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Synthesis and structure of aminobis(η^1-cyclopentadienyl)boranes and related compounds

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Abstract

Amino(diorganyl)boranes of the type $R_2NB(\eta^1\text{-}C_xH_y)_2$ R = various ligands, $C_xH_y = C_5H_5$ (cyclopentadienyl), C_9H_7 (indenyl), $C_{13}H_9$ (fluorenyl) were recently reported as ligands in corresponding [1]borametallocenophanes of the Group IV metals Ti, Zr, and Hf. Several of those ligands including bis(cyclopentadienyl)boranes, cyclopentadienyl(indenyl)boranes, and difluorenylboranes such as ${}^iPr_2NB(\eta^1\text{-}C_5H_5)_2$ (**7**), ${}^iPr_2NB(\eta^1\text{-}C_5H_5)(\eta^1\text{-}C_9H_7)$ (**12**), and $Me_2NB(\eta^1\text{-}C_{13}H_9)_2$ (**13**), were obtained in very high yields and fully characterised. All compounds besides **13** show the expected presence of different constitutional isomers. Compound **7** was chosen as a representative example to assign all isomers by NMR methods. The structures of **12** (one isomer) and **13** in the solid state were determined by X-ray diffraction methods. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Boron/bis(cyclopentadienyl)boranes; Diindenylboranes; Constitutional isomers

1. Introduction

Recently, we started to investigate the chemistry of both strained [1a,b] and unstrained [2a–c] [1]borametallocenophanes, a class of compounds which exhibits an interesting chemistry due to the special properties of the bridging boron atom. For example, the incorporation of a Lewis acidic threefold co-ordinated boron into the bridge of Group IV element metallocenophanes enhances their catalytic activities [3] with respect to Ziegler–Natta type olefin polymerisation [4a,b] which was already demonstrated in a few cases [2b–c,5]. In order to obtain such complexes of the type $[R_2NB(\eta^1\text{-}C_xH_y)_2MCl_2]$ (**1**; R = various ligands, $C_xH_y = C_5H_4$, C_9H_6, $C_{13}H_8$, M = Ti, Zr, Hf) in high yields, we developed a convenient multistep one-pot synthesis which is depicted in Scheme 1 for some representative examples $[(Me_3Si)_2NB(\eta^1\text{-}C_5H_4)_2TiCl_2]$ (**1**) [2a] and $[{}^iPr_2NB(\eta^1\text{-}C_5H_4)(\eta^1\text{-}C_9H_6)MCl_2]$ (**2**, M = Zr; **3**, M = Hf) [2c]. The first step of these reaction sequences affords amino(diorganyl)boranes of the type $R_2NB(\eta^1\text{-}C_xH_y)_2$ [R = various ligands, $C_xH_y = C_5H_5$ (cyclopentadienyl), C_9H_7 (indenyl), $C_{13}H_9$ (fluorenyl)], which we, besides one example [2c], neither isolated nor characterised yet. In the present paper we report on spectroscopic and structural details of aminobis(η^1-cyclopentadienyl)boranes and related compounds.

Main group element compounds with monohapto co-ordinated cyclopentadienyl ligands of the type $R_xE(\eta^1\text{-}C_5H_5)$ (**A**) are known to be highly fluxional molecules undergoing two different sigmatropic rearrangements: On the one hand, a fivefold degenerate 1,2-shift of the R_xE group and on the other hand a non-degenerate 1,2-hydrogen shift which leads to the three different isomers [6]. These isomers exhibit three possible positions of the R_xE-group with respect to the carbon–carbon double bonds in the five-membered ring, namely allylic-allylic (**aa**), vinylic-allylic (**va**), and vinylic-homoallylic (**vh**), respectively. In the case of corresponding boranes $RB(\eta^1\text{-}C_5H_5)_2$ (**B**) with two η^1-cyclopentadienyl ligands one has to expect up to six isomers which may be denoted as **B aa/aa**, **B aa/va** etc (Fig. 1).

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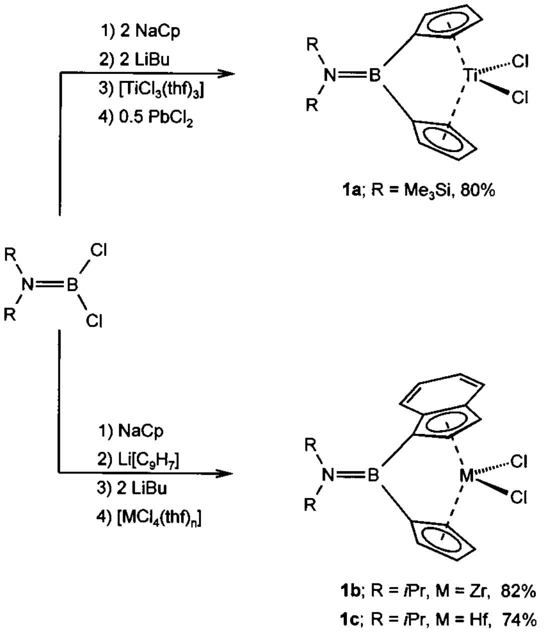
In contrast to the well developed chemistry of mono(η^1-cyclopentadienyl) [7a–h] and mono(η^1-indenyl)boranes [7g,8a–c] only a few examples of the corresponding disubstituted boranes with threefold coordinated boron were reported such as PhB(η^1-$C_5H_4R)_2$ (**4**, R = $SiMe_3$; **5**, R = $SnMe_3$) [9a,b], $PhB(\eta^1$-$C_9H_7)_2$ (**6**) [9c], and $^iPr_2NB(\eta^1$-$C_xH_y)_2$ (**7**, $C_xH_y = C_5H_5$; **8**, $C_xH_y = C_9H_7$) [5]. However, according to the complexity of the NMR spectra, and the thermal reactivity of those compounds preventing them from purification by distillation, complete spectroscopic data including identification of the isomers are mostly not available.



Scheme 1. Multistep synthesis of Group IV [1] borametallocenophanes.

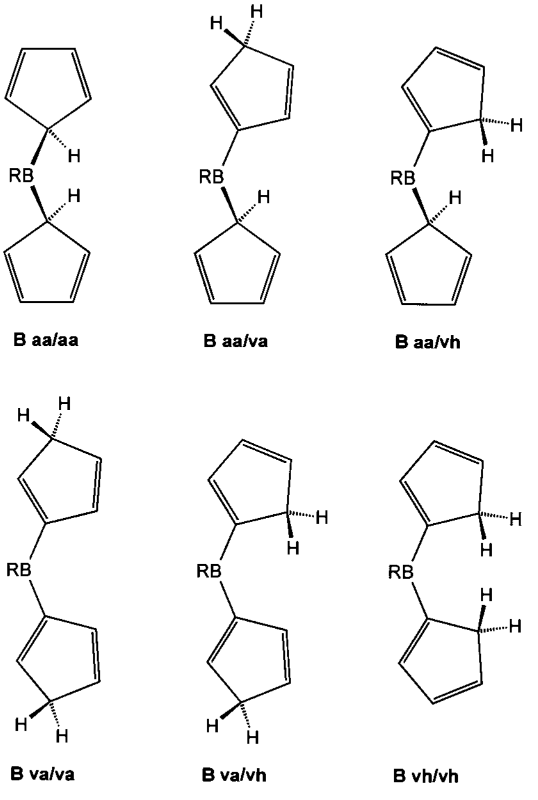


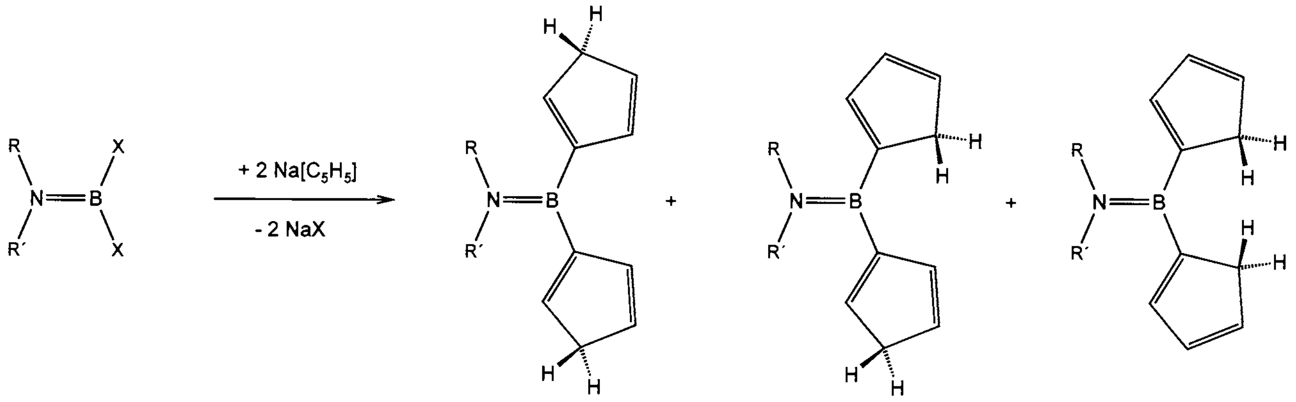
Fig. 1. Constitutional isomers of $B(\eta^1$-$C_5H_5)_2$ (**B**)

2. Results and discussion

2.1. Synthesis and structure of aminobis(η^1-cyclopentadienyl)boranes

According to Eq. (1) the aminobis(η^1-cyclopentadienyl)boranes **9**, **7**, **10**, and **11** were obtained from the reaction of R_2NBX_2 (R = various groups; X = Cl, Br) with two equivalents of $Na[C_5H_5]$ in a hexane slurry at ambient temperature. The dimethylamino derivative **9** could only be obtained from the corresponding dibromoborane; the less reactive Me_2NBCl_2 always produced $Me_2NB(\eta^1$-$C_5H_5)Cl$ even with a fourfold excess of $Na[C_5H_5]$. As monitored by ^{11}B-NMR spectroscopy, the first substitution of a halide by the cyclopentadienide was completed after 10 min in all cases. The second substitution strongly depends on the nature of the amino ligand. The electron withdrawing effect of nitrogen-bound silyl groups enhances the electrophilicity of the boron atom [10a,b], and hence, **10** and **11** are readily formed within 2 and 24 h, respectively, whereas **7** is yielded after two days. All compounds were isolated as crude slightly yellow oils in almost quantitative yields. Multinuclear NMR spectra proved them to be free from significant impurities. Analytically pure compounds were isolated by distillation at about 80°C and 10^{-2} mbar as colourless oils, which in the case of **7** solidified at 15°C. Due to their thermal instability this purification always was accompanied by about 50–80% decomposition of the crude material. At a temperature below 0°C, however, all compounds can be stored for weeks without decomposition. The constitution of **7** and **9**–**11** in solution was deduced from multinuclear NMR spectra and the assignment of all isomers was in the case of **7** achieved by 2-D-COSY, HMQC, and (H, H)-NOE experiments.

For $^iPr_2NB(\eta^1$-$C_5H_5)_2$ (**7**) up to six isomers have to be expected, namely **7 aa/aa**, **7 aa/va**, **7 aa/vh**, **7 va/va**, **7 va/vh**, and **7 vh/vh**. The first three isomers all show at least one η^1-cyclopentadienyl ligand (**aa**), in which boron binds to a saturated carbon atom. As to be expected, these isomers could not be detected after synthesis at ambient temperature, because from the corresponding mono(η^1-cyclopentadienyl)boranes it is known that such **aa** isomers can be obtained only under kinetic control at low temperature; **aa** isomers irre-



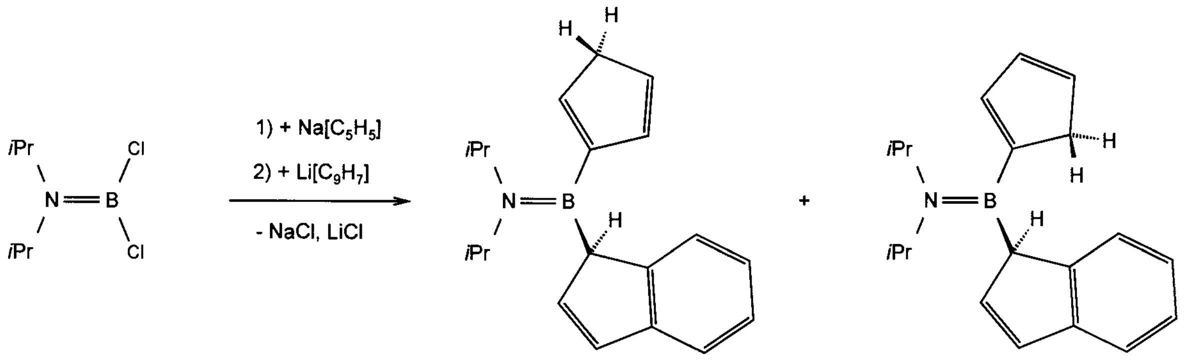
(1)

9 va/va	R = R′ = Me; X = Br	**9 va/vh**	**9 vh/vh**
7 va/va	R = R′ = *i*Pr; X = Cl	**7 va/vh**	**7 vh/vh**
10 va/va	R = *t*Bu, R′= SiMe$_3$; X = Cl	**10 va/vh**	**10 vh/vh**
11 va/va	R = R′= SiMe$_3$; X = Cl	**11 va/vh**	**11 vh/vh**

versibly rearrange into the thermodynamically more stable **va** and **vh** isomers, where boron binds to an unsaturated carbon atom, thus allowing π-interaction with the vinylic π-system into the vacant *pz* orbital at boron [6, 7a,h]. The absence of **7 aa**/**aa**, **7 aa**/**va**, and **7 aa**/**vh**, respectively, was proven by the fact that only –(B)C= and –CH$_2$– but no –(B)CH– moieties were detected in the ^{1}H- and ^{13}C-NMR spectra. Furthermore, the ^{11}B-NMR signal at $\delta = 40.3$ only corresponds to the vinylic isomers **7 va**/**va**, **7 va**/**vh**, and **7 vh**/**vh**, since boron atoms being connected to a saturated carbon atom in such compounds are significantly deshielded [2c]. The presence of two ^{11}B-NMR signals at $\delta = 39.8$ and $\delta = 30.4$ being described for the unspecified isomer mixture of **7** could not be confirmed [5]. **7 va**/**va**, **7 va**/**vh**, and **7 vh**/**vh** are obtained in a 1:1:1 ratio, which becomes clear from the three independent sets of signals in both ^{1}H- and ^{13}C-NMR spectra, being assigned by the methods mentioned above. Virtually the same spectroscopic findings were made for compounds **9**–**11**, however, we refrained from a complete assignment of the isomers in all cases.

2.2. Synthesis and structure of amino(η^1-indenyl)- and -fluorenylboranes

Diisopropylamino(η^1-cyclopentadienyl)(η^1-indenyl)borane (**12**) was obtained in a one pot reaction by subsequent treatment of ^{i}Pr$_2$NBCl$_2$ with Na[C$_5$H$_5$] and Li[C$_9$H$_7$] according to Eq. (2) and isolated as a colourless, crystalline solid in 85% yield. The structure of **12** in solution was deduced from multinuclear NMR spectra including 2-D-COSY, HMQC, and (H, H)-NOE experiments. This compound was obtained as a 1:1 mixture of two isomers, being denoted as **12 va**/**a**, and **12 vh**/**a**. As described for **7** and **9**–**11** under these conditions boron always binds to an unsaturated carbon atom of the cyclopentadienyl ligand, which results



(2)

12 va/a **12 vh/a**

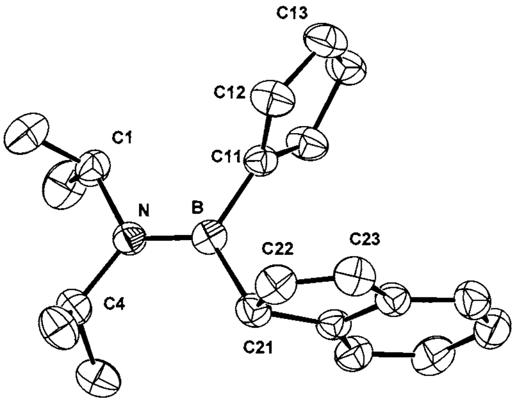
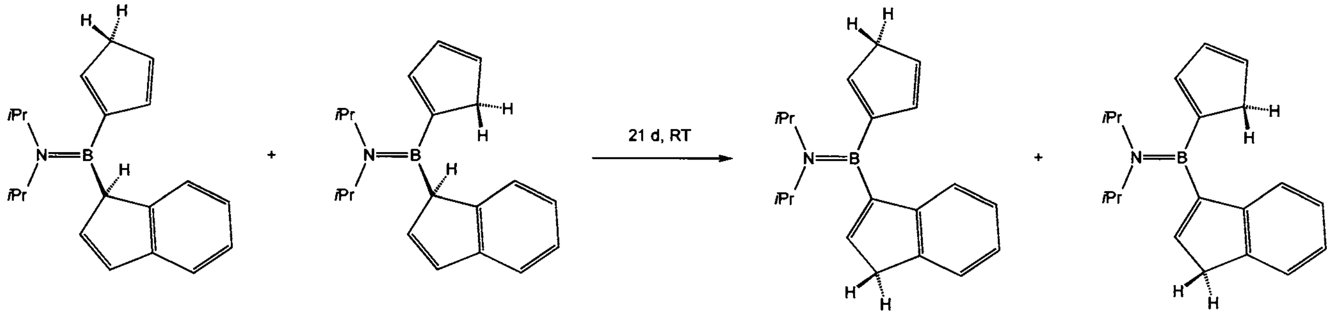


Fig. 2. Structure of **12vh/a** in the crystal (ellipsoids at 30% probability). Selected distances (pm) and angles (°): B–N 140.2(4); B–C11 156.7(4); C11–C12 136.0(4), C12–C13 145.5(4); B–C21 161.1(4); C21–C22 149.8(4); C22–C23 133.1(5); C1–N–B–C21 178.00(24);M C1–N–B–C11 −1.8(4), C4–N–B–C21 −1.0(4); C1–N–C4 113.6(2); C11–B–C21 116.2(3).

in the formation of **va** and **vh** isomers, respectively. In the case of the indenyl ligand, however, boron binds to a saturated carbon atom, thus adopting an allylic position (**a**) here. Within 21 days at ambient temperature a quantitative rearrangement into the thermodynamically more stable isomers **12 va/v** and **12 vh/v** (Eq. (3)) occurs, which was described recently for the corresponding aminodi(η^1-indenyl)borane $(Me_3Si)_2NB(\eta^1\text{-}C_9H_7)_2$ [2c] and related [7g,8a,b] indenylboranes. Characteristic for the vinylic isomers **12 va/v** and **12 vh/v** is for example the ^{11}B-NMR signal at $\delta = 40.8$, which is high field shifted with respect to the signal of **12 va/a** and **12 vh/a** at $\delta = 44.1$.

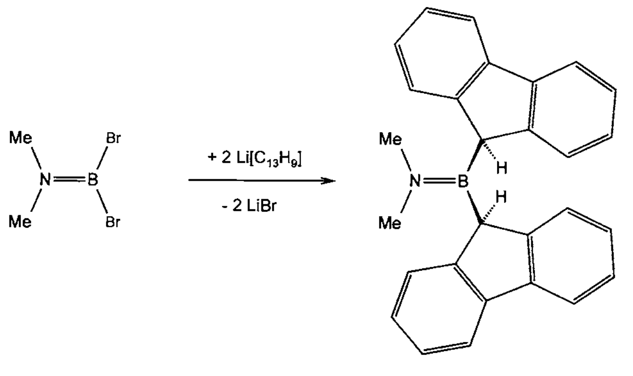


12 va/a **12 vh/a** **12 va/v** **12 vh/v**

(3)

A suitable single crystal of **12 vh/a** was obtained from a solution of the isomeric mixture in hexane at −30°C. The compound crystallises in the space group $P\bar{1}$ and the molecule adopts C_1 symmetry (Fig. 2). Both boron and nitrogen are in a trigonal planar environment and both bonding planes are orientated almost coplanar to each other, which is indicated by the corresponding torsion angles C1–N–B1–C11 = −1.8(4)° and C4–N–B–C21 = −1.0(4)°. This geometry together with a boron–nitrogen distance of 140.2(4) pm proves the presence of a boron–nitrogen double bond. The difference in the boron–carbon distances, B–C11 = 156.7(4) pm versus B–C21 = 161.1(4) pm reflects the different hybridisation of the carbon atoms and possible π-interaction between boron and the vinylic system of the cyclopentadienyl ligand. The geometry of the indenyl ligand and its co-ordination to the boron atom resembles that of known diindenyldiboranes(4) [8c] and diindenylboranes [2c].

Dimethylaminodi(η^1-fluorenyl)borane (**13**) was obtained according to Eq. (4) from Me_2NBBr_2 and two equivalents of $Li[C_{13}H_9]$ in toluene at 0°C, and isolated in 50% yield as a colourless crystalline solid. The compound, which is moderately sensitive towards air and moisture readily, dissolves in aromatic and polar solvents but is only slightly soluble in hexane. The structure of **13** in solution was derived from multinuclear NMR spectra. The ^{11}B-NMR signal at $\delta = 42.3$ is in the expected range for amino(diorganyl)boranes, and besides, a double set of signals for the methyl and fluorenyl ligands, respectively, is observed in both ^{1}H- and ^{13}C-NMR spectra. The latter finding clearly demonstrates that in solution **13** adopts a lower symmetry than C_{2v} which might be expected for a symmetrical amino(diorganyl)borane of the type $R_2N{=}BR'_2$. Two markedly separated ^{1}H-NMR signals for the nitrogen bound methyl groups were observed at $\delta = 1.60$ and 3.21, respectively. Corresponding to the expected range of such NMe_2 groups ($\delta = 2.6$–3.0), one resonance is slightly deshielded, whereas the other one is significantly high field shifted. This gives evidence for different anisotropic effects the two fluorenyl ligands have on the methyl groups in a way that one methyl group points into the centre of one aromatic system, whereas the other one faces the edge of the second fluorenyl ligand. All spectroscopic findings indicate that **13** adopts very similar structures in solution and in the solid state, the latter being described subsequently.



13

(4)

Single crystals of **13** were obtained from a xylene solution (mixture of *o*-, *m*-, *p*-isomers) at −30°C. The compound crystallises in the space group $P2_1/c$ and the molecule adopts approximate C_s symmetry. The presence of a boron–nitrogen double bond is again proved by the same structural features which were described for **12 vh/a** i.e. trigonal planar co-ordination of both boron and nitrogen, the torsion angles C1–N–B–C10 = 1.3(15)° and C2–N–B–C30 = −6.2(15)°, and the boron–nitrogen distance of 140.0(12) pm. The fluorenyl ligands are orientated almost orthogonal to each other enclosing a dihedral angle of 78.2(2)°. Due to this geometry, one nitrogen bound methyl group adopts a position just above the centre of one fluorenyl ligand, while the other methyl group is much closer to the edge of the second aromatic ligand. The latter fluorenyl ligand shows a markedly longer boron–carbon bond (B–C10 = 169.3(13) pm) than the other (B–C30 = 155.9(13) pm) which may be due to the steric requirements of these large groups [11].

3. Conclusions

Several amino(diorganyl)boranes of the type $R_2NB(\eta^1\text{-}C_xH_y)_2$ R = various ligands, $C_xH_y = C_5H_5$ (cyclopentadienyl), C_9H_7 (indenyl), $C_{13}H_9$ (fluorenyl), which are known as intermediates in the synthesis of [1]borametallocenophanes of the Group IV metals Ti, Zr, and Hf, were obtained in high yields by convenient salt elimination reactions. All bis(cyclopentadienyl)derivatives were obtained as mixtures of three constitutional isomers. By NMR methods, it was proven that upon synthesis at ambient temperatures only those isomers were present where the boron atom is connected to an unsaturated carbon atom of the five-membered ring, thus being in a vinylic position. The thermodynamically less stable isomers with bonds between boron and saturated carbon atoms (boron in allylic position) were not detected. Under the same conditions, however, corresponding indenylboranes could be isolated as kinetically controlled allylic isomers, which rearrange to the thermodynamically more stable vinylic isomers at higher temperatures.

4. Experimental

All manipulations were carried out under a dry nitrogen atmosphere with common Schlenk techniques. Solvents and reagents were dried by standard procedures, distilled, and stored under nitrogen over molecular sieves. $(Me_3Si)_2NBCl_2$ [12], $^tBu(Me_3Si)NBCl_2$ [13], $^iPr_2NBCl_2$ [14], $(CH_3)_2NBBr_2$ [15], $Na[C_5H_5]$ [16] were obtained according to literature procedures. Indene and fluorene were used in commercially available quality without further purification (Fa. Merck). NMR: Varian Unity 500 at 499.843 MHz (^1H, internal standard TMS), 150.364 MHz (^{11}B, BF_3OEt_2 in C_6D_6 as external standard), 125.639 MHz ($^{13}C\{^1H\}$, APT, internal standard TMS); all NMR spectra were recorded in CD_2Cl_2 as solvent unless otherwise stated. Mass spectra were recorded on a Finnigan MAT 95 (70 eV) and elemental analyses (C, H, N) were obtained from a Carlo–Erba elemental analyzer, model 1106.

4.1. $Me_2NB(\eta^1\text{-}C_5H_5)_2$ (9)

$Na[C_5H_5]$ (2.20 g, 25.00 mmol) was suspended in 20 ml hexane and a solution of 2.68 g (12.50 mmol) Me_2NBBr_2 in 10 ml hexane was added dropwise at 0°C. The yellow suspension was allowed to come to ambient temperature and stirred for 16 h. The precipitated NaBr was filtered off, washed with 20 ml hexane and the filtrate evaporated in high vacuum. 2.22 g (96%) of **9** were yielded as a yellow oil. Analytically pure **9** was obtained by a trap to trap condensation at 60°C in high vacuum.

^1H-NMR (isomeric mixture of **9 va/va**, **9 va/vh** and **9 vh/vh**): $\delta = 2.66, 2.70, 2.74$ (3 s, 18 H, CH_3); 2.89, 3.01, 3.10 (3 m, 12 H, CH_2); 6.30–7.00 (18 H, CH). ^{13}C-NMR (isomeric mixture of **9 va/va**, **9 va/vh** and **9 vh/vh**): $\delta = 40.97, 41.34, 41.77$ (CH_3), 43.27, 46.70, 47.07 (CH_2); 131.86, 133.31, 136.02, 137.25, 137.66, 138.66, 140.00, 141.25, 142.77. ^{11}B-NMR: $\delta = 37.81$.

MS; m/z (%): 185 (50) [M^+], 170 (10) [$M^+ - Me$], 120 (70) [$M^+ - C_5H_5$], 65 (100) [C_5H_5]. $C_{12}H_{16}NB$ (185.08): Anal. Calc. C, 77.18; H, 8.71; N, 7.57. Found C, 77.21; H, 9.02; N, 7.46%.

4.2. $^iPr_2NB(\eta^1\text{-}C_5H_5)_2$ (7)

$Na[C_5H_5]$ (13.00 g, 147.72 mmol) was suspended in 80 ml hexane and a solution of 13.41 g (73.85 mmol) $^iPr_2NBCl_2$ in 20 ml hexane was added dropwise at 0°C. The yellow suspension was allowed to come to ambient temperature and stirred for two days. The precipitated NaCl was filtered off, washed with 30 ml hexane and the filtrate evaporated in high vacuum. 17.27 g (97%) of **7** were yielded as a yellow oil. 3.56 g (20%) analytically pure **7** was obtained by distillation of the crude material at 55°C in high vacuum as a colourless liquid which solidified at 15°C.

^{1}H-NMR: $\delta = 1.06$ (d, 12H, CH_3, **7 va/va**); 1.08 (d, 12H, CH_3, **7 vh/vh**); 1.13 (d, 12H, CH_3, **7 va/vh**); 2.85 (m, 4H, CH_2, **7 va/va**); 2.94 (m, 4H, CH_2, **7 vh/vh**); 3.03 (m, 4H, CH_2, **7 va/vh**); 3.62 (m, 2H, CH, **7 va/vh**); 3.72 (m, 2H, CH, **7 va/va**); 3.92 (m, 2H, CH, **7 vh/vh**); 6.30, 6.70 (2 m, 6H, CH_{Cp}, **7 va/va**); 6.47, 6.61 (2 m, 6H, CH_{Cp}, **7 vh/vh**); 6.50, 6.60, 6.75 (3 m, 6H, CH_{Cp}, **7 va/vh**). ^{13}C-NMR: $\delta = 23.97$ (CH_3, **7 vh/vh**); 24.39 (CH_3, **7 va/va**); 24.68 (CH_3, **7 va/vh**); 43.13 (CH_2, **7 va/va**); 46.55 (CH_2, **7 vh/vh**); 46.75 (CH_2, **7 va/vh**); 48.35 (CH, **7 va/vh**); 48.76 (CH, **7 va/va**); 49.15 (CH, **7 vh/vh**); 131.80, 134.93, 137.34 (CH_{Cp}, **7 va/va**); 131.87, 133.20, 137.24 (CH_{Cp}, **7 vh/vh**); 135.31, 135.60, 136.82 (CH_{Cp}, **7 va/vh**). ^{11}B-NMR: $\delta = 40.25$. MS; *m/z* (%): 241 (100) [M^+], 226 (95) [$M^+ - Me$], 198 (45) [$M^+ - {}^{i}Pr$]. $C_{16}H_{24}NB$ (241.19): Anal. Calc. C, 79.68; H, 10.03; N, 5.81. Found C, 80.11; H, 9.76; N, 5.63%.

*4.3. $^{t}Bu(Me_3Si)NB(\eta^{1}\text{-}C_5H_5)_2$ (**10**)*

$Na[C_5H_5]$ (6.00 g, 68.18 mmol) was suspended in 25 ml hexane and a solution of 6.75 g (34.09 mmol) $^{t}Bu(Me_3Si)NBCl_2$ in 15 ml hexane was added dropwise at 0°C. The yellow suspension was allowed to come to ambient temperature and stirred for 16 h. The precipitated NaCl was filtered off, washed with 20 ml hexane and the filtrate evaporated in high vacuum. 9.34 g (96%) of **10** was yielded as a yellow oil. 4.67 g (48%) analytically pure **10** was obtained by a trap to trap condensation of the crude material at 90°C in high vacuum as a colourless liquid which solidified at 18°C.

^{1}H-NMR (isomeric mixture of **10 va/va**, **10 va/vh** and **10 vh/vh**): $\delta = 0.18$, 0.22, 0.27 (3 s, 27H, $SiMe_3$); 1.29, 1.35, 1.39 (3 s, 27H, CMe_3); 2.84, 2.91, 2.97 (3 m, 12H, CH_2); 6.30–6.91 (18H, CH). ^{13}C-NMR (isomeric mixture of **10 va/va**, **10 va/vh** and **10 vh/vh**): $\delta = 6.41$, 6.54, 6.73 ($SiMe_3$); 31.93, 33.20, 34.41 (CMe_3); 42.94, 46.00, 55.60 (CH_2); 133.00, 133.10, 137.51, 137.85, 138.85, 138.06, 139.82, 140.24, 141.12 (CH). ^{11}B-NMR: $\delta = 46.01$.

MS; *m/z* (%): 285 (60) [M^+], 270 (100) [$M^+ - Me$], 228 (35) [$M^+ - {}^{t}Bu$], 57 (40) [^{t}Bu]. $C_{17}H_{28}NBSi$ (285.31): Anal. Calc. C, 71.57; H, 9.89; N, 4.91. Found C, 72.02; H, 9.46; N, 5.03%.

*4.4. $(Me_3Si)_2NB(\eta^{1}\text{-}C_5H_5)_2$ (**11**)*

10.09 g (114.66 mmol) $Na[C_5H_5]$ was suspended in 125 ml hexane and a solution of 13.84 g (57.28 mmol) $(Me_3Si)_2NBCl_2$ in 50 ml hexane was added dropwise at 0°C. The yellow suspension was allowed to come to ambient temperature and stirred for 2 h. The precipitated NaCl was filtered off, washed with 30 ml hexane and the filtrate evaporated in high vacuum. 16.92 g (98%) of **11** was yielded as a colourless oil. 3.11 g (18%) analytically pure **11** was obtained by distillation of the crude material at 80°C in high vacuum as a colourless liquid.

^{1}H-NMR (isomeric mixture of **11 va/va**, **11 va/vh** and **11 vh/vh**): $\delta = 0.12$, 0.15, 0.21 (s, 54H, $SiMe_3$); 2.9–3.2 (m, 12H, CH_2); 6.2–7.0 (18H, CH). ^{13}C-NMR (isomeric mixture of **11 va/va**, **11 va/vh** and **11 vh/vh**): $\delta = 3.87$, 4.16, 4.49 ($SiMe_3$); 45.93, 46.04, 46.21 (CH_2); 133.02, 133.38, 137.48, 140.09, 141.58, 143.49, 145.03, 146.27, 146.95 (CH). ^{11}B-NMR: $\delta = 49.02$. MS; *m/z* (%): 301 (50) [M^+], 286 (15) [$M^+ - Me$], 236 (30) [$M^+ - C_5H_5$], 172 (90) [$M^+ - 2C_5H_5$], 97 (100) [$M^+ - SiMe_3 - 2C_5H_5$]. $C_{16}H_{28}NBSi_2$ (301.39): Anal. Calc. C, 63.76; H, 9.36; N, 4.65. Found C, 63.54; H, 10.04; N, 4.39%.

*4.5. $^{i}Pr_2NB(\eta^{1}\text{-}C_5H_5)(\eta^{1}\text{-}C_9H_7)$ (**12**)*

To a suspension of 1.07 g (8.75 mmol) $Li[C_9H_7]$ in 25 ml hexane, a solution of 1.59 g (8.75 mmol) $^{i}Pr_2NBCl_2$ in 5 ml hexane was added dropwise at 0°C. The suspension was allowed to come to ambient temperature and stirred for additional 2 h. The yellow reaction mixture was filtered, and the residue washed with 5 ml hexane. The filtrate was added dropwise to a suspension of 0.77 g (8.75 mmol) $Na[C_5H_5]$ in 25 ml hexane at 0°C. After warming to room temperature (r.t.) and additional stirring for 16 h the suspension was filtered, and the residue was washed with 10 ml of hexane. All volatiles were removed in high vacuum and the remaining solid was crystallised from hexane at −30°C to yield 2.32 g (91%) of **12** as a colourless crystalline solid.

^{1}H-NMR (isomeric mixture of **12 va/a** and **12 vh/a**): $\delta = 0.81$ (d, 6H, CH_3); 1.27 (d, 6H, CH_3); 3.19 (m, 1H, CH); 3.69 (m, 1H, CH); 2.21–2.45 (2H, CH_{2Cp}); 4.01 (m, 1H, $CH_{ind}B$); 5.97–7.5 (9H, $CH_{ind,\ Cp}$). ^{13}C-NMR (isomeric mixture of **12 va/a** and **12 vh/a**): $\delta = 22.39$, 25.88 (CH_3); 45.39, 49.13 (CH); 42.59, 46.5 (CH_{2Cp}); 52.07 ($CH_{ind}B$); 120.99, 123.67, 124.00, 125.47, 130.68, 131.18, 132.63, 133.68, 133.95, 136.64, 137.33, 137.81 ($CH_{ind,\ Cp}$); 146.40, 148.30 (C_{ind}).^{11}B-NMR: $\delta = 41.86$. MS; *m/z* (%): 291 (20) [M^+], 276 (15) [$M^+ - Me$], 176 (40) [$M^+ - C_9H_7$], 116 (100) [$C_9H_7^+$]. $C_{20}H_{26}NB$ (291.25): Anal Calc. C, 82.48; H, 9.00; N, 4.81. Found C, 83.22; H, 8.68; N, 4.79%.

*4.6. $Me_2NB(\eta^{1}\text{-}C_{13}H_9)_2$ (**13**)*

To a solution of 3.32 g (19.98 mmol) fluorene in 80 ml toluene, 12.5 ml (20.00 mmol) 1.6 M LiBu in hexane solution was added dropwise at 0°C. The yellow solution was warmed to ambient temperature and stirred for 12 h. The precipitated yellow Li[$C_{13}H_9$] was filtered off, washed with 50 ml hexane and dried in high vacuum to yield Li[$C_{13}H_9$] as a yellow solid in quantitative yield. Li[$C_{13}H_9$] was suspended in 50 ml toluene and treated with a solution of 2.14 g (8.99 mmol) Me_2NBBr_2 in 20 ml toluene at 0°C. The reaction mixture was warmed to ambient temperature and stirred for an additional 16 h. The colourless suspension was filtered, the residue washed with 20 ml toluene and the filtrate was reduced to a volume of 15 ml and stored at − 30°C. After 24 h a crop of 1.73 g (50%) of **13** was yielded as a crystalline, colourless solid. ^{1}H-NMR (CD_2Cl_2): $\delta = 1.60$ (s, 3H, CH_3); 2.74 (s, 1H, CHB); 3.21 (s, 3H,CH_3); 4.65 (s, 1H, CHB); 6.60–8.00 (16H, CH). ^{13}C-NMR (CD_2Cl_2): $\delta = 39.11$, 41.64 (CH_3); 41.88, 45.58 (br, CHB); 119.78, 120.64, 124.38, 125.44, 125.61, 126.58, 127.03, 129.17 (CH); 141.31, 142.49, 147.44, 148.37 (C). ^{11}B-NMR: $\delta = 42.31$. MS m/z (%): 385 (60) [M^+], 220 (100) [$M^+ - C_{13}H_9$], 165 (50) [$C_{13}H_9^+$]. $C_{28}H_{24}NB$ (385.32): Anal. Calc. C, 87.28; H, 6.28; N, 3.64. Found C, 87.91; H, 5.98; N, 3.72%.

X-ray structure determinations of **12 vh/a** and **13**: Intensity data for both structures were collected on an ENRAF-Nonius CAD4 diffractometer, Cu–K_α radiation equipped with incident beam graphite monochromator ($\lambda = 1.5418$ Å).

Compound **12 vh/a**, $T = 293$ K, colourless parallelepiped of approximate dimensions 0.7 × 0.6 × 0.4 mm^3 mounted in a stream of dinitrogen on a glass fibre. Crystal data: triclinic space group $P\bar{1}$, $a = 8.0659(8)$, $b = 9.7904(8)$, $c = 11.724(2)$ Å, $\alpha = 107.081(9)$, $\beta = 90.253(9)$, $\gamma = 93.331(7)°$, $V = 883.3(4)$ Å^3, $Z = 2$, $D_{calc} = 1.10$ g cm^{-3}, $\mu = 4.3$ cm^{-1}. 4599 reflections, 2398 independent observations with $I > 1\sigma(I)$, $\theta_{max} = 72°$, solution with direct methods (SHELXS 97 [17]), refinement on F (local version of the SDP suite [18]) with anisotropic displacement parameters for all non-hydrogen atoms. Methyl H atoms were treated as riding with refined isotropic U_{eq}, remaining hydrogen atoms were refined isotropically. 267 variables, $R_w = 0.074$, $R = 0.078$, max./min. electron density from final difference Fourier 0.25 and − 0.26 eÅ^{-3}.

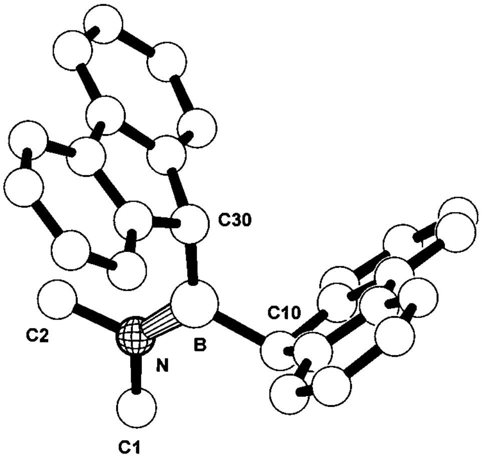


Fig. 3. Structure of **13** in the crystal. Selected distances (pm) and angles (°): B–N 140.0(12); B–C30 155.9(13); B–C10 169.3(13); C1–N–C2 109.2(7); C30–B–C10 118.7 (9); C1–N–B–C10 1.3(15); C2–N–B–C30 − 6.2(15).

Compound **13**, $T = 291$ K, colourless approximately isometric block (diameter ca. 0.3 mm) mounted in a capillary. Crystal data: monoclinic space group $P2_1/c$, $a = 9.535(3)$, $b = 16.311(4)$, $c = 15.858(4)$ Å, $\beta = 92.53(3)°$, $V = 2464(2)$ Å^3, $Z = 4$, $D_{calc} = 1.18$ g cm^{-3}, $\mu = 4.7$ cm^{-1}. The crystal contains two molecules of xylene per unit cell which partially evaporates during data collection. An intensity loss of 50% was corrected by interpolation between three regularly measured check reflections; 9223 reflections, 4193 independent, $\theta_{max} = 65°$, solution with direct methods (SHELXS 97 [17]), refinement on F^2 (SHELXL 97 [17]) with isotropic displacement parameters for all non-hydrogen atoms and H atoms in riding geometry. Due to the necessarily low quality of the data set refinement attempts with anisotropic displacement parameters gave no physically meaningful results. 140 variables, wR_2(all data) = 0.2450, R_1 (for data with $I > 2\sigma(I)$) = 0.1295, max./min. electron density from final difference Fourier 0.52 and − 0.45 eÅ^{-3} Fig. 3.

5. Supplementary data

Crystallographic data (excluding structure factors) for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 149 850 for compound **12 vh/a**, and CCDC no. 149 851 for compound **13**. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: + 44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk).

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