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New zwitterionic heterocycles derived from 1-chloro(dimethyl)silyl-1-borylalkenes and 2-lithio-1-methylimidazole and 1-lithio-indazole

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Abstract

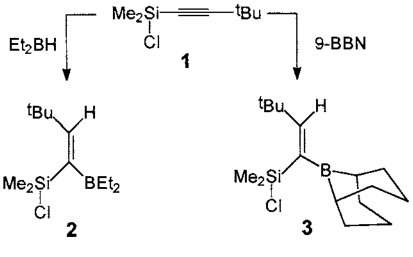
The 1-alkynyl(chloro)dimethylsilane $^{t}BuC{\equiv}CSiMe_2Cl$ (**1**) reacts with tetraethyl-diborane(6) or 9-borabicyclo[3.3.1]nonane dimer, $(9\text{-}BBN)_2$, to give the (*Z*)-1-chloro-dimethylsilyl-1-diethylboryl-alkenes **2** and **3**. These alkenes react with 2-lithio-1-methylimidazole or 1-lithio-indazole by formation of LiCl and of **4**, **5** and **9** together with small amounts of **6**, **7** or **8** as minor products. In **4** and **5**, a zwitterionic structure is present which can be alternatively described as a borane adduct of a carbene. All new compounds were characterised by ^{1}H-, ^{11}B-, ^{13}C-, ^{15}N- and ^{29}Si-NMR spectroscopy, and the molecular structure of **5** was determined by X-ray structural analysis. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Boron; Heterocycles; Hydroboration; Imidazole NMR multinuclear; Silanes; X-ray

1. Introduction

Useful synthons for heterocyclic chemistry can be prepared by 1,2-hydroboration of 1-alkynyl(chloro)dimethylsilane. This has been shown recently for compound **1**, in which the ^{t}Bu group guarantees a high stereoselectivity of the hydroboration reaction [1]. As shown in Scheme 1, the hydroboration of **1** with 9-BBN [2a] affords **3**, analogous to the known alkene **2** [1]. Some aspects of the reactivity of **2** have already been explored [1]; however, it appeared that the products containing the Et_2B group were difficult to crystallise. Therefore, **3** was prepared in this work in order to obtain products of which eventually single crystals would become available.

A surprising aspect of the previous work [1] was the reaction of **2** with 2-lithio-thiazoles which has afforded selectively **A**. Based on NMR spectroscopic evidence, the zwitterionic structure **A** has been proposed in which the boron atom possesses four B–C bonds and the silicon atom is linked to the azole nitrogen atom. The other readily conceivable isomer with a coordinative N_{azole}–B bond was not detected at all. In this work we have used 2-lithio-1-methylimidazole for the reaction with **2** in order to find out whether the nature of the azole system is important with regard to the product distribution. In this context we have also studied the reaction of **2** with N-lithio-indazole. Furthermore, the reaction of **3** with 2-lithio-1-methylimidazole was car-



Scheme 1.

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Table 1
^{11}B-, ^{13}C- and ^{29}Si-NMR data [a] of the alkenes **2** and **3**

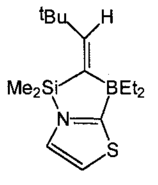
Compound BR_2	**3** 9-BBN	**2** BEt_2
$\delta^{13}C(^{t}Bu\mathbf{C}H=)$	163.6 [66.0] [b,c]	152.5
$\delta^{13}C(B\mathbf{C}(Si)=)$	145.1 (br)	149.0 (br)
$\delta^{13}C(Si\mathbf{Me})$	7.1 [57.7] [b]	5.2
$\delta^{13}C(B\mathbf{R}_2)$	32.2 (br), 33.6, 23.7	21.6 (br), 9.4
$\delta^{13}C(^{t}\mathbf{Bu})$	36.6, 30.5	36.6. 30.4
$\delta^{29}Si$	+17.8	+15.7
$\delta^{11}B$	+82.1	+82.0

[a] Measured in C_6D_6 at 20°C; coupling constants $J(^{29}Si, ^{13}C)$ [± 0.1 Hz] are given in brackets; (br) denotes a broad ^{13}C resonance signal as the result of partially relaxed scalar $^{13}C–^{11}B$ coupling.

[b] Measured from the ^{29}Si-NMR spectrum; isotope induced shifts $^{1}\Delta^{12/13}C_{Me}(^{29}Si) = +0.5$ ppb and $^{1}\Delta^{12/13}C_{C=}(^{29}Si) = -1.5$ ppb.

[c] ^{13}C satellites were observed: $^{1}J(=^{13}C, ^{13}C_{(^{t}Bu)}) = 40.9$ Hz; $^{1}J(^{13}C=^{13}C) = 55.6$ Hz.

ried out in order to isolate crystalline material for X-ray structural analysis.

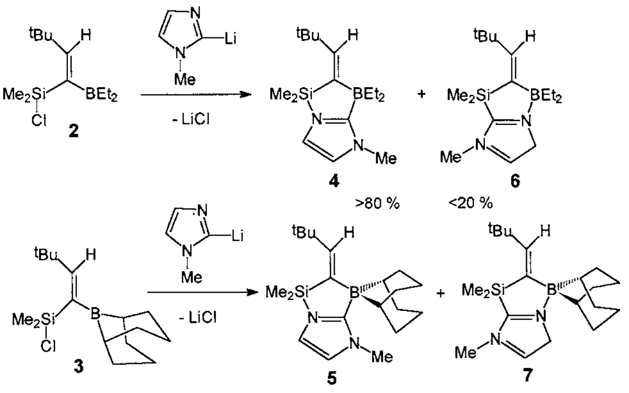


A

2. Results and discussion

2.1. Hydroboration of 1-alkynyl(chloro)dimethylsilanes (1) with 9-BBN′

The reaction of **1** with Et_2BH (tetraethyldiborane(6)[3]) affords selectively the alkene **2** as reported [1]. Analogously, **1** reacts with 9-BBN to give **3** as the sole product (Scheme 1). Similar to the case of **2**, rather harsh reaction conditions were required to achieve hydroboration. The reaction was carried out in hexane, and it required heating at reflux for 20 h. NMR data of **2** (for comparison) and **3** are given in Table 1. For both **2** and **3**, the ^{11}B- and ^{29}Si-NMR data do not indicate any significant bonding interaction via a potential Si–Cl–B bridge.



Scheme 2.

2.2. Reactions of the 1-silyl-1-boryl-alkenes 2 and 3 with 2-lithio-1-methylimidazole and NMR spectroscopic characterisation of the new heterocycles

There are two electrophilic centres in each of the alkenes **2** and **3**. Imidazoles lithiated in 2-position can offer the nitrogen(3) and the carbon atom in 2-position as nucleophilic centres. As shown in Scheme 2, mixtures of isomers **4** and **6** or **5** and **7** were obtained in most cases. However, in each case the zwitterionic derivative was in large excess, and after purification by crystallisation, the compounds **4** or **5** could be isolated in high purity. By this, crystalline material of **5** was just of sufficient quality to determine the molecular structure (vide infra).

The structures of **4** and **5** in solution are supported by the ^{13}C-NMR spectra (Table 2), in particular by inspection of the range for the olefinic carbon atoms (Fig. 1): three sharp and two broad signals (for the boron-bonded carbon atoms [4]) are present, whereas for the other isomers **6** and **7** (with Si–C and B–N bonds) four sharp signals are detected (one broad signal is very weak and could not be assigned with certainty). The broad ^{13}C resonance signal of the imidazole ring is found at a rather high frequency. This indicates the significant contribution of a canonic structure in which the carbenoid [1,5] carbon atom bears the formally positive charge.

The ^{15}N-NMR spectrum of **5** shows two signals of which one ($\delta^{15}N$ −211.3) is close to that of 1-methylimidazole itself ($\delta^{15}N(1)$ −219.2, N(3) −119.1 [6]), and the other one at a higher frequency ($\delta^{15}N$ −182.0) is assigned to the nitrogen atom linked to silicon. This shielding is increased by 62.9 ppm with respect to that of N(3) in 1-methylimidazole and indicates the engagement of the lone pair of electrons at the nitrogen atom in Si–N bonding. A similar shift difference (−56.2 ppm) has been observed between **A** and thiazole [1]. The assignments are in agreement with GIAO calculations based on the RHF/6-31G* optimised geometry [7].

^{29}Si-NMR signals of **4** and **5** are shifted to lower frequency when compared with **A**. In the reaction solutions, a second small signal is evident at much lower

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[3] The formula Et_2BH is used for simplicity: tetraethyldiborane(6) is usually obtained and used as a mixture with triethylborane and small amounts of other ethyldiboranes(6) [3].

Table 2
^{11}B-, ^{13}C-, $^{14/15}$N-, ^{29}Si-NMR data of the heterocycles **4**, **5**, **A**, **9** [a]

Compound BR$_2$	**4** [b] BEt$_2$	**5** [c] 9-BBN	**A** BEt$_2$	**9** [d] BEt$_2$
δ^{13}C(^{t}Bu **C**H=)	157.1	157.3 [e]	157.9	159.2
δ^{13}C(B**C**(Si)=)	145.2 (br) (51.0)	147.5 (br) (53.0)	142.1 (br) [67.3]	140.9 (br)
δ^{13}C(N**C**)	124.1	123.8 [f]	132.2	142.6
δ^{13}C(=**C**)/(**CB**)	117.9/182.9 (br) (55.0)	119.0 [f]/186.0 (br) (56.0)	123.3/219.3 (br)	111.7, 122.4, 122.6, 125.3, 128.6, 129.8
δ^{13}C(Si**Me**$_2$)	1.9 [54.0]	3.7 [54.0]	2.3 [53.7]	1.5 [56.2]
δ^{13}C(B**R**$_2$)	18.9 (br) (50.0), 12.6	28.5 (br) (55.0), 33.1, 34.5, 25.4, 25.3	21.2 (br), 11.5	20.5 (br), 10.5
δ^{13}C(N**Me**)	33.5	37.5	–	–
δ^{13}C(**^{t}Bu**)	36.6, 30.8	36.2, 31.0	36.9, 30.4	36.8, 30.7
δ^{29}Si	+13.1	+8.7	+22.1	+11.2
δ^{11}B	−10.0	−9.1	−7.6	+2.4
$\delta^{14/15}$N	n.m.	−182.9, ^{15}N–Si; −211.3, ^{15}N–Me	−138.0, ^{14}N–Si	n.m.

[a] Measured in C_6D_6 at 20°C.; n.m. not measured; coupling constants $J(^{29}\mathrm{Si}, ^{13}\mathrm{C})$ are given in brackets [±0.2 Hz] and $^1J(^{13}\mathrm{C}, ^{11}\mathrm{B})$ in parentheses (±5 Hz); (br) denotes a broad ^{13}C resonance signal as the result of partially relaxed scalar ^{13}C–^{11}B coupling.

[b] Some relevant NMR data of isomer **6** (Scheme 2): δ^{13}C 0.7 (Me$_2$Si), 10.8 (Et$_2$B, CH$_3$), 122.4, 124.3, 157.1, 156.5 (olefinic carbon atoms); δ^{11}B +1.2; δ^{29}Si −14.8.

[c] Some relevant NMR data of isomer **7** (Scheme 2): δ^{11}B +2.0; δ^{29}Si −18.4.

[d] Some relevant NMR data of isomer **8** (Scheme 3): δ^{13}C 2.4 (Me$_2$Si), 10.9 (Et$_2$B, CH$_3$), 158.4 (^{t}Bu**C**H=), δ^{29}Si 16.9.

[e] ^{13}C satellites were observed: $^1J(^{13}\mathrm{C}{=}^{13}\mathrm{C}) = 73.6$ Hz.

[f] ^{13}C satellites were observed: $^1J(={}^{13}\mathrm{C}, ^{13}\mathrm{C}_{(^t\mathrm{Bu})}) = 41.4$ Hz, $^1J(^{13}\mathrm{C}{=}^{13}\mathrm{C}) = 62.1$ Hz.

frequency which belongs to the isomers **6** and **7**, respectively. Similarly, the ^{11}B-NMR spectra of the reaction solutions show an intense signal in a range approaching that known for tetraorganoborates [8] and a second fairly weak and broad signal at higher frequency for the isomers **6** or **7**.

*2.3. Ab initio calculations of the parent compound of **4** and **6***

The ab initio calculations (RHF/6-31G* [7a,b]) carried out for the parent compounds of **4** or **5** and their isomers **6** or **7** show that the isomer with C–B and N–Si bonds, corresponding to **4** or **5**, is more stable by 7.3 kcal mol^{-1} (the opposite was found for the compounds in which the Si atom is replaced by carbon: the isomer with B–N and C–C bonds is more stable by 11.4 kcal mol^{-1}). The calculated (GIAO [7b,c]) ^{11}B-, ^{13}C- and ^{15}N-isotropic magnetic shieldings based on the RHF/6-31G* optimised geometry are in reasonable agreement with the experimental data taking into account the influence of substituents at the silicon and boron atoms (the X-ray structural analysis of **5** shows a considerable distortion from a planar skeleton whereas the calculations for the unsubstituted parent compounds yield a completely planar skeleton).

*2.4. Reaction of **2** with N-lithio-indazole*

In N-lithio-indazole both nitrogen atoms are nucleophilic sites. The result of the reaction of **2** with N-lithio-indazole is shown in Scheme 3. Among other minor unidentified products, mainly two isomers **8** and **9** are formed (ratio ca. 1:5). Upon heating, the isomer **8** slowly rearranges into **9** (δ^{29}Si 11.2) as indicated by the decreasing intensity of the ^{29}Si-NMR signal of **8** (δ^{29}Si 16.0). However, there are numerous other compounds present in small amounts and **9** could not be obtained in high purity. A compound **B**, comparable with **9**, has

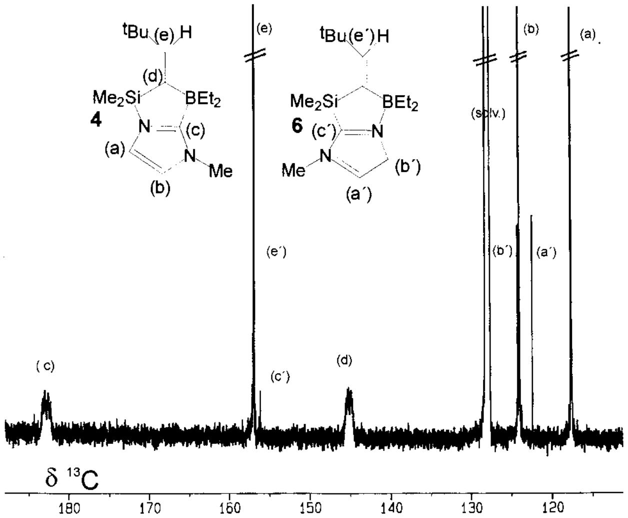
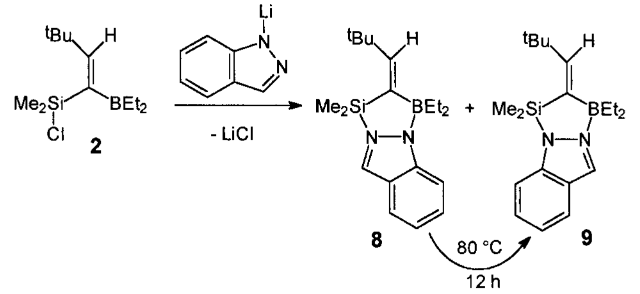


Fig. 1. 125.8 MHz ^{13}C{^{1}H}-NMR spectrum of **4** (5% in C_6D_6, 22 ± 1°C. the range of the olefinic carbon atoms is shown with the assignments as indicated.



Scheme 3.

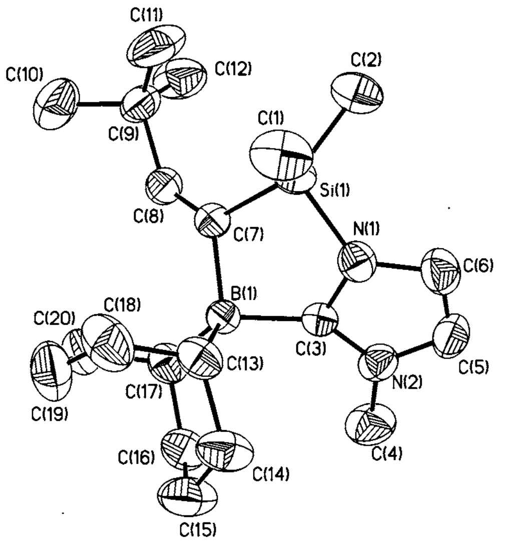
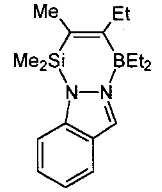


Fig. 2. Molecular structure of **5**; selected bond lengths (pm) and angles (°): Si1–N1, 181.2(4); Si1–C2, 184.9(5); Si1–C7, 185.8(4); B1–C13, 163.3(7); B1–C17, 164.5(7); B1–C3, 167.1(7); N1–C3, 136.1(5); N1–C6, 139.4(6); N2–C3, 135.5(5); N2–C5, 137.7(6); N2–C4, 146.1(6); C6–C6, 135.2(6); C7–C8, 133.0(6); N1Si1C7, 90.73(18); C3B1C7, 98.2(3); Si1C7B1, 106.8(3); N2C3B1, 142.2(3); C6N1Si1, 131.9(3); C7C8C9, 133.0(4).

been prepared under similar conditions (heating at > 80°C), and has been isolated as a single isomer, characterised by X-ray structural analysis [9].



B

2.5. X-Ray structural analysis of the heterocycle 5

The unit cell contains two independent molecules of **5**. The differences in the strucural parameters are very small and one of the molecular structures of **5** is shown in Fig. 2. The bicyclic system is non-planar: the Si(1)C(7)B(1) plane forms an angle of 138.2° with the planar imidazole ring. The geometry at the C=C–^{t}Bu unit is also distorted as shown by the angles formed between the plane Si(1)C(7)B(1) and the Si(1)C(7)C(8) (8.8°), B(1)C(7)C(8) (8.2°) planes. The Si(1)–N(1) bond is rather long (181.2(4) pm) when compared with Si–N$_{amine}$ bond lengths, considering that N(1) is a truly sp^2 hybridised nitrogen atom; It is also slightly longer than in **B** (179.1(2) pm [9]). Both the boron and the silicon atom are in the centres of strongly distorted tetrahedrons owing to the small endocyclic bond angles N(1)Si(1)C(7) (90.73(18)°) and C(3)B(1)C(7) (98.2(3)°). The bonds N(1)–C(3) (136.1(5) pm) and N(2)–C(3) (133.5(6) pm) are markedly shorter than the corresponding N(1)–C(6) (139.5(6) pm) and N(2)–C(5) (137.7(6) pm) bonds. The bond C(5)–C(6) is slightly longer than a normal C=C bond, whereas the bond length C(7)–C(8) (133.0(6) pm) is exactly in the range of C=C bonds. The wide angle C(7)C(8)C(9) (133.0(4)°) reflects steric interactions between the bulky ^{t}Bu and the Me$_2$Si group.

3. Conclusions

The synthetic potential of the 1,1-organometallic-substituted alkenes of type **2** and **3** in heterocyclic chemistry has been demonstrated. The proposed zwitterionic structure with Si–N and B–C bonds is now firmly established by direct structural evidence. 'Expected' isomers (with Si–C and N–B bonds) can be detected in the reaction solutions.

4. Experimental

4.1. Starting materials and measurements

All preparations and handling of samples was carried out under an inert atmosphere (Ar or N$_2$), and carefully dried glass ware and dry solvents were used. BuLi (1.6 M) in hexane, 1-methyimidazole, indazole, (9-BBN)$_2$ and Et$_3$B were commercial products. The 1-alkynyl(chloro)dimethylsilane, **1** [10,11], and the reagent 'Et$_2$BH' [3] were prepared as described and the hydride concentration (1.17%) was determined by ^{11}B-NMR spectroscopy [12].

NMR spectra were recorded by using ARX 250 and DRX 500 instruments, equipped with multinuclear units. Samples dissolved in C$_6$D$_6$ (10–20%) in 5 mm (o.d.) tubes were measured at 22 ± 1°C. Chemical shifts are given with respect to solvent signals [δ^1H (C$_6$D$_5$H) = 7.15; δ^{13}C (C$_6$D$_6$) = 128.0; and external references [δ^{11}B (BF$_3$·OEt$_2$) = 0, Ξ(^{11}B) = 32.083971

MHz; $\delta^{15}N$ ($MeNO_2$, neat) = 0, $\Xi(^{15}N) = 10.136767$ MHz; $\delta^{29}Si$ (Me_4Si) = 0, $\Xi(^{29}Si) = 19.867184$ MHz]. ^{15}N-NMR spectra were recorded by the refocused INEPT pulse sequence with ^{1}H decoupling [13], taking advantage of the scalar coupling $^{15}N-^{1}H$ (across two and three bonds with a magnitude of ca. 7 Hz). All ^{29}Si-NMR spectra were measured using the same technique, based on $^{2}J(^{29}Si, ^{1}H_{Me})$ (ca. 7 Hz) and $^{3}J(^{29}SiC{=}C^{1}H)$ (ca. 23 Hz). Isotope induced chemical shifts $^{1}\Delta^{12/13}C(^{29}Si)$ (ppb) are given with a negative sign if the signal of the heavy isotopomer is shifted to low frequency with respect to that of the lighter isotopomer.

*4.2. (Z)-1-Chloro(dimethyl)silyl-1-(9-borabicyclo[3.3.1]non-9-yl)-3,3-dimethyl-but-1-ene (**3**)*

The alkyne **1** (5.02 g; 28.6 mmol) was dissolved in hexane (25 ml) and 9-BBN (3.48 g; 28.6 mmol) was added. The reaction mixture was heated at reflux for 20 h. After removing the solvent in vacuo, the product **3** is left as a colourless oil (> 97% pure according to ^{1}H-NMR spectra) and can be used for further transformations without purification. ^{1}H-NMR (250 MHz; C_6D_6): $\delta^{1}H = 0.50$ (s, 6H, Me_2Si); 1.06 (s, 9H, ^{t}Bu); 1.39–2.1 (m, 14H, 9-BBN); 6.70 (s, 1H, H–C=; $^{3}J(^{29}Si, ^{1}H) = 22.0$ Hz).

*4.3. 2-[(Z)-1-(3,3-Dimethyl)butenylidene]-1,3-dihydro-1,1,4-trimethyl-3,3-diethyl-1-sila-3-borata-4-aza-6a-aza-pentalene (**4**) and other heterocycles (**5** and **9**)*

N-Methylimidazole (0.164 g; 2 mmol) in hexane (20 ml) was cooled to − 50°C, a solution of BuLi in hexane (2 mmol) was added, and the mixture was allowed to warm to room temperature (r.t.) and kept stirring for 2 h. Then the colourless suspension was cooled again to − 50°C, and **2** (0.488 g; 2 mmol) was added in one portion. After warming to r.t., stirring for 12 h, insoluble material was filtered off, and most of the solvent was removed in vacuo. Crystallisation from hexane at − 20°C afforded colourless crystals of **4** (0.48 g; 82%; m.p. 79°C). ^{1}H-NMR (250 MHz; C_6D_6): $\delta^{1}H = 0.43$ (s, 6H, Me_2Si); 0.88–0.97 (m, 10H, Et_2B); 1.17 (s, 9H, ^{t}Bu);3.04 (s, 3H, NMe), 6.75 (s, 1H, H–C=); 5.93 (d, $^{3}J(^{1}H, ^{1}H) = 1.8$ Hz, 1H, HCN); 6.15 (d, $^{3}J(^{1}H, ^{1}H) = 1.8$ Hz, 1H, HCN).

Compound **5** (93%; colourless crystals; m.p. 134°C) was isolated in the same way as described for **4**, and also recrystallised from hexane to give suitable single crystals. **5**: ^{1}H-NMR (250 MHz; C_6D_6): $\delta^{1}H = 0.45$ (s, 6H, Me_2Si); 1.25, 1.17–2.70 (m, 14H, 9-BBN); 1.18 (s, 9H, ^{t}Bu); 3.00 (s, 3H, NMe), 7.02 (s, 1H, H–C=); 5.69 (d, $^{3}J(^{1}H, ^{1}H) = 1.8$ Hz, 1H, HCN); 6.20 (d, $^{3}J(^{1}H, ^{1}H) = 1.8$Hz, 1H, HCN).

Compound **9** (85%; yellow oil; ca. 85% pure, containing unidentified impurities) was obtained as described for compound **4**. Attempts to crystallise pure **9** from pentane or hexane at − 78°C have not been successful as of yet. ^{1}H-NMR (250 MHz; C_6D_6): $\delta^{1}H = 0.66$ (s, 6H, Me_2Si), 0.97–1.0 (m, 10H, Et_2B), 1.28 (s, 9H, ^{t}Bu), 6.80 (s, 1H, H–C=); 7.10, 7.29, 7.51 (m, 4H, C_6H_4), 7.81 (s, 1H, HCN).

*4.4. Crystal structure of **5***

Intensity data collection was carried out on a Siemens P4 diffractometer with Mo–K_α radiation ($\lambda = 71.073$ pm, graphite monochromator). The measuring temperature was 296 K. $C_{20}H_{35}BN_2Si$, colourless prism of dimensions $0.25 \times 0.15 \times 0.14$ mm, crystallises monoclinic in the space group $P2_1/n$ (no. 14), $a = 1140.97(18)$, $b = 1914.4(3)$, $c = 1916.3(3)$ pm, $\beta = 95.786(10)°$, $Z = 8$, $\mu = 0.117$ mm^{-1}, 9000 reflections collected in the range $4 \leq 2\theta \leq 50°$, 7297 reflections independent, 3860 reflections assigned to be observed ($I > 2\sigma(I)$), full-matrix least-squares refinement against F^2 with 434 parameters converged at R_1/wR_2 values of 0.076/0.198. All non-hydrogen atoms were treated anisotropically, the hydrogen atoms were refined on calculated positions applying the riding model with fixed isotropic temperature factors. The max/min residual electron density was 0.38/ − 0.40 e Å^{-3}.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 139041 for compound **5**. Copies of the data can be obtained free of charge from The Director, CCDC, 12 Union Rd., Cambridge CB2 1EX, UK (fax: + 44-1223-336033; e-mail: deposit@ccdc.com.ac.uk or www: http://www.ccdc.cam.ac.uk).

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References

[1] B. Wrackmeyer, A. Badshah, E. Molla, A. Mottalib, J. Organomet. Chem. 584 (1999) 98.

[2] (a) J.A. Soderquist, J.C. Colberg, L. DelValle, J. Am. Chem. Soc. 111 (1989) 4873. (b) R. Köster, G. Seidel, R. Boese, B. Wrackmeyer, Z. Naturforsch. Teil B 50 (1995) 439.

[3] R. Köster, G. Bruno, P. Binger, Liebigs Ann. Chem. 644 (1961) 1.

[4] B. Wrackmeyer, Progr. NMR Spectrosc. 12 (1979) 227.

[5] (a) N. Kuhn, G. Henkel, T. Kratz, J. Kreutzberg, R. Boese, A.H. Maulitz, Chem. Ber. 126 (1993) 2041. (b) I.I. Padilla-Martinez, M.J. Rosalez-Hoz, R. Contreras, S. Kerschl, B. Wrackmeyer, Chem. Ber. 127 (1994) 343. (c) A. Wacker, H. Pritzkow, W. Siebert, Eur. J. Inorg. Chem. (1998) 843. (d) I.I. Padilla-Martinez, F.J. Martinez-Martinez, A. Lopez-Sandoval, K.I. Giron-Castillo, M.A. Brito, R. Contreras, Eur. J. Inorg. Chem. (1998) 1547.

[6] S. Berger, S. Braun, H.-O. Kalinowski, NMR Spectroscopy of the Non-Metallic Elements, Wiley, Chichester, 1996, p. 165.

[7] (a) T. Clark, A Handbook of Computational Chemistry, Wiley, New York, 1985. (b) M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.A. Robb, J.R. Cheeseman, T. Keith, G.A. Petersson, J.A. Montgomery, K. Raghavachari, M.A. Al-Laham, V.G. Zakrzewski, J.V. Ortiz, J.B. Foresman, J. Cioslowski, B.B. Stefanov, A. Nanayakkara, M. Challacombe, C.Y. Peng, P.Y. Ayala, W. Chen, M.W. Wong, J.L. Andres, E.S. Replogle, R. Gomperts, R.L. Martin, D.J. Fox, J.S. Binkley, D.J. Defrees, J. Baker, J.P. Stewart, M. Head-Gordon, C. Gonzalez, J.A. Pople, GAUSSIAN 94, Revision E.1, Gaussian, Inc., Pittsburgh, PA, 1995. (c) I. Ando, G.A. Webb, Theory of NMR Parameters, Academic Press, London, 1983, pp. 47–82 and Refs. cited therein.

[8] H. Nöth, B. Wrackmeyer, in: P. Diehl, E. Fluck, R. Kosfeld (Eds.), Nuclear Magnetic Resonance Spectroscopy of Boron Compounds in NMR — Basic Principles and Progress, vol. 14, Springer, Berlin, 1978.

[9] B. Wrackmeyer, J. Süß, W. Milius, Chem. Ber. 129 (1996) 147.

[10] H. Lang, U. Lay, Z. Anorg. Allg. Chem. 596 (1991) 7.

[11] B. Wrackmeyer, G. Kehr, J. Süß, Chem. Ber. 126 (1993) 2221.

[12] B. Wrackmeyer, H.-J. Schanz, R. Köster, Fresenius, J. Anal. Chem. 362 (1998) 378.

[13] (a) G.A. Morris, R. Freeman, J. Am. Chem. Soc. 101 (1979) 760. (b) G.A. Morris, J. Am. Chem. Soc. 102 (1980) 428. (c) G.A. Morris, J. Magn. Reson. 41 (1980) 185. (d) D.P. Burum, R.R. Ernst, J. Magn. Reson. 39 (1980) 163.