Nucleophilic Aromatic Substitution with 2,3-Dihydro-1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene

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Dedicated to Professor Ekkehard Lindner on the occasion of his 75th birthday

2,3-Dihydro-1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (**1**) reacts with an excess of hexafluorobenzene in the presence of boron trifluoride diethyletherate to give 1,3-diisopropyl-4,5-dimethyl-2-(perfluorophenyl)imidazolium tetrafluoroborate (**2**). Solutions of **2** exhibit an equilibrium consisting also of hexafluorobenzene and 2,2′-(perfluoro-1,4-phenylene)bis(1,3-diisopropyl-4,5-dimethylimidazolium)bis(tetrafluoroborate) (**3**) which is obtained from **1** and hexafluorobenzene in the ratio 2 : 1 on a preparative scale. Similar to **2**, 2-(4-cyano-2,3,5,6-tetrafluorophenyl)-1,3-diisopropyl-4,5-dimethylimidazolium tetrafluoroborate (**4**), 2-(2,4-dicyano-2,5,6-trifluorophenyl)-1,3-diisopropyl-4,5-dimethylimidazolium tetrafluoroborate (**5**), and 2-(4,6-difluoro-1,3,5-triazin-2-yl)-1,3-diisopropyl-4,5-dimethylimidazolium tetrafluoroborate (**6**) are obtained from **1** and perfluorobenzonitrile, 1,3-dicyano-2,4,5,6-tetrafluorobenzene, and 2,4,6-trifluoro-1,3,5-triazin, respectively. The FAB mass spectra of compounds **2** – **6** and the results of the crystal structure analyses of compounds **2** – **4** are discussed.

Key words: Carbenes, Heterocycles, Fluorine, Nucleophilic Aromatic Substitutions, Mass Spectrometry, Crystal Structure

Introduction

Starting with the pioneering work of Meisenheimer [1], the addition-elimination mechanism of the nucleophilic aromatic substitution has found continuous interest [2]. More recently, this type of reaction has been extended to perfluorinated arenes predominantly by reactions with anionic nucleophiles [3, 4]. Much less is known on the substitution of fluoride by neutral nucleophiles such as amines [5] and *in situ* prepared nucleophilic carbenes [6].

Stable heterocyclic carbenes have been in the center of interest as strong nucleophiles [7] beginning with their synthesis about 20 years ago [8, 9]. To the best of our knowledge, their reaction with pentafluoropyridine [10] is a single example of nucleophilic aromatic substitution with these carbenes.

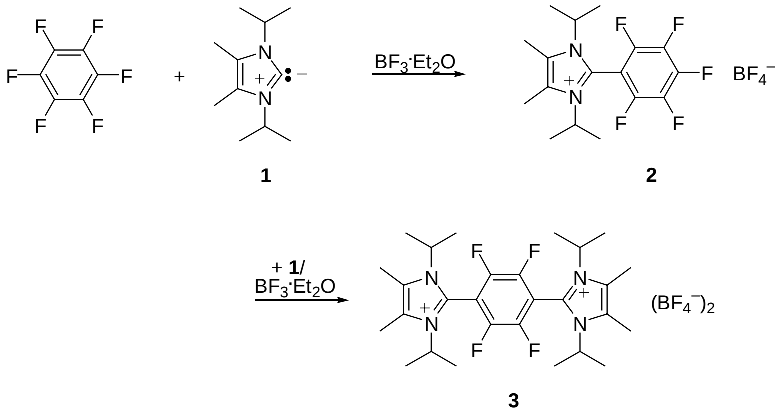
We have become interested in the synthesis of perfluoroaryl-substituted imidazolium salts and report now on our results of the reactions of nucleophilic carbenes with perfluorinated arenes.

Results and Discussion

Reaction of 2,3-dihydro-1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene with fluorinated arenes

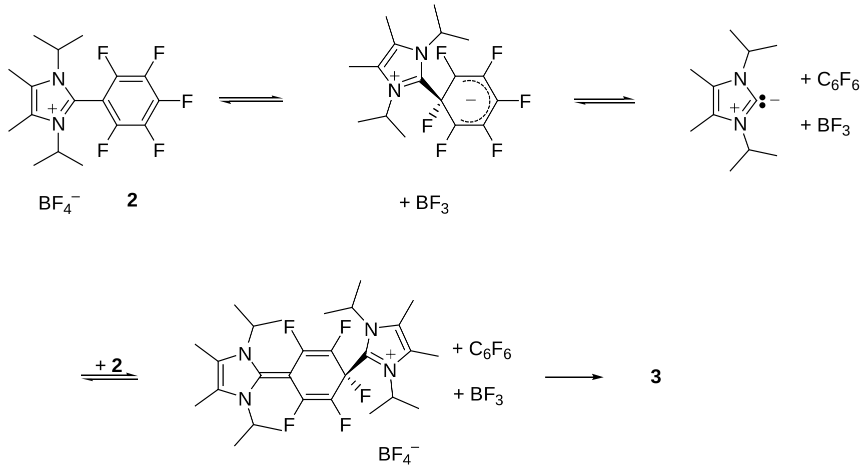
2,3-Dihydro-1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (**1**) undergoes nucleophilic aromatic substitution with fluorinated arenes in diethyl ether to yield imidazolium compounds (Scheme 1). Apparently, owing to the nucleophilic character of fluoride in organic solvents, equilibria are formed which need the addition of boron trifluoride to generate stable salts. To avoid the formation of carbene adducts [11], BF_3 diethyletherate should not be in contact with the unreacted carbene.

With hexafluorobenzene, the pentafluorophenylimidazolium salt **2** is formed as the initial product.



Scheme 1.

$$BF_4^- \rightleftharpoons BF_3 + F^-$$



Scheme 2.

Apparently, the fluorinated arene ring is activated towards nucleophilic aromatic substitution by introduction of the electron-withdrawing heterocyclic substituent. To avoid the formation of the dicationic salt **3**, an excess of hexafluorobenzene is needed. On standing of **2** in solution for some hours, the formation of **3** and hexafluorobenzene is detected. This dismutation reaction is an experimental proof for the reversibility of the formation of the Meisenheimer complex. The regenerated carbene is trapped by excess **2** with the formation of **3** (Scheme 2). Using stoichiometric amounts of the carbene and hexafluorobenzene (2 : 1), **3** is prepared easily on a preparative scale.

In pentafluorobenzonitrile, **1** attacks the 4-position selectively to give the 4-cyano-2,3,5,6-tetrafluorophenylimidazolium salt **4**. Similarly in 1,3-dicyano-2,4,5,6-tetrafluorobenzene, substitution of fluoride is preferred over substitution of cyanide. The 6-position is attacked regioselectively resulting in the formation of the 2,4-dicyano-3,5,6-trifluorophenylimidazolium salt **5**. This reflects the superior quality of *ortho/para*-placed cyano groups to stabilize the negative charge in the intermediate Meisenheimer complexes. Surprisingly, only mono-substitution of fluoride is observed with *s*-trifluorotriazin to give the salt **6** (Scheme 3).

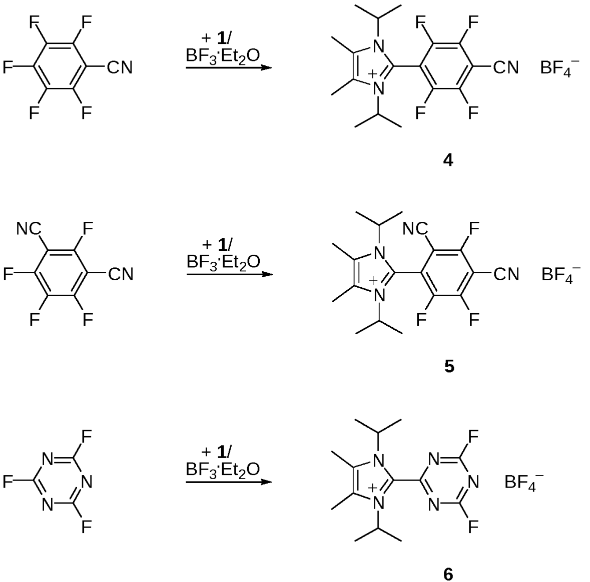
The imidazolium salts **2**–**6**, obtained as stable colorless crystals in good yield, have been characterized by elemental analysis and NMR spectroscopy (see Experimental Section).

Crystal structure analyses

Because of the limited information to be drawn from the (in part) complicated ^{13}C and ^{19}F NMR spectra, we have determined the crystal structures of the salts **2**,

Table 1. Crystal data and structure refinement for $C_{17}H_{20}BF_9N_2$ (**2**), $C_{32}H_{46}B_2F_{12}N_6$ (**3** · $2CH_3CN$), $C_{18}H_{20}F_4N_3BF_4$ (**4** · CH_3CN).

	2	**3** · $2CH_3CN$	**4** · CH_3CN
Empirical formula	$C_{17}H_{23}BF_9N_2$	$C_{32}H_{46}B_2F_{12}N_6$	$C_{20}H_{23}BF_8N_4$
Formula weight	434.16	764.37	482.23
Temperature, K	210(2)	173(2)	173(2)
λ, Å		0.71073	
Crystal system	monoclinic	monoclinic	orthorhombic
Space group	$P2_1/n$	$P2_1/c$	$P2_12_12_1$
a, Å	11.003(2)	14.185(2)	1122.1(1)
b, Å	10.721(1)	7.154(1)	1122.1(1)
c, Å	16.841(3)	23.128(3)	1837.1(2)
β, deg	101.03(2)	125.43(1)	90
Volume, Å^3	1949.9(5)	1912.3(4)	2313.2(3)
Z	4	4	4
D_{calcd}, g cm^{-3}	1.479	1.327	1.385
μ (MoK_α), mm^{-1}	0.147	0.120	0.128
$F(000)$, e	888	796	992
θ, deg	2.44 – 25.95	2.87 – 25.94	5.74 – 26.36
Refls. coll.	21093	20505	32539
Refls. indep.	3786	3677	4660
Refinement method		Full-matrix least-squares on F^2	
Param. refined	342	328	337
Goodness-of-fit on F^2	0.980	0.894	1.157
Final $R_1/wR2[I \geq 2\sigma(I)]$	0.0494 / 0.1353	0.0531 / 0.1340	0.0719 / 0.1259
Final $R_1/wR2$ (all data)	0.0650 / 0.1424	0.0744 / 0.1443	0.0916 / 0.1332
$\Delta\rho_{fin}$ (max / min), e Å^{-3}	+0.654 / −0.394	+0.433 / −0.281	+0.242 / −0.200



Scheme 3.

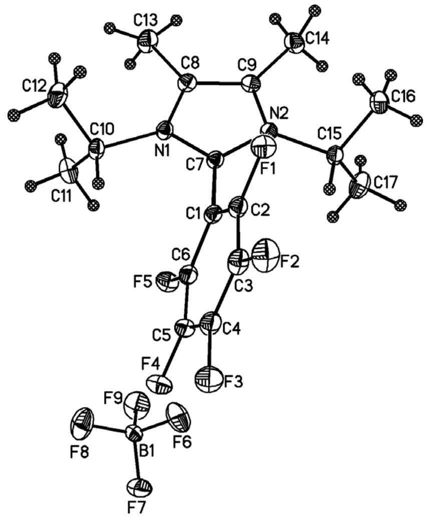


Fig. 1. View of the ion pair of $C_{17}H_{23}BF_9N_2$ (**2**) in the crystal.

3 · $2CH_3CN$, and **4** · CH_3CN (Table 1, Figs. 1 – 3). The central C–C bonds connecting the five- and six-membered rings [**2**: 1.473(2); **3** · $2CH_3CN$: 1.476(2); **4** · CH_3CN: 1.471(5) Å] are at the short end of the range observed for C(sp^2)–C(sp^2) single bonds [12]. The relative orientation of the rings inside the cations is near by perpendicular (**2**: 63(1)°; **3** · $2CH_3CN$: 68(1)°; **4** · CH_3CN: 73.0(1)°). In the six-membered rings, the C–C bond lengths [**2**: 1.370(3) – 1.396(3); **3** · $2CH_3CN$: 1.376(3) – 1.389(3); **4** · CH_3CN: 1.364(5) – 1.393(5) Å] and C–F bond lengths [**2**: 1.330(3) – 1.338(2); **3** · $2CH_3CN$: 1.335(2) – 1.337(2); **4** · CH_3CN: 1.329(4) – 1.343(4) Å] are as expected,

Table 2. Selected bond lengths (Å) and angles (deg) for $C_{17}H_{23}BF_9N_2$ (**2**).

C(1)–C(6)	1.387(3)	C(6)–C(1)–C(2)	117.5(2)
C(1)–C(2)	1.396(3)	C(6)–C(1)–C(7)	122.0(2)
C(1)–C(7)	1.473(2)	C(2)–C(1)–C(7)	120.5(2)
C(2)–F(1)	1.335(2)	C(3)–C(2)–C(1)	121.5(2)
C(2)–C(3)	1.370(3)	C(2)–C(3)–C(4)	119.3(2)
C(3)–F(2)	1.330(3)	C(3)–C(4)–C(5)	120.8(2)
C(3)–C(4)	1.376(3)	C(6)–C(5)–C(4)	119.2(2)
C(4)–F(3)	1.331(2)	C(5)–C(6)–C(1)	121.7(2)
C(4)–C(5)	1.378(3)	N(1)–C(7)–N(2)	108.9(2)
C(5)–F(4)	1.332(3)	C(7)–N(1)–C(8)	108.3(2)
C(5)–C(6)	1.371(3)	C(9)–C(8)–N(1)	107.2(2)
C(6)–F(5)	1.338(2)	C(8)–C(9)–N(2)	107.5(2)
C(7)–N(1)	1.340(2)	C(7)–N(2)–C(9)	108.1(2)
C(7)–N(2)	1.348(2)	C(7)–N(2)–C(9)	108.1(2)
N(1)–C(8)	1.389(2)		
C(8)–C(9)	1.359(3)		
C(9)–N(2)	1.384(2)		

Table 3. Selected bond lengths (Å) and angles (deg) for $C_{32}H_{46}B_2F_{12}N_6$ (**3** · $2CH_3CN$)[a].

C(1)–C(2)	1.380(2)	C(2)–C(1)–C(3)	115.9(2)
C(1)–C(3)	1.389(3)	C(2)–C(1)–C(4)	121.7(2)
C(1)–C(4)	1.476(2)	C(3)–C(1)–C(4)	122.4(2)
C(2)–F(1)	1.335(2)	C(3)#1–C(2)–C(1)	122.1(2)
C(2)–C(3)#1	1.376(3)	C(2)#1–C(3)–C(1)	122.0(2)
C(3)–F(2)	1.337(2)	N(2)–C(4)–N(1)	108.8(2)
C(4)–N(2)	1.335(2)	N(2)–C(4)–C(1)	126.2(2)
C(4)–N(1)	1.340(2)	N(1)–C(4)–C(1)	125.0(2)
N(1)–C(5)	1.388(2)	C(4)–N(1)–C(5)	108.4(2)
C(5)–C(6)	1.356(3)	C(6)–C(5)–N(1)	106.8(2)
C(6)–N(2)	1.382(3)	C(5)–C(6)–N(2)	107.6(2)
		C(4)–N(2)–C(6)	108.4(2)

[a] Symmetry transformation used to generate equivalent atoms: #1 $1-x$, $1-y$, $1-z$.

as are the geometric parameters of the imidazolium fragments [7]. For individual bond lengths and angles see Tables 2–4. The structures of the cations in the salts **5** and **6** have also been confirmed by preliminary data of single crystal structure analyses.

FAB mass spectra

The imidazolium tetrafluoroborate **2** dissolved in a *m*-nitrobenzylic alcohol matrix exhibits an abundant ion at $m/z = 347$ (rel. int. 100 %) in the FAB spectrum. This ion represents the imidazolium cation. The successive elimination of propene from the isopropyl substituents results in two fragments of minor intensities at $m/z = 305$ (15 %) and $m/z = 263$ (22 %). Compound **3**, containing a bis-imidazolium dication, shows a relatively weak signal for the doubly charged species at $m/z = 254$ (10 %). The FAB mass spectrum is dominated by peaks at $m/z = 595$ (48 %) and 465 (100 %). The ion at 595 corresponds to an ion pair composed of the dication and one tetrafluoroborate anion. This is substantiated by the appearance of a satellite peak at 594 for the contribution of the ^{10}B isotope (∼ 20 %). The base peak at $m/z = 465$ is generated by internal dealkylation of the dicationic subunit of the $m/z = 595$

Table 4. Selected bond lengths (Å) and angles (deg) for $C_{20}H_{23}BF_8N_4$ (**4** · CH_3CN).

C(1)–N(2)	1.331(4)	N(2)–C(1)–N(5)	109.1(3)
C(1)–N(5)	1.336(4)	N(2)–C(1)–C(11)	125.0(3)
C(1)–C(11)	1.471(5)	N(5)–C(1)–C(11)	125.7(3)
C(3)–C(4)	1.350(5)	C(4)–C(3)–N(2)	106.9(3)
C(3)–N(2)	1.389(4)	C(3)–C(4)–N(5)	107.7(3)
C(4)–N(5)	1.384(5)	C(12)–C(11)–C(16)	117.8(3)
C(11)–C(12)	1.382(5)	C(12)–C(11)–C(1)	122.1(3)
C(11)–C(16)	1.393(5)	C(16)–C(11)–C(1)	120.1(3)
C(12)–F(16)	1.341(4)	C(13)–C(12)–C(11)	121.5(3)
C(12)–C(13)	1.369(5)	C(12)–C(13)–C(14)	120.0(3)
C(13)–F(13)	1.329(4)	C(15)–C(14)–C(13)	118.7(3)
C(13)–C(14)	1.393(5)	C(15)–C(14)–C(131)	120.5(4)
C(14)–C(15)	1.383(5)	C(13)–C(14)–C(131)	120.7(3)
C(14)–C(131)	1.433(5)	C(16)–C(15)–C(14)	120.7(3)
C(15)–F(14)	1.342(4)	C(15)–C(16)–C(11)	121.1(3)
C(15)–C(16)	1.364(5)	N(131)–C(131)–C(14)	178.8(5)
C(16)–F(15)	1.343(4)	C(1)–N(2)–C(3)	108.2(3)
C(131)–N(131)	1.135(5)	C(1)–N(5)–C(4)	108.1(3)

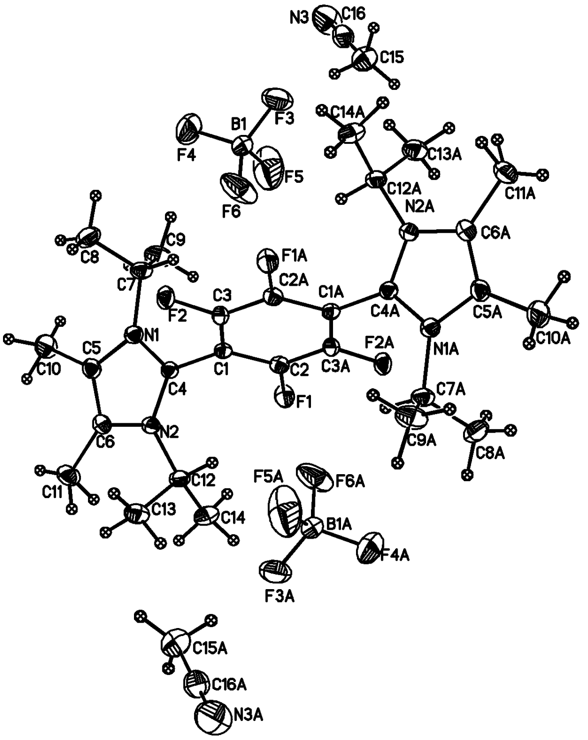


Fig. 2. View of the ion triple of $C_{32}H_{46}B_2F_{12}N_6$ (**3** · $2CH_3CN$) in the crystal.

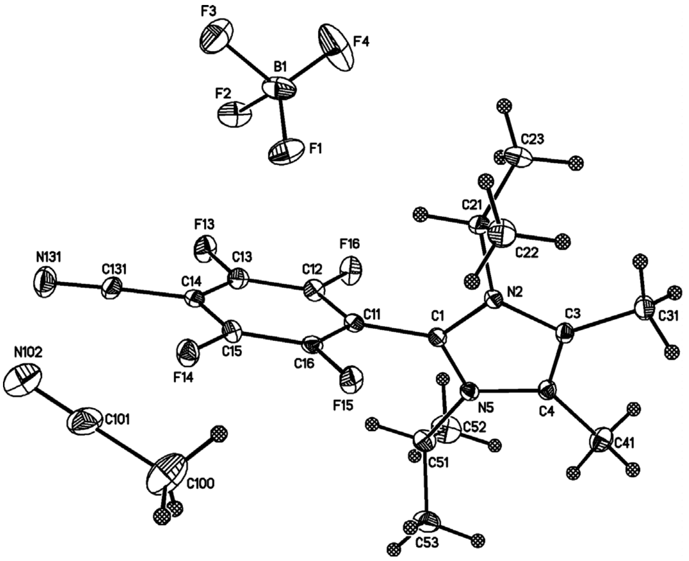
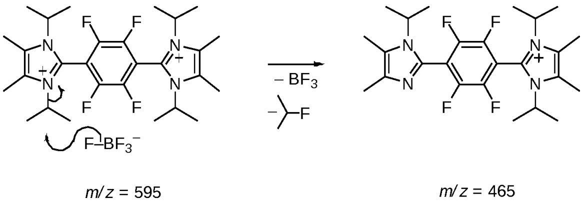
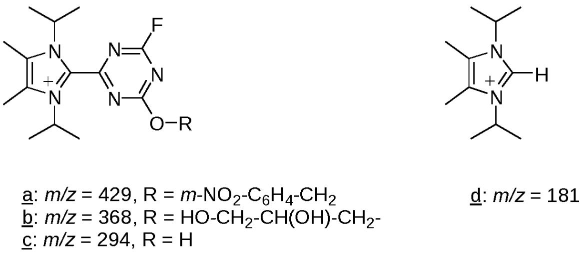


Fig. 3. View of the ion pair of $C_{20}H_{23}BF_8N_4$ ($\mathbf{4} \cdot CH_3CN$) in the crystal.



Scheme 4.



Scheme 5.

ion according to Scheme 4. This fragmentation process cancels one positive and the negative charge of the ion pair and yields a singly charged cation. Subsequent expulsion of up to three propene molecules is responsible for the formation of ions at *m/z* = 423 (6 %), 361 (10 %) and 339 (8 %).

The imidazolium salts **4** and **5** behave like compound **2** in the FAB experiment and yield intense imidazolium cation peaks at *m/z* = 354 (100 %) and 361 (100 %), respectively, followed by fragments of minor intensity for the loss of one and two propenes (**4**: *m/z* = 312, 270; **5**: *m/z* = 319, 277).

At first glance, the FAB spectrum of the monosubstitution product of trifluoro-1,3,5-triazine (compound **6**) looks rather confusing. Apart from the expected peak for the corresponding imidazolium cation at *m/z* = 296 (28 %) a peak at *m/z* = 429 (46 %) appears when the measurement is performed with *m*-nitrobenzylic alcohol as matrix material (Scheme 5). The formation of this cation can be rationalized by nucleophilic displacement of fluorine in **6** by an *m*-nitrobenzyloxy group of the matrix yielding the cationic species a. When the matrix glycerol (containing traces of water) is offered as a potential nucleophile, peak a is shifted to *m/z* = 368 (b) and 294 (c). Ions b and c are the substitution products obtained by attack of glycerol and water, respectively, on the imidazolium salt **6** prior to the transfer of ions from the matrix into the gas phase.

The FAB spectrum of **6**, measured in glycerol, exhibits a further peak at *m/z* = 181. Depending on the experimental conditions of the FAB experiment, this peak can become the base peak. The only reasonable structure to describe this ion is the 1,4-diisopropyl-2,3-dimethyl-imidazolium ion d. Its formation would require the reductive elimination of the 2,4-difluoro-1,3,5-triazinyl substituent in **6**. Tentatively, we suggest that the secondary carbinol function of glycerol transfers a hydride to the C2-position of **6**.

Experimental Section

FAB mass spectra (positive mode): The FAB spectra were recorded on a TSQ 70 quadrupol mass spectrometer with xenon atoms as bombarding particles (kinetic energy *ca.* 8 keV). Unless otherwise stated, *m*-nitrobenzyl alcohol was used as matrix material at an ion source temperature of *ca.* 50 °C. For results see text.

All experiments were performed in purified solvents under argon. 2,3-Dihydro-1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (**1**) was obtained according to a published procedure [9].

CCDC 737798 (**2**), CCDC 737799 (**3** · 2CH_3CN) and CCDC 737800 (**4** · CH_3CN) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

$C_{17}H_{20}BF_9N_2$ (**2**)

2,3-Dihydro-1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (**1**, 0.460 g, 2.55 mmol) was added to a solution of hexafluorobenzene (2.00 mL, 17.33 mmol) in 35 mL of diethyl ether at −70 °C. The mixture was stirred for 12 h at r. t., and trifluoroborane diethyletherate (0.32 mL, 2.77 mmol) was added dropwise. After stirring for further 4 h at r. t., the resulting precipitate was isolated, washed with diethyl ether, and dried *in vacuo*. Yield after recrystallization from acetonitrile/diethyl ether: 0.860 g (78 %), colorless plates. – ^{1}H NMR (CD_3CN): δ = 1.36 (d, 12 H, 1,3-CH*Me*$_2$, ^3J = 6.6 Hz), 2.33 (s, 6 H, 4,5-Me), 4.37 (sept, 2 H, C*H*Me$_2$). – ^{11}B NMR (CD_3CN, $BF_3 \cdot Et_2O$ ext.): δ = −1.38. – ^{19}F NMR (CD_3CN, CCl_3F ext.): δ = −152.1 (BF_4), −135.7, −147.0, −159.8 (2,6-F, 3,5-F, 4-F). – Elemental analysis for $C_{17}H_{20}BF_9N_2$ (434.15): calcd. C 47.03, H 4.64, N 6.45; found C 47.03, H 4.81, N 5.76.

$C_{28}H_{40}B_2F_{12}N_4$ (**3**)

To a solution of 2,3-dihydro-1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (**1**, 0.490 g, 2.72 mmol) in 35 mL of diethyl ether, hexafluorobenzene (0.157 mL, 1.36 mmol) was added at −70 °C. The mixture was stirred for 12 h at r. t., and trifluoroborane diethyletherate (0.172 mL, 1.36 mmol) was added dropwise. After stirring for further 4 h at r. t., the resulting precipitate was isolated, washed with diethyl ether, and dried *in vacuo*. Yield after recrystallization from acetonitrile/diethyl ether: 0.928 g (56 %), colorless needles. – ^{1}H NMR (CD_2Cl_2): δ = 1.52 (d, 12 H, 1,3-CH*Me*$_2$, ^3J = 6.7 Hz), 2.41 (s, 6 H, 4,5-Me), 4.61 (sept, 2 H, C*H*Me$_2$). – ^{11}B NMR (CD_2Cl_2, $BF_3 \cdot Et_2O$ ext.): δ = −1.41. – ^{13}C NMR (CD_2Cl_2): δ = 9.0 (4,5-Me), 19.3 (1,3-CH*Me*$_2$), 52.9 (1,3-*C*HMe$_2$), 106.4 – 145.6 (m, C_{Ph}), 126.2 ($C_{Im}{}^2$), 129.1 ($C_{Im}{}^{4,5}$). – ^{19}F NMR (CD_2Cl_2, CCl_3F ext.): δ = −153.4 (BF_4), −132.0 (2,3,5,6-F). – Elemental analysis for $C_{28}H_{40}B_2F_{12}N_4$ (682.20): calcd. C 49.29, H 5.91, N 8.21; found C 49.19, H 6.24, N 7.84.

$C_{18}H_{20}BF_8N_3$ (**4**)

To a solution of 2,3-dihydro-1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (**1**, 0.370 g, 2.05 mmol) in 35 mL of diethyl ether, pentafluorobenzonitrile (0.246 mL, 2.04 mmol) was added at −70 °C. The mixture was stirred for 12 h at r. t., and trifluoroborane diethyletherate (0.260 mL, 2.24 mmol) was added dropwise. After stirring for further 4 h at r. t., the resulting precipitate was isolated, washed with diethyl ether, and dried *in vacuo*. Yield after recrystallization from acetonitrile/diethyl ether: 0.780 g (86 %), colorless plates. – ^{1}H NMR (CD_3CN): δ = 1.52 (d, 12 H, 1,3-CH*Me*$_2$, ^3J = 6.7 Hz), 2.55 (s, 6 H, 4,5-Me), 4.57 (sept, 2 H, C*H*Me$_2$). – ^{11}B NMR (CD_3CN, $BF_3 \cdot Et_2O$ ext.): δ = −1.33. – ^{13}C NMR (CD_3CN): δ = 9.3 (4,5-Me), 20.0 (1,3-CH*Me*$_2$), 53.1 (1,3-*C*HMe$_2$), 106.6 – 149.3 (m, C_{Ph}), 108.6 (CN), 128.6 ($C_{Im}{}^2$), 130.8 ($C_{Im}{}^{4,5}$). – ^{19}F NMR (CD_3CN), CCl_3F ext.): δ = −152.2 (BF_4), −130.0, −133.1 (2,6-F, 3,5-F). – Elemental analysis for $C_{18}H_{20}BF_8N_3$ (441.17): calcd. C 49.00, H 4.57, N 9.52; found C 49.48, H 4.60, N 9.89.

$C_{19}H_{20}BF_7N_4$ (**5**)

To a solution of 2,3-dihydro-1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (**1**, 0.461 g, 2.56 mmol) in 35 mL of diethyl ether, tetrafluoroisophtalonitrile (0.511 g, 2.55 mmol) was added at −70 °C. The mixture was stirred for 12 h at r. t., and trifluoroborane diethyletherate (0.323 mL, 2.79 mmol) was added dropwise. After stirring for further 4 h at r. t., the resulting precipitate was isolated, washed with diethyl ether, and dried *in vacuo*. Yield after recrystallization from acetonitrile/diethyl ether: 0.980 g (86 %), colorless crystals. – ^{1}H NMR (CD_3CN): δ = 1.37 (d, 12 H, 1,3-CH*Me*$_2$, ^3J = 6.7 Hz, 2.37 (s, 6 H, 4,5-Me), 4.33 (sept, 2 H, C*H*Me$_2$). – ^{11}B NMR (CD_3CN, $BF_3 \cdot Et_2O$ ext.): δ = −1.34. – ^{13}C NMR (CD_3CN): δ = 9.5 (4,5-Me), 20.2 (1,3-CH*Me*$_2$), 53.6 (1,3-*C*HMe$_2$), 99.7 – 162.1 (m, C_{Ph}), 106.0, 108.9 (CN),; 127.4 ($C_{Im}{}^2$), 131.2 ($C_{Im}{}^{4,5}$). – ^{19}F NMR (CD_3CN), CCl_3F ext.): δ = −152.4 (BF_4), −99.3, −112.1, −129.5 (2-F, 3-F, 5-F). – Elemental analysis for $C_{19}H_{20}BF_7N_4$ (448.18): calcd. C 50.92, H 4.50, N 12.50; found C 50.60, H 4.48, N 11.63.

$C_{14}H_{20}BF_6N_5$ (**6**)

To a solution of 2,3-dihydro-1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (**1**, 0.475 g, 2.63 mmol) in 35 mL of diethyl ether, cyanuric trifluoride (0.22 mL, 2.61 mmol) was added at −70 °C. The mixture was stirred for 12 h at r. t., and trifluoroborane diethyletherate (0.334 mL, 2.91 mmol) was added dropwise. After stirring for further 4 h at r. t., the resulting precipitate was isolated, washed with diethyl ether, and dried *in vacuo*. Yield after recrystallization from acetonitrile/diethyl ether: 0.850 g (85 %), colorless needles. –

^{1}H NMR (CD_3CN): δ = 1.42 (d, 12 H, 1,3-CH*Me*$_2$, ^3J = 6.7 Hz), 2.32 (s, 6 H, 4,5-Me), 4.80 (sept, 2 H, C*H*Me$_2$). – ^{11}B NMR (CD_3CN, $BF_3 \cdot Et_2O$ ext.): δ = −1.34. – ^{13}C NMR (CD_3CN): δ = 9.7 (4,5-Me), 19.9 (1,3-CH*Me*$_2$), 53.0 (1,3-*C*HMe$_2$), 129.1 ($C_{Im}{}^2$), 130.8 ($C_{Im}{}^{4,5}$), 167.1 (t, $C_{triaz}{}^2$, ^3J = 6.9 Hz), 170.6 – 172.9 (m, $C_{triazz}{}^{4,6}$). – ^{19}F NMR (CD_3CN, CCl_3F ext.): δ = −152.1 (BF_4), −33.5 (3,5-F). – Elemental analysis for $C_{14}H_{20}BF_6N_5$ (383.14): calcd. C 43.89, H 4.26, N 18.18; found C 43.93, H 5.60, N 18.04.

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