Structure and Properties of Substituted Imidazolium, Triazolium, and Tetrazolium Poly(1,2,4-triazolyl)borate Salts

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Azolium poly(1,2,4-triazolyl)borate salts were prepared by using a simple and highly effective method. The hydrotris(1,2,4-triazolyl)borate organic salts were synthesized in high yields by metathesis reactions of $Ag[HB(tz)_3]$ with substituted imidazolium, triazolium, and tetrazolium iodides. Barium dihydrobis(1,2,4-triazolyl)borate, $Ba[H_2B(tz)_2]$, was used as a precursor to prepare substituted imidazolium and triazolium dihydrobis(1,2,4-triazolyl)borates by reaction with azolium sulfates to form dihydrobis(1,2,4-triazolyl)borate salts. The dihydrobis(1,2,4-triazolyl)borate and hydrotris(1,2,4-triazolyl)borate anions, when paired with different azolium cations, gave rise to salts with interesting crystalline and physicochemical properties. These new borate salts melt at relatively low temperatures to give thermally stable ionic liquids. Some of them exhibit conductivities similar to that of KCl in acetonitrile−water mixtures.

Introduction

Ionic liquids are low-melting salts that are stable, are recyclable, and are readily manipulated. They are being utilized as replacements for organic solvents in chemical processes and reactions, for extracting organic compounds from aqueous waste streams, and as electrolytes for various electrochemical devices.[1,2] It is worthwhile to attempt to develop new ionic liquids which may have these or other advantageous properties.[3] Among the ionic liquids that are currently receiving attention are those which contain borate anions.[4]

A new class of low-melting *N*,*N'*-dialkylimidazolium salts with carborane counterions, $[(C_m\text{mim})(1\text{-R-CB}_{11}H_{11})]$, have been reported. The carborane anion provides the possibility of developing a novel superacid medium that is more strictly nonoxidizing than that previously attainable and where the conjugate base (i.e., the anion) has the lowest nucleophilicity presently available.[5] A novel fluorine-containing room-temperature ionic liquid, 1-butyl-3-methylimidazolium tetrakis[*p*-{dimethyl(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)silyl}phenyl]borate, $[\text{bmim}][B(Ar_f)_4]$, was used as a solvent for the homogeneous hydrosilylation of 1-octene catalyzed by a fluorine-containing version of Wilkinson's catalyst.[6]

Weakly coordinating fluoroanions in borate salts, namely the (perfluoroalkyl)trifluoroborates, combined with a 1-(alkyl or alkyl ether)-3-methylimidazolium cation to yield hydrophobic ionic liquids, $[(C_m\text{mim})(R_FBF_3)]$, have been prepared and characterized. These new salts have low melting points, extremely low glass transition temperatures, and low viscosities.[7] Some of them are shown in Chart 1.

The metal dihydrobis(1,2,4-azolyl) borates, $M[H_2B(az)_2]$, and hydrotris(1,2,4-azolyl)borates, $M[HB(az)_3]$ (az = triazolyl, pyrazolyl, imidazolyl) have been widely studied over a vast range of chemistry.[8−11] A very interesting use of these metal borate salts is in the preparation of boron-based organic cations which is achieved by the alkylation of metal tetrakis(azolyl)borates. These materials have been proposed for use as phase-transfer catalysts.[12] However, dihydrobis(1,2,4-triazolyl)borate or hydrotris(1,2,4-triazolyl)borate salts with heterocyclic cations have not been reported.

We have a continuing interest in ionic liquids for solvent applications as well as energetic nitrogen-rich salts, many of which meet the ionic liquid criteria. A large number of salts that are triazole derivatives have been reported to be energetic materials.[13] Three features of triazole-based borates that make them attractive candidates for further investigation include (a)

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(1) For recent reviews, see, for example: (a) *Ionic Liquids as Green Solvents*; Rogers, R. D., Seddon, K. R., Eds.; ACS Symposium Series No. 856; American Chemical Society: Washington, DC, 2003. (b) *Ionic Liquids in Synthesis*; Wasserscheid, P., Welton, T., Eds.; Wiley-VCH: Weinheim, Germany, 2003; (c) Forsyth, S. A.; Pringle, J. M.; MacFarlane, D. R. *Aust. J. Chem.* **2004**, *57*, 113−119.

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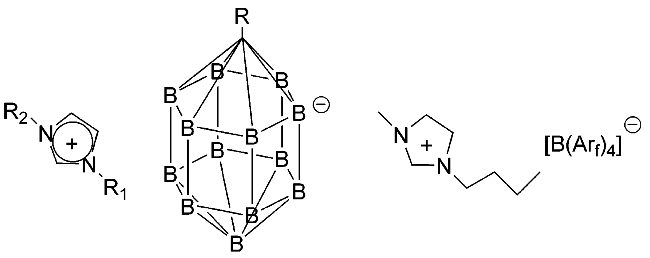
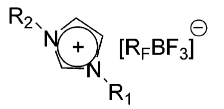
Chart 1. Structures of Some Known Borate Ionic Liquids[a]



a. Inert Carborane anion ionic liquid $[Cmmim][1\text{-}R\text{-}CB_{11}H_{11}]$

b. ionic liquid as solvent $[BMIm][B(Ar_f)_4]$



c. Perfluoroalkyltrifluoroborate ionic liquid $[Cmmim][R_FBF_3]$

[a] Legend: (a) ref 5; (b) ref 6; (c) ref 7.

1,2,4-triazole has a positive heat of formation (109 kJ/mol), which suggests that poly(1,2,4-triazolyl)borates could be energetic materials, (b) greater electron-withdrawing properties relative to those of imidazole- and pyrazole-based borates give characteristics that should differ accordingly, and (c) the dihydrobis(1,2,4-triazolyl)borate, $[H_2B(tz)_2]^-$, and hydrotris(1,2,4-triazolyl)borate, $[HB(tz)_3]^-$, anions are asymmetric bulky organic anions, which may encourage lower melting points. Since many ionic liquids arise because of the asymmetry of their bulky organic cations such as 1,3-dialkylimidazolium, it is useful to study the properties of organic salts based on the asymmetric bulky borate anion. Therefore, in this work, we report the synthesis, characterization, and properties of some new azolium poly(triazolyl)borates.

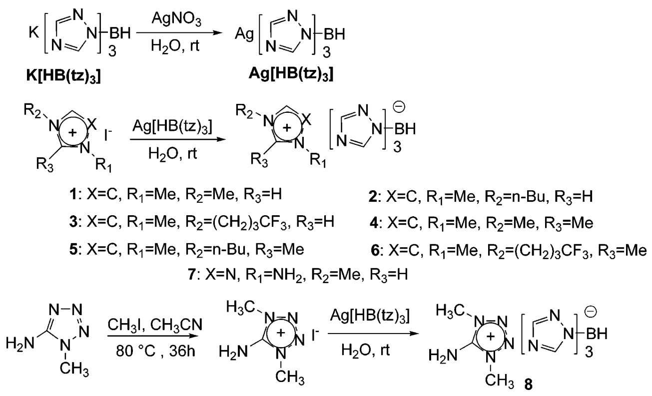
Results and Discussion

The poly(triazolyl)borate organic salts were synthesized as shown in Schemes 1 and 2. For ease of separation of the products, the potassium salts were converted to either the silver or barium derivative. The silver salt of hydrotris(1,2,4-triazolyl)borate, $Ag[HB(tz)_3]$, was prepared as shown,[8a] by combining potassium hydrotris(1,2,4-triazolyl)borate and silver nitrate in water at 25 °C. The hydrotris(1,2,4-triazolyl)borate organic salts (**1**−**7**) were prepared in high yields by metathesis reactions between $Ag[HB(tz)_3]$ and imidazolium or triazolium iodides. Quaternization of 5-amino-1-methyltetrazole with methyl iodide at 80 °C for 36 h in acetonitrile gave 5-amino-1,4-dimethyltetrazolium iodide, which when further reacted with $Ag[HB(tz)_3]$ resulted in **8**.

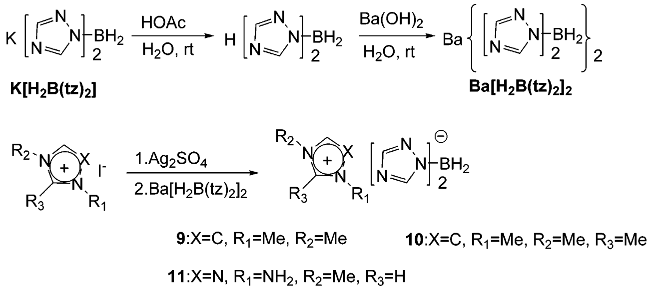
It was not possible to synthesize silver dihydrobis(1,2,4-triazolyl)borate salts by using silver nitrate and potassium dihydrobis(1,2,4-triazolyl)borate, $K[H_2B(tz)_2]$, since the silver ion was reduced to elemental silver.[8b] Therefore, barium dihydrobis(1,2,4-triazolyl)borate, $Ba[H_2B(tz)_2]$, was used as the precursor. Careful acidification of an aqueous solution of $K[H_2B(tz)_2]$ with equimolar amounts of acetic acid yields the corresponding free acid as a water-insoluble solid that was converted to barium dihydrobis(1,2,4-triazolyl)borate, $Ba[H_2B(tz)_2]_2$, by neutralization with barium hydroxide. Combining $Ba[H_2B(tz)_2]_2$ and imidazolium or triazolium sulfate in water at 25 °C gave the dihydrobis(1,2,4-triazolyl)borate salts **9**−**11** (Scheme 2).

Hydrotris(1,2,4-triazolyl) borate, $[HB(tz)_3]^-$, and dihydrobis(1,2,4-triazolyl)borate anions, $[H_2B(tz)_2]^-$, were reacted with different cations to give solids or liquids. The new borate salts were characterized by ^1H, ^{13}C, and ^{11}B NMR spectral and elemental analyses. ^{11}B NMR spectra of **1**−**8** show the ^{11}B doublet peak at −0.38 to −0.49 ppm and coupling between the boron and hydrogen atom. In the boron spectra of **9**−**11** is displayed the clear ^{11}B triplet peak at −6.29 to −6.30 ppm as well as coupling between the boron and the two hydrogen atoms. In general, these newly synthesized borate salts, **1**−**11**, are immiscible with diethyl ether, hexane, and toluene and miscible with methanol, ethanol, acetonitrile, and water.

Scheme 1. Synthesis of Hydrotris(1,2,4-triazolyl)borate Organic Salts



Scheme 2. Synthesis of Dihydrobis(1,2,4-triazolyl)borate Organic Salts



The new borate salts **1**−**11** are the first examples of organic poly(triazolyl)borate salts, some of which are room-temperature ionic liquids. Introduction of a longer chain on the imidazole ring lowers the melting point to <100 °C. For example, changing the cation from 1,3-dimethylimidazolium to 1-butyl-3-methylimidazole or 1-(1,1,1-trifluorobutyl)-3-methylimidazole lowers the melting point of the borate salt. A different cation can change the melting point also: e.g., 4-amino-1-methyl-1,2,4-triazolium and 5-amino-1,3-dimethyltetrazolium cations paired with borate anions give room-temperature ionic liquids. The physicochemical properties of the new borate salts are given in Table 1.

Of particular interest is the density (*d*), as well as the melting point (T_m), decomposition temperature (T_d), and conductivity (*k*), of these salts. The densities of the new borate salts were found to be anion dependent and to increase in direct proportion to the number of 1,2,4-triazolyl substituents on the boron atom. An increase in the length of the alkyl chain on the imidazolium cation also decreases the density of the salts. The melting points of the salts were determined by differential scanning calorimetry (DSC). Three factors found to affect the melting points include (1) the size of the anion, (2) the nature of the cation, and (3) the substituent group on the cation. The melting points of the hydrotris(1,2,4-triazolyl)borate salts are higher than those of dihydrobis(1,2,4-triazolyl)borate salts with the same cation: e.g.,

Table 1. Physicochemical Properties of the Borate Organic Salts

compd	T_g (°C)[a]	T_d (°C)[b]	density[c]	κ (μS cm^{-1})[d]	state[e]
[mmim][HB(tz)$_3$][f] (**1**)	115.4	217.0	1.36	8.03	solid
[*n*-bmim][HB(tz)$_3$] (**2**)	−45.2	202.0	1.27	7.61	liquid
[*n*-CF$_3$bmim][HB(tz)$_3$] (**3**)	−33.1	229.8	1.38	6.84	liquid
[mmmim][HB(tz)$_3$] (**4**)	130.1	253.6	1.39	6.46	solid
[*n*-bmmim][HB(tz)$_3$] (**5**)	−40.9	253.1	1.27	7.46	liquid
[*n*-CF$_3$bmmim][HB(tz)$_3$] (**6**)	55.7	256.9	1.42	7.29	solid
[NH$_2$mtz][HB(tz)$_3$] (**7**)	−18.6	158.5	1.39	7.09	liquid
[NH$_2$mmttz][HB(tz)$_3$] (**8**)	11.8	81.7	1.24	7.23	liquid
[mmim][H$_2$B(tz)$_2$] (**9**)	120.7	214.8	1.29	8.51	solid
[mmmim][H$_2$B(tz)$_2$] (**10**)	116.6	218.1	1.30	8.20	solid
[NH$_2$mtz][H$_2$B(tz)$_2$] (**11**)	−35.3	107.4	1.23	7.49	liquid

[a] Glass transition temperature (DSC). [b] Decomposition temperature (TGA). [c] In units of g cm^{-3} at 25 °C. [d] Conductivity at 25 °C; the conductivity for a KCl solution (0.5 mM) is 8.63 μS cm^{-1} [e] At 25 °C. [f] Legend: im, imidazole; tz, triazole; ttz, tetrazole; m, methyl; *n*-b, *n*-butyl; *n*-CF$_3$b, *n*-(trifluoromethyl)butyl.

4 melts at 130 °C, which is higher than the melting point for compound **10** ($T_g = 116$ °C). The bulkier substituent on the imidazolium cation decreases the melting point. Changing from 1,3-dimethylimidazolium to 1-butyl-3-methylimidazolium to 1-(1,1,1-trifluorobutyl)-3-methylimidazolium causes a decrease in the melting point. When **2** ($T_g = -45.2$ °C) is compared with **1** ($T_g = 115.4$ °C), the melting point is seen to increase by nearly 160 °C, changing from a liquid to solid. The fluorinated butyl chain on the imidazolium ring gives a high transition point, $T_g = 56$ °C, for **6**. The thermal stabilities, which range from 80 to 250 °C depending on the cation, were determined by TGA. The tetrazolium-ring-containing salt **8** has the lowest decomposition temperature at 81.7 °C, and salts with the 4-amino-1,2,4-triazolium cation also exhibit low decomposition temperatures at 107.4 °C (**11**) and 158.5 °C (**7**). In general, dihydrobis(1,2,4-triazolyl)borate salts are thermally less stable: e.g., compare the analogous hydrotris(1,2,4-triazolyl)borate salts **1** and **9** with $T_d = 217.0$ and 214.8 °C, respectively, and **4** and **10** with $T_d = 253.56$ and Td 218.8 °C, respectively, where the differences likely arise from the greater innate thermal stability of the hydrotris(1,2,4-triazolyl)borate anion relative to that of the dihydrobis(1,2,4-triazolyl)borate anion.

Borate anions have good chemical and electrochemical stabilities that can be applied, for example, in lithium ion batteries as nonaqueous electrolytes.[14] The conductivities of these new borate salts were determined in 0.5 mM acetonitrile solutions. When they were compared with KCl solutions of the same concentration (0.5 mM in mixed solvent (95:5 acetonitrile−water), the salts exhibited similar conductivities. Compounds **9** and **10** have the highest conductivities at 8.51 and 8.19 μS cm^{-1}, respectively (8.63 μS cm^{-1} for KCl). In general, salts with the [H$_2$B(tz)$_2$] anion are more highly conducting than those with the [HB(tz)$_3$] anion when they share a common cation. This is not surprising, since smaller, more agile anions would be expected to contribute more favorably to a higher conductivity. This same effect is observed when the number of substituents on the cation is reduced (reducing the cation size): e.g., compare 1,3-dimethylimidazolium and 1,2,3-trimethylimidazolium cations paired with the same borate anion, **9** (8.51 μS cm^{-1}) and **10** (8.20 μS cm^{-1}), and **1** (8.03 μS cm^{-1}) and **4** (6.46 μS cm^{-1}).

The structure of compound **4** is shown in Figure 1a. Suitable colorless platelike crystals were obtained by slow concentration of an ethanol/diethyl ether solution of **4**. The borate anion is tetrahedral (N−B−N angles ca. 109−110° and H−B−N ca. 106−111°), and the triazoles all have the same handed twist. Although there have been very few unchelated tris(imidazole)borate structures reported in the literature, this feature is also seen in sodium hydrogentris(3-methyl-2-thioimidazolinyl)borate hydrate,[15] sodium hydrogentris(3-ethylimidazolium-1-yl)borate−bis(tetrafluoroborate),[16] and hexaaquacalcium bis(hydrogen tris(3-methyl-2-thioimidazolyl)borate) tetrahydrate.[17] These compounds all have B−N distances similar to those of **4** (ca. 1.55 Å). The structure of **9** is shown in Figure 2 from crystals obtained in the same manner as **4**. The coordination environment and bond distances in **9** are very similar to those of the tris(triazolyl)borate **4** and other bis(triazolyl)borates in the literature.[9,10,18] Weak hydrogen bonding is extensive in the extended structure of both **4** (C···N ca. 3.0−3.4 Å) and **9** (C···N ca. 3.2−3.4 Å) and is illustrated in Figures 1b and 2b. An extended 3D network is formed in **4** between the planar cation and the borate,

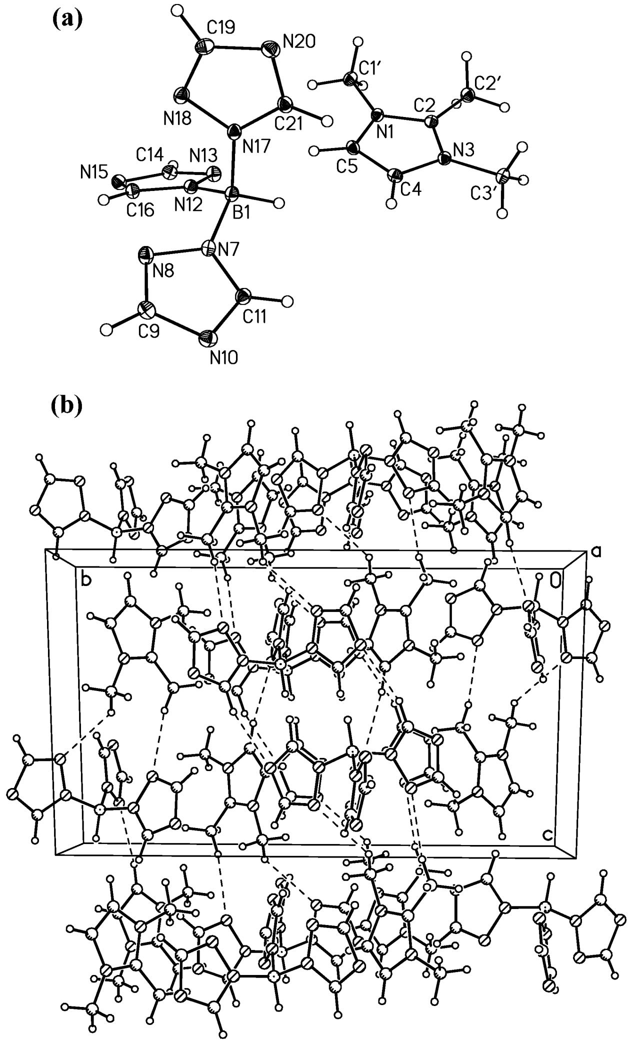


Figure 1. (a) Thermal ellipsoid plot (30%) of **4**. Hydrogen atoms are included but are unlabeled for clarity. (b) Packing diagram of **4** viewed down the *a* axis. Dashed lines indicate hydrogen bonding.

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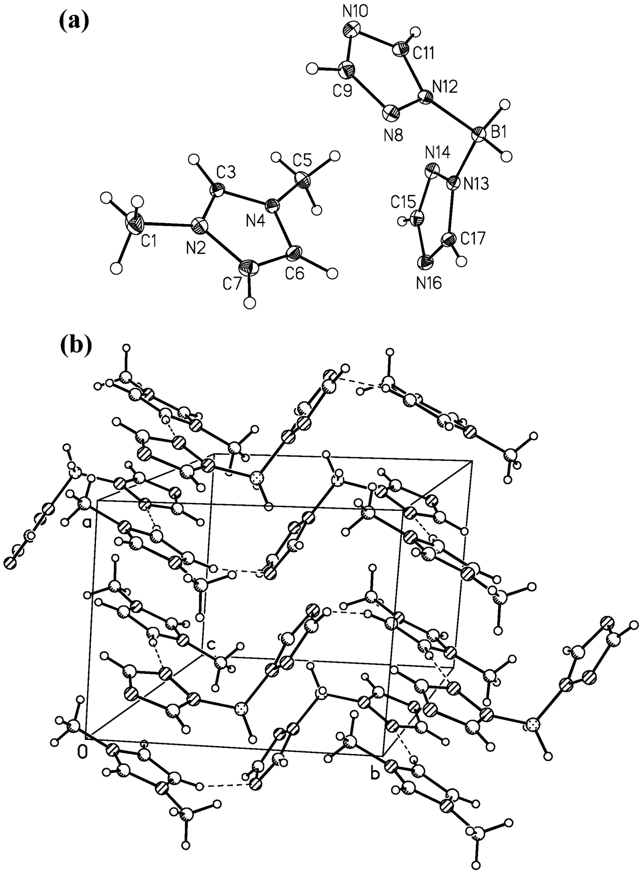

Figure 2. (a) Thermal ellipsoid plot (30%) of **9**. Hydrogen atoms are included but are unlabeled for clarity. (b) Packing diagram of **9** viewed down the *c* axis. Dashed lines indicate hydrogen bonding.

while in **9** a stepped sheet is seen. Crystallographic data and structure refinement parameters of compounds **4** and **9** are given in the Supporting Information.

Conclusion

A new and highly effective method was developed for the preparation of dihydrobis(1,2,4-triazolyl)borate and hydrotris(1,2,4-triazolyl)borate organic salts where the dihydrobis(1,2,4-triazolyl)borate and hydrotris(1,2,4-triazolyl)borate anions are paired with substituted azolium cations to give interesting crystalline and physicochemical properties. These new borate salts melt at relatively low temperatures, giving rise to several thermally stable ionic liquids. Some of them exhibit conductivities similar to those of equimolar KCl solutions in acetonitrile/water.

Experimental Section

General Considerations. All the reagents used were analytical reagents purchased from commercial sources and used as received. The following materials were prepared and purified according to the reported procedures: potassium hydrotris(1,2,4-triazolyl)borate[19] and dihydrobis(1,2,4-triazolyl)borate,[19] 1,3-dimethylimidazolium iodide,[20] 1,2,3-trimethylimidazolium iodide,[20] 1-methyl-*n*-butylimidazolium iodide,[21] 1,2-dimethyl-*n*-butylimidazolium iodide,[21] 1-methyl-3-(4,4,4-trifluorobutyl)imidazolium iodide,[22] 1,2-dimethyl-3-(4,4,4-trifluorobutyl)imidazolium iodide,[22] 1-amino-3-methyltriazolium iodide,[23] and 5-amino-1-methyltetrazole.[24] ^{1}H, ^{19}F, and ^{13}C NMR spectra were recorded on a 300 MHz nuclear magnetic resonance spectrometer operating at 300.13, 282, and 75.48 MHz, respectively. ^{11}B NMR spectra were recorded on a 500 MHz nuclear magnetic resonance spectrometer operating at 160.18 MHz. Chemical shifts were reported relative to Me$_4$Si for ^{1}H, and ^{13}C, CCl$_3$F for ^{19}F, and BF$_3$·Et$_2$O for ^{11}B. The solvent was d_6-DMSO unless otherwise specified. The melting and decomposition points were recorded on a differential scanning calorimeter and a thermogravimetric analyzer, respectively, at a scan rate of 10 °C/min. Conductivities were determined on a Model 1056 EC METER instrument. IR spectra were recorded using NaCl plates for neat liquids and KBr pellets for solids. Elemental analyses were performed on an EXETER CE-440 elemental analyzer. Nitrogen analyses tend to be lower than calculated values, due to the formation of refractory boron nitrides.[25,26] Densities of solid salts were measured at room temperature using a Micromeritics Accupyc 1330 gas pycnometer.

X-ray Crystallography. Crystals of compounds **4** (**9**) were removed from the flask, a suitable crystal was selected and attached to a glass fiber, and data were collected at 90(2) K using a Bruker/Siemens SMART APEX instrument (Mo Kα radiation, $\lambda = 0.71073$ Å) equipped with a Cryocool NeverIce low-temperature device. Data were measured using ω scans of 0.3° (ω and ψ scans of 0.5°) per frame for 10 s for both **4** and **9**, and a full sphere of data was collected. A total of 2400 (2565) frames was collected with a final resolution of 0.83 Å. Cell parameters were retrieved using SMART[27] (APEX2[28]) software and refined using SAINTPlus[29] on all observed reflections. Data reduction and correction for Lp and decay were carried out using the SAINTPlus software. Absorption corrections were applied using SADABS.[30] The structure was solved by direct methods and refined by least-squares methods on F^2 using the SHELXTL program package.[31] The structure was solved in space group space group $P2_1/c$ (No. 14) ($P\bar{1}$ (No. 2)) by analysis of the systematic absences. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms bonded to B1 for **9** were located and independently refined. No decomposition was observed during data collection. Details of the data collection and refinement as well as further characterization data are provided in the Supporting Information.

Synthesis of 5-Amino-1,4-dimethyltetrazolium Iodide. 5-Amino-1-methyltetrazole (0.198 g, 2.0 mmol), methyl iodide (5 mmol), and 30 mL of acetonitrile were sealed in a Pyrex glass tube in vacuo by cooling to liquid-nitrogen temperature and then heated at 80 °C for 24 h. After it was cooled to 25 °C, the tube was opened and methyl iodide (3 mmol) was added. The reaction was continued at 80 °C for 12 h. The colorless solid obtained was removed by filtration and washed with diethyl ether to give 5-amino-1,4-dimethyltetrazolium iodide in 90% yield.

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General Procedure for the Preparation of Hydrotris(1,2,4-triazolyl)borate Organic Salts 1−8. After potassium hydrotris(1,2,4-triazolyl)borate (K[HB(tz)$_3$];[19] 0.510 g, 2.0 mmol) was placed in 20 mL of water at 25 °C and stirred for 5 min, an aqueous solution (10 mL) of $AgNO_3$ (0.340 g, 2.0 mmol) was added. The solution was stirred for 0.5 h. The colorless precipitate, silver hydrotris(1,2,4-triazolyl)borate (Ag[HB(tz)$_3$]), was filtered off and washed with distilled water three times (3 × 20 mL).[8a] Twenty milliliters of distilled water was added, and the mixture was stirred for 5 min at 25 °C. Then a solution (15 mL) of imidazolium iodide (2.0 mmol) was added. After the addition, the solution was stirred for 0.5 h and silver iodide was removed by filtration. The filtrate was concentrated in vacuo to give the crude products **1**−**8** in high yields. Recrystallization from ethanol−diethyl ether (1:10) gave the pure compounds in high yields.

Synthesis of Barium Dihydrobis(1,2,4-triazolyl)borate, Ba{[H$_2$B(tz)$_2$]$_2$}. The synthesis used is a slight modification of the literature procedure.[8b] To a solution of 1.0 g (0.0053 mol) of potassium dihydrobis(1,2,4-triazolyl)borate in 5 mL of water was added 0.33 g (0.0055 mol) of glacial acetic acid. The solid was filtered, washed with water (3 × 5 mL), and then stirred with barium hydroxide (0.026 mol) with 20 mL of distilled water for 1 h. The solution was filtered, and the filtrate was concentrated in vacuo to give a white solid, which was recrystallized from ethanol−dichloromethane (1:5) and dried at 100 °C to give barium dihydrobis(1,2,4-triazolyl)borate in 65% yield.

General Procedure for the Preparation of Dihydrobis(1,2,4-triazolyl)borate Organic Salts 9−11. Imidazolium iodide (2 mmol) was dissolved in water, and an aqueous solution of Ag_2SO_4 (1 mmol) was added. After 30 min, the precipitate was filtered, the solid was washed with water, and barium dihydrobis(1,2,4-triazolyl)borate (Ba{[H$_2$B(tz)$_2$]$_2$}; 1 mmol) was added. The solution was further stirred for 30 min, and the precipitate was removed ($BaSO_4$). The water was removed at reduced pressure, and the residue was recrystallized from ethanol−diethyl ether (1:10) to obtain the compounds **9**−**11** in high yields.

1,3-Dimethylimidazolium Hydrotris(1,2,4-triazolyl)borate (1; [mmim][HB(tz)$_3$]). Yield: 90%, colorless solid. ^{1}H NMR (δ (ppm)): 8.98 (s, 1H), 8.08 (s, 1H), 7.80 (s, 3H), 7.64 (d, J = 0.9 Hz, 2H), 3.82 (s, 6H). ^{13}C NMR (δ (ppm)): 152.96, 148.56, 138.37, 124.78, 36.99. ^{11}B NMR (δ (ppm)): −0.40 (d, J_{BH} = 110.5 Hz). IR (KBr, cm^{-1}): 3426 (b), 3116 (s), 2472 (s), 2293 (s), 1575 (s), 1087 (s), 879 (s), 623 (s). Anal. Calcd for $C_{11}H_{16}BN_{11}$ (253.17): C, 42.19; H, 5.15; N, 49.20. Found: C, 41.82; H, 4.89; N, 47.23.

1-Methyl-3-*n*-butylimidazolium Hydrotris(1,2,4-triazolyl)borate (2; [*n*-bmim][HB(tz)$_3$]). Yield: 85%, colorless liquid. ^{1}H NMR (δ (ppm)): 9.11 (s, 1H), 8.15 (s, 1H), 7.86 (s, 3H), 7.75 (s, 1H), 7.68 (s, 1H), 4.15 (t, J = 7.1 Hz, 2H), 3.84 (s, 3H), 1.78−1.71 (m, 2H), 1.29−1.21 (m, 2H), 0.89 (t, J = 7.3 Hz, 3H). ^{13}C NMR (δ (ppm)): 151.56, 147.17, 136.36, 123.49, 122.14, 48.42, 35.62, 31.19, 18.64, 13.09. ^{11}B NMR (δ (ppm)): −0.43 (d, J_{BH} = 84.9 Hz). IR (KBr, cm^{-1}): 3427 (b), 3016 (s), 2471 (s), 1592 (s), 1506 (s), 1320 (s), 881 (s), 654 (s). Anal. Calcd for $C_{14}H_{22}BN_{11}\cdot 0.4H_2O$ (362.42): C, 46.35; H, 6.29; N, 42.49. Found: C, 45.97; H, 6.13; N, 41.61.

1-Methyl-3-(4,4,4-trifluorobutyl)imidazolium Hydrotris(1,2,4-triazolyl)borate (3; [*n*-CF$_3$bmim][HB(tz)$_3$]). Yield: 83%, colorless liquid. ^{1}H NMR (δ (ppm)): 9.08 (s, 1H), 8.10 (s, 3H), 7.82 (s, 3H), 7.75 (t, J = 1.2 Hz, 1H), 7.67 (t, J = 0.9 Hz, 1H), 4.23 (t, J = 7.2 Hz, 2H), 3.83 (s, 3H), 2.34−2.26 (m, 2H), 2.07−2.01 (m, 2H). ^{13}C NMR (δ (ppm)): 151.54, 147.16, 136.68, 123.64, 122.03, 47.37, 40.25, 35.66, 29.61, 29.24, 22.23, 22.19. ^{11}B NMR (δ (ppm)): −0.41 (d, J_{BH} = 110.7 Hz). ^{19}F NMR (δ (ppm)): −64.67 (s, 3F). IR (KBr, cm^{-1}): 3407 (b), 3116 (s), 2460 (s), 1651 (s), 1571 (s), 1145 (s), 732 (s), 682 (s). Anal. Calcd for $C_{14}H_{19}BN_{11}F_3$ (409.19): C, 41.11; H, 4.88; N, 35.66. Found: C, 39.47; H, 4.70; N, 36.61.

1,2,3-Trimethylimidazolium Hydrotris(1,2,4-triazolyl)borate (4; [mmmim][HB(tz)$_3$]). Yield: 92%, colorless solid. ^{1}H NMR (δ (ppm)): 8.09 (s, 3H), 7.81 (s, 3H), 7.54 (s, 2H), 3.73 (s, 6H), 2.53 (s, 3H). ^{13}C NMR (δ (ppm)): 152.96, 148.57, 146.03, 123.26, 35.99, 10.41. ^{11}B NMR (δ (ppm)): −0.40 (d, J_{BH} = 112.1 Hz). IR (KBr, cm^{-1}): 3427 (b), 3109 (s), 2471 (s), 1506 (s), 1407 (s), 1088 (s), 881 (s), 654 (s). Anal. Calcd for $C_{12}H_{18}BN_{11.}H_2O$ (345.19): C, 41.76; H, 5.84; N, 44.64. Found: C, 41.96; H, 5.50; N, 42.82.

1,2-Dimethyl-3-*n*-butylimidazolium Hydrotris(1,2,4-triazolyl)borate (5; [*n*-bmmim][HB(tz)$_3$]). Yield: 82%, colorless liquid. ^{1}H NMR (δ (ppm)): 9.11 (s, 1H), 8.15 (s, 1H), 7.86 (s, 3H), 7.75 (s, 1H), 7.68 (s, 1H), 4.15 (t, J = 7.1 Hz, 2H), 3.84 (s, 3H), 1.78−1.71 (m, 2H), 1.29−1.21 (m, 2H), 0.89 (t, J = 7.3 Hz, 3H). ^{13}C NMR (δ (ppm)): 151.56, 147.17, 136.36, 123.49, 122.14, 48.42, 35.62, 31.19, 18.64, 13.09. ^{11}B NMR (δ (ppm)): −0.43 (d, J_{BH} = 84.9 Hz). IR (KBr, cm^{-1}): 3427 (b), 3016 (s), 2471 (s), 1592 (s), 1506 (s), 1320 (s), 881 (s), 654 (s). Anal. Calcd for $C_{14}H_{22}BN_{11.}0.4H_2O$ (374.42): C, 46.35; H, 6.29; N, 42.49. Found: C, 45.97; H, 6.13; N, 41.61.

1,2-Dimethyl-3-(4,4,4-trifluorobutyl)imidazolium Hydrotris(1,2,4-triazolyl)borate (6; [*n*-CF$_3$bmmim][HB(tz)$_3$]). Yield: 85%, colorless solid. ^{1}H NMR (δ (ppm)): 8.11 (s, 1H), 7.83 (s, 3H), 7.64 (d, J = 2.1 Hz, 1H), 7.60 (d, J = 2.1 Hz, 1H), 4.17 (t, J = 7.2 Hz, 2H), 3.56 (s, 3H), 2.56 (s, 3H), 2.38−2.32 (m, 2H), 1.98−1.93 (m, 2H). ^{13}C NMR (δ (ppm)): 151.49, 147.15, 144.49, 128.95, 125.29, 120.58, 45.93, 34.55, 29.97, 21.98, 9.02. ^{11}B NMR (δ (ppm)): −0.49 (d, J_{BH} = 101.1 Hz). ^{19}F NMR (δ (ppm)): −64.69 (s, 3F). IR (KBr, cm^{-1}): 3397 (b), 3113 (s), 2449 (s), 1590 (s), 1504 (s), 1146 (s), 873 (s), 735 (s). Anal. Calcd for $C_{15}H_{21}BN_{11}F_3$ (423.21): C, 42.51; H, 5.04; N, 36.41. Found: C, 41.84; H, 5.04; N, 35.71.

1-Amino-3-methyltriazolium Hydrotris(1,2,4-triazolyl)borate (7; [NH$_2$mtz][HB(tz)$_3$]). Yield: 90%, colorless liquid. ^{1}H NMR (δ (ppm)): 10.06 (s, 1H), 9.14 (s, 1H), 8.10 (s, 3H), 7.82 (s, 3H), 6.96 (s, 2H), 4.01 (s, 3H). ^{13}C NMR (δ (ppm)): 151.43, 147.01, 144.78, 142.73, 38.74. ^{11}B NMR (δ (ppm)): −0.38 (d, J_{BH} = 112.1 Hz). IR (KBr, cm^{-1}): 3426 (b), 3116 (s), 2472 (s), 2293 (s), 1575 (s), 1087 (s), 879 (s), 623 (s). Anal. Calcd for $C_9H_{14}BN_{13}\cdot 1.5H_2O$ (342.12): C, 31.58; H, 5.02; N, 53.23. Found: C, 31.45; H, 4.54; N, 53.04.

5-Amino-1,4-dimethyltetrazolium Hydrotris(1,2,4-triazolyl)borate (8; [NH$_2$mmttz][HB(tz)$_3$]). Yield: 82%, colorless liquid. ^{1}H NMR (δ (ppm)): 9.18 (br, 2H), 8.13 (s, 3H), 7.84 (s, 3H), 3.86 (s, 6H). ^{13}C NMR (δ (ppm)): 151.41, 148.42, 147.09, 33.89. ^{11}B NMR (δ (ppm)): −0.39 (d, J_{BH} = 108.3 Hz). IR (KBr, cm^{-1}): 3456 (b), 2473 (s), 2056 (s), 1699 (s), 1505 (s), 1147 (s), 969 (s), 878 (s). Anal. Calcd for $C_9H_{15}BN_{14}$ (330.17): C, 32.74; H, 4.58; N, 59.40. Found: C, 32.62; H, 4.51; N, 53.60.

1,3-Dimethylimidazolium Dihydrobis(1,2,4-triazolyl)borate (9; [mmim][H$_2$B(tz)$_2$]). Yield: 86%, colorless solid. ^{1}H NMR (δ (ppm)): 8.99 (s, 1H), 7.93 (s, 1H), 7.63 (d, J = 1.2 Hz, 4H), 3.83 (s, 6H). ^{13}C NMR (δ (ppm)): 150.78, 147.16, 136.89, 123.27, 35.48. ^{11}B NMR (δ (ppm)): −6.29 (t, J_{BH} = 99.3 Hz). IR (KBr, cm^{-1}): 3100 (b), 2389 (s), 1593 (s), 1154 (s), 1238 (s), 959 (s), 1012 (s), 680 (s). Anal. Calcd for $C_9H_{15}BN_8$ (246.15): C, 43.93; H, 6.14; N, 45.54. Found: C, 43.63; H, 5.96; N, 44.18.

1,2,3-Dimethylimidazolium Dihydrobis(1,2,4-triazolyl)borate (10; [mmim][H$_2$B(tz)$_2$]). Yield: 83%, colorless solid. ^{1}H NMR (δ (ppm)): 7.95 (s, 2H), 7.65 (s, 2H), 7.57 (S, 2H), 3.75 (s, 6H), 2.51 (s, 3H). ^{13}C NMR (δ (ppm)): 150.89, 147.27, 121.83, 34.56, 8.98. ^{11}B NMR (δ (ppm)): −6.29 (t, J_{BH} = 98.4 Hz). IR (KBr, cm^{-1}): 3149 (b), 2417 (s), 2273 (s), 1726 (s), 1497 (s), 1012 (s), 757 (s), 636 (s). Anal. Calcd for $C_{10}H_{17}BN_8$ (260.17): C, 46.18; H, 6.60; N, 43.08. Found: C, 45.33; H, 6.48; N, 41.56.

1-Amino-3-methyltriazolium Dihydrobis(1,2,4-triazolyl)borate (11; [NH$_2$mtz][H$_2$B(tz)$_2$]). Yield: 82%, colorless liquid. ^{1}H NMR (δ (ppm)): 10.06 (s, 1H), 9.12 (s, 1H), 7.94 (S, 2H), 7.64

(s, 2H), 6.97 (s, 2H), 4.02 (s, 2H). ^{13}C NMR (δ (ppm)): 150.79, 147.18, 144.77, 142.73, 64.67, 38.73, 14.94. ^{11}B NMR (δ (ppm)): −6.30 (t, J_{BH} = 98.7 Hz). IR (KBr, cm^{-1}): 3290 (b), 3130 (s), 2414 (s), 2280 (s), 1624 (s), 1504 (s), 875 (s), 680 (s). Anal. Calcd for $C_7H_{13}BN_{10}\cdot H_2O$ (266.15): C, 31.60; H, 5.68; N, 52.64. Found: C, 31.78; H, 5.20; N, 53.27.

5-Amino-1-methyltetrazole.[21] Yield: 35%, colorless solid. Mp: 223−225 °C. ^{1}H NMR (δ (ppm)): 6.06 (s, 2H), 3.70 (s, 3H).

5-Amino-1,4-dimethyltetrazolium Iodide ([NH$_2$mttz]I). Yield: 85%, colorless solid. ^{1}H NMR (δ (ppm)): 9.07 (s, 2H), 3.88 (s, 6H). ^{13}C NMR (δ (ppm)): 148.42, 34.12. Anal. Calcd for $C_3H_8N_5I$ (273.23): C, 14.95; H, 3.35; N, 29.06. Found: C, 15.09; H, 3.23; N, 29.51.

Barium Dihydrobis(1,2,4-triazolyl)borate (Ba[H$_2$B(tz)$_2$]$_2$). Yield: 80%, colorless solid. ^{1}H NMR (δ (ppm)): 8.30 (s, 2H), 7.97 (s, 2H). ^{13}C NMR (δ (ppm)): 152.77, 149.58. ^{11}B NMR (δ (ppm)): −6.71 (t, J_{BH} = 108.6 Hz). Anal. Calcd for $C_8H_{12}B_2N_{12}Ba\cdot 3H_2O$ (490.08): C, 19.58; H, 3.62; N, 34.28. Found: C, 19.71; H, 3.35; N, 32.74.

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Supporting Information Available: Figures, tables, and CIF files giving boron NMR spectra, various atomic parameters, and crystallographic data for **4** and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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