16.9 kcalmol<sup>-1,[4]</sup> For the dianion of  $B_4Me_4^{[10]}$  the distorted tetrahedral form according to our computations lies only 4.9 kcalmol<sup>-1</sup> above the folded two-electron aromtic compound; its planarization requires 7.3 kcalmol<sup>-1</sup>. Thus, an increasing number of boron atoms in four-membered two-electron aromatic compounds facilitates the planarization as well as the fluctuation of the skeletal bonds.

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- [6] The synthesis of **5** will be described elsewhere.
- [7] Crystal structure analyses: 3a·Li(Et<sub>2</sub>O)<sub>3</sub>: A colorless crystal  $(0.45 \times 0.35 \times 0.25 \text{ mm}^3)$  was measured at 193 K on an IPDS area detector system (Stoe) with  $Mo_{K\alpha}$  radiation.  $C_{40}H_{76}B_3LiO_3Si_2$ , monoclinic, space group  $P2_1/c$ , Z=4, a=1183.4(1), b=2277.6(2), c = 1756.7(1) pm,  $\beta = 98.32(1)^\circ$ ,  $V = 4685.0(6) \times 10^{-30} \text{ m}^3$ ,  $\rho_{\text{calcd}} = 0.993 \text{ Mgm}^{-3}$ , 50384 reflections up to  $\theta = 25.84^\circ$ , 8557 independent ( $R_{\text{int}} = 0.1160$ ), 3910 with  $I > 2\sigma(I)$ . The structure was solved with direct methods and refined against  $F^2$  with full matrix. Hydrogen atoms were considered as riding at calculated positions,  $wR_2 = 0.1527$  for all reflections, R = 0.0691for observed reflections. Limited accuracy due to the disorder of the diethyl ether in the Li(Et<sub>2</sub>O)<sub>3</sub> cation. 4: Pale yellow crystal  $(0.30 \times 0.15 \times 0.05 \text{ mm}^3)$  C<sub>28</sub>H<sub>46</sub>B<sub>3</sub>ClSi<sub>2</sub>, monoclinic, space group C2/c, Z=8, a=3031.1(2), b=988.1(1), c=2217.6(1) pm,  $\beta=$ 111.06(1)°,  $V = 6198.1(8) \times 10^{-30} \text{ m}^3$ ,  $\rho_{\text{ber}} = 1.086 \text{ Mgm}^{-3}$  measurement as for  $3a \cdot \text{Li}(\text{Et}_2\text{O})_3$ , 12475 reflections up to  $\theta = 24.0^\circ$ , 4627 independent ( $R_{int} = 0.1414$ ), 1857 with  $I > 2\sigma(I)$  (only very thin platelets available). The structure was solved analogously to that of **3a**, resulting in  $wR_2 = 0.1144$  for all reflections, and R =0.0539 for the observed reflections. CCDC-187178 (3a·Li- $(Et_2O)_3$ ) and CCDC-187179 (4) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.can.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Centre, 12 Union Road,

Cambridge CB21EZ, UK; Fax: (+44)1223-336033; or deposit @ccdc.cam.ac.uk).

- [8] The line shape analysis was carried out with WIN-DYNA 32, Bruker Analytik GmbH, Version 1.01; the changes in the chemical shifts in the investigated temperature interval were considered to be linear and the line widths of the trimethylsilyl groups were used as the reference line widths. The rate constants of the ring inversion  $k_{\text{RInv}}$  were computed from the difference in rate constants of the enantiomerization without ring inversion  $k_{\text{tet}}$  (coalescence of the methyl groups and protons at the aromatic group) and the enantiomerization with ring inversion  $k_{\text{total}}$  (coalescence of the methylene protons) according to  $k_{\text{RInv}} = k_{\text{total}} - k_{\text{tet}}$ .
- [9] Tetrahedra of CB<sub>3</sub> anions are, like those of the isoelectronic B<sub>4</sub> dianions, distorted.<sup>[10]</sup> There are three forms for distorted tetrahedra of the type 6a: two enantiomers with short C–BDur edges (the transition state between 3b and 3a), and one with a short C–BCH<sub>2</sub>R edge (the transition state of the degenerate rearrangement of 3a).
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#### **Boron-Containing Rings**

### A Diboracyclopropane with a Planar-Tetracoordinate Carbon Atom and a Triborabicyclobutane\*\*

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Dedicated to Professor Paul von Ragué Schleyer

Known molecules with a planar-tetracoordinate carbon atom<sup>[1]</sup> contain metal centers.<sup>[2]</sup> According to computations<sup>[3]</sup> the prototype of such molecules *without* metal centers is the diboracyclopropane **1u** (Scheme 1). Derivatives of the lower energy isomer **2u** with planar-tetracoordinate *boron* atoms<sup>[4]</sup>

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## Communications



**Scheme 1.** Structures and energy differences computed at the B3LYP/ 6-31G\* level for classical diboracyclopropane **1 u**\*, its lower energy form with a planar-tetracoordinate carbon atom **1 u**, and for **2 u** with two planar-tetracoordinate boron atoms.<sup>[Bb,c]</sup> A solid line denotes a 2c2e bond, a dashed triangle a 3c2e  $\sigma$  bond, a circle a 3c2e  $\pi$  bond: **1 u** and **2 u** are two-electron aromatic compounds.



**Scheme 2.** Synthesis of the C-boryldiboracyclopropane 1a by methylation of 3a, its isomerization to 2a, and the synthesis of 4a.  $R = SiMe_3$ , Dur = 2,3,5,6-tetramethylphenyl,  $MeX = MeOSO_2CF_3$ .

are known experimentally, the classical form  $1u^*$  with a tetrahedral carbon atom does not represent an energy minimum. We report herein on the synthesis, NMR spectroscopic characterization, and facile isomerization of the derivative 1a to 2a at low temperature (Scheme 2). To compare the chemical shift of the planar-tetracoordinate carbon atom of 1a with that of a similarly substituted carbon atom without a planar environment, we describe in addition 4a, the first derivative of triborabicyclobutane. Density functional computations<sup>[5]</sup> for the models 1b and 2b (Scheme 3) as well as for the transition state TS1b/2b of the isomerization  $1b \rightarrow 2b$  support our argumentation.

The reaction of the triboracyclobutanide  $3a^{[6]}$  in  $[D_8]$ THF with methyl trifluoromethanesulfonate in an NMR tube at -90 °C affords a mixture of the *C*-boryldiboracyclopropane **1a** and of **2a** (ca. 3:1).<sup>[7]</sup> At this temperature **1a** does not rearrange appreciably into **2a**. In contrast, at -70 or -65 °C this isomerization occurs with half lives of 61 and 7 min, respectively. Compound **3a** reacts with dichloro(trimethylsilylmethyl)borane to give a product mixture, from which **4a** can be separated by crystallization (Scheme 2). Its constitution and that of **2a**<sup>[8]</sup> are confirmed by X-ray structure analyses<sup>[9]</sup> (Figure 1). Compound **4a** contains a folded CB<sub>3</sub> four-membered ring with relatively short C–B distances and a short C–B diagonal to the pentacoordinate boron atom bearing the trimethylsilylmethyl and the chloroboryl groups.

The constitution of **1a** is derived from its NMR-spectroscopic data (Table 1), in particular from the comparison of the chemical shift of its skeletal carbon atom with that computed for **1b** (Scheme 3). Figure 2 shows the relevant section of the

<sup>13</sup>C NMR spectrum of the above-mentioned mixture. Ten sharp signals are observed (eight singlets and two doublets) in the region between  $\delta = 140$  and 132 ppm, which show that the Duryl groups are not equivalent and are bound to a ring with different sides. Three additional, broad singlets at  $\delta = 143.7$ , 133.2, and 126.4 ppm need to be assigned to boron-bound carbon atoms, one of which is the skeletal carbon atom of the diboracyclopropane ring, the other two the ipso-carbon atoms of the Duryl groups.<sup>[10]</sup> Independent of the assignment of these signals, the skeletal carbon atom of 1a is deshielded by at least 53 ppm as compared to the quite similarly substituted, distorted-tetrahedral carbon atom in **4a** ( $\delta$ (<sup>13</sup>C) = 73.3 ppm). GIAO-NMR computations gave a chemical shift of  $\delta =$ 143.6 ppm for the exactly planar-tetracoordinate carbon atom of the model molecule 1b. This agrees very well with the experimental value of  $\delta = 143.7$  ppm for **1a**, which shows that the skeletal carbon atom of the diboracyclopropane ring of 1a



Scheme 3. Computed<sup>[5]</sup> energy diferences between 1 b, 2 b, and the transition state TS1b/2b.



*Figure 1.* Structure of **4a** in the crystal. Selected bond lengths [pm] and angles [°]: C1-B1 150.2(3), B1-B2 173.9(3), B2-B3 173.3(3), B3-C1 149.4(3), C1-B2 174.5(3), B2-B4 169.4(3); B1-C1-B3 105.7(2), C1-B1-B2 64.7(1), C1-B3-B2 65.0(1), B1-B2-B3 87.0(1), C2-B2-B4 134.2(2), C1-B2-B4 102.2(1), B1-C1-B2-B3 -124.7(2).

Table 1: Selected physical and spectroscopic properties of 1 a, 2 a, and 4 a.

**1** a: yield estimated by NMR spectroscopy 75 %; <sup>1</sup>H NMR (500 MHz, [D<sub>8</sub>]THF, -90 °C):  $\delta$  = 6.88, 6.87 (each s, each 1 H, *p*-H), 3.40 (s, 4 H, DME), 3.24 (s, 6 H, DME), 2.28, 2.18, 2.15, 2.12, 1.97, 1.84, 1.24, 1.00 (each s, each 3 H, *o*- and *m*-Me), 1.21, 0.73 (each d, each 1 H, B-CH<sub>2</sub>Si), 1.10 (s, 3 H, B-Me), 0.23, 0.03 ppm (each s, each 9 H, SiMe<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, [D<sub>8</sub>]THF, -90 °C):  $\delta$  = 143.7 (br. s, 1 C, CB<sub>3</sub>), 139.7, 139.6, 138.2, 137.6, 134.5, 134.4, 134.2, 134.0, 133.3, 132.5 (each s, each 1 C, *o*and *m*-C), 133.4, 132.5 (each d, each 1 C, *p*-C), 133.2, 126.4 (each br. s, each 1 C, *i*-C), 72.4, 58.8 (each 2 C, DME), 22.0, 21.8, 21.3, 12.1, 20.9, 20.1, 19.6, 19.4 (each q, each 1 C, *o*- and *m*-Me), 16.6 (br. q, 1 C, MeB), 9.1 (br. t, 1 C, BCH<sub>2</sub>Si), 1.1, 1.0 ppm (each q, each 3 C, SiMe<sub>3</sub>)

**2a**: colorless crystals; m.p. 109 °C (decomp); yield 78%; <sup>1</sup>H NMR (500 MHz,  $[D_8]$ THF, -90 °C):  $\delta$  = 6.90 (s, 2 H, *p*-H), 2.24, 2.23, 2.16 (each s, in total 24 H, *o*- and *m*-CH<sub>3</sub>), 0.88 (br.s, 2 H, BCH<sub>2</sub>), 0.76 (br.s, 3 H, BCH<sub>3</sub>), -0.04, -0.5 ppm (each s, each 9 H, Me<sub>3</sub>Si); <sup>13</sup>C NMR (125 MHz,  $[D_8]$ THF, -90 °C):  $\delta$  = 137.2, 137.1, 134.8, 134.7 (each s, each 2 C, *o*- and *m*-C), 134.2 (br.s, 2 C, *i*-C), 133.0 (br.s, 1 C, CB<sub>2</sub>), 132.3 (d, 2 C, *p*-C), 22.6, 20.1, 20.0 (in total 8 C, *o*- and *m*-CH<sub>3</sub>), 19.8 (br.t, 1 C, BCH<sub>2</sub>), 13.4 (br.q, 1 C, BCH<sub>3</sub>), 0.9, 0.4 ppm (each q, each 3 C, Me<sub>3</sub>Si); <sup>11</sup>B NMR (96 MHz,  $[D_{10}]$ Et<sub>2</sub>O, 27 °C):  $\delta$  = 80 (1 B), 40 ppm (2 B)

**4a**: colorless crystals; m.p. 118 °C; yield ca. 50%; <sup>1</sup>H NMR (500 MHz,  $CD_2Cl_2$ , -40 °C):  $\delta = 7.10$  (s, 2 H, *p*-H), 2.52, 2.46, 2.20(each s, in total 24 H, *o*- and *m*-Me), 0.23, 0.03, (each s, each 2 H, H<sub>2</sub>CSi, localized by C/H correlation), 0.08, -0.04, -0.57 ppm (each s, each 9 H, Me<sub>3</sub>Si); <sup>13</sup>C NMR (125 MHz,  $CD_2Cl_2$ , -40 °C):  $\delta = 142.2$ , 140.5, 133.7, 133.6 (each s, each 2 C, *o*- and *m*-C), 135.0 (d, 2 C, *p*-C), 132.1 (br. s, 2 C, *i*-C), 73.3 (br. s, 1 C, CB<sub>3</sub>), 21.4, 21.1, 20.3, 20.2 (each q, in total 8 C, *o*- and *m*-Me), 18.1, 12.8 (each br.t, each 1 C, CH<sub>2</sub>Si), 2.1, 1.1, 0.2 ppm (each q, each 3 C, Me<sub>3</sub>Si); <sup>11</sup>B NMR (96 MHz, CDCl<sub>3</sub>, -20 °C):  $\delta = 58$  (br. s, 3 B), 5.8 ppm (1B). Above -20 °C **4a** is converted partly to an isomer with  $\delta$ (<sup>11</sup>B) = -1.0 ppm, crystallization of the mixture leads to the re-formation of **4a** 



**Figure 2.** Section (145 to 125.5 ppm) of the <sup>13</sup>C NMR spectrum of a 3:1 mixture of **1a** and **2a**. The insert shows an expansion of the region between  $\delta = 133.2$  and 136.6 ppm. The signals of **2a** are marked by an asterisk (\*); their intensities increase as the temperature is raised, those of the other signals decrease: after 30 min at -65 °C only the signals of **2a** are observed.

is planar-tetracoordinate. DFT computations<sup>[5]</sup> for the models **1b**, **2b**, and the transition state **TS1b/2b** of the isomerization **1b** $\rightarrow$ **2b** reveal that **2b** is 11.6 kcal mol<sup>-1</sup> lower in energy than **1b**<sup>[11]</sup> and that the barrier of the isomerization (20.6 kcal mol<sup>-1</sup>) is low.<sup>[12]</sup> The facile isomerization to **2a** thus provides additional support for the structure of **1a**.

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- [5] All geometries were optimized by employing the B3LYP hybrid functional together with the 6-31G(d) basis set. The transition state TS1b/2b was characterized by its intrinsic reaction coordinate. Relative energies are corrected for zero-point energies and are based on energy computations with 6-311+ G(d,p), likewise the computed chemical shifts (GIAO-NMR). a) Gaussian 98 (Revision A.7), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, 1998; b) A. D. Becke, J. Chem. Phys. 1993, 98, 1372; A. D. Becke, J. Chem. Phys. 1993, 98, 5648; c) C. Lee, W. Yang, R. G. Parr, Phys. Rev. B 1988, 37, 785.
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- [7] The methylating reagent was added to a solution of **3a** in  $[D_8]$ THF at -120 °C, which had been frozen in an NMR tube with the aid of liquid nitrogen. Thereafter the components were warmed to -90 °C in the NMR spectrometer.
- [8] The structure of 2a in the crystal resembles that of the starting material of 3a,<sup>[6]</sup> which bears a chlorine atom instead of the methyl group at the boron atom of the boryl bridge of 2a. Selected distances in 2a [pm]: C1–B1 145.5(7), C1–B2 143.9(8), B1–B2 167.7 (10), B1–B3 192.4(9), B2–B3 192.8(8).
- [9] Crystal structure analysis of **4a**: A colorless crystal  $(0.60 \times 0.30 \times 0.05 \text{ mm}^3)$  was measured on at 193 K on an IPDS area detector system (Stoe) with Mo<sub>Ka</sub> radiation. C<sub>32</sub>H<sub>57</sub>B<sub>4</sub>ClSi<sub>3</sub>, monoclinic, space group P2/c, Z=4, a=1186.3(1), b=1185.9(1), c= 2697.2(1) pm,  $\beta$ =91.55(1)°, V=3793.1(5)×10<sup>-30</sup> m<sup>3</sup>,  $\rho_{calcd}$ = 1.059 Mg m<sup>-3</sup>, 29451 reflections up to  $\theta$ =25.94°, 6979 independent ( $R_{int}$ =0.0584), 4901 with  $I > 2\sigma(I)$ . The structure was solved with direct methods and refined against all  $F^2$  data with full matrix,  $wR_2$ =0.0997 for all reflections, R=0.0391 for the observed reflections. CCDC-185030 (**4a**) contains the supplementary crystallographic data for this paper. These data can be

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obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

- [10] The other broad signals of the boron-bound carbon atoms at  $\delta = 16.6$  and 9.1 ppm are not singlets, and thus clearly not assignable to the skeletal carbon atom.
- [11] For the classical **1b**\* with a distorted tetrahedral coordinate ring carbon atom computations at this level give two imaginary frequencies and an energy 8.9 kcal mol<sup>-1</sup> higher than for **1b**. The chemical shift of the ring carbon atom computed at the level used for **1b** was  $\delta = 103.6$  ppm.
- [12] The barrier of the isomerization of 1u to 2u was computed to be 22.0 kcal mol<sup>-1,[3c]</sup>

#### Long-Range Electronic Coupling

# Long-Range Electronic Coupling in Various Oxidation States of a $C_4$ -Linked Tris( $\beta$ -diketonato)ruthenium Dimer\*\*

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Despite an increasingly varied experimental data basis<sup>[1]</sup> and sophisticated theoretical approaches<sup>[2]</sup> there is still only a rudimentary understanding of which factors govern the extent

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of interaction between metal centers in formally symmetrical mixed-valent compounds. Such compounds can be considered as intermediates in "degenerate" inner-sphere metal-to-metal electron transfer. The interplay between metal configurations, the metal-ligand interface, and the properties of the ligand bridge has to be considered. Although the mere metal-metal distance has often been used as a guideline<sup>[3]</sup> in the absence of other, less accessible parameters, it is clear from several experiments<sup>[1]</sup> that the electronic properties of the ligands mediating the metal-metal interaction may be more relevant than the metal-metal separation. However, the correlation between metal configurations and the bridge type also requires consideration, especially when using alternatives to the often studied d<sup>5</sup>/d<sup>6</sup> combination,<sup>[1,3]</sup> familiar from prototypes, such as the Creutz-Taube ion<sup>[3a]</sup> [(H<sub>3</sub>N)<sub>5</sub>Ru- $(\mu-pz)Ru(NH_3)_5^{5+}$  (pz = pyrazine) or partially oxidized biferrocenyl species.[4]

Herein we describe the extraordinarily varied results for two different mixed-valent configurations that are accessible by single-electron transfer from the structurally characterized diruthenium(III) complex **1**.<sup>[5]</sup> The distinguishing feature of the ligand bridge is an unsaturated, cumulene-like, C<sub>4</sub> spacer which, in contrast to other C<sub>4</sub>-bridged dinuclear systems,<sup>[6]</sup> interacts with the metals through conventional Werner-type coordination, namely through  $\beta$ -diketonato chelate ligation.<sup>[5]</sup>

The complex **1** could be characterized crystallographically,<sup>[7]</sup> it has an almost linear C<sub>4</sub> chain with localized singlebond/triple-bond alternation (Figure 1). At 13.1359(6) Å the metal-metal separation is much longer than in directly C<sub>4</sub>connected diruthenium complexes (ca. 8.0 Å),<sup>[6]</sup> and the chelate rings are virtually perpendicular (90.9°).



The crystallographically determined orthogonality agrees with the EPR spectroscopic observation at 4 K of a half-field signal at g = 4.83 in addition to the main broad resonance at about 2.00, which indicate a triplet state. Stepwise oneelectron reduction of the metal centers in 1 occurs at closely spaced potentials,<sup>[5]</sup> yielding a relatively<sup>[1,3]</sup> small value of the comproportionation constant  $K_c = 10^{1.9[5]}$  of the Ru<sup>III,II</sup> intermediate 1-. No intervalence charge-transfer (IVCT) transition could be observed in the visible and near-infrared regions  $(\varepsilon < 100 \,\mathrm{M}^{-1} \mathrm{cm}^{-1})$ , and the IR vibrational spectroelectrochemical study at -40 °C<sup>[8]</sup> clearly revealed the reversible emergence of distinctly split alkyne stretching bands (Figure 2a and b). The latter indicates dissymmetry and thus localized valences on the vibrational time scale of about  $10^{-12}$  s, that is, Class II behavior according to the Robin and Day classification.<sup>[9]</sup> The EPR spectra taken at 4 K in CH<sub>2</sub>Cl<sub>2</sub>