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sented here proceeds along path b, and not along path a (Scheme 1).

The alkenyltitanium intermediate of type C (Scheme 1, $ML_n = Ti(OiPr)_2$) can be trapped by iodine in excellent yield (Table 1, entry 7). This intermediate reacted with an aldehyde to give the adduct in high yield (entries 8, 11–13), thus allowing the extension of the side chain after the cyclization by an one-pot procedure (Scheme 3).



Scheme 3. Trapping with an aldehyde of the intermediate obtained from 1 and the 2,7-enynyl carbonate 7.

The sequence of cyclization followed by trapping with an aldehyde has been widely utilized in the case of lithium- and magnesium-ene reactions for synthesis of polysubstituted cycloalkanes and corresponding natural products.^[1a] The present reaction, which can be regarded as synthetically equivalent, at least in part, to these intramolecular metallo-ene reactions, should also find wide applicability in organic synthesis. Moreover, several functionalities that are labile under the reaction conditions for the magnesium- and lithium-ene reactions are not attacked by the titanium compounds (see Table 1, entries 12 and 13). Thus, the present reaction could offer an even wider range of possibilities, which we are currently investigating.

Experimental Section

Typical procedure (synthesis of 20, Table 1, entry 11): To a solution of 9 (0.082 g, 0.308 mmol) and [Ti(OiPr)₄] (0.113 mL, 0.385 mmol) in ether (3.0 mL) was added iPrMgCl (0.65 mL, 1.13 m in ether, 0.739 mmol) at -50 °C, and the reaction mixture was subsequently allowed to warm to room temperature. After the reaction mixture had been stirred for 1 h, propanal (0.033 mL, 0.462 mmol) was added, and the mixture was stirred for a further hour. Aqueous workup (1 N HCl) and column chromatography (silica gel, hexane/AcOEt 30/1) provided 20 (0.054 g, 74% yield) as a 58:42 mixture of diastereoisomers. ¹H NMR (300 MHz, CDCl₃): major diastereoisomer: $\delta = 0.74 - 0.89$ (m, 6 H), 1.17 - 1.64 (m, 12 H), 1.65 - 1.79 (m, 1 H), 1.82-2.08 (m, 2H), 2.11-2.34 (m, 2H), 3.26-3.36 (m, 1H), 4.27-4.36 (m, 1H), 4.89-4.96 (m. 1 H), 5.80 (ddd, J = 17.0, 10.2, 6.82 Hz, 1 H); minor diastereoisomer: $\delta = 0.74 - 0.89$ (m, 6H), 1.17 - 1.64 (m, 12H), 1.65 - 1.79 (m, 1H), 1.82 - 2.08 (m, 2H), 1.82 (m, 2H), 2.11-2.34 (m, 2H), 3.26-3.36 (m, 1H), 4.27-4.36 (m, 1H), 4.78-4.85 (m, 1 H), 5.61–5.73 (m, 1 H); ¹³C NMR (75 MHz, CDCl₃): $\delta = 10.49$, 10.88, 14.09, 22.50, 23.41, 23.47, 27.66, 28.23, 28.69, 28.83, 29.52, 29.57, 30.09, 30.26, 32.77, 33.64, 45.15, 45.60, 74.36, 74.41, 112.74, 113.00, 134.90, 135.20, 141.45, 141.61, 142.35, 142.60

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Lett. 1994, 35, 7939; g) W. Oppolzer, C. Robyr, Tetrahedron 1994, 50, 415; h) W. Oppolzer, A. Fürstner, Helv. Chim. Acta 1993, 76, 2329.

- [2] a) K. S. Knight, R. M. Waymouth, Organometallics 1994, 13, 2575; b) T. Takahashi, D. Y. Kondakov, N. Suzuki, *ibid*. 1994, 13, 3411; c) A. J. Bird, R. J. K. Taylor, X. Wei, Synlett 1995, 1237.
- [3] No carbon-carbon bond-forming reaction with the resulting organozirconium complexes has been reported.
- [4] a) M. T. Reetz, Organotitanium Reagents in Organic Synthesis, Springer, Heidelberg, 1986; b) D. Seebach, B. Weidmann, L. Widler, Modern Synthetic Methods. Transition Metals in Organic Synthesis (Ed.: R. Scheffold), Otto Salle, Frankfurt am Main, 1983.
- [5] a) K. Harada, H. Urabe, F. Sato, Tetrahedron Lett. 1995, 36, 3203; b) A. Kasatkin, T. Nakagawa, S. Okamoto, F. Sato, J. Am. Chem. Soc. 1995, 117, 3881; c) H. Urabe, T. Hata, F. Sato, Tetrahedron Lett. 1995, 36, 4261; d) S. Okamoto, A. Kasatkin, P. K. Zubaidha, F. Sato, J. Am. Chem. Soc. 1996, 118, 2208; e) T. Yamazaki, A. Kasatkin, Y. Kawanaka, F. Sato, J. Org. Chem. 1996, 61, 2266; f) A. Kasatkin, T. Yamazaki, F. Sato, Angew. Chem. 1996, 108, 2091; Angew. Chem. Int. Ed. Engl. 1996, 35, 1966; g) K. Suzuki, H. Urabe, F. Sato, J. Am. Chem. Soc. 1996, 118, 8729; h) Y. Gao, K. Harada, F. Sato, J. Chem. Soc. Chem. Commun. 1996, 533, and references therein.
- [6] The production of 4 was verified by the treatment of the reaction mixture with D₂O, which gave (*E*)-5-deuterio-4-*n*-propyl-1,4-octadiene (>97% D) in 70% yield.
- [7] Intermolecular reactions of alkynylzirconium and -tantalum complexes with allyl-X have been reported. Zr: a) T. Takahashi, N. Suzuki, M. Kageyama, D. Y. Kondakov, R. Hara, *Tetrahedron Lett.* 1993, 34, 4811; b) T. Takahashi, D. Y. Kondakov, N. Suzuki, *Chem. Lett.* 1994, 259; c) N. Suzuki, D. Y. Kondakov, M. Kageyama, M. Kotora, R. Hara, T. Takahashi, *Tetrahedron* 1995, 51, 4519. Ta: d) K. Takai, M. Yamada, H. Odaka, K. Utimoto, T. Fujii, I. Furukawa, *Chem. Lett.* 1995, 315.
- [8] W. A. Nugent, D. F. Taber, J. Am. Chem. Soc. 1989, 111, 6435.
- [9] Interestingly, only the shown diastereomer 26 was obtained.

Reduction of Dicarbapentaboranes(5) to 1,2-Diborata-4-boracyclopentadienes: Antiaromatic Compounds with 4π-Electron Systems**

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Dedicated to Professor Gerhard E. Herberich on the occasion of his 60th birthday

The tetragonal pyramidal constitutions 2-4 have been assigned to the reduction products of *closo*-dicarbapentaboranes(5) 1.^[1, 2] Such structural changes are expected to accompany the transition from *closo* to *nido* compounds with 2n+2 and 2n+4 skeletal electrons, respectively.^[3]



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- [**] This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

For recent reviews: a) W. Oppolzer, Comprehensive Organic Synthesis, vol. 5 (Eds.: B. M. Trost, I. Fleming), Pergamon, Oxford, 1991, p 29; b) P. Knochel, Comprehensive Organic Synthesis, vol. 4 (Eds.: B. M. Trost, I. Fleming), Pergamon, Oxford, 1991, p 865; c) W. Oppolzer, Angew. Chem. 1989, 101, 39; Angew. Chem. Int. Ed. Engl. 1989, 28, 38; d) J. F. Normant, A. Alexakis, Synthesis 1981, 841. For most renet papers: e) C. Meyer, I. Marek, G. Courtemanche, J. F. Normant, J. Org. Chem. 1995, 60, 863; f) W. Oppolzer, F. Schröder, Tetrahedron

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We now show that reduction of 1a,b leads to five-membered rings, the 1,2-diborata-4-boracyclopentadienes 5a,b. Ab initio computations reveal that the unsubstituted parent five-membered ring 5u is also lower in energy than all tetragonal-pyramid isomers. Nonetheless, 5u is a 4π -electron antiaromatic compound.



The dicarbapentaborane(5) 1a is formed by thermolysis of the aminomethylenborane 6 (Dur = duryl, i.e, 2,3,5,6-tetramethylphenyl), while 1b is obtained by treating 1a with methanol in the presence of hydrochloric acid. Borane 6 is available from the borataalkyne $7^{[4]}$ and bis(trimethylsilyl)aminodifluoroborane. Reduction of 1a,b with potassium in diethyl ether gives 1,2-diborata-4-boracyclopenta-dienes 5a,b. Oxidation of the latter with hexachloroethane, iodine, or air leads to re-formation of 1a,b.^[5]

The constitutions of **1a,b** and **5a** were confirmed by X-ray analyses. The similarity of the NMR data (Table 1) of **5a** and **5b** verifies the constitution of the latter. Figure 1 shows the structure of **5a** in the crystal obtained from toluene.^[6]

The five-membered ring of **5a** bears duryl substituents on the adjacent boron atoms, and trimethylsilyl groups on the carbon atoms. One potassium ion is coordinated to a toluene molecule and the five-membered ring, and the other to a toluene molecule and the two duryl substituents. The Si3-N1-Si4 plane of the bis(trimethylsilyl)amino substituent at B3 is twisted by 85° relative to the C1-B3-C2 plane. The B1-C1 [150.7(5) pm] and B2-C2 [149.0(5) pm] bonds are considerably shorter than B3-C1 and B3-C2 [155.6(5) and 157.7(4) pm]. The five-membered ring is folded by 25° along the C-C axis.

We performed MP2/6-31 + G* computations on the parent compounds to clarify the geometric and energetic relationships without the influence of substituents. The planar five-membered ring **5u** with C_{2v} symmetry is an energy minimum that lies 2.2, 14.2, 27.1, and 9.7 kcalmol⁻¹ below the tetragonal pyramids **2u**-4u and the dianion **8** with a *closo* structure, respectively.^[7]

In the presence of a η^5 -coordinating Li⁺ counterion, the C₂B₃ ring is folded considerably: by 44.1° in **5u**-Li and by 40.1° in **5u**-Li₂. In solution **5a** is likely to be a free, solvated dianion with a planar five-membered ring. This is indicated by the ¹¹B NMR chemical shifts of $\delta = 48$ and 63 calculated for **5u** with GIAO-MP2/tzpdz,^[8] which match the measured value of 62 ppm much better than those calculated for **5u**-Li and **5u**-Li₂ (see Figure 2).

With four cyclically conjugated π -electrons, **5u** is antiaromatic. The bond lengths alternate considerably^[10, 11] (computed for **5u**: B2-C3: 150.4 pm, C3-B4: 155.6 pm);^[12] energetic and magnetic criteria are also characteristic of antiaromaticity.^[13] An antiaromatic destabilization^[10] of 30.3 kcalmol⁻¹ is estiTable 1. Some physical properties of 1 a,b, 5 a,b, and 6.

1a: colorless solid, m.p. > 380 °C, yield 69%. ¹H NMR (500 MHz, CDCl₃, -40 °C): $\delta = -0.02$ (s, 18H, SiMe₃), 0.17 (s, 18H, SiMe₃), 1.91, 2.12, 2.19, 2.28 (each s, each 6H, *o*- and *m*-CH₃), 6.96 (s, 2H, *p*-H); ¹³C NMR (125 MHz, CDCl₃, -40 °C): $\delta = -0.6$ (q, 6C, SiMe₃), 4.3 [q, 6C, N(SiMe₃)], 20.3, 21.0, 22.9 (each q, total of 8C, *o*- and *m*-CH₃), 117.5 (s, 2C, CB₃), 131.2 (d, 2C, *p*-C), 133.2, 133.5, 135.7, 135.9 (each s, each 2C, *o*- and *m*-C), 133.8 (s, 2C, *i*-C). ¹¹B NMR (96 MHz, toluene, 90 °C): $\delta = 22$, 29 (ratio 1:2).

1b: colorless solid, m.p. 144 °C (no decomp.), yield 100%. ¹H NMR (500 MHz, CDCl₃, -40 °C): $\delta = -0.02$ (s, 18 H, SiMe₃), 2.06, 2.21, 2.25, 2.28 (each s, each 6H, o and m-CH₃), 3.86 (s, 3 H, OCH₃), 6.99 (s, 2 H, p-H); ¹³C NMR (125 MHz, CDCl₃, -40 °C): $\delta = -0.3$ (q, 6C, SiMe₃), 19.4, 20.0, 20.3, 21.7 (each q, total of 8C, o- and m-CH₃), 108.4 (s, 2 C, CB₃), 130.9 (d, 2 C, p-C), 132.8, 133.0, 134.7, 134.9 (each s, each 2 C, o- and m-C); ¹¹B NMR (96 MHz, CDCl₃, -90 °C): $\delta = 19$, 32 (ratio 1:2).

5a: red solid, m.p. 160-170 °C at 0.0025 Torr (decomp), yield: 98%. ¹H NMR (500 MHz, $[D_8]$ THF, 0 °C): $\delta = -0.37$, 0.29 (each s, each 18 H, SiMe₃), 1.11 (t, total of 12 H, Et₁₂O), 2.02, 2.18 (each s, each 12 H, o- and m-CH₃), 3.37 (q, total of 8 H, Et₂O), 6.41 (s, 2 H, p-H); ¹³C NMR (125 MHz, $[D_8]$ THF, 0 °C): $\delta = 5.9$, 6.1 (each q, each 6 C, SiMe₃), 15.7 (q, total of 4 C, Et₂O), 20.2, 21.4 (each q, each 4 C, o- and m-CH₃), 66.2 (t, total of 4 C, Et₂O), 111.3 (s, 2 C, CB₂), 125.0 (d, 2 C, p-H), 131.9, 132.1 (each s, each 4 C, o- and m-C), 169.0 (s, 2 C, i-C); ¹¹B NMR (96 MHz, toluene, 25°C): $\delta = 62$.

5b: red solid, m.p. >251 °C (decomp), yield: 99%. ¹H NMR (500 MHz, $[D_8]$ THF, -20 °C): $\delta = -0.28$ (each s, each 18 H, SiMe₃), 2.04, 2.22 (s, 12 H, 3 oand m-CH₃), 3.88(s, 3H, OMe), 6.36 (s, 2H, p-H); ¹³C NMR (125 MHz, $[D_8]$ THF, -20 °C): $\delta = 5.3$ (q, 6C, SiMe₃), 20.6, 21.2 (each q, each 4C, o- and m-CH₃), 98.9 (br s, 2C, CB₂), 124.9 (d, 2C, p-C), 131.7 (s, o- and m-C), 168.5 (br s, 2C, CC); ¹¹B NMR (96 MHz, Et₂O, 25 °C): $\delta = 59$.

6: pale yellow solid, m.p. 68 °C, yield: 98%. ¹H NMR (300 MHz, CDCl₃, -40 °C): $\delta = 0.18$, 0.21 (each s, each 18 H, SiMe₃), 2.28, 2.44 (each s, each 12 H, *o*- and *m*-CH₃), 6.95 (s, 2H, *p*-H); ¹³C NMR (125 MHz, CDCl₃, -40 °C): $\delta = 1.8$ [6 C, N(SiMe₃)], 4.6 (6C, SiMe₃), 20.1, 21.5 (each 4C, *o*- and *m*-CH₃), 51.0 (br 2C, BCB), 98.6 (br, 1C, sp² CB), 129.9 (2C, *p*-C), 132.5, 134.0 (each s, each 4C, *o*- and *m*-CH₃), 146.5 (br, 2C, *i*-C); ¹¹B NMR (96 MHz, toluene, 90 °C): $\delta = 61$, 51 (ratio 2:1).



Figure 1. Crystal structure of **5a**. Selected interatomic distances [pm] and angles [°]: B1-B2 178.0(5), B1-C1 150.7(5), B2-C2 149.0(5), C1-B3 155.6(4), C2-B3 157.7(4), B1-C10 160.3(5), B2-C20 159.0(5), B3-N1 153.7(4), C1-Si1 181.7(3), C2-Si2 182.4(3), B1-K1 323.4(4), B2-K1 321.2(4), C1-K1 293.3(3), C2-K1 289.3(3), B3-K1 297.2(3); C1-B1-B2 107.6(3), B1-B2-C2 106.0(3), B2-C2-B3 103.4(2), B1-C1-B3 102.1(2), C1-B3-C2 15.3(3), Si3-N1-Si4 120.7(2). Interplanar angles C1-B1-B2-C2 to C1-B3-C2 25(1), C1-B3-C2 to Si3-N1-Si4 85(1).

mated for 5u by Equation (a), which balances strain effects as far as possible. In addition, 5u shows a paramagnetically in-





Figure 2. Computed relative energies (E_{rel}) and nucleus independent chemical shifts (NICS, at the positions marked by dots) as well as ¹¹B chemical shifts (δ) for various $C_2B_3H_5^{2-}$ minima.

creased susceptibility: the value Λ is -9.4 ppm cgs [calculated with IGLO/II for Equation (a)].^[14]

Such paramagnetic ring currents, which are characteristic of antiaromatic compounds, cause upfield shifts outside rings and downfield shifts inside rings. We have suggested recently nucleus-independent chemical shifts (NICS) as a criterion for (anti)aromaticity. NICS is based on magnetic shieldings, which have long been calculated by simple methods,^[15] and now can be computed with modern ab initio technique.^[16] To conform with the usual experimental convention, NICS is the negative value of the shielding evaluated, for example, at the center of a ring. Aromaticity is characterized by negative NICS values, antiaromaticity by positive NICS, and nonaromatic compounds by values close to zero. With a NICS value of 16.5 ppm (GIAO- $SCF/6-31 + G^*//MP2(fc)/6-31 + G^*)$, 5u is clearly antiaromatic. Loss of planarity and consequently of cyclic conjugation in 5u-Li and 5u-Li, eliminates the antiaromaticity. This is shown by the NICS values of 2.1 and -2.0 ppm for **5u**-Li and **5u**-Li₂, respectively.

In accordance with empirical rules,^[3b] the carbon atoms prefer nonadjacent low-coordinate sites in the *nido* structure (tetragonal pyramid). However, more negative NICS values (computed in the center of the open face; see Figure 2) are found in order of decreasing stability (2u > 3u > 4u). Hence, the larger electron delocalization is associated with the less stable isomers. As has already been demonstrated for bis(heterobicycle)s, the stability of isomers does not necessarily parallel the degree of aromaticity when other factors are important.^[17]

The two-electron reduction of dicarbapentaboranes(5) does not lead to tetragonal pyramids, but to five-membered rings. The unsubstituted five-membered ring has been characterized as antiaromatic on the basis of geometric, energetic, and magnetic criteria.

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- [1] R. W. Rudolph, W. R. Pretzer, Inorg. Chem. 1972, 11, 1974-1978; R. W. Rudolph, Acc. Chem. Res. 1976, 9, 446-452.
- [2] a) R. Köster, G. Seidel, B. Wrackmeyer, Angew. Chem. 1984, 96, 520-521, Angew. Chem. Int. Ed. Engl. 1984, 23, 512; b) R. Köster, G. Seidel, B. Wrackmeyer, ibid. 1985, 97, 317-318 and 1985, 24, 317-318; c) R. Köster, G. Seidel, B. Wrackmeyer, D. Bläser, R. Boese, M. Bühl, P. von R. Schleyer, Chem. Ber. 1991, 124, 2715-2724.
- [3] a) R. E. Williams, Inorg. Chem. 1971, 10, 210-214; b) Chem. Rev. 1992, 92, 177 - 207.
- [4] J. Allwohn, M. Pilz, R. Hunold, W. Massa, A. Berndt, Angew. Chem. 1990, 102, 1084–1086, Angew. Chem. Int. Ed. Engl. 1990, 29, 1032.
- [5] 2.3,4-Triethyl-1,5-dimethyldicarbapentaborane(5) can also be reduced with two equivalents of cesium and reoxidized by iodine [2b]. Unfortunately, no ¹¹B chemical shifts were reported for the reduction product. Oxidation of the other reduction products gave C_4B_6 clusters (i.e., dimers). The ¹¹B NMR data of the reduction product of pentaethyldicarbapentaborane, $\delta = -14.2$ and -37.1, differ strongly from the values computed for $2\mathbf{u}-4\mathbf{u}$ and $\mathbf{8}$. Therefore, a pyramidal structure can definitively be ruled out. The reduction product may be a dimer of a radical anion of pentaethyldicarbapentaborane.

2Θ

- X-ray structure analysis with a four-circle diffractometer (CAD4, Enraf-Nonius) with Cu_{Ka} radiation ($\lambda = 154.178$ pm) at -60° C: colorless crystals of **5a** ($C_{48}H_{77}B_3K_2NSi_4$), crystal dimensions $0.5 \times 0.3 \times 0.2$ mm, orthorhombic, space group $P2_12_{11}$, Z = 4, a = 1295.0(1), b = 1767.9(1), c = 2372.2(1) pm, $V_{\text{EZ}} = 5430.8(6) \times 10^{-30}$ m³, $\rho_{\text{caled}} = 1.09$ gcm⁻³; total of 20119 reflections collected in ω scan mode for $2\theta = 136^{\circ}$; LP correction and semiempirical absorption correction (Ψ scans, $\mu = 26.0 \text{ cm}^{-1}$, $T_{\min \max} = 0.52, 0.66$); all 9908 independent reflections used in subsequent calculations. The structure was solved by direct methods and refined with full matrix against the F^2 data. All hydrogen atoms could be localized. They were considered in the calculation riding on their bonding partners in groups with common isotropic temperature factors. The methyl group of one toluene molecule was disordered over two alternative orientations. Anisotropic temperature factors were used for all heavy atoms, $wR_2 = 0.1275$ and R = 0.0492 for 7785 reflections with $F_0 > 4\sigma(F_0)$. The maximum residual electron density was 0.33 eÅ⁻³. A Flack Parameter x = 0.00(1) proves that the correct enantiomer has been refined. The crystallographic data (without structure factors) were deposited as "supplementary publication no. CCDC-179-165 at the Cambridge Crystallographic Data Center. Copies of the data can be requested free of charge from: The Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: Int. code + (1223) 336-033; e-mail; deposit(\hat{a} : chemerys.cam.ac.uk)
- [7] Relative energies correspond to MP2(fc)/6-31+G*+0.93 ZPE data. Geometry optimizations and frequency calculations were performed with Gaussian 94: M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, J. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. Y. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challcombe, 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. Blinkley, D. J. DeFrees, J. Baker, J. J. P. Stewart, M. Head-Gordon, C. Gonzalez, J. A. Pople, Gaussian Inc., Pittsburgh, PA, 1995.
- [8] GIAO-MP2: 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: J. F. Stanton, J. Gauss, J. D. Watts, W. J. Lauderdale, R. J. Bartlett, Quantum Theory Project, University of Florida, Fl, 1991, 1992). The abbreviation tzpdz designates triple-zeta plus polarization basis sets for heavy elements and double-zeta for hydrogen: A. Schäfer, H. Horn, R. Ahlrichs, J. Chem. Phys. 1992, 97, 2571-2577.
- [9] The antiaromatic cyclopentadienyl cation also is lower in energy (by 12.3 kcalmol⁻¹) than the isomeric C₅H₅⁺ square pyramid: M. N. Glukhovtsev, B. Reindl, P. von R. Schleyer, *Mendeleev Commun.* 1993, 100-101.
- [10] P. von R. Schleyer, P. K. Freeman, H. Jiao, B. Goldfuss, Angew. Chem. 1995, 107, 332-335, Angew. Chem. Int. Ed. Engl. 1995, 34, 337.
- [11] A gallacyclopentadiene with a long single bond between short C=C double bonds is described in: A. H. Cowley, F. P. Gabbai, A. Decken, Angew. Chem. 1994, 106, 1429-1431, Angew. Chem. Int. Ed. Engl. 1994, 33, 1370.
- [12] An NH₂ substituent on the boron atom between the C atoms of 5u has no significant influence on the C-B distances in the ring, even if it conjugates with the B atom (B-N 149.7 pm, B-N-H 115.2°; C-B 150.2, 155.9) or is twisted by 90° (B-N 157.4 pm, B-N-H 104.5°; C-B 150.4, 154.5 pm).
- [13] P. von R. Schleyer, H. Jiao, Pure Appl. Chem. 1996, 68, 209-218.
- [14] a) W. Kutzelnige, Isr. J. Chem. 1980, 19, 193-200; b) M. Schindler, W. Kutzelnigg, J. Chem. Phys. 1982, 76, 1919-1933. c) W. Kutzelnigg, U. Fleischer, M. Schindler, NMR Basic Princ. Prog. 1990, 23, 165-262.
- [15] A. Pasquarello, M. Schlüter, R. C. Haddon, Science 1992, 257, 1660-1661.
- [16] P. von R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao, N. J. R. van E. Hommes, J. Am. Chem. Soc. 1996, 118, 6317-6318.
- [17] G. Subramanian, P. von R. Schleyer, H. Jiao, Angew. Chem. 1996, 108, 2824– 2827, Angew. Chem. Int. Ed. Engl. 1996, 35, 2638–2641.