

Synthesis and Characterization of Imidazolium Salts with the Weakly Coordinating $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ Anion

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Dedicated to Professor Heribert Offermanns on the occasion of his 75th birthday

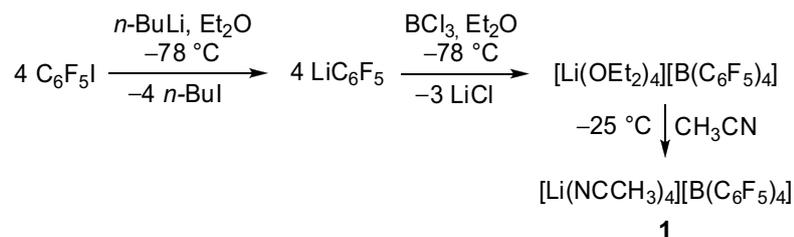
Key words: Imidazolium Salt, Weakly Coordinating Anion, Tetrafluoroborate, Crystal Structures

Introduction

Weakly coordinating anions (WCAs) have been a subject of intensive research in the past decades due to their increasing importance in coordination chemistry and catalysis [1–6]. These applications have grown out of basic research into the special properties of anions containing hydrocarbon and fluorocarbon functionality such as $[\text{SO}_3\text{CF}_3]^-$, $[\text{B}(\text{C}_6\text{F}_5)_4]^-$, $[\text{OTeF}_5]^-$ [7]. Owing to the importance of WCAs both in fundamental and applied chemistry, a new class of WCAs has recently been developed. Robert *et al.* reported the anions $[(\text{C}_6\text{F}_5)_3\text{M-LN-M}(\text{C}_6\text{F}_5)_3]^-$, with $\text{M} = \text{B}$ or Al and the linking group LN being azide, dicyanamide, and imidazolidine, which were found to be the most stable and effective activators for olefin polymerization reactions [8, 9]. $[\text{CB}_{11}\text{H}_{12}]^-$ and related carborane anions developed by Reed *et al.* were applied in many systems, despite the expensive and time-consuming multistep procedure of their preparation [10].

The $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ anion, commonly abbreviated as BAr^{F} , is much more stable as compared to the other anions and frequently used as a counteranion for electrophilic cations [7, 11]. It can be introduced by salt metathesis reaction of reagents such as $\text{Li}[\text{B}(\text{C}_6\text{F}_5)_4]$, which was first reported

in 1963 [12], $[\text{Mn}(\text{NCCH}_3)_6][\text{B}(\text{C}_6\text{F}_5)_4]_2$ [13], $[\text{H}(\text{OEt}_2)_2][\text{B}(\text{C}_6\text{F}_5)_4]$ [14], $[\text{Li}(\text{OEt}_2)_4][\text{B}(\text{C}_6\text{F}_5)_4]$ [15], $[\text{HN}^t\text{Bu}_3][\text{B}(\text{C}_6\text{F}_5)_4]$ [16], $[\text{Bu}_4\text{N}][\text{B}(\text{C}_6\text{F}_5)_4]$ [17], the superacid $[\text{C}_6\text{Me}_3\text{H}_4][\text{B}(\text{C}_6\text{F}_5)_4]$ [18], $[\text{Cp}_2\text{Zr}(\text{CH}_3)][\text{B}(\text{C}_6\text{F}_5)_4]$ [19, 20], $[\text{Ag}(\text{NCCH}_3)_4][\text{B}(\text{C}_6\text{F}_5)_4]$ [21], and $[\text{M}(\text{NCCH}_3)_6][\text{B}(\text{C}_6\text{F}_5)_4]$ ($\text{M} = \text{Cr}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}$) [22, 23] with labile or sometimes even covalently bound halides. Recently, imidazolium-based ionic liquids (ILs) have received considerable attention in different research fields [24–30]. The synthesis of ILs bearing $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ anions and organic cations such as imidazolium could represent an approach to combine the advantages of unreactive and stabilizing WCAs and eco-friendly ILs with low vapor pressure. Since $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ -based organic salts with imidazolium cations are quite rare [31, 32], we focused on the synthesis of new ionic compounds consisting of imidazolium cations and $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ anions *via* metathesis reactions. In this report, we present the precursors $[\text{Li}(\text{NCCH}_3)_4][\text{B}(\text{C}_6\text{F}_5)_4]$ (**1**) and $[\text{Ag}(\text{NCCH}_3)_4][\text{B}(\text{C}_6\text{F}_5)_4]$ (**2**) as metathesis reagents for the conversion of imidazolium bromides $[\text{Bmim}]\text{Br}$ and $[\text{Dbmim}]\text{Br}$ ($\text{Bmim} = 1$ -butyl-3-methylimidazolium; $\text{Dbmim} = 1,2$ -dimethyl-3-butylimidazolium) to yield the imidazolium-based salts $[\text{Bmim}][\text{B}(\text{C}_6\text{F}_5)_4]$ (**3**) and $[\text{Dbmim}][\text{B}(\text{C}_6\text{F}_5)_4]$ (**4**) with the $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ anion.

Scheme 1. Synthesis of the precursor $[\text{Li}(\text{NCCH}_3)_4][\text{B}(\text{C}_6\text{F}_5)_4]$ (**1**).

Results and Discussion

Synthesis of $[\text{Li}(\text{NCCH}_3)_4][\text{B}(\text{C}_6\text{F}_5)_4]$ (**1**)

The alkali metal salt $[\text{Li}(\text{OEt}_2)_4][\text{B}(\text{C}_6\text{F}_5)_4]$ was prepared according to literature procedures [23], but using $\text{C}_6\text{F}_5\text{I}$ instead of $\text{C}_6\text{F}_5\text{Br}$. The reaction of 1 equiv. LiC_6F_5 with 0.25 equiv. BCl_3 in a mixture of diethyl ether and *n*-hexane at low temperatures leads to the formation of $[\text{Li}(\text{OEt}_2)_4][\text{B}(\text{C}_6\text{F}_5)_4]$ under precipitation of LiCl . Subsequent crystallization of $[\text{Li}(\text{OEt}_2)_4][\text{B}(\text{C}_6\text{F}_5)_4]$ from a concentrated solution in acetonitrile yields $[\text{Li}(\text{NCCH}_3)_4][\text{B}(\text{C}_6\text{F}_5)_4]$ (**1**) as colorless crystals in a moderate yield of 41% (Scheme 1). Compound **1** exhibits very good solubility in polar organic solvents such as acetonitrile and diethyl ether. It is stable at room temperature and can be handled in air for a short period of time (5 min). The ^1H NMR spectrum shows one broad singlet at 1.96 ppm originating from free acetonitrile, as a consequence of a fast scrambling with CD_3CN solvent molecules. The ^{19}F NMR spectrum exhibits one broad singlet at -133.8 ppm (arising from 8 *o*-F atoms), one triplet at -164.0 ppm (attributed to 4 *p*-F atoms) and one multiplet which can be assigned to 8 *m*-F atoms. According to elemental analysis, the number of acetonitrile molecules coordinated to the lithium cation is four (see Experimental Section). Compound **1** has been further characterized by means of IR spectroscopy. The

ν_{CN} absorption band in the IR spectra is shifted from 2254 cm^{-1} for free acetonitrile to 2279 cm^{-1} for compound **1**. The higher energy vibration in the ν_{CN} region (2293 and 2306 cm^{-1} for free acetonitrile and **1**, respectively) can be assigned to a combination of the symmetrical CH_3 deformation and the C–C stretch that borrows its intensity from the ν_{CN} band. These results

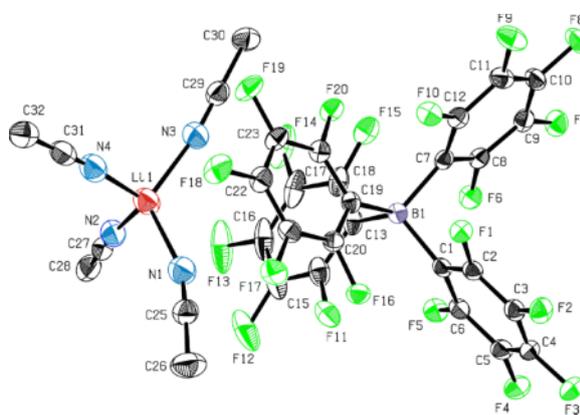


Fig. 1. ORTEP view of **1** with displacement ellipsoids at the 50% probability level. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Li1–N1 2.033(3), Li1–N2 2.041(3), Li1–N3 2.010(3), Li1–N4 2.044(3); Li1–N1–C25 160.2(2), Li1–N2–C27 169.1(2), Li1–N3–C29 169.9(2), Li1–N4–C31 175.5(2), N1–Li1–N2 104.6(2), N2–Li1–N4 120.3(2), N3–Li1–N4 105.5(2), N1–Li1–N4 103.0(2), N1–Li1–N3 121.6(2), N2–Li1–N4 120.3(2).

	1	$[\text{Li}(\text{OEt}_2)_4][\text{B}(\text{C}_6\text{F}_5)_4]$ [15]
Bond lengths (min–max)		
Li–O	–	1.936(4)–1.957(4)
Li–N	2.010(3)–2.044(3)	–
B–C	1.654(2)–1.657(2)	1.651(3)–1.658(3)
Bond angles (min–max)		
O–Li–O	–	104.2(2)–116.9(2)
N–Li–N	103.0(2)–121.6(2)	–
C–B–C	100.8(1)–114.5(1)	101.6(2)–114.5(2)

Table 1. Comparison of selected bond lengths (Å) and angles (deg) in **1** and $[\text{Li}(\text{OEt}_2)_4][\text{B}(\text{C}_6\text{F}_5)_4]$ [15].

Compound	δ (^{19}F) (ppm)		
$[\text{Ag}(\text{NCCH}_3)_4][\text{B}(\text{C}_6\text{F}_5)_4]$	-168.4	-164.0	-133.8
$[\text{Bmim}][\text{B}(\text{C}_6\text{F}_5)_4]$	-165.6	-161.7	-131.3
$[\text{Dbmim}][\text{B}(\text{C}_6\text{F}_5)_4]$	-166.0	-161.5	-132.4

Table 2. ^{19}F NMR chemical shifts of $[\text{Ag}(\text{NCCH}_3)_4][\text{B}(\text{C}_6\text{F}_5)_4]$, $[\text{Bmim}][\text{B}(\text{C}_6\text{F}_5)_4]$ and $[\text{Dbmim}][\text{B}(\text{C}_6\text{F}_5)_4]$ in DMSO.

are in good agreement with what has previously been reported for related Cu(I) [33] and Ag(I) [21] complexes.

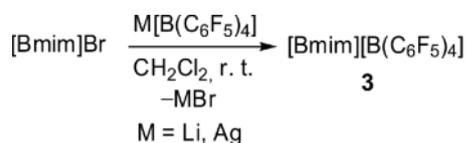
Crystal structure of **1**

The molecular structure of compound **1** is presented in Fig. 1. The compound crystallizes in the monoclinic space group $P2_1/n$ with one ion pair in the asymmetric unit. Both central atoms (lithium and boron) exhibit a tetrahedral coordination environment. Selected bond lengths are given in Table 1. The Li–N bond lengths (average 2.03 Å) are longer than the Li–O bond lengths of $[\text{Li}(\text{OEt}_2)_4][\text{B}(\text{C}_6\text{F}_5)_4]$ described by Martin *et al.* (average 1.95 Å) [15], which are also listed in Table 1. According to the non-coordinating nature of the $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ anion, the B–C bond lengths in **1** and $[\text{Li}(\text{OEt}_2)_4][\text{B}(\text{C}_6\text{F}_5)_4]$ are similar. Since the steric demand of the “end-on”-coordinated linear acetonitrile molecules is lower than that of the “side-on”-coordinated diethyl ether molecules, the N–Li–N bond angles in **1** exhibit a broader range (103 to 122°) than the related O–Li–O bond angles in Martin’s diethyletherate (104 to 117°).

Synthesis of the new imidazolium- BAR^{F} compounds **3** and **4**

In order to obtain the imidazolium salts **3** and **4**, two different starting materials, $[\text{Li}(\text{NCCH}_3)_4][\text{B}(\text{C}_6\text{F}_5)_4]$ and $[\text{Ag}(\text{NCCH}_3)_4][\text{B}(\text{C}_6\text{F}_5)_4]$ (**2**), were used (Scheme 2). The latter was prepared according to the literature [21].

The metathesis reaction of **1** with $[\text{Bmim}]\text{Br}$ leads to the formation of **3** in a yield of 62% within 2 h at room temperature. In order to increase the yield and reduce the reaction time, we



Scheme 2. Synthesis of $[\text{Bmim}][\text{B}(\text{C}_6\text{F}_5)_4]$ (**3**).

selected $[\text{Ag}(\text{NCCH}_3)_4][\text{B}(\text{C}_6\text{F}_5)_4]$ as the precursor for the synthesis of the imidazolium- BAR^{F} compound. In the metathesis reaction, silver cations were exchanged by imidazolium cations. The metathesis was performed using dry CH_2Cl_2 in the dark at room temperature. The reaction mixture was stirred for 10 min, and then filtered through siliceous earth on a Schlenk frit. The solvent was removed under high vacuum. The product was washed with dry *n*-hexane and then dried *in vacuo*. Typical yields of the purified product were around 89%. In the ^{19}F NMR spectra of compounds $[\text{Bmim}][\text{B}(\text{C}_6\text{F}_5)_4]$ and $[\text{Dbmim}][\text{B}(\text{C}_6\text{F}_5)_4]$ the fluorine signals are shifted about 2 ppm toward low field, compared to those of $[\text{Ag}(\text{NCCH}_3)_4][\text{B}(\text{C}_6\text{F}_5)_4]$ (Table 2), indicating that the bromide salts ($[\text{Bmim}]\text{Br}$ and $[\text{Dbmim}]\text{Br}$) have reacted with $[\text{Ag}(\text{NCCH}_3)_4][\text{B}(\text{C}_6\text{F}_5)_4]$.

Crystal structures of compounds **3** and **4**

Crystals of $[\text{Bmim}][\text{B}(\text{C}_6\text{F}_5)_4]$ and $[\text{Dbmim}][\text{B}(\text{C}_6\text{F}_5)_4]$ suitable for X-ray crystal structure analysis were obtained by slow diffusion of *n*-hexane into a dichloromethane solution of the corresponding compound. **3** and **4** are very stable in air for a long time (at least one day) and soluble in polar organic solvents such as ethers and dichloromethane.

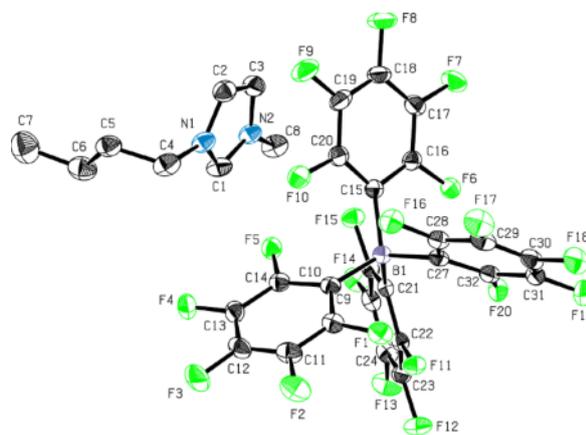


Fig. 2. ORTEP view of **3** with displacement ellipsoids at the 50% probability level. H atoms are omitted for clarity.

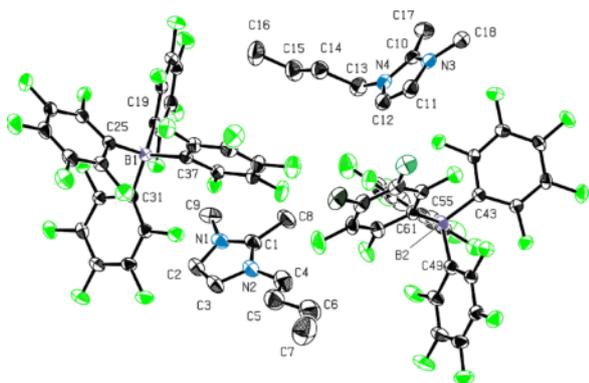


Fig. 3. ORTEP view of **4** with displacement ellipsoids at the 30% probability level. H atoms are omitted for clarity.

The molecular structures are presented in Figs. 2 and 3. Both compounds crystallize in the monoclinic space group $P2_1/c$. The asymmetric unit consists of one anion and one $[\text{Bmim}]^+$ cation (**3**) or of two ion pairs $[\text{Dbmim}]^+[\text{B}(\text{C}_6\text{F}_5)]^-$ (**4**). No significant cation...anion contacts are observed.

Thermal characterization of compounds **1**, **3** and **4**

Samples of compounds **1**, **3** and **4** were examined by thermogravimetric analysis (TGA) in combination with online fragment detection *via* coupled mass spectroscopy (MS), applying a temperature program with a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ between 30 and $1000\text{ }^\circ\text{C}$. For compound **1**, a total weight loss of about 87% of

the original mass was detected. Compound **1** shows its first decomposition onset at $135\text{ }^\circ\text{C}$ and is associated with a weight loss of *ca.* 9% of the original mass. The second and final decomposition starts at $220\text{ }^\circ\text{C}$ and corresponds to a weight loss of 70% at $400\text{ }^\circ\text{C}$. The first step originates from the loss of CH_3CN molecules as indicated by detection of CH_3^+ and CN^- fragments. The second maximum in the MS curves of CH_3CN , CH_3^+ and CN^- fragments is at $285\text{ }^\circ\text{C}$. Simultaneously, maxima in the MS curves of $\text{Li}(\text{CH}_3\text{CN})^+$ and C_6F_5^+ fragments, resulting from the stepwise decomposition of the $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ anion, are observed at $285\text{ }^\circ\text{C}$. The ionic compounds **3** and **4** exhibit a thermal stability beyond $240\text{ }^\circ\text{C}$ ($245\text{ }^\circ\text{C}$ for **3**, $270\text{ }^\circ\text{C}$ for **4**). Furthermore, the thermal behavior of the salts was studied by differential scanning calorimetry (DSC), as shown in Fig. 4. Both crystalline salts displayed a sharp melting transition on heating, and crystallized on cooling from the melt. The melting and crystallization points of **3** and **4** are $145, 97\text{ }^\circ\text{C}$ and $151, 70\text{ }^\circ\text{C}$, respectively.

Conclusions

In summary, the imidazolium- BAr^{F} compounds **3** and **4** were synthesized using two different precursors. Compounds **3** and **4** are imidazolium salts bearing the BAr^{F} anion which were characterized by X-ray single-crystal structure analysis. Whereas the yield of **3** is about 62% when using **1** as starting material (after 2 h at $25\text{ }^\circ\text{C}$), the yield increases to 89% when **2** is employed (after 10 min at $25\text{ }^\circ\text{C}$). The crystal structure of **1** was also elucidated by single-crystal X-ray diffraction. The two new imidazolium salts **3** and **4** have decomposition temperatures (at $245\text{ }^\circ\text{C}$ for **3** and at $270\text{ }^\circ\text{C}$ for **4**) indicative of high thermal stability.

Experimental Section

General methods

All reactions were performed in an argon atmosphere using standard Schlenk techniques. Solvents were dried by standard procedures (*n*-hexane and diethyl ether over sodium/benzophenone; CH_2Cl_2 over CaH_2), distilled under argon and used immediately or stored over molecular sieves. ^1H , ^{11}B and ^{19}F NMR spectra were recorded on a Bruker Avance DPX-400 spectrometer. IR spectra were recorded on a Varian FTIR-670 spectrometer, using a Glad-iATR accessory with a diamond ATR element. Elemental

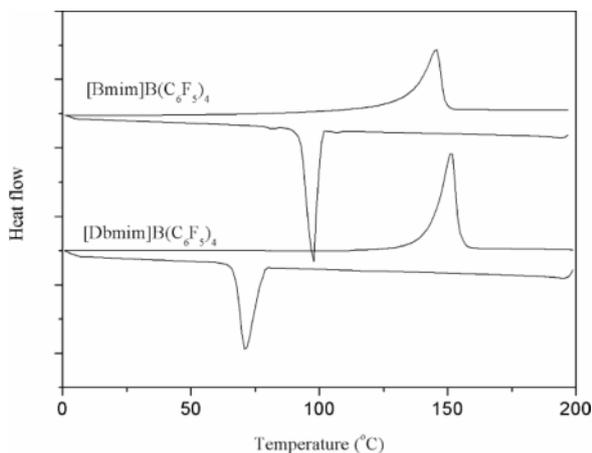


Fig. 4. Characteristic DSC traces for **3** and **4** showing the melting and crystallization points.

analyses were performed with a Flash EA 1112 series elemental analyzer. Thermogravimetric analysis in combination with online fragment detection *via* coupled mass spectroscopy (TGA-MS) was conducted utilizing a Netzsch STA 409 PC system. Typically, about 10 mg of each sample was heated from 30 to 1000 °C at 10 °C min⁻¹. Differential scanning calorimetric analysis (DSC) was performed on a DSCQ2000 from TA instrument (Waters) in the temperature range from 0 to 200 °C at 10 °C min⁻¹. Fast atom bombardment mass spectrometry (FAB-MS) was carried out with a Finnigan MAT 90 mass spectrometer. The compound $[\text{Ag}(\text{NCCH}_3)_4][\text{B}(\text{C}_6\text{F}_5)_4]$ was synthesized according to the literature [21]. All chemicals were purchased from Aldrich, Acros Organics and ABCR and used without further purification.

Synthesis of $[\text{Li}(\text{NCCH}_3)_4][\text{B}(\text{C}_6\text{F}_5)_4]$ (**1**)

A 2.5 M solution of *n*-BuLi in hexane (6.8 mL, 17 mmol) is slowly added to a mixture of $\text{C}_6\text{F}_5\text{I}$ (5.0 g, 17 mmol) in 15 mL diethyl ether *via* syringe at -78 °C. After 1 h of stirring at -78 °C, a 1 M solution of BCl_3 in hexane (4.3 mL, 4.3 mmol) is transferred to the pale-yellow reaction mixture *via* a syringe within 5 min. The resulting suspension (LiCl is precipitating immediately) is allowed to warm to room temperature. After filtration the solution is dried under vacuum to yield a sticky colorless solid that is washed several times with pentane. A concentrated solution in acetonitrile is stored at -25 °C to yield colorless crystals of **1**. The crystalline product is collected and washed with *n*-hexane. Upon drying under vacuum, 1.5 g (41% yield, 1.8 mmol) of a colorless solid **1** is isolated. - ¹H NMR (400 MHz, CD_3CN , 298 K, ppm): $\delta = 1.96$ (s, 12H, 4 CH_3CN). - ¹⁹F NMR (377 MHz, CD_3CN , 298 K, ppm): $\delta = -133.8$ (s, 8F, *o*-F), -164.0 (t, 4F, *p*-F) and -168.4 (m, 8F, *m*-F). - $\text{C}_{32}\text{H}_{12}\text{BF}_{20}\text{LiN}_4$ (850.2): calcd. C 45.21, H 1.42, N 6.59; found C 44.21, H 1.36, N 6.22. - Selected IR bands: $\nu = 2279$ (w, CN), 2306 (w) cm^{-1} .

Method 1 for the synthesis of **3** and **4**

In a Schlenk tube, $[\text{Li}(\text{NCCH}_3)_4][\text{B}(\text{C}_6\text{F}_5)_4]$ (72 mg, 90 μmol) and $[\text{Bmim}]\text{Br}$ (20 mg, 90 μmol) are dissolved in 10 mL CH_2Cl_2 . The mixture is stirred at room temperature for 2 h, and then filtered *via* a cannula. After removal of the solvent under high vacuum, the product is washed with dry *n*-hexane three times and then dried in a high vacuum for 4 h.

Method 2 for the synthesis of **3** and **4**

To a solution of $[\text{Ag}(\text{NCCH}_3)_4][\text{B}(\text{C}_6\text{F}_5)_4]$ (0.738 g, 1 mmol) in CH_2Cl_2 , a solution of imidazolium bromide ($[\text{Bmim}]\text{Br}$: 0.218 g, 1 mmol; $[\text{Dbmim}]\text{Br}$: 0.223 g, 1 mmol) in CH_2Cl_2 is added at room temperature and the mixture

stirred for 10 min under exclusion of light, whereupon a colorless precipitate forms. The solution is filtered *via* a cannula and the solvent removed *in vacuo*. The product is washed with dry *n*-hexane three times and then dried in a high vacuum for 4 h.

Yield of $[\text{Bmim}][\text{B}(\text{C}_6\text{F}_5)_4]$: 0.73 g (89%). - ¹H NMR (400 MHz, $[\text{D}_6]\text{DMSO}$, 296 K, ppm): $\delta = 0.89$ (t, 3H, CH_2CH_3), 1.25 (m, 2H, CH_2), 1.76 (m, 2H, CH_2), 3.85 (s, 3H, NCH_3), 4.16 (t, 2H, NCH_2), 7.71 (m, 1H, NCH), 7.77 (m, 1H, NCH), 9.12 (s, 1H, NCHN). - ¹⁹F NMR (377 MHz, $[\text{D}_6]\text{DMSO}$, 296 K, ppm): $\delta = -131.3$ (s, 8F, *o*-F), -161.7 (t, 4F, *p*-F), -165.6 (m, 8F, *m*-F). - ¹¹B NMR (128 MHz, $[\text{D}_6]\text{DMSO}$, 296 K, ppm): $\delta = -16.7$ (s). - $\text{C}_{32}\text{H}_{14}\text{N}_2\text{BF}_{20}$ (818.3): calcd. C 46.91, H 1.97, N 3.42; found C 46.25, H 2.10, N 3.87. - IR: $\nu = 480$ (w), 573 (w), 660 (m), 683 (m), 739 (m), 772 (m), 974 (vs), 1082 (vs), 1272 (m), 1373 (w), 1486 (vs), 1513 (s), 1642 (m), 1953 (w), 2159 (w), 2545 (vw) cm^{-1} . - FAB-MS: m/z (%) = 138.8, $[\text{Bmim}]^+$, 678.8, $[\text{B}(\text{C}_6\text{F}_5)_4]^-$.

Yield of $[\text{Dbmim}][\text{B}(\text{C}_6\text{F}_5)_4]$: 0.76 g (92%). - ¹H NMR (400 MHz, $[\text{D}_6]\text{DMSO}$, 296 K, ppm): $\delta = 0.89$ (t, 3H, CH_2CH_3), 1.27 (m, 2H, CH_2), 1.68 (m, 2H, CH_2), 2.58 (s, 3H, NCH_3), 3.75 (s, 3H, $\text{NC}(\text{CH}_3)\text{N}$), 4.11 (t, 2H, NCH_2), 7.61 (m, 1H, NCH), 7.64 (m, 1H, NCH). - ¹⁹F NMR (377 MHz, $[\text{D}_6]\text{DMSO}$, 296 K, ppm): $\delta = -132.4$ (s, 8F, *o*-F), -161.5 (t, 4F, *p*-F), -166.0 (m, 8F, *m*-F). - ¹¹B NMR (128 MHz, $[\text{D}_6]\text{DMSO}$, 296 K, ppm): $\delta = -16.8$ (s). - $\text{C}_{33}\text{H}_{17}\text{N}_2\text{BF}_{20}$ (832.3): calcd. C 47.56, H 2.18, N 3.36; found C 46.63, H 2.48, N 3.89. - IR: $\nu = 477$ (vw), 573 (w), 621 (w), 659 (m), 683 (w), 830 (m), 975 (vs), 1081 (s), 1163 (m), 1274 (m), 1374 (w), 1458 (vs), 1512 (s), 1567 (w), 1592 (w), 1642 (m), 1957 (m), 2158 (m), 2547 (w) cm^{-1} . - FAB-MS: m/z (%) = 152.9, $[\text{Dbmim}]^+$, 678.8, $[\text{B}(\text{C}_6\text{F}_5)_4]^-$.

Single-crystal X-ray structure determinations

Intensity data were collected on an X-ray diffractometer equipped with a CCD detector (APEX II, κ -CCD), a rotating anode (Bruker AXS, FR591) or a fine-focus sealed tube with MoK_α radiation ($\lambda = 0.71073$ Å), and a graphite monochromator using the SMART software package [34]. The measurements were performed on single crystals coated with Paratone oil and mounted on glass capillaries. Each crystal was frozen under a stream of nitrogen. A matrix scan using at least 20 centered reflections was used to determine the initial lattice parameters. Reflections were merged and corrected for Lorenz and polarization effects, scan speed, and background using SAINT [35]. Absorption corrections, including odd and even ordered spherical harmonics were performed using SADABS [36]. Space group assignments were based upon systematic absences and successful refinement of the structures. The structures were solved using the Bruker APEX suite of programs [37] and were refined against all data

Table 3. Crystallographic details of **1**, **3** and **4**.

	1	3	4
Formula	C ₃₂ H ₁₂ BF ₂₀ LiN ₄	C ₃₂ H ₁₅ B F ₂₀ N ₂	C ₃₃ H ₁₇ BF ₂₀ N ₂
<i>M_r</i>	850.21	818.27	832.30
Crystal size, mm ³	0.45 × 0.62 × 0.74	0.36 × 0.54 × 0.65	0.18 × 0.22 × 0.72
Crystal system	monoclinic	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> , Å	11.4260(5)	18.5317(5)	32.4863(10)
<i>b</i> , Å	16.3172(7)	11.0850(3)	11.0613(3)
<i>c</i> , Å	19.1740(9)	17.8002(5)	18.7999(6)
β, deg	106.537(2)	104.890(2)	105.476(2)
<i>V</i> , Å ³	3426.9(3)	3533.8(2)	6510.6(3)
<i>Z</i>	4	4	8
<i>D</i> _{calcd.} , g cm ^{−3}	1.65	1.54	1.70
μ(MoK _α), mm ^{−1}	0.2	0.2	0.2
<i>F</i> (000), e	1680	1624	3312
<i>hkl</i> range	±13, ±19, ±23	±22, ±13, ±21	±39, ±13, ±22
((sinθ)/λ) _{max} , Å ^{−1}	0.604	0.603	0.603
Refl. measd / unique / <i>R</i> _{int}	78515 / 6347 / 0.021	70191 / 6486 / 0.022	202926 / 11919 / 0.037
Param. refined	526	500	1015
<i>R</i> (<i>F</i>) / <i>wR</i> (<i>F</i> ²) ^a (all refls.)	0.0312 / 0.0788	0.0356 / 0.0847	0.0468 / 0.1061
GoF (<i>F</i> ²) ^b	0.93	1.04	1.02
Δρ _{fin} (max / min), e Å ^{−3}	0.28 / −0.21	0.31 / −0.19	0.46 / −0.28

^a $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$, where $P = (\text{Max}(F_o^2, 0) + 2F_c^2) / 3$;
^b $\text{GoF} = [\sum w(F_o^2 - F_c^2)^2 / (n_{\text{obs}} - n_{\text{param}})]^{1/2}$.

using SHELXL-97 [38] in conjunction with SHELXLE [39]. Hydrogen atoms were assigned to ideal positions and refined using a riding model with an isotropic displacement parameter 1.2 times that of the attached carbon atom (1.5 times for methyl hydrogen atoms). If not mentioned otherwise, non-hydrogen atoms were refined with anisotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing $\sum w(F_o^2 - F_c^2)^2$ with the SHELXL-97 weighting scheme. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from International Tables for Crystallography [40]. Images of the crystal structures were

generated by PLATON [41]. Further details are summarized in Table 3.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 889186 (**1**), 889187 (**3**) and 889188 (**4**). Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

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