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Reaction of a Stable Conjugated Primary Enamine with Piers' Borane

Ilona Peuser,[a] Roland Fröhlich,[a][‡] Gerald Kehr,[a] and Gerhard Erker*[a]

Dedicated to Professor Willi Keim on the occasion of his 75th birthday

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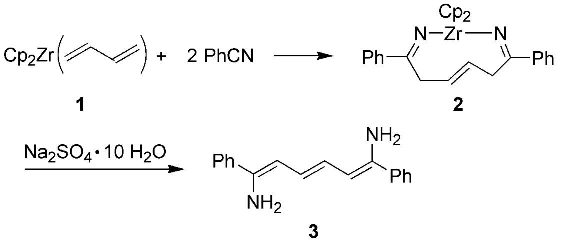
Treatment of 1,6-diamino-1,6-diphenyl-1,3,5-hexatriene (**3**) with 2 mol-equiv. of $HB(C_6F_5)_2$ results in tautomerization of the stable primary enamine to its bis(imine) tautomer, which is stabilized by twofold imine/borane Lewis base/Lewis acid adduct formation to yield an 11:6:1 mixture of *E*,*E*-**5**, *E*,*Z*-**5** and *Z*,*Z*-**5**. Within several hours at room temperature, these systems undergo subsequent hydroboration of the central remaining C=C double bond followed by internal imine–alkylborane coordination to yield the six-membered N,B heterocycle **6** featuring a pendant $–CH_2–C(Ph)=NH[B(H)(C_6F_5)_2]$ group. Compound **6** was characterized by X-ray diffraction.

Introduction

The strong Lewis acid $B(C_6F_5)_3$[1] has been shown to be able to induce tautomerization reactions and to stabilize otherwise unstable carbonyl compounds relative to their favoured enol forms by adduct formation.[2] Piers' borane $[HB(C_6F_5)_2]$[3] is also a strongly electrophilic reagent that might be able to influence tautomerization equilibria in a similar way. At the same time $HB(C_6F_5)_2$ is a reactive hydroboration agent.[4] We will here describe an example where these two reactivities in their combination lead to an interesting product formation. We chose the 1,6-diamino-1,3,5-hexatriene derivative **3** as the substrate for our study. This unusual compound[5–7] was obtained starting from (butadiene)zirconocene (**1**)[8] as described previously by us.[5] The reaction of **1** with 2 mol-equiv. of benzonitrile gave the metallacycle **2** (see Scheme 1). Subsequent controlled hydrolysis removed the zirconocene template to give the stable conjugated primary enamine derivative **3** in good yield. The reaction of **3** with Piers' borane will be described in this account.



Scheme 1.

Results and Discussion

The diaminohexatriene **3** was mixed with 2 mol-equiv. of Piers' borane $[HB(C_6F_5)_2]$ (**4**) in toluene solution at ambient temperature. This resulted in a rapid isomerization reaction of the enamine moieties to their imine isomers combined with imine–borane adduct formation.[9] After removal of the solvent, an oil was obtained that contained three isomeric products: *E*,*E*-**5**, *E*,*Z*-**5** and *Z*,*Z*-**5** in an 11:6:1 ratio. The structure of the very minor compound of this mixture was only tentatively assigned as the third possible isomer *Z*,*Z*-**5** (see Scheme 2, Figure 1).

The ^1H NMR spectrum clearly shows the presence of three primary ketimine isomer adducts. The major component of the mixture features a pair of symmetry-equivalent ketimine moieties [=NH resonance at $\delta = 9.65$ (s, 2 H) ppm (see Figure 1) with a single corresponding ^{13}C NMR resonance at $\delta = 181.7$ ppm]. Consequently, we observe only one ^1H NMR signal of the central –CH=CH– unit at $\delta = 4.99$ ppm (^{13}C NMR: $\delta = 126.8$ ppm) and a single ^1H NMR CH_2 resonance at $\delta = 3.20$ ppm (m, 4 H; ^{13}C NMR: $\delta = 34.7$ ppm). There is a very broad BH ^1H NMR signal (not differentiated between the isomers) at $\delta \approx 4.25$ ppm, and a single broad ^{11}B NMR resonance at $\delta = –15.0$ ppm, as expected for a four-coordinate boron centre. The major component shows three corresponding ^{19}F NMR "borate" signals of the symmetry-equivalent pair of C_6F_5 substituents at the boron atom [$\delta = –134.4$ (*o*), –157.7 (*p*), –163.1 (*m*) ppm]. The small separation of the *p*- and *m*-C_6F_5 ^{19}F NMR resonances further supports the presence of four-coordinate

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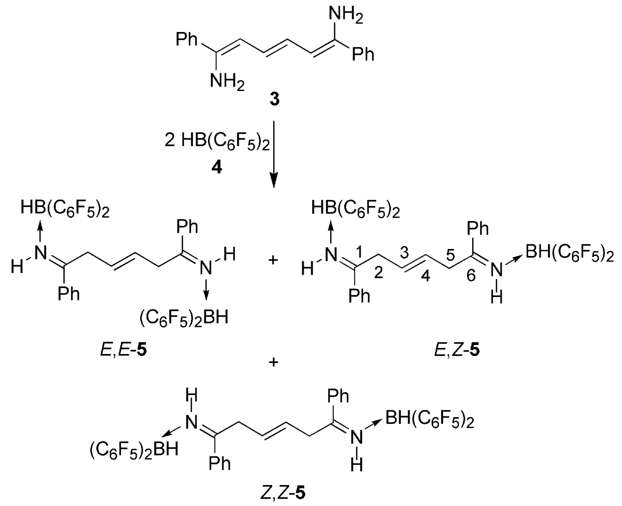
[a] Organisch-Chemisches Institut der Universität Münster,
Corrensstraße 40, 48149 Münster, Germany
Fax: +49-251-8336503
E-mail: erker@uni-muenster.de

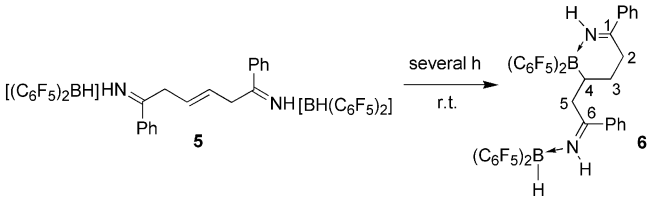
[‡] X-ray crystal structure analysis



Scheme 2.

boron centres[10] in this major product, to which we assign the structure of *E*,*E*-**5**. The second isomer, to which we assign the structure of *E*,*Z*-**5**, shows a 1:1 intensity pair of =NH ^{1}H NMR signals (δ = 9.88, 9.47 ppm; ^{13}C NMR: δ = 184.4, 181.5 ppm). It features a pair of ^{1}H NMR signals of the central (*E*)–CH=CH– unit (δ = 5.17, 4.92 ppm; $^3J_{HH}$ = 15.6 Hz) and a pair of CH$_2$ resonances (δ = 3.53, 2.46 ppm).

Keeping a solution of the mixture of the isomers of **5** in benzene or toluene at room temperature for several hours resulted in the observation of a subsequent rearrangement of all three compounds to give a single new product (see Scheme 3). On a preparative scale this was obtained by treatment of the diaminohexatriene starting material **3** with 2 mol-equiv. of HB(C$_6$F$_5$)$_2$ followed by stirring of the reaction mixture overnight. After removal of the volatiles in vacuo, the obtained solid was washed with pentane and dried to finally give the product **6** in approximately 55% yield as a colourless solid. Compound **6** was characterized by X-ray diffraction (single crystals were obtained from a dichloromethane/pentane solvent mixture) (see Figure 2).



Scheme 3.

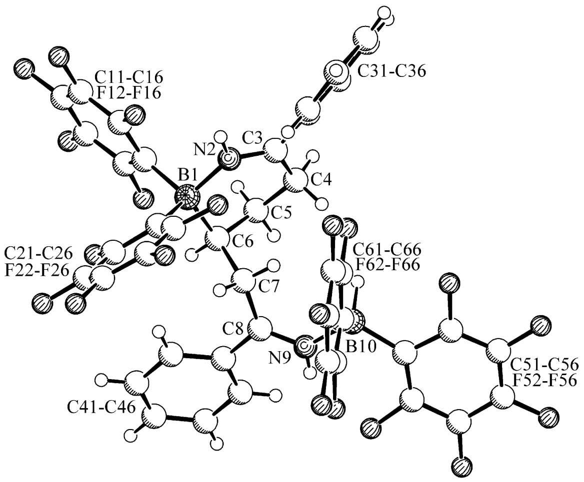


Figure 2. View of the molecular structure of compound **6**.

The result of the X-ray crystal structure analysis shows that one of the HB(C$_6$F$_5$)$_2$ molecules has undergone a hydroboration reaction of the central carbon–carbon double bond of the system. This has resulted in the formation of an alkylborane product that is stabilized by intramolecular B–N(imine) adduct formation of the strongly electrophilic three-coordinate boron centre. Consequently, the new product **6** contains a six-membered heterocyclic subunit that features a strong B–N interaction [B1–N2 1.584(5) Å] to the primary imine functional group. The coordinated imine

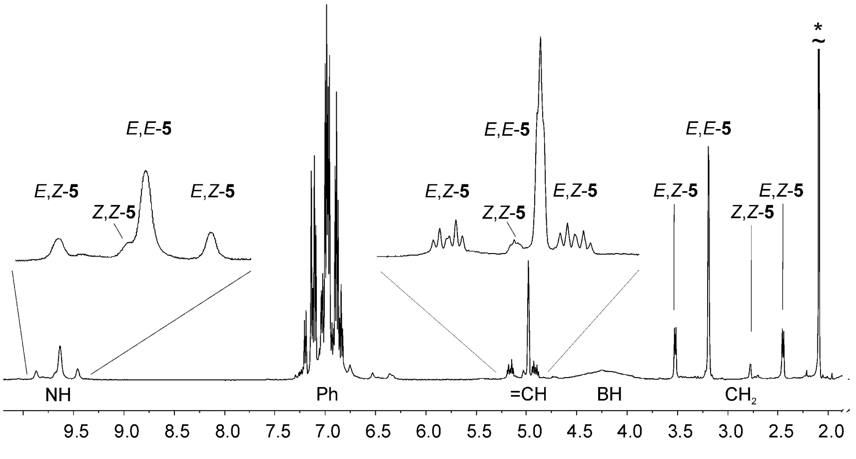


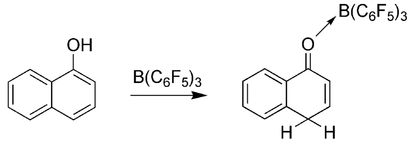
Figure 1. ^{1}H NMR spectrum of the mixture of *E*,*E*-, *E*,*Z*- and *Z*,*Z*-**5** isomers (500 MHz, [D$_6$]benzene, 298 K; *: toluene).

function is characterized by an N2–C3 bond length of 1.293(4) Å and bond angles N2–C3–C4 of 120.1(3)°, N2–C3–C31 of 119.7(3)° and a C3–N2–B1 angle of 129.1(3)°. The boron atom is four-coordinate featuring bond angles of 106.8(3)° (N2–B1–C6), 104.6(3)° (N2–B1–C11), 109.8(3)° (N2–B1–C21), 117.5(3)° (C6–B1–C11), 106.4(3)° (C21–B1–C11) and 111.5(3)° (C6–B1–C21). The six-membered ring attains a distorted cyclohexene-like half-chair conformation (see Figure 2).

Ring-carbon atom C6 bears the –CH_2–imine substituent [C6–C7 1.543(5) Å, C7–C8 1.487(5) Å]. It contains the second imine functionality [pertinent bonding features: C8–N9 1.291(4) Å; angles: C7–C8–N9 120.1(3)°, C7–C8–C41 120.6(3)°, N9–C8–C41 119.2(3)°], which still has the intact second $HB(C_6F_5)_2$ unit coordinated to its nitrogen atom [N9–B10 1.579(5) Å; angle: C8–N9–B10 129.5(3)°]. The boron atom B10 is also tetracoordinate featuring two C_6F_5 substituents, the hydride and the imine moiety bonded to it [B10–C61 1.626(5) Å, B10–C51 1.622(5) Å; angles: N9–B10–C51 111.0(3)°, N9–B10–C61 110.8(3)°, C51–B10–C61 110.2(3)°]. The ^{13}C NMR spectrum of compound **6** shows a pair of iminium-type C=N resonances at δ = 189.9 and 183.0 ppm, respectively. The corresponding =NH ^1H NMR resonances show up as a pair of broad signals at δ = 10.08 and 9.69 ppm. The hydroboration reaction has created a new chiral centre. Therefore, the three CH_2 groups feature pairs of diastereotopic hydrogen atoms each. Also, the pair of C_6F_5 substituents inside the heterocyclic six-membered ring is diastereotopic. This differentiation extends as far as to the terminal *N*-bonded –$B(H)(C_6F_5)_2$ unit. Consequently, we observe a total of four sets of C_6F_5 ^{19}F NMR resonances [$\delta(C_6F_5^A)$ = –134.3 (2 F), –157.7 (1 F), –162.9 (2 F) ppm; $\delta(C_6F_5^B)$ = –134.7 (2 F), –157.4 (1 F), –163.0 (2 F) ppm; $\delta(C_6F_5^C)$ = –135.3 (2 F), –156.6 (1 F), –162.3 (2 F) ppm; $\delta(C_6F_5^D)$ = –135.5 (2 F), –155.8 (1 F), –161.8 (2 F) ppm]. The small $\Delta\delta(m/p)$ difference is typical for a situation involving four-coordinate boron.[10]

Conclusions

This study shows that Piers' borane $HB(C_6F_5)_2$ is a powerful Lewis acid. Similarly, as it had previously been shown for its congener $B(C_6F_5)_3$, the bis(pentafluorophenyl)borane system is able to kinetically effect tautomerization and to thermodynamically stabilize an otherwise unfavourable tautomer by coordination. This had been demonstrated, for example, for $B(C_6F_5)_3$ by the transformation of the naphthol (**7**) to its benzocyclohexadienone tautomer adduct **8** (see Scheme 4);[2] here it is demonstrated for $HB(C_6F_5)_2$ by the transformations of the thermodynamically favoured conjugated diaminohexatriene **3** to the double adduct **5** of its tautomeric bis(imine) form.



7 **8**

Scheme 4.

In contrast to the $B(C_6F_5)_3$ adducts, the $HB(C_6F_5)_2$–imine adducts contain pairs of active H–[B] reagents. One of these is eventually used for the hydroboration of the single remaining C=C double bond, located in the central position of the adducts **5**. The detailed mechanistic pathway of this transformation remains to be studied, but it is clear that the resulting hydroboration products undergo a rapid subsequent intramolecular borane–imine adduct formation that leads to the observed internally stabilized final product **6**. It will be seen whether such internal imine adducts might eventually show reactivities reminiscent of those of remotely related frustrated N/B Lewis pairs.[11,12]

Experimental Section

General Procedures: All syntheses involving air- and moisture-sensitive compounds were carried out by using standard Schlenk-type glassware or in a glove box under argon. Solvents were dried by the procedure according to Grubbs[13] or were distilled from appropriate drying agents and stored under argon. The following instruments were used for physical characterization of the compounds: NMR spectra: Bruker ARX 300 spectrometer (^1H NMR: 300 MHz; ^{13}C NMR: 75 MHz), Bruker AMX 400 (^1H NMR: 400 MHz; ^{13}C NMR: 100 MHz), Varian Inova 500 (^1H NMR: 500 MHz; ^{13}C NMR: 126 MHz; ^{19}F NMR: 470 MHz; ^{11}B NMR: 160 MHz). ^1H NMR and ^{13}C NMR chemical shifts (δ) are given relative to TMS and referenced to the solvent signal (^{19}F NMR rel. to external $CFCl_3$; ^{11}B rel. to external $BF_3{\cdot}Et_2O$). NMR spectroscopic assignments are supported by additional 1D and 2D NMR experiments. Elemental analyses were performed with an Elementar Vario El III. IR spectra were recorded with a Varian 3100 FT-IR (Excalibur Series). Melting points were obtained with a DSC Q20 (TA Instruments). X-ray crystal-structure analysis: Data set was collected with a Nonius KappaCCD diffractometer. Programs used: data collection COLLECT (B. V. Nonius, 1998), data reduction Denzo-SMN,[14] absorption correction Denzo,[15] structure solution SHELXS-97,[16] structure refinement SHELXL-97,[17] graphics SCHAKAL (E. Keller, 1997).

***E*,*E*-/*E*,*Z*-/*Z*,*Z*-5:** 1,6-Diamino-1,6-diphenyl-1,3,5-hexatriene (**3**) (70.0 mg, 0.26 mmol) was dissolved in toluene (20 mL). To this yellow solution bis(pentafluorophenyl)borane (184.5 mg, 0.52 mmol) was added. The reaction mixture was stirred at room temperature for 7 min. Afterwards, the solvent was removed in vacuo. The precipitated yellow oil was washed with pentane (2 × 8 mL) and the now beige solid (192.3 mg, 77%) dried in vacuo overnight. *E*,*E*-**5**/*E*,*Z*-**5**/*Z*,*Z*-**5** = 11:6:1. M.p. 123.3 °C (dec.). ^1H NMR (500 MHz, C_6D_6, 298 K): *E*,*E*-**5**: δ = 9.65 (br. s, 2 H, NH), 6.99 (m, 2 H, *p*-Ph), 6.98 (m, 4 H, *o*-Ph), 6.90 (m, 4 H, *m*-Ph), 4.99 (m, 2 H, 3,4-H), 4.25 (br., 2 H, BH), 3.20 (m, 4 H, 2,5-H) ppm; *E*,*Z*-**5**: δ = 9.88 (br. s, 1 H, NH^1), 9.47 (br. s, 1 H, NH^6), 7.21 (m, 2 H, *o*-Ph^1), 7.05 (m, 1 H, *p*-Ph^1), 7.00 (m, 2 H, *m*-Ph^1), 6.94 (m, 1 H, *p*-Ph^6), 6.87 (m, 2 H, *m*-Ph^6), 6.84 (m, 2 H, *o*-Ph^6), 5.17 (dt, $^3J_{H,H}$ = 15.6, $^3J_{H,H}$ = 6.3 Hz, 1 H, 3-H), 4.92 (dt, $^3J_{H,H}$ = 15.6, $^3J_{H,H}$ = 6.8 Hz, 1 H, 4-H), 4.25 (br., 2 H, BH), 3.53 (d, $^3J_{H,H}$ = 6.2 Hz, 2 H, 2-H), 2.46 (d, $^3J_{H,H}$ = 6.7 Hz, 2 H, 5-H) ppm; *Z*,*Z*-**5**: δ = 9.70 (br. s, 1 H, NH), 5.04 (m, 2 H, 3,4-H), 2.79 (m, 4 H, 2,5-H), n.o. (Ph) ppm.

^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 298 K): *E*,*E*-**5**: δ = 181.7 (C-1,6), 133.5 (*i*-Ph), 134.4 (*p*-Ph), 130.0 (*m*-Ph), 126.6 (*o*-Ph), 126.8 (C-3,4), 34.7 (C-2,5) ppm; *E*,*Z*-**5**: δ = 184.4 (C-6), 181.5 (C-1), 134.8 (*p*-Ph^1), 133.4 (*i*-Ph^1), 132.8 (*p*-Ph^6), 132.8 (C-3), 131.9 (*i*-Ph^6), 130.2 (*m*-Ph^1), 128.5 (*m*-Ph^6), 127.7 (*o*-Ph^6), 126.9 (*o*-Ph^1), 124.1 (C-4), 42.3 (C-5), 34.6 (C-2) ppm; *Z*,*Z*-**5**: δ = 184.1 (C-1,6), 130.3 (C-3,4), 42.7 (C-2,5), n.o. (Ph) ppm; no differentiation of the C_6F_5 groups: δ = 148.0 (dm, $^1J_{F,C}$ = 238.7 Hz, C_6F_5), 139.9 (dm, $^1J_{F,C}$ = 249.2 Hz, *p*-C_6F_5), 137.5 (dm, $^1J_{F,C}$ = 252.6 Hz, C_6F_5), 118.6 (br., *i*-C_6F_5) ppm. ^{19}F NMR (470 MHz, C_6D_6, 298 K): *E*,*E*-**5**: δ = –134.4 (m, 2 F, *o*-C_6F_5), –157.7 (t, $J_{F,F}$ = 20.5 Hz, 1 F, *p*-C_6F_5); –163.1 (m, 2 F, *m*-C_6F_5) ppm; *E*,*Z*-**5**: δ = –134.4 (m, 2 F, *o*-C_6F_5), –134.5 (m, 2 F, *o*-C_6F_5), –157.5 (t, $J_{F,F}$ = 20.3 Hz, 1 F, *p*-C_6F_5), –158.1 (t, $J_{F,F}$ = 20.7 Hz, 1 F, *p*-C_6F_5), –163.1 (m, 2 F, *m*-C_6F_5), –163.5 (m, 2 F, *m*-C_6F_5) ppm. ^{11}B{^{1}H} NMR (160 MHz, C_6D_6, 298 K): δ = –15 ($\nu_{1/2}$ = 420 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 3352 (w, NH), 2477 (w, BH) cm^{-1}. $C_{42}H_{20}B_2F_{20}N_2$ (954.2): calcd. C 52.87, H 2.11, N 2.94; found C 52.74, H 2.29, N 2.91.

Compound 6: 1,6-Diamino-1,6-diphenyl-1,3,5-hexatriene (100.0 mg, 0.38 mmol) was dissolved in toluene (30 mL). To this solution bis(pentafluorophenyl)borane (263.7 mg, 0.76 mmol) was added. The yellow solution was stirred at room temperature overnight. Afterwards, the solvent of the now colourless solution was removed in vacuo. The precipitated white product was washed with pentane (20 mL) and dried in vacuo overnight (200.0 mg, 55%). M.p. 183 °C. ^{1}H NMR (500 MHz, C_6D_6, 298 K): δ = 10.08 (br. s, 1 H, NH^1), 9.69 (br. s, 1 H, NH^6), 7.22 (m, 2 H, *o*-Ph^6), 7.16 (m, 2 H, *o*-Ph^1), 7.00 (m, 1 H, *p*-Ph^6), 6.98 (m, 1 H, *p*-Ph^1), 6.94 (m, 2 H, *m*-Ph^6), 6.89 (m, 2 H, *m*-Ph^1), 4.34 (br., 1 H, BH), 3.31 (dd, $^2J_{H,H}$ = 14.4, $^3J_{H,H}$ = 12.4 Hz, 1 H, 5-H), 2.84, 2.03 (each m, each 1 H, 2-H), 2.70 (dd, $^2J_{H,H}$ = 14.4, $^3J_{H,H}$ = 3.8 Hz, 1 H, 5-H), 2.25 (m, 1 H, 4-H), 1.54, 1.45 (each m, each 1 H, 3-H) ppm. ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 298 K): δ = 189.9 (C-6), 183.0 (C-1), 148.2 (dm, $^1J_{F,C} \approx$ 238 Hz, C_6F_5), 140.0 (dm, $^1J_{F,C} \approx$ 259 Hz, C_6F_5), 137.6 (dm, $^1J_{F,C} \approx$ 250 Hz, C_6F_5), 135.1 (*i*-Ph^6), 134.5 (*p*-Ph^1), 133.8 (*p*-Ph^6), 133.5 (*i*-Ph^1), 129.94, 129.92 (*m*-Ph^{1,6}), 126.5 (*o*-Ph^6), 125.9 (*o*-Ph^1), 32.8 (C-5), 28.0 (C-2), 22.7 (br., C-4), 21.7 (C-3) ppm. ^{19}F NMR (470 MHz, C_6D_6, 298 K): δ = –134.3 (m, 2 F), –157.7 (t, $J_{F,F}$ = 20.6 Hz, 1 F), –162.9 (m, 2 F, $C_6F_5{}^A$); –134.7 (m, 2 F), –157.4 (t, $J_{F,F}$ = 20.5 Hz, 1 F), –163.0 (m, 2 F, $C_6F_5{}^B$); –135.3 (m, 2 F), –156.6 (t, $J_{F,F}$ = 20.8 Hz, 1 F), –162.3 (m, 2 F, $C_6F_5{}^C$); –135.5 (m, 2 F), –155.8 (t, $J_{F,F}$ = 20.8 Hz, 1 F), –161.8 (m, 2 F, $C_6F_5{}^D$) ppm. ^{11}B{^{1}H} NMR (160 MHz, C_6D_6, 298 K): δ = –15 ($\nu_{1/2}$ = 200 Hz, B^6), –6 ($\nu_{1/2}$ = 360 Hz, B^1) ppm. IR (KBr): $\tilde{\nu}$ = 3363 (s, NH), 2393 (w, BH) cm^{-1}. $C_{42}H_{20}B_2F_{20}N_2$ (954.2): calcd. C 52.87, H 2.11, N 2.94; found C 52.45, H 2.17, N 2.72.

X-ray Crystal Structure Analysis of 6: Empirical formula $C_{42}H_{20}B_2F_{20}N_2$, M = 954.22, colourless crystal, 0.25 × 0.10 × 0.03 mm, a = 11.7813(8), b = 13.5712(9), c = 14.3960(9) Å, α = 64.063(4), β = 85.653(4), γ = 86.702(3)°, V = 2063.2(2) Å^3, $\rho_{calcd.}$ = 1.536 g cm^{-3}, μ = 1.374 mm^{-1}, empirical absorption correction (0.725 ≤ T ≤ 0.960), Z = 2, triclinic, space group $P\bar{1}$ (no. 2), λ = 1.54178 Å, T = 223(2) K, ω and ϕ scans, 23938 reflections collected ($\pm h$, $\pm k$, $\pm l$), [$(\sin\theta)/\lambda$] = 0.60 Å^{-1}, 6707 independent (R_{int} = 0.087) and 4239 observed reflections [$I \geq 2\sigma(I)$], 604 refined parameters, R = 0.056, wR_2 = 0.170, max. (min.) residual electron density 0.31 (–0.27) e Å^{-3}, hydrogen atoms at N and B from difference Fourier map, others calculated and refined as riding atoms. CCDC-742130 contains 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.

Acknowledgments

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