

## Kurzzmitteilung / Short Communication

## An Uncomplexed 1,2,3-Triborolane Derivative

Anton Meller\*, Dietmar Bromm, Walter Maringgele, Andreas Heine, Dietmar Stalke, and George M. Sheldrick

Institut für Anorganische Chemie der Universität Göttingen,  
Tammannstraße 4, D-3400 Göttingen

Received October 18, 1989

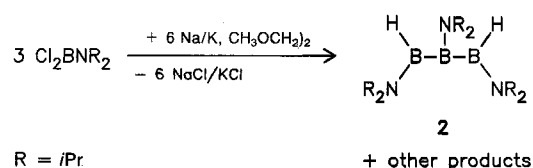
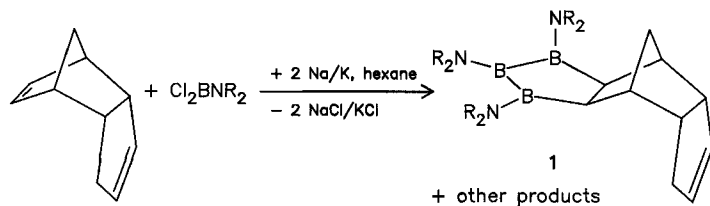
**Key Words:** 1,2,3-Triborolane / Dicyclopentadiene / Dichloro(diisopropylamino)borane, dehalogenation product of / Triborane(5), 1,2,3-tris(diisopropylamino)-

(3 $\alpha$ ,4 $\beta$ ,4a $\beta$ ,7a $\beta$ ,8 $\beta$ ,8a $\alpha$ )-1,2,3-Tris(diisopropylamino)-1,2,3,3a,4,4a,5,7a,8,8a-decahydro-4,8-methanoindeno[5,6-d]-1,2,3-triborol (1) is formed from dicyclopentadiene and dichloro(diisopropylamino)borane upon treatment with sodium/potassium alloy in

hexane. 1,2,3-Tris(diisopropylamino)triborane(5) (2) was also obtained. 1 is characterized by elemental analyses, spectroscopic data, and by an X-ray structure analysis, 2 by its MS and NMR data.

Generally, C<sub>2</sub>B<sub>3</sub> systems exist in form of carboranes<sup>1)</sup>, and C<sub>2</sub>B<sub>3</sub>H<sub>7</sub> is known as *nido*-1,2-dicarbapentaborane<sup>2)</sup>. So far C<sub>2</sub>B<sub>3</sub> ring systems have been obtained only stabilized as  $\eta^5$ -ligands in transition-metal complexes<sup>3)</sup>. A triple decker, containing an ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Co<sub>2</sub>C<sub>2</sub>B<sub>3</sub>H<sub>5</sub> cluster, has been obtained by the reaction of Na[B<sub>5</sub>H<sub>8</sub>] with CoCl<sub>2</sub> and Na[C<sub>5</sub>H<sub>5</sub>] upon partial insertion of C<sub>5</sub>H<sub>5</sub> into the pentaborane anion<sup>4)</sup>. The formation of the species 2,2,3,3,4,4-hexafluoro-2,3,4-trisilabicyclo[3.2.2]nona-6,8-diene from the reaction of the difluorocarbene analog SiF<sub>2</sub> has been reported<sup>5)</sup>.

We have isolated compound 1, which incorporates the first C<sub>2</sub>B<sub>3</sub> ring system without complexation, from the reaction of dicyclopentadiene with dichloro(diisopropylamino)borane upon treatment with sodium/potassium alloy in hexane. Apparently, a diradical [B(NR<sub>2</sub>)<sub>2</sub>]<sub>2</sub>B(NR<sub>2</sub>)<sub>2</sub><sup>••</sup> (R = *i*Pr) is added to one of the double bonds of dicyclopentadiene. If the dehalogenation of Cl<sub>2</sub>BNR<sub>2</sub> is performed in 1,2-dimethoxyethane or hexane without an equally reactive partner, 1,2,3-tris(diisopropylamino)triborane(5) (2) is obtained<sup>6)</sup>.

R = *i*Pr

+ other products

The spectroscopic data are consistent with the reported structures (see Experimental). However, for 1 the <sup>1</sup>H- and <sup>13</sup>C-NMR spectra are too complicated to allow unequivocal assignments.

**Crystal Structure of 1**

The molecular structure of 1 is depicted in Figure 1. Atomic coordinates and equivalent isotropic displacement parameters are

given in Table 1, selected bond lengths and angles in Table 2. The atoms B1, N1, C3, and C6 lie on a crystallographic mirror plane perpendicular to the B<sub>3</sub>C<sub>2</sub> five-membered ring. In this ring the B<sub>3</sub> and BCCB planes form an envelope.

Table 1. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\times 10^3$ ) [ $\text{\AA}^2$ ] of 1 [ $U(\text{eq})$  defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor]

	x	y	z	U(eq)
B(1)	1356(2)	2500	919(4)	32(1)
B(2)	1933(2)	3229(2)	1439(3)	33(1)
N(1)	747(2)	2500	128(3)	40(1)
N(2)	1846(1)	3791(1)	2544(2)	36(1)
C(1)	2675(1)	2974(2)	793(3)	33(1)
C(2)	2815(1)	3169(2)	-793(3)	43(1)
C(3)	2429(2)	2500	-1577(4)	48(2)
C(4)	3574(2)	2969(2)	-1206(3)	48(1)
C(5)	4146(2)	3192(2)	-193(4)	63(1)
C(6)	4434(2)	2500	397(5)	53(2)
C(7)	408(2)	3225(3)	-417(4)	82(2)
C(8)	-224(2)	3494(3)	355(5)	93(2)
C(9)	704(3)	3639(4)	-1473(9)	210(4)
C(10)	2403(1)	4271(2)	3208(3)	41(1)
C(11)	2786(2)	4787(2)	2130(3)	59(1)
C(12)	2891(2)	3773(2)	4126(3)	59(1)
C(13)	1155(2)	3927(2)	3167(4)	62(1)
C(14)	1122(2)	3738(3)	4738(4)	110(2)
C(15)	893(2)	4765(3)	2847(6)	117(2)

Table 2. Selected bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] of 1

B(1)-B(2)	1.724 (4)	B(1)-B(2A)	1.724 (4)
B(2)-C(1)	1.609 (4)	C(1)-C(2)	1.541 (4)
C(1)-C(1A)	1.591 (5)	C(2)-C(3)	1.533 (4)
C(2)-C(4)	1.547 (4)	C(3)-C(2A)	1.533 (4)
C(4)-C(5)	1.500 (4)	C(4)-C(4A)	1.575 (6)
C(5)-C(6)	1.401 (4)	C(6)-C(5A)	1.401 (4)
B(2)-B(1)-N(1)	134.1(1)	B(2)-B(1)-B(2A)	90.5(3)
N(1)-B(1)-B(2A)	134.1(1)	B(1)-B(2)-N(2)	127.3(3)
B(1)-B(2)-C(1)	106.1(2)	N(2)-B(2)-C(1)	124.0(2)
B(1)-N(1)-C(7)	124.0(2)	B(2)-C(1)-C(2)	117.3(2)
B(2)-C(1)-C(1A)	105.5(1)	C(2)-C(1)-C(1A)	102.3(1)
C(1)-C(2)-C(3)	102.7(2)	C(1)-C(2)-C(4)	111.0(2)
C(3)-C(2)-C(4)	100.3(2)	C(2)-C(3)-C(2A)	94.2(3)
C(2)-C(4)-C(5)	118.8(3)	C(2)-C(4)-C(4A)	102.5(2)
C(5)-C(4)-C(4A)	104.5(2)	C(4)-C(5)-C(6)	109.4(3)
C(5)-C(6)-C(5A)	112.1(4)		

The C1–C1A–B2A–B1–B2 ring and the C1–C1A–C2A–C3–C2 ring form a cradle with a distance of 3.115 Å between B1 and C3. This may result from steric effects involving the bulky *i*Pr groups. The mirror plane perpendicular to the plane of the C4–C4A–C5A–C6–C5 five-membered ring requires the double bond to be disordered, with an average apparent C–C bond length of 1.40 Å. Steric hindrance probably also accounts for the envelope form, because a planar ring with N(*i*Pr)<sub>2</sub> groups at each boron atom would be energetically less favorable.

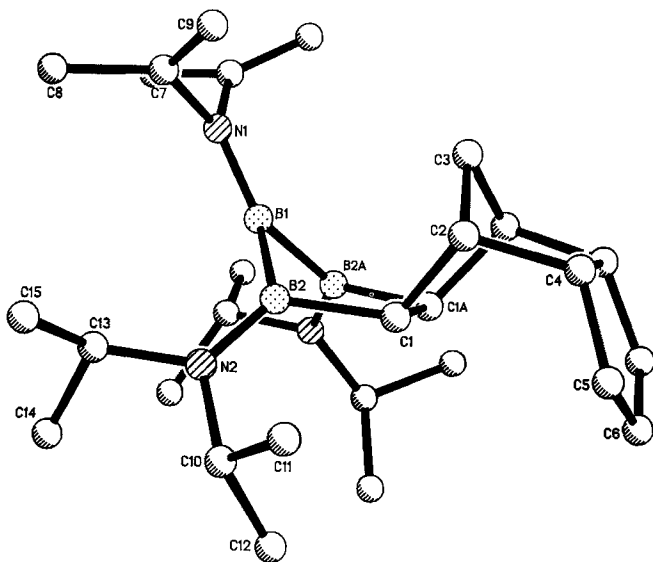


Figure 1. Molecular structure of **1**

Support by the Volkswagenstiftung and the Fonds der Chemischen Industrie is gratefully acknowledged.

## Experimental

Elemental analyses: Mikroanalytisches Laboratorium Beller, Göttingen. — NMR (standards): <sup>1</sup>H, <sup>13</sup>C (TMS, int.), <sup>11</sup>B (Et<sub>2</sub>O–BF<sub>3</sub>, ext.); Bruker AM 250. — MS: EI (70 eV), FI; Varian AMT CH 5. — Cl<sub>2</sub>BN(*i*Pr)<sub>2</sub><sup>7</sup>. — All reactions are performed in dry N<sub>2</sub> and in dry solvents.

(3 $\alpha$ ,4 $\beta$ ,4 $\alpha\beta$ ,7 $\alpha\beta$ ,8 $\beta$ ,8 $\alpha\alpha$ )-1,2,3-Tris(d*is*isopropylamino)-1,2,3,3a,4,4a,5,7a,8,8a-decahydro-4,8-methanoindeno[5,6-*d*]-1,2,3-triborol (**1**): Dicyclopentadiene (59.4 g, 0.45 mol) and dichloro(d*is*isopropylamino)borane (82.0 g, 0.45 mol) are dissolved in hexane (250 ml). The mixture is added dropwise with vigorous stirring to a suspension of sodium/potassium alloy (5.75 g Na, 29.33 g K, 1.00 mol) in hexane (1 l) during 30 min. The reaction mixture is stirred for ca. 12 h and heated to reflux for 20 h. After filtration through a glass frit under N<sub>2</sub> pressure and distillation of the hexane, the green residue is kept at 0°C for 72 h, and colorless crystals are collected by filtration. The yield of **1** (after recrystallization from acetone) is 7.40 g [11% relative to Cl<sub>2</sub>BN(*i*Pr)<sub>2</sub>], mp 170°C. — MS (EI): *m/z* (%) = 465 (15); (FI): *m/z* (%) = 465 (100) [M]<sup>+</sup>. — NMR (CDCl<sub>3</sub>):  $\delta^{11}\text{B} = 55$  ( $h_{1/2} \approx 1180$  Hz), shoulder at 62.

C<sub>28</sub>H<sub>54</sub>B<sub>3</sub>N<sub>3</sub> (465.19) Calcd. C 72.29 H 11.70 B 6.97 N 9.04  
Found C 72.86 H 12.12 B 6.57 N 8.48

1,2,3-Tris(d*is*isopropylamino)triborane(5) (**2**): This is obtained in varying quantities (5–15%) from dehalogenation reactions of Cl<sub>2</sub>BN(*i*Pr)<sub>2</sub> in hexane or 1,2-dimethoxyethane together with other products. It crystallizes from distillation fractions bp 50–75°C/0.1 mbar in colorless needles, mp  $\leq 30^\circ\text{C}$ . — MS (EI): *m/z* = 335; (FI): *m/z* (%) = 335 (100). — NMR (CDCl<sub>3</sub>):  $\delta^{11}\text{B} = 44$  ( $h_{1/2} = 770$  Hz) and 58 ( $h_{1/2} \approx 755$  Hz), ratio 2:1;  $\delta^1\text{H} = 1.09$  (d), 1.11 (d), and 1.12 (d) (<sup>3</sup>*J*<sub>HH</sub> = 6.75 Hz, 12 CH<sub>3</sub>), 3.16 (sept), 3.34 (sept), and 3.60 (sept) (<sup>3</sup>*J*<sub>HH</sub> = 6.75 Hz 6 CH), 4.8–5.6 (br., 2 BH). — IR (KBr):  $\nu(\text{BH}) = 2390$  cm<sup>-1</sup> (br.).

C<sub>18</sub>H<sub>44</sub>B<sub>3</sub>N<sub>3</sub> (335.02) Calcd. C 64.53 H 13.24 B 9.68 N 12.54  
Found C 64.50 H 13.05 B 9.60 N 12.41

Crystal Data for C<sub>28</sub>H<sub>54</sub>B<sub>3</sub>N<sub>3</sub><sup>8</sup>: Single crystals were obtained from a solution of **1** in acetone. A crystal (0.7 × 0.7 × 0.7 mm) was mounted on a Stoe-Siemens four-circle diffractometer. Orthorhombic, space group *Pnma* with *a* = 9.342(1), *b* = 16.793(2), *c* = 19.248(2) Å, *V* = 3020 Å<sup>3</sup>, molecular mass 465.2 g/mol, *Z* = 4, *D*<sub>calc.</sub> = 1.023 g/cm<sup>3</sup>,  $\mu = 0.05$  mm<sup>-1</sup>, *F*(000) = 1032. Data were collected at –85°C using Mo-*K*<sub>α</sub> radiation ( $\lambda = 0.71073$  Å) and a 2 $\Theta$  range of 8–50°. 3156 reflections were measured of which 2731 were independent, and 1971 considered observed with *F* ≥ 4 $\sigma$ (*F*) were used in the refinement. Absorption corrections were unnecessary. The structure was determined by direct methods (SHELXS-86)<sup>9</sup>. All non-hydrogen atoms were refined anisotropically. A riding model with idealized hydrogen geometry was employed for H-atom refinement, and the hydrogen thermal parameters were refined isotropically with those of atoms bonded to the same carbon atom constrained to be equivalent. The disorder involving the C=C bond was modelled successfully by refining the C5–C6 unit using partially occupied H atoms at C5. 160 parameters were refined, and a weighting scheme [*w*<sup>-1</sup> =  $\sigma^2 \cdot (|F_o| + g \cdot |F_c|)^2$ ; *g* = 0.0007] was used. The final values for *R* and *R*<sub>w</sub> were 0.077 and 0.082, respectively, with the final Fourier difference map showing a maximum of 0.32 and a minimum of –0.28 e Å<sup>-3</sup>.

## CAS Registry Numbers

**1**: 124442-69-9 / **2**: 124442-70-2 / Cl<sub>2</sub>BN(*i*Pr)<sub>2</sub>: 44873-49-6 / dicyclopentadiene: 77-73-6

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