Figure 2. The NMR spectra of the methyl group region of the *p*-toluidine in 1 M NaCl at 30 °C. The concentration of *p*-toluidine is 3.8 × 10⁻³ M. The large peak at 2.10 is due to sodium acetate, and the small peaks at both sides of this peak are spinning sidebands and carbon satellite peaks.

to a maximum molecular weight.[9] The repeat unit of our polymer is not flexible, and branching is imperfect;[10] thus, no definite steric saturation point at the surface could be found based on a molecular model. We cannot explain what causes the molecular growth to stop.

A molecular model[11] of the polymer (Figure 1) reveals a globular structure with many cavities. The average opening size of the.cavities was measured to be in the range of 5 Å.

A water-soluble derivative of the polymer was prepared by metalation with *n*-BuLi at −78 °C in THF, followed by reaction with CO_2.[12] The polymer was isolated as its Li salt. The titration curve of this salt with 0.1 M HCl showed a broad pK_a value for the acid group, ranging from 3.0 to 5.0. The conversion to carboxylate was estimated to be 70% of theory based on elemental analysis and the NMR spectrum after the carboxy group had been reduced to a hydroxymethyl function with borane. The carboxylate form of the polymer is very soluble in water (greater than 1 g/mL), without much change in the viscosity of the solution. The carboxylic acid ended polymer is water insoluble. The NMR spectrum of the acid-ended polymer in THF shows several well-resolved groups of peaks in the aromatic region, but the carboxylate polymer in an aqueous solution gives only a broad peak. This might be due to the ordered structure of the water in the cavities restricting the rotation of the phenyl rings more than a loosely bound organic solvent does.

The complexation with *p*-toluidine, a guest molecule, was studied by NMR.[13] All *p*-toluidine NMR peaks shifted upfield and broadened as the polymer was added. The effect is strongly

dependent on the ionic strength of the media, namely, with a polymer to *p*-toluidine ratio of 0.53, the chemical shift of the methyl group was 1.76[14] in 1.28 M and 2.03 in 0.13 M Na_2SO_4 solution. When the ratios were higher than 2.5 in a 1.9 M solution, the chemical shift reached a limiting value of 1.59. The equilibrium constant of the complex was determined in 1 M NaCl solution. At a 0.5 molar ratio of polymer to *p*-toluidine, the chemical shift change ($\Delta\delta$) of the methyl group and AB quartets of the phenyl ring were 0.08, 0.08 (ortho proton), and 0.10 (meta proton) ppm, respectively; at a molar ratio of 10, $\Delta\delta$ values of 0.66, 0.72, and 0.84 were found (Figure 2). An accurate equilibrium constant is difficult to obtain, since the polymer could form multiple complexes with *p*-toluidine when the ratio of host to guest is low. If we make two approximations, (1) only a 1:1 complex is formed and (2) the chemical shift for the methyl group of the complexed *p*-toluidine is 1.59, then an equilibrium constant of 510 (±150) M⁻¹ is estimated.[15]

In conclusion, an array of aromatic polymeric chains was able to generate an environment that resembles a micellar structure.[16] This microenvironment resembles a Flory–Dill model[3a] in the sense that all of the chains are pointing toward the center of the globular structure, but the accessibility of the cavity to water and connectivity of the chains is applicable to a Menger model.[3b]
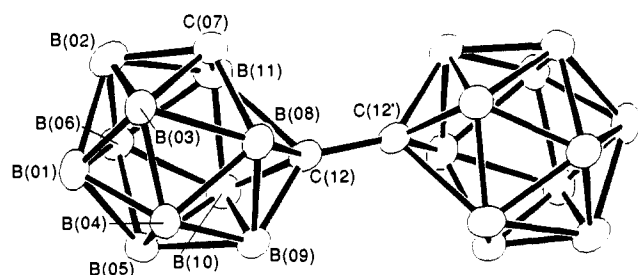
(9) De Gennes, P. G.; Hervet, H. *J. Phys. (Paris)* 1983, *44*, L351–L360.

(10) If the polymer (DP > 24, equivalent to three tiers) is fully branched, the ratio of the number of carbons (4-position) between two carbons connected to bromide to the number of carbons (1-position) connected to phenyl ring is 0.25. In the ¹³C NMR spectrum, the peaks due to these two kinds of carbon are well separated, and the branching factor was found to be in the range of 70%. The NMR spectrum was obtained by 20-s pulse delay while NOE was suppressed. The relaxation time of the quaternary carbon was found to be less than 5 s.

(11) Chem-X, developed and distributed by Chemical Design Ltd., Oxford, England.

(12) In a small-scale reaction, the yield of the lithiation was confirmed to be over 95% by quenching of the anion with trimethylchlorosilane. When the anion was quenched with MeOH, IR peaks at 700 and 799 cm⁻¹, due to monosubstituted benzene, appeared in addition to the peaks corresponding to trisubstituted benzene.

(13) This polymer solution also showed dissolution ability. A 10% solution of the lithium carboxylate polymer in water dissolves 1.1 mg of naphthalene in 1 mL of solution. The same amount of polymer in 0.1 M K_2HPO_4 solution also enhanced the solubility of methyl red and methyl orange 30 times and twice, respectively.

(14) Sodium acetate was used as an internal standard with the chemical shift 2.100. The chemical shift of sodium acetate was invariable relative to the water peak in addition of the polymer. The pH of the solution was 9.6.

(15) The 10 data points were plotted to an equation $R/r = 1 + 1/[Kt(1 - r)]$ where R is the molar ratio between the polymer and *p*-toluidine, r is the ratio between the $\Delta\delta$ at the given R and the maximum $\Delta\delta$, and t is the concentration of *p*-toluidine. The correlation factor for the fit was 0.82.

(16) The term micelle was introduced in 1858 by a Swiss botanist, C. van Naegeli, who described a cell as an aggregate of 9000 molecules of starch packed in a crystalline array. Polymers were believed to have micellar structures (the micellar theory) until the 1920s.

Multiple-Bond Character between Two Carborane Polyhedra: The Two-Electron Reduction of Biscarborane

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In an effort to extend the chemistry and possibly determine the molecular structure of the $[nido\text{-}C_2B_{10}H_{12}]^{2-}$ anion,[1–3] a valuable synthon for numerous metallacarboranes,[4–8] biscarborane[9] was

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(8) Alcock, N. W.; Taylor, J. G.; Wallbridge, M. G. H. *J. Chem. Soc., Dalton Trans.* 1987, 1805.

(9) The term biscarborane here refers to 1-1'-(*closo*-1',2'-$C_2B_{10}H_{11}$)-*closo*-1,2-$C_2B_{10}H_{11}$. (a) Dupont, J. A.; Hawthorne, M. F. *J. Am. Chem. Soc.* 1964, *86*, 1643. (b) Paxson, T. E.; Callahan, K. P.; Hawthorne, M. F. *Inorg. Chem.* 1973, *12*, 708.
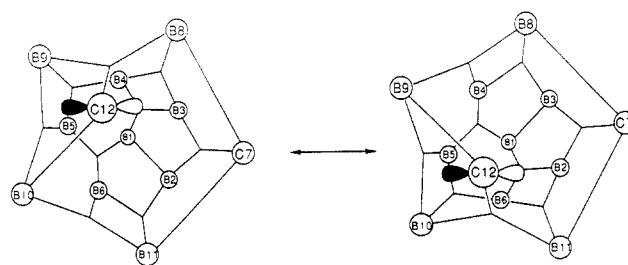
Figure 1. The molecular structure of **1** with thermal ellipsoids drawn at 50% probability. The terminal hydrogen atoms have been omitted for clarity. The distance 1.95 Å was arbitrarily chosen as the cutoff point for the representation of connectivity between boron and carbon.

Figure 2. Two resonance structures which represent the bonding within **1**. The singly occupied p orbital on C12 combines with its counterpart on C12′ to form a double bond. The apparent change in position of C12 between structures does not represent atomic motion, but is done to enhance the clarity of the illustration. C12 = sp^2 C, C7 = CH, and B = BH.

reduced by two electrons. One possible course for this reaction would result in the formation of a species that contained one carborane cage opened by the reduction and analogous to the [*nido*-$C_2B_{10}H_{12}$]$^{2-}$ anion, while the second closo cage would serve solely as an ancillary group, which would aid in forming an ordered crystal. However, the ^{11}B FT-NMR spectrum of the product did not exhibit the pattern[10] expected for this reaction course. Presented herein is the characterization of the species (**1**) that was actually formed. The molecular structure of [P(C_6H_5)$_3$C-H_3]$_2$(**1**) was determined by single-crystal X-ray diffraction and is also presented. The anion, **1**, represents the first example of a species that exhibits multiple-bond character between the carbon atoms of two adjacent carborane cages.

When a THF solution of biscarborane is reacted with 2 equiv of sodium metal or sodium naphthalide solution, the intensely orange disodium salt Na_2(**1**) is formed.[11] The salt [P(C_6H_5)$_3$-CH_3]$_2$(**1**) can be isolated in moderate yields by the metathesis reaction of Na_2(**1**) with [P(C_6H_5)$_3CH_3$]Br. Crystals of [P(C_6-H_5)$_3CH_3$]$_2$(**1**) were obtained from an acetonitrile solution,[11] and one of these was employed in a single-crystal X-ray diffraction experiment to determine the molecular structure of [P(C_6H_5)$_3$-CH_3]$_2$(**1**),[12] Figure 1.

The molecular structure of **1** consists of two crystallographically equivalent $C_2B_{10}H_{11}$ carborane cages related by an inversion center located at the center of the C12–C12′ bond, which connects the cages. The C12–C12′ distance is 1.377 (4) Å, which reveals the existence of substantial double-bond character.[13] The reduction has resulted in the cleavage of the polyhedral C–C bonding interaction that exists in biscarborane (C7–C12 2.414 (4) Å). The C12–B9 and C12–B10 interatomic distances, 1.628 (4) and 1.643 (4) Å, respectively, are short but within the normal range for C–B bond distances in carboranes.[14] However, the C12–B8 and C12–B11 interatomic distances, 1.838 (4) and 1.925 (4) Å, respectively, are in the area of uncertainty[14] for what may be considered a bonding interaction.

The pentagon formed by the atoms C7–B8–B9–B10–B11 (upper belt) is not planar. C7 is 0.361 Å out of the least-squares plane formed by B8–B9–B10–B11 (plane *B*), in the direction of the plane formed by B2–B3–B4–B5–B6 (lower belt). The atoms of the lower belt are within 0.06 Å of the least-squares plane through themselves. The angle between plane *B* and the lower belt is 4.9°. The angle between plane *B* and the plane described by B8–C7–B11 is 19.4°. The angle between plane *B* and the plane described by B9–B10–C12 is 50°. The angle between the vector

described by C12–C12′ and the plane described by B9–B10–C12 is 36°.

The structure of **1** is closely related to the structure of the most stable isomer[15] of [*nido*-$C_2B_{10}H_{13}$]$^-$ (**2**), described by Tolpin and Lipscomb[15b] (0941 styx topology). In the latter ion, a methylene group is held in an endo fashion to two nearest-neighbor boron atoms (B9 and B10 in Figure 1) by a pair of two-electron two-center bonds. The sp^3 carbon atom in this methylene group may accommodate this bonding scheme without prohibitive stereochemical consequences. In **1**, the methylene bridge of **2** has been conceptually converted to a divalent sp^2 carbon (C12 and C12′) derived from an alkene moiety with concomitant opening of the divalent carbon bond angle from an ideal 109° to 120°. In order to accommodate this increased angle between divalent carbon atom orbitals, C12 (and C12′) moves near the center of the pentagonal face and may attain additional stabilization through long three-center bonds utilizing B8–B9 and B10–B11 as illustrated in the resonance structures of Figure 2. The two equivalent structures are only two of many that satisfy the overall geometry of **1**. The observation of two long and two short C12–B interatomic distances is in agreement with this description. Most probably the fact that the two long C12–B interatomic distances (1.838 (4) and 1.925 (4) Å) and to a lesser extent other symmetry-related interatomic distances are unequal is due to packing forces within the crystal lattice.

Solutions of Na_2(**1**) may be air-oxidized to regenerate the starting bicarborane. The addition of 2 equiv of sodium or sodium naphthalide solution to a THF solution of Na_2(**1**) results in the complete uptake of the reductant, loss of the intense orange color of **1**, and the formation of a light yellow solution. The characterization of the product(s) formed during this reaction is not yet complete. However, it seems likely that a two-electron reduction of **1** would result in loss of the multiple-bond character between C12 and C12′ with the formation of a [(*nido*-$C_2B_{10}H_{11}$)$^{2-}$]$_2$ species. The characterization of this species and the investigation of the chemistry of **1** are in progress. The uptake of two or four electrons by biscarborane has stimulated an interest in the partial reduction of larger carborane oligomers. The synthesis of carborane oligomers containing more than two repeat units is currently in progress.

Supplementary Material Available: Complete details of the synthesis and characterization of **1**, complete details of the solution of the structure of **1**, and tables of crystallographic data, positional and thermal parameters, interatomic distances and angles, and torsion angles for **1** (11 pages); listing of observed and calculated structure factors for **1** (16 pages). Ordering information is given on any current masthead page.

(10) A pattern consisting of 10 resonances due to the reduced cage and six resonances due to the ancillary cage would be expected for a [*nido-closo*]$^{2-}$ species. The observed ^{11}B FT-NMR spectra consisted of only five resonances,[11] thus indicating the existence of a mirror plane within the molecule.

(11) Complete experimental details on the synthesis of **1** and details of the characterization of **1** are presented in the supplementary material.

(12) Complete crystallographic details are given in the supplementary material.

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