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Formation of a dihydroborole by catalytic isomerization of a divinylborane†

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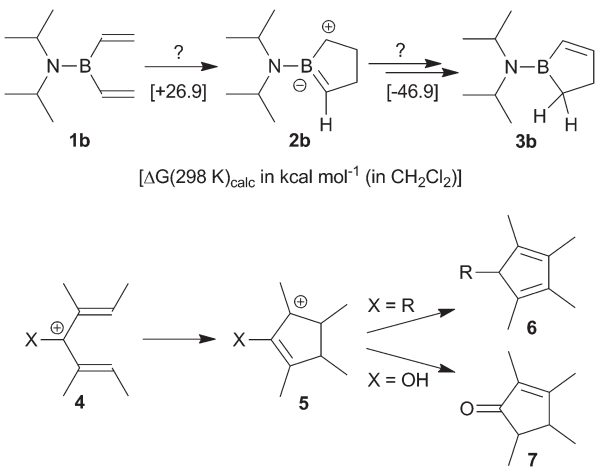
Diphenylamino(divinyl)borane (**1a**) adds two molar equivalents of Piers' borane [$HB(C_6F_5)_2$] to give the expected double hydroboration product. In contrast diisopropylamino(divinyl)borane (**1b**) reacts cleanly already with one molar equivalent of $HB(C_6F_5)_2$ to give the α-borylated tetrahydroborole derivative **10** in good yield. Subsequent treatment of **10** with benzaldehyde proceeded by retro-hydroboration to give the hydroboration product of the aldehyde plus the dihydroborole **3b**. We were able to achieve the divinylborane to dihydroborole isomerization (**1b** to **3b**) catalytically: treatment of diisopropylamino(divinyl)borane (**1b**) with 15 mol% of Piers' borane at elevated temperature gave (diisopropylamino)dihydroborole **3b** in good yield.

Introduction

Organic pentadienyl cations can be cyclized to give their cyclopentenyl cation isomers.[1] This thermally induced electrocyclization reaction provides the principal basis for a variety of important synthetic protocols such as *e.g.* the acid induced formation of many substituted cyclopentadienes from the respective bis(alkenyl)carbinols[2] or the Nazarov cyclization of pentadienones to the corresponding cyclopentenone products (Scheme 1) under strongly acidic reaction conditions.[3]

Boron containing heterocycles serve as important building blocks *e.g.* in organic materials chemistry.[4] Therefore, developing novel synthetic entries to cyclic boron derivatives *e.g.* dihydroboroles, is of an increasing interest.[5] Since divinylboranes are isoelectronic neutral organoelement analogues of the organic pentadienyl cations one might have envisaged that some such systems might be prone to isomerization to give the dihydroborole heterocycles. A DFT study (see below) will show for the example investigated in this study that the thermal divinylborane to dihydroborole rearrangement is very unlikely to become realized.[6] However, we found a surprising solution to carry out this interesting cycloisomerization reaction by taking a completely different catalytic pathway. These new developments will be described in this article.



Scheme 1

Results and discussion

The DFT study

We investigated the potential thermally induced ring closure reaction of (diisopropylamino)divinylborane (**1b**, preparation see below) to its corresponding dihydroborole isomer (**3b**) *via* the hypothetical intermediate **2b** (see Scheme 1), the putative diisopropylaminoboron analogue of the cyclopentenyl cation intermediate in the pentadienyl cation ring closure sequence.

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† Electronic supplementary information (ESI) available: Additional experimental and analytical details, spectral data and crystallographic data for all compounds described. CCDC 982551–982553 and 983316. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4dt01423e

‡ X-ray crystal structure analyses.

§ Computational chemistry. B. S. is member of the Center for Multiscale Theory and Computation (CMTC) of the University of Münster.

The calculation was carried out using the double hybrid density functional B2PLYP with the D3 dispersion correction and the large Gaussian AO basis set def2-TZVP. Thermal and solvent corrections (at 298.15 K with solvent CH_2Cl_2) were included to yield ΔG values of about 1–2 kcal mol^{-1} accuracy (for details see the ESI†).[7] The overall **1b** to **3b** cyclization reaction is strongly exergonic, both in the gas phase and in solution (CH_2Cl_2). The overall conversion of a pair of C=C double bonds to a combination of a C–C single bond and a C=C double bond in the product shows the expected high exergonicity of *ca.* 20 kcal mol^{-1}. However according to this DFT calculation the formation of the potential intermediate **2b** in this cyclization of the divinylborane (**1b**) is strongly endergonic, namely by ΔG(298 K) = +27.6 kcal mol^{-1}, in the gas phase. In solution the energetic situation is actually quite similar (CH_2Cl_2: ΔG(298 K) = +26.9 kcal mol^{-1}). Since the activation barrier of the **1b** to **2b** interconversion would probably be even markedly higher it is unlikely that a thermally induced overall **1b** to **3b** ring closing isomerization can easily be realized. We actually could confirm this experimentally. Even prolonged heating of the divinylborane starting material **1b** at 200 °C did not lead to the desired compound (for details see the ESI†). However, we found a different way for synthesizing **3b** from **1b** in a rather convenient way.

Experimental studies, stoichiometric reactions

We first used (diphenylamino)divinylborane (**1a**) as the starting material that we reacted with Piers' borane [$HB(C_6F_5)_2$].[8] It was prepared by treatment of $(Ph_2N)BCl_2$ [9] with a slight excess (2.5 mol equivalent) of vinylmagnesium bromide in THF–ether. The product **1a** was obtained as a colorless crystalline solid in 76% yield. In solution it shows the typical $^1H/^{13}C$ NMR features of the pair of symmetry-equivalent vinyl substituents at boron (^1H: δ 6.02, 5.87, 5.85; ^{13}C: δ 139.0, 134.1) and a typical ^{11}B NMR resonance at δ 39.0.

Compound **1a** was characterized by an X-ray crystal structure analysis (see Fig. 1). There are two crystallographically independent molecules in the crystal, but they are chemically equivalent. Compound **1a** shows a planar arrangement of the four carbon substituents at the central N=B unit[9c,10] [molecule A: N1A–B1A: 1.416(2) Å, $\sum N1^{BCC}$ = 360.0°, $\sum B1^{NCC}$ = 360.0°, θ C11A–N1A–B1A–C1A: −4.5(2)°; molecule B: N1B–B1B: 1.419(2) Å, $\sum N1^{BCC}$ = 360.0°, $\sum B1^{NCC}$ = 360.0°, θ C11B–N1B–B1B–C1B: 5.8(2)°]. The phenyl substituents at nitrogen are both rotated out of the central molecular plane. The divinylborane subunit in **1a** has attained a U-shaped conformation [molecule A: B1A–C1A: 1.559(2) Å, C1A–C2A: 1.317(2) Å, B1A–C3A: 1.561(2) Å, C3A–C4A: 1.322(2) Å, θ C2A–C1A–B1A–C3A: −28.0(2)°, C1A–B1A–C3A–C4A: −29.0 (2)°; for further details see the ESI†].

We then reacted the divinylborane **1a** with Piers' borane [$HB(C_6F_5)_2$] in toluene in a 1 : 2 molar ratio. Hydroboration took place rapidly at both vinyl groups at r.t. Workup including crystallization from pentane at −32 °C over 2 d eventually gave the product **8** as a crystalline solid in a *ca.* 50% yield (Scheme 2). In solution we have monitored a ^{11}B NMR signal of the symmetry-equivalent pair of newly introduced $B(C_6F_5)_2$ groups at δ 70.7, *i.e.* in a typical range of strongly Lewis acidic trigonal planar $RB(C_6F_5)_2$ boranes. The ^{11}B NMR resonance of the Ph_2N=B unit occurs at δ 47.5. In addition we have observed the typical ^{19}F NMR signals of the $B(C_6F_5)_2$ substituents [δ −130.3 (*o*), −149.2 (*p*), −162.2 (*m*)] and the $^1H/^{13}C$ NMR features of the phenyl substituents at nitrogen. The pair of $-CH_2-CH_2-$ groups bridging between the boron atoms give rise to ^1H NMR signals at δ 1.97 and 0.95, respectively (^{13}C: δ 25.8, 11.7).

We followed the reaction by *in situ* NMR spectroscopy. In CD_2Cl_2 solution the reaction between **1a** and $HB(C_6F_5)_2$ was complete after *ca.* 20 min at r.t. We monitored the formation of two 1 : 2 addition products in a *ca.* 80 : 20 ratio, the major of which we have tentatively assigned the structure of **8**. The minor product was not positively identified. From the NMR spectra it could contain a unit derived from Markovnikov borane addition. The reaction between **1a** and $HB(C_6F_5)_2$ in a 1 : 1 molar ratio was more complex: it gave a mixture containing **8** and remaining unreacted **1a** as the major components plus some unidentified minor products (for details including the depicted spectra see the ESI†).

Compound **8** was characterized by X-ray diffraction (see Fig. 2). In the crystal it features a close to C_2-symmetric structure. The central Ph_2N=B unit shows a short N1–B1 bond (1.407(6) Å). The $CH_2-CH_2-B(C_6F_5)_2$ moieties attached at the boron atom B1 each show a close to antiperiplanar conformational orientation (θ B1–C1–C2–B2 173.9(4)°, B1–C3–C4–B3 167.6(4)°, B1–C1 1.591(6) Å, B1–C3 1.568(6) Å, B2–C2 1.558(6) Å,

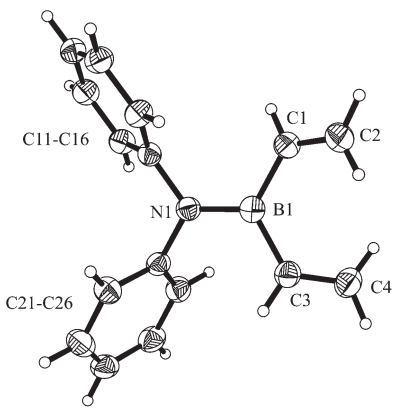
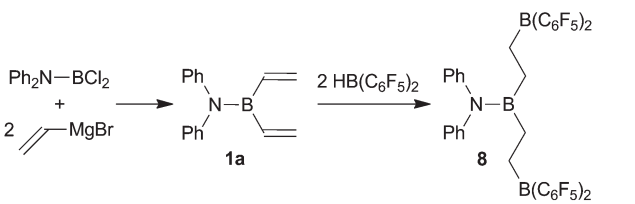


Fig. 1 Molecular structure of compound **1a** (thermal ellipsoids are shown with 30% probability).



Scheme 2

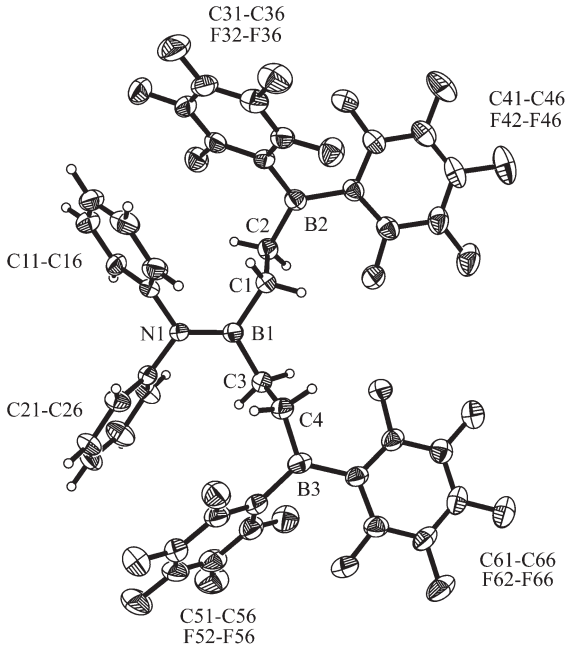


Fig. 2 A view of the molecular structure of compound **8** (thermal ellipsoids are shown with 30% probability).

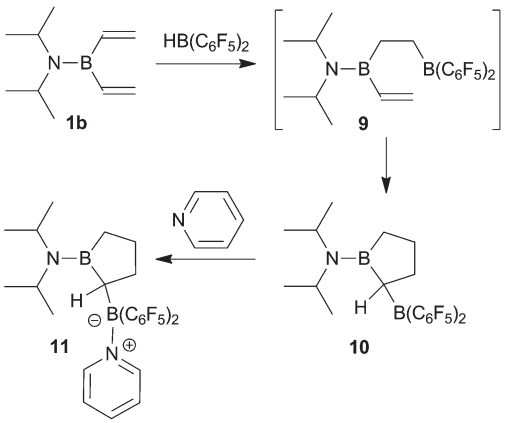
B3–C4 1.551(6) Å). The bonding geometry at the nitrogen N1 atom is trigonal planar ($\sum N1^{BCC}$ = 360.0°) as well as the bonding geometries at all three boron atoms in compound **8** ($\sum B1^{NCC}$ = 360.0°, $\sum B2^{CCC}$ = 359.7°, $\sum B3^{CCC}$ = 359.8°).

We prepared the slightly more bulky starting material **1b** analogously by treatment of $(^{i}C_3H_7)_2NBCl_2$[9] with a slight excess (2.8 equiv.) of vinylmagnesium bromide in THF–ether. The product **1b** was obtained as a colorless oil in 43% yield. It shows a typical ^{11}B NMR feature at δ 37.7 in dichloromethane solution and the typical ^{1}H and ^{13}C NMR signals of the pairs of homotopic vinyl groups at boron and isopropyl substituents at nitrogen (for details see the ESI†).

We treated compound **1b** with Piers' borane [$HB(C_6F_5)_2$]. In contrast to the corresponding reaction of **1a** (see above) it takes only 1 molar equivalent of the borane to achieve a complete conversion of (diisopropylamino)divinylborane to a saturated reaction product. The reaction was complete within *ca.* 15 min at ambient temperature and we isolated the product **10** in >90% yield as a colorless oil. Although we do not know the mechanistic details of this reaction at this time, the formation of the cyclic product **10** can formally be explained by an anti-Markovnikov hydroboration of one of the vinyl units of the starting material (to generate **9**) followed by a formal 1,2-alkylborane addition reaction to the remaining C=C double bond (see Scheme 3).

Compound **10** shows the ^{1}H/^{13}C NMR signals of a pair of chemically inequivalent isopropyl groups at nitrogen each featuring a pair of diastereotopic methyl groups. The compound is characterized by showing two ^{11}B NMR resonances [$B(C_6F_5)_2$: δ 71.7, $^{i}Pr_2NB$: δ 49.2].

For the purpose of further characterization we reacted compound **10** with pyridine.[11] This gave the corresponding



Scheme 3

$B(C_6F_5)_2$(pyridine) adduct **11** that was isolated as a colorless solid in 70% yield. We obtained single crystals from a benzene–pentane solution that allowed for the characterization of compound **11** by X-ray diffraction. In the crystal compound **11** shows a tetrahydroborole framework (see Fig. 3). It has the $B(C_6F_5)_2$(pyridine) unit bonded to carbon atom C1. Its boron atom (B2) shows a typical pseudotetrahedral coordination geometry. The B2–N11 bond length is only slightly shorter than the adjacent B2–C(pentafluorophenyl) bond lengths. Boron atom B1 is part of the five-membered heterocyclic core of compound **11**. It shows a trigonal planar geometry (sum of the bond angles at $\sum B1^{NCC}$: 359.6°) as does the adjacent nitrogen atom N1 (sum of the three bond angles at $\sum N1^{BCC}$: 359.8°). The N1–B1 bond (1.404(2) Å) is much shorter

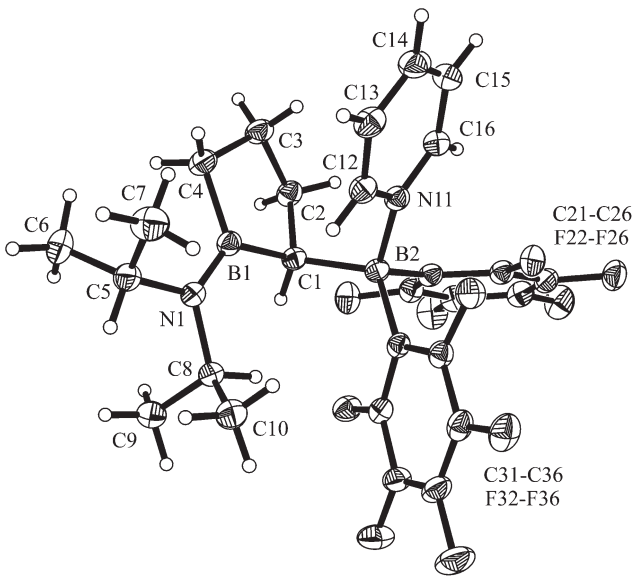


Fig. 3 Molecular structure of compound **11** (thermal ellipsoids are shown with 30% probability). Selected bond lengths (Å) and angles (°); B1–C1 1.615(2), C1–C2 1.573(2), C2–C3 1.528(2), C3–C4 1.525(2), B1–C4 1.600(2), C1–B2 1.646(2), B2–N11 1.636(2), B2–C21 1.667(2), B2–C31 1.666(2), B1–N1 1.404(2), N1–C5 1.487(2), N1–C8 1.482(2), C1–B1–N1 127.4(1), C1–B1–C4 107.6(1), C5–N1–C8 113.7(1), C5–N1–B1–C1 179.6(1).

than the B2–N11 linkage (1.636(2) Å) indicating substantial double bond character of the N1–B1 linkage by nitrogen to boron π-back-donation.

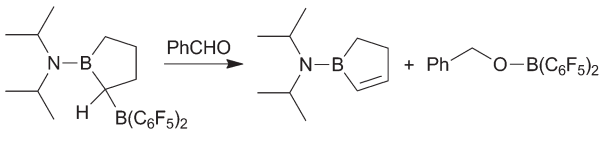
In solution compound **11** shows ^{11}B NMR signals at δ 52.0 and δ 1.9, respectively. The broad [B]CH[B] ^{13}C NMR resonance was observed at δ 23.1.

We also reacted the product **10** with benzaldehyde (r.t., benzene). This resulted in a retro-hydroboration reaction and formation of the dihydroborole product **3b** and compound **12**, the trapping product of the *in situ* liberated borane [HB(C$_6$F$_5$)$_2$] with benzaldehyde (Scheme 4; for the characterization of **3b** see below). Compound **12** was independently synthesized by treatment of benzaldehyde with Piers' borane. Compound **12** was characterized spectroscopically and by an X-ray crystal structure analysis (for details including a view of the molecular structure in the crystal see the ESI†).

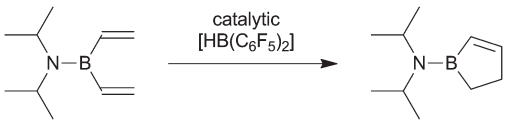
Catalytic dihydroborole formation

The reaction of **10** with benzaldehyde giving **3b** and **12** indicated equilibration of **10** with **3b** and [HB(C$_6$F$_5$)$_2$] by rapid reversible hydroboration/dehydroboration reactions. This observation made it tempting to search for a formation of the dihydroborole **3b** by catalytic conversion of the divinylborane **1b**. This isomerization reaction should be strongly exergonic (see above). We found that compound **3b** can indeed be obtained from **1b** by treatment with catalytic quantities of [HB(C$_6$F$_5$)$_2$] at elevated temperatures. Orientating experiments showed that treatment of **1b** with 5 mol% of [HB(C$_6$F$_5$)$_2$] in toluene solution at 100 °C resulted in a *ca*. 20% conversion to the dihydroborole isomer **3b** within *ca*. 1 d, but then the reaction stopped. Utilization of 10 mol% of the [HB(C$_6$F$_5$)$_2$] catalyst resulted in *ca*. 70% conversion at 100 °C after 2 days, and we obtained a close to quantitative ring closing isomerization of **1b** to **3b** within 1 h at 100 °C by using 15 mol% [HB(C$_6$F$_5$)$_2$] as catalyst. For the catalytic formation of **3b** from **1b** on a preparative scale we used even harsher conditions (*i.e.* 36 h, 200 °C in a sealed ampoule using 8 mol% of the [HB(C$_6$F$_5$)$_2$] catalyst) since we knew about the high thermal stability of the dihydroborole **3b** from separate experiments. Workup involving condensation of the product eventually gave the dihydroborole product **3b** in 62% yield. The reaction on a preparative scale can also be performed using standard glassware, under milder conditions (r.t., 4 days, 15 mol% [HB(C$_6$F$_5$)$_2$]; for details see the ESI†) (Scheme 5).

Compound **3b** shows the ^{1}H/^{13}C NMR resonances of a pair of inequivalent isopropyl substituents at nitrogen. The endocyclic C=C double bond at boron gives rise to ^{1}H NMR signals



Scheme 4



Scheme 5

at δ 7.13 and 6.27 ($^3J_{HH}$ = 8.1 Hz) with corresponding ^{13}C NMR signals at δ 162.0 and 135.4, respectively. The ^{1}H NMR resonances of the remaining CH_2–CH_2–moiety of the heterocycle are detected at δ 2.29 and 1.03 (^{13}C: 32.6 and 15.2). Compound **3b** features a ^{11}B NMR resonance at δ 46.6.

Conclusions

Formally, divinylboranes are the neutral analogues of the pentadienyl cations. Therefore, one might have expected some divinylborane systems undergoing ring-closure reactions similar to their pentadienyl cation analogues. Our DFT results have, however, shown that the formation of **3b** from **1b** by a route involving **2b** is unfavorable because of the high energy content of this zwitterionic borata–alkene/carbenium ion type intermediate.[12] Since the overall **1b** to **3b** isomerization is markedly exergonic we had to search for a different kinetically viable pathway of this ring-closure reaction. It was found in the treatment of **1b** with catalytic amounts of Piers' borane [HB(C$_6$F$_5$)$_2$]. The reaction is likely to involve the intermediates **9** and **10**. The later was isolated upon carrying out the reaction stoichiometrically. It can be assumed that the retro-hydroboration step from **10** may close the cycle in the catalytic variant of this reaction liberating the dihydroborole product **3b** and the chain-propagating borane [HB(C$_6$F$_5$)$_2$]. Thereby the apparently in this case unfavorable "bora-Nazarov" ring closing rearrangement could successfully be circumvented by a completely different catalytic divinylborane to dihydroborole isomerization.

Experimental section

Preparation of 1-(diisopropylamino)-2,3-dihydroborole (3b)

(Diisopropylamino)divinylborane (**1b**) (350 mg, 2.12 mmol) in toluene (8 mL) and bis(pentafluorophenyl)borane (60 mg, 0.17 mmol, 0.08 eq.) were stirred for 15 minutes in an ampoule. Then the ampoule was sealed and taken into an autoclave. After 36 h at 200 °C, all volatiles were carefully removed in vacuum at room temperature. Compound **3b** was condensed from the obtained yellow residue at 8×10^{-3} mbar and 100 °C as a colorless oil (218 mg, 62%). Elemental analysis: calcd for $C_{10}H_{20}BN$: C, 72.76; H, 12.21; N, 8.48. Found: C, 72.79; H, 12.19; N, 8.66. ^{1}H NMR (500 MHz, [D$_8$]-toluene, 298 K): δ = 7.13 (br dm, $^3J_{HH}$ = 8.1 Hz, 1H, =CH), 6.27 (dm, $^3J_{HH}$ = 8.1 Hz, 1H, BCH), 3.48, 3.24 (each hept, $^3J_{HH}$ = 6.8, 6.9 Hz, each 1H, isopropyl CH), 2.29 (m, 2H, CH_2), 1.03

(m, 2H, BCH_2). $^{13}C\{^1H\}$ NMR (126 MHz): δ = 162.0 (=CH), 135.4 (br, BCH=), 50.5, 46.4 (isopropyl CH), 32.6 (CH_2), 15.2 (br, BCH_2). $^{11}B\{^1H\}$ NMR (160 MHz): δ = 46.6.

Preparation of compound 8

The reaction mixture of divinyl(diphenylamino)borane (**1a**) (70 mg, 0.3 mmol) and bis(pentafluorophenyl)borane (208 mg, 0.6 mmol, 2 eq.) in toluene (2 mL) was stirred for 20 minutes. Then the suspension was filtered. The filtrate was concentrated, pentane (0.5 mL) was added and after 2 days at −32 °C compound **8** was obtained as long colorless needles (144 mg, 52%). The obtained crystals were suitable for the X-ray single crystal structure analysis. Elemental analysis: calcd for $C_{40}H_{18}B_3F_{20}N$: C, 51.94; H, 1.96; N, 1.51. Found: C, 51.89; H, 1.85; N, 1.43. In CD_2Cl_2 solution a mixture of **8** and **8′** was detected (*ca.* 79 : 21). *Major isomer* **8**: ^1H NMR (500 MHz, CD_2Cl_2, 298 K): δ = 1.97 (m, 2H, CH_2B), 0.95 (m, 2H, $NBCH_2$). $^{13}C\{^1H\}$ NMR (126 MHz): δ = 25.8 (br, CH_2B), 11.7 (br, $NBCH_2$). ^{19}F NMR (470 MHz): δ = −130.3 (2F), −149.2 (1F), −162.2 (2F). $^{11}B\{^1H\}$ NMR (160 MHz): δ = 70.7 (B), 47.5 (BN). *Minor isomer* **8′**: ^1H NMR (500 MHz): δ = 3.08 (q, $^3J_{HH}$ = 6.4 Hz, 1H, CH), 2.00/1.66 (each m, each 1H, CH_2B), 1.08/0.97 (each m, each 1H, $NBCH_2$), 1.34 (d, $^3J_{HH}$ = 6.4 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (126 MHz): δ = 148.8, 148.4 (i), 129.41, 129.35 (*m*), 128.1, 127.7 (*o*), 126.31, 126.25 (*p*)(Ph), 37.0 (br, CH), 24.5 (br, CH_2B), 10.8 (br, $NBCH_2$), 12.2 (CH_3). ^{19}F NMR (470 MHz): δ = −130.1, −131.3 (each 2F), −149.2^t, −151.5 (each 1F), −162.1, −162.5 (each 2F). $^{11}B\{^1H\}$ NMR (160 MHz): δ = 70.7 (B), 47.5 (BN).

Generation of compound 10

A solution of bis(pentafluorophenyl)borane (69 mg, 0.2 mmol) and (diisopropylamino)divinylborane (33 mg, 0.2 mmol) in dichloromethane (1 mL) was stirred for 15 minutes at room temperature. Then all volatiles were removed in vacuum and a colorless oil was obtained (94.8 mg, 93%). ^1H NMR (600 MHz, CD_2Cl_2, 298 K): δ = 3.36, 3.28 (each hept, $^3J_{HH}$ = 6.7, 7.0 Hz, each 1H, CH), 2.70 (t, $^3J_{HH}$ = 6.8 Hz, 1H, BCH), 1.95/1.74 (each 1H), 1.52 (2H), 1.28/1.11 (each 1H)(CH_2), 1.24/1.23, 0.95/0.87 (each d, $^3J_{HH}$ = 7.0, 6.7 Hz, each 3H, CH_3). $^{13}C\{^1H\}$ NMR (151 MHz): δ = 56.5, 45.6 (CH), 46.5 (br, BCH), 31.9, 27.9, 21.2 (CH_2), 24.2, 24.1, 22.0, 21.5 (CH_3). ^{19}F NMR (564 MHz): δ = −131.0 (2F), −151.4 (1F), −162.4 (2F). $^{11}B\{^1H\}$ NMR (192 MHz): δ = 71.7 (B), 49.2 (BN).

Preparation of compound 11

Compound **10** was generated *in situ* by reaction of (diisopropylamino)divinylborane (**1b**) (33 mg, 0.2 mmol) and bis(pentafluorophenyl)borane (69 mg, 0.2 mmol) in dichloromethane (2 mL). After 15 minutes stirring pyridine (16 μL, 0.2 mmol) was added and the obtained reaction solution was stirred for additional 10 minutes. Then it was concentrated to *ca.* 0.5 mL and pentane (4 mL) was added. Compound **11** was obtained as a colorless solid after storing the reaction mixture at −32 °C for one day (82 mg, 70%). Crystals suitable for the X-ray single crystal structure analysis were obtained from a benzene–pentane solution of compound **11** at −32 °C. M.p.: 120 °C. Decomp.: ~240 °C. Elemental analysis: calcd for $C_{27}H_{26}B_2F_{10}N_2$: C, 54.95; H, 4.44; N, 4.75. Found: C, 54.20; H, 4.21; N, 4.49. ^1H NMR (500 MHz, CD_2Cl_2, 298 K): δ = 3.78, 3.23 (each hept, $^3J_{HH}$ = 6.7, 7.0 Hz, each 1H, CH), 1.91 (br, 1H, BCH), 1.91/1.44, 1.23/0.25, 0.87/0.24 (each 1H, CH_2), 1.17/1.15, 1.02/0.44 (each d, $^3J_{HH}$ = 7.0, 6.7 Hz, each 3H, CH_3). $^{13}C\{^1H\}$ NMR (126 MHz): δ = 52.6, 45.0 (CH), 31.6, 25.3, 21.1 (CH_2), 24.4, 24.2, 22.5, 20.2 (CH_3), 23.1 (br, BCH). ^{19}F NMR (470 MHz): δ = −129.1, −130.0 (each 2F), −159.4, −160.4 (each 1F), −164.5, −165.4 (each 2F). $^{11}B\{^1H\}$ NMR (160 MHz): δ = 52.0 (BN), 1.9 (py-B).

Acknowledgements

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Notes and references

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