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.

Acknowledgment. We are grateful to the National Science Foundation for support of this work (DMR-9014487).

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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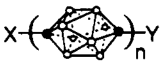
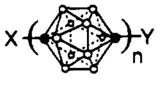
Terminally functionalized transparent rigid-rod molecules are expected to be useful in the "tinkertoy" construction of molecular superstructures,[1-3] as spacers in investigations of energy and electron[4,5] transfer rates, spin density propagation,[6] etc., and for many other purposes. The rods known 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**.



1



2

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

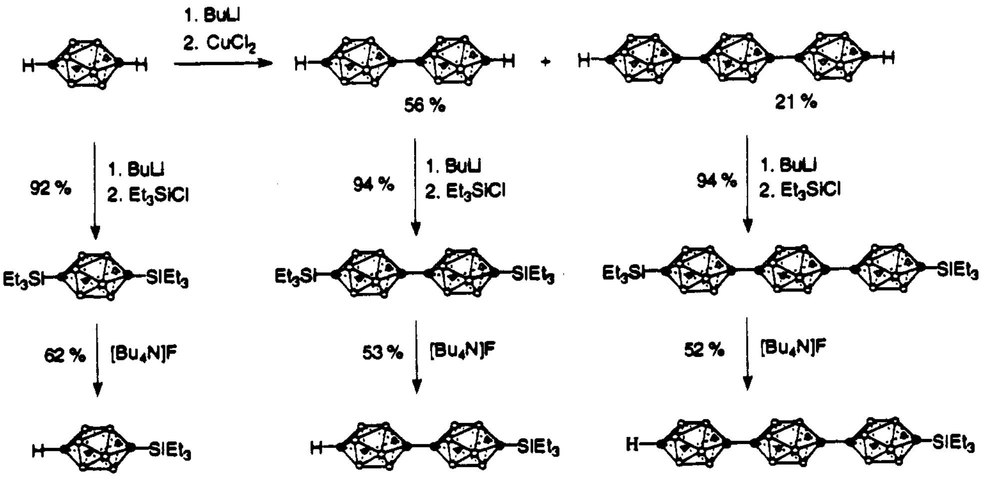


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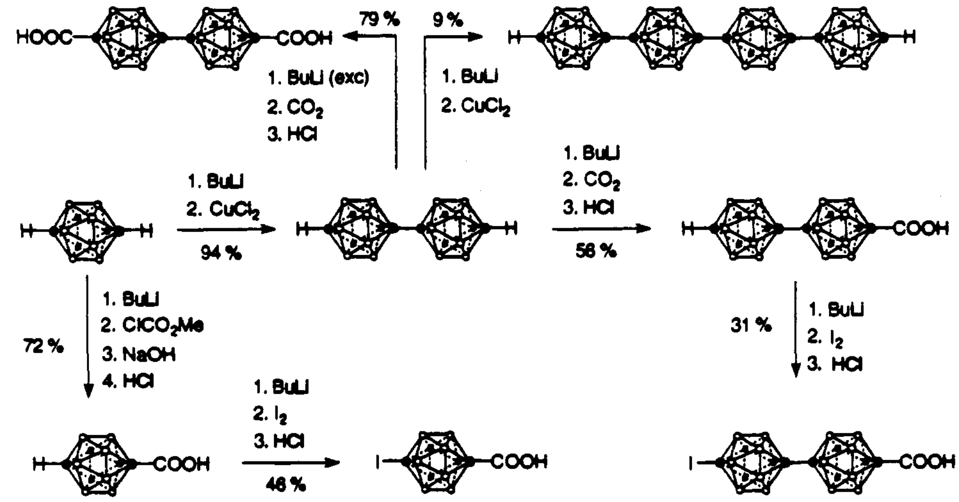
Table I. ^{11}B Chemical Shifts in Selected Oligo-*p*-Carboranes **1** and **2**[a]

	X	Y	*n*	δ_1	δ_2	δ_3	δ_4	δ_5	δ_6
1[b]	H	H	1	−13.8	−13.8				
			2	−13.7	−9.8	−9.8	−13.7		
			3	−13.7	−9.8	−9.8	−9.8	−9.8	−13.7
	H	SiEt$_3$[c]	1	−12.0	−12.0				
			2	−13.8	−10.0	−8.1	−12.3		
			3	−13.7	−9.9	−9.9	−9.9	−8.0	−12.2
	SiEt$_3$	SiEt$_3$	1	−10.1	−10.1				
			2	−12.3	−8.3	−8.3	−12.3		
			3	−12.2	−8.0	−10.1	−10.1	−8.0	−12.2
2[d]	H	H	1	−15.8	−15.8				
			2	−15.8	−12.2	−12.2	−15.8		
			4		insoluble, characterized by IR and MS only				
	H	COOH	1	−15.2	−13.5				
			2	−15.9	−12.6	−12.6	−14.6		
			2[b,e]	−15.25	−12.5	−12.5	−14.25		
	I	COOH	1	−10.3	−12.4				
			2	−10.9	−10.9	−12.7	−14.4		
	COOH	COOH	1[b,e]	−14.1	−14.1				
			2[e]	−14.2	−12.8	−12.8	−14.2		

[a] δ_1 refers to the chemical shift (in ppm, relative to BF$_3$–Et$_2$O) of the four (in **1**) or five (in **2**) equivalent boron atoms in the positions closest to substituent X; δ_2 refers to the next closest group of equivalent boron atoms, etc. Measured on a Varian VXR 300 instrument. Solvent: CDCl$_3$. Standard: B(OMe)$_3$. [b] External standard. [c] Assignments based on 2D ^{11}B NMR measurements. [d] Internal standard. [e] In acetone-d_6.

Scheme II



the diameter ratio of ~1.4, we would have expected A = ~50 Å^2 if the packing were identical). At 20 mN/m, A = ~40 Å^2. The stable monolayer transfers well onto standard substrates to yield sturdy L–B monolayers and multilayers with transfer ratios between 0.8 and 0.9. The activation of the iodine atoms by irradiation is currently under investigation.

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Supplementary Material Available: Listings of experimental procedures and spectral data for the *p*-carboranes (9 pages). Ordering information is given on any current masthead page.

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(1) Kaszynski, P.; Michl, J. *J. Am. Chem. Soc.* **1988**, *110*, 5225.

(2) Michl, J.; Kaszynski, P.; Friedli, A. C.; Murthy, G. S.; Yang, H.-C.; Robinson, R. E.; McMurdie, N. D.; Kim, T. In *Strain and Its Implications in Organic Chemistry*; de Meijere, A., Blechert, S., Eds.; NATO ASI Series 273; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1989; p 463.

(3) Kaszynski, P.; Friedli, A. C.; Michl, J. *J Am. Chem. Soc.* **1991**, *114*, 601.

(4) Zimmerman, H. E.; Goldman, T. D.; Hirzel, T. K.; Schmidt, S. P. *J. Org. Chem.* **1980**, *45*, 3933.

(5) Leland, B. A.; Joran, A. D.; Felker, P. M.; Hopfield, J. J.; Zewail, A. H.; Dervan, P. B. *J. Phys. Chem.* **1985**, *89*, 5571.

(6) McKinley, A. J.; Ibrahim, P. N.; Balaji, V.; Michl, J. *J. Am. Chem. Soc.*, in press.

(7) Gilardi, R.; Maggini, M.; Eaton, P. E. *J. Am. Chem. Soc.* **1988**, *110*, 7232. Eaton, P. E.; Tsanaktsidis, J. *J. Am. Chem. Soc.* **1990**, *112*, 876. Hassenrück, K.; Radziszewski, J. G.; Balaji, V.; Murthy, G. S.; McKinley, A. J.; David, D. E.; Lynch, V. M.; Martin, H.-D.; Michl, J. *J. Am. Chem. Soc.* **1990**, *112*, 873.

(8) Hassenrück, K.; Murthy, G. S.; Lynch, V. M.; Michl, J. *J. Org. Chem.* **1990**, *55*, 1013.

(9) Kenny, P. W.; Miller, L. L. *J. Chem. Soc., Chem. Commun.* **1988**, 84.

(10) Baše, K.; Michl, J. Presented at BUSA 3, Washington State University, Pullman, WA, July 8–11, 1992, Abstract No. 70.

(11) Tebbe, F. N.; Garrett, P. M.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1968**, *90*, 869.

(12) Heying, T. L.; Ager, J. W.; Clark, S. L.; Mangold, D. L.; Goldstein, H. L.; Hillerman, M.; Polak, R. J.; Szymanski, J. W. *Inorg. Chem.* **1963**, *2*, 1089.

(13) Zakharkin, L. I.; Kovredov, A. I. *Zh. Obshch. Khim.* **1974**, *44*, 1860.

(14) Zakharkin, L. I.; Kovredov, A. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1973**, 1428.

(15) Yields of purified products.

(16) Complete standard spectral data have been obtained and will be published in a full report.

(17) Yang, H. C.; Magnera, T. F.; Lee, C.; Bard, A. J.; Michl, J. *Langmuir*, in press.

(18) Atavin, E. G.; Mastryukov, V. S.; Golubinskii, A. V.; Vilkov, L. V. *J. Mol. Struct.* **1980**, *65*, 259.

(19) Bohn, R. K.; Bohn, M. D. *Inorg. Chem.* **1971**, *10*, 350. Dorofeeva, O. V.; Mastryukov, V. S.; Vilkov, L. V.; Golubinskii, A. V.; Kovredov, A. I. *Zh. Strukt. Khim.* **1988**, *29*, 137.

(20) Friedli, A. C.; Lynch, V. M.; Kaszynski, P.; Michl, J. *Acta Crystallogr. B* **1990**, *46*, 377.