9-Borabarbaralanes

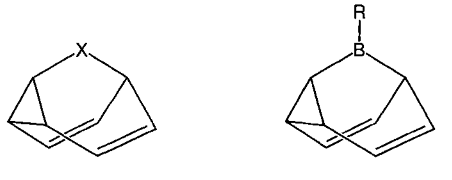
Gerhard E. Herberich,* Hans-W. Marx, Stefan Moss, Paul von Ragué Schleyer,* and Trixie Wagner

Abstract: The reaction of MgCOT(thf)$_x$ with tBuBF$_2$ or PhBCl$_2$ affords the first 9-borabarbaralanes **2** (C$_8$H$_8$BR, **a**: R = tBu; **b**: R = Ph). With the aminoboron dihalides BCl$_2$NiPr$_2$ and BCl$_2$N(SiMe$_3$)tBu 9-borabicyclo[4.2.1]-nona-2,4,7-trienes **3** (**a**: R = NiPr$_2$, **b**: R = N(SiMe$_3$)tBu) and the *trans*-9-borabicyclo[4.3.0]nona-2,4,7-triene **4** are obtained. The bicyclic compounds **3a** and **3b** are converted into 9-borabarbaralanes **2c** and **2d**, respectively, by irradiation in solution as well as by heating. All 9-borabarbaralanes **2** are fluxional in solution. In the crystalline state, the *B*-phenyl derivative **2b** displays a well-ordered van der Waals crystal structure. The theoretical prediction that the degenerate Cope rearrangement in barbaralanes will be retarded by π-acceptor groups in the 9 position has been verified. Quantum chemical calculations employing density functional theory support and help interpret the experimental findings. The isoelectronic 9-barbaralyl cations, in contrast, have such high Cope barriers that other rearrangement pathways are followed instead.

Keywords
ab initio calculations · barbaralanes · borabarbaralanes · Cope rearrangements

Introduction

Barbaralanes **1** [X = CH$_2$ (**1a**),[1] CO (**1b**),[2] CH$^+$ (**1c**),[3-5] CMe$^+$ (**1d**)[4e]] and their 9-hetero analogues (e.g., X = SiMe$_2$,[6a] NCN,[6b] NH,[6c] PPh,[6d] PMe$_2^+$,[6e] P(NMe$_2$)Cl$^+$,[6f] S,[6g] SO$_2$[6h]) are fascinating molecules exhibiting fluxional behavior (Scheme 1). The completely degenerate barbaralyl cation (**1c**) has been studied thoroughly, experimentally[3,4] as well as theoretically.[3,5] The hitherto unknown 9-borabarbaralanes **2** are isoelectronic with **1c,d**. We now describe the first representatives **2a–d** of this class of compound and report theoretical studies on the model compounds **2e–g**.[7]



1 **2**

Scheme 1. Barbaralanes: X = CH$_2$ (**1a**), CO (**1b**), CH$^+$ (**1c**), CMe$^+$ (**1d**). 9-Borabarbaralanes: R = tBu (**2a**), Ph (**2b**), NiPr$_2$ (**2c**), N(SiMe$_3$)tBu (**2d**), H (**2e**), Me (**2f**), NH$_2$ (**2g**).

Results and Discussion

The reaction of MgCOT(thf)$_x$[8] (COT = 1,3,5,7-cyclooctatetraene) with organoboron dihalides tBuBF$_2$ and PhBCl$_2$ gave the 9-borabarbaralanes **2a,b**, respectively. These compounds are extremely air- and moisture-sensitive. They are fluxional at ambient temperature in solution, as expected, showing apparent C_{2v} symmetry in their ^{1}H and ^{13}C NMR spectra.

The X-ray crystal structure determination of **2b** (Table 1, Fig. 1)[9] reveals a well-ordered van der Waals crystal. Orientational disorder of the C$_8$B skeleton would result in apparent C_{2v} molecular symmetry. However, disorder is ruled out by the observation of the quite different interatomic distances for C2–C8 [152.9(1) pm] and C4···C6 [239.1(1) pm]. Furthermore, the thermal parameters of the C2, C4, C6, and C8 atoms are

Table 1. Selected bond lengths [pm] and bond angles [°] for **2b** (experimental) and **2e** (calculated, RBecke3LYP/6-311G**).

	2b	**2e**		**2b**	**2e**
B–C1	153.7(1)	153.1	C7–C8	147.0(1)	147.9
B–C5	158.2(1)	158.3	C3–C4	132.8(1)	133.8
B–C11	155.6(1)		C6–C7	132.6(1)	133.8
C1–C2	153.5(1)	154.1	C4–C5	151.8(1)	153.1
C1-C8	153.1(1)	154.1	C5–C6	152.0(1)	153.1
C2–C8	152.9(1)	153.9	C4···C6	239.1(1)	240.3
C2–C3	147.0(1)	147.9			
C1-B-C5	111.95(6)	113.1	C2-C3-C4	121.78(8)	121.6
B-C1-C2	113.25(7)	113.4	C6-C7-C8	121.95(8)	121.6
B-C1-C8	114.68(7)	113.4	C3-C4-C5	120.50(8)	119.8
C2-C1-C8	59.82(5)	59.9	C5-C6-C7	120.14(8)	119.8
C1-C2-C8	59.98(5)	60.0	C4-C5-C6	103.78(7)	103.4
C1-C8-C2	60.20(5)	60.0	B-C5-C4	107.30(7)	108.1
C1-C2-C3	118.49(7)	118.8	B-C5-C6	108.63(7)	108.1
C1-C8-C7	118.31(7)	118.8			

---

[*] Prof. Dr. G. E. Herberich, Dr. H.-W. Marx, Dipl.-Chem. T. Wagner
Institut für Anorganische Chemie
RWTH Aachen, D-52056 Aachen (Germany)
Fax: Int. code +(241)8888-288
Prof. Dr. P. von R. Schleyer, Dr. S. Moss
Computer-Chemie-Centrum
Institut für Organische Chemie der Universität Erlangen-Nürnberg
Henkestr. 42, D-91054 Erlangen (Germany)
Fax: Int. code +(9131)85-9132

0947-6539/96/0204-0458 $ 15.00+.25/0

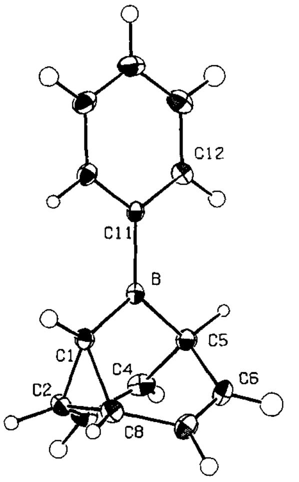
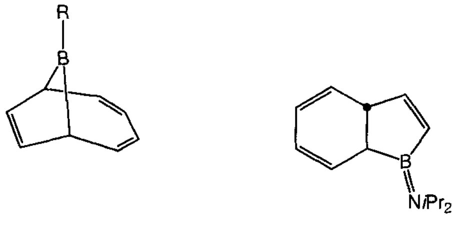


Fig. 1. Molecular structure of **2b**.

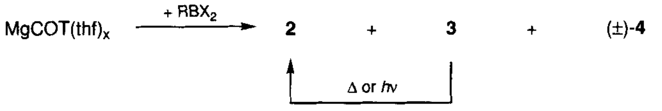
inconspicuous and exhibit only slight anisotropies. Hence, the fluxional behavior is frozen out in the crystalline state. The structure of the parent compound **2e** was also calculated by means of density functional theory (RBecke3LYP/6-311G**).[10] The bond lengths obtained for **2e** are in fair agreement with those observed experimentally for compound **2b**.

The reaction of the aminoboron dihalide BCl_2NiPr_2 with MgCOT(thf)$_x$ (in the dark, below 20 °C) yielded a mixture (ca. 1:1) of the two isomeric bicyclic compounds **3a** and **4** (Scheme 2 and 3); varying small amounts of barbaralane **2c** were also present in the product mixture. The known triene **3a**, originally synthesized by the reaction of $K_2C_8H_8$ with BCl_2NiPr_2,[11] could be separated and purified by crystallization. The second isomer **4** could only be characterized by NMR spectroscopy and is the first example of a *trans*-9-borabicyclo[4.3.0]nona-2,4,7-triene. Irradiation (pentane, 20 °C) converted **3a** to aminoborabarbaralane **2c** in quantitative yield. When heated (100 °C/20 h), **3a** decomposed in part but also underwent slow isomerization to **2c**.



3 **4**

Scheme 2. R = N*i*Pr$_2$ (**3a**), N(SiMe$_3$)*t*Bu (**3b**).



Scheme 3.

The sterically crowded unsymmetrical aminoboron dihalide $BCl_2N(SiMe_3)tBu$ reacted with MgCOT(thf)$_x$ to produce the triene **3b** exclusively (Scheme 2). The crystalline borabarbaralane **2d** was formed quantitatively from **3b** by irradiation in solution or by heating (150 °C, 3 h).

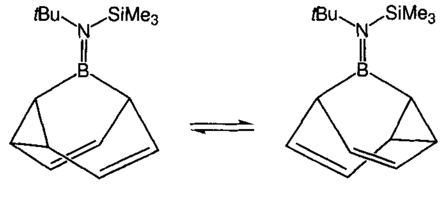
The triene **3b** exhibits effective C_s symmetry despite the different substituents at the nitrogen atom. The B–N rotational barrier is lowered from the typical 60–100 kJ mol^{-1} range[12] to $\Delta G^{\ddagger}_{273} = 51(2)$ kJ mol^{-1}. Rotational barriers of [(trimethylsilyl)amino]boranes have not been measured before, but the geometry of **5c**[13] also hints at a low rotational barrier. The aminoborane group of this compound is twisted by 45°; the B–N bond length of 143.3(6) pm is elongated considerably.[14] These results can be compared with DFT calculations (RBecke3LYP/6-311 + G**) on the (silylamino)borane **5b** as a model compound.

The B–N bond length determined experimentally for **5c** is between that calculated for the energy minimum (140.4 pm) and the transition state (145.8 pm) for B–N rotation in **5b**. Furthermore the rotational barrier of the parent compound H_2BNH_2 (**5a**), 128 kJ mol^{-1} calculated at the same level, is only reduced to 111 kJ mol^{-1}[15] in the silyl derivative **5b** (via a C_1 transition

$H_2B{=}NH_2$ **5a** $H_2B{=}NH(SiH_3)$ **5b** $Ph_2B{=}N(SiMe_3)tBu$ **5c**

state). Hence, the electronic effect of a silyl substituent on the aminoborane rotational barriers is minor. Larger reductions, as in **5c**, must be due to other, presumably steric, effects.

Borabarbaralanes **2** undergo a dynamic skeletal rearrangement in solution; **2b** exhibits C_s symmetry in its NMR spectra only at low temperatures (< −60 °C). At room temperature effective C_{2v} symmetry is observed. Hence, C1 and C5 are equivalent as are C2/8 and C4/6. The rearrangement of **2b** is degenerate and nearly so for **2a** and **2c**, owing to the low symmetries of the substituents at the boron atoms. The determination of the rearrangement barriers in degenerate cases is straightforward by means of ^{13}C NMR spectroscopy.[16, 17] The free energies of activation $\Delta G^{\ddagger}$ are 45.7(4) kJ mol^{-1} for **2a** ($\Delta G^{\ddagger}_{278}$) and 40.5(7) kJ mol^{-1} for **2b** ($\Delta G^{\ddagger}_{248}$). The dynamics of the *B*-diisopropylamino group in **2c** can be frozen out ($T < 250$ K); on the other hand, the slow-exchange limit of the skeletal rearrangement could not be reached. Finally, the two structural isomers expected for **2d** (Scheme 4) can be discerned spectroscopically in the slow-exchange region [ratio 2:1, −95 °C/67.9 MHz].



2d **2d'**

Scheme 4. Skeletal rearrangement of compounds **2d**.

The skeletal rearrangements of compounds **1** with a barbaralane skeleton show a mechanistic dichotomy.[3, 4e] Both **1a** and **1b** automerize through Cope rearrangements. When a π acceptor (like boron) is substituted at position 9 of the borabaralane skeleton, the barrier to Cope rearrangement is raised. A different mechanism is followed in barbaralyl cations **1c,d**, owing to the positive charge at C9. For **1c**, two different dynamic processes can be distinguished by ^{13}C NMR spectroscopy.[3, 4] At −135 °C, **1c** is completely (!) degenerate showing one signal for all nine carbon atoms,[4d] while at −150 °C two signals are found (6:3).[4f] In a thorough theoretical study, Cremer, Ahlberg et al. have shown that the dynamic behavior of **1c** at −150 °C is due to a series of divinylcyclopropylmethyl cation rearrangements;[5] Cope rearrangements are mimicked, but are not involved because of their much higher barrier.[5] The same situation holds for the 9-methylbarbaralyl cation **1d**,[4c, 3d, 18] whose structure is even closer to that of 9-borabarbaralanes **2**, especially to the *tert*-butyl derivative **2a**.

The cyclopropyl group is a fairly strong π donor.[19] Calculations by Clark, Schleyer et al. reveal that one of the two Walsh HOMOs interacts strongly with the LUMO of π acceptor groups such as BH_2 or CH_2^+.[20a] This results in a stabilization of the ground state of **2**, a shortening of the distal bond C2–C8, and an increase of the Cope barrier.

These predictions have been confirmed for the 9-borabarbaralanes, both experimentally and by a DFT computational investigation of the model compounds **2e–g** (Table 2). The good performance of the Becke3LYP level of theory with the parent Cope rearrangement[21] suggests that it may also work well in the present case. The comparison of the calculated vicinal and distal C–C bond lengths shows that the BH group and a vinylic C–C double bond are comparable acceptors. The cyclopropane ring of the parent compound **2e** is a nearly equilateral triangle. The acceptor strength of the BR group is reduced in the methyl compound **2f** and much more so in the amino derivative **2g**. The distal C–C bond in **2g** is 3.0 pm longer than the vicinal bond, while in **2e** the difference is only 0.2 and in **2f** 0.6 pm. Hence, the amino group is a more powerful donor than the methyl group. The barrier to the Cope rearrangement follows the same trend: the free activation energy at 0 K varies as **2e**>**2f**≫**2g**. Consistent with these results, the Cope barriers of **2a,b** can be determined experimentally, whereas the slow exchange temperature region is not reached for **2b**·NMe$_3$ even at −90 °C/125.7 MHz. In addition, the theoretically predicted barriers are in good agreement with the experimental values.

Table 2. Experimental and calculated (RBecke3LYP/6-311G**) bond lengths [pm] and free activation energies ΔG^{*} of the Cope rearrangement [kJ mol^{-1}] for 9-borabarbaralanes **2** (Scheme 1).

	2a	**2b**	**2e**	**2f**	**2g**
C–C$_{vic}$ [a]	–	153.1, 153.5	153.9	153.7	152.7
C–C$_{dist}$ [a]	–	152.9	154.1	154.3	155.7
Δ(C–C)	–	0.2, 0.6	0.2	0.6	3.0
$\Delta G^{*}(0)$			41.1	39.4	35.0
$\Delta G^{*}(T)$	45.7(4) [b]	40.5(7) [c]	43.3 [d]	39.3 [d]	37.1 [d]

[a] Vicinal bonds: C1–C2 and C1–C8; distal bonds: C2–C8. [b] T = 278 K. [c] T = 248 K. [d] T = 300 K, calculated.

Although the 9-barbaralyl cations **1c,d** and the 9-borabarbaralanes **2** are isoelectronic, the latter are more akin to barbaralane (**1a**) and barbaralone (**1b**) in their dynamic behavior, and also undergo true Cope rearrangements.

Experimental Section

General: All manipulations of compounds were carried out by standard Schlenk techniques. All the products are extremely oxygen- and moisture-sensitive. NMR spectra were recorded on Varian VXR 300 (^{1}H 300 MHz), Varian Unity 500 (^{1}H 500, ^{13}C 125.7 MHz), Bruker WH-270, (^{13}C 67.9 MHz), and Jeol JNM-PS 100 (^{11}B 32 MHz) instruments.

9-*tert*-Butyl-9-borabarbaralane (2a): *t*BuBF$_2$ (1.8 g, 17 mmol) was added to a suspension of MgCOT(thf)$_{2.5}$ (4.6 g, 14.9 mmol) in pentane (50 mL) at −78 °C. The reaction mixture was allowed to warm up to 20 °C and was stirred for 12 h. The salts that precipitated out were filtered. Distillative workup gave **2a** (1.2 g, 47%) as a yellowish liquid; b.p. 80–90 °C/15 mbar. MS, *m/z* (%): 172 (82, M^+), 139 (100, $M^+ - C_3H_7$). ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): δ = 5.55 (m, 3-/7-H), 4.1 (br, 2-/4-/6-/8-H), 2.17 (m, 1-/5-H), 0.92 (s, *t*Bu). ^{11}B NMR (CDCl$_3$): δ = 83. ^{13}C NMR (67.9 MHz, CH$_2$Cl$_2$/CD$_2$Cl$_2$, 183 K, *J* in Hz): δ = 128.78 (d, 164.6, C4/6), 121.87 (d, 159.6, C3/7), 35.24 (d, C5), 34.91 (d, 166.2, C2/8), 25.56 (q, 124.5, Me), 24.22 (s, *C*Me$_3$), 18.05 (d, 156.2, C1); $T_c = 278 \pm 15$ K, $\Delta\nu$ = 6371 Hz, $\Delta G^{\ddagger}_{278} = 45.8 \pm 2.6$ kJ mol^{-1} for C2/4/6/8; $T_c = 248 \pm 5$ K, $\Delta\nu$ = 1167 Hz, $\Delta G^{\ddagger}_{248} = 44.1 \pm 0.9$ kJ mol^{-1} for C1/5. Rate constants were determined by simulation of band shapes and gave $\Delta G^{\ddagger}_{278} = 45.7 \pm 0.4$ kJ mol^{-1}.

9-Phenyl-9-borabarbaralane (2b): As described for **2a**, reaction of MgCOT(thf)$_{2.5}$ (6.42 g, 20.8 mmol) and PhBCl$_2$ (3.3 g, 20.8 mmol) gave **2b** (1.8 g, 44%) as a yellowish oil that solidified very slowly; bp. 70–80 °C/5 × 10^{-6} bar. MS, *m/z* (%): 192 (14, M^+), 104 (100, $C_8H_8^+$). ^{1}H NMR (500 MHz, CD$_2$Cl$_2$, 183 K): δ = 7.90 (m, 2H$_o$), 7.6–7.4 (m, H$_p$ and 2H$_m$), 5.80 (m, 4-/6-H), 5.59 (m, 3-/7-H), 3.25 (m, 5-H), 2.65 (m, 2-/8-H), 2.10 (m, 1-H). ^{11}B NMR (CDCl$_3$): δ = 73. ^{13}C NMR (67.9 MHz, CH$_2$Cl$_2$/CD$_2$Cl$_2$, 178 K, *J* in Hz): δ = 136.68 (s, C$_i$), 135.46 (d, 159.6, 2C$_o$), 132.70 (d, hidden, C$_p$), 128.74 (d, 164.3, C4/6), 127.68 (d, 158.6, 2C$_m$), 122.01 (d, 158.9, C3/7), 35.45 (d, 165.5, C2/8), 34.68 (d, 126, C5), 19.10 (d, 156.9, C1); $T_c = 248 \pm 15$ K, $\Delta\nu$ = 6333 Hz, $\Delta G^{\ddagger}_{248} = 40.7 \pm 2.6$ kJ mol^{-1} for C2/4/6/8; $T_c = 223 \pm 10$ K, $\Delta\nu$ = 1096 Hz, $\Delta G^{\ddagger}_{223} = 39.6 \pm 1.9$ kJ mol^{-1} for C1/5. Rate constants were determined by simulation of band shapes and gave $\Delta G^{\ddagger}_{248} = 40.5 \pm 0.7$ kJ mol^{-1}.

9-Phenyl-9-borabarbaralane trimethylamine (2b·NMe$_3$): An excess of NMe$_3$ was added to a solution of **2b** (0.4 g, 2.0 mmol) in hexane (10 mL) at −78 °C. Crystallization of the resulting solid from hot hexane gave **2b**·NMe$_3$ (0.4 g, 80%) as a white powder; decomp. 110 °C. MS, *m/z* (%): 192 (35, $M^+ - NMe_3$), 114 (100, $192 - C_6H_6$). ^{1}H NMR (500 MHz, CD$_2$Cl$_2$, 25 °C): δ = 7.50 (m, 2H$_o$), 7.20 (m, 2H$_m$), 7.12 (m, H$_p$), 5.61 (br, 3-H, *cis* position to NMe$_3$), 4.98 (br, 7-H, *trans* position to NMe$_3$), 4.17 and 3.93 (br, 2-/4-/6-/8-H), 2.43 (s, NMe$_3$), 1.87 (m, 1-/5-H). ^{11}B NMR (CDCl$_3$): δ = 1. ^{13}C{^{1}H} NMR (125.7 MHz, CD$_2$Cl$_2$, 25 °C): δ = 150 (br, C$_i$), 134.67 (2C$_o$), 126.80 (2C$_m$), 125.35 (C$_p$), 123.6 and 120.9 (br, C3 and C7), 80.00 and 78.57 (C2/4 and C6/8), 51.24 (NMe$_3$), 21.7 (C1/5). Estimation of an upper limit for ΔG^{*}: $T_c < 213$ K, $\Delta\nu < 13.5$ kHz, $\Delta G^{\ddagger}_{213} < 34$ kJ mol^{-1}.

Synthesis of 9-diisopropylamino derivatives 2c/3a/4: As described for **2a**, MgCOT(thf)$_{2.5}$ (5.36 g, 17.4 mmol) was treated with BCl$_2$N*i*Pr$_2$ (3.0 g, 16.5 mmol) in pentane (80 mL), and the mixture was stirred for 3 d at 20 °C. Workup gave a mixture of **2c/3a/4** (2.98 g, 84%). Crystallization from ether yielded **3a** (1.06 g, 30%) [11]. Distillative workup of the mother liquor gave a pale yellow oil (1.66 g, 47%) containing **3a** and **4** (ratio 1:3.5) and a small amount of **2c** (ca. 5% based on BCl$_2$N*i*Pr$_2$, data given below). **4**: ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C, *J* in Hz): δ = 6.97 (br d, 8.3, 7-H), 6.55 (ddm, 9.46, 3.05, 2-H), 6.39 (dm, 9.4, 5-H), 6.11 (dd, 8.3, 2.9, 8-H), 6.06 (m, 3-H), 5.98 (m, 4-H), 3.06 (dm, 15.3, 6-H), 1.72 (br dm, 15.3, 1-H); for N*i*Pr$_2$ 3.96 and 3.40 (both signals: sept, 6.9, NCH), 1.27, 1.22, 1.19, 1.18 (all four signals: d, 6.9, Me). ^{11}B NMR (CDCl$_3$): δ = 41. ^{13}C{^{1}H} NMR (125.7 MHz, CDCl$_3$): δ = 155.25 (C7), 134.5 (br, C8), 133.79 (C5), 132.77 (C2), 126.52 (C3), 124.70 (C4), 50.07 (br, 1 NC), 48.11 (C6), 45.56 (br, 1 NC), 35 (br, C1), 25.32, 24.73, 22.56 and 22.28 (4 Me); the assignment was confirmed by COSY- and HETCOR experiments.

9-[*tert*-Butyl(trimethylsilyl)amino]-9-borabicyclo[4.2.1]nona-2,4,7-triene (3b): As described for **2a**, MgCOT(thf)$_{2.5}$ (4.0 g, 13.0 mmol) was treated with BCl$_2$N(SiMe$_3$)*t*Bu (2.9 g, 12.8 mmol). The resulting oil was recrystallized from Et$_2$O and gave **3b** (2.98 g, 86%) as colorless crystals; m.p. 39–41 °C, b.p. 70–80 °C/5 × 10^{-6} bar. MS, *m/z* (%): 259 (2, M^+), 57 (100, $C_4H_9^+$). ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C): δ = 5.90 (m, 2-/5-H), 5.70 (m, 3-/4-H), 5.56 (m, 7-/8-H), 2.44 (m, 1-/6-H), 1.33 (s, *t*Bu), 0.29 (s, SiMe$_3$). ^{11}B NMR (CDCl$_3$): δ = 54. ^{13}C NMR (67.9 MHz, CDCl$_3$, 25 °C, *J* in Hz): δ = 135.5 (d, 159.3, C2/5), 127.6 (d, 164.2, C7/8), 124.2 (d, 154.6, C3/4), 58.0 (s, *C*Me$_3$), 39.2 (br d, C1/6), 34.1 (q, 125.9, C*Me*$_3$), 6.9 (q, 118.7, SiMe$_3$); ^{13}C{^{1}H} NMR (213 K): δ = 136.7 and 135.1 (C2, C5), 128.8 and 124.0 (C7, C8), 125.0 and 122.1 (C3, C4), 57.9 (*C*Me$_3$), 38.8 and 38.3 (C1, C6), 33.7 (C*Me*$_3$), 6.7 (SiMe$_3$); $T_c = 258 \pm 10$ K, $\Delta\nu$ = 104 Hz, $\Delta G^{\ddagger}_{258} = 51.2 \pm 2.1$ kJ mol^{-1} for C2/5; $T_c = 273 \pm 10$ K, $\Delta\nu$ = 461 Hz, $\Delta G^{\ddagger}_{273} = 50.9 \pm 1.9$ kJ mol^{-1} for C7/8; $T_c = 263 \pm 10$ K, $\Delta\nu$ = 193 Hz, $\Delta G^{\ddagger}_{263} = 50.9 \pm 2.0$ kJ mol^{-1} for C3/4; $T_c = 243 \pm 10$ K, $\Delta\nu$ = 30.3 Hz, $\Delta G^{\ddagger}_{243} = 50.6 \pm 2.2$ kJ mol^{-1} for C1/6.

9-(Diisopropylamino)-9-borabarbaralane (2c): Compound **3a** (0.89 g, 4.1 mmol) in pentane (50 mL) was irradiated for 5 d (mercury high pressure lamp TQ150, Original Hanau, 150 W). Distillative workup and recrystallization from Et$_2$O/hexane (2:1) gave **2c** (0.65 g, 73%) as colorless crystals; m.p. 57–59 °C, b.p. 65 °C/5 × 10^{-6} bar. MS, *m/z* (%): 215 (87, M^+), 200 (100, $M^+ - Me$). ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C, *J* in Hz): δ = 5.58 (m, 3-/7-H), 4.0 (br, 2-/4-/6-/8-H), 3.68 (sept, 6.8, 2NCH), 1.88 (m, 2-/5-H), 1.15 (d, 6.8, 4Me). ^{11}B NMR (CDCl$_3$): δ = 45. ^{13}C{^{1}H} NMR (125.7 MHz, CDCl$_3$, 313 K): δ = 123.25 (C3/7), 79 (br, C2/4/6/8), 48.18 (NCH), 23.86 (Me), 21 (br, C1/5); ^{13}C{^{1}H} NMR (218 K): δ = 129 (br, C4/6), 122.96 (C3/7), 51.8 (br, NCH), 44.2 (br, NCH), 29 (very br, C5 and C2/8), 25.11 (2Me), 21.92 (2Me), 10.0 (br, C1); $T_c = 263 \pm 10$ K, $\Delta\nu$ = 960 Hz, $\Delta G^{\ddagger}_{263} = 47.4 \pm 1.9$ kJ mol^{-1} for NCH; $T_c = 253 \pm 10$ K, $\Delta\nu$ = 401 Hz, $\Delta G^{\ddagger}_{253} = 47.3 \pm 2.0$ kJ mol^{-1} for Me.

9-[*tert*-Butyl(trimethylsilyl)amino]-9-borabarbaralane (2d): As described for **2c**, irradiation of a solution of **3b** (2.46 g, 9.5 mmol) in pentane (100 mL) and workup as above gave **2d** (2.21 g, 90%) as colorless crystals; m.p. 54–56 °C, b.p. 90–100 °C/5 × 10^{-6} bar. MS, *m/z* (%): 259 (3, M^+), 57 (100, $C_4H_9^+$). ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C): δ = 5.57 (m, 3-/7-H), 4.05 (br, 2-/4-/6-/8-H), 1.88 (m, 1-/5-H), 1.33 (s, *t*Bu), 0.24 (s, SiMe$_3$). ^{11}B NMR (CDCl$_3$): δ = 58. ^{13}C NMR (67.9 MHz, CH$_2$Cl$_2$/CD$_2$Cl$_2$, 25 °C, *J* in Hz): δ = 123.15 (d, 157.9, C3/7), 80.8 (br d, 159, C2/4/6/8), 55.84 (s, *C*Me$_3$), 33.67 (q, 125.3, C*Me*$_3$), 27.2 (br d, C1/5), 6.16 (q, 118.8, SiMe$_3$); ^{13}C NMR (178 K), major isomer: δ = 129.51 (d, 160.0, C4/6), 122.39 (d, 158.9, C3/7), 54.76 (s, *C*Me$_3$), 37.06 (d, 130.1, C5), 32.27 (q, 124.8, C*Me*$_3$), 31.09 (d, 162.7, C2/8), 15.43 (d, 152.4, C1), 5.60 (q, 118.6, SiMe$_3$); minor isomer: δ = 129.34 (d, 160, C4/6), 122.12 (d, 159.6, C3/7), 55.73 (s, *C*Me$_3$), 35.09 (d, 127, C5), 32.81 (q, 125.0, C*Me*$_3$), 28.86 (d, C2/8), 17.34 (d, 153,0, C1), 5.06 (q, 118.7, SiMe$_3$).

Table 3. Number of imaginary frequencies (NIMAG), total energies E_{tot} [a.u.], vibrational energies E_{th} at 0 and 300 K [kJ mol^{-1}], entropies S [kJ mol^{-1} K^{-1}] of **2e–g** (Scheme 1) and their transition states **2e-ts** to **2g-ts**, and corresponding free activation energies $\Delta G^{\neq}$ of the Cope rearrangement.

	2e	**2e-ts**	**2f**	**2f-ts**	**2g**	**2g-ts**
point group	C_s	C_{2v}	C_s	C_s	C_s	C_{2v}
NIMAG	0	1	0	1	0	1
E_{tot} [a]	−335.13139	−335.11376	−374.47534	−374.45832	−390.56920	−390.55395
$E_{th}(0)$ [b]	372.3	367.1	442.3	437.0	420.6	415.6
$\Delta G^{\neq}(0)$		41.1		39.4		35.0
$E_{th}(300)$ [b]	388.8	383.2	463.3	457.6	439.8	434.3
$S(300)$ [c]	0.326	0.318	0.371	0.370	0.349	0.341
$\Delta G^{\neq}(300)$		43.3		39.3		37.1

[a] RBecke3LYP/6-311G**. [b] RHF/6-31G* value, scaled by 0.89. [c] RHF/6-31G*.

Computational Details: Calculations were carried out with the Gaussian-92 Program package [10]. Geometries were fully optimized at RHF/6-31G* and RBecke3LYP/6-311G** [10]. Stationary points were characterized as minima or saddle points by analytic second-derivative computation of harmonic vibrational frequencies. These provided the zero-point vibrational energies (ZPE), entropies, and thermochemical data. The free activation energies $\Delta G^{\neq}$ given in Table 3 are defined as $\Delta G^{\neq} = \Delta E_{tot} + \Delta E_{th}(T) - T\Delta S(T)$ for $T = 300$ K. E_{tot} are the RBecke3LYP/6-311G** energies, and for E_{th} and S the RHF/6-31G* data were used. E_{th} and ZPE were scaled by an empirical factor of 0.89.

Acknowledgement: We thank Dipl.-Chem. Matthias Hofmann for helpful discussions. This work was supported by the Volkswagen-Stiftung, the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the Convex Computer Corporation.

Received: September 11, 1995 [F209]

---

[1] a) U. Biethan, H. Klusacek, H. Musso, *Angew. Chem.* **1967**, *79*, 152–153; *Angew. Chem. Int. Ed. Engl.* **1967**, *6*, 176; b) H. Tsuruta, K. Kurabayashi, T. Mukai, *Tetrahedron Lett.* **1967**, 3775–3779.

[2] a) J. B. Lambert, *Tetrahedron Lett.* **1963**, 1901–1906; b) W. von E. Doering, W. R. Roth, *Angew. Chem.* **1963**, *75*, 27–35; *Angew. Chem. Int. Ed. Engl.* **1963**, *2*, 115; W. von E. Doering, B. M. Ferrier, E. T. Fossel, J. H. Hartenstein, M. Jones, Jr., G. Klumpp, R. M. Rubin, M. Saunders, *Tetrahedron* **1967**, *23*, 3943–3963.

[3] Reviews: a) R. E. Leone, P. von R. Schleyer, *Angew. Chem.* **1970**, *82*, 889–919; *Angew. Chem. Int. Ed. Engl.* **1970**, *9*, 860; b) R. E. Leone, J. C. Barborak, P. von R. Schleyer, in *Carbonium Ions* (Eds.: G. A. Olah, P. von R. Schleyer), Wiley Interscience, New York, **1973**, Vol. 4, pp. 1837–1899; c) P. Ahlberg, G. Jonsäll, C. Engdahl, *Adv. Phys. Org. Chem.* **1983**, *19*, 223–379. d) P. Ahlberg in *Stable Carbocations* (Eds.: G. K. S. Prakash, P. von R. Schleyer), Wiley, **1995**, in press.

[4] a) P. Ahlberg, D. L. Harris, S. Winstein, *J. Am. Chem. Soc.* **1970**, *92*, 4454–4456; b) C. Engdahl, G. Jonsäll, P. Ahlberg, *J. Chem. Soc. Chem. Commun.* **1979**, 626–627; c) P. Ahlberg, C. Engdahl, G. Jonsäll, *J. Am. Chem. Soc.* **1981**, *103*, 1583–1584; d) C. Engdahl, G. Jonsäll, P. Ahlberg, *ibid.* **1983**, *105*, 891–897; e) G. Jonsäll, P. Ahlberg, *J. Chem. Soc. Chem. Commun.* **1984**, 1125–1127; f) Cf. ref. [5] and references therein.

[5] D. Cremer, P. Svensson, E. Kraka, P. Ahlberg, *J. Am. Chem. Soc.* **1993**, *115*, 7445–7456.

[6] a) T. J. Barton, M. Juvet, *Tetrahedron Lett.* **1975**, *30*, 2561–2564; b) A. G. Anastassiou, A. E. Winston, E. Reichmanis, *J. Chem. Soc. Chem. Commun.* **1973**, 779–780; c) A. G. Anastassiou, E. Reichmanis, A. E. Winston, *Angew. Chem.* **1976**, *88*, 382–383; *Angew. Chem. Int. Ed. Engl.* **1976**, *16*, 370; d) T. J. Katz, J. C. Carnahan, Jr., G. M. Clarke, N. Acton, *J. Am. Chem. Soc.* **1970**, *92*, 734–735; e) G. Märkl, B. Alig, *Tetrahedron Lett.* **1983**, *24*, 3981–3984; f) S. A. Weissman, S. G. Baxter, A. M. Arif, A. H. Cowley, *J. Am. Chem. Soc.* **1986**, *108*, 529–531; g) A. G. Anastassiou, B. Y.-H. Chao, *J. Chem. Soc. Chem. Commun.* **1972**, 277; h) L. A. Paquette, U. Jacobsson, M. Oku, *ibid.* **1975**, 115–116; G. G. Christoph, S. Hardwick, U. Jacobsson, Y.-B. Koh, R. Moerck, L. A. Paquette, *Tetrahedron Lett.* **1977**, 1249–1252.

[7] For other carbocation boron analogies, see J. M. Schulmann, R. L. Disch, P. von R. Schleyer, M. Bühl, M. Bremer, W. Koch, *J. Am. Chem. Soc.* **1992**, *114*, 7897–7901.

[8] H. Lehmkuhl, S. Kintopf, K. Mehler, *J. Organomet. Chem.* **1972**, *46*, C1–C2; after drying in a high vacuum we find $x = 2$–2.5 for the composition of Mg-COT(thf)$_x$.

[9] a) X-ray structure determination of **2b**: crystals of **2b** for the structure determination were crystallized from pentane at −30 °C. Crystal dimensions 0.6 × 0.6 × 1.0 mm^3, formula $C_{14}H_{13}B$, formula weight 192.07 g mol^{-1}; cell parameters $a = 1238.9(4)$, $b = 651.9(2)$, $c = 1302.9(4)$ pm, $\beta = 100.53(3)°$; $V = 1.035(1)$ nm^3; monoclinic, space group $P2_1/n$ (no. 14), $Z = 4$, $d_{calcd} = 1.233$ g cm^{-3}, $F(000) = 408.0$, $\mu = 4.74$ cm^{-1}; ENRAF-Nonius CAD4, $\lambda = 154.18$ pm, 2076 reflections measured ($5 < \theta < 70°$, $\omega - \theta$ scans), 1840 reflections with $I > 3\sigma(I)$, 1795 independent reflections with $I > 2\sigma(I)$ for 189 parameters, structure solution and refinement with SDP [9b]. All non-hydrogen atoms were refined anisotropically, all hydrogen atoms were treated isotropically. Empirical absorption correction with DIFABS [9c], sec. extinction coefficient $E = 4.82 \times 10^{-6}$ [9d], $R = 0.045$, $R_w = 0.062$, GOF = 2.878, residual electron density 0.186×10^{-6} e pm^{-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-401605. b) B. A. Frenz, *The ENRAF-Nonius CAD4-SDP—a Real-Time System for Concurrent X-Ray Data Collection and Crystal Structure Determination*, in *Computing in Crystallography* (Eds.: H. Schenk, R. Olthof-Hazekamp, H. van Koningsveld, G. C. Bassi), University of Delft **1978**; SDP-PLUS, Version 1.1 (1984) and VAXSDP, Version 2.2 (**1985**); c) N. Walker, D. Stuart, *Acta Crystallogr. Sect. A* **1983**, *39*, 158–166; d) W. H. Zachariasen, *Acta Crystallogr.* **1963**, *16*, 1139–1144.

[10] a) *Gaussian 92/DFT*, Revision F.2, M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. W. Wong, J. B. Foresman, M. A. Robb, M. Head-Gordon, E. S. Replogle, R. Gomperts, J. L. Andres, K. Raghavachari, J. S. Binkley, C. Gonzalez, R. L. Martin, D. J. Fox, D. J. Defrees, J. Baker, J. J. P. Stewart, J. A. Pople, Gaussian, Pittsburgh PA, **1993**; b) *New Methods and Features in Gaussian 92/DFT (adding density functional capabilities to Gaussian 92)*, Gaussian, Pittsburgh, PA, **1993**; c) J. W. Labanowski, J. Andzelm, *Density Functional Methods in Chemistry*, Springer, New York, **1991**; d) R. G. Parr, W. Yang, *Density Functional Theory of Atoms and Molecules*, Oxford University Press, New York, **1989**.

[11] W. Maringgele, D. Stalke, A. Heine, A. Meller, G. M. Sheldrick, *Chem. Ber.* **1990**, *123*, 489–490.

[12] D. Imbery, A. Jaeschke, H. Friebolin, *Org. Magn. Reson.* **1970**, *2*, 271–281.

[13] D. Männig, H. Nöth, H. Prigge, A.-R. Rotsch, S. Gopinathan J. W. Wilson, *J. Organomet. Chem.* **1986**, *310*, 1–20.

[14] Typical bond lengths for aminoboranes B–N 141 pm: P. Paetzold, *Adv. Inorg. Chem.* **1987**, *31*, 123–170.

[15] Data for H_2BNH_2: C_{2v} ground state, B–N 139.1 pm, C_s transition state for internal rotation; data for $H_2BNHSiH_3$: C_s ground state, B–N 140.4 pm, C_1 transition state.

[16] H. Friebolin, *Ein- und zweidimensionale NMR-Spektroskopie*, 2nd ed., VCH, Weinheim, **1992**.

[17] J. Sandström, *Dynamic NMR Spectroscopy*, Academic Press, London, **1984**.

[18] P. Ahlberg, J. B. Grutzner, D. L. Harris, S. Winstein, *J. Am. Chem. Soc.* **1970**, *92*, 3478–3480.

[19] Cf. ref. [20a] and references therein.

[20] a) T. Clark, G. W. Spitznagel, R. Klose, P. von R. Schleyer, *J. Am. Chem. Soc.* **1984**, *106*, 4412–4419; b) R. Hoffmann, W.-D. Stohrer, *J. Am. Chem. Soc.* **1971**, *93*, 6941–6948; c) F. H. Allen, *Acta Crystallogr. Sect. B* **1980**, *36*, 81–96.

[21] H. Jiao, P. von R. Schleyer, *Angew. Chem.* **1995**, *107*, 329–332; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 334–337.