Reduction of base-stabilized difluoroboranes to induce rearrangement reactions†‡

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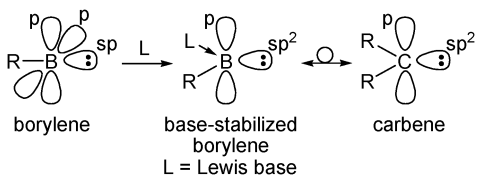
Lewis base-stabilized difluoroboranes **2**, **4-pyr** and **4-^{i}Pr**, having an oxazoline- or amine-tethered amide ligand, were synthesized and fully characterized. The treatment of **2** with KC_8 led to its complete consumption, and the rearranged product **5-H**, probably originating from C–O bond cleavage and B–O bond formation, could be isolated as a major Dip-containing product in 18% yield. From deuterium labelling experiments and diffusion control reactions, the formation of **5-H** could be explained by a radical mechanism. The reduction of **4-pyr** and **4-^{i}Pr** using one-electron reducing agents also gave the rearranged products **13-pyr** and **13-^{i}Pr** in 21 and 19% yields, respectively, *via* C–N bond cleavage and B–N bond formation. The mechanism for the formation of **13-pyr** and **13-^{i}Pr** is suggested to contain a benzylic radical intermediate.

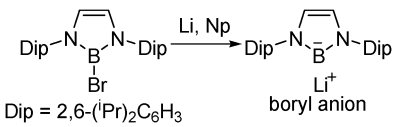
Introduction

Borylene is the boron analog of carbene and nitrene, and is also sometimes called borene or boranediyl. It includes a boron atom with an oxidation state of +1 and is a highly reactive species that has only ever been observed in inert gas matrices at low temperature.[1] There have been no reports on its isolation in a condensed phase to date.[2] Isolated examples are not borylene itself but its adducts with a Lewis acid[3] or with transition metals.[4] One may expect that the coordination of a Lewis base to borylene would provide a base-stabilized borylene, an isoelectronic species to carbene (eqn (1)), which has also never been synthesized. Considering the well-developed chemistry of heavy group 13 metal(I) (Al, Ga, In, Tl) compounds,[5] electronic and steric stabilization by using nitrogen-containing boracycles could afford the chance to isolate a base-stabilized borylene.



(1)

Recently, boryl anions[6] and NHC-stabilized diborenes,[7] possessing an oxidation state of +1, have been synthesized by reduction of the corresponding halogenated precursors (eqn (2) and eqn (3)). The former can be considered an isoelectronic species to base-stabilized borylene and the latter may be regarded as a dimer of it. Based on our previous approach for the synthesis of boryl anions,[6] we conceived that N-containing heterocyclic haloboranes could be good precursors of base-stabilized borylenes. Although there have been many reports on the synthesis of *N*-heterocyclic haloboranes,[8] no reduced product has been fully identified so far. Herein, we report our attempts to synthesize base-stabilized borylenes. The reduction of base-stabilized difluoroboranes, however, resulted in the isolation of unexpected rearrangement products.



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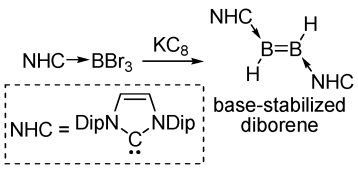
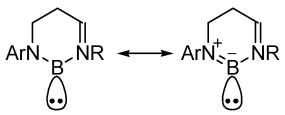


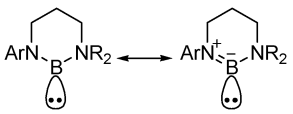
(3)

Results and discussion

Difluoroboranes **2**, **4-pyr** and **4-^{i}Pr** (eqn (4) and eqn (5)) were designed based on the following expectations. Intramolecular coordination of the imine or amine lone pair to a vacant p-orbital of the central boron atom stabilizes the borylene. A nitrogen atom was introduced as a covalent ligand on the boron atom so that the remaining lone pair on the amide nitrogen would further stabilize the boron center by a mesomeric effect.



(4)



(5)

Difluoroboranes **2**, **4-pyr** and **4-^{i}Pr** were synthesized from corresponding iminoamine **1**[9] or diamines **3-pyr** and **3-^{i}Pr** *via*

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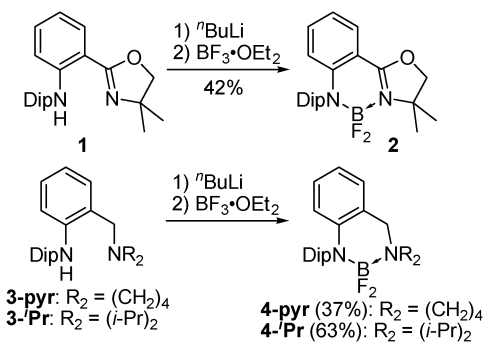
deprotonation, followed by a reaction with $BF_3{\cdot}OEt_2$, in moderate yields (Scheme 1). The ^{11}B NMR signal of the difluoroboranes appeared as a broad triplet [δ_B = 1.2 (**2**), 1.6 (**4-pyr**) and 3.0 (**4-^{i}Pr**)], indicating the intramolecular coordination of a nitrogen atom in the oxazoline or amine to form an sp^3-type borate structure. Two distinct doublets of the methyl protons and one septet of the methine protons of the Dip group may indicate restricted rotation of the Dip–N bond in all cases. Additionally, two fluorine atoms and two methyl groups of the oxazoline moiety in **2** are magnetically equivalent in its ^{19}F and ^1H NMR spectra, supporting the restricted rotation of the Dip group.

X-Ray crystallographic analyses revealed the solid state structures of difluoroboranes **2**, **4-pyr** and **4-^{i}Pr** (Fig. 1, Fig. 2 and Fig. 3). All of the compounds contain a nitrogen-coordinated sp^3 aminodifluoroborane moiety. The relationship between the shorter B1–N1 bonds [1.528(4) and 1.522(4) Å for **2**, 1.502(3) Å for **4-pyr** and 1.5162(19) Å for **4-^{i}Pr**] and the longer B1–N2 bonds [1.560(4) and 1.560(4) Å for **2**, 1.612(3) Å for **4-pyr** and 1.6554(19) Å for **4-^{i}Pr**] is analogous to the shorter B–N single bond (1.50 Å) and the longer B←N dative bond (1.66 Å) calculated in the molecule $H_2N{-}B(H)_2{\leftarrow}NH_3$.[10] The B–N bond lengths in previously reported dihaloborane β-diiminate complexes[8d,i–m] lie mid-way between the B1–N1 and B1–N2 bond lengths in **2**, **4-pyr** and **4-^{i}Pr** because the π-electrons in the diiminato moiety are delocalized by conjugation. The N1–B1–N2 bond angles around the central boron atom [107.1(2) and 107.5(2)° for **2**, 108.58(17)° for **4-pyr** and 108.46(11)° for **4-^{i}Pr**] showed a nearly ideal sp^3 hybridization of the boron center. In contrast, amidinato- or guanizinato-dihaloborane compounds have a distorted sp^3 boron atom [N–B–N 82–85°] due to their four-membered ring.[8a–c,e–h] The boron-containing six-membered rings in **2** are nearly coplanar, as the distances the boron atoms are from the mean plane of the remaining five atoms are only 0.2086(45) and 0.2360(44) Å. On the contrary, the N2 atom in **4-pyr** and **4-^{i}Pr** is located above the mean plane of the other five atoms by 0.7211(29) and 0.4775(20) Å, respectively, due to repulsions among the substituents on the B1 and N2 atoms.

The reduction of difluoroborane **2** with KC_8 in toluene led to the formation of diaminoalkoxyborane **5-H** in 18% yield (Scheme 2). Although **5-H** was not the predominant species, as detected by NMR spectroscopy of the crude mixture, it is a major Dip-containing product. None of the other side products could be assigned. The rearranged structure of **5-H**



Scheme 1 The syntheses of base-stabilized difluoroboranes **2** and **4**.

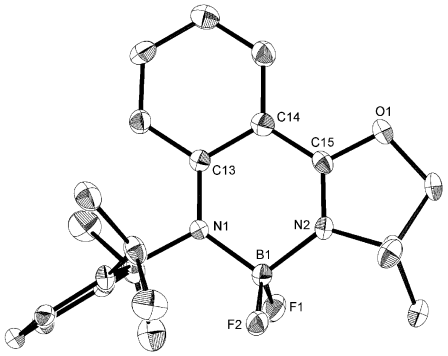


Fig. 1 An ORTEP drawing of **2** (50% thermal ellipsoids; one of two independent molecules and all hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (°): B1–N1 1.528(4), 1.522(4), B1–N2 1.560(4), 1.560(4), B1–F1 1.395(4), 1.404(4), B1–F2 1.389(4), 1.391(4), N1–C13 1.369(4), 1.373(4), C13–C14 1.427(4), 1.420(4), C14–C15 1.420(4), 1.432(4), N2–C15 1.306(4), 1.306(4), N1–B1–N2 107.1(2), 107.5(2), F1–B1–F2 108.3(3), 107.8(2).

was characterized by the following analyses. No oxazoline sp^2 carbon was detected in its ^{13}C NMR spectrum and, instead, benzylic 2H protons appeared in its ^1H NMR spectrum. Furthermore, the ^{11}B NMR spectrum of the product showed a slightly shifted signal at δ_B 25, indicating the existence of a three-heteroatom substituted boron center. By using deuterated toluene as the solvent, the benzylic position was selectively deuterated to afford **5-D**. This labelling experiment indicated that the two benzylic protons came from the toluene. Additionally, the reduction of **2** without stirring led to the formation of dimeric compound **6** (Scheme 3), probably *via* dimerization of radical intermediate **7b** at the benzylic position (*vide infra*). The dimeric structure of **6** was confirmed by ESI-TOF MS and the preliminary result of an X-ray crystallographic analysis (see the Experimental section). There may be a possibility to form a diastereomeric isomer of **6**. During the interaction between two molecules of radical intermediate **7b**, steric repulsion among bulky Dip groups and dimethyloxazoline moieties may help to produce one diastereomer of **6** exclusively.

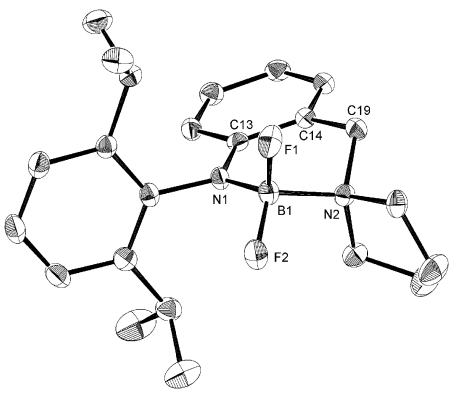


Fig. 2 An ORTEP drawing of **4-pyr** (50% thermal ellipsoids; hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (°): B1–N1 1.502(3), B1–N2 1.612(3), B1–F1 1.401(3), B1–F2 1.390(3), N1–C13 1.394(3), C13–C14 1.416(3), C14–C19 1.498(3), N2–C19 1.508(3), N1–B1–N2 108.58(17), F1–B1–F2 108.75(18).

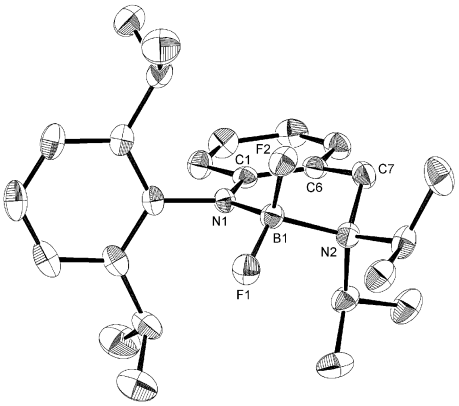
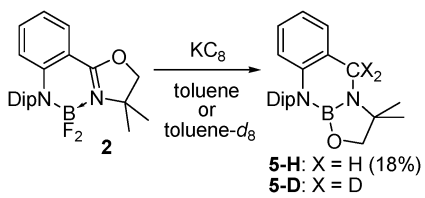


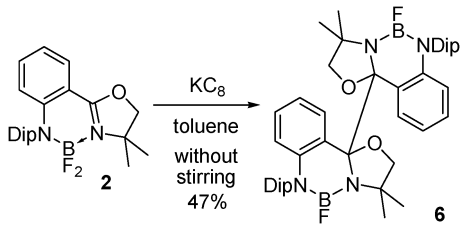
Fig. 3 An ORTEP drawing of **4-^{i}Pr** (50% thermal ellipsoids; hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (°): B1–N1 1.5162(19), B1–N2 1.6554(19), B1–F1 1.3783(18), B1–F2 1.3917(18), N1–C1 1.3885(17), C1–C6 1.4069(19), C6–C7 1.493(2), N2–C7 1.5143(18), N1–B1–N2 108.46(11), F1–B1–F2 108.90(11).

Based on the above observation, we propose a reaction mechanism for the formation of **5-H** and **6**, as shown in Scheme 4.[11] A one-electron transfer from KC_8 to **2** could remove one fluoride ion to generate boron-centered radical species **7a**, which can also be drawn as a resonance structure of benzylic radical **7b**. A subsequent radical–radical coupling of **7b** under diffusion-controlled conditions could afford dimer **6**. Under stirring conditions, **7b** could abstract a hydrogen atom from the solvent, toluene, at the benzylic position to form diaminofluoroborane **8**. This compound could be further reduced, again eliminating fluoride, to form a second boron-centered radical species, **9**. Oxygen could then migrate to the boron center *via* a 1,3-shift reaction to afford benzylic radical **10**.[12] The second hydrogen abstraction from the solvent by **10** could finally give product **5-H**.

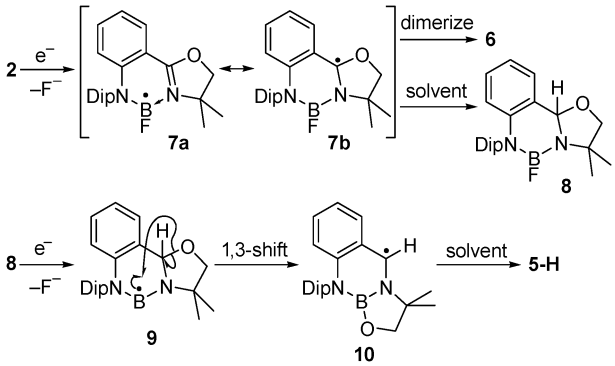
Amine-coordinated difluoroboranes **4-pyr** and **4-^{i}Pr** were also reduced with a one-electron transfer reagent. The reaction of **4-pyr** with Li/DTBB (DTBB = 4,4′-di-*tert*-butylbiphenyl) gave amine-rearranged product **13-pyr** in 21% yield (Scheme 5). A similar rearrangement reaction was observed for **13-^{i}Pr** with KC_8 to give **13-^{i}Pr** in 19% yield (Scheme 6). As observed in the reduction of **2**, no other products could be characterized, although the yields of the major Dip-containing products **13-pyr** and **13-^{i}Pr** were rather low. The ^{13}C NMR spectra of **13-pyr** and **13-^{i}Pr** showed broad benzylic signals due to a connection between the benzylic carbon and the quadrupolar boron nucleus. The chemical shift of the ^{11}B NMR signal (δ_B 33 for both **13-pyr** and **13-^{i}Pr**) also indicated the formation of a diaminocarbylborane. Finally, the structures of **13-pyr**



Scheme 2 The reduction of base-stabilized difluoroborane **2** with KC_8 in toluene or toluene-d_8.



Scheme 3 The reduction of base-stabilized difluoroborane **2** with KC_8 under diffusion-controlled conditions.



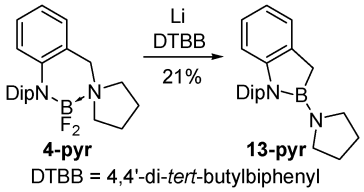
Scheme 4 A plausible mechanism for the formation of **5-H** and **6**.

and **13-^{i}Pr** were unambiguously determined by X-ray crystallographic analysis (Fig. 4 and Fig. 5). The boron center is sp^2 hybridized within the resulting five-membered ring as the sum of the angles around the central boron atom is 360°. Apparently shorter B1–N1 [1.4387(19) Å for **13-pyr** and 1.4583(19) Å for **13-^{i}Pr**] and B1–N2 [1.395(2) Å for **13-pyr** and 1.4088(19) Å for **13-^{i}Pr**] bond lengths than those seen in **13-pyr** and **13-^{i}Pr**, and the coplanarity among the boron plane and the two nitrogen planes, reflect a strong π–π interaction between the boron and the two nitrogen atoms. The longer B–N bond lengths in **13-^{i}Pr** may reflect the steric bulkiness of the N^{i}Pr$_2$ group compared to those of **13-pyr**.

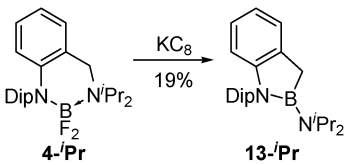
We suggest a mechanism for the formations of **13-pyr** and **13-^{i}Pr**, as illustrated in Scheme 7. A one-electron reduction of **4-pyr** and **4-^{i}Pr** by Li/DTBB or KC_8 results in the elimination of one fluoride ion to form boron-centered radical species **14**. Subsequent C–N bond cleavage leads to the formation of benzylic radical **15**. The further reduction of **15** generates benzylic anion **16**, which undergoes intramolecular nucleophilic substitution on the boron center to afford the rearranged products **13-pyr** and **13-^{i}Pr**.

Conclusion

Lewis base-stabilized difluoroboranes, **2**, **4-pyr** and **4-^{i}Pr**, having an oxazoline- or amine-tethered amide ligand, were synthesized and fully characterized. The treatment of **2** with KC_8 led to its complete consumption. The reaction mixture contained rearranged product **5-H**, probably formed *via* C–O bond cleavage and B–O bond formation, as a minor product. From deuterium labelling experiments and diffusion control reactions, the formation of **5-H** could be explained by a radical mechanism. We were able to isolate **13-pyr** and **13-^{i}Pr** as one



Scheme 5 The reduction of **4-pyr** with Li/DTBB.



Scheme 6 The reduction of **4-^{i}Pr** with Li/DTBB.

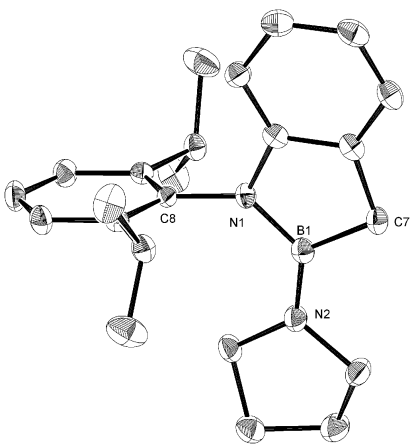


Fig. 4 An ORTEP drawing of **13-pyr** (50% thermal ellipsoids; hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (°): B1–N1 1.4387(19), B1–N2 1.395(2), B1–C7 1.5896(19), N1–C8 1.4395(16), N1–B1–N2 127.51(12), N1–B1–C7 107.15(11), N2–B1–C7 125.34(12).

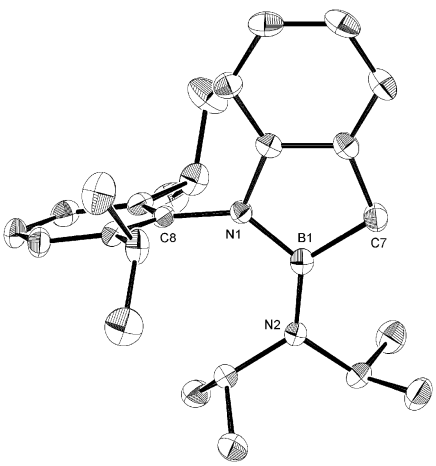
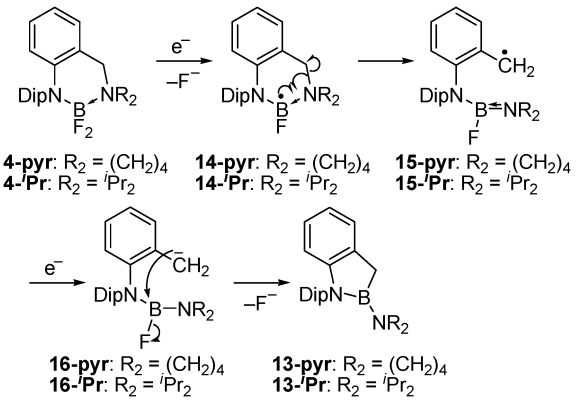


Fig. 5 An ORTEP drawing of **13-^{i}Pr** (50% thermal ellipsoids; hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (°): B1–N1 1.4583(19), B1–N2 1.4088(19), B1–C7 1.603(2), N1–C8 1.4357(17), N1–B1–N2 126.52(12), N1–B1–C7 105.30(11), N2–B1–C7 128.15(12).



Scheme 7 A plausible mechanism for the formation of **13**.

of the reduction products of **4-pyr** and **4-^{i}Pr** using one-electron reducing agents, formed *via* C–N bond cleavage and B–N bond formation. The mechanism for the formation of **13-pyr** and **13-^{i}Pr** is also suggested to contain a benzylic radical intermediate.

Experimental section

General

All manipulations, except for the purification of difluoroboranes, were carried out by standard Schlenk techniques under an argon atmosphere purified by passing it through a hot column packed with a BASF R3-11 catalyst, or in an argon-filled glove box (Miwa MFG), unless otherwise noted. ^{1}H, ^{11}B{^{1}H}, ^{13}C{^{1}H} and ^{19}F NMR spectra were recorded on 500 or 400 MHz spectrometers with residual protonated solvent for ^{1}H, deuterated solvent for ^{13}C{^{1}H}, external $BF_3{\cdot}OEt_2$ for ^{11}B{^{1}H} and external $CFCl_3$ for ^{19}F being used as references. Elemental analyses were performed by the Microanalytical Laboratory of the Department of Chemistry, Faculty of Science, Graduate School of Science, The University of Tokyo. X-Ray crystallographic analyses were recorded on a Rigaku Mercury CCD diffractometer. High resolution mass spectra (ESI-TOF, THF solution) were measured on a JEOL AccuTOF JMS-T100LP instrument with calibration using PEG as an internal reference. Melting points were measured on an MPA100 Optimelt automated melting point system and are uncorrected. Toluene, THF, pentane and hexane were purified by passing them through a solvent purification system. Low temperature reactions at −35 °C were performed with an SW-M01 small stirrer (Nissin Laboratory Instruments) in the freezer of a glove box. Amine-oxazoline ligand **1**[9] and 1-bromo-2-(pyrrolidin-1-yl-methyl)benzene[13] were synthesized according to literature procedures. Purifications by GPC were performed by an LC-928 recycling preparative HPLC (JAI) equipped with a JAI GEL 1H-2H column; the solvent was $CHCl_3$.

Syntheses

2. To an ethereal solution (12 mL) of **1** (751 mg, 2.14 mmol) in a 20 mL Schlenk flask was added a hexane solution of *n*-BuLi (1.66 M, 1.42 mL, 2.35 mmol) at −78 °C under an argon atmosphere. After the solution was stirred at the same temperature for 5 min, the cooling bath was removed and the

flask was kept at room temperature for 1 h without any heating. The resulting yellow-green suspension, containing a yellow precipitate, was cooled again to −78 °C. Then, freshly distilled $BF_3{\cdot}OEt_2$ (290 μL, 2.35 mmol) was added to the flask. After the addition was complete, the cooling bath was immediately removed to induce the color change of the resulting suspension to orange. The resulting suspension was stirred at room temperature without any heating to produce a yellowish-green suspension. All of the volatiles were removed under reduced pressure and the residue was purified by silica gel column chromatography (CH_2Cl_2–hexane = 1 : 1) to give a pale yellow solid of **2** (362 mg, 42%).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.01 (d, J = 7 Hz, 6H), 1.26 (d, J = 7 Hz, 6H), 1.68 (s, 6H), 3.07 (dq, J = 7 Hz, 7 Hz, 2H), 4.48 (d, J = 1 Hz, 2H), 6.23 (d, J = 9 Hz, 1H), 6.63 (t, J = 7 Hz, 1H), 7.22–7.29 (m, 3H), 7.36 (t, J = 8 Hz, 1H), 7.67 (d, J = 8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 24.1 (CH_3), 24.9 (CH_3), 26.6 (CH_3), 28.1 (CH_3), 65.1 (4°), 81.8 (CH_2), 101.1 (4°), 115.0 (CH), 115.8 (CH), 124.2 (CH), 127.4 (CH), 127.6 (CH), 127.6 (CH), 135.7 (4°), 135.9 (CH), 148.1 (4°), 152.3 (4°), 165.7 (4°); ^{11}B{^{1}H} NMR ($CDCl_3$, 160 MHz): δ 1.2 (t, $^1J_{FB}$ = 25 Hz); ^{19}F NMR ($CDCl_3$, 471 MHz): δ −130.6 (br q); mp 193.8–198.8 °C (decomp.). Anal. calc. for $C_{23}H_{29}BF_2N_2O$: C, 69.36; H, 7.34; N, 7.03. Found: C, 69.36; H, 7.46; N, 6.95%.

3-pyr. 1-Bromo-2-(pyrrolidin-1-yl-methyl)benzene (9.89 g, 41.4 mmol), 2,6-diisopropylaniline (7.34 g, 41.4 mmol), $Pd(OAc)_2$ (743 mg, 3.31 mmol), ^{t}BuP (1.34 g, 6.62 mmol), NaO^{t}Bu (5.17 g, 53.8 mmol) were placed into a 500 mL Schlenk flask in a glove box. Toluene (150 mL) was added to the mixture and the flask connected to a condenser. The resulting apparatus was brought out from the glove box and the reaction mixture refluxed at 130 °C for 2 d. After cooling the flask to room temperature, the solution was filtrated through a pad of Celite® on Silica gel to remove inorganic salts, and the residue was washed with toluene. All the volatiles were evaporated *in vacuo*. The crude mixture was heated at 260 °C under reduced pressure to remove unreacted aryl bromide and 2,6-diisopropylaniline, giving a brown oil (8.32 g, >95%, containing a trace amount of 2,6-diisopropylaniline). The obtained material was used for the next step without any further purification.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.11 (d, J = 7 Hz, 6H), 1.17 (d, J = 7 Hz, 6H), 1.79 (m, 4H), 2.54 (m, 4H), 3.13 (sept, J = 7 Hz, 2H), 3.74 (s, 2H), 6.15 (d, J = 8 Hz, 1H), 6.62 (t, J = 7 Hz, 1H), 7.00 (t, J = 8 Hz, 1H), 7.08 (d, J = 7 Hz, 1H), 7.20–7.26 (m, 3H), 7.88 (br s, 1H).

4-pyr. To an ethereal solution (15 mL) of **3-pyr** (1.97 g, 5.38 mmol) in an 80 mL Schlenk flask was added a hexane solution of *n*-BuLi (1.57 M, 3.60 mL, 5.65 mmol) at −78 °C under an argon atmosphere. After the solution had been stirred at the same temperature for 5 min, the cooling bath was removed and the flask kept at room temperature for 1 h without any heating. The resulting suspension was cooled again to 0 °C and $BF_3{\cdot}OEt_2$ (0.700 mL, 5.65 mmol) added dropwise. After the addition was complete, the cooling bath was immediately removed and the resulting reaction mixture stirred at room temperature for 1.5 h without any heating. All the volatiles were removed *in vacuo*. The crude product was then recrystallized by the diffusion of hexane into a saturated $CHCl_3$ solution of the crude product to give colorless crystals (755 mg, 37% yield).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.99 (d, J = 7 Hz, 6H), 1.21 (d, J = 7 Hz, 6H), 2.04–2.16 (br m, 4H), 3.05–3.14 (br m, 2H), 3.19 (dq, J = 7 Hz, 7 Hz, 2H), 3.50–3.60 (br m, 2H), 4.18 (s, 2H), 5.95 (d, J = 8 Hz, 1H), 6.54 (t, J = 7 Hz, 1H), 6.92–7.00 (m, 2H), 7.20–7.26 (m, 1H), 7.28–7.34 (m, 1H); ^{11}B NMR ($CDCl_3$, 160 MHz): δ 1.4; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 22.6 (CH_2), 24.3 (CH_3), 25.0 (CH_3), 27.9 (CH_2), 53.9 (CH), 58.6 (CH_2), 113.7 (CH), 113.8 (CH), 115.0 (CH), 124.4 (CH), 127.0 (4°), 127.6 (CH), 129.3 (CH), 136.8 (4°), 148.0 (4°), 149.0 (4°); ^{19}F NMR ($CDCl_3$, 470 MHz): δ −156.6.

^{1}H NMR (C_6D_6, 500 MHz): δ 1.05 (br m, 2H), 1.17 (br m, 2H), 1.19 (d, J = 7 Hz, 6H), 1.50 (d, J = 7 Hz, 6H), 2.37 (br m, 2H), 3.19 (br m, 2H), 3.50 (s, 2H), 3.57 (sep, J = 7 Hz, 2H), 6.23 (d, J = 8 Hz, 1H), 6.58 (t, J = 7 Hz, 1H), 6.65 (d, J = 7 Hz, 1H), 6.94 (t, J = 8 Hz, 1H), 7.32 (m, 3H); ^{11}B NMR (C_6D_6, 160 MHz): δ 1.6 (br t); ^{19}F NMR (C_6D_6, 470 MHz): δ −158.1 (br).

mp: 123.1–136.2 °C (decomp.). Anal. calc. for $C_{23}H_{31}BF_2N_2$: C, 71.88; H, 8.13; N, 7.29. Found: C, 71.78; H, 8.21; N, 7.09%.

3-^{i}Pr. To a 100 mL round-bottomed flask were added 2-bromobenzyl bromide (15.9 g, 63.6 mmol), toluene (*ca.* 30 mL) and diisopropylamine (16.1 g, 159 mmol), and the solution was refluxed for 2 d in air. After cooling the reaction mixture to room temperature, the organic salts were filtered off through a pad of Celite® and the filtrate pumped to remove toluene and excess amine. The residue was dissolved in CH_2Cl_2 and the resulting solution passed through a short silica gel column. The solution was evaporated, giving crude 2-bromobenzyldiisopropylamine. The product was then brought into a glove box. In the glove box, to a 500 mL three-necked flask equipped with a rubber septum and a three-way stopcock were added the crude aryl bromide, 2,6-diisopropylaniline (11.6 g, 65.4 mmol), $Pd(OAc)_2$ (1.17 g, 5.23 mmol), ^{t}BuP (2.11 g, 10.5 mmol), NaO*t*-Bu (8.17 g, 85.0 mmol) and 300 mL of toluene. After the flask had been brought out from the glove box, it was equipped with a condenser and the reaction mixture was then refluxed for 46 h. After cooling the flask to room temperature, the reaction mixture was filtered through a pad of Celite® to remove inorganic salts and the filtrate evaporated *in vacuo*. The crude product was recrystallized from refluxing hexane to give **3-^{i}Pr** (17.2 g, 47.0 mmol, 73% over two steps).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.08 (d, J = 7 Hz, 6H), 1.11 (d, J = 7 Hz, 12H), 1.16 (d, J = 7 Hz, 6H), 3.11–3.21 (m, 4H), 3.84 (s, 2H), 6.07 (d, J = 8 Hz, 1H), 6.62 (t, J = 7 Hz, 1H), 6.96 (d, J = 8 Hz, 1H), 7.09 (d, J = 6 Hz, 1H), 7.21 (m, 2H), 7.48 (s, 1H); ^{13}C NMR (C_6D_6, 126 MHz): δ 20.3 (CH_3), 23.4 (CH_3), 25.0 (CH_3), 28.2 (CH), 46.9 (CH), 49.0 (CH_2), 111.8 (CH), 116.6 (CH), 123.1 (4°), 123.8 (CH), 126.4 (CH), 128.1 (CH), 130.5 (CH), 135.9 (4°), 147.1 (4°), 148.6 (4°); mp: 124.5–126.4 °C (decomp.); HRMS-ESI (m/z): [M + H$^+$] calc. for $C_{25}H_{39}N_2^+$ 367.3113; found 367.3110.

4-^{i}Pr. An ether (40 mL) solution of **3-^{i}Pr** (3.13 g, 8.55 mmol) in an 80 mL Schlenk flask was cooled to −78 °C under an argon atmosphere. A hexane solution of *n*-BuLi (1.57 M, 5.71 mL, 8.98 mmol) was then added dropwise to the reaction mixture. After the solution had been stirred at the same temperature for 5 min, the cooling bath was removed and the flask kept at room temperature for 1 h without any heating. The resulting suspension was cooled again to 0 °C and $BF_3{\cdot}OEt_2$ (1.13 mL, 8.98 mmol) added dropwise. After the addition was complete, the cooling bath was immediately removed and the resulting reaction mixture stirred at room temperature overnight. All the volatiles were then removed *in vacuo*. After the Schlenk flask had been brought into a glove box, the crude product was triturated with hexane and the resulting suspension filtered through a pad of Celite®. After the solvents had been removed from the filtrate, the crude product was re-precipitated by adding its saturated THF solution to an excess amount of hexane to give **4-^{i}Pr** (2.24 g, 5.42 mmol, 63% yield).

^{1}H NMR (C_6D_6, 500 MHz): δ 0.89 (d, J = 6 Hz, 6H), 1.18 (d, J = 7 Hz, 6H), 1.20 (d, J = 7 Hz, 6H), 1.50 (d, J = 7 Hz, 6H), 3.31–3.42 (br m, 2H), 3.55 (dq, J = 7 Hz, 7 Hz, 2H), 3.78 (br s), 6.17 (d, J = 8 Hz, 1H), 6.59 (m, 1H), 6.65 (d, J = 6 Hz, 1H), 6.92 (m, 1H), 7.29–7.37 (m, 3H); ^{13}C NMR (C_6D_6, 100 MHz): δ 20.9 (CH_3), 24.8 (CH_3), 25.4 (CH_3), 28.4 (CH), 55.7 (CH), 56.7 (CH_2), 113.5 (CH), 114.7 (4°), 115.4 (CH), 124.8 (CH), 127.5 (CH), 127.7 (CH), 129.5 (CH), 137.9 (4°), 148.9 (4°), 149.4 (4°); ^{11}B NMR (C_6D_6, 160 MHz): δ 3.0 (br t); ^{19}F NMR (C_6D_6, 470 MHz): δ −138.0 (br); mp: 145.2–170.9 °C (decomp.). Anal. calc. for $C_{25}H_{37}BF_2N_2$: C, 72.46; H, 9.00; N, 6.76. Found: C, 72.21; H, 9.25; N, 6.58%.

The reduction of 2 to give 5-H. To a 50 mL vial containing a glass stirrer bar was added **2** (376 mg, 0.944 mmol), KC_8 (1.22 g, 9.00 mmol) and toluene (15 mL) at room temperature in a glove box. The resulting mixture was stirred at room temperature for 2 d and filtered through a pad of Celite®. All the volatiles were removed from the filtrate under reduced pressure. The solid residue was extracted with hexane in six times and the combined hexane solution evaporated. The crude product was purified by recycling HPLC ($CHCl_3$ eluent) to give a solid of **5-H** (61.0 mg, 18%).

^{1}H NMR (CD_2Cl_2, 500 MHz): δ 1.06 (d, J = 7 Hz, 6H), 1.14 (d, J = 7 Hz, 6H), 1.27 (s, 6H), 2.99 (dq, J = 7 Hz, 7 Hz, 2H), 3.87 (s, 2H), 4.42 (s, 2H), 6.07 (dd, J = 8 Hz, 1 Hz, 1H), 6.79 (dt, J = 7 Hz, 1 Hz, 1H), 6.91 (dt, J = 8 Hz, 1 Hz, 1H), 7.09 (d, J = 7 Hz, 1H), 7.24 (d, J = 8 Hz, 2H), 7.34 (dd, J = 8 Hz, 1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 23.7 (CH_3), 24.3 (CH_3), 24.4 (CH_3), 42.3 (CH_2), 58.5 (4°), 77.4 (CH), 79.8 (CH_2), 114.8 (CH), 119.7 (CH), 122.0 (4°), 124.2 (CH), 127.4 (CH), 127.9 (CH), 128.0 (CH), 135.0 (4°), 144.3 (4°), 147.6(4°); ^{11}B NMR (C_6D_6, 160 MHz): δ 25 (br s); HRMS-ESI (m/z): calc. for $C_{23}H_{30}BN_2O^+$ 361.2451; found 361.2450.

The reduction of 2 without stirring to give 6. **2** (21.8 mg, 54.7 μmol), KC_8 (37.0 mg, 274 μmol) and 1.0 mL of toluene were added to a 20 mL vial in a glove box. The mixture was kept unstirred for 3 d at room temperature and then filtrated through a pad of Celite® to remove inorganic salts and excess KC_8. All the volatiles were removed under reduced pressure and the crude product purified by recrystallization (twice) by the diffusion of hexane into a saturated $CHCl_3$ solution of the crude product to give a colorless solid of **6** (9.8 mg, 47%).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.59 (s, 6H), 1.05 (d, J = 7 Hz, 6H), 1.12 (d, J = 8 Hz, 6H), 1.14 (d, J = 8 Hz, 6H), 1.15 (s, 6H), 1.29 (d, J = 7 Hz, 6H), 2.61 (sept, J = 7 Hz, 2H), 2.85 (d, J = 8 Hz, 2H), 3.30 (d, J = 8 Hz, 2H), 3.64 (sept, J = 7 Hz, 2H), 6.18 (dd, J = 8 Hz, 1 Hz, 2H), 6.97 (dt, J = 7 Hz, 1 Hz, 2H), 7.05 (dt, J = 8 Hz, 1 Hz, 2H), 7.29 (dd, J = 8 Hz, 1 Hz, 2H), 7.33 (dd, J = 8 Hz, 1 Hz, 2H), 7.41 (dt, J = 8 Hz, 1 Hz, 2H), 7.59 (dd, J = 8 Hz, 1 Hz, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz). Two signals were observed as a doublet, probably due to through-space ^{13}C–^{19}F coupling:[14] δ 23.8 (CH_3), 24.5 (CH_3), 24.7 (CH_3), 25.2 (CH_3), 25.4 (CH_3), 27.2 (CH), 28.3 (d, J = 4 Hz, CH_3), 28.4 (CH), 62.0 (4°), 78.7 (CH_2), 100.4 (d, J = 6 Hz, 4°), 114.3 (CH), 120.4 (CH), 124.3 (CH), 124.4 (CH), 124.7 (4°), 128.1 (CH), 128.4 (CH), 129.7 (CH), 134.5 (4°), 144.4 (4°), 147.6 (4°), 148.1 (4°); ^{11}B{^{1}H} NMR ($CDCl_3$, 160 MHz): δ 23 (br s), ^{19}F NMR ($CDCl_3$, 471 MHz): δ −127.7 (s); mp: 207.8–210.7 °C (decomp.); HRMS-ESI (m/z): [M + H$^+$] calc. for $C_{46}H_{59}B_2F_2N_4O_2$ 759.4792; found 759.4823.

The reduction of 4-pyr to form 13-pyr. A 20 mL vial equipped with a glass stirrer bar was charged with **4-pyr** (217 mg, 0.564 mmol), lithium powder (39.2 mg, 5.64 mmol) and di-*tert*-butylbiphenyl (30.1 mg, 0.113 mmol) in a globe box. To the vial, cooled to −35 °C, was added pre-cooled THF (10 mL, −35 °C). After stirring the reaction mixture at −35 °C for 15 h, the solution was filtered through a pad of Celite® to remove inorganic salts. The resulting filtrate was evaporated under reduced pressure. The crude product was recrystallized by slow evaporation of a benzene solution to give **13-pyr** (42.1 mg, 0.122 mmol, 21%).

^{1}H NMR (C_6D_6, 500 MHz): δ 1.06 (d, J = 7 Hz, 6H), 1.16 (d, J = 7 Hz, 6H), 1.24–1.27 (m, 2H), 1.34–1.39 (m, 2H), 2.30 (s, 2H), 2.62 (t, J = 7 Hz, 2H), 3.01 (t, J = 7 Hz, 2H), 3.22 (sep, J = 7 Hz, 2H), 6.22 (d, J = 8 Hz, 1H), 6.89 (t, J = 7 Hz, 1H), 7.01 (t, J = 8 Hz, 1H), 7.19 (d, J = 8 Hz, 2H), 7.27 (t, J = 8 Hz, 1H), 7.34 (d, J = 7 Hz 1H); ^{13}C NMR (C_6D_6, 100 MHz): δ 20.1 (br, CH_2), 23.9 (CH_3), 24.7 (CH_3), 25.8 (CH_2), 27.1 (CH_2), 28.7 (CH), 46.3 (CH_2), 49.9 (CH_2), 109.8 (CH), 119.3 (CH), 124.0 (CH), 126.6 (CH), 127.3 (CH), 127.9 (CH), 131.3 (4°), 138.1 (4°), 147.5 (4°), 156.0 (4°); ^{11}B NMR (C_6D_6, 160 MHz): 33 (br); mp 58.1–65.1 °C (decomp.). Anal. calc. for $C_{23}H_{31}BN_2$: C, 79.77; H, 9.02; N, 8.09. Found: C, 79.55; H, 9.21; N, 7.70%.

The reduction of 4-^{i}Pr to form 13-^{i}Pr. A 20 mL vial equipped with a glass stirrer bar was charged with **4-^{i}Pr** (170 mg, 0.410 mmol) and KC_8 (160 mg, 4.10 mmol) in a globe box. To the vial, cooled to −35 °C, was added pre-cooled THF (3 mL, −35 °C). After stirring the reaction mixture at −35 °C for 2.5 h, the solution was filtered through a pad of Celite® to remove inorganic salts. The resulting filtrate was evaporated under reduced pressure. The crude product was then recrystallized

Table 1 Crystallographic data and structure refinement details for **2**, **4-pyr**, **4-^{i}Pr**, **6**, **13-pyr** and **13-^{i}Pr**

	2	**4-pyr**	**4-^{i}Pr**	**6**	**13-pyr**	**13-^{i}Pr**
Formula	$C_{23}H_{29}BF_2N_2O$	$C_{23}H_{31}BF_2N_2$	$C_{25}H_{37}BF_2N_2$	$C_{46}H_{58}B_2F_2N_4O_2$	$C_{23}H_{31}BN_2$	$C_{25}H_{37}BN_2$
f_w	398.29	384.31	414.38	758.58	346.31	376.38
T/K	103(2)	103(2)	103(2)	103(2)	103(2)	103(2)
λ/Å	0.71070	0.71070	0.71070	0.71070	0.71070	0.71070
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/a$	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a/Å	11.866(5)	13.975(6)	10.9370(13)	10.393(8)	9.440(5)	9.969(4)
b/Å	12.250(5)	11.390(5)	11.0234(10)	17.539(13)	10.504(5)	10.684(5)
c/Å	15.775(7)	14.556(7)	20.180(2)	11.564(9)	10.892(5)	11.315(5)
α (°)	100.107(4)	90	90	90	89.733(3)	85.714(13)
β (°)	100.940(4)	114.7635(19)	101.4026	99.422(5)	107.726(6)	77.331(12)
γ (°)	104.311(5)	90	90	90	103.128(7)	83.324(13)
V/Å^3	2121.0(15)	2104.0(16)	2384.9(4)	2080(3)	999.4(8)	1166.4(9)
Z	4	4	4	2	2	2
D_c/g cm^{-3}	1.247	1.213	1.154	1.211	1.151	1.072
μ/mm^{-1}	0.087	0.082	0.077	0.079	0.066	0.061
F(000)	848	824	896	812	376	412
Crystal size/mm	0.40 × 0.15 × 0.13	0.35 × 0.25 × 0.10	0.60 × 0.55 × 0.55	0.40 × 0.40 × 0.10	0.60 × 0.45 × 0.35	0.40 × 0.35 × 0.20
2θ range (°)	3.32–25.00	3.08–25.00	3.12–25.00	3.06–25.00	3.41–25.00	3.08–25.00
Reflections collected	13859	13221	14829	13022	6464	7627
Independent reflections	7298	3570	4067	3592	3415	4007
R_{int}	0.0325	0.0378	00263	0.0627	0.0147	0.0218
Parameter	535	257	279	259	239	261
GOF on F^2	1.104	1.124	1.117	1.268	1.069	1.081
R_1	0.0797	0.0585	0.0449	0.1355	0.0401	0.0430
wR_2 [$I > 2\sigma(I)$]	0.1969	0.1406	0.1024	0.3076	0.0923	0.1006
R_1	0.1021	0.0697	0.0495	0.1656	0.0471	0.0520
wR_2 (all data)	0.2153	0.1493	0.1053	0.3278	0.0968	0.1066

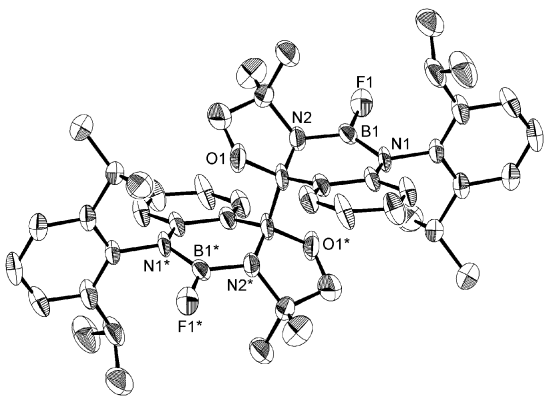


Fig. 6 An ORTEP drawing of dimeric compound **6** (50% thermal ellipsoids; hydrogen atoms are omitted for clarity). Half of the molecule is the asymmetric unit; the numbers with asterisks refer to the second half of the molecule.

by slow evaporation of a hexane solution to give **13-^{i}Pr** (30.0 mg, 0.0797 mmol, 19%).

^{1}H NMR (C_6D_6, 500 MHz): δ 0.77 (d, J = 7 Hz, 6H), 1.01 (d, J = 7 Hz, 6H), 1.18 (d, J = 7 Hz, 6H), 1.21 (d, J = 7 Hz, 6H), 2.52 (s, 2H), 3.03 (s, 1H), 3.20 (sep, J = 7 Hz, 2H), 3.60 (s, 1H), 6.12 (m, 1H), 6.90 (m, 1H), 6.95 (m, 1H), 7.18 (m, 2H), 7.24 (m, 1H), 7.30 (m, 1H). ^{13}C NMR (C_6D_6,100 MHz): δ 22.1 (CH_3), 22.2 (br CH_2), 23.7 (CH_3), 24.3 (CH_3), 25.4 (CH_3), 28.6 (CH), 44.3 (CH), 47.4 (CH), 111.0 (CH), 119.4 (CH), 124.5 (CH), 126.0 (CH), 126.7 (CH), 127.7 (CH), 131.5 (4°), 139.6 (4°), 147.1 (4°), 155.4 (4°); ^{11}B NMR (C_6D_6, 160 MHz): 33 (br); mp 98.2–100.1 °C. Anal. calc. for $C_{25}H_{37}BN_2$: C, 79.78; H, 9.91; N, 7.44. Found: C, 79.67; H, 10.01; N, 7.20%.

X-Ray crystallography

Details of the crystal data and a summary of the intensity data collection parameters for **2**, **4-pyr**, **4-^{i}Pr**, **6**, **13-pyr** and **13-^{i}Pr** are listed in Table 1. In each case, a suitable crystal was mounted with mineral oil onto a glass fiber and transferred to the goniometer of a Rigaku Mercury CCD diffractometer with graphite-monochromated Mo-K$_\alpha$ radiation (λ = 0.71070 Å). The structures were solved by direct methods using SIR-97[15] and refined by full-matrix least-squares techniques against F^2 (SHELXL-97).[16] The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed using AFIX instructions. The quality of the data for **6** (Fig. 6) was not good enough for it to be discussed in detail.

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Notes and references

1 (*a*) L. Andrews, P. Hassanzadeh, J. M. L. Martin and P. R. Taylor, *J. Phys. Chem.*, 1993, **97**, 5839–5847; (*b*) P. Hassanzadeh and L. Andrews, *J. Phys. Chem.*, 1993, **97**, 4910–4915; (*c*) L. Andrews, D. V. Lanzisera, P. Hassanzadeh and Y. Hannachi, *J. Phys. Chem. A*, 1998, **102**, 3259–3267; (*d*) H. F. Bettinger, *J. Am. Chem. Soc.*, 2006, **128**, 2534–2535.

2 (*a*) P. L. Timms, *J. Am. Chem. Soc.*, 1967, **89**, 1629–1632; (*b*) P. L. Timms, *J. Am. Chem. Soc.*, 1968, **90**, 4585–4589; (*c*) P. L. Timms, *Acc. Chem. Res.*, 1973, **6**, 118–123; (*d*) B. Pachaly and R. West, *Angew. Chem., Int. Ed. Engl.*, 1984,

23, 454–455; (*e*) T. Mennekes, P. Paetzold and R. Boese, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 899–900; (*f*) T. Mennekes, P. Paetzold, R. Boese and D. Bläser, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 173–175; (*g*) W. J. Grigsby and P. P. Power, *J. Am. Chem. Soc.*, 1996, **118**, 7981–7988; (*h*) M. Ito, N. Tokitoh, T. Kawashima and R. Okazaki, *Tetrahedron Lett.*, 1999, **40**, 5557–5560; (*i*) S. M. van der Kerk, J. Boersma and G. J. M. van der Kerk, *Tetrahedron Lett.*, 1976, **17**, 4765–4766; (*j*) S. M. van der Kerk, A. L. M. van Eekeren and G. J. M. van der Kerk, *J. Organomet. Chem.*, 1980, **190**, C8–C10; (*k*) S. M. van Der Kerk, J. C. Roos-Venekamp, A. J. M. van Beijnen and G. J. M. van Der Kerk, *Polyhedron*, 1983, **2**, 1337–1343; (*l*) S. M. van der Kerk, P. H. M. Budzelaar, A. L. M. van Eekeren and G. J. M. van der Kerk, *Polyhedron*, 1984, **3**, 271–280; (*m*) J. J. Eisch and H. P. Becker, *J. Organomet. Chem.*, 1979, **171**, 141–153; (*n*) R. Schlögl and B. Wrackmeyer, *Polyhedron*, 1985, **4**, 885–892; (*o*) A. Meller, W. Maringgele, G. Elter, D. Bromm, M. Noltemeyer and G. M. Sheldrick, *Chem. Ber.*, 1987, **120**, 1437–1439.

3 (*a*) A. H. Cowley, V. Lomeli and A. Voigt, *J. Am. Chem. Soc.*, 1998, **120**, 6401–6402; (*b*) D. Vidovic, M. Findlater, G. Reeske and A. H. Cowley, *Chem. Commun.*, 2006, 3786–3787; (*c*) P. Greiwe, A. Bethäuser, H. Pritzkow, T. Küler, P. Jutzi and W. Siebert, *Eur. J. Inorg. Chem.*, 2000, 1927–1929.

4 Since the first report on transition metal-borylene complexes, many examples of borylene complexes have appeared. The first example: (*a*) H. Braunschweig and T. Wagner, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 825–826; (*b*) The following are general review papers on borylene complexes: H. Braunschweig, *Angew. Chem., Int. Ed.*, 1998, **37**, 1786–1801; (*c*) H. Braunschweig and M. Colling, *Eur. J. Inorg. Chem.*, 2003, 393–403; (*d*) H. Braunschweig, *Adv. Organomet. Chem.*, 2004, **51**, 163–192; (*e*) H. Braunschweig and G. R. Whittell, *Chem.–Eur. J.*, 2005, **11**, 6128–6133; (*f*) H. Braunschweig and D. Rais, *Heteroat. Chem.*, 2005, **16**, 566–571; (*g*) H. Braunschweig, C. Kollann and D. Rais, *Angew. Chem., Int. Ed.*, 2006, **45**, 5254–5274; (*h*) H. Braunschweig, C. Kollann and F. Seeler, *Struct. Bonding*, 2008, **130**, 1–27; (*i*) S. Aldridge and D. L. Coombs, *Coord. Chem. Rev.*, 2004, **248**, 535–559; (*j*) D. Vidovic, G. A. Pierce and S. Aldridge, *Chem. Commun.*, 2009, 1157–1171.

5 (*a*) M. N. Sudheendra Rao, H. W. Roesky and G. Anantharaman, *J. Organomet. Chem.*, 2002, **646**, 4–14; (*b*) H. W. Roesky, *Inorg. Chem.*, 2004, **43**, 7284–7293; (*c*) C. Janiak, *Coord. Chem. Rev.*, 1997, **163**, 107–216; (*d*) P. Jutzi and G. Reumann, *J. Chem. Soc., Dalton Trans.*, 2000, (14), 2237–2244; (*e*) H. Schmidbaur, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 893–904; (*f*) C. Dohmeier, D. Loos and H. Schnöckel, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 129–149; (*g*) P. Jutzi and N. Burford, *Chem. Rev.*, 1999, **99**, 969–990; (*h*) G. Linti and H. Schnöckel, *Coord. Chem. Rev.*, 2000, **206–207**, 285–319; (*i*) R. J. Baker and C. Jones, *Dalton Trans.*, 2005, 1341–1348; (*j*) C. Gemel, T. Steinke, M. Cokoja, A. Kempter Roland and A. Fischer, *Eur. J. Inorg. Chem.*, 2004, 4161–4176; (*k*) R. J. Baker, R. D. Farley, C. Jones, M. Kloth and D. M. Murphy, *J. Chem. Soc., Dalton Trans.*, 2002, 3844–3850; (*l*) R. J. Baker, C. Jones, M. Kloth and J. A. Platts, *Angew. Chem., Int. Ed.*, 2003, **42**, 2660–2663; (*m*) R. J. Baker, C. Jones and J. A. Platts, *J. Am. Chem. Soc.*, 2003, **125**, 10534–10535; (*n*) R. J. Baker, C. Jones and J. A. Platts, *Dalton Trans.*, 2003, 3673–3674; (*o*) R. J. Baker, C. Jones, M. Kloth and J. A. Platts, *Organometallics*, 2004, **23**, 4811–4813; (*p*) R. J. Baker, C. Jones and M. Kloth, *Dalton Trans.*, 2005, 2106–2110; (*q*) S. Aldridge, R. J. Baker, N. D. Coombs, C. Jones, R. P. Rose, A. Rossin and D. J. Willock, *Dalton Trans.*, 2006, 3313–3320; (*r*) S. P. Green, C. Jones, K. A. Lippert, D. P. Mills and A. Stasch, *Inorg. Chem.*, 2006, **45**, 7242–7251; (*s*) C. Jones, P. C. Junk, J. A. Platts and A. Stasch, *J. Am. Chem. Soc.*, 2006, **128**, 2206–2207; (*t*) C. Jones, D. P. Mills, J. A. Platts and R. P. Rose, *Inorg. Chem.*, 2006, **45**, 3146–3148; (*u*) C. Jones, D. P. Mills and R. P. Rose, *J. Organomet. Chem.*, 2006, **691**, 3060–3064; (*v*) P. L. Arnold, S. T. Liddle, J. McMaster, C. Jones and D. P. Mills, *J. Am. Chem. Soc.*, 2007, **129**, 5360–5361; (*w*) S. P. Green, C. Jones, D. P. Mills and A. Stasch, *Organometallics*, 2007, **26**, 3424–3430; (*x*) S. P. Green, C. Jones and A. Stasch, *Inorg. Chem.*, 2007, **46**, 11–13; (*y*) C. Jones, R. P. Rose and A. Stasch, *Dalton Trans.*, 2007, 2997–2999; (*z*) C. Jones, A. Stasch, G. J. Moxey, P. C. Junk and G. B. Deacon, *Eur. J. Inorg. Chem.*, 2009, 3593–3599; (*aa*) C. Jones, A. Stasch and W. D. Woodul, *Chem. Commun.*, 2009, 113–115; (*ab*) S. T. Liddle, J. McMaster, D. P. Mills, A. J. Blake, C. Jones and W. D. Woodul, *Angew. Chem., Int. Ed.*, 2009, **48**, 1077–1080; (*ac*) S. T. Liddle, D. P. Mills, B. M. Gardner, J. McMaster, C. Jones and W. D. Woodul, *Inorg. Chem.*, 2009, **48**, 3520–3522; (*ad*) G. J. Moxey, C. Jones, A. Stasch, P. C. Junk, G. B. Deacon, W. D. Woodul and P. R. Drago, *Dalton Trans.*, 2009, 2630–2636.

6 (*a*) Y. Segawa, M. Yamashita and K. Nozaki, *Science*, 2006, **314**, 113–115; (*b*) T. B. Marder, *Science*, 2006, **314**, 69–70; (*c*) H. Braunschweig, *Angew. Chem., Int. Ed.*, 2007, **46**, 1946–1948; (*d*) M. Yamashita, Y. Suzuki, Y. Segawa and K. Nozaki, *J. Am. Chem. Soc.*, 2007, **129**, 9570–9571; (*e*) Y. Segawa, M. Yamashita and K. Nozaki, *Angew. Chem., Int. Ed.*, 2007, **46**, 6710–6713; (*f*) M. Yamashita, Y. Suzuki, Y. Segawa and K. Nozaki, *Chem. Lett.*, 2008, **37**, 802–803; (*g*) T. Kajiwara, T. Terabayashi, M. Yamashita and K. Nozaki, *Angew. Chem., Int. Ed.*, 2008, **47**, 6606–6610; (*h*) Y. Segawa, Y. Suzuki, M. Yamashita and K. Nozaki, *J. Am. Chem. Soc.*, 2008, **130**, 16069–16079; (*i*) T. Terabayashi, T. Kajiwara, M. Yamashita and K. Nozaki, *J. Am. Chem. Soc.*, 2009, **131**, 14162–14163.

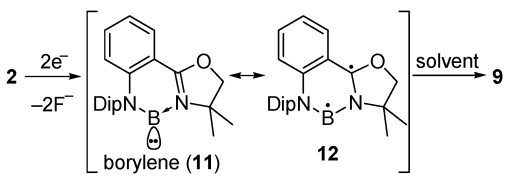
7 (*a*) Y. Wang, B. Quillian, P. Wei, C. S. Wannere, Y. Xie, R. B. King, H. F. Schaefer, P. v. R. Schleyer and G. H. Robinson, *J. Am. Chem. Soc.*, 2007, **129**, 12412–12413; (*b*) Y. Wang, B. Quillian, P. Wei, Y. Xie, C. S. Wannere, R. B. King, H. F. Schaefer, P. v. R. Schleyer and G. H. Robinson, *J. Am. Chem. Soc.*, 2008, **130**, 3298–3299.

8 (*a*) N. J. Hill, M. Findlater and A. H. Cowley, *Dalton Trans.*, 2005, 3229–3234; (*b*) M. Findlater, N. J. Hill and A. H. Cowley, *Polyhedron*, 2006, **25**, 983–988; (*c*) Z. Lu, N. J. Hill, M. Findlater and A. H. Cowley, *Inorg. Chim. Acta*, 2007, **360**, 1316–1322; (*d*) D. Vidovic, M. Findlater and A. H. Cowley, *J. Am. Chem. Soc.*, 2007, **129**, 8436–8437; (*e*) M. Findlater, N. J. Hill and A. H. Cowley, *Dalton Trans.*, 2008, 4419–4423; (*f*) S. Aldridge, R. J. Calder, D. L. Coombs, C. Jones, J. W. Steed, S. Coles and M. B. Hursthouse, *New J. Chem.*, 2002, **26**, 677–686; (*g*) G. A. Pierce, N. D. Coombs, D. J. Willock, J. K. Day, A. Stasch and S. Aldridge, *Dalton Trans.*, 2007, 4405–4412; (*h*) C. Jones, D. P. Mills, A. Stasch and W. D. Woodul, *Main Group Chem.*, 2010, **9**, DOI: 10.1080/10241220902962937, ASAP article; ; (*i*) F. P. Macedo, C. Gwengo, S. V. Lindeman, M. D. Smith and J. R. Gardinier, *Eur. J. Inorg. Chem.*, 2008, 3200–3211; (*j*) A. H. Cowley, Z. Lu, J. N. Jones and J. A. Moore, *J. Organomet. Chem.*, 2004, **689**, 2562–2564; (*k*) B. Qian, S. W. Baek and M. R. Smith Iii, *Polyhedron*, 1999, **18**, 2405–2414; (*l*) K.-H. Park and W. J. Marshall, *J. Org. Chem.*, 2005, **70**, 2075–2081; (*m*) N. Kuhn, A. Kuhn, M. Speis, D. Bläser and R. Boese, *Chem. Ber.*, 1990, **123**, 1301–1306.

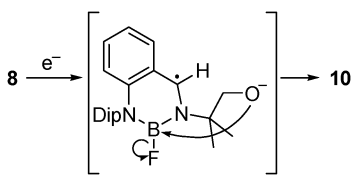
9 C.-T. Chen, C.-Y. Chan, C.-A. Huang, M.-T. Chen and K.-F. Peng, *Dalton Trans.*, 2007, 4073–4078.

10 G. Leroy, M. Sana and C. Wilante, *Theor. Chim. Acta*, 1993, **85**, 155–166.

11 There is another possibility for a mechanism involving the formation of borylene **11** by reduction. A subsequent hydrogen abstraction from its resonance form, biradical **12**, could afford diaminoborylradical species **9**. However, the borylene mechanism can be ruled out based on the formation of dimeric compound **6**.



12 There is another possibility for an initial elimination of alkoxide from intermediate **8**, followed by the nucleophilic attack of alkoxide towards the B–F moiety to form intermediate **10**.



13 S. R. Wilson, P. A. Zucker, R. R. C. Huang and A. Spector, *J. Am. Chem. Soc.*, 1989, **111**, 5936–5939.
14 (*a*) M. Barfield, S. R. Walter, K. A. Clark, G. W. Gribble, K. W. Haden, W. J. Kelly and C. S. L. Houllier, *Org. Magn. Reson.*, 1982, **20**, 92–101; (*b*) F. R. Jerome and K. L. Servis, *J. Am. Chem. Soc.*, 1972, **94**, 5896–5897.
15 A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori and R. Spagna, *J. Appl. Crystallogr.*, 1999, **32**, 115–119.
16 G. M. Sheldrick, *SHELXL-97, Program for refinement of crystal structures*, University of Göttingen, Germany, 1997.

