significantly different organometallic monomer structures are under active investigation in our group.

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Synthesis of a New Small-Cage Carborane *nido*-4,5-$C_2B_6H_{10}$ and Structural Characterization of Its Conjugate Anion *nido*-4,5-$C_2B_6H_9^-$

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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.[2] For example, the reaction of *arachno*-6,8-$C_2B_7H_{12}^-$ with acetonitrile was found to produce the new tricarbon carborane *nido*-6-CH_3-5,6,9-$C_3B_7H_9^-$. We have now found that the reaction of acetonitrile with the isomeric carborane anion *arachno*-4,5-$C_2B_7H_{12}^-$ proceeds in a different fashion to form the new carborane anion *nido*-4,5-$C_2B_6H_9^-$ in high yields.[3]

$$\textit{arachno}\text{-4,5-}C_2B_7H_{12}^- + CH_3CN \xrightarrow{\Delta} \textit{nido}\text{-4,5-}C_2B_6H_9^- + {}^1\!/\!_3Et_3B_3N_3H_3 \quad (1)$$

In a typical reaction, *arachno*-4,5-$C_2B_7H_{13}$[4] was deprotonated with KH in THF at −50 °C. An excess of dry CH_3CN was then added, and the solution was refluxed for ~1 day. Removal of the volatiles left a slightly air-sensitive off-white solid, K^+*nido*-4,5-$C_2B_6H_9^-$ ($\mathbf{1}^-$), in essentially quantitative yield.[5] Fractionation of the volatile materials also gave an equivalent amount of *N*,*N*,*N*-triethylborazine.

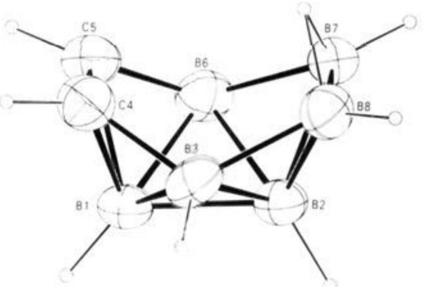
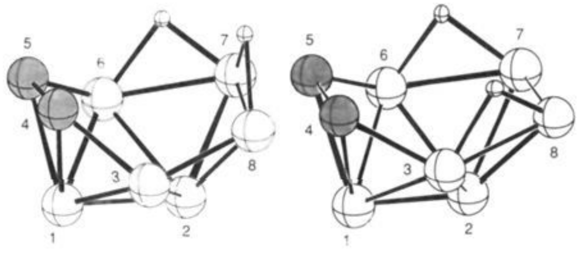


Figure 1. ORTEP drawing of the cage structure of Bu_4N^+*nido*-4,5-$C_2B_6H_9^-$ ($\mathbf{1}^-$). Selected bond distances (Å): B1–B2, 1.749 (7); B1–B3, 1.794 (7); B1–C4, 1.687 (7); B1–C5, 1.686 (6); B1–B6, 1.805 (7); B2–B3, 1.792 (7); B2–B6, 1.833 (7); B2–B7, 1.715 (6); B2–B8, 1.710 (7); B3–C4, 1.566 (7); B3–B8, 1.699 (7); C4–C5, 1.400 (7); C5–B6, 1.562 (7); B6–B7, 1.709 (7); B7–B8, 1.666 (7); B7–H78, 1.219 (35); B8–H78, 1.294 (35).



1a 1b

Figure 2. Possible structures for *nido*-4,5-$C_2B_6H_{10}$: HF/3-21G optimized geometries[18-20] for the asymmetric (**1a**) and symmetric (**1b**) isomers. Terminal hydrogens have been omitted from the figure for clarity.

The *arachno*-4,5-$C_2B_7H_{12}^-$ anion, unlike the *arachno*-6,8-$C_2B_7H_{12}^-$ isomer, contains a BH_2 structural unit.[4a] Thus, the differences observed in the reactivity of these two carborane anions with acetonitrile undoubtedly arise because of the base-induced cleavage of a BH_3 group[6] from the 4,5-isomer with subsequent rearrangement of the resulting $CH_3CN{\cdot}BH_3$ adduct to 1,3,5-$Et_3B_3N_3H_3$.[7]

The new carborane *nido*-4,5-$C_2B_6H_{10}$ (**1**) was obtained by protonation of a dry CH_2Cl_2 suspension of K^+*nido*-4,5-$C_2B_6H_9^-$ with gaseous HCl at −78 °C. Unoptimized, isolated yields of >60% of this colorless air-sensitive liquid that slowly decomposes at room temperature were obtained using standard vacuum fractionation techniques at a −50 °C trap.[8]

$$K^+\textit{nido}\text{-4,5-}C_2B_6H_9^- + HCl \xrightarrow[-78\ ^\circ C]{CH_2Cl_2} \underset{\mathbf{1}}{\textit{nido}\text{-4,5-}C_2B_6H_{10}} + KCl \quad (2)$$

The carbons apart isomer of this carborane, 4,7-$C_2B_6H_{10}$, was first isolated in 1973 by Williams[9] in <5% yields, and later by Burg[10] in 37% yields, from the reactions of *closo*-1,5-$C_2B_3H_5$ and diborane. The two $C_2B_6H_{10}$ carboranes are examples of 8-vertex, 20 skeletal electron, nido cluster systems and, on the basis of skeletal electron counting rules,[11] would be expected to adopt open-cage structures based on a tricapped trigonal prism missing one high coordination vertex. However, the only structurally characterized 8-vertex nido cluster with this geometry is *nido*-

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(1) Department of Chemistry, Korea University, Seochang 208 Jochiwon, Choongnam, Korea, 339-800.

(2) (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.

(3) Onak has also recently synthesized the isomeric *nido*-3,5-$C_2B_6H_9^-$ anion: T. Onak, personal communication.

(4) (a) Hermanek, S.; Jelinek, T.; Plesek, J.; Stibr, B.; Fusek, J. *J. Chem. Soc., Chem. Commun.* **1987**, 927–928. (b) Stibr, B.; Hermanek, S.; Plesek, J. *Inorg. Synth.* **1983**, *22*, 237–238.

(5) Spectroscopic data for K^+*nido*-4,5-$C_2B_6H_9^-$: ^{11}B NMR (160.5 MHz, THF) (ppm, *J*, Hz) 4.9 (d, B7,8, J_{BH} = 135), −15.7 (d, B2, J_{BH} = 129), −17.1 (d, B3, 6, J_{BH} = 124), −36.4 (d, B1, J_{BH} = 157, J_{BB} = 20), 2D ^{11}B–^{11}B established the connectivities B7,8–B2, B7,8–B3,6, B2–B1, B2–B3,6; ^{13}C NMR (50.3 MHz, THF-d_8) (ppm, *J*, Hz) 108.4 (br); ^{1}H NMR (500 MHz, THF-d_8) (ppm, *J*, Hz) 5.5 (s, CH), 3.9 (q, BH, J_{BH} = 128), 2.1 (q, BH, J_{BH} = 123), 0.8 (q, BH, J_{BH} = 123), −0.3 (q, BH, J_{BH} = 158), −6.3 (br, BHB); mp 92–93 °C ($Bu_4N^+C_2B_6H_9^-$).

(6) *arachno*-4,5-$C_2B_7H_{13}$ also undergoes a one-boron degradation upon reaction with aqueous sodium cyanide to give the *hypho*-$C_2B_6H_{12}^-$ anion. See: Jelinek, T.; Plesek, J.; Hermanek, S.; Stibr, B. *Main Group Met. Chem.* **1987**, *10*, 397–398.

(7) Emeleus, H. J.; Wade, K. *J. Chem. Soc.* **1960**, 2614–2617.

(8) Spectroscopic data for *nido*-4,5-$C_2B_6H_{10}$: ^{11}B NMR (160 MHz, CD_2Cl_2) (ppm, *J*, Hz) 7.8 (br, B7,8), −7.3 (d, B1, J_{BH} = 176), −12.4 (d, B3,6, J_{BH} = 143), −26.6 (d, B2, J_{BH} = 146); 2D ^{11}B–^{11}B NMR established the connectivities B7,8–B3,6, B7,8–B2, B1–B3,6, B1–B2, B3,6–B2; ^{1}H NMR (200 MHz, toluene-d_8, ^{11}B spin decoupled) (ppm) 6.2 (CH), 3.0 (BH), 2.6 (BH), 2.0 (BH), 1.2 (BH), −3.4 (BHB); exact mass calcd for $^{12}C_2{}^{11}B_6{}^1H_{10}$ 100.1341, found 100.1349; mp ≈ −50 °C.

(9) Gotcher, A. J.; Ditter, J. F.; Williams, R. E. *J. Am. Chem. Soc.* **1973**, *95*, 7514–7516.

(10) Reilly, T. J.; Burg, A. B. *Inorg. Chem.* **1974**, *13*, 1250.

(11) (a) Williams, R. E. *Inorg. Chem.* **1971**, *10*, 210–214. (b) Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1–66. (c) Williams, R. E. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 67–142. (d) Rudolph, R. W. *Acc. Chem. Res.* **1976**, *9*, 446–452. (e) Williams, R. E. *Electron Deficient Boron and Carbon Clusters*; Olah, G. A., Wade, K., Williams, R. E., Eds.; Wiley: New York, 1991; pp 11–93. (f) Williams, R. E. *Chem. Rev.* **1992**, *92*, 177–207.

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$(\eta\text{-}C_5H_5)_2Co_2SB_5H_7$.[12] Other isoelectronic clusters, such as *nido*-B_8H_{12},[13] *nido*-$(\eta^6\text{-}(CH_3)_6C_6)FeMe_4C_4B_3H_3$,[14] and *nido*-$(\eta\text{-}C_5H_5)CoPh_4C_4B_3H_3$,[15] have been shown to adopt structures based on a 10-vertex bicapped square antiprism missing two vertices, which is the same geometry expected for 8-vertex arachno clusters.[11] Thus, the question of which is the preferred geometry for 8-vertex nido cages has been a longstanding problem in cluster chemistry.[11e,f]

The NMR spectra obtained for 4,7-$C_2B_6H_{10}$ were originally interpreted as consistent with either static arachno or fluxional nido structures in solution. A recent ab initio/IGLO/NMR study[16] strongly favors the static structure for 4,7-$C_2B_6H_{10}$; however, its structure has not yet been crystallographically confirmed.

A single-crystal X-ray study of Bu_4N^+*nido*-4,5-$C_2B_6H_9^-$ confirmed the arachno-type structure shown in Figure 1,[17] and it is thus the first structural confirmation of this geometry for the parent carborane system. The carbon atoms occupy adjacent positions on the puckered six-membered open face with the single bridge hydrogen located at the B3–B6 edge, across from the carbons.

Ab initio[18]/IGLO[19]/NMR calculations[20] likewise favor an arachno-type geometry for *nido*-4,5-$C_2B_6H_{10}$, with the asymmetric placement of hydrogens in structure **1a** (C_1 symmetry) being favored over the symmetric arrangement in **1b** (C_s) (Figure 2). The 160.5-MHz ^{11}B NMR spectra[4,7] of K^+*nido*-4,5-$C_2B_6H_9^-$ and *nido*-4,5-$C_2B_6H_{10}$ both display a 2:1:2:1 ratio of resonances suggesting similar cage geometries, but also suggest a symmetric (**1b**) rather than asymmetric (**1a**) arrangement of bridging protons in the parent. However, the broad appearance of the B3,6 resonance in the spectrum of **1** suggests dynamic behavior. Indeed, rapid bridge-proton rearrangements across the B3–B8, B7–B8, and B6–B7 edges in **1** could account for both the apparent mirror symmetry present in the ^{11}B NMR spectrum and the broad nature of the B3–B6 resonance.

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Supplementary Material Available: Tables of positional parameters, anisotropic temperature factors, bond distances, and bond angles (12 pages); table of observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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[12] Zimmerman, G. J.; Sneddon, L. G. *J. Am. Chem. Soc.* **1981**, *103*, 1102–1111.

[13] Enrione, R. E.; Boer, F. P.; Lipscomb, W. N. *Inorg. Chem.* **1964**, *3*, 1659–1666.

[14] Micciche, R. P.; Briguglio, J. J.; Sneddon, L. G. *Organometallics* **1984**, *3*, 1396–1402.

[15] Zimmerman, G. J.; Sneddon, L. G. *Inorg. Chem.* **1980**, *19*, 3650–3655.

[16] Bausch, J. W.; Bühl, M.; Prakash, G. K. S.; Schleyer, P. v. R.; Williams, R. E. *Inorg. Chem.*, in press.

[17] Structural data: monoclinic, space group $P2_1/n$; $a = 10.374$ (1), $b = 15.440$ (2), $c = 15.116$ (2) Å, $\beta = 97.06$ (1)°, $V = 2402.9$ (9) Å^3, $Z = 4$, and $d_{calcd} = 0.941$ g/cm^3. The data were collected at −45 °C. The structure was solved by direct methods (Multan 11/82). Non-hydrogen atoms were refined anisotropically and cage hydrogens isotropically. Other hydrogen atoms were not refined. $R_1 = 0.051$ and $R_2 = 0.060$.

[18] *Gaussian 90*, Revision H: Frisch, M. J.; Head-Gordon, M.; Trucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M.; Binkley, J. S.; Gonzalez, C.; DeFrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Topiol, S.; Pople, J. A.; Gaussian, Inc., Pittsburgh, PA, 1990.

[19] (a) Kutzelnigg, W. *Isr. J. Chem.* **1980**, *19*, 193. (b) Schindler, M.; Kutzelnigg, W. *J. Chem. Phys.* **1982**, *76*, 1919–1933. Review: (c) Kutzelnigg, W.; Fleisher, U.; Schindler, M. In *NMR, Basic Principles and Progress*; Springer Verlag: Berlin, 1990; pp 165–262.

[20] At the HF/3-21G level of ab initio theory, **1a** is ~22 kcal/mol more stable than **1b**. DZ//3-21G IGLO ^{11}B NMR chemical shifts for **1b** are δ 45.0 (B1), 29.2 (B7,8), −2.7 (B3,6), and −15.8 (B2), while those for **1a** are δ 38.9 (B8), 2.4 (B1), −12.7 (B3), −10.8 (B7), −16.4 (B6), and −20.7 (B2). Averaging the values of B3,B6 and B7,B8 for **1a** give the shifts for the proposed dynamic structure of **1** in solution of 14.1 (B7,8), 2.4 (B1), −14.5 (B3,6), and −20.7 (B2).

An ab Initio Study on the Mechanism of the Ketene–Imine Cycloaddition Reaction

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The ketene–imine cycloaddition reaction is one of the most widely used methods in the synthesis of the β-lactamic rings.[1,2]

In 1907, Staudinger[3] reported the first synthesis of a β-lactam by a [2 + 2] cycloaddition of diphenylketene with benzylideneaniline at 200 °C. The Staudinger reaction is now widely employed in the preparation of β-lactams, because it provides direct access to these compounds from simple precursors; in addition, there is increasing interest in the problem of control of the induction of asymmetry in the reaction.[4]

Nevertheless, despite the synthetic interest, the actual mechanism of the Staudinger reaction is still unclear.[1] The most widely accepted mechanism involves the participation of a ketene generated from an acid halide precursor under basic conditions;[5] the ketene generated in situ will cycloadd to the imine, leading to the β-lactam derivative (see Figure 1). According to the experimental results of Moore and co-workers,[6] the cycloaddition of the ketene to the imine is a two-step zwitterionic process rather than a concerted one (Figure 1). This mechanistic proposal is supported by the detection of the zwitterionic intermediate by infrared spectroscopy in thermal reactions of ketenes with imines[7a] and by a detailed kinetic analysis with low-temperature FT-IR spectroscopy.[7b]

The related reaction of ketene with alkenes has been studied theoretically by Burke,[8] by Bernardi and co-workers,[9] and by Wang and Houk.[10] The results of these calculations show that this reaction has a very asynchronic transition structure, with an appreciable charge separation, but no intermediates were located.

In this communication we report the first ab initio study on the mechanism of the Staudinger reaction.[11] Ketene plus form-

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[1] For a review, see: Holden, K. G. In *Chemistry and Biology of β-lactam antibiotics*; Vol. 2, Morin, R. B., Gorman, M., Eds.; Academic Press, Inc.: New York–London, 1982; p 114.

[2] See, for example: Georg, G. I.; He, P.; Kant, J.; Mudd, J. *Tetrahedron Lett.* **1990**, *31*, 451. Arrieta, A.; Leccea, B.; Palomo, C. *J. Chem. Soc., Perkin Trans. 1* **1987**, 845. Ram, B.; Bose, A. K. *Synthesis* **1976**, 689.

[3] Staudinger, H. *Justus Liebigs Ann. Chem.* **1907**, *356*, 51.

[4] Hubschwerlen, C.; Schmid, G. *Helv. Chim. Acta* **1983**, *66*, 2206. Cooper, R. D. G.; Daugherty, B. W.; Boyd, D. B. *Pure Appl. Chem.* **1987**, *59*, 485. Evans, D. A.; Williams, J. M. *Tetrahedron Lett.* **1988**, *29*, 5065. Ikota, N. *Chem. Pharm. Bull.* **1990**, *38*, 1601.

[5] Duran, F.; Ghosez, L. *Tetrahedron Lett.* **1970**, 245. Hegedus, L. S.; Montgomery, J.; Narukawa, Y.; Snustad, D. C. *J. Am. Chem. Soc.* **1991**, *113*, 5784.

[6] Moore, H. W.; Hughes, G.; Srinivasachar, K.; Fernandez, M.; Nguyen, N. V.; Schoon, D.; Tranne, A. *J. Org. Chem.* **1985**, *50*, 4231.

[7] (a) Pacansky, J.; Chang, J. S.; Brown, D. W.; Schwarz, W. *J. Org. Chem.* **1982**, *47*, 2233. (b) Lynch, J. E.; Riseman, S. M.; Laswell, W. L.; Tschaen, D. M.; Volante, R.; Smith, G. B.; Shinkai, I. *J. Org. Chem.* **1989**, *54*, 3792.

[8] Burke, L. A. *J. Org. Chem.* **1985**, *50*, 3149.

[9] Bernardi, F.; Bottoni, A.; Olivucci, M.; Robb, M. A.; Schlegel, H. B.; Tonachini, G. *J. Am. Chem. Soc.* **1988**, *110*, 5993. Bernardi, F.; Bottoni, A.; Robb, M. A.; Venturini, A. *J. Am. Chem. Soc.* **1990**, *112*, 2106.

[10] Wang, X.; Houk, K. N. *J. Am. Chem. Soc.* **1990**, *112*, 1754.

[11] The calculations were performed with the GAUSSIAN 90 series of programs: Frisch, M. J.; Head-Gordon, M.; Trucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M.; Binkley, J. S.; Gonzalez, G.; Defrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. E.; Stewart, J. J. P.; Topiol, S.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1990.

0002-7863/92/1514-6249$03.00/0