# FULL PAPER

# Designing Ionic Liquids: 1-Butyl-3-Methylimidazolium Cations with Substituted Tetraphenylborate Counterions

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The hydrophobic, low melting, 1-butyl-3-methylimidazolium (BMIm) salts [BMIm][BPh$_4$] (**1**), [BMIm][B(C$_6$H$_4$Me-4)$_4$] (**2**), [BMIm][B{C$_6$H$_4$(CF$_3$)-4}$_4$] (**3**), [BMIm][B{C$_6$H$_3$(CF$_3$)$_2$-3,5}$_4$] (**4**), [BMIm][B{C$_6$H$_4$(C$_6$F$_{13}$)-4}$_4$] (**5**), [BMIm][B{C$_6$H$_4$(SiMe$_3$)-4}$_4$] (**6**), [BMIm][B{C$_6$H$_4${SiMe$_2$(CH$_2$CH$_2$CF$_3$)}-4}$_4$] (**7**), [BMIm][B{C$_6$H$_4${SiMe$_2$C$_8$H$_{17}$}-4}$_4$] (**8**) and [BMIm]-[B(C$_6$H$_4${SiMe$_2$(CH$_2$CH$_2$C$_6$F$_{13}$)}-4)$_4$] (**9**) have been prepared. Systematic variation of the substituents on the tetraphenylborate anion allowed an assessment of their influence on the physical properties of the imidazolium salts. Structural investigations using NMR and IR spectroscopy, combined with single crystal X-ray structure determinations for **2**, **3**, **5** and **6**, revealed hydrogen-bonding interactions between the imidazolium ring protons and the borate anion, both in the solid state and in solution. These interactions are weakened upon the introduction of electron-withdrawing substituents

in the anion and follow the order 3,5-(CF$_3$)$_2$ < –C$_6$F$_{13}$ < –CF$_3$ < –SiMe$_2$CH$_2$CH$_2$C$_6$F$_{13}$ < –SiMe$_2$CH$_2$CH$_2$CF$_3$ < –$H$ < –Me < –SiMe$_3$. The melting points of the salts depend primarily on the bulk of the lipophilic substituents, and decrease with increasing size. Bulky lipophilic substituents dramatically enhance the solubility of the imidazolium borates **8** and **9** in hexane and reduce their relative polarity. These unique properties make imidazolium borates **8** and **9** interesting as amphiphilic ionic liquids with low polarity. Attempts to crystallise **7** resulted in decomposition. A single-crystal X-ray structure determination of the product, isolated in 6% yield, showed that a carbene–tris[4-{dimethyl(3,3,3-trifluoropropyl)silyl}phenyl]borane adduct was formed.

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## Introduction

The extremely low vapour pressure[1] of room-temperature ionic liquids (ILs) based on *N,N*-dialkylimidazolium cations and weakly coordinating anions (Scheme 1) makes them an interesting alternative to highly volatile organic solvents, such as CH$_2$Cl$_2$, that cause environmental concern and are subject to ever more stringent regulations.[2] The

X$^-$ = e.g. AlCl$_4^-$, BF$_4^-$, PF$_6^-$, CF$_3$SO$_3^-$
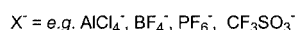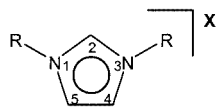
Scheme 1

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miscibility of ILs with other solvents can also be controlled, through a careful choice of the ions,[3] making them attractive as easily containable solvents. Especially noteworthy is their use as a polar phase in biphasic solvent systems, which is of interest for catalyst recycling. In such a system, the advantages of both homogeneous and heterogeneous catalysis, good catalyst efficiency under mild reaction conditions and facile catalyst recovery, respectively, can be combined.[1]

The physical properties, and chemical and physical stability of an IL govern its suitability as a reaction medium. The potential of ILs as solvents for catalysis was first demonstrated with the discovery of 1-ethyl-3-methylimidazolium tetrafluoroborate,[4] which combines the favourable properties of a liquid salt with high air and water stability. Subsequently, a broad range of cation-anion combinations has been developed,[5] and their chemical and physical properties,[5,6] as well as their application as solvents in catalysis, examined[1,7] These studies focussed on varying the alkyl substitution pattern on the imidazolium ring, while the anions employed have predominantly remained limited to inorganic or small organic anions such as BF$_4^-$, PF$_6^-$, SbF$_6^-$, NO$_2^-$, CF$_3$SO$_3^-$, [N(CN)$_2$]$^-$ and [N(SO$_2$CF$_3$)$_2$]$^-$.[1,5a,6a] The incorporation of large and lipo-

philic organic anions is virtually unexplored,[5a,7e,8] even though anions such as tetraphenylborates[9] and carboranes[10] efficiently delocalise their negative charge, resulting in a very low coordinating strength. The interaction of the anions, and to a lesser extent the cation, with solvent or substrate molecules plays a major role in determining the (im)miscibility of an IL with other liquids.[11] Large organic anions permit a broad range of substituents, which could allow the facile tailoring of an ionic liquid. In a first example of this approach[12] we showed that $-SiMe_2(CH_2CH_2C_6F_{13})$ substituents produced an imidazolium salt, [BMIm][B(C_6H_4{SiMe_2(CH_2CH_2C_6F_{13})}-4)_4] (9), that is highly miscible with apolar solvents. Furthermore, 9 displayed phase behaviour similar to perfluorinated solvents when combined with apolar organic solvents. This facilitated efficient catalyst recycling by biphasic separation following a reaction under homogeneous conditions[12] − a unique feature for ionic liquids.

After this initial demonstration a more systematic study of the effects of a range of alkyl-, perfluoroalkyl- and silyl-substituted tetraarylborates on the physical properties of the corresponding [BMIm]+-salts was performed.

## Results and Discussion

**Synthesis:** A series of 1-butyl-3-methylimidazolium salts of tetraphenylborate and alkyl-, perfluoroalkyl- and silyl-substituted derivatives thereof was prepared by metathesis of the sodium borates with dialkylimidazolium halides (Scheme 2). All imidazolium salts were purified by washing
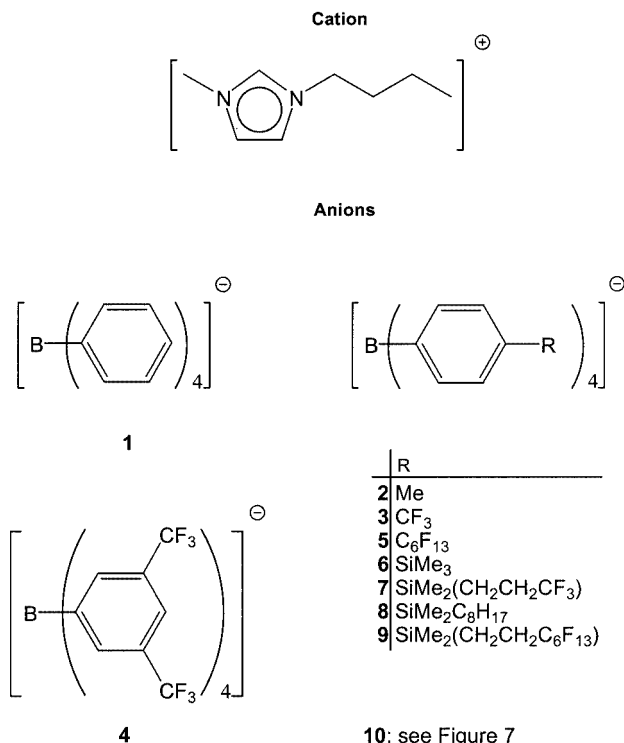
a solution in $CH_2Cl_2$ or toluene with demineralised water, followed by removal of residual water with $MgSO_4$ and subsequent drying of the IL in vacuo.

The resulting compounds were characterised by $^1H$, $^{13}C\{^1H\}$ and $^{11}B\{^1H\}$ NMR spectroscopy, IR spectroscopy and elemental analysis, and found to be pure. Furthermore, for 4, 5, 7 and the previously communicated 9,[12] elemental analyses found no evidence of contamination by trace amounts of chloride or iodide. The remaining compounds were not analysed for halide ions. As the synthetic and workup procedures were identical, they were presumed to be halogen free at the level detectable by elemental analysis. The salts 2−9 are not hygroscopic, are stable in air, and are insoluble in water. Crystals suitable for single-crystal X-ray structure determination were obtained for 2, 3, 5 and 6. Single crystals of 2, 3 and 5 were grown by slow diffusion of hexane into $CH_2Cl_2$ solutions of these imidazolium salts. Crystals of 6 were obtained by slow evaporation of acetone from a concentrated solution. The molecular structures of 2 (Figure 1), 3 (Figure 2), 5 (Figure 3) and 6 (Figure 4) are



Figure 1. ORTEP drawing of the molecular structure of 2, with ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity

**Cation**



**Anions**



| | R |
|---|---|
| 2 | Me |
| 3 | CF_3 |
| 5 | C_6F_{13} |
| 6 | SiMe_3 |
| 7 | SiMe_2(CH_2CH_2CF_3) |
| 8 | SiMe_2C_8H_{17} |
| 9 | SiMe_2(CH_2CH_2C_6F_{13}) |

**10**: see Figure 7

Scheme 2



Figure 2. ORTEP drawing of the molecular structure of 3 showing hydrogen bonding between cations and anions. Ellipsoids are shown at the 50% probability level. Hydrogen atoms, except for those participating in hydrogen-bonding interactions, are omitted for clarity
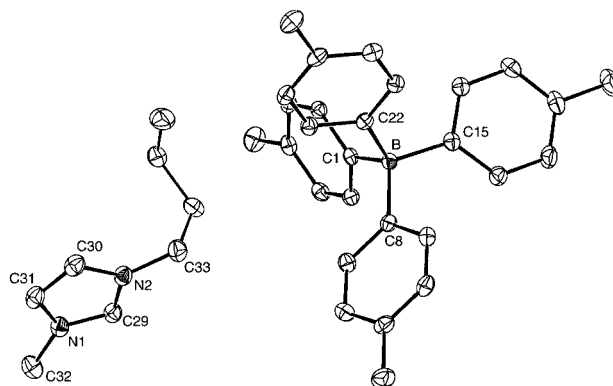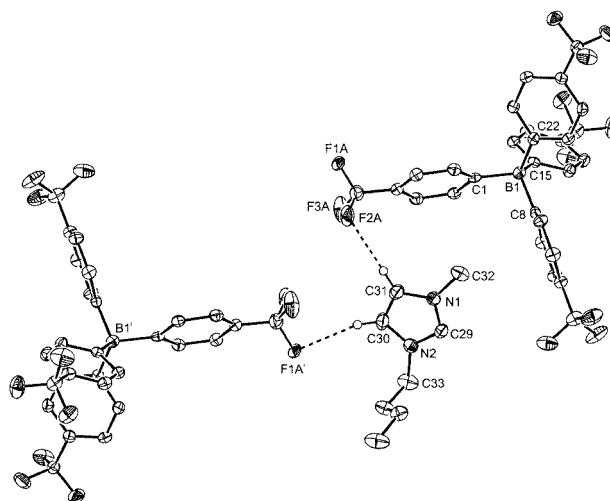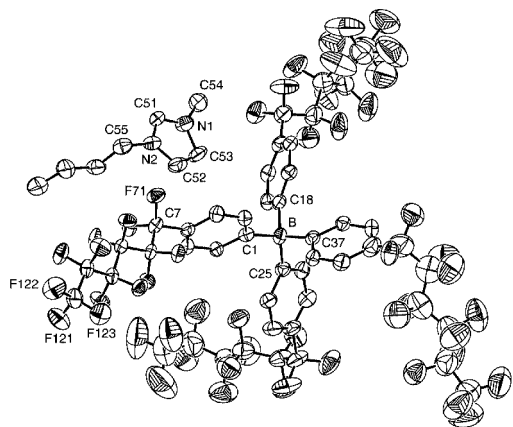
Figure 3. ORTEP drawing of the molecular structure of **5**, with ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity
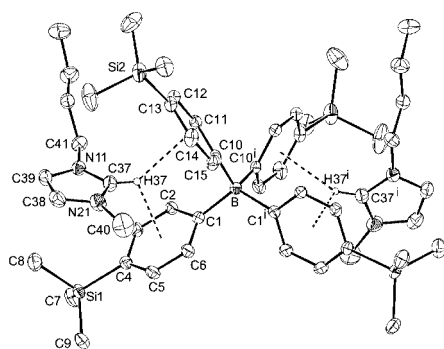


Figure 4. ORTEP drawing of the unit cell of **6**, with ellipsoids at the 30% probability level. Hydrogen atoms, except for those participating in hydrogen-bonding interactions, are omitted for clarity

represented; relevant bond angles and distances are collected in Table 1.

The 1-butyl-3-methylimidazolium cation, common to all four structures, shows little variation in bond lengths and

angles for each compound, having a planar pentagonal imidazolium ring that contains two pairs of C−N bonds, with C(2)−N bonds (1.32−1.33 Å) that are shorter than the C(4)−N and C(5)−N bonds (1.37−1.40 Å). Although the precision of the bond lengths in **6** and especially in **5** is poor due to the considerable structural disorder, they are similar to those of **2** and **3**. The configuration of the imidazolium ring is identical to those observed in related structures, such as [BMIm][BPh$_4$],[8] [EMIm][CB$_{11}$H$_{(12-n)}$X$_n$] (X = Cl, Br, I, $n$ = 0, 1),[13] [OMIm][CB$_{11}$H$_6$Cl$_6$],[13] and [EMIm]X (X = Br, I, AlBr$_4$)[14] [N−C(2) 1.29−1.33 Å, N−C(4) and N−C(5) 1.35−1.38 Å, N−C(2)−N 108−109°], showing that the ring's internal dimensions are largely insensitive to its environment. The orientation of the butyl substituent relative to the imidazolium ring differs with each anion due to packing effects in the respective crystal lattices.

The anions all consist of a tetraphenylborate core, with different *para* substituents. The bond lengths and angles show that substitution does not significantly affect the geometry around the boron atom, with all anions having a slightly distorted tetrahedral configuration with practically identical B−C distances (1.64−1.65 Å) and C−B−C angles (103−113°). These data correspond with that previously reported for the borate anions in [BMIm][BPh$_4$],[8] and [(THF)$_2$Na(18-crown-6)][B{C$_6$H$_4$(SiMe$_3$)-4}$_4$] and [Rh(dppe)$_2$][B{C$_6$H$_4$(SiMe$_3$)-4}$_4$][15] (B−C 1.64−1.72 Å, C−B−C 106−112°). Unfortunately, no molecular structures of complexes containing [B(C$_6$H$_4$Me-4)$_4$]$^-$, [B{C$_6$H$_4$(CF$_3$)-4}$_4$]$^-$ and [B{C$_6$H$_4$(C$_6$F$_{13}$)-4}$_4$]$^-$ are available for comparison.

In the crystal lattice the ions in **2** and **3** form well-defined layers of cations and anions. In **2** the interlayer distances between hydrogen atoms on the imidazolium ring and the π-electron system of the phenyl groups of the anions are around 2.8 Å (Table 2), suggesting that the layers of cations

Table 1. Selected bond angles [°] and distances [Å] for **2**, **3**, **5** and **6**

| [a] | | **2** | **3** | **5** | **6** |
|---|---|---|---|---|---|
| | B−C(1) | 1.6476(18) | 1.645(3) | 1.651(17) | 1.641(4) |
| | B−C(8) | 1.6422(18) | 1.641(3) | 1.650(17) | 1.648(4) |
| | B−C(15) | 1.6484(18) | 1.647(3) | 1.622(17) | 1.646(4) |
| | B−C(22) | 1.696(17) | 1.647(3) | 1.653(17) | 1.645(4) |
| N(1)−C(2) | N(1)−C(29) | 1.3270(17) | 1.324(3) | 1.327(16) | 1.312(4) |
| N(1)−C(5) | N(1)−C(31) | 1.3768(17) | 1.370(3) | 1.406(17) | 1.376(4) |
| N(3)−C(2) | N(2)−C(29) | 1.3325(17) | 1.323(3) | 1.310(16) | 1.327(4) |
| N(3)−C(4) | N(2)−C(30) | 1.3791(17) | 1.374(3) | 1.369(17) | 1.365(4) |
| C(4)−C(5) | C(30)−C(31) | 1.350(2) | 1.343(3) | 1.34(2) | 1.333(5) |
| | C(1)−B−C(8) | 103.59(9) | 104.64(16) | 105.2(9) | 105.3(2) |
| | C(1)−B−C(15) | 111.28(10) | 112.89(16) | 113.6(10) | 111.5(2) |
| | C(1)−B−C(22) | 109.85(9) | 112.22(165 | 110.2(10) | 111.7(2) |
| | C(8)−B−C(15) | 113.30(10) | 111.66(15) | 112.7(10) | 111.1(2) |
| | C(8)−B−C(22) | 113.24(10) | 111.95(16) | 112.1(10) | 113.1(2) |
| | C(15)−B−C(22) | 105.67(9) | 103.72(16) | 103.2(9) | 104.3(2) |
| | N(1)−C(29)−N(2) | 108.57(11) | 109.38(18) | 109.7(10) | 108.6(3) |
| | C(29)−N(1)−C(32) | 125.51(12) | 126.33(18) | 126.1(11) | 126.5(3) |
| | C(29)−N(2)−C(33) | 125.24(11) | 125.61(18) | 124.4(10) | 125.8(3) |

[a] Atom numbers refer to atoms according to the numbering scheme used for **2** and **3** and to the equivalent atoms in **5** and **6**.

and anions are inter-connected by weak hydrogen-bonding interactions (for a representative picture of this hydrogen-bonding pattern between layers, see Figure 5).[16,17] Similar behaviour has been reported for [BMIm][BPh$_4$].[8] In **3**, such layering of cations and anion was not observed. However, weak hydrogen bonding is present: The C(2)−H and C(4−H imidazolium protons are in close contact with the CF$_3$ groups of neighbouring anions (see Figure 2 and Table 2). Some of the inter-ionic H···F interactions may be unavoidable, due to steric congestion, but the H···F of F to C(4)−H (2.44 Å) clearly indicates weak hydrogen-bonding interactions.[18] The packing diagram of **6** did not reveal the separation of cations and anions into distinct layers. Nevertheless, the cations' orientation allows attractive interactions between C(2)−H and the π-systems of neighbouring phenyl rings (Figure 4). Their distance (2.65 Å) is similar to that for the C−H···π interactions in **2**, suggesting weak hydrogen bonding.

Table 2. Hydrogen−π interactions in the solid state of **2**, **5** and **6** and hydrogen−fluorine interactions in the solid state of **3**

| | H···C$_g$ [Å] | C···C$_g$ [Å] | C−H···C$_g$ [°] |
|---|---|---|---|
| **2** | | | |
| C(29)−H(29)···C$_g$5[a] | 2.40 | 3.3506(13) | 180 |
| C(30)−H(30)···C$_g$3[b] | 2.52 | 3.4076(16) | 155 |
| **5** | | | |
| C(51)−H(51)···C$_g$4[c] | 3.08 | 3.233(13) | 91 |
| C(51)−H(51)···C$_g$5[c] | 2.51 | 3.370(12) | 155 |
| C(52)−H(52)···C$_g$2 | 2.67 | 3.525(14) | 153 |
| C(53)−H(53)···C$_g$3 | 2.64 | 3.514(15) | 157 |
| **6** | | | |
| C(37)−H(37)···C$_g$4 | 2.81 | 3.340(3) | 116 |
| C(37)−H(37)···C$_g$6 | 2.65 | 3.331(3) | 130 |
| | H···F [Å] | C···F [Å] | C−H···F [°] |
| **3** | | | |
| C(30)−H(30)···F(1a)[d] | 2.49 | 3.401(9) | 161 |
| C(31)−H(31)···F(2a) | 2.44 | 3.378(6) | 172 |

[a] 1 − x, y + 0.5, 0.5 − z. [b] 1 − x, 1 − y, 1 − z. [c] − x, 1-y, z + 0.5. [d] − x, 1 − y, −z. Note that the CF$_3$ group is rotationally disordered.
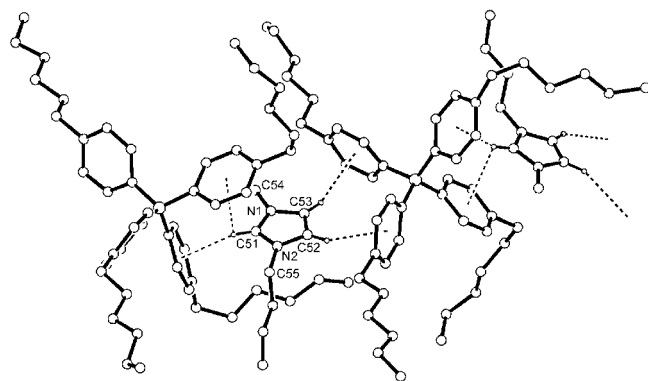


Figure 5. Representation of hydrogen bridging interactions in the crystal lattice of **5**. Hydrogen and fluorine atoms have been omitted for clarity

In the crystal lattice of fluorous borate salt **5**, an alternative ion ordering could be discerned. Instead of layers of cations and anions, a division into fluorous and non-fluorous regions is present (Figure 6). The perfluoroalkyl parts of the ions are assembled in fluorous regions, which alternate with non-fluorous layers that contain the organic and charged parts of the salts. In other words, the structure organises the imidazolium cations and the tetraarylborate cores of the anions into layers with the perfluoroalkyl groups pointing outwards (Figure 5). In these organic domains, the cations and anions form chains with each cation being connected to two anions through hydrogen···π interactions (Figure 5) and vice versa. Furthermore, the butyl substituents of the cation are also oriented towards the fluorous domains. Such layered structures are well known for perfluoroalkyl-substituted compounds,[19] and are related to the inability of the perfluoroalkyl groups to participate in stabilising interactions with other molecules. This lack of interaction excludes these substituents from the ionic organic layers, allowing optimum inter-ion interactions not involving the fluorous tails. The absence of interactions with neighbouring molecules is also reflected in the high disorder in the fluorous tails.
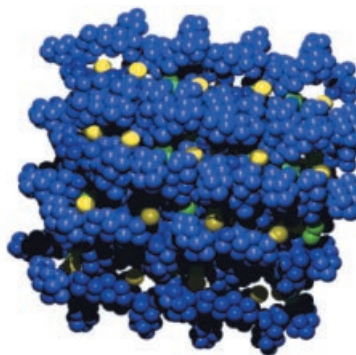


Figure 6. Packing diagram of **5** (F = blue, B = yellow, N = green, all other atoms are omitted for clarity)

During attempts to crystallise **7** from a saturated solution in warm MeOH/H$_2$O (v:v, 95:5), a crystalline material was isolated in low yield (6%). A single-crystal X-ray diffraction study of this material showed, unexpectedly, it to be a carbene−tris[4-{dimethyl(3,3,3-trifluoropropyl)-silyl}phenyl]borane adduct. The molecular structure **10** (formula see Figure 7) shows a carbene connected to the boron atom of a BAr$_3$ moiety through the C(2) carbon of the imidazolium ring, which has replaced the fourth phenyl group present in the original tetraarylborate anion. The geometry around the boron centre is a slightly distorted tetrahedral one with C−B−C angles between 105.53(11)° and 113.26(11)°, and B−C bond lengths of 1.642(2)−1.657(2) Å for the phenyl substituents and 1.659(2) Å for the carbene moiety (Table 3). These values are similar to those for the tetraarylborate anions in **2**, **3**, **5** and **6**, suggesting that the nature of the boron atom in **10** is identical and that it formally bears a single negative charge. The chemical shift in the $^{11}$B{$^1$H} NMR supports
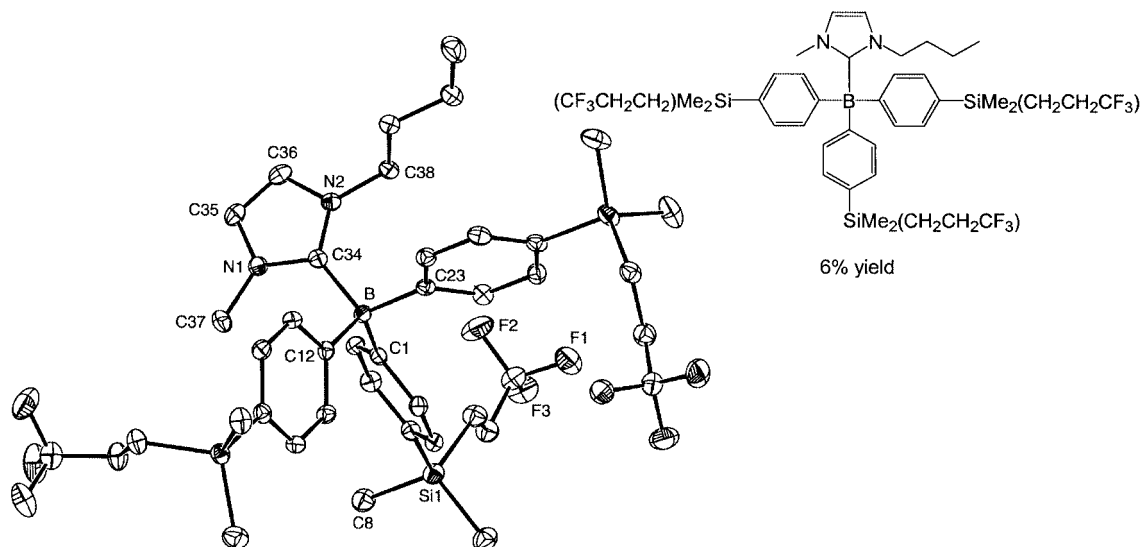
Figure 7. ORTEP drawing of the molecular structure of **10**, with ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity

Table 3. Selected bond angles [°] and distances [Å] for **10**

| Bond lengths | | Bond angles | |
|---|---|---|---|
| B−C(1) | 1.642(2) | C(1)−B−C(12) | 113.26(11) |
| B−C(12) | 1.645(2) | C(1)−B−C(23) | 110.78(12) |
| B−C(23) | 1.657(2) | C(1)−B−C(34) | 105.53(11) |
| B−C(34) | 1.659(2) | C(12)−B−C(34) | 108.01(11) |
| | | C(23)−B−C(34) | 112.28(11) |
| N(1)−C(34) | 1.3611(19) | | |
| N(1)−C(35) | 1.3784(19) | N(1)−C(34)−N(2) | 104.20(12) |
| N(2)−C(34) | 1.3583(18) | | |
| N(2)−C(36) | 1.3845(19) | C(34)−N(1)−C(37) | 126.93(12) |
| C(35)−C(36) | 1.337(2) | C(34)−N(2)−C(38) | 128.29(12) |

this suggestion, as the observed resonance corresponds with that of other [BAr$_4$]$^-$ (Ar = aryl) ions.[20]

However comparing the five-membered carbene ring with the imidazolium rings in the molecular structures for **2**, **3**, **5** and **6** reveals a consistent deviation in the bond lengths. The lengthening of the N−C(2) bonds in **10** compared to those in the imidazolium borate salts, N−C(34) 1.3612(19) Å (**10**) vs. N−C(2) 1.312(4)−1.3325(19) Å, combined with the shortening of the C−C bond, C(35)−C(36) 1.337(2) Å (**10**) vs. C−C 1.333(5)−1.350(2) Å, and a reduced N−C−N angle, 104.20(12)° in **10**, indicate a reduced aromatic character in the pentacycle. The bond lengths in **10** correspond with those observed for carbene adducts of transition-metals, in which the N−C bonds have single bond character and the C−C bond has a double bond character.[21] Bond lengths in such carbene moieties are around 1.36−1.40 Å for N−C(2), 1.31−1.34 Å for C(4)−C(5), with an angle of 101−104° for N(1)−C(2)−N(3). The similar angles and distances observed in **10** show it to be a carbene−borane adduct. A similar geometry has been reported for 2-borane-1,3-diethyl-4,5-dimethylimidazolin (**11**), for which N(1)−C(2) and N(3)−C(2) of 1.352(2) Å, N(1)−C(5) and N(2)−C(4)

of 1.393(2) Å, C(4)−C(5) of 1.350(2) Å and N−C−N of 104.7(1)° were observed (Scheme 3).[22] However, the B−C(2) of 1.659(2) Å in **10** deviates significantly from that in **11** [1.603(3) Å] as well as that in the only related compound 2-(1,3,2-diazaborolyl)-1,3,4,5-tetramethylimidazolium bromide (**12**) that has been studied using single-crystal X-ray crystallography [1.580(11) Å].[23]
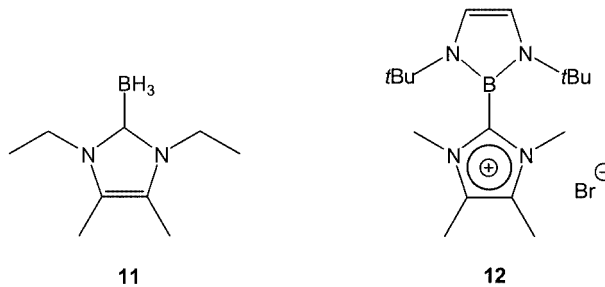


Scheme 3

The B−C(2) bond length is highly dependent on its σ-character.[22] Delocalisation of the electron density on the boron through the phenyl substituents in **10** results in a partial positive charge on the boron.[24] This lowers its ability to participate in the σ-bond with C(34) in comparison to the boron atom in **11** and **12**, where such a delocalisation is not possible. Hence, B−C(34) in **10** is somewhat longer than this bond in **11** and **12**.

The slightly acidic proton at C(2) of the imidazolium ring (p$K_a$ = 7.5),[25] supplemented by the increased basicity of the borate's aryl groups due to the silyl substitution, may well be responsible for the conversion of **7** into **10**. Proton abstraction from the imidazolium moiety by one of the aryl groups will afford **10** as well as dimethyl(3,3,3-trifluoropropyl)silylbenzene. A related decomposition mode of the tetraphenylborate anion is found in the reaction of [Ru(η$^3$-1,2,3-η$^2$-5,6-(1,5-cyclooctadienyl))][BPh$_4$] with HF, HBF$_4$ and HPF$_6$, to form [Ru{η$^3$-1,2,3-η$^2$-5,6-(1,5-cycloocta-

dienyl)}($\eta^6$-PhBF$_3$)].[26] Given the weak acidity of the C(2)H proton compared to the strong acids HF, HBF$_4$ and HPF$_6$, and the absence of any transition metals that may lead to hydrides, the formation of **10** is still remarkable. Another explanation that cannot be completely ruled out is the involvement of traces of low-valent late transition metals that can oxidatively add imidazolium cations to give *N*-heterocyclic carbene hydride complexes.[27]

**Infrared Spectroscopy:** The aromatic C−H stretching vibrations in the imidazolium ring result in three highly characteristic infrared bands, between 3200 and 3050 cm$^{-1}$, that depend on the presence and strength of hydrogen-bonding interactions between these protons and the anions of the ionic liquid.[5a,28] For **1**, **2** and **6−9** the bands for $\nu$[C(5)−*H*] and $\nu$[C(4)−*H*] are observed at approximately 3140 and 3105 cm$^{-1}$. Furthermore, a separate stretching frequency at 3080 cm$^{-1}$ was observed, which corresponds with $\nu$[C(2)−*H*]. For compounds **3** and **5** these vibrations are shifted to higher frequencies, with bands at 3150, 3110 and 3091 cm$^{-1}$, respectively (Table 4). Furthermore, for **4**, a further shift for $\nu$[C(5)−*H*] and $\nu$[C(4)−*H*] to 3179 and 3130 cm$^{-1}$ was seen, while the absorption corresponding with $\nu$[C(2)−*H*] was not detectable. This shift is caused by a reduction in the strength of the C−H bonds in the imidazolium ring as their participation in hydrogen-bonding interactions increases.[29] Therefore, the shift of the stretching vibrations to higher frequencies in the imidazolium salts containing borate anions with electron-withdrawing substituents indicates that the hydrogen-bridging interactions are weakened by these substituents. For related imidazolium salts similar observations have been reported; [EMIm]X (X = Cl$^-$, Br$^-$, I$^-$ and AlBr$_4^-$) shows IR bands at 3150, 3135 and 3080 cm$^{-1}$;[14] [BMIm]X (X = BF$_4^-$, PF$_6^-$) at 3166 and 3123 cm$^{-1}$,[28b] and [EMIm]X (X = various carboranes) at 3165, 3150 and 3110 cm$^{-1}$.[5a] In these salts an increase in the strength of the hydrogen bonds between the cation and the anion also resulted in lower $\nu$(CH) stretching frequencies.

The sensitivity of the C−H stretching frequencies to the strength of the hydrogen-bonding interactions varies with the position on the imidazolium ring. Whereas $\nu$[C(4)−*H*] and $\nu$[C(5)−*H*] change by more than 30 cm$^{-1}$, a maximum shift of 20 cm$^{-1}$ in $\nu$[C(2)−*H*] was observed. The H(2) proton bears the largest positive charge ($\delta^+$) of the aromatic imidazolium protons[6f,30] and is, therefore, the strongest hydrogen-bond donor. Upon reduction of the hydrogen-bonding capabilities of the anion the relatively strong C(2)H···$\pi$ interactions remain intact, but the weaker bonds C(4)−*H* and C(5)−*H* are more likely to be significantly affected. This results in the relatively low sensitivity of $\nu$[C(2)−*H*] to a reduced participation of the imidazolium cation in hydrogen bonding.

**$^1$H NMR Spectroscopy:** The dependence of the $^1$H NMR chemical shifts of the imidazolium ring protons on various borate anions and different concentrations was investigated. The chemical shifts C(2)−*H*, C(4)−*H*, C(5)−*H*, NC*H$_2$* and NC*H$_3$* for 0.08 M solutions of **1−9** in dry [D$_6$]acetone (Table 5) proved to be highly sensitive to the substituent on the borate anion. The largest variations were observed for the C(2)−*H* resonances, which shifted by as much as 1.7 ppm, depending on the anion. With [BMIm][BPh$_4$] (**1**) as a reference compound, the imidazolium salts containing an anion with CF$_3$ or C$_6$F$_{13}$ substituents exhibit a positive $\Delta\delta$, i.e., the imidazolium proton resonances shift to lower field relative to **1** (Figure 8). Conversely, alkyl- or non-fluorous silyl substituents induce a negative $\Delta\delta$, except for [BMIm][B{C$_6$H$_4$(SiMe$_2$C$_8$H$_{17}$)-4}$_4$] (**8**) which shows no significant shifts relative to **1**. Furthermore, the largest downfield shifts were observed for the compounds with perfluoroalkyl groups connected directly to the phenyl rings of the anion.

For imidazolium compounds the chemical shifts of the protons on the ring are determined by both hydrogen-bonding interactions and shielding due to ring current effects of the tetraarylborate anions and of neighbouring imidazolium cations.[3a] Hydrogen bonding causes the protons to shift to lower field, and shielding of the protons from the magnetic field by the aromatic system of the borate and imidazolium aromatic systems results in an upfield shift.[31]

Table 4. Infrared spectroscopic data for the aromatic stretching region (3200−3050 cm$^{-1}$), corresponding with C−H stretching frequencies in the imidazolium cation

| IL | R | $\nu$[C(5)−*H*] and $\nu$[C(4)−*H*] | | $\nu$[C(2)−*H*] |
|---|---|---|---|---|
| **1** | H | 3132 (w) | 3099 (w) | 3082 (m) |
| **2** | Me | 3140 (w) | 3103 (w) | 3078 (m) |
| **3** | CF$_3$ | 3150 (w) | 3113 (w) | 3088 (m) |
| **4** | 3,5-(CF$_3$)$_2$ | 3179 (w) | 3130 (w) | −[a] |
| **5** | C$_6$F$_{13}$ | 3157 (w) | 3110 (w) | 3094 (w) |
| **6** | SiMe$_3$ | 3138 (w) | 3107 (w) | 3079 (m) |
| **7** | SiMe$_2$(CH$_2$)$_2$CF$_3$ | 3144 (w) | 3107 (m) | 3077 (m) |
| **8** | SiMe$_2$C$_8$H$_{17}$ | 3134 (w) | 3107 (w) | 3074 (m) |
| **9** | SiMe$_2$(CH$_2$)$_2$C$_6$F$_{13}$ | 3136 (w) | 3107 (w) | 3074 (m) |

[a] Not observed.

Table 5. $^1$H NMR chemical shifts ($\delta$ in ppm) for 0.08 M solutions of **1−9** in [D$_6$]acetone



| IL | R | *H$^2$* | *H$^4$* | *H$^5$* | NC*H$_2$* | NC*H$_3$* |
|---|---|---|---|---|---|---|
| **1** | H | 8.08 | 7.48 | 7.40 | 4.08 | 3.74 |
| **2** | Me | 7.58 | 7.41 | 7.33 | 3.97 | 3.65 |
| **3** | CF$_3$ | 9.06 | 7.77 | 7.71 | 4.37 | 4.06 |
| **4** | 3,5-(CF$_3$)$_2$ | 9.12 | 7.84 | 7.77 | 4.41 | 4.11 |
| **5** | C$_6$F$_{13}$ | 9.07 | 7.78 | 7.72 | 4.38 | 4.06 |
| **6** | SiMe$_3$ | 7.42 | 7.28 | 7.20 | 4.00 | 3.69 |
| **7** | SiMe$_2$(CH$_2$)$_2$CF$_3$ | 8.29 | 7.64 | 7.57 | 4.21 | 3.89 |
| **8** | SiMe$_2$C$_8$H$_{17}$ | −[a] | −[a] | −[a] | 4.04 | 3.77 |
| **9** | SiMe$_2$(CH$_2$)$_2$C$_6$F$_{13}$ | 8.40 | 7.66 | 7.60 | 4.23 | 3.91 |

[a] Obscured by resonances of tetraarylborate anion.
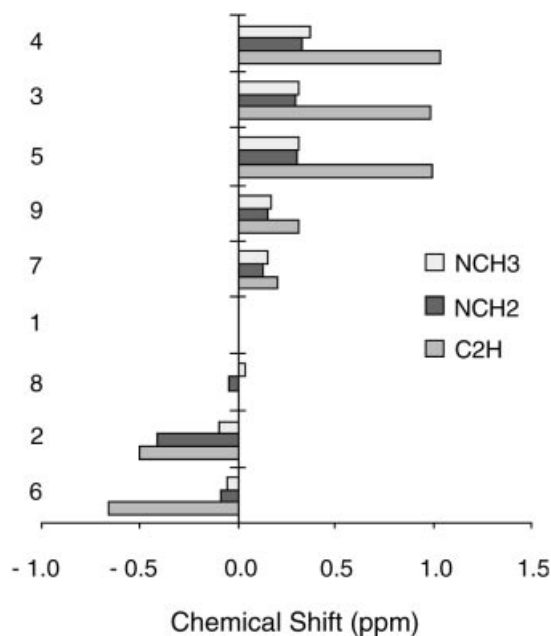
Figure 8. $^1$H NMR chemical shifts for **2−9** relative to [BMIm][BPh$_4$] (**1**)
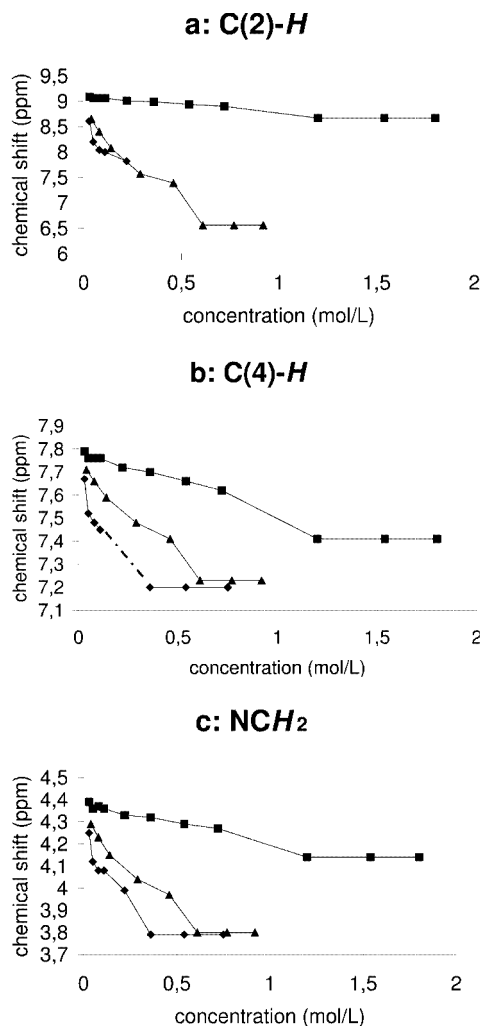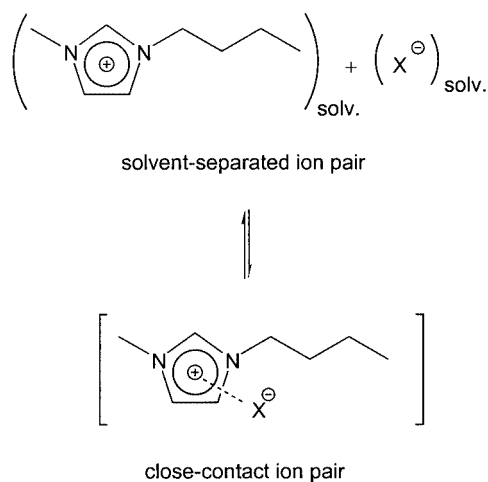


Figure 9. Concentration dependence of the $^1$H NMR chemical shifts (δ in ppm) in [D$_6$]acetone for **1**, **3** and **9**. ◆ = [BPh$_4$]$^-$. ■ = [B{C$_6$H$_4$(CF$_3$)-4}$_4$]$^-$. ▲ = [B(C$_6$H$_4${SiMe$_2$(CH$_2$CH$_2$C$_6$F$_{13}$)}-4)$_4$]$^-$. ·-·-·-: peaks in this concentration range were obscured by resonances of the tetraarylborate anion

The IR data established that the hydrogen-bonding strength is reduced when electron-withdrawing groups are present on the borate anion. This would correspond with an upfield shift in the $^1$H NMR spectrum;[31] however, the opposite effect is observed because the weakened cation−anion interactions reduce the proximity of the imidazolium protons to the π-orbitals of the anion. This reduces the magnetic shielding experienced by these protons. As a negative Δδ is observed with increasing hydrogen-bond strength, the effect of the shielding apparently outweighs the influence of the hydrogen-bonding interactions on the chemical shift.

Although magnetic shielding proved to be the most important factor in determining the chemical shift of C(2)−H, C(4)−H and C(5)−H, the C−H···π interactions affect the sensitivity of the chemical shift of the imidazolium protons to the nature of the anion. As C(2)−H is the strongest hydrogen-bond donor of the imidazolium ring protons it will be closer to the phenyl rings of the borate anion than C(4)−H and C(5)−H, and therefore the shielding C(2)−H experiences will be increased. This is reflected in the enhanced sensitivity of its chemical shift towards changes in the anion.

The concentration dependence of the chemical shifts of the imidazolium ring protons of **1**, **3** and **9** in acetone was investigated in the range 0.03−1.80 M. As reported previously,[3a] the $^1$H NMR signals of these protons were anion- and concentration-dependent (Figure 9). The order of magnitude of these effects varied with each proton, with C(2)−H being the most sensitive. Smaller displacements were observed for the pairs of signals corresponding with C(4)−H and C(5)−H and with NCH$_3$ and NCH$_2$. The pro-

tons within these pairs displayed comparable concentration-related shifts.

Compounds **1** and **9** show similar behaviour − the resonances shifting to higher field at higher molarities. The C(2)−H signal displayed the largest Δδ (Δδ = −2.09 ppm) when increasing the concentration of **9** from 0.04 to 0.92 M (Figure 9). For **1** a similar trend could be discerned; however, broadening of the C(2)−H resonance at concentrations above 0.22 M prevented accurate observation. No change in the chemical shifts was observed above 0.36 M and 0.61 M for **1** and **9**, respectively. The imidazolium ring protons of **3** showed a more modest concentration-related displacement, the C(2)−H signal shifting by a mere −0.4 ppm over the concentration range 0.11 to 1.20 M. Below 0.11 M and above 1.20 M, all of the chemical shifts of **3** were constant.

The changes in the chemical shifts upon increasing concentration of the imidazolium salts in acetone can be explained by an equilibrium between a solvent-separated ion pair and a close-contact ion pair (Scheme 4).[3a]

Scheme 4

Figure 10. Thermogravimetric analysis for [BMIm][B{$C_6H_4$Me-4}$_4$] (**2**) and [BMIm][B{$C_6H_4$($CF_3$)-4}$_4$] (**3**)

With increasing concentration, this equilibrium shifts to the right, resulting in an increase in close-contact ion pairing. In such ion-pairs the magnetic shielding of the imidazolium ring protons by the phenyl groups of the anion will be stronger than in the solvent-separated ion pairs, which explains the observed shift of the proton resonances to higher field with increasing concentrations Further increases in proton shielding in concentrated solutions are caused by ring stacking of the cations.[3a,32] This predominantly affects the C(2)−H proton,[3a] which could explain the high concentration sensitivity of the corresponding signal in comparison with the other imidazolium proton resonances.

The reduced cation−anion interactions in **3**, which contains the more weakly coordinating [B{$C_6H_3$($CF_3$)-4}$_4$]$^-$ anion, reduces the amount of close-contact ion pairing at a given concentration. This results in weaker magnetic shielding on the imidazolium ring protons and, thus, in a smaller $\Delta\delta$ than observed for **1** and **9**. Furthermore, as hydrogen bonding interactions in **3** are weaker, cation−cation aggregation at higher concentration will be weaker, further reducing shielding of the imidazolium protons with respect **1** and **9**. This weakening of the inter-ionic interactions in **3** is supported by the IR data.

**Melting Points and Thermal Stability:** For the imidazolium salts **1**−**9** the melting points and thermal stability were
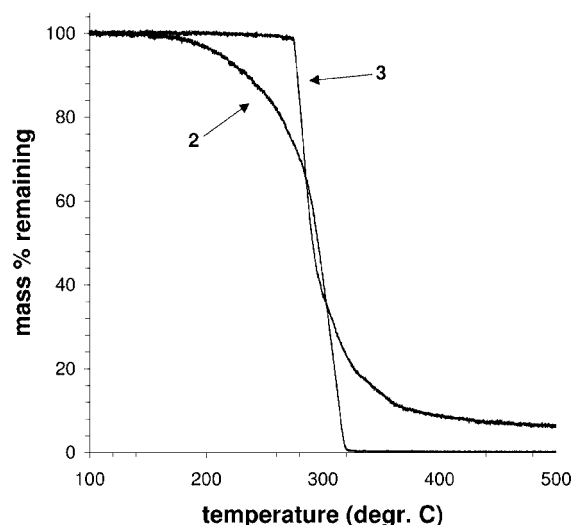
determined (Table 6). All compounds are white solids that melt well above room temperature, except for **8** and **9** for which DSC measurements indicated possible glass transition temperatures in the range −20 °C to −10 °C.[33] Whereas the NMR and IR data showed an obvious influence of the electron-withdrawing $CF_3$ and $C_6F_{13}$ substituents on cation−anion interactions, such a correlation with the observed melting points is difficult. However, the increasing bulk and orientational flexibility of the substituents[34] clearly depress the melting points of the imidazolium borates, as observed for **8** and **9** and to a lesser extent in **5** and **7**, since the bulky substituents disturb the most efficient packing of ions in the crystal lattice.[35]

The thermal stability of the compounds was assessed by thermogravimetric analysis under nitrogen, heating **1**−**9** from 100 to 500 °C at 5 °C/min. All compounds were stable up to 170 °C, after which the alkyl- and silyl-substituted salts **1**, **2**, **7**, **8** and **9** started to decompose. For all ionic liquids the decomposition process was complete above 450 °C (Figure 10). The only exception is $SiMe_3$-substituted **6**, which decomposes at 250 °C.

The borate anions with $CF_3$ or $C_6F_{13}$ substituents directly connected to the aryl rings yielded more stable salts, with decomposition starting, on average, 70 °C higher than

Table 6. Melting points and liquid range of imidazolium salts **1**−**9**

| | Anion | Melting point [°C] | Decomposition temperature [°C] | Liquid range [°C] |
|---|---|---|---|---|
| **8** | [B{$C_6H_4$($SiMe_2C_8H_{17}$)-4}$_4$]$^-$ | −20[a] | 170 | 190 |
| **9** | [B($C_6H_4${$SiMe_2$($CH_2CH_2C_6F_{13}$)}-4)$_4$]$^-$ | −10[a] | 190 | 200 |
| **5** | [B{$C_6H_4$($C_6F_{13}$)-4}$_4$]$^-$ | 90 | 225 | 135 |
| **7** | [B($C_6H_4${$SiMe_2$($CH_2CH_2CF_3$)}-4)$_4$]$^-$ | 104 | 175 | 71 |
| **4** | [B{$C_6H_3$($CF_3$)$_2$−3,5}$_4$]$^-$ | 109 | 245 | 136 |
| **1** | [$BPh_4$]$^-$ | 126 | 185 | 59 |
| **3** | [B{$C_6H_4$($CF_3$)-4}$_4$]$^-$ | 152 | 275 | 123 |
| **2** | [B($C_6H_4$Me-4)$_4$]$^-$ | —[b] | 173 | —[b] |
| **6** | [B{$C_6H_4$($SiMe_3$)-4}$_4$]$^-$ | —[b] | 250 | —[b] |

[a] DSC measurements suggest a glass transition around this temperature. [b] No melting point observed before the onset of decomposition.

for the alkyl- or silyl-substituted compounds. As the only variable in these studies is the anion, the changes in the decomposition temperature are connected with the stability of the tetraarylborate anions. The increased thermal stability for **3−5** is a direct result of the increased delocalisation of the negative charge due to the electron-withdrawing substituents on the phenyl groups of the anion.[9] The high stability of **6** is remarkable and remains unexplained as this anion does not contain stabilising functionalities, and because the other silyl-substituted anions do not show increased stability over [BPh$_4$]$^-$.

**Polarity:** For **8** and **9**, which are liquids at room temperature, the relative polarity was estimated by measuring $\lambda_{max}^{abs}$ of the solvatochromatic dye Nile Red dissolved in these ILs. The observed solvatochromatic shifts, and the molar transition energy ($E_{NR}$) calculated using $\lambda_{max}^{abs}$, indicate that **8** is less polar than **9**, and that both are considerably less polar than the common ILs [BMIm]BF$_4$ and [BMIm]PF$_6$ (Table 7).[36] Nevertheless, the polarity of **8** and **9** is of the same order of magnitude as that of a polar solvent such as acetone.

Earlier work using Nile Red to assess the polarity of *N*,*N*-dialkylimidazolium ILs showed that, in general, the polarity

decreased with increasing anion size. This was correlated with a reduction in electron density and, correspondingly, a reduction in the ability of the anion to interact with the dye. However, only BF$_4^-$, PF$_6^-$, NO$_2^-$, NO$_3^-$ and [N(SO$_2$CF$_3$)$_2$]$^-$ were assessed. When comparing **8** and **9** with these anions, the increased size and efficient charge delocalisation further reduce the relative polarity of the BMIm salts. The relatively high polarity of **9** could be the result of local dipoles, caused by the electron-withdrawing C$_6$F$_{13}$ substituents. Such dipole moments could lead to stronger interactions with the dye molecules and thus increase the relative polarity observed.[36]

**Solubility and Miscibility with Other Liquids:** The solubility of the imidazolium salts in a range of organic solvents was examined (Table 8). All ILs were immiscible with water and showed good solubility in acetone. Furthermore, the solubility in the solvents investigated proved to be highly dependent on the substituents present in the tetraarylborate anions. In methanol the solubility of **1−9** was moderate; however, the imidazolium salts with CF$_3$- and C$_6$F$_{13}$-substituted anions displayed significantly better solubility than those without perfluoroalkyl groups. This was especially evident in **3** and **4**, which exhibit the best solubility in methanol. In acetone, the substituent effect is less evident, with all compounds showing high solubilities. Upon going from acetone to Et$_2$O and hexane, the solubility of the imidazolium borates, except for **8**, decreases rapidly with decreasing solvent polarity. In Et$_2$O the compounds with CF$_3$ or large silyl substituents are still highly soluble, but only **8**, and to some extent **9**, retain significant miscibility with hexane. This is a consequence of the large, lipophilic substituents in the borate anion, which reduce the ILs to relatively apolar compounds and partially compensate the ionic character with a large lipophilic domain. The lipophilic character of **9** has been demonstrated previously,[12] where a phase behaviour resembling that of perfluorinated solvents was observed in combinations of **9** with toluene, hex-1-ene and oct-1-ene. Similar characteristics are expected for highly lipophilic **8**, but were not investigated.

The relatively low solubility in methanol and the immiscibility with water are no doubt the result of the poor hydrogen bonding character of the borate anions in **1−9**.[11] The

Table 7. Polarity of **8** and **9** determined using the solvatochromatic dye Nile Red (values other than for **8** and **9** were taken from ref.[36a] and ref.[37])

| | Liquid | $\lambda_{max}^{abs}$ [nm] | $E_{NR}$ [kcal/mol][a] |
|---|---|---|---|
| | H$_2$O | 593 | 201.7 |
| | [BMIm]BF$_4$ | 551 | 217.2 |
| | MeOH | 550 | 217.7 |
| | [BMIm]PF$_6$ | 548 | 218.5 |
| | [C$_{10}$MIm]BF$_4$[b] | 546 | 219.2 |
| 9 | [BMIm][B(C$_6$H$_4${SiMe$_2$(CH$_2$CH$_2$C$_6$F$_{13}$)}-4)$_4$] | 542 | 220.7 |
| 8 | [BMIm][B{C$_6$H$_4$(SiMe$_2$C$_8$H$_{17}$)-4}$_4$] | 534 | 224.0 |
| | Acetone | 530 | 225.9 |
| | Et$_2$O | 504 | 237.2 |
| | Hexane | 484 | 247.0 |

[a] Calculated from $E_{NR} = (hcN_A/\lambda_{max}^{abs}) \times 10^6$, where $h$ is Planck's constant, $c$ is the speed of light, $N_A$ is Avogadro's number and $\lambda_{max}^{abs}$ is the wavelength of maximum absorption for Nile Red. [b] C$_{10}$MIm = 1-decyl-3-methylimidazolium.

Table 8. Solubility of **1−9** in various organic solvents

| [a] | Anion | Solubility (g/L) | | | |
|---|---|---|---|---|---|
| | | MeOH | Acetone | Et$_2$O | Hexane |
| 1 | [BPh$_4$]$^-$ | 0.8 | 140 | 0.6 | 0.2 |
| 2 | [B(C$_6$H$_4$Me-4)$_4$]$^-$ | 0.09 | 63 | 0.3 | 0.06 |
| 3 | [B{C$_6$H$_4$(CF$_3$)-4}$_4$]$^-$ | 70 | 340 | 180 | 0.2 |
| 4 | [B{C$_6$H$_3$(CF$_3$)$_2$−3,5}$_4$]$^-$ | 66 | 290 | 200 | 0.2 |
| 5 | [B{C$_6$H$_4$(C$_6$F$_{13}$)-4}$_4$]$^-$ | 3.6 | 82 | 53 | 0.08 |
| 6 | [B{C$_6$H$_4$(SiMe$_3$)-4}$_4$]$^-$ | 0.5 | 96 | 14 | 0.2 |
| 7 | [B(C$_6$H$_4${SiMe$_2$(CH$_2$CH$_2$CF$_3$)}-4)$_4$]$^-$ | 12 | 160 | 98 | 0.07 |
| 8 | [B{C$_6$H$_4$(SiMe$_2$C$_8$H$_{17}$)-4}$_4$]$^-$ | 1.8 | 250 | 230 | 250 |
| 9 | [B(C$_6$H$_4${SiMe$_2$(CH$_2$CH$_2$C$_6$F$_{13}$)}-4)$_4$]$^-$ | 33 | 580 | 510 | 19 |

[a] Solubility in g/L of pure solvent at 25 °C.

comparatively high solubility of the $CF_3$-substituted ionic liquids could be due to the additional $O-H \cdots F$ hydrogen bonding possibilities such substituents introduce,[16] which would enhance solvent−solute interactions and thus enhance solubility.

**Application as Solvents:** Based on the melting points of the imidazolium tetraarylborate salts described here, only **8** and **9** qualify as true room-temperature ionic liquids. Although their melting point is significantly higher than that of the widely used [BMIm]$BF_4$ and [BMIm]$PF_6$ salts, which melt at −81 °C and −62 °C, [1a][7a][28b] it allows their application as solvents for reactions at room temperature. The thermal stability of **8** and **9**, up to 170 °C, is sufficient for general application in homogeneous catalysis, even though the borate anion reduces their stability relative to ionic liquids with inorganic anions such as $BF_4^-$.[38] Conversely, the use of the borate anions eliminates the main source of decomposition in [BMIm]$BF_4$ and [BMIm]$PF_6$. Halogen-containing inorganic anions, and especially $PF_6^-$, might form acids in the presence of water.[1a,39] As the conventional ionic liquids often contain trace amounts of water, HF formation is a serious concern, in particular for [BMIm]$PF_6$. In **8** and **9** this is prevented by the elimination of fluorine atoms that are sensitive to hydrolysis and by the possibility of removing even trace amounts of water.[40] However, isolation of **10** when attempting to crystallise **7** shows that chemical stability could be an issue. This indicates that the borate could be prone to decomposition under the influence of the acidic $C(2)-H$ proton of the imidazolium cation.

The high miscibility of **8** and **9** with apolar solvents is unique amongst ionic liquids. [BMIm]$PF_6$ shows limited miscibility with apolar organic liquids such as oct-1-ene (65 g/L);[41] however, the high solubility of **8** and **9**, and the phase behaviour displayed by the latter, is unprecedented. In catalysis this would offer increased solubility of apolar substrates, which could be beneficial in catalytic processes that suffer from phase transfer limitations due to the high polarity of the common ILs. The lipophilic character of **8** and **9** would enable their use as a polar phase that can dissolve and immobilise ionic catalysts, with affinity for apolar substrates.

## Conclusions

An interesting feature of ionic liquids that favours their use as solvents is the possibility of adapting their properties by choosing different cation−anion combinations. This concept has been applied successfully, but a thorough understanding of the effects that govern the physical properties of ionic liquids is lacking. Here the effects of systematically varying the anion on the physical properties of BMIm tetraarylborate salts are reported. The hydrogen-bonding interactions, between the imidazolium ring protons and the borate anion, that are present both in the solid state and in solution are reduced upon introducing electron-withdrawing perfluoroalkyl substituents in the anion. In ad-

dition, bulky silyl substituents depress the melting point of these salts. [BMIm][B{$C_6H_4(SiMe_2C_8H_{17})$-4}$_4$] and [BMIm][B($C_6H_4${$SiMe_2(CH_2CH_2C_6F_{13})$}-4)$_4$] even proved to be liquid down to −10 °C, making them true room-temperature ILs. These two imidazolium borates displayed significant solubility in hexane, due to their large lipophilic anions. As conventional ionic liquids display poor miscibility with apolar compounds, this lipophilic character makes them a unique reaction media. However, before their application as solvents, their stability under reaction conditions should be assessed carefully as they are not chemically inert.

## Experimental Section

**General Procedures:** All reactions were performed under dry $N_2$ using standard Schlenk techniques. Tetrahydrofuran (THF) and diethyl ether ($Et_2O$) were distilled from sodium benzophenone ketyl, $CH_2Cl_2$ from $CaH_2$ and benzene from sodium. Dimethyloctylsilyl chloride,[42] 1-butyl-3-methylimidazolium chloride,[43] 1-butyl-3-methylimidazolium bromide,[44] 1-butyl-3-methylimidazolium iodide,[44] Na[B($C_6H_4$Me-4)$_4$],[45] Na[B{$C_6H_4(CF_3)$-4}$_4$],[46] Na[B{$C_6H_3(CF_3)_2$-3,5}$_4$],[47] Na[B{$C_6H_4(SiMe_3)$-4}$_4$],[15] Na[B{$C_6H_4(C_6F_{13})$-4}$_4$],[48] and [BMIm][B($C_6H_4${$SiMe_2(CH_2CH_2C_6F_{13})$}-4)$_4$] (**9**)[12] were prepared according to literature procedures. All other chemicals were used as received. NMR spectra were recorded with a Varian Inova 300 spectrometer at 25 °C ($\delta$ in ppm and $J$ in Hz) with TMS ($^1$H, $^{13}$C) and $BF_3 \cdot Et_2O$ ($^{11}$B) as external references. Infrared spectra were recorded with a Mattson Galaxy FT-IR 5000 spectrometer at 25 °C under $N_2$ (as KBr pellets). DSC traces were recorded with a Mettler-Toledo DSC-821, and melting points were determined with a Büchi melting point apparatus. UV/Vis absorption spectra were recorded with a Perkin−Elmer Lambda 16 spectrophotometer. TGA measurements were performed with a Perkin−Elmer thermal analysis system 4 coupled to a Perkin−Elmer TGS2 thermogravimmetric system. Elemental analyses were carried out by H. Kolbe, Mikroanalytisches Laboratorium, Mülheim an der Ruhr.

**4-Bromo{dimethyl(3,3,3-trifluoropropyl)silyl}benzene:** $n$BuLi (17.2 mL, 1.54 M in hexanes, 26.5 mmol) was added to a solution of 1,4-dibromobenzene (6.25 g, 26.5 mmol) in $Et_2O$ (100 mL). The resultant mixture was stirred at room-temperature for 5 min and then cooled to −78 °C. Chlorodimethyl(3,3,3-trifluoropropyl)silane (4.55 mL, 26.5 mmol) was added and the mixture warmed to room temperature over 2 h. This mixture was then poured into $H_2O$ (100 mL), extracted with $Et_2O$ (3 × 100 mL) and the combined organic layers dried with $MgSO_4$. Removal of the solvents in vacuo yielded 7.07 (86%) of a colourless oil. $^1$H NMR (CDCl$_3$, 300.1 MHz): $\delta$ = 0.39 (s, SiC$H_3$), 1.01 (m, SiC$H_2$), 2.01 (m, C$H_2$CF$_3$), 7.43 (d, $^3J_{H,H}$ = 7.8 Hz, 2 Ar-$H_m$), 7.58 (d, $^3J_{H,H}$ = 7.8 Hz, 2 Ar-$H_o$) ppm. $^{13}$C{$^1$H} (CDCl$_3$, 75.5 MHz): $\delta$ = −3.4 (s), 7.7 (s), 29.0 (q), 124.5 (s), 131.5 (s), 135.4 (s), 136.5 (s) ppm. $C_9H_{14}BrF_3$ (310.00): calcd. C 42.45, H 5.43, F 18.31; found C 42.22, H 4.65, F 18.18.

**4-Bromo{dimethyl(octyl)silyl}benzene:** Using a procedure similar to that for 4-bromo[dimethyl(3,3,3-trifluoropropyl)silyl]benzene, 1,4-dibromobenzene (14.28 g, 60.5 mmol), $n$BuLi (38 mL, 1.6 M in hexanes, 61.0 mmol) and chlorodimethyloctylsilane (12.62 g, 61.0 mmol) yielded 15.51 g (78%) of a light yellow oil. $^1$H NMR (CDCl$_3$, 300.1 MHz): $\delta$ = 0.25 (s, SiC$H_3$), 0.77 (s, SiC$H_2$), 0.91 (m,

SiC$_7$H$_{14}$C$H_3$), 1.31 (m, SiCH$_2$C$_6$H$_{12}$CH$_3$), 7.38 (d, $^3J_{H,H}$ = 7.8 Hz, 2 Ar-$H_m$), 7.53 (d, $^3J_{H,H}$ = 7.8 Hz, 2 Ar-$H_o$) ppm. $^{13}$C{$^1$H} (CDCl$_3$, 75.5 MHz): δ = −2.8 (s), 0.7 (s), 14.4 (s), 15.9 (s), 22.9 (s), 241. (s), 29.6 (s), 32.2 (s), 33.8 (s), 123.8 (s), 131.1 (s), 135.4 (s), 138.7 (s) ppm. C$_{16}$H$_{27}$Br (326.11): calcd. C 78.70, H 8.41; found C 78.56, H 8.35.

**Sodium Tetrakis{4-[dimethyl(3,3,3-trifluoropropyl)silyl]phenyl}-borate:** $t$BuLi (12.6 mL, 1.5 M in pentane, 20.2 mmol) was added to 4-bromo{dimethyl(3,3,3-trifluoropropyl)silyl}benzene (3.14 g, 10.1 mmol) in Et$_2$O (50 mL) at −78 °C. The mixture was allowed to warm to room temperature over 16 h and then cooled to −78 °C with subsequent addition of BF$_3$·Et$_2$O (0.21 mL, 1.67 mmol). This solution was then warmed to room temperature over 16 h, poured into H$_2$O and saturated with NaCl. After extraction with Et$_2$O (3 × 50 mL) the combined organic layers were dried with MgSO$_4$ and the solvents removed in vacuo. The residue was taken up in THF (25 mL), filtered through Celite and dried in vacuo, yielding 1.33 g (83%) of a white solid. $^1$H NMR ([D$_4$]MeOH, 300.1 MHz): δ = 0.25 (s, 24 H, SiC$H_3$), 0.89 (m, 8 H, SiC$H_2$), 2.01 (m, 8 H, C$H_2$CF$_3$), 7.17 (d, $^3J_{H,H}$ = 7.9 Hz, 8 Ar-$H_m$), 7.37 (m, 8 Ar-$H_o$) ppm. $^{13}$C{$^1$H} ([D$_4$]MeOH, 75.5 MHz): δ = −4.2 (s), 7.7 (s), 28.5 (s), 128.3 (s), 128.3 (s), 130.2 (s), 130.7 (s), 135.9 (s), 166.5 (q, $^1J_{BC}$ = 49.5 Hz, B−C) ppm. C$_{44}$H$_{56}$BF$_{12}$NaSi$_4$ (958.33): calcd. C 55.10, H 5.89, Na 2.40; found C 54.84, H 5.85, Na 2.48.

**Sodium Tetrakis{4-[dimethyl(octyl)silyl]phenyl}borate:** A procedure similar to that for sodium tetrakis{4-[dimethyl(3,3,3-trifluoropropyl)silyl]phenyl}borate and 4-bromo{dimethyl(octyl)-silyl}benzene (5.77 g, 21.5 mmol), $t$BuLi (23.5 mL, 1.5 M in pentane, 35.2 mmol) and BF$_3$·Et$_2$O (0.44 mL, 3.50 mmol) yielded a brown oil. After washing with α,α,α-trifluorotoluene (3 × 5 mL) a white solid (2.42 g; 71%) was collected. $^1$H NMR ([D$_4$]MeOH, 300.1 MHz): δ = 0.21 (s, 24 H, SiC$H_3$), 0.75 (s, 8 H, SiC$H_2$), 0.92 (m, 12 H, C$_7$H$_{14}$C$H_3$), 1.32 (m, 48 H, CH$_2$C$_6$H$_{12}$CH$_3$), 7.19 (d, $^3J_{H,H}$ = 7.8 Hz, 8 Ar-$H_m$), 7.48 (m, 8 Ar-$H_o$) ppm. $^{13}$C{$^1$H} ([D$_6$]-acetone, 75.5 MHz): δ = −2.9 (s), 13.9 (s), 16.2 (s), 22.8 (s), 24.2 (s), 33.9 (s), 130.4 (s), 131.3 (s), 135.9 (s), 165.8 (q, $^1J_{BC}$ = 49.5 Hz, B−C) ppm. C$_{64}$H$_{108}$BNaSi$_4$ (1022.75): calcd. C 75.09, H 10.63; found C 74.88, H 10.75.

**1-Butyl-3-methylimidazolium Tetraphenylborate (1):**[8] In a procedure adapted from the literature (2.18 g, 6.37 mmol) Na[BPh$_4$] and (1.26 g, 5.79 mmol) [BMIm]Br were dissolved in H$_2$O (30 mL) and CH$_2$Cl$_2$ (30 mL). After stirring for 24 h, the layers were separated and the CH$_2$Cl$_2$ layer was washed with water (2 × 50 mL). Drying in vacuo yielded a white solid (2.12 g; 80%). $^1$H NMR ([D$_6$]acetone, 300.1 MHz): δ = 0.92 (t, $^3J_{H,H}$ = 7.4 Hz, CH$_2$C$H_3$), 1.31 (m, C$H_2$CH$_3$), 1.79 (m, NCH$_2$C$H_2$), 3.75 (s, NC$H_3$), 4.09 (t, $^3J_{H,H}$ = 7.4 Hz, NC$H_2$), 6.78 (t, $^3J_{H,H}$ = 7.8 Hz, 4 Ar-$H_p$), 6.94 (t, $^3J_{H,H}$ = 7.5 Hz, 8 Ar-$H_m$), 7.36 (m, 8 Ar-$H_o$), 7.42 [s, C(5)$H$], 7.49 [s, C(4)$H$], 8.19 [s, C(2)$H$] ppm. $^{13}$C{$^1$H} ([D$_6$]acetone, 75.5 MHz): δ = 13.0 (s), 19.5 (s), 32.0 (s), 35.9 (s), 49.5 (s), 122.5 (s), 124.0 (s), 131.0 (s), 135.7 (s), 136.3 (s), 165.0 (q, $^1J_{BC}$ = 49.5 Hz, B−C) ppm. $^{11}$B{$^1$H} ([D$_6$]acetone, 96.3 MHz): δ = −12.21 (s) ppm. C$_{32}$H$_{35}$BN$_2$ (458.29): calcd. C 83.84, H 7.70; found C 83.17, H 7.59.

**1-Butyl-3-methylimidazolium Tetrakis{4-(methyl)phenyl}borate (2):** A mixture of (0.79 g, 1.98 mmol) Na[B(C$_6$H$_4$Me-4)$_4$] and (0.58 g, 2.18 mmol) [BMIm]I was dissolved in H$_2$O (20 mL). After stirring for 2 d the mixture was extracted with CH$_2$Cl$_2$ (2 × 20 mL), dried with MgSO$_4$, filtered and all volatiles removed in vacuo. The resulting solid was washed with hexane (2 × 20 mL) and dried in vacuo, yielding a white solid (0.64 g; 63%). $^1$H NMR ([D$_6$]acetone,

300.1 MHz): δ = 0.93 (t, $^3J_{H,H}$ = 7.4 Hz, CH$_2$C$H_3$), 1.38 (m, C$H_2$CH$_3$), 1.96 (m, NCH$_2$C$H_2$), 2.15 (s, 12 H, ArC$H_3$), 3.79 (s, NC$H_3$), 4.16 (t, $^3J_{H,H}$ = 7.5 Hz, NC$H_2$), 6.75 (d, $^3J_{H,H}$ = 7.5 Hz, 8 Ar-$H_m$), 7.25 (m, 8 Ar-$H_o$), 7.51 [s, C(5)$H$], 7.59 [s, C(4)$H$], 8.12 [s, C(2)$H$] ppm. $^{13}$C{$^1$H} ([D$_6$]acetone, 75.5 MHz): δ = 13.0 (s), 19.3 (s), 20.6 (s), 32.1 (s), 35.9 (s), 49.5 (s), 122.5 (s), 123.9 (s), 126.2 (s), 129.5 (s), 136.3 (s), 161.2 (q, $^1J_{BC}$ = 49.4 Hz, B−C) ppm. $^{11}$B{$^1$H} ([D$_6$]acetone, 96.3 MHz): δ = −12.79 (s) ppm. C$_{36}$H$_{43}$BN$_2$ (514.35): calcd. C 84.03, H 8.42; found C 83.78, H 8.54.

**1-Butyl-3-methylimidazolium Tetrakis{4-(trifluoromethyl)phenyl}-borate (3):** A mixture of Na[B{C$_6$H$_4$(CF$_3$)-4}$_4$] (3.87 g, 6.30 mmol) and [BMIm]I (1.85 g, 6.93 mmol) was dissolved in CH$_2$Cl$_2$ (100 mL). After stirring for 2 d the mixture was poured into demineralised water (40 mL) and the resulting mixture was washed with demineralised water (5 × 40 mL). The organic layer was then dried with MgSO$_4$, filtered and the solvent was removed in vacuo. The resulting solid was washed with hexane (5 × 100 mL) and dried in vacuo, yielding a white solid (2.88 g; 63%). $^1$H NMR ([D$_6$]acetone, 300.1 MHz): δ = 0.95 (t, $^3J_{H,H}$ = 7.4 Hz, CH$_2$C$H_3$), 1.38 (m, C$H_2$CH$_3$), 1.96 (m, NCH$_2$C$H_2$), 4.08 (s, NC$H_3$), 4.39 (t, $^3J_{H,H}$ = 7.2 Hz, NC$H_2$), 7.34 (d, $^3J_{H,H}$ = 8.4 Hz, 8 Ar-$H_m$), 7.42 (m, 8 Ar-$H_o$), 7.74 [s, C(5)$H$], 7.80 [s, C(4)$H$], 9.09 [s, C(2)$H$] ppm. $^{13}$C{$^1$H} ([D$_6$]acetone, 75.5 MHz): δ = 13.0 (s), 19.3 (s), 32.1 (s), 36.1 (s), 49.6 (s), 120.5 (s), 122.5 (s), 124.1 (q, $^1J_{C,F}$ = 30.9 Hz, CF$_3$), 125.0 (s), 131.3 (s), 135.9 (s), 136.7 (s), 167.4 (q, $^1J_{BC}$ = 48.3 Hz, B−C) ppm. $^{11}$B{$^1$H} ([D$_6$]acetone, 96.3 MHz): δ = −12.34 (s) ppm. C$_{36}$H$_{31}$BF$_{12}$N$_2$ (730.24): calcd. C 59.20, H 4.28; found C 59.00, H 4.04.

**1-Butyl-3-methylimidazolium Tetrakis{3,5-(trifluoromethyl)phenyl}-borate (4):** In a procedure similar to **3**, Na[B{C$_6$H$_3$(CF$_3$)$_2$−3,5}$_4$] (1.40 g, 1.58 mmol) and [BMIm]I (0.39 g, 1.42 mmol) yielded a white solid (1.31 g; 82%). $^1$H NMR ([D$_6$]acetone, 300.1 MHz): δ = 0.95 (t, $^3J_{H,H}$ = 6.6 Hz, CH$_2$C$H_3$), 1.38 (m, C$H_2$CH$_3$), 1.97 (m, NCH$_2$C$H_2$), 4.09 (s, NC$H_3$), 4.40 (t, $^3J_{H,H}$ = 7.4 Hz, NC$H_2$), 7.33 (d, 8 Ar-$H_m$), 7.47 (m, 8 Ar-$H_o$), 7.76 [s, C(5)$H$], 7.81 [s, C(4)$H$], 9.18 [s, C(2)$H$] ppm. $^{13}$C ([D$_6$]acetone, 75.5 MHz): δ = 12.9 (s), 19.5 (s), 32.2 (s), 36.0 (s), 49.6 (s), 117.8 (s), 122.0 (s), 122.8 (s), 127.4 (s), 129.3 (q, $^1J_{C,F}$ = 31.8 Hz, CF$_3$), 134.8 (s), 136.8 (s), 162.5 (q, $^1J_{BC}$ = 49.9 Hz, B−C) ppm. $^{11}$B{$^1$H} ([D$_6$]acetone, 96.3 MHz): δ = −12.27 (s) ppm. C$_{40}$H$_{27}$BF$_{24}$N$_2$ (1002.19): calcd. C 47.93, H 2.71, I 0.00; found C, 47.93, H 2.79, I 0.00.

**1-Butyl-3-methylimidazolium Tetrakis{4-(perfluorohexyl)phenyl}-borate (5):** In an analogous procedure to the synthesis of **3**, Na[B{C$_6$H$_4$(C$_6$F$_{13}$)-4}$_4$] (2.39 g, 1.44 mmol) and [BMIm]I (0.42 g, 1.59 mmol) yielded a white solid (0.48 g; 20%). $^1$H NMR ([D$_6$]acetone, 300.1 MHz): δ = 0.95 (t, $^3J_{H,H}$ = 7.4 Hz, CH$_2$C$H_3$), 1.38 (m, C$H_2$CH$_3$), 1.97 (m, NCH$_2$C$H_2$), 4.09 (s, NC$H_3$), 4.40 (t, $^3J_{H,H}$ = 7.2 Hz, NC$H_2$), 7.33 (d, $^3J_{H,H}$ = 8.4 Hz, 8 Ar-$H_m$), 7.47 (m, 8 Ar-$H_o$), 7.76 [s, C(5)$H$], 7.81 [s, C(4)$H$], 9.18 [s, C(2)$H$] ppm. $^{13}$C{$^1$H} ([D$_6$]acetone, 75.5 MHz): δ = 12.8 (s), 19.3 (s), 32.1 (s), 36.0 (s), 49.6 (s), 108.1 (m), 111.3 (m), 115.1 (m), 118.4 (m), 121.4 (m), 122.9 (m), 124.1 (s), 125.7 (s), 135.9 (s), 136.8 (s), 167.7 (q, $^1J_{BC}$ = 49.0 Hz, B−C) ppm. $^{11}$B{$^1$H} ([D$_6$]acetone, 96.3 MHz): δ = −12.31 (s) ppm. C$_{56}$H$_{31}$BF$_{52}$N$_2$ (1730.17): calcd. C 41.67, H 3.45, Cl 0.00; found C 41.88, H 3.61, Cl 0.00.

**1-Butyl-3-methylimidazolium Tetrakis{4-(trimethylsilyl)phenyl}-borate (6):** A mixture of Na[B{C$_6$H$_4$(SiMe$_3$)-4}$_4$] (1.48 g, 2.35 mmol) and [BMIm]Br (0.47 g, 2.14 mmol) was dissolved in acetone (30 mL) and H$_2$O (5 mL). After stirring for 24 h a white solid was collected, taken up in acetone and filtered through Celite. Slow evaporation of solvents yielded 0.61 g (38%) of a white crys-

talline solid. $^1$H NMR ([D$_6$]acetone, 300.1 MHz): $\delta$ = 0.16 (s, 36 H, SiC$H_3$), 0.95 (t, $^3J_{H,H}$ = 7.4 Hz, CH$_2$C$H_3$), 1.37 (m, C$H_2$CH$_3$), 1.90 (m, NCH$_2$C$H_2$), 4.00 (s, NC$H_3$), 4.31 (t, $^3J_{H,H}$ = 7.5 Hz, NC$H_2$), 7.15 (d, $^3J_{H,H}$ = 7.5 Hz, 8 Ar-$H_m$), 7.46 (m, 8 Ar-$H_o$), 7.68 [s, C(5)$H$], 7.74 [s, C(4)$H$], 8.92 [s, C(2)$H$] ppm. $^{13}$C{$^1$H} ([D$_6$]acetone, 75.5 MHz): $\delta$ = $-1.2$ (s), 13.0 (s), 19.4 (s), 32.1 (s), 36.0 (s), 49.5 (s), 122.4 (s), 130.8 (s), 135.8 (s), 136.4 (s), 165.6 (q, $^1J_{BC}$ = 49.3 Hz, B$-$C) ppm. $^{11}$B{$^1$H} ([D$_6$]acetone, 96.3 MHz): $\delta$ = $-12.04$ (s) ppm. C$_{44}$H$_{67}$BN$_2$Si$_4$ (746.45): calcd. C 70.73, H 9.04; found C, 70.86, H 8.94. Single crystals were obtained from acetone.

**1-Butyl-3-methylimidazolium Tetrakis{4-[dimethyl(3,3,3-trifluoro-propyl)silyl]phenyl}borate (7):** A mixture of Na[B(C$_6$H$_4$-{SiMe$_2$(CH$_2$CH$_2$CF$_3$)}-4)$_4$] (0.50 g, 0.52 mmol) and [BMIm]I (0.13 g, 0.47 mmol) was dissolved in acetone (20 mL) and stirred for 4 h. A white precipitate that formed upon the addition of H$_2$O (10 mL) was then collected, washed with H$_2$O (3 × 20 mL) and dried in vacuo. The solid was taken up in toluene (50 mL), washed with demineralised water (2 × 30 mL) and dried in vacuo to yield a white solid (0.45 g, 75%). $^1$H NMR ([D$_6$]acetone, 300.1 MHz): $\delta$ = 0.29 (s, 24 H, SiC$H_3$), 0.96 (m, 8 H, SiC$H_2$), 0.98 (t, $^3J_{H,H}$ = 7.4 Hz, CH$_2$C$H_3$), 1.33 (m, C$H_2$CH$_3$), 1.78 (m, NCH$_2$C$H_2$), 2.17 (m, 8 H, C$H_2$CF$_3$), 3.67 (s, NC$H_3$), 4.02 (t, $^3J_{H,H}$ = 7.5 Hz, NC$H_2$), 7.25 (d, $^3J_{H,H}$ = 7.9 Hz, 8 Ar-$H_m$), 7.36 [s, C(5)$H$], 7.45 [s, C(4)$H$], 7.49 [s, C(2)$H$], 7.56 (m, 8 Ar-$H_o$) ppm. $^{13}$C{$^1$H} ([D$_6$]acetone, 75.5 MHz): $\delta$ = $-2.7$ (s), 8.7 (s), 13.9 (s), 20.2 (s), 33.0 (s), 36.8 (s), 50.4 (s), 123.5 (s), 125.0 (s), 127.7 (s), 129.3 (s), 132.0 (s), 134.6 (s), 135.9 (s), 137.0 (s), 167.0 (q, $^1J_{BC}$ = 49.2 Hz, B$-$C) ppm. $^{11}$B{$^1$H} ([D$_6$]acetone, 96.3 MHz): $\delta$ = $-12.15$ (s) ppm. C$_{52}$H$_{71}$BF$_{12}$N$_2$Si$_4$ (1074.46): calcd. C 58.08, H 6.06, I 0.00; found C 57.86, H 6.10, I 0.00.

**1-Butyl-3-methylimidazolium Tetrakis{4-[dimethyl(octyl)silyl]-phenyl}borate (8):** In a procedure similar to that for **3**, Na[B{C$_6$H$_4$(SiMe$_2$C$_8$H$_{17}$)-4}$_4$] (3.78 g, 3.69 mmol) and [BMIm]I

(1.47 g, 5.40 mmol) yielded a brown oil. This was washed with a hexane/methanol mixture (1:1) (3 × 60 mL), yielding a yellow oil (0.73 g; 17%). $^1$H NMR ([D$_6$]acetone, 300.1 MHz): $\delta$ = 0.17 (s, 24 H, SiC$H_3$), 0.71 (s, 8 H, SiC$H_2$), 0.89 (t, $^3J_{H,H}$ = 7.4 Hz, NC$_3$H$_6$C$H_3$), 0.92 (m, 12 H, SiC$_7$H$_{14}$C$H_3$), 1.27 (m, NC$_2$H$_4$C$H_2$CH$_3$), 1.34 (m, 48 H, SiCH$_2$C$_6$H$_{12}$CH$_3$), 1.72 (m, NCH$_2$C$H_2$), 3.52 (s, NC$H_3$), 3.86 (t, $^3J_{H,H}$ = 7.5 Hz, NC$H_2$), 6.67 [s, C(2)$H$], 7.20 (d, $^3J_{H,H}$ = 7.8 Hz, 8 Ar-$H_m$), 7.27 [s, C(5)$H$], 7.37 [s, C(4)$H$], 7.53 (m, 8 Ar-$H_o$) ppm. $^{13}$C{$^1$H} ([D$_6$]acetone, 75.5 MHz): $\delta$ = $-2.9$ (s), 13.2 (s), 13.9 (s), 16.2 (s), 19.5 (s), 22.8 (s), 24.2 (s), 32.1 (s), 33.9 (s), 35.8 (s), 49.5 (s), 122.2 (s), 123.8 (s), 130.4 (s), 131.3 (s), 134.2 (s), 135.9 (s), 165.8 (q, $^1J_{BC}$ = 49.5 Hz, B$-$C) ppm. $^{11}$B{$^1$H} ([D$_6$]acetone, 96.3 MHz): $\delta$ = $-12.10$ (s) ppm. C$_{72}$H$_{123}$BN$_2$Si$_4$ (1138.89): calcd. C 75.86, H 10.88; found C 75.65, H 11.06.

**Carbene$-$2-Tris[4-{dimethyl(3,3,3-trifluoropropyl)silyl}phenyl]-borane Adduct 10:** Crystallisation of **7** (0.20 g, 0.19 mmol) from a mixture of warm MeOH/H$_2$O (95:5) yielded white crystals (0.01 g; 6%) and a yellow oil that solidified upon standing. The $^1$H NMR spectrum of the oil was identical to that for **7**. The white crystals were suitable for X-ray single crystal analysis. $^1$H NMR ([D$_6$]acetone, 300.1 MHz): $\delta$ = 0.34 (m, 18 H, SiC$H_3$), 0.67 (m, 3 H, CH$_2$C$H_3$), 0.76 (m, 2 H, CH$_2$C$H_2$CH$_3$), 0.94 (m, 6 H, SiC$H_2$), 1.29 (m, 2 H, NCH$_2$C$H_2$), 2.12 (m, 6 H, C$H_2$CF$_3$), 3.09 (s, 3 H, NC$H_3$), 3.51 (m, 2 H, NC$H_2$), 7.33 (m, 12 H), 7.40 (s, 1 H) ppm. $^{13}$C{$^1$H} ([D$_6$]acetone, 75.5 MHz): $\delta$ = $-3.9$ (s), 7.7 (s), 13.1 (s), 19.6 (s), 33.1 (s), 37.8 (s), 49.3 (s), 121.1 (s), 123.3 (s), 126.6 (s), 131.7 (s), 132.2 (s), 135.0 (s) ppm. $^{11}$B{$^1$H} ([D$_6$]acetone, 96.3 MHz): $\delta$ = $-14.90$ (s) ppm.

**Solubility Studies:** Saturated solutions of **1**$-$**9** in a solvent were prepared and allowed to settle at 25 °C for 1 h, until the solution was completely clear upon visible inspection. A sample [2.0(1) mL] was taken while ensuring that no undissolved material was

Table 9. Final unit cell parameters and structural data for **2**, **3**, **5**, **6** and **10**

| | **2** | **3** | **5**[a] | **6** | **10** |
|---|---|---|---|---|---|
| Empirical formula | (C$_{28}$H$_{28}$B)(C$_8$H$_{15}$N$_2$) | (C$_{28}$H$_{16}$BF$_{12}$)(C$_8$H$_{15}$N$_2$) | (C$_{48}$H$_{16}$BF$_{52}$)(C$_8$H$_{15}$N$_2$) | (C$_{36}$H$_{52}$BSi$_4$)(C$_8$H$_{15}$N$_2$)·²/₃(C$_3$H$_6$O) | C$_{41}$H$_{56}$BF$_9$N$_2$Si$_3$ |
| Formula mass | 514.53 | 730.44 | 1730.64 | 785.88 | 842.96 |
| Temperature [K] | 110(2) | 110(2) | 150(2) | 150(2) | 110(2) |
| Crystal system | monoclinic | monoclinic | tetragonal | orthorhombic | monoclinic |
| Space group | $P2_1/c$ (no. 14) | $P2_1/c$ (no. 14) | $P4_1$ (no. 76) | $Pbcn$ (no. 60) | $P2_1/c$ (no. 14) |
| $a$ [Å] | 16.0649(1) | 14.4195(1) | 17.4238(10) | 38.4424(2) | 22.6720(2) |
| $b$ [Å] | 11.1877(1) | 14.4595(2) | | 17.5784(1) | 13.0435(1) |
| $c$ [Å] | 21.1563(1) | 18.0689(2) | 21.457(2) | 22.1918(1) | 15.2549(1) |
| $\beta$ [°] | 127.4728(3) | 116.6921(6) | | | 100.5188(3) |
| $V$ [Å$^3$] | 3017.75(4) | 3365.87(6) | 6514.1(8) | 14996.24(13) | 4435.40(6) |
| $Z$ | 4 | 4 | 4 | 12 | 4 |
| $D_{calcd.}$ [g cm$^{-1}$] | 1.133 | 1.441 | 1.765 | 1.044 | 1.262 |
| Abs. coeff., $\mu$ [mm$^{-1}$] | 0.065 | 0.130 | 0.208 | 0.151 | 0.175 |
| Crystal size [mm] | 0.46 × 0.36 × 0.30 | 0.36 × 0.09 × 0.09 | 0.35 × 0.21 × 0.06 | 0.60 × 0.30 × 0.15 | 0.48 × 0.21 × 0.12 |
| $\theta$ Range [°] | 1.60$-$27.49 | 3.03$-$24.34 | 1.17$-$25.25 | 1.27$-$22.25 | 1.81$-$27.18 |
| Meas./unique refl. | 52337/6914 | 50613/5500 | 102273/6071 | 90497/9463 | 48882/9754 |
| Goodness-of-fit on $F^2$ | 1.046 | 1.087 | 1.262 | 1.049 | 1.041 |
| Resid. density [e·Å$^{-3}$] | $-0.34/0.34$ | $-0.32/0.36$ | $-0.72/1.51$ | $-0.40/0.80$ | $-0.25/0.44$ |
| $R$ [$I > 2\sigma(I)$] | 0.0453 | 0.0399 | 0.1282 | 0.0535 | 0.0365 |
| $R$ (all data) | 0.0559 | 0.0635 | 0.1492 | 0.0668 | 0.0547 |
| $wR_2$ (all data) | 0.1218 | 0.1151 | 0.2864 | 0.1467 | 0.0922 |

[a] Friedel pairs were merged.

sampled. The solvent was removed in vacuo and the residue kept under vacuum (0.1 mbar) for 1 h, after which the weight was constant to within ± 1 mg. The weight of the residue was then determined and the solubility calculated.

**Polarity Measurements:** A Nile Red solution in methanol (1 mL, 1.89 $10^{-3}$ M) was added to 0.5 g of **8** or **9**. After the mixture had become homogeneous, the methanol was evaporated off in vacuo and the maximum absorbance of Nile Red determined by transmission UV/Vis spectroscopy of a thin film of the ionic liquid. An absorption maximum of 534 (**8**) or 542 nm (**9**) was observed, which corresponds to $E_{NR}$s of 224.0 kJ/mol (**8**) and 220.7 kJ/mol (**9**).

**Structure Determination and Refinement of 2, 3, 5, 6 and 10:** X-ray intensities were measured on a Nonius KappaCCD diffractometer with a rotating anode and Mo-$K_\alpha$ radiation (graphite monochromator). The structures were solved by direct methods with the programs SHELXS-97[49] (compounds **2** and **6**) and SIR97[50] (compounds **3**, **5** and **10**). The structures were refined with the program SHELXL-97[51] against $F^2$ of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters, hydrogen atoms were refined as rigid groups. The drawings, structure calculations, and checking for higher symmetry were performed with the program PLATON.[52] In the crystal structure of compound **2**, the *n*-butyl group was refined with a disorder model. For compound **3**, one of the trifluoromethyl groups was rotationally disordered. The absolute structure of compound **5** could not be determined reliably. Friedel pairs were therefore merged in the refinement. In the crystal structure of compound **6**, one of the 1-butyl-3-methylimidazolium ions is located on an inversion centre and is, therefore, disordered. Further details of the crystal structure determinations are given in Table 9. CCDC-207227 (**2**), -207228 (**3**), -207229 (**5**), -207230 (**6**), and -207231 (**10**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk)

## Acknowledgments

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