Monomeric 1-Borylimidazoles: Syntheses, Structure and Reactivity of 1-[Bis(diisopropylamino)boryl]imidazoles

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Dedicated to Prof. Heinrich Nöth on the occasion of his 75th birthday

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Reactions of chlorobis(diisopropylamino)borane with 1-(trimethylsilyl)imidazole and 4,5-dimethyl-1-(trimethylsilyl)imidazole lead to the monomeric 1-borylimidazoles **3a** and **3b**. Treatment of **3a** with the Lewis acid BF_3 results in the quantitative formation of the corresponding trifluoroborane adduct **4a**. In contrast, **3a** reacts with the stronger Lewis acids BCl_3, BBr_3, and BI_3 to partially substitute the diisopropylamino groups and form the corresponding adducts, depending on the Lewis acidity of the reagent; **3a** forms, with $Mo(CO)_5$thf and Cp′$Mn(CO)_2$thf, the complexes 3-[$(OC)_5$Mo]**3a** (**8**) and 3-[$(OC)_2$Cp′Mn]**3a** (**6**). The product compositions agree with spectroscopic and analytical data and with X-ray structure analyses of **3a**, **3b**, **4a**, **8**, and **9**.

Introduction

1-(Diorganoboryl)imidazoles have been prepared either by cleavage of the silicon−nitrogen bond in silylimidazoles with haloboranes or by reaction of (dimethylamino)diethylborane with imidazole. The resulting colorless, glassy materials readily dissolve in organic solvents to form solutions of high viscosity due to intermolecular association by Lewis acid−base interactions.[1] Inherent viscosity and cryoscopical measurements, as well as mass spectrometric data, confirm the presence of polymeric structures.

Analogously, some discrete cyclic tetra-[1a,2] and -pentameric[2c] 1-(diorganoboryl)imidazoles, as well as a boryl-substituted bis(imidazole),[2d] have been obtained. Few monomeric 1-borylimidazoles are known[3] and the reactivity of their unsubstituted nitrogen atom has not been investigated.

This report describes the preparation and characterization of 1-[bis(diorganoamino)boryl]imidazoles. In contrast to former assumptions,[3] bulky substituents are necessary as the electron-donating effects of two small amino groups do not stabilize sufficiently the three-coordinate boron atom to inhibit intermolecular association. Monomeric 1-[bis(diisopropylamino)boryl]imidazoles may be obtained due to the sterically demanding boryl groups. In addition, we examined the reactivity of these compounds toward boron halides of different Lewis acidity, toward BH_3, BEt_3 and photochemically activated carbonylmetal compounds. We previously showed that *N*-borane-substituted imidazoles can be deprotonated to form anionic imidazol-2-ylidenes, which are even more nucleophilic than the classic imidazol-2-ylidenes.[2d,4] Deprotonation of 1-[bis(diisopropylamino)boryl]-3-(trifluoroborio)imidazole is, likewise, possible − despite the electrophilic three-coordinate boron atom − if bulky deprotonation reagents are used.[4d] The anionic carbene reacts with transition metal−halogen compounds to yield (diborylimidazole-2-ylidene)metal complexes containing a reactive boryl group.

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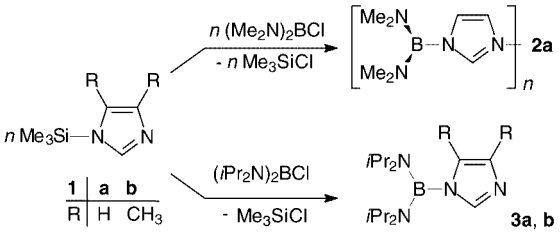
Results and Discussion

Monomeric 1-Borylimidazoles 3a,b

Chlorobis(dimethylamino)borane reacts with 1-(trimethylsilyl)imidazole (**1a**) in THF to yield colorless **2**, which is soluble in $CDCl_3$ (Scheme 1). Its ^{11}B NMR shift is in the region expected for compounds with four-coordinate boron atoms,[5] indicating that **2** undergoes intermolecular association by Lewis acid−base interactions. In contrast, the bulkier reagent chlorobis(diisopropylamino)borane affords the crystalline 1-[bis(diisopropylamino)boryl]imidazoles **3a** and **3b**, which exhibit broad ^{11}B NMR signals in the range typical for three-coordinate boron atoms.[5] The ^1H NMR spectra of **3a** and **3b** show signals for the aromatic hydrogen atoms of both molecules as singlets, the methyl substituents of the imidazole ring in **3b** exhibit only one resonance, whereas two signals appear in the ^{13}C NMR spectrum. The aliphatic resonances of **3a** coincide as a single doublet for the methyl and a septuplet for the methine protons, indicat-

ing that free rotation about the boron−imidazole as well as about the boron−diisopropylamino bonds occurs at room temperature on the NMR time scale. For the same reason the ^{13}C NMR spectrum shows only two resonances for the diisopropylamino substituents as well as three signals for the imidazole ring.



Scheme 1

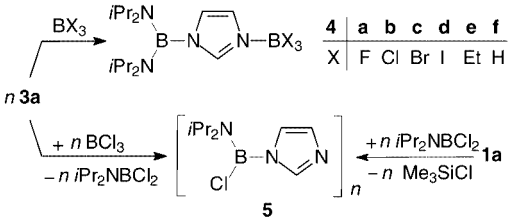
By contrast, in the ^1H NMR spectrum of **3b** the methyl groups of the diisopropylamino substituents appear as two groups of diastereomeric protons, each signal split to a doublet, at slightly different fields. Likewise, two ^{13}C NMR absorptions are assigned to these chemically inequivalent methyl carbon atoms. Thus, in **3b**, due to the methyl substituent at the 5-position of the imidazole ring, free rotation of the diisopropylamino groups about the boron−imidazole bond at room temperature is assumed to be inhibited. Nevertheless, the corresponding methine carbon atoms show only one septuplet as well as one signal in the ^{13}C NMR spectrum on account of the unhindered rotation of all four isopropyl groups about the diisopropylamino−boron axis.

To determine the height of the rotation barrier for the bis(diisopropylamino)boryl group, temperature-dependent NMR experiments have been performed. From the Eyring equation,[6] using the method of the peak separation, a free energy of activation of $\Delta G^{\neq} = 84.6$ kJ/mol of the rotation barrier has been calculated. (The coalescence temperature of the corresponding peaks has been determined by temperature-dependent spectra in [D$_8$]toluene to $T_c = 318$ K; for these signals a frequency difference of up to $|\nu_A - \nu_B| = 7.1$ Hz has been ascertained.) This $\Delta G^{\neq}$ is about 20 kJ/mol higher than that obtained for (2,2′,6,6′-tetramethylpiperidino)boryl-substituted bis(imidazole).[2d]

The EI mass spectrometric data on **3a** and **3b** agree with monomeric structures for both molecules. The highest boron-containing sets of peaks in each case correspond to the respective monomeric molecules, and high-resolution spectra confirm their compositions.

Donor−Acceptor Compounds 4, 5 and 7

Imidazole−trifluoroborane adduct formation has been studied extensively,[7] whereas only one report on imidazole−trichloroborane adducts is available.[7a] We examined the reactivity of **3a** toward the haloboranes BF_3, BCl_3, BBr_3, and BI_3 as well as toward BEt_3 and BH_3 (Scheme 2).



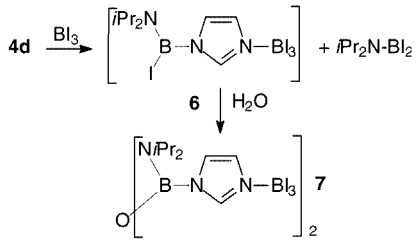
Scheme 2

Treatment of **3a** with the weak Lewis acid BF_3 in THF yields the donor−acceptor compound **4a** quantitatively. The ^{11}B NMR spectrum of **4a** has a broad signal for the three-coordinate boron atom and a sharp 1:3:3:1 quadruplet at high field. Its ^1H NMR spectrum exhibits signals for the ring protons that are slightly shifted down-field compared with the corresponding resonances of **3a**. Only a small influence on the shift of the signals of the diisopropylamino groups is observed. In the ^{13}C NMR spectrum, the imidazole carbon atoms and the diisopropylamino substituents appear nearly unchanged compared with the starting material. Mass spectrometric studies (EI, CI) on **4a** reveal that the Lewis acid−base interaction between the nitrogen and boron atoms is too weak to permit ionization without dissociation.

Treatment of **3a** with the stronger Lewis acid BCl_3 in toluene leads to a small amount of a white precipitate (**5**); NMR spectra of the crude product, obtained by evaporation of the solvent, indicate a product mixture. Recrystallization gave **4b** (68%), which shows a broad signal at low field and a sharp absorption at high field in its ^{11}B NMR spectrum. Accordingly, the ^1H NMR spectrum exhibits a doublet and a septuplet as well as three absorptions in the aromatic region. Additional signals for **3a** and for dichloro(diisopropylamino)borane are found. These observations show that, as well as the expected adduct **4b**, BCl_3 cleaves the diisopropylamino−boron bond of **3a** to give 1-[chloro(diisopropylamino)boryl]imidazole (**5**) as a white precipitate; **5** was obtained separately from **1a** and dichloro(diisopropylamino)borane (Scheme 2).[4d]

Under the same conditions, with the stronger Lewis acids BBr_3 and BI_3, the amount of side products increases, as indicated by the smaller yields of **4c** (55%) and of **4d** (< 30%). However, in contrast to **4c**, purification of **4d** by recrystallization was unsuccessful, due to the formation of [iPr$_2$NH$_2$]I. The ^1H NMR spectra showed increased low-field shifts of the aromatic protons. Additionally, the corresponding signals for the four-coordinate boron atoms are shifted to high field. Apart from the two resonances of the boron atoms of **4c** and **4d**, each ^{11}B NMR spectrum of the crude products shows an additional signal assigned to the (diisopropylamino)haloborane by-products. As (diisopropylamino)diiodoborane, not yet described, was prepared separately by treating diisopropylamine with BI_3. During crystallization of **4d**, extremely air-sensitive yellow crystals of **7** were obtained, confirming that compound **6** is formed

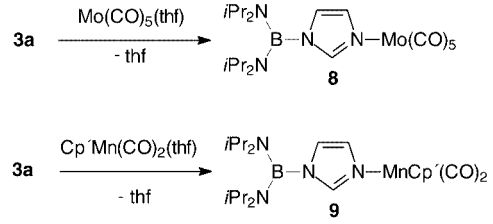
by the reaction of BI_3 and **4d** (Scheme 3). Treatment of **3a** with BEt_3 and BH_3 gave the adducts **4e** and **4f** in excellent yields. Unlike the observed down-field shift of the imidazole proton signals in the ^1H NMR spectrum of the haloborane adducts **4**, the corresponding proton signals of **4e** and **4f** remain nearly unchanged compared to those of **3a**. The ^{11}B NMR resonances for the tetracoordinate boron atoms are at $\delta = -3$ (**4e**) and -20 (**4f**) ppm.



Scheme 3

Formation of Metal Complexes

Examination of the reactivity of **3a** towards photochemically generated $[Mo(CO)_5thf]$ and $Cp'Mn(CO)_2thf$ complexes ($Cp' = C_5H_4Me$)[8] revealed that THF is readily displaced by the two-electron donor ligand **3a** at low temperature to give good yields of **8** and **9**, respectively (Scheme 4).



Scheme 4

In the ^1H NMR spectrum of **8** all resonances remain unchanged compared with those of the starting material, but the corresponding signals in the ^{13}C NMR spectrum appear at slightly different fields. The IR spectrum of **8** exhibits three absorptions, at $\tilde{\nu} = 1979$, 1933 and 1891 cm^{-1}.

Unlike that of **8**, the ^1H NMR spectrum of **9** exhibits clearly broadened lines that are significantly shifted in comparison with the starting material, hinting at the formation of a paramagnetic compound. The reasons for this unexpected paramagnetism at room temperature for the 18VE carbonylmetal complex of manganese(I) lie, as described by Kaim et al.,[9] in the generally small ligand-field splitting of low-valent manganese, which favors spin crossover. Other factors are the ligand strength and coordination geometry. Reduction of the symmetry of the $Cp'Mn(CO)_3$ parent to C_s in **9** and weakening of the bond to the imidazole substituent lead to an arrangement of d orbitals that favors the occupation of magnetically excited states. Conversely, the correlated ^{13}C NMR spectra exhibit all expected resonances as sharp lines at slightly different fields compared with **3a**. Infrared spectroscopy shows two CO bands at $\tilde{\nu} = 2017$ and 1928 cm^{-1}. As with the haloborane adducts **4**, no mass spectrometric data for **8** and **9** could be obtained.

Crystal Structures

To confirm their monomeric structures, we performed X-ray single-crystal analyses of the colorless and orange crystals obtained by cooling hexane solutions of **3a** and **3b**, respectively, to -80 °C. Their molecular structures are shown in Figures 1 and 2.

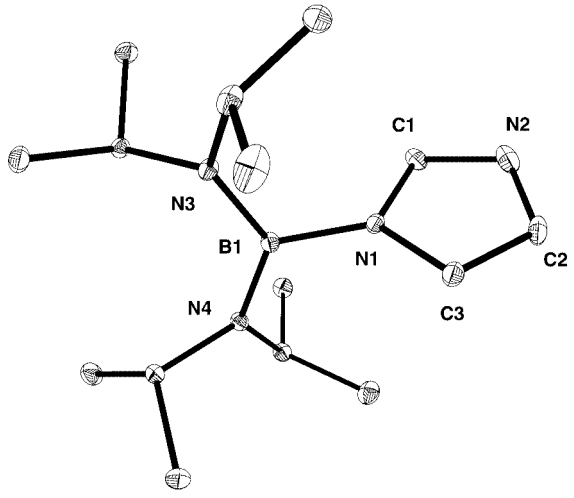


Figure 1. Molecular structure of **3a** in the crystal; hydrogen atoms are omitted for clarity; selected bond lengths [Å] and angles [°]: B1–N1 1.514(2), B1–N3 1.420(1), B1–N4 1.425(1), N1–C1 1.361(2), N1–C3 1.387(2), N2–C1 1.316(2), N2–C2 1.389(3); C1–N1–C3 104.6(1), N2–C1–N1 114.1(2), C1–N2–C2 104.4(1); angle between planes N1/B1/N3/N4 and ring 68.5

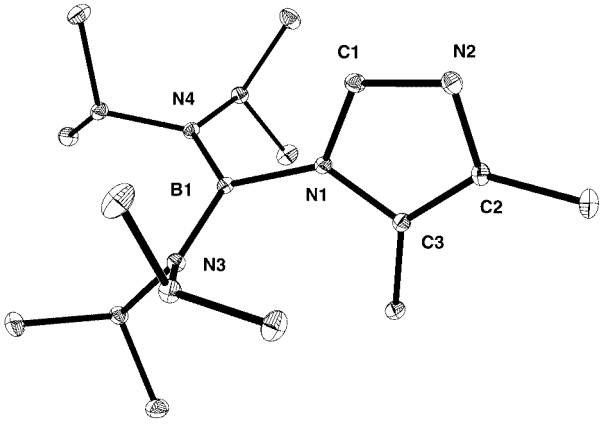


Figure 2. Molecular structure of **3b** in the crystal; hydrogen atoms are omitted for clarity; selected bond lengths [Å] and angles [°]: B1–N1 1.507(1), B1–N3 1.429(1), B1–N4 1.426(1), N1–C1 1.368(1), N1–C3 1.397(1), N2–C1 1.318(1), N2–C2 1.390(1); C1–N1–C3 105.3(1), N2–C1–N1 113.7(1), C1–N2–C2 104.5(1); angle between planes N1/B1/N3/N4 and ring 63.7

In **3a** the imidazole ring is disordered over two positions (3:1); the distances and angles of the higher occupied part are given. The imidazole rings are planar with short internal

ring bond lengths, which are very similar to those in imidazole.[10] More significant differences are found in the ring angles, especially at N1 (decreasing) and C1 (increasing) compared with imidazole.

As expected for a substituted imidazole, the N1/2−C1 bond lengths of **3a** and **3b** show single- and double-bond character.[11] Because the B1−N1 distance is about 0.10 Å longer than that from B1 to the diisopropylamino nitrogen atoms, π-interactions of the vacant p-orbital of B1 with the free electron pair of N1 can be excluded, while the short B1−N2/N3 distances indicate strong interactions with these nitrogen atoms. This is in agreement with the angles between the planes through the imidazole ring and B1 and the adjacent nitrogen atom (**3a**: 68.5°; **3b**: 63.7°).

Single crystals of **4a** have been obtained from a toluene solution. The crystal cell contains two crystallographically independent molecules in the asymmetric unit with very similar distances and angles; only one structure is shown in Figure 3 and the average values are listed.

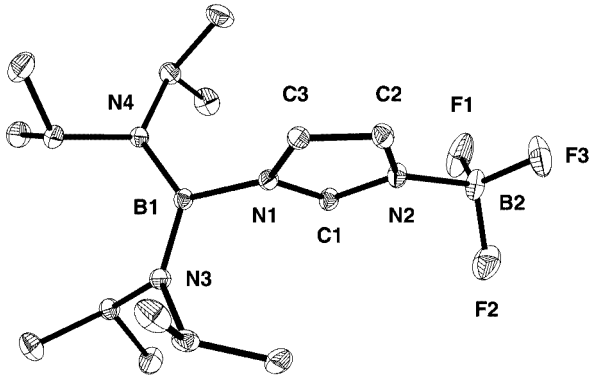


Figure 3. Molecular structure of **4a** in the crystal; hydrogen atoms are omitted for clarity; average values of selected bond lengths [Å] and angles [°]: B1−N1 1.527(2), B1−N3 1.412(2), B1−N4 1.414(2), B2−N2 1.579(2), N1−C1 1.336(2), N1−C3 1.388(2), N2−C1 1.327(2), N2−C2 1.379(2); C1−N1−C3 106.8(1), N2−C1−N1 110.7(1), C1−N2−C2 107.0(1); angle between planes N1/B1/N3/N4 and ring 73.4

Comparing the structural data of **4a** with that of **3a** enables the following observations: First, the N1/N2−C1 distances [N1−C1 1.336(2) Å and N2−C2 1.327(2) Å] exhibit significantly smaller bond-length alternations as at **3a**, indicating uninterrupted aromaticity. Second, the angles at N1 and C1 in **4a** resemble those in imidazole[10] more than in **3a** and **3b**. Third, as expected, the distance [1.577(2) Å] between N2 and the four-coordinate boron atom is longer than between N1 and B1 [1.527(2) Å].

The X-ray diffraction study of yellow **7** confirms the structure; as the quality of the data is poor, however, it will not be further discussed here. Crystals of **8** and **9** suitable for X-ray analysis were grown from a toluene solution. **8** contains four independent molecules in the asymmetric unit. As the obtained distances and angles of these molecules are similar, only one structure is shown in Figure 4, and the range of selected bond lengths and angles is listed. The values for **9** are given in the caption of Figure 5.

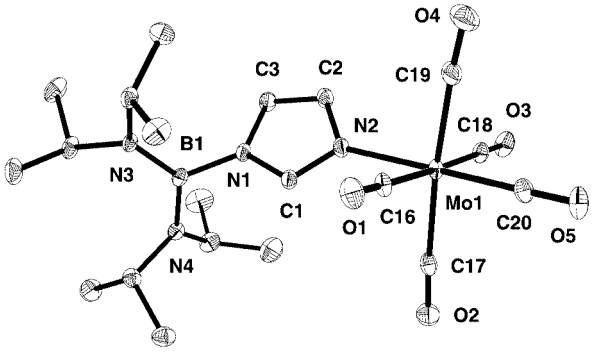


Figure 4. Molecular structure of **8** in the crystal; hydrogen atoms are omitted for clarity; selected bond lengths [Å] and angles [°]: B1−N1 1.517(5)−1.527(5), B1−N3 1.406(5)−1.412(5), B1−N4 1.404(5)−1.422(5), N1−C1 1.344(4)−1.350(5), N2−C1 1.317(5)−1.326(4); C1−N1−C3 105.0(3)−105.4(3), N2−C1−N1 112.9(3)−113.5(3), C1−N2−C2 104.2(3)−105.0(3); angle between planes N1/B1/N3/N4 and ring 108.7−117.9

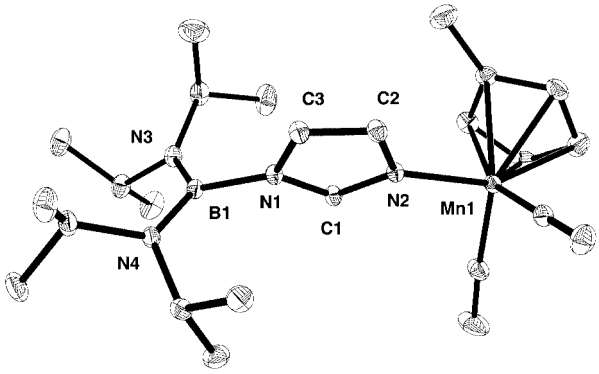


Figure 5. Molecular structure of **9** in the crystal; hydrogen atoms are omitted for clarity; selected bond lengths [Å] and angles [°]: B1−N1 1.527(2), B1−N3 1.416(2), B1−N4 1.423(2), N1−C1 1.353(2), N2−C1 1.327(2); C1−N1−C3 105.7(1), N2−C1−N1 112.5(1), C1−N2−C2 105.0(1); angle between planes N1/B1/N3/N4 and ring 118.8

Both molecules exhibit less bond-length alternations than **3a** but more than **4a** and, following this structural pattern, the angles at N1 and C1 resemble those in imidazole more than those of **3a** and **3b**. Further, the Mo−CO bonds of **8** *trans* to the nitrogen atoms (1.97 Å) are shorter than the average length of the *cis* Mo−C bonds (2.04 Å). This is due to the stronger π-bonding from Mo to CO, indicating good σ-donor and poor π-acceptor capacity of the imidazole ligand.

Conclusion

The monomeric imidazoles **3a** and **4a** are obtained by using electron-donating *and* sterically demanding boryl substituents. Contrary to **3a**, restricted rotation about the B−N(imid.) bond is observed for **4a**. X-ray structure analyses of **3a** and **4a** reveal that π-interaction of the vacant p-

orbital of the boron atoms exists only with the diisopropylamino groups and not with the imidazole nitrogen atoms. Treatment of **3a** with the weak Lewis acids BF_3, BEt_3 and BH_3 leads to the corresponding zwitterionic adducts in excellent yields. In contrast, the stronger Lewis acids BCl_3, BBr_3, and BI_3 give decreasing yields with increasing Lewis acidity. The observed side reactions involve splitting off of the diisopropylamino groups of **3a** and the corresponding adducts. With $Mo(CO)_5$thf and $Cp'Mn(CO)_2$thf the complexes 3-[$(OC)_5$Mo]**3a** (**8**) and 3-[$(OC)_2Cp'Mn$]**3a** (**9**) are formed readily, and X-ray diffraction measurement of **8** reveals the good σ-donor and poor π-acceptor capacity of the borylimidazole ligand.

Experimental Section

General: Reactions were carried out under dry argon, using standard Schlenk techniques. Solvents were dried, distilled and saturated with nitrogen. Glassware was dried with a heat-gun under high vacuum. ^1H, ^{13}C, ^{11}B NMR: Bruker AC 200 spectrometer, with $(CH_3)_4Si$ and $BF_3{\cdot}Et_2O$ as references. IR spectra were recorded with a Bruker IFS 28 Fourier-transformation spectrometer with CaF_2 cells. Mass spectra were obtained with a Finnigan MAT 8200 plus spectrometer using the EI technique. Melting points (uncorrected) were obtained with a Büchi apparatus, using a capillary filled under argon and sealed. Chlorobis(dimethylamino)borane,[12] chlorobis(diisopropylamino)borane[13] and 4.5-dimethyl-1-(trimethylsilyl)imidazol[14] were prepared according to literature procedures. (Trimethylsilyl)imidazole, $BF_3{\cdot}Et_2O$, BBr_3, $BH_3{\cdot}THF$, $BEt_3{\cdot}THF$ and $Cp'Mn(CO)_3$ were purchased from Sigma Aldrich and $Mo(CO)_6$ from Fluka.

1-[Bis(dimethylamino)boryl]imidazole (2): Chlorobis(dimethylamino)borane (190 mg, 1.4 mmol) in THF (10 mL) was added dropwise at −30 °C to a solution of **1a** (200 mg, 1.4 mmol) in THF (40 mL). After slowly warming to room temperature and stirring for 10 h, the solvent was removed in vacuo, leaving the white crude product, m.p. (dec.) > 240 °C. ^1H NMR (200.1 MHz, $CDCl_3$): δ = 0.7−1.2 (m, CH_3), 6.8−7.5 (m, im.) ppm. ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = 1.3 ($\Delta\nu_{1/2}$ = 145 Hz) ppm.

1-[Bis(diisopropylamino)boryl]imidazole (3a): Chlorobis(diisopropylamino)borane (713 mg, 2.9 mmol) in THF (10 mL) was added dropwise at −30 °C to a solution of **1a** (410 mg, 2.9 mmol) in THF (40 mL). The resultant mixture was allowed to warm to room temperature and stirred for 24 h. The solvent was then removed in vacuo, and the remaining solid extracted with hexane and filtered. The product was recrystallized from hexane solution at −80 °C. Yield: 685 mg (85%) of colorless crystals, sensitive to air and moisture, m.p. 67−68 °C. ^1H NMR (200.1 MHz, $CDCl_3$): δ = 0.98 [d, $^3J_{H,H}$ = 6.8 Hz, 24 H, $CH(CH_3)_2$], 3.41 [m, $^3J_{H,H}$ = 6.8 Hz, 4 H, $CH(CH_3)_2$], 6.85 (s, 1 H, C*H*−CH=N), 7.01, (s, 1 H, CH−C*H*=N), 7.47 (s, 1 H, N=CH−N) ppm. ^1H NMR (200.1 MHz, [D_8]THF): δ = 1.04 [d, $^3J_{H,H}$ = 6.8 Hz, 24 H, $CH(CH_3)_2$], 3.47 [m, $^3J_{H,H}$ = 6.8 Hz, 4 H, $CH(CH_3)_2$], 6.90 (s, 2 H, C*H*−C*H*=N), 7.44 (s, 1 H, N−CH=N) ppm. ^1H NMR (200.1 MHz, [D_8]toluene): δ = 1.08 [d, $^3J_{H,H}$ = 6.8 Hz, 24 H, $CH(CH_3)_2$,], 3.45 [m, $^3J_{H,H}$ = 6.8 Hz, 4 H, $CH(CH_3)_2$], 6.92 (s, 1 H, C*H*−CH=N), 7.46 (s, 1 H, CH−C*H*=N), 7.72 (s, 1 H, N−CH=N) ppm. ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = 28 ($\Delta\nu_{1/2}$ = 145 Hz) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 24.4 [$CH(CH_3)_2$], 47.0 [$CH(CH_3)_2$], 122.2 (*C*H−CH=N), 128.1 (CH−*C*H=N), 141.4 (N−CH=N) ppm. ^{13}C NMR (50.3 MHz, [D_8]THF): δ = 25.5 [$CH(CH_3)_2$], 48.5 [$CH(CH_3)_2$], 123.1 (*C*H−CH=N), 129.7 (CH−*C*H=N), 142.8 (N−CH=N) ppm. ^{13}C NMR (50.3 MHz, [D_8]toluene): δ = 24.4 [$CH(CH_3)_2$], 47.0 [$CH(CH_3)_2$], 122.2 (*C*H−CH=N), 128.1 (CH−*C*H=N), 141.4 (N−CH=N) ppm. EI-MS: *m*/*z* (%) = 278 (62) $[M]^+$, 263 (100) $[M - CH_3]^+$, 235 (82) $[M - C_3H_7]^+$, 178 (52) $[M - N(C_3H_7)_2]^+$, 43 (13) $[C_3H_7]^+$. HR-EI: *m*/*z* = 278.2670, calcd. for $C_{15}H_{31}N_4B$ 278.2698 (Δμ = 2.8).

1-[Bis(diisopropylamino)boryl]-4,5-dimethylimidazole (3b): The same procedure as for **3a** was used in treating **1b** (300 mg, 1.8 mmol) with chlorobis(diisopropylamino)borane (443 mg). After workup an air- and moisture-sensitive orange solid was obtained (484 mg; 88%), m.p. 94−95 °C. ^1H NMR (200.1 MHz, $CDCl_3$): δ = 0.96 [d, $^3J_{H,H}$ = 6.8 Hz, 12 H, $CH(CH_3)_2$], 1.01 [d, $^3J_{H,H}$ = 6.8 Hz, 12 H, $CH(CH_3)_2$]], 2.12 [2 s, 6 H, CH_3(im.)], 3.39 [m, $^3J_{H,H}$ = 6.8 Hz, 4 H, $CH(CH_3)_2$], 7.24 (s, 1 H, N=CH−N) ppm. ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = 28 ($\Delta\nu_{1/2}$ = 145 Hz) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 11.2 [CH_3 (im.)], 12.4 [CH_3 (im.)], 23.8 [$CH(CH_3)_2$], 24.6 [$CH(CH_3)_2$], 47.1 [$CH(CH_3)_2$], 124.3 (*C*Me−CMe=N), 133.9 (CMe−*C*Me=N), 138.7 (N−CH=N) ppm. EI-MS: *m*/*z* (%) = 306 (10) $[M]^+$, 211 (100) $[C_{12}H_{28}N_2B]^+$. HR-EI: *m*/*z* = 306.2953, calcd. for $C_{17}H_{35}N_4B$ 306.2947 (Δμ = 0.6).

General Procedure for the Preparation of the 1-[Bis(diisopropylamino)boryl]imidazole Adducts 4: To a solution of **1a** (200 mg, 0.7 mmol) in the corresponding solvent (40 mL), $BF_3{\cdot}OEt_2$ (120 mg, 0.84 mmol) was added at −78 °C to give **4a**; BCl_3 (81 mg, 0.7 mmol) to give **4b**; BBr_3 (174 mg, 0.7 mmol) to give **4c**; BI_3 (274 mg, 0.7 mmol) to give **4d**; $BH_3{\cdot}$thf (0.7 mL, 0.7 mmol; 1 M solution in THF) to give **4e** and $BEt_3{\cdot}$thf (0.7 mL, 1 M solution in THF) to give **4f**. The reaction mixtures were allowed to warm to room temperature and stirred for 7 h.

1-[Bis(diisopropylamino)boryl]imidazole(N^3-B)Trifluoroborane (4a): Yield after evaporation of THF: 242 mg (100%) of a white powder, sensitive to air and moisture, m.p. 112−114 °C. ^1H NMR (200.1 MHz, $CDCl_3$): δ = 1.01 [d, $^3J_{H,H}$ = 6.8 Hz, 24 H, $CH(CH_3)_2$], 3.45 [m, $^3J_{H,H}$ = 7 Hz, 4 H, $CH(CH_3)_2$], 6.98 (s, 1 H, C*H*−CH=N), 7.30 (s, 1 H, CH−C*H*=N), 7.98 (s, 1 H, N=CH−N) ppm. ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = −0.3 (q, $^2J_{B,F}$ = 14 Hz, $\Delta\nu_{1/2}$ 36 Hz, BF_3), 28 [$\Delta\nu_{1/2}$ = 145 Hz, N−B(N*i*Pr$_2$)$_2$] ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 24.4 [$CH(CH_3)_2$], 47.4 [$CH(CH_3)_2$], 122.0 (*C*H−CH=N), 123.7 (CH−*C*H=N), 138.6 (N−CH=N) ppm.

1-[Bis(diisopropylamino)boryl]imidazole(N^3-B)Trichloroborane (4b): A colorless precipitate (20 mg) was filtered off and the volatile compounds of the toluene solution removed under vacuum. The NMR spectra of the crude product show signals of **4b**, **3a** and dichloro(diisopropylamino)borane. The residue was recrystallized from toluene at −18 °C. Yield: 187 mg (68%) of colorless **4b**, which is sensitive to air and moisture, m.p. 145−148 °C. ^1H NMR (200.1 MHz, [D_8]toluene): δ = 0.87 [d, $^3J_{H,H}$ = 6.8 Hz, 24 H, $CH(CH_3)_2$], 3.21 [m, $^3J_{H,H}$ = 6.8 Hz, 4 H, $CH(CH_3)_2$], 6.35 (s, 1 H, C*H*−CH=N), 7.67 (s, 1 H, CH−C*H*=N), 8.60 (s, 1 H, N−CH=N) ppm. ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = 5.3 ($\Delta\nu_{1/2}$ = 30 Hz, BCl_3), 28 [$\Delta\nu_{1/2}$ = 360 Hz, N−B(N*i*Pr$_2$)$_2$] ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 23.7 [$CH(CH_3)_2$], 47.0 [$CH(CH_3)_2$], 124.7 (CH−CH=N), 128.9 (CH−CH=N), 137.4 (N−CH=N) ppm.

1-[Bis(diisopropylamino)boryl]imidazole(N^3-B)Tribromoborane (4c): A yellowish precipitate was filtered off and the volatile compounds of the toluene solution removed under vacuum. The NMR spectra of the crude product show signals of **4c**, **3a** and dibromo(di-

isopropylamino)borane. The residue was then recrystallized from toluene at −18 °C. Yield: 202 mg (55%) of colorless **4c**, which is sensitive to air and moisture, m.p. decomp. > 150 °C. ^{1}H NMR (200.1 MHz, [D$_8$]toluene): δ = 0.90 [d, $^3J_{H,H}$ = 6.8 Hz, 24 H, CH(CH_3)$_2$], 3.23 [m, $^3J_{H,H}$ = 6.8 Hz, 4 H, CH(CH$_3$)$_2$], 6.42 (s, 1 H, CH−CH=N), 7.84 (s, 1 H, CH−CH=N), 8.81 (s, 1 H, N−CH=N) ppm. ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = −11.8 (Δν$_{1/2}$ = 30 Hz, BBr_3), 28 [Δν$_{1/2}$ = 360 Hz, N−B(NiPr$_2$)$_2$] ppm. ^{13}C NMR (50.3 MHz, [D$_8$]toluene): δ = 24.1 [CH(CH_3)$_2$], 47.4 [CH(CH$_3$)$_2$], 124.0 (CH−CH=N), 129.3 (CH−CH=N), 141.1 (N−CH=N) ppm.

1-[Bis(diisopropylamino)boryl]imidazole(N^3−B)Triiodoborane (4d): A yellow precipitate was filtered off and the volatile compounds of the toluene solution were removed under vacuum. The NMR spectra of the crude product show signals of **4d**, **3a** and (diisopropylamino)diiodoborane. The residue was recrystallized from toluene at −18 °C, but was still contaminated with diisopropylammonium iodide. ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 1.06 [d, $^3J_{H,H}$ = 6.8 Hz, 12 H, CH(CH_3)$_2$], 1.58 [d, $^3J_{H,H}$ = 6.8 Hz, 24 H, CH(CH_3)$_2$], 3.48 [m, $^3J_{H,H}$ = 6.8 Hz, 4 H, CH(CH$_3$)$_2$], 3.65 [m, $^3J_{H,H}$ = 6.8 Hz, 4 H, CH(CH$_3$)$_2$], 7.11 (s, 1 H, CH−CH=N), 7.91 (s, 1 H, CH−CH=N), 8.68 (s, 1 H, N−CH=N) ppm. ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = −68.5 (Δν$_{1/2}$ = 50 Hz, BI_3), 28 [Δν$_{1/2}$ = 360 Hz, N−B(NiPr$_2$)$_2$] ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 19.1 [CH(CH_3)$_2$], 24.5 [CH(CH_3)$_2$], 47.4 [CH(CH$_3$)$_2$], 48.6 [CH(CH$_3$)$_2$], 128.2 (CH−CH=N), 129.0 (CH−CH=N), 137.6 (N−CH=N) ppm.

1-[Bis(diisopropylamino)boryl]imidazole(N^3−B)Triethylborane (4e): The volatile compounds of the THF solution were removed under vacuum, leaving **4e** quantitatively as a white powder that is sensitive to air and moisture, m.p. 97−98 °C. ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 0.24 (q, 6 H, CH_2CH$_3$), 0.60 (t, 6 H, CH$_2$CH_3), 1.00 [d, $^3J_{H,H}$ = 6.8 Hz, 24 H, CH(CH_3)$_2$], 3.43 [m, $^3J_{H,H}$ = 6.8 Hz, 4 H, CH(CH$_3$)$_2$], 6.83 (s, 1 H, CH−CH=N), 7.07 (s, 1 H, CH−CH=N), 7.56 (s, 1 H, N−CH=N) ppm. ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = −3 (Δν$_{1/2}$ = 380 Hz, BEt_3), 28 [Δν$_{1/2}$ = 360 Hz, N−B(NiPr$_2$)$_2$] ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 9.7 (CH$_2$$CH_3$), 15.0 ($CH_2CH_3$) 24.4 [CH($CH_3$)$_2$], 47.2 [$C$H(CH$_3$)$_2$], 122.6 ($C$H−CH=N), 123.5 (CH−$C$H=N), 138.3 (N−CH=N).

1-[Bis(diisopropylamino)boryl]imidazole(N^3−B)Trihydroborane (4f): The volatile compounds of the THF solution were removed under vacuum. The residue was then recrystallized from toluene at −18 °C. Yield: 190 mg (93%) of a white powder that is sensitive to air and moisture, m.p. 93−95 °C. ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 1.00 [d, $^3J_{H,H}$ = 6.8 Hz, 24 H, CH(CH_3)$_2$], 3.42 [m, $^3J_{H,H}$ = 6.8 Hz, 4 H, CH(CH$_3$)$_2$], 6.83 (s, 1 H, CH−CH=N), 7.05 (s, 1 H, CH−CH=N), 7.68 (s, 1 H, N−CH=N) ppm. ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = −20 (Δν$_{1/2}$ = 400, $^2J_{B,H}$ = 90 Hz, BH_3), 28 [Δν$_{1/2}$ = 360 Hz, N−B(NiPr$_2$)$_2$] ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 24.4 [CH(CH$_3$)$_2$], 47.3 [CH(CH$_3$)$_2$], 123.1 (CH−CH=N), 126.7 (CH−CH=N), 140.3 (N−CH=N) ppm.

(Diisopropylamino)diiodoborane: Diisopropylamine (160 mg, 1.6 mmol) in toluene (30 mL) was added dropwise at −50 °C to a solution of BI_3 (310 mg, 0.8 mmol) in toluene (100 mL), after which the mixture was refluxed for 5 h. After removal of the diisopropylammonium iodide by filtration, the solvent of the resultant yellow solution was removed in vacuo. The product was recrystallized from hexane/toluene at −15 °C. Yield 170 mg (60%) of a yellow powder that is sensitive to air and moisture, m.p. (decomp.) > 100 °C. ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 1.4 [br., 24 H, CH(CH_3)$_2$], 4.3 [br., 4 H, CH(CH$_3$)$_2$] ppm. ^{11}B NMR (64.2 MHz,

Table 1. Crystal data and structure refinement for **3a**, **3b**, **4a**, **8** and **9**

	3a	**3b**	**4a**	**8**	**9**
Empirical formula	$C_{15}H_{31}BN_4$	$C_{17}H_{35}BN_4$	$C_{15}H_{31}B_2F_3N_4$	$C_{20}H_{31}BMoN_4O_5$	$C_{23}H_{38}BMnN_4O_2$
Formula mass	278.3	306.3	346.1	514.2	468.3
Crystal system	orthorhombic	monoclinic	triclinic	monoclinic	monoclinic
Space group	*Pbca*	$P2_1/c$	$P\bar{1}$	$P2_1/n$	$P2_1/c$
Unit cell					
a [Å]	12.5145(5)	7.5352(3)	9.1347(6)	15.525(2)	8.096(1)
b [Å]	14.4572(6)	15.9599(7)	14.3484(9)	25.507(3)	16.961(2)
c [Å]	19.3949(7)	15.9414(7)	15.693(1)	26.559(3)	18.594(3)
α [°]	90	90	82.041(1)	90	90
β [°]	90	95.843(1)	88.996(1)	101.348(3)	93.036(3)
γ [°]	90	90	81.506(1)	90	90
V [Å^3]	3509.0(2)	1907.2(1)	2014.7(2)	10311(2)	2549.6(6)
Z	8	4	4	16	4
Temperature [K]	103	100	190	190	190
Calcd. density [g/cm^3]	1.053	1.067	1.141	1.325	1.220
Absorp. coeff. [mm^{-1}]	0.06	0.06	0.09	0.54	0.54
F(000)	1232	680	744	4256	1000
Crystal size [mm]	0.30 × 0.27 × 0.14	0.28 × 0.30 × 0.31	0.40 × 0.31 × 0.15	0.41 × 0.17 × 0.07	0.52 × 0.14 × 0.12
θ_{max} [°]	32	31	30.5	26.4	32
Index ranges	0/+18, 0/+21, 0/+28	−11/+10, 0/+23, 0/+22	−13/+13, −20/+20, 0/+22	−19/+19, 0/+31, 0/+33	−12/+11, 0/+25, 0/+27
No. of reflections					
collected	37980	16411	33771	68628	23848
unique	6067	6439	12252	21094	8510
Parameters	327	339	681	1155	432
Final *R* indices					
*R*1 [$I > 2\sigma(I)$]	0.044	0.043	0.055	0.046	0.042
*wR*2	0.128	0.120	0.171	0.116	0.115
Largest diff. peak/hole [e/Å^3]	0.41/−0.17	0.49/0.20	0.86/−0.60	0.75/−0.68	0.46/−0.32

$CDCl_3$): δ = −1 ($\Delta\nu_{1/2}$ = 30 Hz) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 21.9 [$CH(CH_3)_2$], 58.6 [$CH(CH_3)_2$] ppm. CI-MS: *m*/*z* (%) = 238 (100) $[M - I + H]^+$.

1-Bis[diisopropylamino)boryl]imidazole(N^3−*Mo*)(Pentacarbonyl)-molybdenum (8): A solution of freshly prepared $Mo(CO)_5$thf (150 mg, 0.5 mmol) in THF (30 mL) was slowly added to **1a** (140 mg, 0.5 mmol), dissolved in THF (50 mL) at −78 °C. After warming to room temperature and stirring, a brown solution formed. The solvent was then removed in vacuo and the remaining brown oil extracted with toluene. After filtration, the product was crystallized at −30 °C. Yield 170 mg (56%) of a yellow powder that is sensitive to air and moisture (containing traces of **3a**), m.p. (decomp.) > 100 °C. ^1H NMR (200.1 MHz, $[D_8]$THF): δ = 1.04 [d, $^3J_{H,H}$ = 6.8 Hz, 24 H, $CH(CH_3)_2$], 3.47 [m, $^3J_{H,H}$ = 6.8 Hz, 4 H, $CH(CH_3)_2$], 6.90 (s, 2 H, CH−CH=N), 7.43 (s, 1 H, N−CH=N) ppm. ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = 27 ($\Delta\nu_{1/2}$ = 145 Hz) ppm. ^{13}C NMR (50.3 MHz, $[D_8]$THF): δ = 24.0 [$CH(CH_3)_2$], 25.5 [$CH(CH_3)_2$], 48.2 [$CH(CH_3)_2$], 48.5 [$CH(CH_3)_2$], 123.1 (CH−CH=N), 129.1 (CH−CH=N), 129.3 (CH−CH=N), 129.7 (CH−CH=N), 132.6 (N−CH=N), 142.8 (N−CH=N) ppm. IR (THF): $\tilde{\nu}$ = 1979 (s), 1933 (vs), 1891 (w) cm^{-1}.

1-[Bis(diisopropylamino)boryl]imidazole(N^3−*Mn*)Dicarbonyl[η^5-(methylcyclopentadienyl)]manganese (9): The same procedure as for the preparation of **8** was used by treating freshly prepared Cp′$Mn(CO)_2$thf (130 mg, 0.5 mmol) with **1**(139 mg, 0.5 mmol). Crystallization from toluene yielded orange crystals (112 mg, 48%), which are sensitive to air and moisture, m.p. (decomp.) > 110 °C. ^{11}B NMR (64.2 MHz, $[D_8]$THF): δ = 32 ($\Delta\nu_{1/2}$ = 145 Hz) ppm. ^{13}C NMR (50.3 MHz, $[D_8]$THF): δ = 13.5 [$CH(CH_3)_2$], 47.8 [$CH(CH_3)_2$], 83.0 [CH_3(Cp)], 83.4 [CH_3(Cp)], 122.4 (CH−CH=N), 129.4 (CH−CH=N), 142.3 (N−CH=N), 226.7 (C=O) ppm. IR (THF): $\tilde{\nu}$ = 2017 (s), 1928 (vs) cm^{-1}.

Crystal Structure Determinations of 3a, 3b, 4a, 4f, 8, and 9: Crystal data and details of the structure determinations are listed in Table 1. Unique sets of intensity data were collected at low temperature with a Bruker−AXS SMART 1000 diffractometer (Mo-K_α radiation, λ = 0.71073 Å, graphite monochromator, ω-scan). Empirical absorption corrections were applied. The structures were solved by direct methods (SHELXS-86)[15] and refined by least-squares methods based on F^2 with all measured reflections (SHELXS-97).[16] All non-hydrogen atoms were refined anisotropically. The imidazole ring in **3a** is disordered. CCDC-193535 (**3a**), -193536 (**3b**), -193537 (**4a**), -193538 (**8**), -193539 (**9**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk).

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