Formation of Isomeric BAr$_3$ Adducts of 2-Lithio-*N*-methylimidazole

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Dedicated to Professor Hans J. Schäfer on the occasion of his 65th birthday

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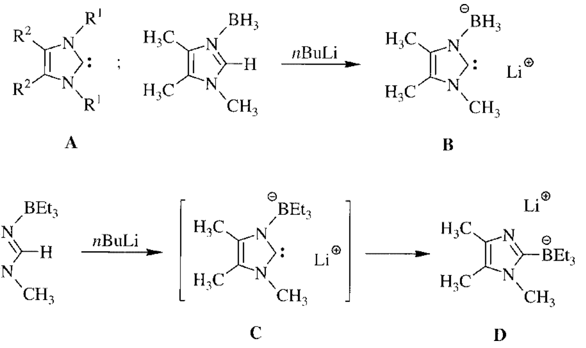
N-Methylimidazole added to the strong organometallic Lewis acid B(C$_6$F$_5$)$_3$ at the donor nitrogen atom to form the adduct **3** (characterized by X-ray diffraction). Deprotonation at the imidazole carbon atom C-2 was achieved by treatment with methyllithium to generate the reactive "Arduengo carbene anion" intermediate **4**, which underwent a rapid subsequent intramolecular nucleophilic aromatic substitution reaction at one of the adjacent C$_6$F$_5$ groups to form the tricyclic betaine-type product **5**. Rearrangement of **4** by 1,2-boron migration was not observed. The respective isomer **7** was prepared independently by deprotonation of *N*-methylimidazole, followed by C-2 addition of B(C$_6$F$_5$)$_3$. The corresponding *N*-methylimidazolide-2–B(C$_6$H$_5$)$_3$ adduct **8** was characterized by X-ray diffraction and shown to have a cyclodimeric structure made up of intermolecular bis(π-arene)(imidazole)lithium units. A DFT study revealed that the *N*-borated Arduengo carbene anions are in general very effectively kinetically protected from undergoing intramolecular rearrangement to their thermodynamically favored 2-boratoimidazole anion isomers by 1,2-BR$_3$ migration.

Introduction

The chemistry of the stable nucleophilic carbenes of the imidazol-2-ylidene type (**A**) has been developed considerably in recent years,[1−7] their use as stabilizing ligands in catalysis included.[8−11] Many other heteroatom combinations have successfully been employed for such carbene stabilization,[7d,12−14] but surprisingly little is known about the use of heteroatom-containing substituents at the nitrogen donor substituents themselves.[15−17] This would, however, be very interesting, since suitably constructed heteroatom moieties at one or both nitrogen atoms of the "Arduengo carbenes" would be expected to change the properties of such systems considerably, and would potentially open up routes to new applications of such compounds.

Siebert has recently described such a system:[17] CH deprotonation of the *N*-methylimidazole−BH$_3$ adduct resulted in the formation of **B** (isolated as a dimer), which may be regarded as an anionic analogue of the neutral imidazol-2-ylidine carbene species **A**. Compound **B** displayed interesting chemistry, largely determined by its nucleophilic character. Surprisingly, the analogous BEt$_3$ adduct **C** was reported by Siebert et al. to be unstable under the reaction conditions and to rearrange spontaneously to **D**.



We have now developed synthetic routes to systems of types **B** and **D** by the use of triarylborane reagents and have characterized some novel chemical and structural features of such anions.

Results and Discussion

Experimental Studies

For this study, the examples of the two imidazolylborate anion types were prepared by two separate routes, since it turned out that they did not spontaneously interconvert un-

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[‡] X-ray crystal structure analyses

[‡‡] Quantum chemical calculations

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der our chosen reaction conditions. The systems described here were all derived from the parent heterocycle, the *N*-methylimidazole precursor **1**.

In the first series of experiments, the neutral starting material **1** was treated with 1 mol-equiv. of the strong organometallic Lewis acid tris(pentafluorophenyl)borane (**2a**).[18−20] The addition reaction was carried out at ambient temperature in pentane (12 h), and furnished the 1:1 addition product **3** as a white solid in > 90% yield. The ^{1}H NMR spectrum of **3** showed a singlet at $\delta = 7.82$ ppm (1 H, 2-H), and the corresponding ^{13}C NMR C-2 resonance was observed at $\delta = 137.7$ ppm. At ambient temperature, the "tetraarylborate" system equilibrates conformationally on the ^{19}F NMR timescale (563 MHz), and so only three ^{19}F NMR resonances were observed (at $\delta = -133.1$, -158.6, and -164.6 ppm), in 2:1:2 ratio. The ^{11}B NMR signal at $\delta = -8.0$ ppm indicated borate formation.

Compound **3** was characterized by X-ray diffraction. The crystal was twinned, but the structure could be solved with a sufficient accuracy. The analysis established that the bulky $B(C_6F_5)_3$ moiety was coordinated to the imidazole N1 nitrogen donor. The resulting N1−B bond length amounts to 1.605(6) Å [1.597(6) Å, the values in brackets correspond to the second independent molecule in the crystal, which is chemically equivalent]. The π-system inside the imidazole ring of the neutral adduct **3** is largely delocalized, as is evident from the respective bond lengths inside the five-membered heterocycle. The N1−C2 bond is the shortest, at 1.317(6) Å [1.303(6) Å], followed by the adjacent C2−N3 linkage at 1.336(6) Å [1.333(6) Å]. The N1−C5 [1.380(6) Å [1.389(6) Å]) and the N3−C4 bonds [1.380(6) Å [1.376(7) Å]) are almost identical in length. The C4−C5 bond is shorter [1.342(7) Å [1.350(8) Å]), whereas the exocyclic N3−C6 bond is much longer, at 1.469(6) Å [1.458(7) Å].

The conformational arrangement of **3** in the crystal is such that two of the C_6F_5 rings at the boron atom, together with the imidazole ring, form a three-bladed propeller arrangement[21] {with the dihedral angle N1−B−C11−C12 being −57.5(6)° [128.4(5)°] and N1−B−C21−C22 amounting to −65.0(5)° [106.5(5)°]}. The remaining C_6F_5 ring serves as the pivot. Its plane is rotated towards a perpendicular orientation relative to the *N*-methylimidazole ring {dihedral angles N1−B−C31−C32 179.2(4)° [+3.5(7)°], C2−N1−B−C31 −120.3(5)° [−118.3(5)°], Figure 1).

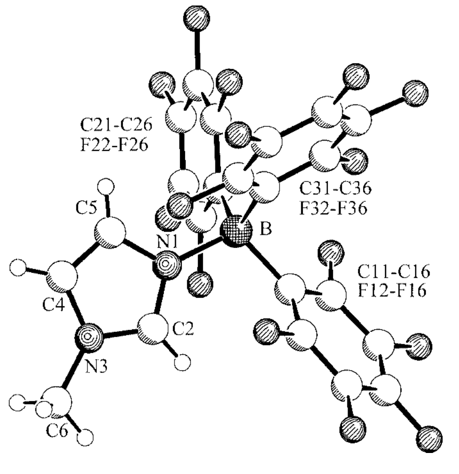
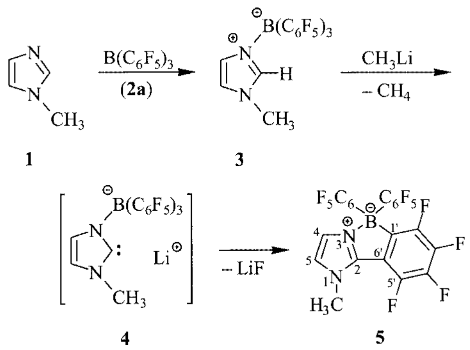


Figure 1. Projection of the molecular structure of **3**, showing the propeller-like arrangement of two C_6F_5 rings and the imidazole ring at the B−C31 pivot (only one of the two independent molecules is depicted); selected bond lengths [Å] and angles [°]: N1−C2 1.317(6)/1.303(6), N1−C5 1.380(6)/1.389(6), N1−B 1.605(6)/1.597(6), C2−N3 1.336(6)/1.333(6), N3−C4 1.380(6)/1.376(7), N3−C6 1.469(6)/1.458(7), C4−C5 1.342(7)/1.350(8), B−C11 1.640(7)/1.643(7), B−C21 1.654(7)/1.643(7), B−C31 1.632(7)/1.640(7); C2−N1−C5 106.8(4)/106.6(4), C2−N1−B 127.7(4)/129.0(4), C5−N1−B 125.5(4)/124.3(4), N1−C2−N3 110.3(4)/111.3(4), C2−N3−C4 107.7(4)/107.2(4), C2−N3−C6 125.6(4)/126.5(5), C4−N3−C6 126.7(4)/126.3(5), N3−C4−C5 106.4(4)/106.7(5), C4−C5−N1 108.8(4)/108.1(5), N1−B1−C11 108.5(4)/108.9(4), N1−B1−C21 101.8(4)/103.1(4), N1−B1−C31 112.6(4)/112.5(4), C11−B−C21 115.0(4)/116.5(4), C11−B−C31 105.2(4)/104.0(4), C21−B−C31 113.8(4)/112.0(4)

Treatment of **3** with methyllithium resulted in methane liberation, with formation of the product **5** (see Scheme 1). The ^{1}H NMR spectrum of **5** showed that the 2-H proton had been removed as expected, but the probably initially generated "anionic Arduengo carbene" product **4** proved unstable under the reaction conditions. It underwent a rapid intramolecular nucleophilic aromatic substitution with formation of a C−C bond to one of the three adjacent C_6F_5 rings at the boron atom.[22] The ^{13}C NMR resonance of the C-2 carbon atom was consequently observed at $\delta = 147.3$ ppm (shifted ca. 50 ppm to high field from a typical value for a boron-substituted carbene **B**[23]). The remaining $^{1}H/^{13}C$ NMR resonances of the imidazole nucleus appeared at $\delta = 6.99/122.2$ (4-H/C-4) and $\delta = 6.29/126.7$ (5-H/C-5). The $N-CH_3$ ^{1}H NMR resonance was observed as a doublet at $\delta = 3.08$ ppm. Detailed NMR analysis, including selective $^{1}H/^{19}F$ decoupling, revealed that this was due to $^{1}H/^{19}F$ long-range coupling between the $N-CH_3$ protons and the 5′-F atom at the annelated C_6F_4 ring ($^{6}J_{H,F} = 4.0$ Hz).[24−26] The corresponding N-CH_3/5′-F coupling was determined at $^{5}J_{C,F} = 16.7$ Hz.[27−30]



Scheme 1

The ^{11}B NMR resonance of product **5** occurred at $\delta = -7.6$ ppm. The product exhibited the signals of a pair of symmetrically equivalent C_6F_5 substituents at the boron atom [^{19}F NMR: $\delta = -133.7$, -157.1, -163.1 (*o*-, *p*-, *m*-F) ppm; ^{13}C NMR: $\delta = 148.4$, 140.3, 137.6 (C-*o*, -*p*, -*m*)] and, in addition, a typical set of four C−F signals corresponding to the annelated C_6F_4 moiety [$^{19}F/^{13}C$ NMR: δ = −131.0/148.2 (2′-F/C-2′), −151.1/140.5 (3′-F/C-3′), −156.2/142.1 (4′-F/C-4′), −135.7/141.5 (5′-F/C-5′)]. Figure 2 shows the typical appearance of the ^{19}F NMR spectrum of the product **5**.

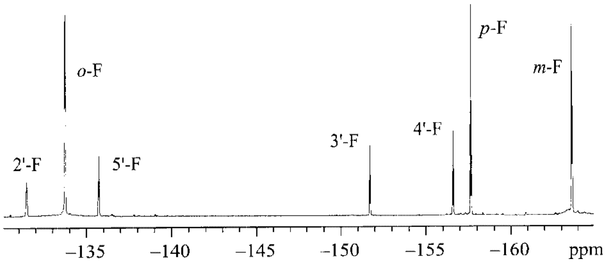
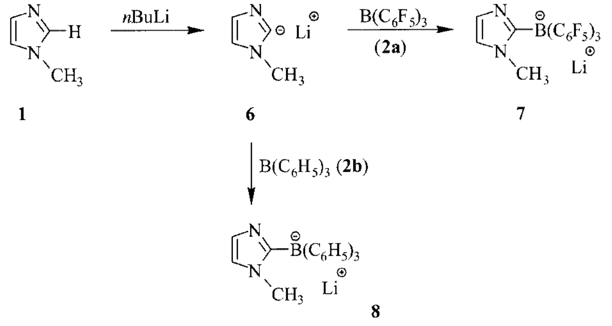


Figure 2. ^{19}F NMR spectrum of the cyclic betaine product **5** (in [D_6]benzene/[D_8]THF, 10:1, 563.6 MHz, at ambient temperature)

This experiment showed that, in this system, the *C*-borato anion **D**-type products could not be obtained by rearrangement of their Arduengo carbene anion isomers **C**. The respective system **4** was probably generated from **3** on treatment with the base methyllithium, but was shown to be unstable not with regard to rearrangement, but with regard to the much more favored intramolecular S_{NAr} reaction resulting in the observed final product **5**. In this system we therefore had to prepare the *C*-borato **D**-type isomer of the Arduengo carbene anion by a different route.

N-Methylimidazole was deprotonated at C-2 by prolonged treatment (3 d) with *n*-butyllithium at ambient temperature, as described in the literature,[31−38] to yield 2-lithio-1-methylimidazolide (**6**). This was then treated with 1 mol-equiv. of $B(C_6F_5)_3$ to yield the corresponding borate anion product **7** cleanly (see Scheme 2).



Scheme 2

Comparison of characteristic NMR spectroscopic data between compounds **6** and **7** showed that the electrophilic borane had selectively added at carbon atom C-2 of the imidazolide ring system. Most characteristically, the ^{13}C NMR resonance of the carbon atom C-2 had shifted from a very lowfield value of δ = 201.7 ppm in **6** by ca. +40 ppm to δ = 162.2 ppm in **7**. The 4-H and 5-H ^{1}H NMR resonances were also found at smaller values in **7** (δ = 6.61, 6.58 ppm) relative to the starting material **6** (δ = 7.23, 6.89 ppm). In addition, the ^{11}B NMR resonance of **7** was found at δ = −16.6 ppm, in the range typical for a *C*-bonded borate[39−40] [the *N*-bonded tris(pentafluorophenyl)borate systems typically show ^{11}B NMR resonances between δ = −7 and −9 ppm].

We also treated **6** with $B(C_6H_5)_3$ and obtained the salt **8** [^{13}C NMR: δ = 174.0 (C-2); ^{1}H NMR: δ = 6.69, 6.66 (4-H, 5-H); ^{11}B NMR: δ = −9.4]. Product **8** was characterized by X-ray crystal structure analysis. This shows the $B(C_6H_5)_3$ group attached at the imidazolide *carbon* atom C2. The C2−B bond length is found at a typical value of 1.634(2) Å. The imidazole π-system in compound **8** is delocalized, similar values as in **3** (see above) being observed: the C4−C5 bond is the shortest in the five-membered ring, at 1.334(2) Å, followed by C2−N3 [1.344(2) Å] and C2−N1 [1.367(2) Å]. The N1−C5 [1.373(2) Å] and N3−C4 bonds [1.374(2) Å] are almost equal in length. The N1−C6 linkage is much longer, at 1.453(2) Å.

The extraordinary structural feature of compound **8** is the coordinative attachment of the lithium cation to the complex anion moiety. It is bonded to N3 [Li−N3 distance: 1.922(3) Å]. One of the phenyl groups at the boron atom is rotated conformationally in such a way [θ(C2−B−C21−C22) = 86.9(2)°] that its π-face is located within bonding distance above Li. An unsymmetrical intramolecular π-arene−lithium interaction results from this orientation, with Li−C(phenyl) distances of 2.467(4) (C26), 2.641(4) (C21), 2.982(4) (C25), 3.192(4) (C22), 3.526(4) (C24), and 3.600(4) Å (C23). The coordination sphere of the lithium cation is completed by a similarly significant intermolecular π-arene−Li interaction with the C11* to C16* phenyl−B ring of an adjacent molecule of **8**. The observed *intermolecular* Li−C(phenyl)* distances are similar [2.393(4) (C15*), 2.515(4) (C16*), 2.629(4) (C14*), 2.895(4)

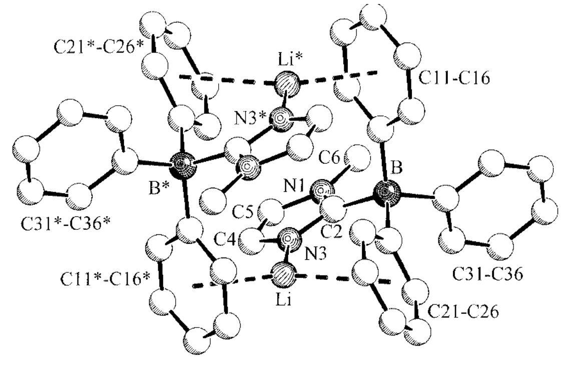
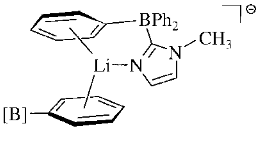
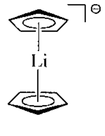


Figure 3. View of the dimeric lithiocene-type structure of **8** in the crystal; selected bond lengths [Å] and angles [°]: Li−N3 1.922(3), N1−C2 1.367(2) N1−C5 1.373(2), N1−C6 1.453(2), C2−N3 1.344(2), N3−C4 1.374(2), C4−C5 1.334(2), B−C2 1.634(2), B−C11 1.640(2), B−C21 1.650(2), B−C31 1.635(2); C2−N1−C5 108.9(1), C2−N1−C6 128.1(1), C5−N1−C6 123.0(1), N1−C2−N3 107.8(1), C2−N3−C4 107.0(1), C2−N3−Li 124.7(1), C4−N3−Li 128.3(1), N3−C4−C5 110.3(1), N1−C4−C5 106.0(1), N1−C2−B 128.1(1), N3−C2−B 124.1(1), C2−B−C11 109.3(1), C2−B−C21 106.6(1), C2−B−C31 110.8(1), C11−B−C21 111.4(1), C11−B−C31 109.9(1), C21−B−C31 108.8(1)

(C11*), 2.958(4) (C13*), and 3.066(4) Å (C12*)] to the *intramolecular* π-arene−lithium bond lengths observed in **8** (Figure 3).[41−43] The lithium−arene interaction is probably largely electrostatic in nature, as is usually observed in organolithium chemistry,[44−48] and the anionic nature of the hetaryltris(aryl)borate unit therefore facilitates the formation of this cyclodimeric structure of **8** in the solid state. Compound **8** thus represents a (dimeric) example of a distorted anionic donor ligand stabilized bis(π-arene)Li−L$^-$ lithiocene-type structure, the π-arene-derived bent lithiocene relative of the often observed Cp-derived lithiocene anions[49−51] **9**. The arene(centroid)−Li−arene(centroid) angle in **8** is 133.1°.



8



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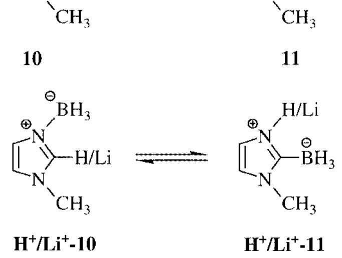
Theoretical Studies

Our experimental investigation had shown that the Arduengo carbene anion **4** generated in situ underwent a favored intramolecular aromatic nucleophilic substitution reaction to yield **5** rather than rearrange to the isomeric anion **7**. We were able to show by independent synthesis that **7** was stable and isolable under the applied reaction conditions. The observed resistance of **4** to rearrangement prompted us to investigate the isomerization hypersurface by theoretical methods with regard to the relative energies of the isomeric anions involved, as well as the energy profiles of their putative thermally induced interconversions with suitable model systems.

For quantum chemical investigation of the equilibrium between *N*-borane-substituted and *C*-borane-substituted imidazol-2-ylidene anions we chose the B3LYP density functional.[52−53] The structures were fully optimized without symmetry restrictions by use of the Turbomole program.[54] A triple zeta Gaussian AO basis set with additional polarization functions (TZVP)[55] was used in the optimization of the geometries and energy calculations. The calculated reaction energies for the rearrangement shown in Scheme 3 are given in Table 1.



Scheme 3

Table 1. Reaction energies for the rearrangement of the borane (B3LYP/TZVP)

Starting compound	$\Delta_R E$ [kcal mol^{-1}]
10a (R = H)	−17.4
10b (R = CH_3)	−12.8
10c [R = (C_6H_5)]	−13.7
10d [R = (C_6F_5)]	−15.8
Li$^+$-10a	−16.9
H$^+$-10a	+5.0

Inspection of Table 1 clearly shows that the borate substituent thermodynamically prefers to be bound to C-2 of the anionic heterocyclic moiety. If the N−C fragment is regarded as an imidazolide, the Lewis acidic borane compensates the negative charge much more efficiently when bound to the carbon atom than when bound to the nitrogen atom. The different borane substituents have only a small influence on the reaction energy.

For the lithiated compound (**Li$^+$-10a**, Li at C-2), which may be viewed as a better model for the experimentally investigated situation, no significant change in the reaction energy is observed, although carbon atom C-2 is now no longer divalent. The metal atom does not change the unfavorable situation of two eclipsed vicinal sp^2 lone pairs at the carbenic center and the nitrogen atom, respectively. Only when the corresponding imidazole−borane complex (**H$^+$-10a**) is considered do we find a reversal of the equilibrium. Now the stronger boron−nitrogen interaction determines the preference for the isomer **H$^+$-10a** over the rearranged **H$^+$-11a**.

We have also localized a transition state for the intramolecular rearrangement of **10a** to **11a**.[56] The rearrangement of the borane does not proceed through the ring plane but is tilted, with a dihedral angle of 117.6° to the ring atoms (Figure 4). This is an indication of the symmetry-forbidden character of the reaction, which is also reflected in the high barrier of 40.5 kcal mol^{-1} on going from **10a** to **11a**.[57]

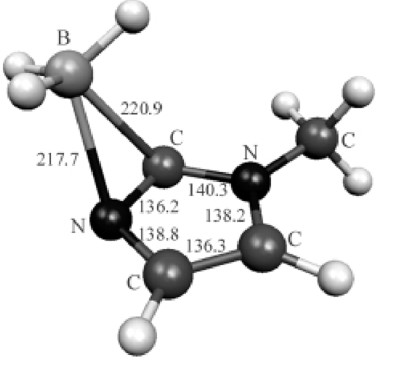


Figure 4. Transition structure of the reaction **10a** → **11a** (B3LYP/TZVP); bond lengths in pm

The nature of the transition structure was confirmed by a frequency calculation, which yielded one imaginary frequency (−119 cm^{-1}). Semiempirical (AM1) calculation of the intrinsic reaction coordinate showed that this structure indeed linked **10a** and **11a**. By restricting the molecular symmetry to C_s, we obtained a second transition structure, with the borane in the plane, but with a much higher energy relative to **10a** (57.9 kcal mol^{-1}).

Attempts to locate a transition state for the shift of a $B(CH_3)_3$ group failed to give a similar stationary point, but ended with a loose complex of the borane with the anion (B−N 3.5 Å; B−C 3.6 Å), with a relative energy of 31.2 kcal mol^{-1} compared with **10b**. It is very likely that the $B(aryl)_3$ compounds, for which we did not try to calculate a barrier, behave in the same manner.

Our theoretical study revealed that the *C*-borated anions of type **D** (e.g. **7**) were thermodynamically favored over their "Arduengo carbene anion" isomers **B**, **C**, and, for example, **4**, but that their interconversion was practically precluded by a very high barrier of the respective 1,2-BR_3 shift. From our theoretical study it must be assumed that any such rearrangement, when experimentally observed,[17] is likely to have proceeded intermolecularly.[7d,60] Thus, we must conclude that the *N*-borato Arduengo carbene anions should exhibit their characteristic chemistry − as observed for **4** in the Experimental Study − when prepared or generated under conditions precluding *intermolecular* rearrangement pathways to their thermodynamically favored *C*-2-borated imidazole anion isomers. We expect that these findings should stimulate the use of such anionic Arduengo carbenes, especially as ligands in transition metal chemistry and catalysis, beyond the chemistry already reported for the special example of the BH_3-derived system **B**.[61]

Experimental Section

General: Reactions with organometallic compounds were carried out under argon in Schlenk-type glassware or in a glovebox. Solvents, including deuterated solvents used for NMR spectroscopy, were dried and distilled under argon prior to use. The following instruments were used for physical characterization of the compounds: Bruker AC 200 P NMR spectrometer (^{11}B: 64 MHz) at 300 K and Varian Unity plus (^{1}H: 600 MHz. ^{13}C: 150 MHz. ^{19}F: 564 MHz) NMR spectrometer at 298 K, a Nicolet 5 DXC FT-IR spectrometer, and a Micromass Quattro LC-Z mass spectrometer for HRMS determination. Elemental analyses were carried out with a Foss-Heraeus CHN-rapid elemental analyzer or a Vario El III micro elemental analyzer; melting points were determined by differential scanning calorimetry (2010 DSC, Du Pont/STA Instruments). Tris(pentafluorophenyl)borane (**2a**) was prepared according to a literature procedure.[18−20] 1-Methylimidazole (**1**) and triphenylborane (**2b**) were commercially available and were used without further purification. 1-Methylimidazole was stored over molecular sieves.

1-Methylimidazole−Tris(pentafluorophenyl)borane (3): Tris(pentafluorophenyl)borane (**2a**, 1.02 g, 2.00 mmol) was added to a suspension of 1-methylimidazole (**1**, 164 mg, 2.00 mmol) in 20 mL of pentane at 0 °C. The reaction mixture was allowed to warm to room temperature and was stirred for another 12 h. The precipitated product was collected by filtration to yield 1.08 g (91%) of **3** as a white solid, m.p. 249 °C. IR (KBr): $\tilde{\nu}$ = 3001, 1649, 1566, 1530, 1380, 1281, 1259, 1100, 991, 865, 751 cm^{-1}. ^{1}H NMR (600 MHz, [D$_6$]benzene): δ = 7.82 (s, 1 H, 2-H), 7.06 (s, 1 H, 4-H), 7.01 (d, $^{3}J_{H,H}$ = 1.2 Hz, 1 H, 5-H), 3.81 (s, 3 H, N−CH_3) ppm. ^{13}C NMR (150 MHz, [D$_6$]benzene): δ = 148.3 (dm, $^{1}J_{C,F}$ = 242 Hz, *o*-Ph), 140.2 (dm, $^{1}J_{C,F}$ = 247 Hz, *p*-Ph), 137.7 (CH, C-2), 137.4 (dm, $^{1}J_{C,F}$ = 246 Hz, *m*-Ph), 127.1 (CH, C-4), 121.9 (CH, C-5), 36.1 (CH_3, N−CH_3) ppm; *ipso*-carbon signal not detected. ^{19}F NMR (564 MHz, [D$_6$]benzene): δ = −133.1 (m, 6 F, *o*-Ph), −158.6 (m, 3 F, *p*-Ph), −164.6 (m, 6 F, *m*-Ph) ppm. ^{11}B NMR (64 MHz, [D$_6$]benzene): δ = −8.0 ($\nu_{1/2}$ = 140 Hz) ppm. $C_{22}H_6BF_{15}N_2$ (594): calcd. C 44.48, H 1.02, N 4.72; found C 43.98, H 1.08, N 5.27.

X-ray Crystal Structure Analysis of 3: Empirical formula $C_{22}H_6BF_{15}N_2$, M = 594.10, colorless crystal 0.25 × 0.20 × 0.10 mm, a = 11.222(2), b = 12.315(2), c = 16.463(3) Å, α = 88.32(1), β = 72.69(2), γ = 86.91(1)°, V = 2168.8(7) Å^3, $\rho_{calcd.}$ = 1.820 g cm^{-3}, μ = 18.15 cm^{-1}, empirical absorption correction from ψ scan data (0.660 ≤ T ≤ 0.839), Z = 4, triclinic, space group $P\bar{1}$ (no. 2), λ = 1.54178 Å, T = 223 K, ω scans, 9282 reflections collected ($-h$, $\pm k$, $\pm l$), [(sin θ)/λ] = 0.62 Å^{-1}, 8808 independent (R_{int} = 0.037) and 5107 observed reflections [$I \geq 2\,\sigma(I)$], 723 refined parameters, R = 0.082, wR^2 = 0.246, max. residual electron density 0.68 (−0.49) e Å^{-3}, crystals were always twinned (thin plates with a small tilt), by use of ω scans to collect the integrated intensities of all individuals, hydrogen atoms calculated and refined as riding atoms.

Treatment of Compound 3 with Methyllithium, Formation of the Heterocycle 5: Benzene/tetrahydrofuran (10:1, 2 mL) was added to a mixture of 1-methylimidazole−tris(pentafluorophenyl)borane (**3**, 100 mg, 168 μmol) and methyllithium (3.70 mg, 168 μmol). The resultant reaction mixture was stirred for 12 h, the solvent was removed in vacuo, and benzene was added. The LiF precipitate was removed by filtration, and evaporation of the solvent in vacuo yielded **5** as a light brown solid, yield: 83 mg (92%), m.p. 76 °C. IR (KBr): $\tilde{\nu}$ = 2966, 1647, 1616, 1519, 1486, 1467, 1382, 1287, 1266, 1098, 1058, 975, 835, 778 cm^{-1}. ^{1}H NMR (600 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran 10:1): δ = 6.99 (d, $^{3}J_{H,H}$ = 1.8 Hz, 1 H, 4-H), 6.29 (d, $^{3}J_{H,H}$ = 1.8 Hz, 1 H, 5-H), 3.08 (d, $J_{H,F}$ = 4.0 Hz, 3 H, N−CH_3) ppm. ^{13}C NMR (150 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, 10:1): δ = 148.4 (dm, $^{1}J_{C,F}$ = 241 Hz, *o*-Ph), 148.2 (dm, $^{1}J_{C,F}$ = 245 Hz, C-2′), 147.3 (C, C-2), 142.1 (dm, $^{1}J_{C,F}$ = 257 Hz, C-4′), 141.5 (dm, $^{1}J_{C,F}$ = 255 Hz, C-5′), 140.5 (dm, $^{1}J_{C,F}$ = 251 Hz, C-3′), 140.3 (dm, $^{1}J_{C,F}$ = 251 Hz, *p*-Ph), 137.6 (dm, $^{1}J_{C,F}$ = 250 Hz, *m*-Ph), 126.7 (CH, C-5), 122.2 (CH, C-4), 116.7 (C, *ipso*-C), 35.6 (CH_3, $J_{C,F}$ = 16.7 Hz, N−CH_3) ppm; signals of C-1′ and C-6′ not detected. ^{19}F NMR (564 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, 10:1): δ = −131.0 (m, 1 F, 2′-F), −133.7 (m, 4 F, *o*-Ph), −135.7 (m, 1 F, 5′-F), −151.1 (m, 1 F, 3′-F), −156.2 (m, 1 F, 4′-F), −157.1 (m, 2 F, *m*-Ph), −163.2 (m, 4 F, *m*-Ph) ppm. ^{11}B NMR (64 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, 10:1): δ = −7.6 ($\nu_{1/2}$ = 130 Hz) ppm. $C_{22}H_5F_{14}N_{22}$ (574): calcd. C 46.03, H 0.88, N 4.88; found C 45.59, H 1.54, N 4.58.

2-Lithio-1-methylimidazole (6):[13] A solution of 1-methylimidazole (1.18 g, 14.1 mmol) in 20 mL of toluene was cooled to −78 °C and treated with an equivalent amount of *n*-butyllithium in hexane (9.00 mL, 14.4 mmol). After the mixture had stirred for 2 d at room temperature, the solvent was removed in vacuo. Pentane was added, the solid was separated by filtration, and the product was dried in vacuo to yield 1.24 g (99%) of **6**. ^{1}H NMR (600 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, 10:1): δ = 7.23 (s, 1 H, 4-H), 6.89 (s, 1 H, 5-H), 3.64 (CH_3, N−CH_3) ppm. ^{13}C NMR (150 MHz, [D$_6$]benzene/[D$_8$]tetrahydrofuran, 10:1): δ = 201.7 (C, C-2), 128.4 (CH, C-4), 117.8 (CH, C-5); 35.7 (CH_3, N−CH_3).

Lithium (1-Methylimidazol-2-yl)tris(pentafluorophenyl)borate (7): Tris(pentafluorophenyl)borane (**2a**, 512 mg, 1.00 mmol) was added to a suspension of 2-lithio-1-methylimidazole (**6**, 88.0 mg, 1.00 mmol) in 20 mL of pentane at room temperature. The reaction mixture was stirred for 24 h. The precipitated product was collected by filtration to yield **7** as a gray solid (380 mg, 63%), m.p. 255 °C. IR (KBr): $\tilde{\nu}$ = 1646, 1523, 1465, 1366, 1282, 1091, 981, 796, 740, 695 cm^{-1}. ^1H NMR (600 MHz, $[D_6]$benzene/$[D_8]$tetrahydrofuran, 10:1): δ = 6.61 (d, $^3J_{H,H}$ = 1.2 Hz, 1 H, 4-H), 6.58 (d, $^3J_{H,H}$ = 1.2 Hz, 1 H, 5-H), 3.17 (s, 3 H, N−CH_3) ppm. ^1H NMR (150 MHz, $[D_6]$benzene/$[D_8]$tetrahydrofuran, 10:1): δ = 162.2 (C, C-2), 148.7 (dm, $^1J_{C,F}$ = 241 Hz, *o*-Ph), 140.3 (dm, $^1J_{C,F}$ = 249 Hz, *p*-Ph), 137.3 (dm, $^1J_{C,F}$ = 250 Hz, *m*-Ph), 125.9 (CH, C-4), 121.2 (CH, C-5), 33.7 (CH_3, N−CH_3) ppm, *ipso*-carbon signal not detected. ^{19}F NMR (564 MHz, $[D_6]$benzene/$[D_8]$tetrahydrofuran, 10:1): δ = −124.6 (m, 1 F, *o*-Ph), −132.7 (m, 1 F, *o*-Ph), −133.0 (br, 3 F, *o*-Ph), −132.6 (m, 1 F, *o*-Ph), −161.6 (br, 2 F, *p*-Ph), −162.8 (m, 1 F, *p*-Ph), −165.6 (m, 1 F, *m*-Ph), −166.0 (br, 5 F, *m*-Ph) ppm. ^{11}B NMR (64 MHz, $[D_6]$benzene/$[D_8]$tetrahydrofuran, 10:1): δ = −16.6 ($\nu_{1/2}$ = 50 Hz) ppm. HRMS: calculated for $[C_{22}H_5N_2BF_{15}]^-$ 593.0310; found 593.0384.

Lithium (1-Methylimidazol-2-yl)triphenylborate (8): As described above, 2-lithio-1-methylimidazole (**6**, 264 mg, 3.00 mmol) in 20 mL of toluene was treated with triphenylborane (**2b**, 762 mg, 3.00 mmol) to yield **8** (619 mg, 62%) as a white solid, m.p. 283 °C. IR (KBr): $\tilde{\nu}$ = 3055, 1580, 1481, 1426, 1385, 1278, 1122, 1154, 1032, 943, 854, 758, 710 cm^{-1}. ^1H NMR (600 MHz, $[D_6]$benzene/$[D_8]$tetrahydrofuran, 10:1): δ = 7.55 (m, 6 H, *o*-Ph), 7.18 (m, 6 H, *m*-Ph), 7.04 (m, 3 H, *p*-Ph), 6.69 (d, $^3J_{H,H}$ = 1.2 Hz, 1 H, 5-H), 6.66 (d, $^3J_{H,H}$ = 1.2 Hz, 1 H, 4-H), 3.06 (s, 6 H, N−CH_3) ppm. ^{13}C NMR (150 MHz, $[D_6]$benzene/$[D_8]$tetrahydrofuran, 10:1): δ = 174.0 (q, $^1J_{CB}$ = 50 Hz, C-2), 160.3 (q, $^1J_{CB}$ = 57 Hz, *ipso*-C), 135.6 (CH, *o*-Ph), 127.1 (CH, *m*-Ph), 124.6 (CH, C-4), 123.5 (CH, *p*-Ph), 120.5 (CH, C-5), 35.4 (CH_3, N−CH_3) ppm. ^{11}B NMR (64 MHz, $[D_6]$benzene): δ = −9.4 ($\nu_{1/2}$ = 44 Hz) ppm. HRMS: calculated for $[C_{22}H_{20}N_2B]^-$ 323.1724; found 323.1781.

X-ray Crystal Structure Analysis of 8: Empirical formula $C_{22}H_{20}BLiN_2$, M = 330.15, light yellow crystal 0.45 × 0.30 × 0.30 mm, a = 10.701(1), b = 14.818(1), c = 11.104(1) Å, β = 91.65(1)°, V = 1760.0(3) $Å^3$, $\rho_{calcd.}$ = 1.246 g cm^{-3}, μ = 0.71 cm^{-1}, empirical absorption correction by SORTAV ($0.969 \le T \le 0.979$), Z = 4, monoclinic, space group $P2_1/n$ (no. 14), λ = 0.71073 Å, T = 198 K, ω and ψ scans, 14410 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda]$ = 0.66 $Å^{-1}$, 4269 independent (R_{int} = 0.050) and 2820 observed reflections [$I \ge 2\,\sigma(I)$], 236 refined parameters, R = 0.050, wR^2 = 0.102, max. residual electron density 0.25 (−0.17) e $Å^{-3}$, hydrogen atoms calculated and refined as riding atoms.

Data sets were collected with Enraf−Nonius CAD4 and Nonius KappaCCD diffractometers, the latter equipped with a rotating anode generator (Nonius FR591). Programs used: data collection EXPRESS (Nonius B.V., 1994) and COLLECT (Nonius B.V., 1998), data reduction MolEN (K. Fair, Enraf-Nonius B.V., 1990) and Denzo-SMN (Z. Otwinowski, W. Minor, *Methods Enzymol.*, **1997**, *276*, 307−326), absorption correction for CCD data SORTAV (R. H. Blessing, *Acta Crystallogr.* **1995**, *A51*, 33−37; R. H. Blessing, *J. Appl. Crystallogr.* **1997**, *30*, 421−426), structure solution SHELXS-97 (G. M. Sheldrick, *Acta Crystallogr.* **1990**, *A46*, 467−473), structure refinement SHELXL-97 (G. M. Sheldrick, Universität Göttingen, 1997), graphics SCHAKAL (E. Keller, Universität Freiburg, 1997). CCDC-173951 (**3**) and -173952 (**8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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