Communications to the Editor

Carboracycles: A Family of Novel Macrocyclic Carborane Derivatives

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We have recently reported the synthesis of rigid rod arrays of icosahedral *p*-carborane cages (carborods) and the structural characterization of a linear tetrameric derivative.[1] As a further result of a program to incorporate reactive carborane clusters within organized supramolecular structures, we report here the first syntheses and structural characterizations of macrocyclic *o*-carborane derivatives in which multiple carborane cages are linked by their C-atoms with hydrocarbon moieties of varying complexity. Currently known carbocyclic carborane derivatives consist of exocyclic ring derivatives in which the two carborane C-atoms of a single *o*-carborane cage are bridged by a hydrocarbon chain,[2a] and a series of cyclic and open-chain oligomers incorporating $C_2B_4H_6$ units were proposed.[2f] The cyclic diketone in which two *o*-carborane cages are linked in a six-membered ring by two carbonyl groups[3] has been structurally characterized[4] and provides the only previously known example of a multicage cycle of which we are aware.

The recently described method for the selective protection of a single carbon vertex in *o*-carborane (CbH_2 hereafter) by attachment of a *tert*-butyldimethylsilyl group[5,6] has greatly enhanced the scope of *o*-carborane derivative chemistry, and the modular attachment of carborane cages (as in monolithiated **1**, (*t*-BuMe$_2$Si)CbLi) to organic electrophiles has allowed the synthesis of the first carboracycles, macrocyclic hydrocarbons which incorporate multiple di-C-functional *o*-carborane cages in their structures. Scheme I summarizes the two general routes leading to both trimethylene- and 1,3-xylyl-linked carboracycles and includes pertinent yield data. Syntheses involve lithiation of (*t*-BuMe$_2$Si)CbH (**1**) with *n*-BuLi, subsequent reaction of the lithiation product with the appropriate bifunctional electrophile, and desilylation of the product to afford the known carboracycle precursors $CH_2(CH_2CbH)_2$ (**2**),[6] 1,3-$C_6H_4(CH_2CbH)_2$ (**3**),[6] or $Cb(CH_2CH_2CH_2CbH)_2$ (**7**).[7] Dimetalation of these precursors with *n*-BuLi in either C_6H_6–Et_2O or THF solution followed by reaction with the desired $BrCH_2RCH_2Br$ produced the cyclodimer cyclo[Cb-1,3-$CH_2C_6H_4CH_2$]$_2$ (**5**),[8] the cyclotrimer cyclo[CH_2-$CbCH_2CH_2$]$_3$ (**8**),[9] and the cyclotetramers cyclo[CH_2CbCH_2-CH_2]$_4$ (**4**),[10] and cyclo[Cb-1,3-$CH_2C_6H_4CH_2$]$_4$ (**6**).[11] Analytical and spectroscopic data support the assigned structures of those compounds.

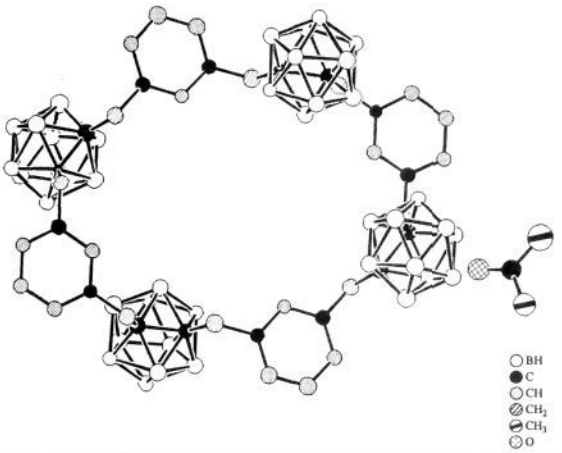

Figure 1. ORTEP representation of **6** with hydrogen atoms removed for clarity.

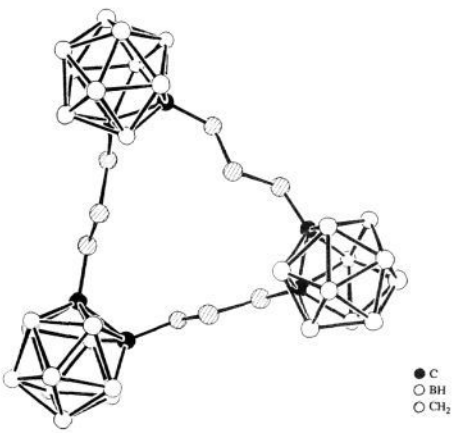

Figure 2. ORTEP representation of **8** with hydrogen atoms removed for clarity.

The structures of carboracycles **4**, **5**, **6**, and **8** were determined by X-ray diffraction studies. Due to space limitations, only the structures of **6** and **8** are presented in Figures 1 and 2, respectively. The structures of **4** and **5** will be published elsewhere.

The modular synthetic methods presented here provide the new macrocyclic carborane derivatives in practical yields by

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(8) Characterization data for **5**: IR (KBr) 2574 (s) ν_{B-H}; ^{1}H NMR (360 MHz, acetone-d_6) δ 7.84 (s, 2 H, H^2-C_6H_4), 7.46–7.31 (m, 6 H, H$^{4-6}$-C_6H_4), 3.99 (s, 8 H, CH_2); ^{13}C NMR (90 MHz, THF-d_8, proton decoupling) δ 135.6 (C^{1,3}-C_6H_4), 132.9 (C^2- or C^5-C_6H_4), 131.1 (C^{4,6}-C_6H_4), 128.1 (C^5- or C^2-C_6H_4), 84.1 (s, sh, C_{carb}), 39.8 (CH_2); ^{11}B NMR (160 MHz, THF) δ –5.08 (d, 4 B, 143), –8.61 (d, 8 B, 129), –12.37 (s, br, 8 B); HR EI-MS (70 eV, 250 °C) *m/e* for $C_{20}H_{36}{}^{10}B_4{}^{11}B_{16}$ calcd 492.4823, found 492.4800.

(9) Characterization data for **8**: mp > 300 °C; ^{1}H NMR (200 MHz, acetone-d_6, 25 °C) δ 1.87 (m, 6 H, CH_2), 2.48 (m, 12 H, $CbCH_2$), 0.69–3.30 (br, 30 H, H_{carb}); ^{13}C{^{1}H} NMR (50.3 MHz, acetone-d_6, 25 °C) δ 21.1 (s, CH_2), 30.5 (s, $CbCH_2$), 80.5 (s, br, C_{carb}); ^{11}B NMR (160 MHz, acetone-d_6, 25 °C) δ 4.90 (d, 6 B), –10.1 (d, 24 B); IR (Nujol) 2586 (s) ν_{B-H}; EI-MS *m/e* 552.5, (M$^+$, 100). Anal. Calcd for $C_{15}B_{30}H_{48}$: C, 32.58; H, 8.77; B, 58.65. Found: C, 33.09; H, 8.67; B, 58.24.

(10) Characterization data for **4**: mp > 300 °C; ^{1}H NMR (360 MHz, DMA-d_9, 70 °C) δ 2.11 (t, 8 H, J_{HH} = 7.2 Hz, CH_2), 2.94 (m, 16 H, $CbCH_2$), 0.69–3.30 (br, 40 H, H_{carb}); ^{11}B{^{1}H} NMR (160 MHz, DMA, 25 °C) δ 5.41 (s, 8 B), –10.60 (d, 32 B); IR (KBr) 2600 (s) ν_{B-H}; EI-MS *m/e* 735.9 (M$^+$, 100). Anal. Calcd for $C_{22}B_{40}H_{68.5}N_{0.5}O_{0.5}$ (**8**·0.5 DMA): C, 33.87; H, 8.79; B, 55.42. Found: C, 33.54; H, 8.39; B, 55.49.

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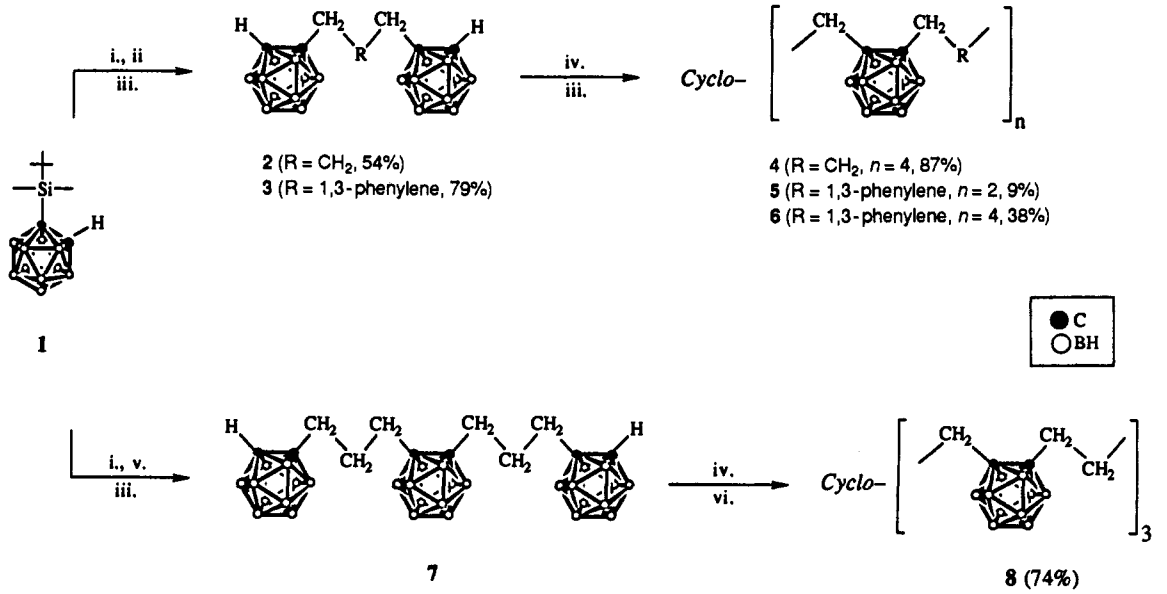
Scheme I[a]



[a] (i) *n*-BuLi/C_6H_6–Et_2O; (ii) $BrCH_2RCH_2Br$; (iii) *t*-Bu_4NF/THF −78 °C → 20 °C; (iv) *n*-BuLi/THF 0 °C → 20 °C; (v) *o*-$B_{10}H_{10}C_2(CH_2CH_2CH_2OTos)_2$; (vi) $BrCH_2CH_2CH_2Br$.

rational routes. The syntheses of **4** and **6** are significant since they proceed by cyclodimerization of **2** and **3**, respectively, in bifunctional nucleophilic displacement reactions. Cycles **5** and **8** are formed via cyclization of **3** and **7**, respectively, in bifunctional nucleophilic displacement reactions.

The potential scope of carboracycle chemistry is vast, and novel structural motifs which utilize the component carborane clusters as sources of nido-cage ligands[12,13] for the construction of macrocyclic arrays of metallacarborane moieties are apparent. More ambitious goals suggest investigations of *rotaxane* and *catenane* analogues of carboracycles[14] and metallacarboracycles.

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Supplementary Material Available. Experimental details for the preparation of **4**, **5**, **6**, and **8**; tables of bond distances and angles, positional and thermal parameters for **6** and **8**; details of the crystallographic data collection, collection and reduction of X-ray data, and solution and refinement of structures **6** and **8** (29 pages); tables of observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page.

(11) Characterization data for **6**: IR (KBr) 2576 (s) ν_{B-H}; ^1H NMR (360 MHz, acetone-d_6) δ 1.76 and 3.61 (m, THF-solvate), 3.94 (s, 16 H, $CbCH_2$), (s, 4 H, H^2-C_6H_4), 7.98–7.43 (m, 16 H, H^{4-6}-C_6H_4); ^{11}B NMR (160 MHz, THF) δ −4.75 (s, br, 8 B), −10.54 (s, br, 32 B); HR FAB-MS for $C_{40}H_{72}{}^{10}B_7{}^{11}B_{33}$, calcd for $(M-H)^-$ 984.9543; found for $(M-H)^-$ 984.9560.

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