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Synthesis and Structure of Stable α-Boranyldiazomethanes: 1,3-Di-*tert*-butyl-2,3-dihydro-1*H*-1,3,2-diazaborolyl-(trimethylsilyl)diazomethane and 1,3-diethyl-2,3-dihydro-1*H*-1,3,2-benzodiazaborolyl-(trimethylsilyl)diazomethane

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Summary: Reaction of equimolar amounts of $Me_3SiC(N_2)Li$ *with the 2-bromo-2,3-dihydro-1H-1,3,2-diazaborolederivatives* $tBuNCH{=}CHN(tBu)BBr$ (**1**), $EtN{-}C(CH{=}CH{-}CH{=}CH)CN(Et)BBr$ (**3**), *and* $tBuNCH{=}C(CH{=}CH{-}CH{=}CH)N{-}B{-}Br$ (**5**) *afforded the 1,3,2-diazaborolyldiazomethanes* $tBuNCH{=}CHN(tBu)B{-}C(N_2)SiMe_3$ (**2**), $EtN{-}C(CH{=}CH{-}CH{=}CH)C{-}N(Et)B{-}C(N_2)SiMe_3$ (**4**), *and* $tBuNCH{=}C(CH{=}CH{-}CH{=}CH)N{-}B{-}C(N_2)SiMe_3$ (**6**). *The X-ray structure analysis of* **2** *revealed a planar five-membered heterocycle which is linked to the carbon atom of the diazomethyl unit via a B−C single bond. π-Interactions between this carbon atom and the boron atom can thus be excluded.*

Introduction

Diazoalkanes are important 1,3-dipoles, which undergo [3+2] cycloadditions with a variety of π-systems as dipolarophiles, in particular, acetylenes,[1] alkenes,[1] thiocarbonyls,[1] phosphaalkynes,[2] and phosphaalkenes.[3] Main-group-element-functionalized diazo compounds have been carefully studied with the exception of group 13 elements. Only two examples of tractable C-substituted α-boryldiazoalkanes with tricoordinate boron atoms are performed in the literature. Ethyl(1,3,2-benzodioxaborol-2-yl)diazoacetate **I** was obtained as a yellow oil from the reaction of $LiC(N_2)CO_2Et$ or $Hg[C(N_2)CO_2Et]_2$ with 2-chloro-1,3,2-benzodioxaborole.[4] In an inert gas atmosphere solutions of **I** are stable at 0 °C for days. The characterization of the compound was limited to spectroscopy. Thermally stable $(iPr_2N)2BC(N_2)H$ (**II**) was synthesized from bis(diisopropylamino)chloroborane and an ethereal solution of $LiC(N_2)H$ at −78 °C.[5] Diazoalkane **II** was isolated as a yellow oil by vacuum distillation and characterized by IR and NMR.

Treatment of boraalkene $iPr_2N{=}B{=}C(SiMe_3)_2$ with trimethylsilyl azide led to an instable product, which on the grounds of an intense band at $\nu = 2041\ cm^{-1}$ in the IR spectrum was regarded as boryldiazoalkane $(iPr_2N)[(Me_3Si)_2N]B{-}C(N_2)SiMe_3$ (**III**).[6]

In addition, a few diazocompounds with tetracoordinate B atoms were reported. Compound $Me_2(H)N{\rightarrow}B(CF_3)_2C(N_2)CO_2Et$ **IV** resulted from the reaction of $(CF_3)_2B{=}NMe_2$ with ethyl diazoacetate,[7] whereas the first α-diazoalkylborates $(iPr_2N)_2(Cl)PC(N_2)BX_3$ (X = F, H) **V** where synthesized from the diazomethylenephosphorane and BF_3 or BH_3, respectively.[8]

The paucity of this class of compounds is presumably due to the ability of Lewis acids to initiate the decomposition of diazoalkanes.[9] π-Electron-donating heteroatoms at the boron atoms in **I** and **II** decrease its electron-definciency and add to the stability of the compounds. An interesting question that remained open concerns the π-interaction of the carbon atom with the boron atom (limiting formula B), as it is observed in boron-stabilized carbanions.[10]

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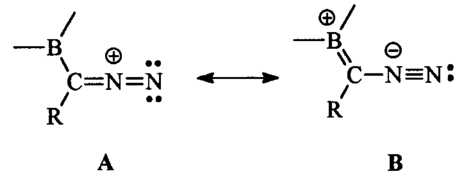
Scheme 1



Experimental Section

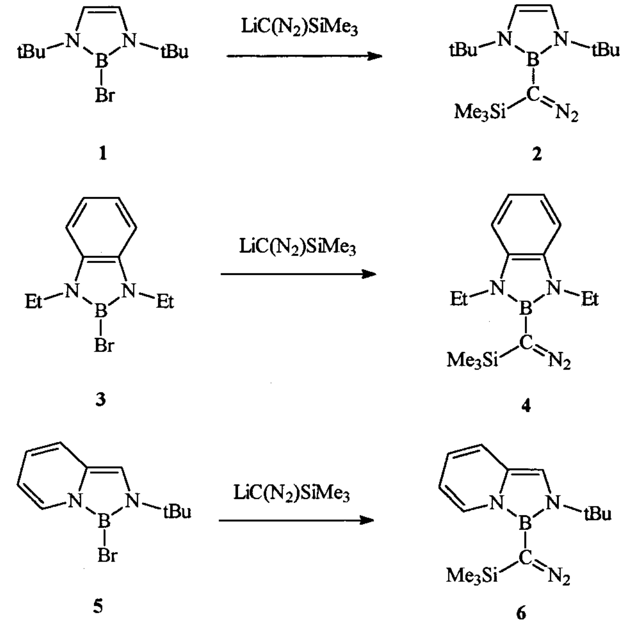
All operations were performed under dry, oxygen-free dinitrogen using standard Schlenk techniques. Solvents were dried by standard methods and freshly distilled under nitrogen prior to use. ^{1}H, ^{11}B, ^{13}C, and ^{29}Si NMR spectra were recorded in C_6D_6 with Bruker AC 100 (^{1}H, 100.13 MHz, ^{11}B, 32.13 MHz) and Bruker Avance DRX 500 (^{1}H, 500.13 MHz, ^{11}B, 160.46 MHz, ^{13}C, 125.75 MHz, ^{29}Si, 99.36 MHz). References: $SiMe_4$ (^{1}H, ^{13}C, ^{29}Si), $BF_3{\cdot}OEt_2$ (^{11}B).

Compounds *t*BuN−CH=CH−N(*t*Bu)BBr (**1**),[11] Et−N−C-(CH=CH−CH=CH)CN(Et)BBr (**3**),[12]and *t*BuN−CH=C(CH=CH−CH=CH)N−BBr (**5**)[13] were synthesized according to literature procedures. A hexane solution of $Me_3SiC(N_2)H$ was purchased commercially.

{*t*BuN−CH=CH−N(tBu)B}C(N$_2$)SiMe$_3$ (2). A solution of 1.5 mL of a 1.6 M solution of *n*-butyllithium (2.4 mmol) in *n*-hexane was added dropwise to a chilled (−78 °C) solution of 1.10 mL of a 2 M solution of (trimethylsilyl)diazomethane in *n*-hexane, and the resulting mixture was stirred for 2 h. Then a solution of **1** (0.56 g, 2.16 mmol) in *n*-hexane (10 mL) was slowly added. It was warmed to 20 °C and stirred for another 3 h. Solvent was removed in vacuo, and to the residue *n*-pentane was added (20 mL). It was filtered, and the filtrate was evaporated to dryness. The residue was distilled by means of a hot-air gun (10^{-6} bar, 300 °C air temperature). The yellow waxy distillate was crystallized from *n*-pentane at −28 °C to afford colorless crystalline **2** (0.48 g, 76% yield). ^{1}H NMR: δ 0.17 (s, 9H, $SiCH_3$), 1.37 (s, 18H, *t*Bu), 6.32 (s, 2H, CH=CH). ^{13}C{^{1}H} NMR: δ −0.7 ($SiMe_3$), 31.9 [s, $C(CH_3)_3$], 53.0 [s, $C(CH_3)_3$], 113.9 (s, HC=CH). ^{11}B{^{1}H} NMR: δ 21.0 s. ^{29}Si{^{1}H} NMR: δ 2.6 s. MS (CI/NH$_3$): *m*/*z* (relative intensity) 293 (100) [M^{+}]. IR (NaCl): ν 2048 s (CN_2) cm^{-1}. Anal. Calcd for $C_{14}H_{29}BN_4Si$ (292.30): C, 57.53; H, 10.00; N, 19.17. Found: C, 57.33; H, 9.99; N, 19.52.

{EtN−C(CH=CH−CH=CH)C−N(Et)B}C(N$_2$)SiMe$_3$ (4). A solution of 2.4 mmol of $Me_3SiC(N_2)Li$ was prepared at −78 °C as described before. Then a solution of **3** (0.51 g, 2.0 mmol) in *n*-hexane (10 mL) was slowly added. The resulting mixture was warmed to ambient temperature and stirred for another 3 h. It was worked up as before, and product **4** was isolated as a light yellow oil by distillation (10^{-6} bar, 300 °C air temperature) (0.46 g, 81% yield). ^{1}H NMR: δ 0.14 (s, 9H, $SiCH_3$), 1.10 (t, $^{3}J_{HH}$ = 7.1 Hz, 6H, CH_2CH_3), 3.55 (q, $^{3}J_{HH}$ = 7.1 Hz, 4H, CH_2CH_3), 6.90 (m, 2H, NCC*H*), 7.07 (m, 2H, NC−CH=C*H*). ^{13}C{^{1}H} NMR: δ −0.5 (s, $SiCH_3$), 16.0 (s, CH_3), 37.9 (s, CH_2), 109.0 (s, NC*C*H), 119.2 (s, NC−CH=*C*H), 137.8 (s, N−C=C−N). ^{11}B{^{1}H} NMR: δ 26.4 s. ^{29}Si{^{1}H} NMR: δ 1.2 s. MS (CI/NH$_3$): *m*/*z* (relative intensity) 287 (100) [M^{+}]. IR (NaCl): ν 2049 s (CN_2) cm^{-1}. Anal. Calcd for $C_{14}H_{23}BN_4Si$ (286.26): C, 58.74; H, 8.10; N, 19.57. Found: C, 58.54; H, 8.12; N, 19.52.

Scheme 2



tBuNCH=C(CH=CH−CH=CH)N−B−C(N$_2$)SiMe$_3$ (6). A solution of 6.8 mmol of (trimethylsilyl)diazomethane in *n*-hexane was combined at −78 °C with 5.6 mmol of *n*-butyllithium as described before. To the reaction mixture was slowly added a solution of 1.28 g (5.1 mmol) of **5** in 20 mL of toluene. It was warmed to room temperature, stirred for 3 h, and evaporated to dryness. The dark residue was extracted with *n*-pentane (20 mL) and filtered. Volatiles were removed in vacuo to give crude **6** (1.27 g, 87% yield). This material could not be purified without decomposition. ^{1}H NMR: δ 0.07 (s, 9H, $SiCH_3$), 1.39 (s, 9H, *t*Bu), 5.67 (t, $^{3}J_{HH}$ = 7.0 Hz, CH); 6.12 (m, 1H, CH), 6.36 (s, 1H, *t*BuN-CH), 6.68 (d, $^{3}J_{HH}$ = 9.4 Hz, 1H, CH), 7.39 (d, $^{3}J_{HH}$ = 7.1 Hz, CH). ^{11}B{^{1}H} NMR: δ 19.4 s. ^{29}Si{^{1}H} NMR: δ 2.45 s. MS (CI)/NH$_3$): *m*/*z* (relative intensity) 287 (33) [M^{+}]. IR (NaCl): ν 2048 s (CN_2) cm^{-1}.

Results and Discussions

Reaction of lithio(trimethylsilyl)diazomethane and 1 equiv of 2,3-dihydro-1*H*-1,3,2-diazaborole derivates **1**, **3**, and **5** in *n*-hexane or *n*-hexane/toluene mixtures in the temperature range −78° and +20 °C afforded the 1,3,2-diazaborolyl(trimethylsilyl)diazomethanes **2**, **4**, and **6** in good yields. Whereas compounds **2** and **4** are thermally robust enough to be purified by vacuum distillation, diazoalkane **6** could not be purified due to its thermolability. Its air and moisture sensitivity prevented chromatography. Product **2** was obtained in the form of colorless crystals from *n*-pentane. Analytically pure **4** remained as a light yellow oil.The IR spectra of the product confirmed the presence of a diazo function by an intense band at ν = 2048 cm^{-1} for the asymmetric CN_2 stretching vibration. In diazoalkane **II** a strong IR absorption at 2071 cm^{-1} (ν CN_2) was observed.[5] The ^{11}B{^{1}H} NMR spectrum of **2** shows a singlet at δ 21.0, which is best compared with the resonances of 2-alkenyl-2,3-dihydro-1*H*-diazaboroles (δ 21.1−23.4).[14] The signal occurs amidst that of 2-alkynyl-1,3,2-diazaboroles

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(δ 15.7) and 2-*n*-alkyl-1,3,2-diazaboroles (δ 26.4).[15] Similar observations were made for **4**, the ^{11}B NMR resonance of which (δ 26.4) falls in the range for EtN−C(CH═CH−CH═CH)C−N(Et)B−X: from δ 15.7 (X = CN) and δ 29.7 (X = CH_3).[12] The ^{11}B NMR signals of 1,2-dihydro[1,3,2]-diazaborolo[1,5α]pyridine *t*BuNCH═C(CH═CH−CH═CH)N−B−X range from δ 8.9 (X = CN) to δ 19.9 (X = S*t*Bu), which includes the ^{11}B NMR signal of **6** (δ 19.4).[13] The ^{1}H NMR spectrum of **2** is characterized by three singlets at δ 0.17, 1.37, and 6.32, which are readily assigned to the hydrogens of the trimethylsilyl, *tert*-butyl, and CH═CH moieties. The ^{13}C nuclei of the HC═CH group in **2** give rise to the resonance at δ 113.9, which compares well with the situation in 2-alkenyl-1,3,2-diazaboroles (δ 112.7−114.2).

X-ray Structural Analysis of 2. The structure of **2** was confirmed by an X-ray crystal structure analysis.[16]

Single crystals of the compound were grown from *n*-pentane at −30 °C. An essential structural feature is a planar five-membered heterocycle which is connected to the trigonal-planar carbon atom (sum of angles 360.0°) of the diazomethyl group via a BC single bond of 1.575(2) Å. In the 2-alkenyl-1,3,2-diazaborole *t*BuN−CH═CH−N(*t*Bu)B−CH═C(Ph)$SnMe_3$ a boron−carbon bond length of 1.581(5) Å was measured.[14] A bonding B−C π-interaction therefore has to be excluded. In line with this, the plane defined by the atoms C(11), Si(1), N(3), and N(4) is orientad nearly perpendicularly to the plane of the heterocycle (interplanar angle 89.4°). The distances C(11)−N(1) [1.300(2) Å] and N(3)−N(4) [1.139(2) Å] well resemble the corresponding bond lengths in $\{(iPr_2N)_2P\}_2CN_2$ [1.28(1) and 1.15(1) Å][17] and are in the range usually observed for diazoalkanes, namely, 1.28−1.32 and 1.12−1.15 Å, respectively.[17] The valence angle at N(3) is 179.1(1)°. The angle B(1)−C(11)−Si(1) of 128.3(1)° is markedly more obtuse than the two remaining angles at C(11) [114.4(1)° and 117.3(1)°], which could mirror the steric strain between the trimethylsilyl group and the *tert*-butyl substituents. As a result of this steric congestion, the exocyclic angles C(11)−B(1)−N(1) [127.6(1)°] and C(11)−B(1)−N(2) [126.8(1)°] exceed angles C(1)−N(1)−C(3) [118.9(1)°] and C(2)−N(2)−C(7) [120.5(1)°]. The bonding parameters within the 1,3,2-diazaborole ring are normal and deserve no further comment.[18]

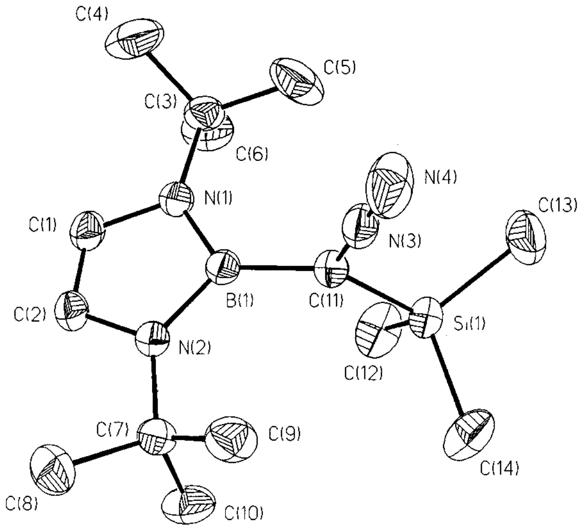

Figure 1.

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Supporting Information Available: Tables of X-ray data, atomic coordinates, thermal parameters, and complete bond lengths and angles and thermal ellipsoid plots for compound **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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