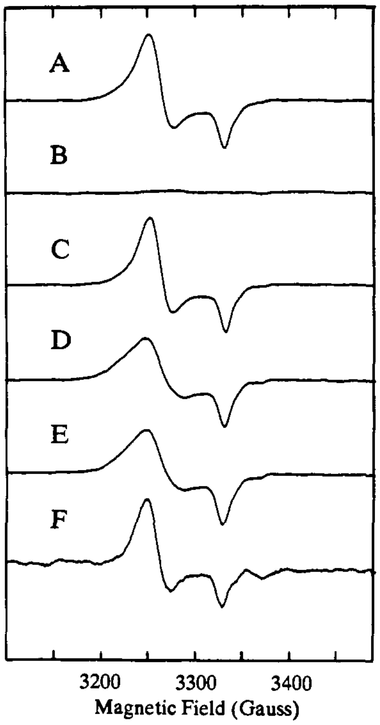

Figure 1. EPR spectra of CODH before and after addition of 1,10-phenanthroline and $NiCl_2$: A, CODH before addition of phen; B, CODH (sample used in A) after phen; C, phen-treated CODH (sample used in B) after addition of Ni^{2+}; D, phen-treated CODH after addition of $^{61}Ni^{2+}$; E, CODH from bacteria grown in ^{61}Ni-enriched media; F, phen-treated CODH (sample used in E) after addition of natural-abundance Ni^{2+}. Sample concentrations: A–D, 2.7 mg/mL; E and F, 1.8 mg/mL. Samples were reduced by CO. EPR conditions: temperature, 130 K; microwave power, 80 mW; microwave frequency, 9.45 GHz.

for one or more of the substrates used in acetyl-CoA synthesis.

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Rigid-Rod Molecules: Carborods. Synthesis of Tetrameric *p*-Carboranes and the Crystal Structure of Bis(tri-*n*-butylsilyl)tetra-*p*-carborane

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The design and synthesis of rigid-rod molecules has recently attracted increasing attention, because of their potential application in nanoarchitecture[1] and the preparation of novel materials.[2] Rod-like molecules containing two to five polycyclic units such as bicyclo[1.1.1]pentane,[3] bicyclo[2.2.2]octane,[4] and cubane[5] have been reported recently. The recognition of the need for small and rigid molecular structures has led us to the synthesis of rods, rings, and related motifs based upon the use of exceedingly stable carborane cages as building blocks. New and efficient synthetic methods have been developed in our laboratory for the synthesis of carborane-containing rigid-rod molecules (carborods) capable of functionalization at their C–H termini. We report here the first successful synthesis of tetrameric *p*-carborane and the crystal structure of bis(tri-*n*-butylsilyl)tetra-*p*-carborane.

Our synthesis of carborane-containing rigid-rod molecules starts with the coupling of two 1,12-$C_2B_{10}H_{12}$ (*p*-carborane) (**1**) cages forming a C–C bond. This was achieved by the reaction of 1-Li-1,12-$C_2B_{10}H_{11}$ with CuCl or $CuCl_2$.[6] Accordingly, we attempted to prepare the tetrameric *p*-carborane in a single reaction by coupling dilithiated **1** with 2 equiv of $CuCl_2$ in refluxing diethyl ether (Scheme IA). The tetrameric **3** was formed in 16% yield and the dimer **2** in 80% yield after a 3-day reaction. We suggest that the dimeric **2** anion is first formed and further coupling gives the tetrameric **3** anion. Acidic workup led to **3** as an insoluble white solid.[7] **2** is soluble in Et_2O, THF, and benzene and was characterized by NMR spectroscopy.[8] The ^{11}B NMR spectrum of **2** contains two peaks corresponding to two types of boron atoms in **2**. The EIMS of **3** exhibits the molecular ion at *m/z* 570.[7] The poor solubility of **3** in organic solvents precluded its complete characterization by NMR spectroscopy. An attempt to functionalize **3** by introducing R_3Si groups was also unsuccessful due to the poor solubility of **3**.

The synthesis of soluble tetrameric *p*-carboranes (**5**) was achieved by functionalizing **2** with a solubility-enhancing trialkylsilyl group to give **4**, which was subsequently monolithiated by *n*-BuLi and coupled by 1 equiv of $CuCl_2$ (Scheme IB; alkyl = *n*-hexyl, *n*-butyl, and isobutyl). **4a–c** were obtained in 52–79% yields and characterized by multinuclear NMR spectroscopy.[9] The ^{11}B NMR spectra of **4a–c** each showed four resonances as expected. **4a–c** are very soluble in common organic solvents, and

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(7) Spectroscopic data for **3**: IR (KBr, cm^{-1}) ν 2612 (B–H), 3101 (C–H); EIMS (70 eV, 150 °C) *m/z* 570 (M^+, 19, calcd for $C_8H_{42}{}^{10}B_8{}^{11}B_{32}$), 427 ($M - C_2B_{10}H_{11}$, 100).

(8) Spectroscopic data for **2**: mp 330–332 °C; ^1H NMR (500 MHz, C_6D_6, ppm) δ 1.6–2.9 (m, B*H*, 20 H), 1.82 (s, carborane C*H*, 2 H); ^{13}C NMR (90 MHz, C_6D_6, decoupled) δ 83.9 (carborane *CC*), 61.7 (carborane *C*H); ^{11}B NMR (160 MHz, THF, 25 °C, $BF_3 \cdot Et_2O$ external, decoupled) δ −12.3, −15.8 (1:1); IR (KBr, cm^{-1}) ν 2606 (B–H), 3064 (C–H); EIMS *m/z* 286 (M^+, 94, calcd for $C_4H_{22}{}^{10}B_4{}^{11}B_{16}$).

(9) Spectroscopic data for **4a**: mp 132–133 °C; ^1H NMR (360 MHz, C_6D_6) δ 2.72 (s, carborane C*H*), 3.4–1.8 (m, B*H*, 20 H), peaks due to *n*-hexyl groups; $^{13}C\{H\}$ NMR (360 MHz, C_6D_6) δ 61.7 (carborane *C*H), 71.8 (carborane *C*Si), 84.2 (carborane *CC*), 87.1 (carborane *CC*), peaks due to *n*-hexyl; $^{11}B\{H\}$ NMR (Et_2O) −15.1, −13.0, −11.5, −10.2; IR (Nujol, cm^{-1}) ν 2612 (B–H), 3026 (C–H); FAB-MS *m/z* 569 (M^+, 20, calcd for $C_{42}H_{60}{}^{10}B_4{}^{11}B_{16}Si$). **4b**: mp 221–222 °C; ^1H NMR (360 MHz, $CDCl_3$) δ 2.68 (s, carborane C*H*), 3.3–1.4 (m, B*H*, 20 H), peaks due to *n*-butyl groups; $^{13}C\{H\}$ NMR (360 MHz, $CDCl_3$) δ 61.3 (carborane *C*H), 71.3 (carborane *C*Si), 83.8 (carborane *CC*), 86.3 (carborane *CC*), peaks due to *n*-butyl; $^{11}B\{H\}$ NMR (Et_2O) −15.3, −13.2, −11.7, −10.4; IR (Nujol, cm^{-1}) ν 2612 (B–H), 3026 (C–H); FAB-MS *m/z* 485 (M^+, 20, calcd for $C_{16}H_{48}{}^{10}B_4{}^{11}B_{16}Si$). **4c**: mp 168–169 °C; ^1H NMR (360 MHz, $CDCl_3$) δ 2.68 (s, carborane C*H*), 3.4–1.6 (m, B*H*, 20 H), peaks due to isobutyl groups; $^{13}C\{H\}$ NMR (360 MHz, $CDCl_3$) δ 61.3 (carborane *C*H), 72.5 (carborane *C*Si), 84.0 (carborane *CC*), 87.2 (carborane *CC*), peaks due to isobutyl groups; $^{11}B\{H\}$ NMR (Et_2O) −14.8, −12.7, −11.3, −10.0; IR (Nujol, cm^{-1}) ν 2620 (B–H), 3039 (C–H); FAB-MS *m/z* 485 (M^+, 20, calcd for $C_{16}H_{48}{}^{10}B_4{}^{11}B_{16}Si$).

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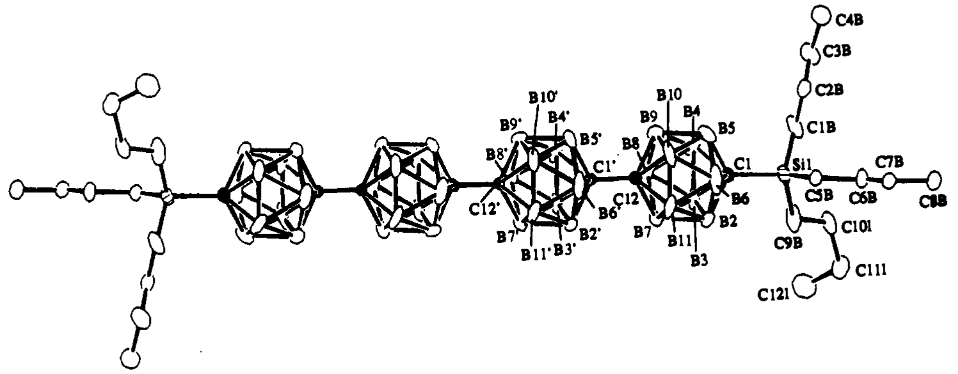
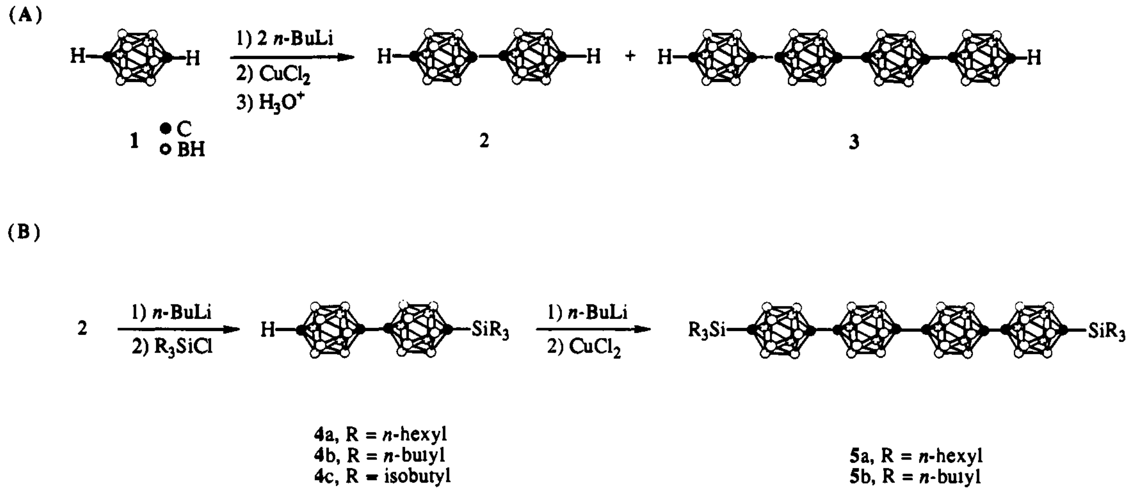


Figure 1. ORTEP representation of **5b** with hydrogen atoms removed for clarity. Some selected interatomic distances (Å) are as follows: C12–C1′ = 1.532 (7), C12′–C12′,2 = 1.533 (7), C1···C12 = 3.157 (7), C1′···C12′ = 3.142 (7), C1···C1,2 = 17.195 (7), C1–Si1 = 1.925 (6), C–B = 1.712 (9) (av), B–B = 1.758 (av). Atoms labeled with ",2" are in the positions related by the inversion symmetry of **5b**.

Scheme I



the coupling of lithiated **4a,b** gives the corresponding **5** in ca. 60% yield. **5a** is soluble in common nonpolar organic solvents, and **5b** is soluble in THF. The increased solubility of **5a,b** would facilitate reactions leading to octameric *p*-carboranes. **5a,b** were characterized[10] by NMR spectroscopy, FAB-MS, and X-ray crystallography (**5b**). The ^{11}B NMR spectra of **5a,b** contain four resonances of equal intensity.

An ORTEP drawing[11] of **5b** is shown in Figure 1. Although the data were collected at −117 °C, one of three *n*-butyl groups is disordered in the crystal. **5b** has a crystallographically imposed inversion symmetry with a rigid-rod structure and consists of four icosahedral cages connected through three C–C bonds. C12′–C12′,2[16] is 1.533 (7) Å, and C1′–C12 is 1.532 (7) Å. Both bonds are shorter than a C(sp^3)–C(sp^3) single bond (1.572 (35) Å)[12] and similar to that observed for bis(*p*-carborane) (1.553 (26) Å) in electron diffraction studies.[13] The intercage C–C bond length is 1.522 (2) Å for 1,1′-bis(*o*-carborane),[14] and the intracage C–C bond is 1.65 (5) Å for *o*-carborane by electron diffraction.[15] In comparison, intercage C–C bond distances are 1.458 Å for cubylcubane[12] and 1.474 Å for 1,4-bis(bicyclo[1.1.1]pent-1-yl)cubane.[3c] The short intercage distances are attributed to the greater s character of the exocyclic 4-coordinate carbon orbitals of cubane and bicyclo[1.1.1]pentane.[3d,12] **5b** is linear within 1° with C1···C12–C1′, C1′···C12′–C12′,2,[16] and C12–C1′···C12′ angles equal to 179.5 (3), 179.0 (4), and 179.8 (3)°, respectively. The *p*-carborane cages of **5b** are not eclipsed with respect to intercage C–C bonds. **5b** has a pseudo-D_{5d} symmetry, and the length of the tetramer is 17.21 Å from C1 to C1,2,[16] excluding the two tri-*n*-butylsilyl groups. To our knowledge, **5b** is the longest rigid-rod molecule to be structurally characterized.[3c]

The efficacious synthesis of bis(tri-*n*-butylsilyl)tetra-*p*-carborane provides a new entry to rigid-rod molecules. The trialkylsilyl capping groups not only increase the solubility of carborod molecules but also provide the possibility of further coupling of carborods with themselves, other organic cage and ring compounds, or electrophilic reagents which introduce functional groups, since trialkylsilyl groups can be easily removed[17] and the resulting C–H bond metalated at will. Subsequently, the monoprotected intermediate can be coupled to give a new carborod of doubled length. In principle, this cycle can be repeated *i* times to give carborods with 2^i *p*-carborane residues,[18] as long as the carborod

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(10) Spectroscopic data for **5a**: mp 185–186 °C; ^{1}H NMR (360 MHz, C_6D_6) δ 3.5–1.8 (m, B*H*, 20 H), peaks due to *n*-hexyl groups; ^{11}B{H} NMR (Et_2O) −14.9, −12.9, −11.4, −10.1; IR (Nujol, cm^{-1}) ν 2622 (B–H), FAB-MS *m/z* 1135 (M$^+$, 18, calcd for $C_{44}H_{118}{}^{10}B_8{}^{11}B_{32}Si_2$). **5b**: mp >360 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ 3.3–1.7 (m, B*H*, 20 H), peaks due to *n*-butyl groups; ^{11}B{H} NMR (Et_2O) −14.9, −12.8, −11.3, −10.0; IR (Nujol, cm^{-1}) ν 2625 (B–H); FAB-MS *m/z* 967 (M$^+$, 20, $C_{32}H_{94}{}^{10}B_8{}^{11}B_{32}Si_2$).

(11) Crystallographic data for **5b**: $C_{32}H_{94}B_{40}Si_2$, triclinic, space group $P\bar{1}$; a = 9.3393 (7) Å, b = 11.1392 (8) Å, c = 15.589 (1) Å, α = 98.633 (2)°, β = 104.448 (2)°, γ = 104.769 (2)°, V = 1479 Å^3, Z = 1, ρ_{calcd} = 1.22 g·cm^{-3}, μ = 0.9 cm^{-1}. Data were collected on a Picker FACS-1 diffractometer, using Mo Kα radiation, to a maximum 2θ = 50°, giving 5198 unique reflections, and the structure was solved by direct methods. The final discrepancy index was R = 0.076, R_w = 0.103 for 2800 independent reflections with $I > 3\sigma(I)$.

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(16) Atoms labeled with ",2" are in the positions related by the inversion symmetry of **5b**.

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products remain soluble. The extension of this synthetic method to other rigid-rod molecules containing organic cages, rings, acetylenic moieties, and organic functional groups is now under active investigation.

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Supplementary Material Available: Tables of positional and thermal parameters, bond lengths and angles, and crystallographic data for **5b** (6 pages); listing of observed and calculated structure factors for **5b** (17 pages). Ordering information is given on any current masthead page.

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(18) A similar process has been reported to synthesize phenylacetylene oligomers. See: Zhang, J.; Moore, J. S.; Xu, Z.; Aguirre, R. A. *J. Am. Chem. Soc.* **1992**, *114*, 2273.

Rigid-Rod Oligo-*p*-Carboranes for Molecular Tinkertoys. An Inorganic Langmuir–Blodgett Film with a Functionalized Outer Surface

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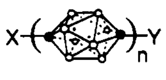
Terminally functionalized transparent rigid-rod molecules are expected to be useful in the "tinkertoy" construction of molecular superstructures,[1-3] as spacers in investigations of energy and electron[4,5] transfer rates, spin density propagation,[6] etc., and for many other purposes. The rods known so far are carbon-based: the oligomers of [1.1.1]-[1-3] and [2.2.2]-propellanes,[4,5] 1,4-cubanediyl,[7] and their various combinations.[8] UV–visible absorbing carbon-based rods such as polyynes, polyphenylenes, and more complicated structures[9] are also known. We have recently disclosed[10] the addition of two further classes of functionalized boron-based rigid rods (**1**, **2**) to this growing list, and we now illustrate their utility by assembling an inorganic Langmuir–Blodgett (L–B) rigid-rod monolayer.

The starting materials are the parent 10-vertex[11] (1,10-$C_2B_8H_{10}$) and 12-vertex[12] (1,12-$C_2B_{10}H_{12}$) *p*-carboranes, **1** ($n = 1, X = Y = H$) and **2** ($n = 1, X = Y = H$). The black dots in their structures stand for C and the white ones for BH. Although oxidative coupling of their Li salts with $CuCl_2$ to the parent dimers **1** ($n = 2, X = Y = H$)[13] and **2** ($n = 2, X = Y = H$)[14] was reported long ago, no derivatives nor higher oligomers were known. We have combined this coupling reaction with standard terminal functionalization procedures that exploit the acidity of the terminal CH groups, a decided advantage over the usual carbon-based rods, and with their facile protection with trialkylsilyl chlorides and deprotection with fluoride to prepare two series of rods, **1** and **2**.



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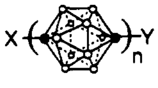

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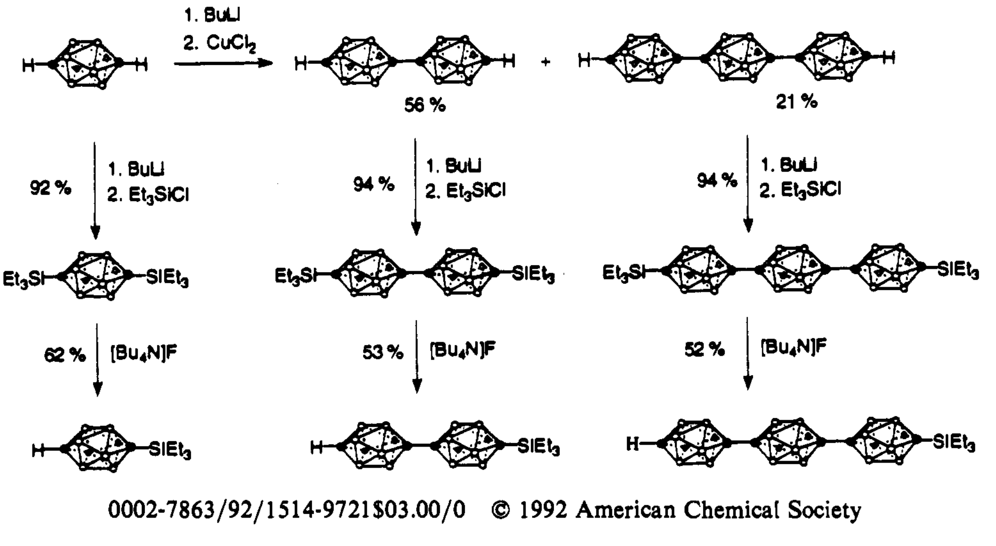
The reactions in Scheme I[15] take advantage of the separability of **1** ($n = 2, X = Y = H$) and **1** ($n = 3, X = Y = H$) by sublimation and outline the preparation of singly silylated rods, n = 1–3, in series **1**. These are useful for further oxidative length doubling and for the selective synthesis of terminally monosubstituted and differentially disubstituted derivatives. A selection from similar results obtained in series **2** is given in Scheme II.[15] Regularities in ^{11}B NMR chemical shifts provide an excellent characterization tool for the new rigid-rod structures,[16] as exemplified in Table I.

We are currently examining the utility of the new rigid rods. The first application attempted was the assembly of a new type of inorganic L–B film. One of the opportunities offered by the reduced mobility in monolayers built from rigid-rod molecules,[17] as opposed to the usual floppy chains, is likely to be a facile derivatization of the outer surface without much concern for interference by undesirable interactions between reactive centers located at the outer ends of neighboring rods. The rods are firmly held in the assembly, and their ends can neither approach very closely nor rotate freely to adopt the conformations optimal for such interactions. In this regard, the relatively thick rods of type **1** (van der Waals diameter D estimated at 7.1 Å[18]), and particularly **2** (D estimated at 7.65 Å[19]), may be preferable to the thinner rods of the staffane type (D = ~5.5 Å[20]).

Of the monocarboxylic acids described in Scheme II, the iodo acid **2** ($n = 1, X = COOH, Y = I$) and the acid **2** ($n = 2, X = COOH, Y = H$) are too soluble in water, but the iodo acid **2** ($n = 2, X = COOH, Y = I$) yields a highly satisfactory Langmuir isotherm on water surface. With Cd^{2+} counterions, the surface area per molecule, extrapolated to zero surface pressure, is A = 44.4 Å^2 (from A = ~26 Å^2 for [n]staffane-3-carboxylates[17] and

Scheme I



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