*Organometallics* **1991,** *10,* 2097-2098

# A Tricyclic Ring System of Six Carbon and Five Boron Atoms from Monoalkylbenzene and Five Formal Borene Units

Walter Maringgele, Uwe Seebold, Andreas Heine, Dietmar Stalke, Mathias Noltemeyer, George M. Sheldrick, and Anton Meller*

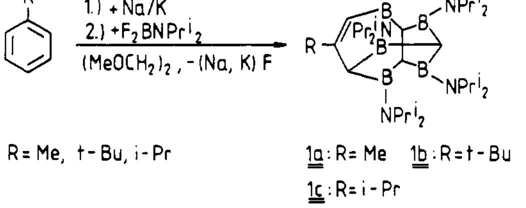
*Institut für Anorganische Chemie, Universität Göttingen, Tammannstrasse 4, D-3400 Göttingen, Germany*

*Received March 11, 1991*

*Summary:* Products of $RC_6H_5{\cdot}5BNR'_2$ are the highest borylated species to be formed in reactions between dehalogenation products of $F_2BN(i\text{-}Pr)_2$ with monoalkylbenzenes. The structures are cages, each consisting of a five-, six-, and seven-membered ring, in which the carbon skeleton has been split into $C_1$, $C_2$, and $C_3$ units, as shown by single-crystal X-ray structure determinations. Mass spectroscopic and $^1H$, $^{11}B$, and $^{13}C$ NMR and elemental analyses are reported.

Generally, reactions of the six-electron species carbene with aromatic compounds lead to the addition of only one carbene molecule to a benzene ring.[1] Due to the anticipated higher reactivity of the four-electron species borene, multiple additions to aromatic rings might occur. Mass spectrometric studies of the system $Cl_2BN(i\text{-}Pr)_2/C_6H_6/Na,K$[2] indicated that up to six "$BN(i\text{-}Pr)_2$" units can be added to benzene. Upon substitution of the benzene ring with methyl groups, only a reduced number of formal "borene" units will react, as one double bond or a cyclopropane ring will be left or formed, respectively, at the carbon atom carrying the alkyl group.[3] Therefore, toluene and other monoalkylated benzenes should add at most five "borene" units. However, it should be noted that the formation of these products can be also explained by stepwise radical reactions/eliminations from borenoids.

Here we report for the first time the isolation and structures of such species formed in the reaction of toluene, *tert*-butylbenzene, and isopropylbenzene with sodium/potassium alloy and $F_2BN(i\text{-}Pr)_2$ in glyme. The cage compounds **1a**, **1b**, and **1c** each consist of a seven-, six-, and five-membered ring with the remaining double bond fixed at the alkylated C atom in the seven-membered ring.



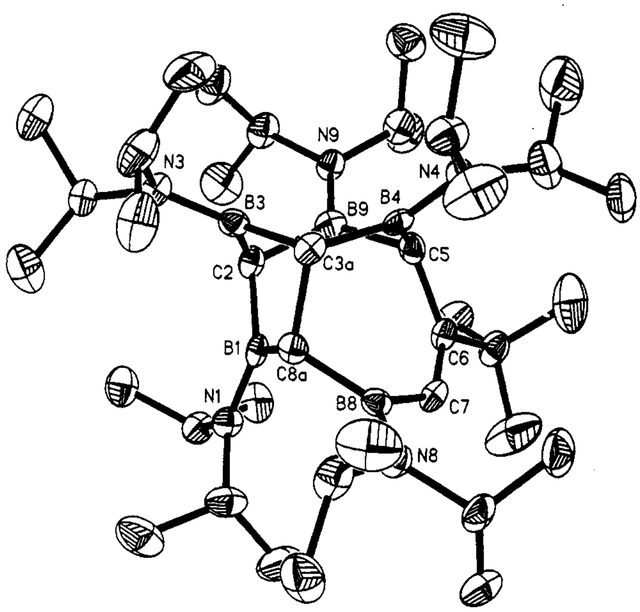


**Figure 1.** Structure of **1b**. Selected bond lengths (pm) and angles (deg) (m = mean): B1—C2 = 158.0 (4), B1—C8a = 160.7 (4), B3—C2 = 160.9 (4), B9—C2 = 158.5 (4), B9—C5 = 161.8 (4), B3—C3a = 159.3 (4), B4—C3a = 157.9 (3), B4—C5 = 160.7 (4), B8—C7 = 156.6 (4), B8—C8a = 158.1 (4), B—N = 141.6 (m), N—C = 147.5 (4) (m), C6═C7 = 134.8 (4), C5—C6 = 153.9 (3), C3a—C8a = 160.9 (3), C6—$CMe_3$ = 154.9 (3); (B1C2B3) = 91.1 (2), (B2C3aC8a) = 91.9 (2), (C6C7B8) = 130.5 (2).

In these reactions, **1a** ($R = CH_3$), which is merely a byproduct of the tetraborylated species,[3] is isolated only in 0.6% yield after repeated distillation and recrystallization of the first solid formed.[4] **1b** (R = *t*-Bu) is obtained, however, in a yield of 32% while **1c** (R = *i*-Pr) is isolated in 22% yield (based on $F_2BN(i\text{-}Pr)_2$).[5]

**1b** was prepared by dropwise addition of 210 g (1.41 mol) of $F_2BN(i\text{-}Pr)_2$ to a stirred suspension of 98 g (2.87 mol) of Na/K alloy (1:4) in 1.2 L of 1,2-dimethoxyethane (DME) and 410 g of *tert*-butylbenzene during 4 h at 25 °C.

---

(1) Regitz, M., Ed. Methoden der Organische Chemie (Houben-Weyl); G. Thieme Vlg.: Stuttgart-New York, 1989; Vol. E19b.

(2) Meller, A.; Bromm, D.; Maringgele, M.; Böhler, D.; Elter, G. *J. Organomet. Chem.* **1988**, *347*, 11.

(3) Meller, A.; Seebold, U.; Maringgele, W.; Noltemeyer, M.; Sheldrick, G. M. *J. Am. Chem. Soc.* **1989**, *111*, 8299.

(4) **1a** ($R = CH_3$): 6-methyl-deca-*N*-isopropyl-1,2,3,3a,4,5,8,8a-octahydro-2,5-epiborano-1,3-diborolo[4,5-*b*]-1,4-diborepine-1,3,4,8,9-pentaamine has been obtained in an analogous procedure as described for **1b** in the text but was isolated in only 0.6% yield. Single crystals were grown after recrystallization from hexane. $C_{37}H_{78}B_5N_5$ (MW 647.11). MS EI (70 eV), *m/z* (relative intensity): 647 (15) [$M^+$], 56 (100); FI 647 (100). High-resolution MS: $C_{37}H_{78}N_5{}^{11}B_5$ calcd 647.67226, found 647.6732; $C_{37}H_{78}N_5{}^{10}B^{11}B_4$ calcd 646.67588, found 646.6763. The colorless crystals (containing one molecule of hexane in the unit cell of two **1a** molecules) have a mp of 322 °C, dec. The hexane is also detected in the MS at 86 (28).

(5) **1c** (R = *i*-Pr) is prepared analogously to **1b** with 430 g of isopropylbenzene. The extraction yielded 17 g of **1c**, which was recrystallized from hexane. Vacuum distillation of the high-boiling fraction from the filtrate in a four-bulb tube yielded 12 g of **1c** with a bp of 235 °C/0.002 mbar (air bath temperature) thus giving a total yield of 29 g (22%) relative to $F_2BN(i\text{-}Pr)_2$. The fraction boiling at 200 °C/0.002 mbar (9 g) consists of a mixture of (isopropylbenzene)$\cdot 4BN(i\text{-}Pr)_2$ and **1c**. The compound did not melt up to 350 °C. Anal. Calcd for $C_{39}H_{82}B_5N_5$ (MW 675.19): C, 69.37; H, 12.24; B, 8.02; N, 10.37. Found: C, 69.24; H, 12.37; B, 7.91; N, 10.11. MS EI (70 eV), *m/z* (relative intensity): 675 (43) [$M^+$], 43 (100) [$C_3H_7{}^+$]. Selected NMR data (250 MHz, $CDCl_3$): $\delta(^1H)$ 5.65 (br, 1 H, H7), 2.30 (singlet, 2 H), 1.87 (s, 2 H) (4 H in 2, 3a, 5, and 8a). Signals of the isopropyl groups are from 0.85 to 1.50 (br, 66 H) and from 2.05 to 4.55 (multiplets, 11 H). NMR: $\delta(^{13}C)$ 163.6 (C6), 124.6 (br, C7), 47.6 (br) + 39.5 (br) + 29.5 (br) (together 4 CH in 2, 3a, 5 and 8a). The signals of the isopropyl groups appear from 20 to 26 ($CH_3$) and from 44 to 50 (CH). NMR: $\delta(^{11}B)$ 46.6 ($h_{1/2}$ = 1080 Hz).

0276-7333/91/2310-2097$02.50/0

Stirring was continued for 2 days at ambient temperature. The solidified alloy was liquefied by the addition of 32 g of K and the stirred suspension refluxed for 2 days. Then the reaction mixture was filtered through a glass frit by $N_2$ pressure, and the solids were extracted in a Soxhlet extractor with hexane/DME (1:1) for 50 h to yield 23.0 g of colorless **1b** (mp 340–350 °C). Recrystallization from hexane gave single crystals. Vacuum distillation of the higher boiling fractions from the filtrate in a four-bulb tube at 235 °C/0.002 mbar (air bath temperature) gave an additional 39 g of **1b**, thus leading to a total yield of 62 g (32%). The fraction collected around 200 °C/0.002 mbar (21 g) consists of a mixture of (*tert*-butylbenzene)·4BN(*i*-Pr)$_2$ and **1b**. Anal. Calcd for $C_{40}H_{84}B_5N_5$ (MW 689.20): C, 69.71; H, 12.29; B, 7.84; N, 10.16. Found: C, 69.65; H, 12.41; B, 7.69; N, 10.12. MS EI (70 eV), *m/z* (relative intensity): 689 (57) [$M^+$], 57 (100) [$C_4H_9^+$]. Selected NMR data (250 MHz, $CDCl_3$): $\delta$($^1$H) 5.79 (br, 1 H, H7), 1.81 (s, 2 H) + 2.36 (s, 2 H) (for H in 2, 3a, 5, and 8a). Signals of the isopropyl groups appear between 0.9 and 1.40 (60 H) and from 3.20 to 4.55 (10 H), while the *t*-Bu group gives a singlet at 1.05 (9 H). NMR $\delta$($^{13}$C) 165.2 (C6), 126.6 (br, C7), 40.1 (C34), 38.2 + 34.2 + 29.4 (br, C2, 3a, 5, 8a). NMR $\delta$($^{11}$B) 45.5 ($h_{1/2}$ = 600 Hz). The signals of the isopropyl groups are from $\delta$ 20 to 32 and 44 to 50, and the $CH_3$ of *t*-Bu is at 30.9.

A single-crystal X-ray structure analysis has been performed for **1b**.[6] Crystals of **1a** have been also studied by X-ray diffraction; however, the latter contain some disordered hexane near the center of symmetry and, accordingly, the formula mass is increased by one-half hexane per molecule. Furthermore, there is disorder of the isopropyl groups (the X-ray data for **1a** were collected at room temperature), so we will not discuss the structure of **1a** further. The results obtained for **1a** are deposited with the supplementary material and confirm that molecules **1a** and **1b** are of the same structural type.

Following the pattern of the products obtained so far from aromatic compounds and dehalogenation products of (dialkylamino)dihaloboranes,[2,3] the three-dimensional structures of $RC_6H_5{\cdot}5BNR'_2$ contain boron atoms only in sp$^2$ and carbon atoms in both sp$^2$ and sp$^3$ bonding situations. In the compounds of type 1 the ring of the aromatic hydrocarbon has been split into one $C_1$, one $C_2$, and one $C_3$ unit. As expected, the smallest angles of the skeleton are observed in the five-membered ring, the largest in the seven-membered ring, which also contains the remaining double bond. The C–C bond lengths increase upon higher substitution with boron atoms relative to normal C–C bond lengths between sp$^3$-hybridized carbon atoms. A complete assignment of the NMR spectra has not been possible due to the overlap of signals and the lack of coupling across the quadrupolar boron nuclei.

These results are not inconsistent with the presence of a free "borene" intermediate.

**Acknowledgment.** The financial support by the Volkswagen-Stiftung (A.M.), Fonds der Chemischen Industrie (A.M. and G.M.S.), and Leibniz program of the Deutsche Forschungsgemeinschaft (G.M.S.) is gratefully acknowledged.

**Supplementary Material Available:** For structures **1a** and **1b**, atomic coordinates and isothermal displacement parameters (Table I), bond lengths (Table II), bond angles (Table III), anisotropic displacement parameters (Table IV), hydrogen atom coordinates and isotropic displacement parameters (Table V), and a table of crystal and diffractometer data and structure solution and refinement (8 pages); listings of observed and calculated structure factors (33 pages). Ordering information is given on any current masthead page.

---

[6] Crystal data for **1b**: $C_{40}H_{84}B_5N_5$, MW = 689.2, triclinic, space group $P\bar{1}$, $a$ = 11.330 (2) Å, $b$ = 11.902 (3) Å, $c$ = 17.931 (4) Å, $\alpha$ = 87.43 (1)°, $\beta$ = 86.94 (1)°, $\gamma$ = 69.32 (2)°, $V$ = 2258.1 Å$^3$, $Z$ = 2, $d_{calcd}$ = 1.014 g/cm$^3$, $\mu$ = 0.057 mm$^{-1}$, $F_{000}$ = 768, $\lambda$(Mo $K\alpha$, graphite monochromator) = 0.7107 Å. The data were collected with use of $2\theta$–$\omega$ scans on a Stoe-Siemens AED diffractometer at 153 K: 5901 measured and unique reflections and 4637 observed reflections with $F \geq 3\sigma(F)$; $2\theta_{max}$ = 45°. The structure was determined by direct methods (SHELXS-86[7]). 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. Refinement of 467 parameters converged with $R$ = 0.059, $R_w$ = 0.060, $w^{-1} = \sigma^2(F) + 0.0006F^2$, and maximum/minimum rest electron density 0.30 e Å$^{-3}$/–0.24 e Å$^{-3}$.

[7] Sheldrick, G. M. *Acta Crystallogr.* 1990, *A46*, 467.

---

# $^{13}$C CP/MAS NMR Spectroscopy of Magnesium–Anthracene and –Cyclooctatetraene Complexes: Graphite-Assisted Degradation of a Magnesium–Anthracene Complex

William M. Brooks, Colin L. Raston,* and Rodney E. Sue

*Division of Science and Technology, Griffith University, Nathan, Brisbane, Queensland 4111, Australia*

Frank J. Lincoln and Justin J. McGinnity

*Department of Physical and Inorganic Chemistry, The University of Western Australia, Nedlands, Western Australia 6009, Australia*

*Received April 9, 1991*

*Summary:* $^{13}$C CP/MAS NMR spectroscopy shows that [Mg(anthracene)(THF)$_2$], derived from decomposition of [Mg(anthracene)(THF)$_3$], has Mg–C9,10 interactions and that Mg(cyclooctatetraene)(THF)$_{2.5}$ has an aromatic dianion: graphite accelerates the decomposition of [Mg(anthracene)(THF)$_3$], in toluene (via [Mg(anthracene)(THF)$_2$]) or diethyl ether, to its constituents, affording highly activated and finely divided magnesium (ca. 6 $\mu$m) rather than an intercalation compound.

The magnesium–anthracene complex [Mg(anthracene)(THF)$_3$] (1; THF = tetrahydrofuran) is an important source of magnesium either via reactions involving the complex directly or from activated magnesium arising from decomposition of 1 to its constituents.[1–6] The decompo-

---

[1] Alonso, T.; Harvey, S.; Junk, P. C.; Raston, C. L.; Skelton, B. W.; White, A. H. *Organometallics* 1987, *6*, 2110.

[2] Harvey, S.; Junk, P. C.; Raston, C. L.; Salem, G. *J. Org. Chem.* 1988, *53*, 3134.

0276-7333/91/2310-2098$02.50/0