985.4 (18) [M^-, $C_{73}H_{15}NO_5$], 746.1 (100) [$C_{61}N^-$], 720.0 (7) [C_{60}^-]; HR-FAB-MS: m/z: 985.0950 [$C_{73}H_{15}NO_5^+$] calcd; 985.0942 found.

High-resolution X-ray structure analysis with low-temperature data:[16] $C_{73}H_{15}NO_5 \cdot C_7H_8$, $M_r = 985.86$, dark brown crystal 0.44 × 0.22 × 0.12 mm, triclinic, space group $P\bar{1}$, $a = 10.0417(2)$, $b = 14.5831(4)$, $c = 16.8772(4)$ Å, $\alpha = 68.277(1)$, $\beta = 75.985(1)$, $\gamma = 84.583(1)^\circ$, $V = 2227.59(9)$ Å^3, $Z = 2$, $T = 123(2)$ K, $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, $\rho_{calcd} = 1.607$ kg dm^{-3}, $F(000) = 1100$, $\mu = 0.1$ mm^{-1}, an empirical absorption correction was carried out, Bruker SMART diffractometer, ω and φ scan, $\theta_{max.} = 50.6^\circ$, $-21 \leq h \leq 20$, $-30 \leq k \leq 30$, $-32 \leq l \leq 36$, 43 s measuring time per frame; of 119878 measured reflections, 44299 were independent and 22618 were observed. The structure was solved by direct methods (SHELXS-97).[17] Refinement (F^2 after the LSQ method with SHELXL-97[18]) and calculation of the difference density in the following order: a) With the reflections from $\theta = 5-28^\circ$, 10592 independent, 8791 observed [$I > 2\sigma(I)$], 867 variables. Isotropic refinement of the hydrogen atoms and anisotropic refinement of the heavy atoms, $R = 0.046$, $wR = 0.11$, $R_{int.} = 0.03$, GOF = 1.07. b) High-angle refinement with the reflections from $\theta = 28-50.6^\circ$, 33719 independent, 13839 observed [$I > 2\sigma(I)$], 775 variables. Anisotropic refinement of the heavy atoms, parameters of the hydrogen atoms were adopted from (a), $R = 0.105$, $wR = 0.154$. The Hirshfeld rigid bond test[19] resulted in a mean deviation of 6.3×10^{-4} Å^2 for the 90 bonds of the fullerene skeleton. An R value of 0.028 was obtained for the fullerene skeleton by applying a T,L,S analysis according to Schomaker and Trueblood.[20] c) With the reflections from $\theta = 5-50.6^\circ$, 44299 independent, 22618 observed [$I > 2\sigma(I)$]. Refinement of the scale factor, $R = 0.081$, $wR = 0.175$. d) Calculation of the structural factors (F_{calcd}) for $\theta = 5-28^\circ$ [$I > 5\sigma(I)$] with the structure model from (b) and the scale factor from (c).

Figure 1 was generated with the program ORTEP3.[21] The difference density sections in Figure 3 were calculated with the program WinGX-98.[22] The rigid bond test and the T,L,S analysis were carried out with the program PLATON.[23]

Received: October 21, 1998 [Z12552IE]
German version: *Angew. Chem.* **1999**, *111*, 1356–1358

Keywords: difference electron density distribution · fullerenes · structure elucidation · X-ray scattering

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2,3,5-Tri-*tert*-butyl-1-carba-*nido*-tetraborane**

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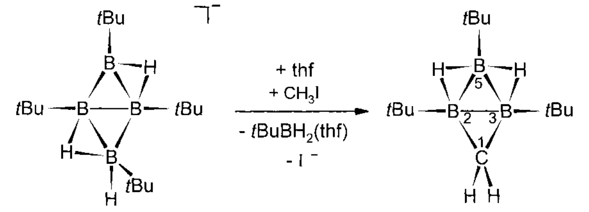
Dedicated to Professor Bernt Krebs
on the occasion of his 60th birthday

In the series of isoelectronic *nido* clusters B_4H_8, CB_3H_7, and NB_3H_6, the *tert*-butyl derivatives $B_4H_4t\text{Bu}_4$[1] and $NB_3H_2t\text{Bu}_4$[2] are well known. We report here on a derivative, $CB_3H_4t\text{Bu}_3$, of the missing link. It is formed by the reaction of iodomethane and the *nido*-tetraborane $[B_4H_3t\text{Bu}_4]^-$[1] in thf in 90% yield [Eq. (a); the numbering of the skeletal atoms follows the IUPAC *nido* cluster rules that attribute the number 4 to the missing atom of the corresponding trigonal-bipyramidal *closo* cluster]. Traces of $B_4H_2t\text{Bu}_4$[3] and $B_4H_4t\text{Bu}_4$[1] cannot be removed from the product.



(a)

The structure of the product follows from the NMR spectra. C_s symmetry is concluded from the equivalence of the *t*Bu(2) and *t*Bu(3) groups and of the bridging protons. The coupling between the methylene protons in *exo*/*endo* position ($^2J = 13$ Hz) and between these and the bridging protons ($^3J(\mu/endo) = {}^3J(\mu/exo) = 6$ Hz) are found at the expected values. Homonuclear 2D couplings are observed between B(2)/B(3) and B(5) and between the methylene protons. All of the five ^{1}H NMR chemical shifts give heteronuclear 2D cross peaks: the μ-H atoms are coupled to both kinds of B atoms, the methylene-H atoms are related to the methylene-C atom, and the methyl-H atoms display 2D hetcor coupling not only with each neighboring C atom, but also with the more remote C

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[**] This work was supported by the Deutsche Forschungsgemeinschaft.

atoms of *t*Bu. No dynamic processes can be observed in the NMR spectra in a temperature range from -50 to $+90\,^{\circ}C$. Replacing the solvent thf with [D$_8$]toluene does not significantly alter the NMR spectra.

Ab initio calculations (B3LYP/6-31++G(d,p))[4] on the parent molecule CB_3H_7 and on its methyl derivative $CB_3H_4Me_3$ lead to minima on the potential energy hypersurfaces that represent bicyclobutane-type *nido* clusters with a CH_2 group in position 1 and hydrogen atoms that bridge B(2)/B(3) and B(5). The computed bond lengths and the angle between the planes through B(2)-B(3)-B(5) and B(2)-B(3)-C(1) for the molecules CB_3H_7, $CB_3H_4Me_3$, and $CB_3H_4tBu_3$ are summarized in Figure 1. The geometric data for the title compound are not significantly changed by going from the 6-31G(d) to the more sophisticated 6-31++G(d,p) level. The optimized geometric parameters were used as a basis for a calculation of the NMR signals using the GIAO method.[5] The computed chemical shifts of the skeletal atoms and the skeleton-bound H atoms of the molecules CB_3H_7, $CB_3H_4Me_3$, and $CB_3H_4tBu_3$, along with the corresponding experimental values, are summarized in Table 1. The good agreement of the calculated and observed values gives clear support for the adopted structure of the title compound.

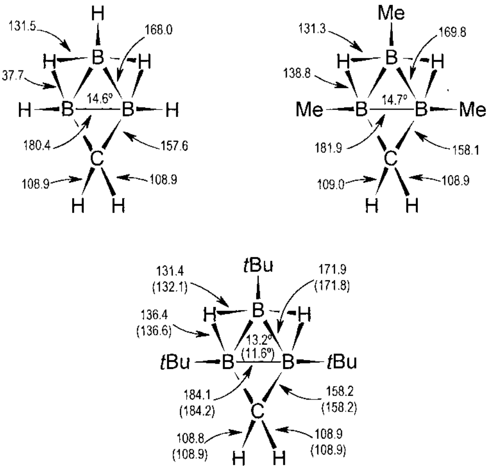

Figure 1. Calculated structure of the molecules CB_3H_7, $CB_3H_4Me_3$, and $CB_3H_4tBu_3$ with distances [pm] and angles [°] between the triangles BBB and BBC (6-31++G(d,p) level; numbers in parentheses: 6-31G(d) level).

Table 1. Calculated[a] and observed chemical shifts δ of $CB_3H_4R_3$ with R = H, Me, *t*Bu.

	CB_3H_7 calcd	$CB_3H_4Me_3$ calcd	$CB_3H_4tBu_3$ calcd	$CB_3H_4tBu_3$ exp.
^{1}H NMR: H$_{exo}$	0.721	0.143	0.226	0.307
^{1}H NMR: H$_{endo}$	2.105	1.789	1.363	1.362
^{1}H NMR: μ-H	-0.820	0.404	0.597	0.781
^{11}B NMR: B(2)	10.9	20.0	21.4	22.4
^{11}B NMR: B(5)	23.4	27.4	30.7	34.5
^{13}C NMR: C(1)	14.6	14.7	11.6	13.2

[a] B3LYP/GIAO at the 6-31++G(d,p) level.

The *closo*-tetraborane $B_4H_2tBu_4$[3] is obtained when the *nido* anion $[B_4H_3tBu_4]^-$ is oxidized by haloalkanes with bigger alkyl groups than methyl. This is shown in Equation (b) for the case of bromoethane.

$$[B_4H_3tBu_4]^- + C_2H_5Br \longrightarrow B_4H_2tBu_4 + C_2H_6 + Br^- \qquad \text{(b)}$$

The isoelectronic four-vertex *nido* clusters $B_4H_4tBu_4$,[1] $CB_3H_4tBu_3$, and $NB_3H_2tBu_4$[2] can be represented by structural formulae that make use of localized two-center, two-electron (2c2e) and three-center, two-electrom (3c2e) bonds and obey the octet rule (Figure 2). An equilibrium (c) between two tautomeric species has been observed in the case of $NB_3H_2tBu_4$.[2]

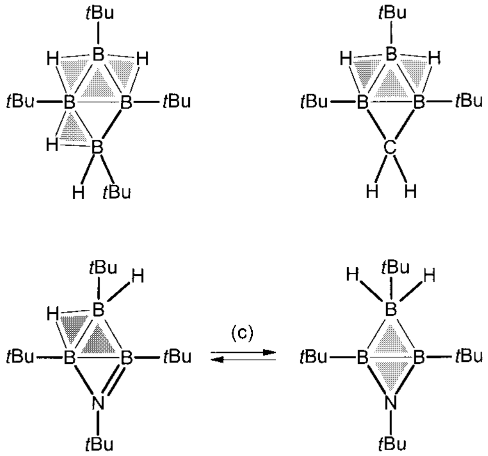

Figure 2. Localized bonds in the isoelectronic molecules $B_4H_4tBu_4$, $CB_3H_4tBu_3$, and $NB_3H_2tBu_4$ (equilibrium of two isomers) (bold lines: (2c2e) bonds; gray triangles: (3c2e) bonds).

The title compound can be derived from the three-vertex *nido* cluster $B_3H_4(tBu)_3$ by replacing two terminal H atoms by a bridging CH_2 group. It can be considered, therefore, to be a member of the family of *nido*-triboranes with B_3H_7 as the parent molecule. Although B_3H_7 itself has not yet been isolated, its *arachno* adducts with Lewis bases L of the type B_3H_7L have been known for many years.[6]

Experimental Section

2,3,5-Tri-*tert*-butyl-1-carba-*nido*-tetraborane: Iodomethane (78 mg, 0.55 mmol) was added to a solution of [K(thp)$_6$][B$_4$H$_3$*t*Bu$_4$] (400 mg, 0,48 mmol; thp = tetrahydropyran)[1] in thf (2 mL) at $-78\,^{\circ}C$. After 1 h stirring at ambient temperature, volatiles were removed in vacuo (5 mbar), and the residue was extracted with hexane (5 mL). The product was distilled into a cooled receiver (25 °C/0.001 mbar; 101 mg). According to NMR spectra, it contained equal amounts of $B_4H_2tBu_4$ and $B_4H_4tBu_4$ (ca. 5 % in total; yield of main product ca. 95 mg, i.e. ca. 90 %). The nonvolatile material (30 mg) that remained from the distillation gave H_2 on acidification. Apparently products of the decomposition of $(tBuBH_2)_2$ were present; this borane underwent an equilibrium with $tBuBH_2$(thf) in thf and decomposed into nonvolatile products of unknown structure after a while.[7] $^1H\{^{11}B\}$ NMR (500 MHz, [D$_8$]toluene): $\delta = 0.307$, 1.362 (2d, t, $^2J = 13$ Hz, $^3J = 6$ Hz; *exo*-H and *endo*-H of CH$_2$; assignment according to Table 1), 1.077, 1.093 (2s, 18H, 9H; *t*Bu), 0.781 (d,d, $^3J_1 = {}^3J_2 = 6$ Hz; 2μ-H); ^{11}B NMR (160.4 MHz,[D$_8$]toluene): $\delta = 22.4$, 34.5 (2:1); ^{13}C NMR (125.7 MHz, [D$_8$]toluene): $\delta = 13.2$ (broad, CH$_2$), 19.7 (C(1) of 3 *t*Bu), 31.85, 32.71 (Me of *t*Bu(2,3) and *t*Bu(5); assignment according to $^{13}C/^1H$ cross peaks).

Received: November 9, 1998 [Z12633IE]
German version: *Angew. Chem.* **1999**, *111*, 1358–1360

Keywords: ab initio calculations · boron · boranes · cluster compounds · electron deficiency

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A New In Vitro Model of Lignin Biosynthesis

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There are still many open questions concerning the structure as well as the peculiar biosynthesis of lignin.[1–3] The most accredited theories go back to the early 1960s, when Freudenberg and co-workers proposed dehydrogenation reactions as the dominating framework of a polymerization process which involves *p*-hydroxycinnamyl alcohols as the primary precursors and building blocks of all lignins.[4, 5] Numerous structural investigations of isolated and synthetic lignins and of model compounds then outlined a composite picture of a very complex, three-dimensional polymeric structure devoid of ordered repeating units, such as in the case of other biological macromolecules.[1, 5–11] According to these studies lignin production is triggered by the enzymatic formation of resonance-stabilized phenoxy radicals, while the polymerization is generally known to run as a non-enzymatic process which advances in a random fashion through radical and ionic steps. We now report that under in vitro homogeneous conditions—which, in principle, could be related to the natural microenvironment[12, 13]—a synthetic lignin is produced. The beginning of the polymerization process appears to be an alternating sequence of radical and ionic steps which generate ordered structures of oligolignols.

The polymerization of the monomeric precursor by random coupling reactions cannot be studied in vivo; many theories on lignin structure and biosynthesis rely upon in vitro experiments on the polymerization of coniferyl alcohol (**1**, Figure 1),[5, 7, 14] which is the most common natural lignin

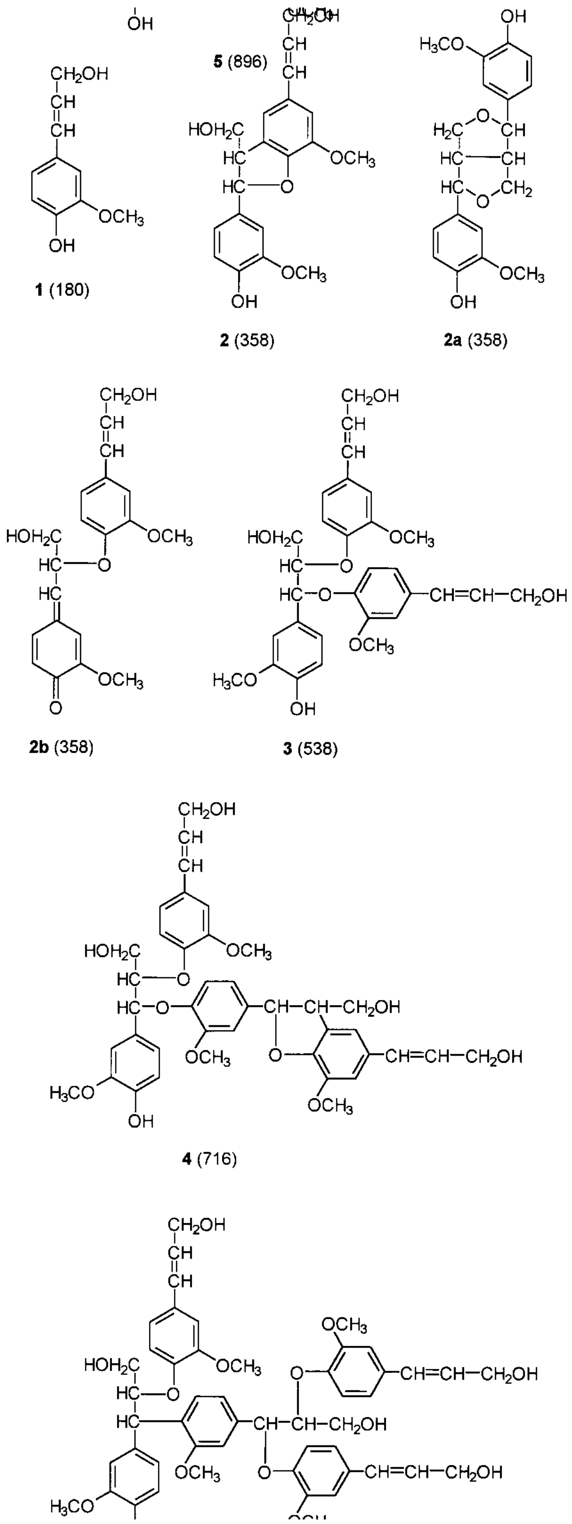
1 (180)
5 (896)
2 (358)
2a (358)
2b (358)
3 (538)
4 (716)

Figure 1. Schematic representation of oligolignols (molecular weights are given in parentheses).

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