COMMUNICATIONS

precursor $[Cp*Ir(PPh_3)(S_2fc)]$ (**6b**).^[19] In the very stable 18electron complexes **6a** and **6c** $[S_2fc]$ functions as a two-electron ligand. The dimeric structure of **5** has been confirmed by an X-ray crystal structure analysis for the selenium analogue, $[Cp_2^*Ir_2(Se_2fc)_2]$.

In summary, the 1,1'-ferrocenedithiolato unit $[S_2fc]$ is a versatile ligand system which may function as a two-electron (in **6a** and **6b**), four-electron (in **5**), or six-electron donor (in **1**-4) and which may act as either chelating or bridging ligand.

Experimental Procedure

1: A green solution of $[(Cp^*CoCl_2)_2]$ [9] (0.42 g, 0.80 mmol) in THF (20 mL) and an orange solution of $[fc(SLi)_2]$ (0.45 g, 1.1 mmol) in THF (100 mL) were combined at -78 °C. The color of the homogeneous mixture changed to violet. The solution was stirred for 3 h at room temperature. After removal of the solvent, the residue was separated by column chromatography on silica gel (Merck, Kieselgel 60). Elution with pentane/CH₂Cl₂ (1:2) gave 1. Recrystallization from CHCl₃/toluene/hexane mixtures at -25 °C gave violet microcrystals of 1 (0.15 g, 30.1%, m.p. 248 °C). EI-MS (70 eV): prominent peaks at m/z (%): 943 (100) $[M^+]$, 808 (10) $[M^+ - Cp^*]$, 636 (48) $[Cp_2^*Co_2(S_2fc)^+]$, 501 (22) $[Cp^*Co_2(S_2fc)^+]$, 442 (42) $[Cp^*Co(S_2fc)^+]$; strong peaks due to the ferrocene oligomers (m/z 370 $[Fc_2^+]$, 554 $[Fc(fc)Fc^+]$, 738 $[Fc(fc)_2Fc^+]$) were also observed. The effective magnetic moment was found to be 5.6 μ_{B} at room temperature; it decreases with decreasing temperature to reach 3.4 μ_{B} at 6 K [20].

2. The reaction of $[(Cp*RhCl_2)_2]$ [15] (0.24 g, 0.38 mmol) with $[fc(SLi)_2]$ (0.31 g, 0.76 mmol) in THF (130 mL) was started at -78 °C and then continued for 4 h at room temperature. Chromatography over silica (with CH₂Cl₂/hexane mixtures for elution) gave several bands; isolation of the first (violet) zone which follows [FcH] and recrystallization from hexane or pentane gave violet crystals of (2) (0.12 g, 41 %, m.p. 168 °C). ¹H NMR (CDCl₃): $\delta = 1.99$ (s, C₅Me₅, 30H), 3.74, 4.39 (vt, fc, 4 + 4H); E1-MS (70 eV): *m/z* 723 (100%) [$M^+ - H$].

Received: December 29, 1993 Revised version: December 13, 1995 [Z 6592 IE] German version: Angew. Chem. **1995**, 107, 716

Keywords: cobalt compounds · complexes with sulfur ligands · iridium compounds · rhodium compounds · sandwich complexes

- Reviews: a) D. A. Buckingham, C. R. Clark in Comprehensive Coordination Chemistry, Vol. 4 (Eds.: G. Wilkinson, R. D. Gillard, J. A. McCleverty), Pergamon, 1987, p. 635-900; b) R. D. W. Kemmitt, D. R. Russell in Comprehensive Organometallic Chemistry, Vol. 5 (Eds.: G. Wilkinson, F. G. A. Stone, E. W. Abel), Pergamon, 1982, p. 1-276.
- [2] C. H. Wei, L. F. Dahl, Inorg. Chem. 1967, 6, 1229-1236.
- [3] P. D. Frisch, L. F. Dahl, J. Am. Chem. Soc. 1972, 94, 5082-5084.
- [4] S. Otsuka, A. Nakamura, T. Yoshida, Liebigs Ann. Chem. 1968, 719, 54-60.
- [5] a) H. Werner, K. Leonhard, Angew. Chem. 1979, 91, 663-664; Angew. Chem. Int. Ed. Engl. 1979, 18, 663; b) H. Werner, K. Leonhard, O. Kolb, E. Röttinger, H. Vahrenkamp, Chem. Ber. 1980, 113, 1654-1662.
- [6] a) J. Fortune, A. R. Manning, F. S. Stephens, J. Chem. Soc. Chem. Commun. 1983, 1071 - 1072; b) A. R. Manning, L. O'Dwyer, P. A. McArdle, D. Cunningham, J. Organomet. Chem. 1995, 474, 173-176.
- [7] G. Henkel, W. Tremel, B. Krebs, Angew. Chem. 1983, 95, 314; Angew. Chem. Int. Ed. Engl. 1983, 22, 318; Angew. Chem. Suppl. 1983, 307-322.
- [8] C. H. Wei, L. F. Dahl, J. Am. Chem. Soc. 1968, 90, 3960-3969, 3977-3983.
- [9] U. Kölle, B. Fuss, Chem. Ber. 1984, 117, 743-752.
- [10] Data for the crystal structure analysis of C₄₀H₄₆Co₃Fe₂S₄ (1): diffractometer: Siemens P4 (Mo_{Ka}, λ = 0.71073 Å, graphite monochromator); monoclinic, P2/ n, a = 12.558(3), b = 10.151(2), c = 15.792(3) Å, β = 107.54(2)°, Z = 2, violetblack platelet, dimensions 0.04 × 0.38 × 0.40 mm. Measured range: 4.0° ≤ 2 θ ≤ 45.0°; measured octant hkl, T = 298 K; measured reflections: 5235; independent reflections: 2516 (R_{ini} = 0.049); observed reflections: 1746 (F > 4.0 σ(F)); structure solution with direct methods (SHELXTL PLUS (VMS)); number of refined parameters: 222; R = 0.0493; wR = 0.0599 (w⁻¹ = σ²(F) + 0.0020 F²); maximum/minimum residual electron density: 0.54/-0.49 eÅ⁻³. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-58076.
- [11] G. Henkel, S. Weissgräber, Angew. Chem. 1992, 104, 1382–1383; Angew. Chem. Int. Ed. Engl. 1992, 31, 1368–1369.
- [12] A. Shaver, S. Morris, R. Turrin, V. W. Day, *Inorg. Chem.* 1990, 29, 3622-3623.
 [13] R. Minkwitz, H. Borrmann, J. Nowicki, Z. Naturforsch. B 1992, 47, 915-918.

- [14] C. R. Pulliam, J. B. Thoden, A. M. Stacy, B. Spencer, M. H. Englert, L. F. Dahi, J. Am. Chem. Soc. 1991, 113, 7398-7410.
- [15] J. W. Kang, K. Moseley, P. M. Maitlis, J. Am. Chem. Soc. 1969, 91, 5970-5977.
- [16] D. Seyferth, B. W. Hames, Inorg. Chim. Acta 1983, 77, L1-L2.
- [17] W. R. Cullen, A. Talaba, S. J. Rettig, Organometallics 1992, 11, 3152-3156.
- [18] a) R. Hoffmann, Angew. Chem. 1982, 94, 725-739; Angew. Chem. Int. Ed. Engl. 1982, 21, 711-724; b) F. G. A. Stone, ibid. 1984, 96, 85-96 and 1984, 23, 89-99.
- [19] M. Herberhold, G.-X. Jin, A. L. Rheingold, G. F. Sheats, Z. Naturforsch. B 1992, 47, 1091–1098.
- [20] W. Bronger, RWTH Aachen, personal communication, 1995.

Heteroatom-Substituted Bicyclo[1.1.1]pentanes with Two Boron Atoms as Electron-Deficient Centers**

Matthias Menzel, Christine Wieczorek, Sigrid Mehle, Jürgen Allwohn, Heinz-Jürgen Winkler, Markus Unverzagt, Matthias Hofmann, Paul von Ragué Schleyer, Stefan Berger, Werner Massa, and Armin Berndt*

Dedicated to Professor Peter Paetzold on the occasion of his 60th birthday

The dicarbapentaboranes(5) $(1)^{[2]}$ are the only known bicyclo[1.1.1]pentane derivatives^[1] with boron atoms as electrondeficient centers. Here we report on the synthesis, X-ray crystal structures, and NMR data of the 2-methylene (**3a**) and 2-sila (**4a**) derivatives of dibora-

bicyclo[1.1.1]pentane 2. In addition, we computed the geometries and the chemical shifts of the unsubstituted (u) parent compounds 2u, 3u, and 4u by ab initio methods to rationalize the observed properties of 3a and 4a.

1,4-Diboraspiro[2.3]hex-5-ene 6 can be obtained from methyleneborane $5^{[3]}$ and 2-butyne at -30 °C. It isomerizes to 3a in less than one hour at



10 °C. A plausible^[4] reaction mechanism involving low energy intermediates^[5] is given. (The bonds marked in Scheme 1 with open arrows and black arrowheads are broken and formed, respectively).

The X-ray crystal structure^[6] of **3a** (Fig. 1) shows a surprising feature: the C2–B4 distance (188.3 pm) is significantly shorter than the C2–B5 distance (197.7 pm) even though higher

[*] Prof. Dr. A. Berndt, Dr. M. Menzel, Dr. C. Wieczorek, Dr. S. Mehle, Dr. L.Allwohn, Dipl. Chem. H. J. Winkler, M. Universated Prof. Dr. S. Berner

Dr. J. Allwohn, Dipl.-Chem. H.-J. Winkler, M. Unverzagt, Prof. Dr. S. Berger, Prof. Dr. W. Massa

- Fachbereich Chemie der Universität
- D-35032 Marburg (Germany)
- Telefax: Int. code + (6421)288917

Dipl.-Chem. M. Hofmann, Prof. Dr. P. von R. Schleyer

- Computer-Chemie-Centrum der Universität
 - Nägelsbachstrasse 25, D-91052 Erlangen (Germany)
- [**] This work was supported by the Deutsche Forschungsgemeinschaft, the Volkswagen-Stiftung, the Convex Computer Corporation, and the Fonds der Chemischen Industrie.

COMMUNICATIONS







Fig. 1. Crystal structure of 3a. Relevant distances [pm] and angles [°] (in addition to Table 1): C1-B4 153.9(3), C3-B4 160.9(4), C1-B5 157.5(3), C3-B5 154.1(4), C1-C2 156.4(4), C3-C2 152.9(3), C1 ··· C3 217.4(4), C2-C6 136.4(3); C1-B4-C3 87.3(2), C3-B5-C1 88.4(2), C1-C2-C3 89.2(2), B4-C1-C2 74.7(2), B4-C3-C2 73.7(2), B5-C1-C2 78.1(2), B5-C3-C2 80.1(2); C1-C2-C6-Si1 -23.6(3), C1-C2-C6-Si2 156.6(2)

symmetry is possible. In contrast, in the ¹³C NMR spectrum of 3a signals of only one kind of duryl group were observed even at -80 °C. Hence, the boron atoms are equivalent in solution according to NMR spectroscopy. The boron chemical shift for



3a ($\delta(^{11}B) = 34$) is far from the usual range for 1,3-diboretanes 7 $(\delta(^{11}B) = 82 \pm 2^{[7]})$ but close to that of dicarbapentaborane(5) 1 a $(\delta({}^{11}\overline{B}) = 21)$.

The MP2(fc)/6-31G* geometry^[8] 3u (Fig. 2), like that of 3a, exhibits a short (170.7 pm, C2–B4) and a long (208.1 pm, C2– B5) carbon-boron distance. The C_{2v} structure $3u^*$ with equal distances for C2-B4 and C2-B5 (188.4 pm) is 3.0 kcalmol⁻¹ higher in energy than 3u and is the transition structure for the rapid exchange of the chemical environments of the boron atoms in 3u.^[10] GIAO-MP2/tzpdz calculations^[9] (Fig. 2) gave boron chemical shifts of $\delta(^{11}B) = 6.2$ (B4) and 34.9 (B5) for 3u. The average value, 20.6, is in accord with the experimental value $\delta^{(11}B) = 34$, when the effects of the different substituents are taken into account (compare $\delta(^{11}B) = 1.9$ for $1u^{[2]}$ and 21 for 1a). The C=C bond in 3u hardly influences the strong shielding



3u. and 4u.

© VCH Verlagsgesellschaft mbH. D-69451 Weinheim, 1995

Table 1. Computed (2u, 3u, 4u) and experimental distances (3a, 4a) [pm] and chemical shieldings of framework atoms.

	2 u (X = C2)	3u (X = C2)	3a (X = C2)	4u (X = Si)	$\textbf{4a}\;(X=Si)$
X-B4	178.4	170.7	188.3(3)	224.0	223.2(6)
X-B5	217.3	208.1	197.7	224.0	225.2(6)
B4-B5	190.7	193.1	194.9(3)	186.2	187.6(6)
$\delta(^{13}C1,C3)$	72.0	76.8	91.7	82.2	98.6
δ(¹¹ B4)	10.9	6.2	34	39.2	46
$\delta(^{11}B5)$	40.0	34.9	34	39.1	46
δ(X)	-1.4	101.4	124.2	-140.4	- 99.6
δ(¹³ C6)	_	106.8	80.2	-	-

of the boron atoms.^[11] The GIAO-MP2 δ (¹¹B) NMR shifts of 2u (10.9 (B4) and 40.0 (B5)) are only about 5 ppm larger than those of 3u. The lowest energy structure of $2u(C_s)$, like 3u, has a short C2-B4 distance (178.4 pm) and a long C2-B5 distance (217.3 pm). The C_{2v} symmetry form, $2u^*$, a transition structure with equal C2-B distances (201.1 pm), is 3.2 kcalmol⁻¹ higher in energy than 2u. Strong hyperconjugation between the strained C1-C2,C3 bonds and B4 and between the B4-C1,C3 bonds and B5 results in the strong boron shieldings in 3u and 2u. Analogous interactions of a boron atom with four neighboring strained C-B bonds give rise to the strong boron shielding in dicarbapentaborane 1 (see above). This was shown by means of an NBO analysis^[12] involving a second-order perturbative estimation of donor-acceptor interactions. In addition, in 3u π -electron density is transferred from the C2–C6 bond to B4, and there is back donation from the B4-C1,C3 bonds into the C2-C6 π^* orbital. Analogous but weaker interactions take place in 2u, where C-H σ and σ^* orbitals act as donors and acceptors, respectively.

Hence, the nonclassical characteristics of 1 are not changed when one boron atom is replaced by an sp² (3) or an sp³ (2) carbon atom. In the related 2-sila-4,5-diborabicyclo[1.1.1]pentanes 4, the nonclassical character of 1 is also conserved to a large extent. Borataalkyne $8^{[13]}$ reacts with chlorodimethylsilane to give 4a, probably via intermediates 9–11 (Scheme 2). The crystal structure of 4a is shown in Figure 3.^[6] Important distances and the chemical shifts of the framework atoms are listed with those calculated for 4u in Table 1. The experimental distances of 4a differ little from those computed for 4u. The chemical shift of the boron atoms in 4a ($\delta = 46$) lies between the values of classical 1,3-diboretanes 7 and the nonclassical dicar-



Scheme 2. Synthesis of 4a. Mes = 2,4,6-trimethylphenyl.



Fig. 3. Crystal structure of **4a**. Relevant distances [pm] and angles [°] (in addition to Table 1): C1-B4 158.3(6), C3-B4 159.9(6), C1-B5 159.2(6), C3-B5 156.9(7), C1-Si2 189.4(5), C3-Si2 189.3(4), C1 ··· C3 231.7(6); C1-B4-C3 93.4(4), C3-B5-C1 94.4(4), C1-Si2-C3 75.4(2), B4-C1-Si2 78.6(3), B4-C3-Si2 79.2(3), B5-C1-Si2 80.6(3), B5-C3-Si2 80.1(3).

bapentaboranes 1. The chemical shifts computed for 4u, $\delta(^{11}B) = 39.1$ and $\delta(^{29}Si) = -140.4$, agree with the experimental values of 4a (see Table 1), as long as the substituent effects are taken into account. Note the strong shielding of the bridging silicon atom in 4a, $\delta(^{29}Si) = -99.6$. The Si atoms in the SiMe₂ bridges in trisilabicyclo[1.1.1]pentanes 12a, $b^{[14]}$ form C1-Si-C3 angles (79.5°) comparable to those in 4a (75.4°), but the ²⁹Si chemical shifts of -4.9 (12a) and 31.9 (12b) differ. Therefore, the small angle at the Si2 atom of 4a is not the source of the strong shielding.^[15] No unusual chemical shifts are observed in bicyclo[1.1.1]pentanes, either.^[17]

The strong shielding of framework atoms in heterobicyclo[1.1.1]pentanes is apparently due to the presence of electrondeficient centers. The second-order perturbative estimation of donor-acceptor interactions with NBO analysis^[12] revealed that hyperconjugation of the C-B bonds in 4u and in 1u is equally strong. However, there are twice as many C-B bonds per boron atom in the latter. The hyperconjugation in 4u is significantly weaker, because Si-C bonds are not as effective as C-B bonds as hyperconjugative donors. 2-Sila-4,5-diborabicyclo[1.1.1]pentanes 4 differ from dicarbapentaboranes(5) 1 only in the magnitude of the nonclassical interactions. These sila

derivatives 4 are the simplest^[18] examples of heterodicarboranes. Physical data for 1a, 3a, 4a, and 6 are listed in Table 2.

Experimental Procedure

6 and **3a**: 2-Butyne (0.18 g, 3.25 mmol) was added dropwise to a solution of **5** (1.49 g, 3.25 mmol) in 30 mL of pentane cooled to -78 °C. After the mixture had warmed to -30 °C, all volatile components were removed under high vacuum, and the pale yellow solid **6** was dissolved in 50 mL of pentane with cooling. The pale yellow suspension was warmed to 7 °C and stirred at this temperature until a clear red solution formed. The volatile material was removed under vacuum, the resulting yellow residue taken up in hexane at 0 °C, and the solid that precipitated removed by filtration through a D4 frit. **3a** crystallized from hexane at -30 °C as yellow cubes.

4a: Chlorodimethylsilane (2.0 g, 21.2 mmol) was added dropwise to a solution of **8** (4.19 g, 7.07 mmol) in 50 mL of diethyl ether cooled at -20 °C. The mixture was kept at -10 °C for 2 h and then stirred and

COMMUNICATIONS

Table 2. Selected physical data for compounds 1a, 3a, 4a, and 6.

1a (colorless crystals): m.p. > 200 °C, yield: 69%. $^{-1}$ H NMR (500 MHz, CDCl₃, -30 °C): $\delta = -0.03$ (s, 18 H, SiMe₃), 2.15, 2.23 (each s, each 18 H, o- and m-CH₃), 7.03 (s, 3 H, p-H); 13 C NMR (125 MHz, CDCl₃, -30 °C): $\delta = -1.3$ (6C, SiMe₃), 20.4, 20.9 (each 6C, o- and m-CH₃), 127.0 (2C, CB₃), 131.5, 133.5, 136.4 (total of 15C, o-, m-, p-C), 132.4 (br., 3 C, i-C); 11 B NMR (96 MHz, CDCl₃, 25 °C): $\delta = 21$ 3a (yellow crystals): m.p. 62 °C, yield: 75%. $^{-1}$ H NMR (400 MHz, CDCl₃, -40 °C): $\delta = 0.24$ (s, 18H, SiMe₃), 1.97 (s, 6H, CH₃), 2.20, 2.34 (each s, total of 24 H, o- and m-CH₃), 7.15 (s, 2 H, p-H); 13 C NMR (125 MHz, CD₂Cl₂, -60 °C): $\delta = 3.9$ (q, 6C, SiMe₃), 1.26 (q, 2C, CH₃), 19.4, 19.9 (each q, 8 C, o- and m-CH₃), 80.2 (s, 1 C, ^{-1}J (C, Si) = 58 Hz, CSi₂), 91.7 (s, 2 C, CB₂), 124.2 (br.s, 1 C, $=CC_2$), 132.6 (d, 2 C, p-C), 133.8, 136.7 (each s, each 4 C, o- and m-C), 142.5 (br.s, 2 C, i-C); 11 B NMR (96 MHz, pentane, 10 °C): $\delta = 34$

4a (colorless crystals): m.p. 165 °C, yield: 73%. – ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 0.01 (s, 18 H, SiMe₃), 0.39 (s, 6 H, SiMe₂), 2.22 (18 H, *o*- and *p*-CH₃), 6.75 (s, 4H, *m*-H), ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ = 0.3 (q, 6C, SiMe₃), 5.0 (q, 2C, SiMe₂), 21.0 (q, 2C, *p*-CH₃), 23.4 (q, 4C, *o*-CH₃), 98.6 (s, 2C, CB₂), 128.0 (d, 4C, *m*-C), 133.9 (br.s, 2C, *i*-C), 137.6 (s, 2C, *p*-C), 140.1 (s, 4C, *o*-C); ¹¹B NMR (96 MHz, CDCl₃, 25 °C): δ = 46; ²⁹Si NMR (79 MHz, CDCl₃, 25 °C): δ = -11.0 (s, 25 siMe₃), -99.6 (s, 1Si, SiMe₂)

6 (pale yellow solid): yield: quantitative by NMR spectroscopy. $-^{13}$ C NMR (125 MHz, CDCl₃, -30° C): $\delta = 2.3, 2.9$ (each q, each 3 C, SiMe₃), 13.6, 15.8 (each q, each 1 C, CH₃), 19.2 (br.), 19.3 (br.), 19.6 (br.), 19.8 (br.), 20.1 (br.), 20.3 (each q, 8C, o- and m-CH₃), 24.6 (s, 1 C, CSi₂), 51.2 (br.s, 1 C, CB₂), 130.3, 132.7 (each d, each 1 C, p-C), 131.0, 133.0, 133.3, 136.3 (each s, 6 C, o- and m-C), 138.1 (br.s, 1 C, i-C), 144.0 (br.s, 2 C, o-C of Dur on three-membered ring), 155.8 (s, 1 C, =CC₂), 164.5 (br.s, 1 C, =CB)

warmed to 25 °C for another 10 h. The volatile components were removed under vacuum, the residue was treated with pentane, and the the lithium chloride was removed with a D4 frit. The pentane soluton was concentrated and cooled to -20 °C to yield 2.5 g of 4a as fine needles.

Received: June 22/July 22, 1995 Revised version: December 6, 1995 [Z 7065/7158 IE] German version: Angew. Chem. **1995**, 107, 728

Keywords: bicyclopentanes · boron compounds · hyperconjugation

- a) D. Bromm, U. Seebold, M. Noltemeyer, A. Meller, Chem. Ber. 1991, 124, 2645-2649; b) M. Bühl, J. Gauss, M. Hofmann, P. von R. Schleyer, J. Am. Chem. Soc. 1993, 115, 12385-12390, and references therein.
- [2] R. Köster, M. A. Grassberger, Angew. Chem. 1967, 79, 197-219; Angew. Chem. Int. Ed. Engl. 1967, 6, 218-240; M. A. Grassberger, R. Köster in Methoden Org. Chem. (Houben-Weyl) 4th ed. 1952 - Vol. XIII/3c, 1984, pp. 156-214.
- [3] A. Berndt, Angew. Chem. 1993, 105, 1034-1058; Angew. Chem. Int. Ed. Engl. 1993, 32, 985-1009, and references therein.
- [4] For the small activation energy for allyl shifts in borylallyl compounds see M. Bühl, P. von R. Schleyer, M. A. Imbrahim, T. Clark, J. Am. Chem. Soc. 1991, 113, 2466-2471, and references therein.
- [5] The triple bond of 2-butyne is cleaved during the reaction with 5 by insertion of two B-Dur fragments and one C=C(SiMe₃)₂ moiety. Similar insertions were reported for the reaction of alkynes with B₄H₁₀: M. A. Fox, R. Greatrex, M. Hofmann, P. von R. Schleyer, Angew. Chem. 1995, 106, 2384-2386; Angew. Chem. Int. Ed. Engl. 1995, 33, 2298-2300, and references therein.
- [6] X-ray structure analyses were conducted with a four-circle diffractometer (CAD4, Enraf-Nonius) with Cu_{Ka} radiation ($\lambda = 154.178$ ppm) at -80 °C. The structures were solved by direct methods and refined with full matrix against the F_o^2 data employing the SHELXL-93 system (**3a**) or against the F_o^1 data with the SHELXTL-plus (**4a**) system. Anisotropic temperature factors were used for all non-hydrogen atoms. **3a**. C₃₂H₅₀B₂Si₂, crystal dimensions 0.5 × 0.3 × 0.3 mm³, triclinic, space group P1, Z = 2, a = 880.4(2), b = 1190.0(2), c = 1600.7(3) pm, $\alpha = 88.73(3)$, $\beta = 88.97(3)$, $\gamma = 79.88(3)^\circ$, $V = 1650.3 \times 10^{-30}$ m³, $\rho_{\text{cated}} = 1.031$ g cm⁻³; total of 5259 reflections collected in ω -scan mode up to 2 $\theta = 150^{\circ}$; 5120 out of 5123 independent reflections used in subsequent calculations after LP correction; no absorption correction ($\mu = 10.8 \text{ cm}^{-1}$). The hydrogen atoms were considered in the calculations to be ,riding'' on their bonding partners in groups with common isotropic temperature factors. Final wR₂ = 0.1622 and R = 0.050 for 3825 reflections with $F_{\rho} > 4\sigma(F_{\rho})$. The maximum residual electron density was 0.27 e Å⁻³. **4a**:

 $C_{28}H_{46}B_2Si_3$, crystal dimensions $0.5 \times 0.3 \times 0.6$ mm³, monoclinic, space group $P2_1/c$, Z = 4, a = 1337.6(5), b = 1347.9(2), c = 1779.2(7) pm, $\beta = 106.81(2)^\circ$, $V = 3070.6 \times 10^{-30}$ m³, $\rho_{calcd} = 1.057$ gcm⁻³; total of 4544 reflections collected in ω -scan mode up to $2\theta = 110^\circ$; 3256 (with $F_e > 3\sigma(F_e)$) out of 3849 independent reflections used in subsequent calculations after LP correction; no absorption correction ($\mu = 14.1$ cm⁻¹). All hydrogen atoms could be localized by difference Fourier synthesis and were considered in the calculations as riding on their bonding partners in groups with common isotropic temperature factors. Employing weights of $w = 1/\sigma^2(F_e)$ resulted in R = 0.063 and wR = 0.058. The maximum residual electron density was 0.50 e Å⁻³. Further details of the crystal structure investigation may be obtained from the Fachin-formationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (FRG), on quoting the depository number CSD-58797.

- [7] G. Schmidt, G. Baum, A. Berndt, Angew. Chem. 1986, 98, 1123-1124; Angew. Chem. Int. Ed. Engl. 1986, 25, 1111-1112.
- [8] Geometry optimizations and frequency calculations were performed with Gaussian 92 to determine the nature of the stationary points: M. J. Frisch, G. W. Trucks, M. Head-Gordon, P. M. W. Gill, M. W. Gomperts, J. L. Andres, K. Raghavachari, J. S. Binkley, C. Gonzalez, R. I. Martin, D. J. Fox, D. J. Defrees, J. Baker, J. J. P. Stewart, J. A. Pople, Gaussian 92, Gaussian, Inc., Pittsburgh, PA, USA, 1992.
- [9] For GIAO-MP2 see a) J. Gauss, Chem. Phys. Lett. 1992, 191, 614; b) J. Gauss, J. Chem. Phys. 1993, 99, 3629-3643. The method was implemented in ACESII: ACESII, an ab initio program system by J. F. Stanton, J. Gauss, J. D. Watts, W. J. Lauderdale, R. J. Bartlett, Quantum Theory Project, University of Florida, 1991 and 1992. tzpdz stands for "triple zeta plus polarization" basis sets for heavy atoms and "double zeta" basis sets for hydrogen atoms: A. Schäfer, H. Horn, R. Ahlrichs, J. Chem. Phys. 1992, 97, 2571-2577.
- [10] The notably different NMR shifts of the C atoms in the C=C bonds in **3a** and **3u** are likely to be due to the trimethylsilyl substituents, which induce a negative partial charge at C6 (stabilized by the α -Si effect) and a positive partial charge at C2. IGLO(II) computations for **3u'** (two SiH₃ substituents at C6) show significant shielding of C6 ($\delta(^{13}C) = 95.0$) and deshielding of C2 ($\delta(^{13}C) = 142.2$) relative to the data computed for **3u** at the same level ($\delta(^{13}C) = 112.5$ (C6) and 118.0 (C2)). The difference $\Delta\delta(^{13}C)$ (C2,6) is 47 ppm for **3u'**, close to the experimental difference of 44 ppm. **3u'** was too large for GIAO-MP2/tzpdz computations.
- [11] Siebert et al. reported strong shielding for the boron atom of a 3-methylenboretane derivative: M. Enders, H. Pritzkow, W. Siebert, Angew. Chem. 1992, 104, 628-629; Angew. Chem. Int. Ed. Engl. 1992, 31, 606-607.
- [12] NBO = natural bond orbital: A. E. Reed, L. A. Curtiss, F. Weinhold, Chem. Rev. 1988, 88, 899-926.
- [13] J. Allwohn, M. Pilz, R. Hunold, W. Massa, A. Berndt, Angew. Chem. 1990, 102, 1084-1085; Angew. Chem. Int. Ed. Engl. 1990, 29, 1032-1033.
- [14] W. Ando, H. Yoshida, K. Kurishima, M. Sugiyama, J. Am. Chem. Soc. 1991, 113, 7790-7792.
- [15] The Si atoms in siliranes are considerably shielded: δ ⁽²⁹Si) = -49.3 to -58.8 [16].
- [16] R. L. Lambert, D. Seyferth, J. Am. Chem. Soc. 1972, 94, 9246-9248; P. Boudjouk, E. Black, R. Kumarathasan, Organometallics 1991, 10, 2095-2096, and references therein.
- [17] M. Barfield, J. Am. Chem. Soc. 1993, 115, 6916-6928, and references therein.
- [18] Heterodicarbaboranes with four and more boron atoms: L. J. Todd in Metal Interactions with Boron Clusters (Ed.: R. N. Grimes), Plenum, New York, 1982, pp. 145-171; J. Kim, S. Kim, Y. Do, J. Chem. Soc. Chem. Commun. 1992, 938-939, and references therein; A. K. Saxena, N. S. Hosmane, Chem. Rev. 1993, 93, 1081-1124.