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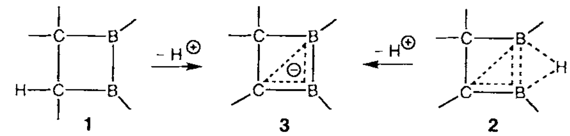
1,2-Diboretanides: Homoaromatic 2π-Electron Compounds with High Inversion Barriers[**]

Dirk Steiner, Heinz-Jürgen Winkler, Christian Balzereit, Thorsten Happel, Matthias Hofmann, Govindan Subramanian, Paul von Ragué Schleyer, Werner Massa, and Armin Berndt*

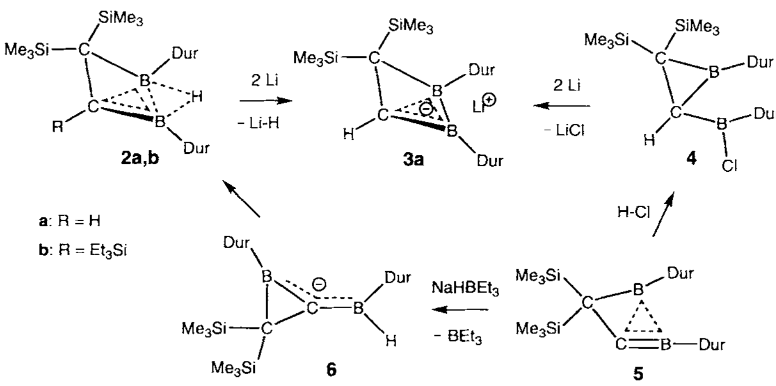
Dedicated to Professor Kurt Dehnicke
on the occasion of his 65th birthday

1,2-Diboretanes with amino substitutents on the boron atoms have the classical structures **1**.[1] When such π-donor groups are absent the nonclassical form **2**, which contains two three-center–two-electron (3c,2e) bonds, is more stable.[2] We describe herein the corresponding anions of **1** and **2**, 1,2-diboretanides **3**, which have one 3c,2e bond and serve as a link between classical and nonclassical 1,2-diboretanes (Scheme 1).



Scheme 1.

The lithium 1,2-diboretanide **3a** is formed by the reaction of the nonclassical 1,2-diboretane **2a**[2] or of the chloroborylborirane **4**[3] with lithium in diethyl ether (Scheme 2). Compound **2a** can be obtained almost quantitatively from the methyleneborane **5**[4] in two steps. Treatment of **5** with $NaHBEt_3$ in toluene gives the hydride adduct **6**, which is then allowed to react with cyclopentadiene to yield **2a**. The constitution of **3a** is deduced from the NMR data (Table 1) by means of the NMR/GIAO/ab initio method.[5] Note the agreement of the chemical shifts of the framework atoms with values computed at the GIAO-MP2/tzp level for unsubstituted **3u** and **3u'** (Table 2).[6] Figure 1 shows the structure of **3a** in the crystal.[7]



Scheme 2.

The geometry of the four-membered ring in the 1,2-diboretanide **3a** strongly resembles those of the nonclassical 1,2-diboretanes **2u** and **2b**;[2] the lithium ion coordinated by one di-

Table 1. Some physical properties of compounds **3a** and **6**.

3a: Solid, m.p. 157 C (decomp.), yield: 75%. ^1H NMR (300 MHz, C_6D_6, 25 C): $\delta = 0.09, 0.32$ (each s, each 9H, $SiMe_3$), 2.05, 2.14, 2.28, 2.43, 2.61 (each s, total of 24H, *o*- and *m*-CH_3), 4.69 (s, 1H, CHB), 6.72, 6.77 (each s, each 1H, *p*-H); ^{13}C NMR (125 MHz, C_6D_6, 25 C): $\delta = 1.6, 2.7$ (each q, each 3 C, each $(CH_3)_3Si$), 19.8, 20.5, 20.8, 21.0, 21.3, 21.5 (each q, total of 8 C, *o*- and *m*-CH_3), 32.0 (br. s, 1 C, CSi_2), 84.8 (br. d, 1 C, CHB, $^1J(C,H) = 161$ Hz), 130.0, 131.7, 132.5, 133.9, 134.1, 137.1, 137.4 (total of 10 C, *o*-, *m*- and *p*-C), 139.2, 146.5 (each br. s, each 1 C, each *ipso*-C); ^{11}B NMR (96 MHz, C_6D_6, 25 C): $\delta = 5, 58$.

6: yellow solid, m.p. 170 °C (decomp.), yield ca. 90%. ^1H NMR (500 MHz, $[D_8]THF$, −30 C): $\delta = -0.02$ (s, 18H, $SiMe_3$), 2.07, 2.10, 2.27, 2.38 (each s, each 6H, *o*- and *m*-CH_3), 5.65 (br. s, 1H, BH), 6.48, 6.70 (each s, each 1H, *p*-H); ^{13}C NMR (125 MHz, $[D_8]THF$, −30 C): $\delta = 2.0$ (q, 6 C, $SiMe_3$), 19.5, 20.6, 20.8, 21.0 (each q, each 2 C, *o*- and *m*-CH_3), 106.1, (br. s, 1 C, BCB), 127.1, 132.0 (each d, each 1 C, *p*-C), 130.1, 131.4, 134.8, 142.5 (each s, each 2C, *o*- and *m*-C), 138.1, 155.8 (each br. s, each 1 C, *ipso*-C), the signal of the C atom carrying the trimethylsilyl groups could not be observed; ^{11}B NMR (96 MHz, $[D_8]$toluene, 25 °C): $\delta = 44$ ($\nu_{1/2}$ = ca. 2600 Hz).

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Table 2. Experimental (**2a**, **3a**) and computed (**2u**, **3u′**, **3u**) [a] chemical shifts of framework atoms, and distances [pm].

	2a	**2u**	**3a**	**3u′**	**3u**
$\delta(^{11}B1)$	5.0	−2.6	5.0	−3.8	−1.3
$\delta(^{11}B2)$	44.0	43.5	58.0	53.8	60.8
$\delta(^{13}C3)$	73.8	71.2	84.8	90.4	72.6
$\delta(^{13}C4)$	30.6	24.2	32.0	28.9	27.9
B1-B2		171.7	165.5(4)	162.2	161.3
B2-C3		146.4	146.0(4)	148.4	149.1
C3-C4		150.0	154.2(4)	149.9	151.1
C4-B1		157.0	162.9(4)	158.2	159.7
B1-C3		170.5	171.1(4)	171.8	174.9

[a] MP2(FU) 6-31G*-optimized geometries. ^{11}B and ^{13}C NMR computations with GIAO-MP2 tzp.

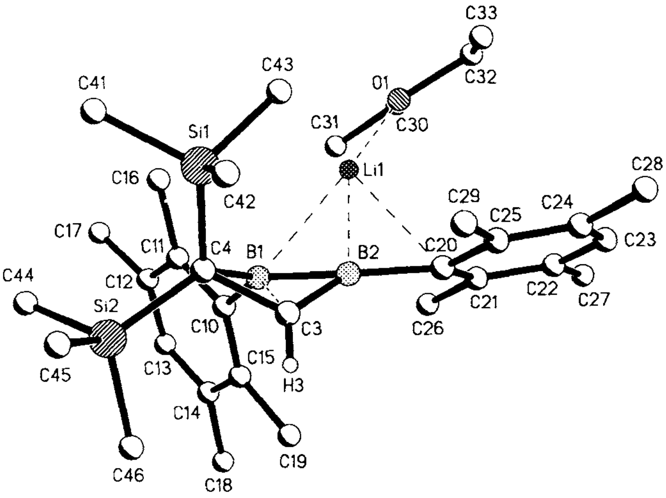

Fig. 1 Structure of **3a** in the crystal. Important interatomic distances [pm] and angles [°]: B1–B2 165.5(4), B1–C3 171.1(4), B1–C4 162.9(4), B1–C10 160.9(4), B2–C3 146.0(4), B2–C20 157.8(4), C3–C4 154.2(4), Li1–B1 250.8(7), Li1–B2 224.6(7), Li1–C20 259.8(7), Li1–O1 187.2(6), C4–Si1 186.2(2), C4–Si2 187.9(3); B2-B1-C4 97.5(2), B2-B1-C10 136.1(2), C4-B1-C10 123.1(2), B1-B2-C3 66.3(2), B1-B2-C20 151.8(2), C3-B2-C20 138.7(2), B2-C3-C4 110.7(2), C3-C4-B1 65.2(2), Si1-C4-Si2 116.7(1). Folding angle at B1–C3 140.0(2).

ethyl ether molecule adopts the position of the bridging H atom in **2u** and **2b**. However, the B1–B2 distance of 165.5(4) pm in **3a** (computed[8] to be 162.2 pm for **3u′**, Table 2) is considerably shorter than the corresponding distances in **2b** (179.9(3) pm) and **2u** (171.7 pm): the interaction of the B–B bond with the Li^+ ion in **3a** is electrostatic, whereas that with the H^+ ion in **2b** and **2u** is multicenter covalent. The Wiberg bond indices (WBIs) and charges obtained by natural population analysis (NPA) of the HF/6-31G* wavefunction clearly characterize the B-H-B bridge as a covalent 3c,2e bond, while the Li^+ ion in **3u′** is bound essentially electrostatically (Fig. 2).

The short B1–C3 distance (**3a**: 171.1(4) pm, **3u′**: 171.8 pm) and the corresponding WBI (0.528) indicate a strong 1,3-interaction, which also is consistent with the high barrier of ring inversion of **3a**. Two sharp signals for the geminal trimethylsilyl groups in the ^1H and ^{13}C NMR spectra at 25 °C broaden at higher temperatures. The barrier of 19.5 kcal mol^{-1}, determined from the coalescence temperature (130 °C in [D$_{10}$]*o*-xylene) in the ^1H NMR spectrum and the difference of the chemical shifts at slow exchange ($\Delta\delta = 100$ Hz), is considerably higher than all barriers reported for the homoaromatic 2π-electron compounds **7**–**9** (Fig. 3).[9]

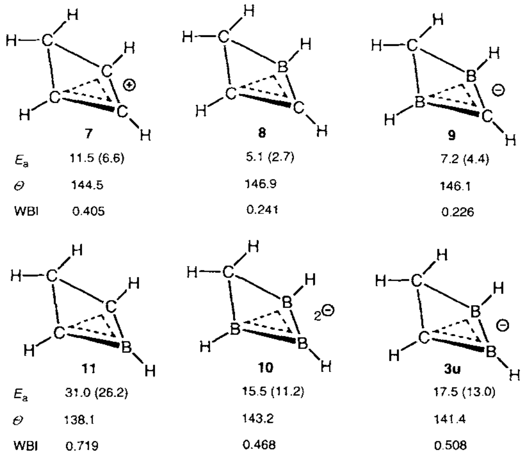

Fig. 3. MP2(FU)/6-31G*//MP2(FU)/6-31G* + ZPE inversion barriers E_a [kcal mol^{-1}], dihedral angles θ [°], and Wiberg bond indices (WBIs) for isoelectronic homoaromatic 2π-electron compounds. Inversion barriers at B3LYP/6-311 + G**//B3LYP/6-311 + G** + ZPE level are given in parentheses for comparison.

MP2/6-31G* calculations gave inversion barriers of 17.5 and 20.4 kcal mol^{-1} (Fig. 3) for the unsubstituted **3u** and **3u′**, respectively. Hence, such high barriers are characteristic for 1,2-diboretanides. Two related members of the family of homoaromatic 2π-electron compounds are still unknown, the homotriborirane dianion **10** and the borabicyclobutane **11**; their computed barriers are 15.5 and 31.0 kcal mol^{-1}, respectively (Fig. 3).

The inversion barriers given in Figure 3 reflect the degree of cyclic delocalization and the magnitude of homoaromaticity in the four-membered rings. The barriers correlate both with the folding angles between the two planes of the three-membered rings (correlation coefficient 0.98) and with the WBI of the transannular bonds (correlation coefficient 0.96).

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Keywords: ab initio calculations · boron compounds · heterocycles · homoaromaticity · strained rings

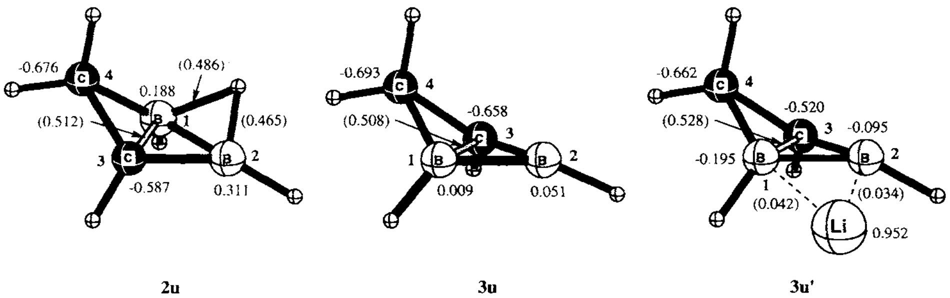

Fig. 2. Natural population analysis (NPA) charges and Wiberg bond indices (WBIs, in parentheses) for **2u**, **3u**, and **3u′** at the MP2(FU)/6-31G* level.

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[7] X-ray structure analysis: colorless crystals of **3a** ($C_{28}H_{45}B_2Si_2Li \cdot Et_2O$) were investigated with a four-circle diffractometer (CAD4, Enraf-Nonius) at −70 C with $Cu_{K\alpha}$ radiation ($\lambda = 154.178$ pm). Crystal dimensions $0.6 \times 0.3 \times 0.3$ mm^3, monoclinic, space group $P2_1/c$, $Z = 4$, $a = 1287.5(3)$, $b = 1536.0(3)$, $c = 1745.2(3)$ pm, $\beta = 90.88(3)^\circ$, $V = 3450.9 \times 10^{-30}$ m^3, $\rho_{calc} = 1.040$ gcm^{-3}; a total of 4630 reflections were measured up to $2\theta = 110^\circ$ with $\omega/2\theta$ scans; 4329 independent reflections were used after LP correction in subsequent calculations; no absorption correction ($\mu = 10.7$ cm^{-1}). The structure was solved by direct methods and refined with full matrix against the F^2 data. Some of the H atoms could be localized from difference Fourier syntheses, the rest were calculated. Anisotropic temperature factors were used for all other atoms. $wR_2 = 0.1489$ resulted, corresponding to $R = 0.0517$ for 3614 reflections $> 4\sigma(F_0)$, the maximum residual electron density was 0.31 eÅ^{-3}. Crystallographic data (excluding structure factors) for the structure(s) reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-179-67. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: Int. code +(1223) 336-033; e-mail: teched@chemcrys.cam.ac.uk).

[8] MP2(FU)/6-31G* geometries computed 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. Binkley, D. J. DeFrees, J. Baker, J. J. P. Stewart, M. Head-Gordon, C. Gonzalez, J. A. Pople, Gaussian Inc., Pittsburgh, PA, USA, **1995**.

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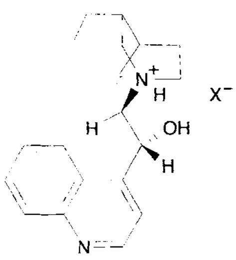
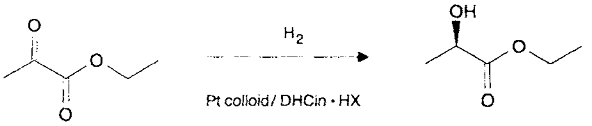
Enantioselective Hydrogenations on Platinum Colloids**

Helmut Bönnemann* and Gerhard A. Braun

Metal colloids with dimensions of a few nanometers are important for catalysis research because of their high proportion of surface atoms.[1] These colloids can either be employed as catalysts in quasi-homogeneous phases[2] or serve as precursors for heterogeneous catalysts.[3] Their stabilization in solution at concentrations necessary for catalysis is achieved by polymers,[4] ligands,[5] or surfactants.[6] In several cases it was possible to show that the stabilizer affects the catalytic selectivity.[7] Herein, we report on a chiral induction by the stabilizer in a colloid-catalyzed hydrogenation. Using as an example a platinum sol stabilized by the protonated alkaloid dihydrocinchonidine (DHCin), we examined the influence of the stabilizer on the enantioselective hydrogenation of ethylpyruvate to (*R*)-ethyllactate [Eq. (a)] in a quasi-homogeneous phase.



DHCin · HX:
X = Cl, AcO, HCO_2



(a)

The enantioselective hydrogenation of α-oxoesters on heterogeneous platinum catalysts in the presence of cinchona alkaloids was reported for the first time by Y. Orito.[8] Over the last few years, these chirally modified heterogeneous catalysts have been systematically studied with respect to catalyst preparation,[9a] catalyst structure,[9b, c, d] reaction conditions,[9e, f, g] and kinetics.[9h, i] The structure of the modifier has been varied,[10a] and the interaction between the substrate and the alkaloid has been modeled.[10b, c]

In order to synthesize colloidal platinum, an aqueous solution of a platinum salt is reduced in the presence of protonated DHCin. The normally water-insoluble alkaloid is initially transformed into the water-soluble hydroformate, and then added by syringe to an aqueous platinum tetrachloride solution. The formate reacts to yield carbon dioxide, and the resulting platinum sol (**2**) is stabilized by the hydrochloride of DHCin [Eq. (b)].

$$\mathrm{PtCl_4} + (2-n)\ \mathrm{DHCin{\cdot}HCO_2H} + n\ \mathrm{HCO_2H} \longrightarrow \underset{\textbf{2}}{\mathrm{Pt_{colloid}}\ [\mathrm{DHCinH^+\ Cl^-}]_{2-n}} + (2+n)\ \mathrm{HCl} + 2\ \mathrm{CO_2} \qquad \text{(b)}$$

$n = 0$–1.75

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