-butylimidazole tetrafluoroborate **10**

This salt was synthesised following a similar method to **9** using sodium tetrafluoroborate (0.24 g, 2.15 mmol) and 1-(ferrocenylmethyl)-3-butylimidazolium bromide (0.43 g, 1.08 mmol) to yield a brown powder of **10** (0.33 g, 75%); mp 73 °C; IR (ATR cm^{-1}) 3147, 3094, 2961, 1561, 1466, 1152, 1035, 822, 752, 625, 499, 481; ^1H NMR ($CDCl_3$) 9.1900 (1H, s, NCH), 7.1199 (2H, m, 2 × NCH), 5.23 (2H, s, CH_2), 4.38 (2H, t, *J* 1.8, C_5H_4), 4.24 (2H, t, *J* 1.8, C_5H_4), 4.16 (5H, s, C_5H_5), 1.82 (2H, m, CH_2), 1.33 (4H, m, CH_2), 0.93 (3H, t, *J* 7.2, CH_3); ^{13}C NMR ($CDCl_3$) 207, 136, 121, 77.24, 69.8, 69.5, 69.2, 50, 32, 19, 13; *m/z* (ESI) 124.9 (0.3%), 181.2 (12.1%), 182 (1.2%), 197 (2.2%), 198.6 (100%), 199.3 (15%), 322.7 (27%), 323.7 (M^+-BF_4, 5.4%); Anal. Calc. for $C_{18}H_{23}N_2Fe^+$; $[M^+]$ 323.12051.

4.3.3. 1-(Ferrocenylmethyl)-3-octylimidazolium tetrafluoroborate **11**

This salt was synthesised following a similar method to **9** using an excess of sodium tetrafluoroborate (0.52 g, 4.71 mmol) and 1-(ferrocenylmethyl)-3-octylimidazolium bromide (0.39 g, 0.83 mmol) to yield an orange-yellow paste identified as **11** (0.38 g, 97%); IR (ATR cm^{-1}) 2927, 1561, 1014, 773, 550, 526, 483; ^1H NMR ($CDCl_3$) 9.17 (1H, s, NCH), 7.09 (1H, s, NCH), 7.07 (1H, s, NCH), 5.22 (2H, s, CH_2), 4.38 (2H, t, *J* 1.8, C_5H_4), 4.25 (2H, t, *J* 1.8, C_5H_4), 4.23 (5H, s, C_5H_5), 4.14 (2H, m, CH_2), 1.26 (12H, m, 6 × CH_2), 0.85 (3H, m, CH_3); ^{13}C NMR ($CDCl_3$) 135.9, 121.2, 121.1, 77.2, 69.9, 69.5, 69.3, 50.3, 50.0, 31.6, 30.1, 29, 28.8, 26.2, 22.6, 14.0; *m/z* (ESI) 197.1 (2.9%), 198.6 (100%), 199.4 (12%), 377.2 (2.8%), 378.9 ($M^+-BF_4^-$, 59%), 379.7 (14%), 380.8 (2.6%); Anal. Calc. for $C_{22}H_{29}N_2Fe^+$; $[M^+]-BF_4$, 377.16801.

4.3.4. 1-(6-Ferrocenylhexyl)-3-methylimidazolium tetrafluoroborate **12**

This salt was synthesised following a similar method to **9** using sodium tetrafluoroborate (0.46 g, 4.18 mmol) and 1-(6-ferrocenylhexyl)-3-methylimidazolium iodide (2.00 g, 4.18 mmol) to give a yellow solid identified as **12** (1.79 g, 98%); mp 91 °C; IR (KBr cm^{-1}) 3088, 2928, 2860, 1636, 1584, 1564, 1471, 1375, 1312, 1258, 1174, 1103, 1084, 1041, 1000, 808, 730, 653, 616; ^1H NMR ($CDCl_3$) 9.94 (1H, s, NCH), 7.51 (1H, t, *J* 1.7, NCH), 7.41 (1H, t, *J* 1.7, NCH), 4.29 (2H, t, *J* 7.4, CH_2), 4.09 (3H, s, NCH_3), 4.08 (5H, s, C_5H_5), 4.03 (4H, m, C_5H_4), 2.30 (2H, t, *J* 7.5, CH_2), 1.89 (2H, m, CH_2), 1.47 (2H, m, CH_2), 1.35 (4H, m, 2 × CH_2); ^{13}C NMR ($CDCl_3$) 137.10, 124.10, 122.53, 89.41, 68.92, 68.50, 67.49, 50.59, 37.52, 31.40, 30.61, 29.86, 29.86, 29.23, 26.52; *m/z* (FAB) 351 (M^+-BF_4,

100%), 200 (11), 154 (6), 137 (10), 121 (10), 121 (10), 109 (10); (Found: $[M^+]-BF_4$, 351.152401. $C_{20}H_{27}N_2Fe\ BF_4$ requires $[M^+]-BF_4$, 351.15236).

*4.3.5. 1-(6-Ferrocenylhexyl)-3-butylimidazolium tetrafluoroborate **13***

This salt was synthesised following a similar method to **9** using sodium tetrafluoroborate (0.70 g, 6.34 mmol) and 1-(6-ferrocenylhexyl)-3-butylimidazolium bromide (3.00 g, 6.34 mmol) to give a brown oil identified as **13** (2.83 g, 93%); IR ($CHCl_3$ cm^{-1}) 3153, 3095, 3031, 2937, 2861, 1697, 1564, 1467, 1362, 1288, 1219, 1165, 1062, 858, 821, 670, 520, 483; ^1H NMR ($CDCl_3$), 8.96 (1H, s, NCH), 7.34 (2H, m, 2 × NCH), 4.20 (4H, m, 2 × CH_2), 4.10 (5H, s, C_5H_5), 4.05 (4H, m, C_5H_4), 2.31 (2H, t, *J* 7.3, CH_2), 1.87 (4H, m, 2 × CH_2), 1.48 (2H, m, CH_2), 1.35 (6H, m, 3 × CH_2), 0.96 (3H, t, *J* 7.2, CH_3); ^{13}C NMR ($CDCl_3$), 136.24, 122.65, 122.57, 89.49, 68.95, 68.52, 67.52, 50.47, 50.26 32.38, 31.33, 30.50, 29.85, 29.20, 26.47, 19.80, 13.79; *m*/*z* (FAB) 480 (M^+, 10%), 393 (100%), 347 (8), 272 (12), 200 (10), 179 (9), 165 (8), 151 (17), 138 (18), 121 (18); (Found: $[M^+]$, 480.202425. $C_{23}H_{33}N_2FeBF_4$ requires $[M^+]$, 480.202232).

*4.3.6. 1-(6-Ferrocenylhexyl)-3-octylimidazolium tetrafluoroborate **14***

This salt was synthesised following a similar method to **9** using sodium tetrafluoroborate (0.63 g, 5.68 mmol) and 1-(6-ferrocenylhexyl)-3-octylimidazolium bromide (3.00 g, 5.67 mmol) to give a brown oil identified as **14** (2.80 g, 92%); IR ($CHCl_3$ cm^{-1}) 3026, 2933, 2860, 1695, 1586, 1563, 1468, 1207, 1163, 1065, 822, 670, 514, 485; ^1H NMR ($CDCl_3$), 9.17 (1H, s, NCH), 7.25 (2H, m, 2 × NCH), 4.97 (8H, m, 2 × CH_2 and C_5H_4), 4.14 (5H, s, C_5H_5), 1.76 (8H, m, 4 × CH_2), 1.30 (14H, m, 7 × CH_2), 0.91 (3H, t, *J* 7.2, CH_3); ^{13}C NMR ($CDCl_3$), 136.24, 122.65, 122.57, 89.49, 68.95, 68.52, 50.47, 32.38, 31.33, 30.50, 29.85, 29.20, 26.47, 19.80, 13.79; *m*/*z* (FAB) 536 (M^+, 24%), 450 (100), 404 (8), 328 (8), 293 (5), 271 (10), 250 (11), 236 (12), 221 (11), 207, (20), 186 (5), 151 (4), 137 (9), 121 (25), 109 (13); (Found: $[M^+]$, 536.264943. $C_{27}H_{41}N_2FeBF_4$ requires $[M^+]$, 536.264832).

*4.3.7. 1-(Ferrocenylmethyl)-3-methylimidazole hexafluorophosphate **15***

This salt was synthesised following a similar method to **9** using sodium hexafluorophosphate (0.13 g, 0.76 mmol) and 1-(ferrocenylmethyl)-3-methylimidazolium iodide (0.30 g, 0.74 mmol) to yield 0.23 g, 72% of an orange crystals identified as **15**; mp 66–68 °C; IR (ATR cm^{-1}) 3429, 1624, 1567, 1331, 1150, 812, 619, 554, 500, 480; ^1H NMR ($CDCl_3$) 9.05 (1H, s, NCH), 7.11 (1H, s, NCH), 7.0868 (1H, s, NCH), 5.22 (2H, s, CH_2), 4.39 (2H, t, *J* 1.8, C_5H_4), 4.23 (7H, t, *J* 1.8, C_5H_4), 4.24 (5H, s, C_5H_5), 3.94 (3H, s, CH_3); ^{13}C NMR ($CDCl_3$) 136.06, 122.79, 121.23, 78.02, 77.23, 69.97, 69.59, 69.19, 50.18; *m*/*z* 197 (2.3%), 198.6 (100%), 199.3 (13.1%), 280.6 ($M^+-PF_6^+$, 4.5%); Anal. Calc. for $C_{15}H_{17}N_2Fe^+$; $[M^+]-PF_6$, 281.07411.

*4.3.8. 1-(Ferrocenylmethyl)-3-butylimidazolium hexafluorophosphate **16***

This salt was synthesised following a similar method to **9** using sodium hexafluorophosphate (0.30 g, 1.81 mmol) and 1-(ferrocenylmethyl)-3-butylimidazolium bromide (0.43 g, 1.08 mmol) to yield a brown powder identified as **16** (0.48 g, 96%); mp 70 °C; IR (ATR cm^{-1}) 3639, 3167, 2934, 1562, 1448, 1154, 820, 775, 555, 501, 478; ^1H NMR ($CDCl_3$) 8.62 (1H, s, NCH), 7.15 (1H, s, NCH), 7.13 (1H, s, NCH), 5.17 (2H, s, CH_2), 4.37 (2H, t, *J* 1.8, C_5H_4), 4.25 (2H, t, *J* 1.8, C_5H_4), 4.22 (5H, s, C_5H_5), 4.11 (2H, t, *J* 5.8, CH_2), 1.81 (2H, m, CH_2), 1.32 (2H, m, CH_2), 0.93 (3H, m, CH_3); ^{13}C NMR ($CDCl_3$) 134.8, 121.6, 121.5, 78.1, 77.2, 69.9, 69.5, 69.3, 50.0, 31.8, 19.4, 13.3; *m*/*z* 125 (1.7%), 181.2 (13.6%), 182.1 (1.6%), 197 (2.4%), 198.6 (100%), 199.3 (13.3%), 241.9 (4%), 322.8 ($M^+-PF_6^-$, 12.7%), 323.7 (2.8%); Anal. Calc. for $C_{18}H_{23}N_2Fe^+$; $[M^+]-PF_6$, 323.12051.

*4.3.9. 1-(Ferrocenylmethyl)-3-octylimidazolium hexafluorophosphate **17***

This salt was synthesised following a similar method to **9** using an excess of sodium hexafluorophosphate (0.55 g, 3.27 mmol) and 1-(ferrocenylmethyl)-3-octylimidazolium bromide (0.39 g, 0.84 mmol) to yield an orange-yellowish paste identified as **17** (0.42 g, 95%); mp 74 °C; IR (ATR cm^{-1}) 2928, 1709, 1366, 1233, 1150, 824, 556, 501, 483; ^1H NMR ($CDCl_3$) 8.61 (1H, s, NCH), 7.12 (1H, s, NCH), 7.09 (1H, s, NCH), 5.17 (2H, s, CH_2), 4.36 (2H, t, *J* 1.8, C_5H_4), 4.26 (2H, t, *J* 1.8, C_5H_4), 4.23 (5H, s, C_5H_5), 4.09 (2H, t, *J* 7.1, CH_2), 1.24 (12H, m, 6 × CH_2), 0.85 (3H, m, CH_3); ^{13}C NMR ($CDCl_3$) 134.9, 121.4, 77.97, 77.2, 69.97, 69.50, 69.3, 50.3, 31.6, 29.9, 28.9, 26.2, 22.6, 14.0; *m*/*z* (ESI) 197.0 (2.9%), 198.6 (100%), 199.3 (12.9%), 293 (1.2%), 377 (1.4%), 378.1 (1.1%), 378.9 ($M^+-PF_6^-$, 27%), 379.7 (7.2%); Anal. Calc. for $C_{22}H_{29}N_2Fe^+$; $[M^+]-PF_6$, 377.16801.

*4.3.10. 1-(6-Ferrocenylhexyl)-3-methylimidazolium hexafluorophosphate **18***

This salt was synthesised following a similar method to **9** using sodium hexafluorophosphate (0.70 g, 4.18 mmol) and 1-(6-ferrocenylhexyl)-3-methylimidazolium iodide (2.00 g, 4.18 mmol) to yield a yellow solid identified as **18** (1.99 g, 96%), mp 93 °C; IR (KBr cm^{-1}) 3083, 2944, 2925, 2858, 1575, 1635,1575, 1565, 1468, 1460,1434, 1320, 1224, 1163, 1105, 1039, 1022, 1003, 854, 762, 725, 661, 625, 556, 487; ^1H NMR ($CDCl_3$) 9.18, (1H, s, NCH), 7.33 (1H, t, *J* 1.7, NCH), 7.29 (1H, t, *J* 1.7, NCH), 4.21 (2H, t, *J* 7.5, CH_2), 4.11 (5, s, C_5H_5), 4.06 (4H, m, C_5H_4), 3.99 (3H, s, NCH_3), 2.32 (2H, t, *J* 7.5, CH_2), 1.89 (2H, m, CH_2), 1.46 (2H, m, CH_2), 1.36 (4H, m, 2 × CH_2); ^{13}C NMR ($CDCl_3$) 136.86, 123.87, 122.31, 89.55, 69.03, 68.60, 67.57, 50.61, 37.05, 31.29, 30.39, 29.84, 29.16, 26.47; *m*/*z* (FAB) 496 (M^+, 20%), 351 (M^+-PF_6, 100%), 329 (6), 306 (6), 284 (5), 268 (14), 230 (11), 212 (11), 199 (38), 186 (12), 176 (45), 165 (4), 151 (18), 137 (28), 121 (35), 109 (35); (Found: $[M^+]$, 496.116636. $C_{20}H_{27}N_2FePF_6$ requires $[M^+]$, 496.116546).

*4.3.11. 1-(Ferrocenylmethyl)-3-methylimidazole hexafluoroantimonate **19***

This salt was synthesised following a similar method to **9** using sodium hexafluoroantimonate (0.1958 g, 0.7568 mmol) and 1-(ferrocenylmethyl)-3-methylimidazolium iodide (0.3092 g, 0.7596 mmol) to yield an orange powder identified as **19** (0.26 g, 66%); mp 66 °C; IR (ATR cm^{-1}) 3072, 1706, 1566, 1445, 1409, 1325, 1238, 1149, 1104, 1027, 999.7, 816, 734, 653, 619, 499, 480; ^1H NMR ($CDCl_3$) 9.94 (1H, s, NCH), 7.27 (1H, s, NCH), 7.23 (1H, s, NCH), 5.34 (2H, s, CH_2), 4.45 (2H, m, C_5H_4), 4.29 (7H, m, C_5H_5, C_5H_4), 4.02 (3H, m, CH_3); ^{13}C NMR ($CDCl_3$) 135.56, 123.16, 121.62, 77.82, 77.23, 70.04, 69.68, 69.31, 50.42; *m*/*z* (ESI) 197.1 (2.6%), 198.6 (100%), 199.2 (15%), 280.6 ($M^+-SbF_6^-$), 4.4%); Anal. Calc. for $C_{15}H_{17}N_2Fe^+$; $[M^+]-SbF_6$, 281.07411.

*4.3.12. 1-(Ferrocenylmethyl)-3-butylimidazolium hexafluoroantimonate **20***

This salt was synthesised following a similar method to **9** using sodium hexafluoroantimonate (0.38 g, 1.47 mmol) and 1-(ferrocenylmethyl)-3-butylimidazolium bromide (0.43 g, 1.08 mmol) to yield dark brown-greenish powder identified as **20** (0.46 g, 77%); mp 52 °C; IR (ATR cm^{-1}) 3155, 2965, 1561, 1467, 1321, 1239, 1148, 1105, 828, 749, 650, 482; ^1H NMR ($CDCl_3$) 8.44 (1H, s, NCH), 7.16 (1H, s, NCH), 7.12 (1H, s, NCH), 5.07 (2H, s, CH_2), 4.42 (2H, s, C_5H_4), 4.29 (7H, m, C_5H_4, C_5H_5), 4.09 (2H, m, CH_2), 1.81 (2H, m, CH_2), 1.35 (2H, m, CH_2), 0.94 (3H, m, CH_3); ^{13}C NMR ($CDCl_3$) 134, 121.7, 77.3, 77.0, 70.6, 70.1, 69.9, 50.1, 31.8, 30.9, 19.4, 13.3;

m/*z* (ESI) 125.0 (2.4%), 181.1 (14.2%), 181.9 (1.4%), 197.0 (2.9%), 198.5 (100%), 199.3 (14.9%), 200.5 (1.4%), 320.8 (2.6%), 322.7 ($M^+-SbF_6^-$, 2.4%); Anal. Calc. for $C_{18}H_{23}N_2Fe^+$; $[M^+]-SbF_6$, 323.12051.

4.3.13. 1-(ferrocenylmethyl)-3-octylimidazolium hexafluoroantimonate ***21***

This salt was synthesised following a similar method to **9** using an excess of sodium hexafluoroantimonate (0.5332 g, 2.061 mmol) and 1-(ferrocenylmethyl)-3-octylimidazolium bromide (0.3850 g, 0.8402 mmol) to yield a dark brown-greenish oil identified **21** (0.4819 g, 93.4%); IR (ATR cm^{-1}) 3155, 2928, 1709, 1561, 1467, 1320, 1148, 1106, 828, 746, 652, 501, 482; 1H NMR (CDCl3) 8.44 (1H, s, NCH), 7.20 (1H, s, NCH), 7.14 (1H, s, NCH), 4.86 (2H, s, CH_2), 4.60 (2H, s, C_5H_4), 4.47 (7H, m, C_5H_4, C_5H_5), 4.09 (2H, s, CH_2), 1.29 (12H, m, C_6H_{12}), 0.86 (3H, m, CH_3); ^{13}C NMR ($CDCl_3$) 134.64, 121.96, 121.91, 77.34, 77.23, 50.65, 50.20, 31.65, 30.06, 29.70, 28.98, 28.86, 26.27, 22.59, 14.07; *m*/*z* (ESI) 197.1 (2.7%), 198.6 (100%), 199.3 (14.3%), 378.8 (M+$-SbF_6^-$, 10%), 379.8 (1.7%); Anal. Calc. for $C_{22}H_{29}N_2Fe^+$; $[M^+]-SbF_6$, 377.16801.

4.3.14. 1-(6-Ferrocenylhexyl)-3-methylimidazolium hexafluoroantimonate ***22***

This salt was synthesised following a similar method to **9** using sodium hexafluoroantimonate (1.08 g, 4.18 mmol) and 1-(6-ferrocenylhexyl)-3-methylimidazolium iodide (2.00 g, 4.18 mmol) to give a yellow solid identified as **22** (2.33 g, 95%), mp 68 °C; IR (KBr cm^{-1}) 3164, 3119, 2924, 2857, 1628, 1572, 1467, 1431, 1374, 1337, 1319, 1224, 1165, 1105, 1022, 1002, 922, 840, 821, 759, 726, 661, 625, 514, 484, 423; ^1H NMR ($CDCl_3$) 9.58, (1H, s, NCH), 7.41 (1H, t, *J* 1.7 NCH), 7.33 (1H, t, *J* 1.7, NCH), 4.26 (2H, t, CH_2), 4.10 (5H, s, C_5H_5), 4.04 (7H, m, CH_3 and C_5H_4), 3.99 (3H, s, NCH_3), 2.32 (2H, t, *J* 7.5, CH_2), 1.90 (2H, m, CH_2), 1.49 (2H, m, CH_2), 1.36 (4H, m, $2 \times CH_2$); ^{13}C NMR ($CDCl_3$), 136.88, 124.00, 122.45, 89.46, 68.95, 68.54, 67.51, 50.63, 37.32, 31.31, 30.52, 29.85, 29.21, 26.50; *m*/*z* (FAB) 587 (M^+, 11%) 351 (100), 268 (10), 230 (11), 212 (10), 199 (30), 186 (10), 151 (20), 137 (24), 121 (28), 109 (30); (Found: $[M^+]$, 587.054774. $C_{20}H_{27}N_2FeSbF_6$ requires $[M^+]$, 587.054432).

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2010.01.019.

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