We also note that the monomeric 1^+ (and the dication 1^{2+}), but not our dimerized 1^+, is seen (λ_{max} 560 nm) in the channels of the oxidizing zeolite Na–ZSM-5, where π-dimerization should be prohibited by the channel size.[2d] Because the monomer/dimer equilibration is fast in solution, it is abundantly clear that the bond between monomers is weak and does not perturb the electronic structure very much. This rules out a carbon–carbon bound dimer of the type involved in polymerization of thiophenes.

Terthiophenes blocked with 2,5″-dibromo- or 2,5″-bis(methylthio) groups behave in a qualitatively identical fashion, with the additional features that more stable dications are formed and identified optically and that evidence for further aggregation of the cation radicals beyond the dimer stage occurs at high concentration.[8,9] The cation radicals have spectra shifted to slightly longer wavelengths than those from **1**.

The formation of dimer structures at such low concentrations has important implications for oxidized conducting polymers. In the solid polymer the cation radicals are more concentrated, and there must be extensive intermolecular interactions of the type demonstrated here. Clearly, *diamagnetic π-dimers can be an alternative to diamagnetic bipolarons* as an explanation for the small ESR signal from highly oxidized polythiophenes. π-Dimers and π-stacks[1a,9] can also help explain optical spectra. Indeed we believe that this hypothesis will explain certain data already reported for oxidized oligothiophenes in solution.[2a] Considering the high formation constant of these dimers, we suggest that π-stacks (analogous to those present in conducting charge-transfer salts[1a,7a]) should be considered as conducting entities in polythiophene and other conducting polymers.

Acknowledgment. We acknowledge financial support from the National Science Foundation and the Office of Naval Research. Experiments on other oligothiophenes which led us to study **1** were conducted by Nancy Phillips and Kent Hubbard. Chuan Jian Zhong helped with the ESR experiment. M.G.H. acknowledges the University of Minnesota Graduate School for a Stanwood Johnston Memorial Fellowship.

---

(9) To be reported in a full paper.

A New Monocarbon Insertion Reaction. Synthesis and Structural Characterization of the First Polyhedral Arachno Tricarbon Carborane: *arachno*-6-$(NCCH_2)$-5,6,7-$C_3B_7H_{12}$

Kai Su, Beverly Barnum, Patrick J. Carroll, and
Larry G. Sneddon*

Department of Chemistry
University of Pennsylvania
Philadelphia, Pennsylvania 19104-6323

Received January 10, 1992

We have previously shown that nitrile carbons are susceptible to nucleophilic attacks by polyhedral borane anions and that these reactions can result in either CN or monocarbon cage-insertion products in high yields.[1] These results suggested that other species such as polarized acetylenes might also be susceptible to similar nucleophilic reactions and that these reactions could result in new routes for either mono- or dicarbon insertions into polyhedral boranes. In agreement with these expectations, we report here that the *arachno*-6,8-$C_2B_7H_{12}^-$ anion reacts readily with cyanoacetylene to give the first example of a polyhedral arachno tricarbon carborane, *arachno*-6-$(NCCH_2)$-5,6,7-$C_3B_7H_{12}$.

In a typical reaction, a cyanoacetylene/THF solution was added dropwise to a stirred solution containing an equivalent amount of the *arachno*-6,8-$C_2B_7H_{12}^-$ anion at room temperature. The reaction mixture was then neutralized with HCl, the THF vacuum evaporated, the residue extracted with CH_2Cl_2, and the extract filtered through silica gel. Evaporation of the filtrate gave an 82% yield of crude product. Further sublimation (50 °C) gave white *arachno*-6-$(NCCH_2)$-5,6,7-$C_3B_7H_{12}$ as a slightly air-sensitive crystalline solid.[2]

$$\textit{arachno}\text{-6,8-}C_2B_7H_{12}^- + HC{\equiv}CCN \xrightarrow[\text{2. H}^+]{\text{1. room temperature}} \textit{arachno}\text{-6-}(NCCH_2)\text{-5,6,7-}C_3B_7H_{12}$$

In contrast to the numerous dicarbon carboranes, only a few tricarbon carboranes have been reported: *nido*-2,3,4-$R_2C_3B_3H_5$,[3] *nido*-2,3,5-$R_5C_3B_3H$[4] (R = alkyl or H), *closo*-$C_3B_5H_7$,[5] *nido*-5,6,10-$(CH_3)_3C_3B_7H_9$,[6] *nido*-6-CH_3-5,6,9-$C_3B_7H_{10}$,[1,7] and *hypho*-$C_3B_4H_{12}$.[8] The *arachno*-6-$(NCCH_2)$-5,6,7-$C_3B_7H_{12}$ is both the first example of a polyhedral tricarbon carborane in the arachno electronic class[9] and the first tricarbon carborane to be structurally characterized.[18]

The structure of *arachno*-6-$(NCCH_2)$-5,6,7-$C_3B_7H_{12}$ as determined by a single-crystal X-ray study is shown in the ORTEP drawing in Figure 1.[10] Consistent with its 26-skeletal-electron count, the tricarbon carborane adopts a cage geometry based on an icosahedron missing two vertices, similar to those which have been either confirmed or proposed for other 10-vertex arachno cage systems such as the borane $B_{10}H_{14}^{2-}$,[11] monocarbon carborane 6-$CB_9H_{14}^-$,[12] and dicarbon carborane 6,9-$C_2B_8H_{14}$[13] analogues. The three carbons are adjacent in the 5,6,7-vertex positions on

---

(1) (a) Kang, S. O.; Furst, G. T.; Sneddon, L. G. *Inorg. Chem.* **1989**, *28*, 2339–2347. (b) Kang, S. O.; Sneddon, L. G. *Electron Deficient Boron and Carbon Clusters*; Olah, G. A., Wade, K., Williams, R. E., Eds.; Wiley: New York, 1991; pp 195–213.

(2) Spectroscopic data: ^{11}B NMR (64.2 MHz, CD_2Cl_2) (ppm, Hz) 10.7 (d, B2, J_{BH} = 187), −3.7 (d of d, B8, B10, J_{BH} = 151, $J_{BH(br)}$ = 26), −25.1 (d, B1, B3, J_{BH} = 168), −26.1 (d, B9, J_{BH} obscured), −41.1 (d, B4, J_{BH} = 151); two-dimensional ^{11}B–^{11}B NMR established the connectivities B2–B1,3, B8,10–B1,3, B8,10–B9, B8,10–B4, B1,3–B4, B9–B4; ^{13}C NMR (50.3 MHz, CD_2Cl_2) (ppm, Hz) 116.7 (s, C12), 39.2 (d, C6, J_{CH} = 170), 27.1 (t, C11, J_{CH} = 137), 11.5 (d, C5, C7, J_{CH} = 170); ^1H NMR (200 MHz, CD_2Cl_2 ^{11}B spin decoupled) (ppm, Hz) 4.1 (BH), 2.9 (BH), 2.8 (CH, d, J_{HH} = 7.0), 2.1 (BH, t, $J_{HH(br)}$ = 8.6), 2.0 (BH), 1.3 (CH), 0.2 (BH), −0.1 (CH, t, J_{HH} = 7.0), −3.0 (BHB); exact mass calcd for $^{12}C_5{}^{11}B_7{}^{14}N^1H_{14}$ 165.1778, found 165.1780; mp 71–72 °C.

(3) (a) Bramlett, C. L.; Grimes, R. N. *J. Am. Chem. Soc.* **1966**, *88*, 4269–4270. (b) Grimes, R. N.; Bramlett, C. L. *J. Am. Chem. Soc.* **1967**, *89*, 2557–2560. (c) Grimes, R. N.; Bramlett, C. L.; Vance, R. L. *Inorg. Chem.* **1968**, *7*, 1066–1070.

(4) (a) Kuhlmann, T.; Pritzkow, H.; Zenneck, U.; Siebert, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 965–966. (b) Zwecker, J.; Pritzkow, H.; Zenneck, U.; Siebert, W. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1099–1100. (c) Zwecker, J.; Kuhlmann, T.; Pritzkow, H.; Siebert, W.; Zenneck, U. *Organometallics* **1988**, *7*, 2316–2324. (d) Siebert, W.; Schafer, V.; Brodt, G.; Fessenbecker, A.; Pritzkow, H. *Abstracts of Papers*, 200th National Meeting of the American Chemical Society, Washington, DC, Aug 1990; American Chemical Society: Washington, DC, 1990; INOR 381.

(5) Thompson, M.; Grimes, R. N. *J. Am. Chem. Soc.* **1971**, *93*, 6677–6679.

(6) Stibr, B.; Jelinek, T.; Janousek, Z.; Hermånek, S.; Dråkovå, E.; Plzåk, Z.; Plesek, J. *J. Chem. Soc., Chem. Commun.* **1987**, 1106–1107.

(7) (a) Plumb, C. A.; Carroll, P. J.; Sneddon, L. G. *Organometallics*, in press. (b) Plumb, C. A.; Carroll, P. J.; Sneddon, L. G. *Organometallics*, in press. (c) Plumb, C. A.; Sneddon, L. G. *Organometallics*, in press.

(8) Greatrex, R.; Greenwood, N. N.; Kirk, M. *J. Chem. Soc., Chem. Commun.* **1991**, 1510.

(9) The formal $R_4C_3B_2H^{3-}$ anions derived from the diborole heterocycles $R_4C_3B_2H$ developed by Siebert also fall into the arachno electronic class, but the neutral *arachno*-$R_4C_3B_2H_4$ is not known. See, for example: (a) Siebert, W. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 943–958. (b) Siebert, W. *Pure Appl. Chem.* **1987**, *59*, 947–954. (c) Siebert, W. *Pure Appl. Chem.* **1988**, 1345–1348. (d) Attwood, A. T.; Fonda, K. K.; Grimes, R. N.; Brodt, G.; Hu, D.; Zenneck, U.; Siebert, W. *Organometallics* **1989**, *8*, 1300–1303. (e) Brodt, G.; Kuhlmann, T.; Siebert, W. *Chem. Ber.* **1989**, *122*, 829–831.

(10) Structural data: space group $P2_12_12_1$, a = 6.895 (1) Å, b = 9.881 (1) Å, c = 14.798 (5) Å, V = 1008.1 (6) Å^3, Z = 4, and d_{calcd} = 1.079 g/cm^3. The structure was solved by direct methods. Refinement was by full-matrix least-squares techniques based on F to minimize the quantity $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F)$. Non-hydrogen atoms were refined anisotropically, and hydrogen atom positions were refined with constant isotropic B's of 6.0 Å^2. Refinement converged to R_1 = 0.053 and R_2 = 0.062.

(11) Kendall, D. S.; Lipscomb, W. N. *Inorg. Chem.* **1973**, *12*, 546–551.

(12) Stibr, B.; Jelinek, T.; Plesek, J.; Hermanek, S. *J. Chem. Soc., Chem. Commun.* **1987**, 963–964.

(13) (a) Stibr, B.; Plesek, J.; Hermanek, S. *Collect. Czech. Chem. Commun.* **1974**, *39*, 1805–1809. (b) Stibr, B.; Plesek, J.; Hermanek, S. *Chem. Ind. (London)* **1972**, 963–964. (c) Wermer, J. R.; Hosmane, N. S.; Alexander, J. J.; Siriwardane, U.; Shore, S. G. *Inorg. Chem.* **1986**, *25*, 4351–4354.

0002-7863/92/1514-2730$03.00/0 © 1992 American Chemical Society

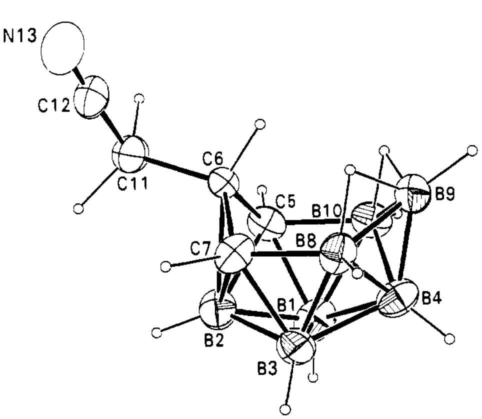

Figure 1. ORTEP drawing of the molecular structure of *arachno*-6-$(NCCH_2)$-5,6,7-$C_3B_7H_{12}$. Selected bond lengths (Å) and angles (deg): C5–C6, 1.552 (6); C7–B8, 1.620 (6); B3–B8, 1.821 (8); C5–B1, 1.699 (7); B4–B8, 1.810 (8); C5–B2, 1.710 (8); B4–B9, 1.699 (9); C5–B10, 1.644 (7); B4–B10, 1.832 (8); B8–B9, 1.803 (8); C6–C7, 1.549 (6); B1–B2, 1.640 (9); B1–B3, 1.677 (9); B8–H89, 1.183 (40); C6–B2, 2.015 (8); B1–B4, 1.770 (8); B9–B10, 1.821 (8); B1–B10, 1.804 (9); C7–B2, 1.750 (7); B2–B3, 1.667 (8), C7–B3, 1.742 (7); B3–B4, 1.742 (9); C5–C6–C7, 100.9 (3); B8–B9–B10, 101.4 (4); C6–C7–B8, 110.1 (4); C6–C5–B10, 110.5 (4); C7–B8–B9, 115.1 (4); C5–B10–B9, 113.3 (4).

the puckered six-membered open face, with the C6 carbon having both *exo*-CH_2CN and *endo*-H substituents. Bridging hydrogen atoms are also present at the B8–B9 and B9–B10 edges.

Although the gross cage geometry is consistent with skeletal-electron counting predictions, examination of the interatomic cage distances reveals features that may be attributed to a hybrid "classical"/"nonclassical" nature of the cluster. The C6–C5 (1.552 (6) Å) and C6–C7 (1.549 (6) Å) distances are in the range expected for carbon–carbon single bonds. Furthermore, the C6–B2 distance is quite long (2.015 (8) Å) and the B2–B1, B2–B3, and B1–B3 distances are unusually short (~1.64–1.68 Å), when compared to similar distances in the isoelectronic analogues above or to those in *nido*-$B_{10}H_{14}$.[14] These distances suggest a reduced bonding interaction between C6 and B2 and largely localized two-center single bonds between the C6 carbon and C5 and C7. Thus, the cluster could be considered to be composed of both "classical" electron-precise and "nonclassical" electron-deficient components. In the limit where C6 and B2 are nonbonding, then instead of being considered part of the cluster framework, C6 might be viewed as a carbon–carbon bridging exopolyhedral substituent on the starting carborane framework, i.e., *arachno*-$(\mu\text{-RCH})C_2B_7H_{11}$. We have previously discussed,[1b,15] similar structural features and alternative bonding descriptions for the related hybrid nine-vertex compounds *hypho*-1-CH_2-2,5-$S_2B_6H_8$ and *hypho*-1-BH_2-2,5-$S_2B_6H_9$.

Reactions between neutral polyhedral boranes and alkynes are thought to proceed by initial electrophilic attack of the borane at the alkyne π-electron density and generally result in two-carbon insertions.[16] Clearly, the reaction reported herein involves a different reaction pathway and, accordingly, results in monocarbon rather than dicarbon insertion. The observed adjacent-carbon structure of *arachno*-6-$(NCCH_2)$-5,6,7-$C_3B_7H_{12}$ is consistent with the reaction sequence shown in Figure 2 involving an initial nucleophilic attack of the *arachno*-6,8-$C_2B_7H_{12}^-$ at the γ-carbon atom of the cyanoacetylene, followed by monocarbon insertion and acetylene reduction in the manner shown to produce the tricarbon carborane with a CH_2CN substituent at C6. Additional support for this sequence comes from ^{11}B NMR spectra taken immediately after the cyanoacetylene addition, but before acidification, which show the formation of a new species exhibiting seven different doublet resonances[17] consistent with the structure of the asymmetric intermediate indicated in the figure. We are presently using isotopic labeling studies to determine the details of this reaction, as well as investigating the extensions of this new carbon-insertion reaction to other polyhedral borane anions.

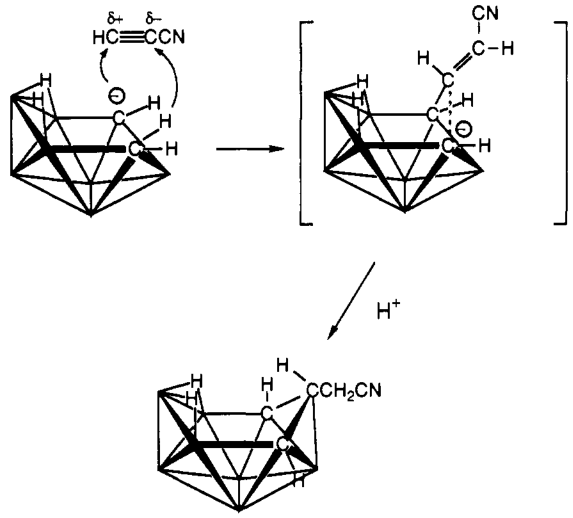

Figure 2. Possible reaction sequence leading to the formation of *arachno*-6-$(NCCH_2)$-5,6,7-$C_3B_7H_{12}$.

Acknowledgment. We thank the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research.

Supplementary Material Available: Tables of positional parameters, anisotropic temperature factors, bond distances, bond angles, and least-squares planes for *arachno*-6-$(NCCH_2)$-5,6,7-$C_3B_7H_{12}$ (10 pages); listing of observed and calculated structure factors for *arachno*-6-$(NCCH_2)$-5,6,7-$C_3B_7H_{12}$ (4 pages). Ordering information is given on any current masthead page.

---

[14] Tippe, A.; Hamilton, W. C. *Inorg. Chem.* **1969**, *8*, 464–470.

[15] Kang, S. O.; Sneddon, L. G. *J. Am. Chem. Soc.* **1989**, *111*, 3281–3289.

[16] Onak, T. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. D., Eds.; Pergamon: New York, 1982; pp 411–457.

[17] ^{11}B NMR (64.2 MHz, THF): 9.3, 0.9, −8.1, −17.3, −36.4, −42.5, −44.5 ppm.

[18] Several tetracarbon carboranes may also be viewed as arachno tricarbon carboranes with bridging methylene groups; see: ref 6 and Finster, D. C.; Grimes, R. N. *J. Am. Chem. Soc.* **1981**, *103*, 2675–2683.

Identification of the Imino–Oxo Form of 1-Methylcytosine

M. Szczesniak, J. Leszczyński,† and W. B. Person*

Department of Chemistry
University of Florida
Gainesville, Florida 32611-2046
Department of Chemistry
Jackson State University
Jackson, Mississippi 39217

Received October 31, 1991

Interest in the tautomerism of nucleic acid bases[1] was stimulated by the suggestion by Watson and Crick[2] that this effect may be responsible for spontaneous point mutations. It has been agreed that the bases display predominantly amino-oxo tautomeric forms

---

† Jackson State University.

[1] See: (a) Pullman, B.; Pullman, A. *Adv. Heterocycl. Chem.* **1971**, *13*, 77. (b) Kwiatkowski, J. S.; Pullman, B. *Adv. Heterocycl. Chem.* **1975**, *18*, 199. (c) Elguero, J.; Marzin, C.; Katritzky, A. R.; Linda, P. *Advances in Heterocyclic Chemistry*; Academic Press: New York, 1976, Suppl. 1. (d) Shugar, D.; Psoda, A. In *Landolt*-Bornstein—*New Series—Biophysics. Part I. Nucleic Acids VII/1D*; Springer Verlag: Berlin, 1990 pp 308–348 and references therein.

[2] Watson, J. D.; Crick, F. H. C. *Nature* **1953**, *171*, 964.

0002-7863/92/1514-2731$03.00/0 © 1992 American Chemical Society