with the molar ratio of tartrate to allenylboronic acid of 1:2 gave 1-cyclohexyl-3-butyn-1-ol with 75% ee. Thus, the optical yield appeared to decrease by the presence of remaining allenylboronic acid, and the ratio of 2:1 was used in subsequent experiments.[10] (2) A single mechanistic feature dominates the chiral tilt since most of the reactions examined so far fit the transition state of **1**. (3) Aromatic and α,β-unsaturated aldehydes gave lower enantioselectivities. It is well-known, however, that benzylic as well as allylic alcohols may be prepared with satisfactory enantioselectivities by the existing techniques.[11] (4) Generally DIPT gave a slightly higher enantiomeric excess than DET.

It seems clear that the methodology described herein has a vast potential in organic synthesis. Acetylenic alcohols may be transformed into other important classes of functionalities including β-hydroxyl ketones and *Z*-homoallylic alcohols.

Acknowledgment. Financial supports from the Ministry of Education, Japanese Government (Grant-in-Aid 57118008) and Asahi Glass Foundation are acknowledged.

Registry No. L(+)-DET, 87-91-2; D-(−)-DET, 13811-71-7; L-(+)-DIPT, 2217-15-4; D-(−)-DIPT, 62961-64-2; cyclohexanecarbaldehyde, 2043-61-0; hexanal, 66-25-1; trimethylacetaldehyde, 630-19-3; benzaldehyde, 100-52-7; *p*-nitrobenzaldehyde, 555-16-8; *p*-methoxybenzaldehyde, 123-11-5; 2-furaldehyde, 98-01-1; *trans*-2-hexenal, 6728-26-3; *trans*-cinnamaldehyde, 14371-10-9; 1-perillaldehyde, 2111-75-3; allenylboronic acid, 83816-41-5; (*S*)-1-cyclohexyl-3-butyn-1-ol, 83816-42-6; (*R*)-1-cyclohexyl-3-butyn-1-ol, 83816-43-7; (*S*)-1-nonyn-4-ol, 81077-12-5; (−)-5,5-dimethyl-1-hexyn-4-ol, 83816-44-8; (*S*)-1-phenyl-3-butyn-1-ol, 83816-45-9; (*R*)-1-phenyl-3-butyn-1-ol, 83816-46-0; (+)-1-*p*-nitrophenyl-3-butyn-1-ol, 83816-47-1; (−)-1-*p*-methoxyphenyl-3-butyn-1-ol, 83816-48-2; (+)-1-(2-furyl)-3-butyn-1-ol, 83816-49-3; (*S*)-*trans*-5-nonen-1-yn-4-ol, 83816-50-6; (+)-*trans*-6-phenyl-5-hexen-1-yn-4-ol, 83816-51-7; 1-(4-(1-methylethenyl)cyclohexen-1-yl)-3-butyn-1-ol, 83816-52-8.

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[10] The reaction of allenylboronic acid with aldehydes in THF was slow at −78 °C unless the reaction was warmed to 0 °C. Thus, with the ratio of 1:2, the yield of the reaction drops to 32%.

[11] Recent preparation of optically active benzyl and allyl alcohols: (a) Noyori, R.; Tomino, I.; Tanimoto, Y. *J. Am. Chem. Soc.* **1979**, *101*, 3129. (b) Martin, V. S.; Woodard, S. S.; Katsuki, T.; Yamada, Y.; Ikeda, M.; Sharpless, K. B. *J. Am. Chem. Soc.* **1981**, *103*, 6237.

Structure of the $[B_2H_7]^-$ Anion

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Ever since it was first synthesized by Brown and co-workers in 1957,[1] the $[B_2H_7]^-$ anion has attracted a considerable amount of attention. As perhaps the only example of a species containing an unsupported[2] B–H–B bond, it provided investigators with the ideal system for probing the details of the three-center two-electron linkage. Various spectroscopic investigations provided support for the single-H-bridged model,[3] $[H_3B(\mu\text{-}H)BH_3]^-$. Ab initio calculations have concluded that the central B–H–B linkage of the $[B_2H_7]^-$ anion is linear,[4] at least in the gas phase, while other calculations on the isoelectronic $[C_2H_7]^+$ cation have predicted that the central C–H–C backbone is bent.[5] Meanwhile, an X-ray structure determination on the closely related $[B_2(C_4H_8)_2H_3]^-$ anion unambiguously showed a bent (140°) B–H–B core.[6] In this paper we report the single-crystal X-ray structural characterization of the $[B_2H_7]^-$ anion in $[(Ph_3P)_2N]^+[B_2H_7]^-\cdot CH_2Cl_2$.

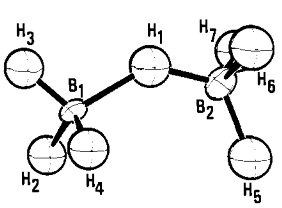

Figure 1. The structure of the $[B_2H_7]^-$ anion.

Table I. Selected Distances (Å) and Angles (deg) in $[(Ph_3P)_2N]^+[B_2H_7]^-\cdot CH_2Cl_2$

N–P(1)	1.583 (3)	C–Cl(1)	1.764 (5)
N–P(2)	1.586 (3)	C–Cl(2)	1.752 (5)
P(1)–N–P(2)	138.6 (2)	Cl(1)–C–Cl(2)	112.1 (3)
B(1)···B(2)	2.107 (7)	H(1)–B(1)–H(2)	115 (3)
B(1)–H(1)	1.27 (5)	H(1)–B(1)–H(3)	108 (3)
B(1)–H(2)	1.11 (4)	H(1)–B(1)–H(4)	105 (3)
B(1)–H(3)	0.90 (4)	H(2)–B(1)–H(3)	96 (4)
B(1)–H(4)	0.91 (5)	H(2)–B(1)–H(4)	111 (4)
B(2)–H(1)	1.00 (5)	H(3)–B(1)–H(4)	122 (4)
B(2)–H(5)	1.09 (5)	H(1)–B(2)–H(5)	123 (4)
B(2)–H(6)	1.11 (5)	H(1)–B(2)–H(6)	98 (3)
B(2)–H(7)	1.07 (5)	H(1)–B(2)–H(7)	103 (3)
		H(5)–B(2)–H(6)	107 (3)
B(1)–H(1)–B(2)	136 (4)°	H(5)–B(2)–H(7)	108 (3)
		H(6)–B(2)–H(7)	118 (3)
	Average Values		
$B\text{–}H_t$	1.03	$H_t\text{–}B\text{–}H_t$	110
$B\text{–}H_b$	1.14	$H_t\text{–}B\text{–}H_b$	109

The title compound was prepared according to the following reaction sequence, which employed procedures similar to those described previously in the preparation of $[B_2H_7]^-$ salts:[3d,7]

$$[(Ph_3P)_2N]^+Cl^- + LiBH_4 \xrightarrow[\text{room temp}]{CH_2Cl_2/Et_2O} [(Ph_3P)_2N]^+[BH_4]^- + LiCl\downarrow \quad (1)$$

$$[(Ph_3P)_2N]^+[BH_4]^- + {}^1/{}_2B_2H_6 \xrightarrow[-78\ ^\circ C]{CH_2Cl_2} [(Ph_3P)_2N]^+[B_2H_7]^- \quad (2)$$

Crystals of $[(Ph_3P)_2N]^+[B_2H_7]^-\cdot CH_2Cl_2$ were grown at room temperature from a CH_2Cl_2 solution into which $(C_2H_5)_2O$ was allowed to diffuse slowly. The clear, colorless crystals showed a tendency to become opaque when removed from the mother liquor. Therefore, they were rapidly loaded into thin-walled capillaries at −78 °C immediately after removal from the solution in which they were grown.

$[(Ph_3P)_2N]^+[B_2H_7]^-\cdot CH_2Cl_2$ crystallizes in the triclinic space group $P\bar{1}$, with $a = 9.589$ (10) Å, $b = 10.578$ (9) Å, $c = 17.014$ (18) Å, $\alpha = 90.61$ (8)°, $\beta = 93.58$ (9)°, $\gamma = 93.86$ (8)°. X-ray diffraction data were collected at low temperature (−96 °C) on a Syntex P2$_1$ diffractometer. The positions of all non-hydrogen atoms were revealed in a single E map generated by direct methods,[8] and these were refined anisotropically to yield an initial

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[1] (a) Brown, H. C.; Stehle, P. F.; Tierney, P. A. *J. Am. Chem. Soc.* **1957**, *79*, 2020. (b) Brown, H. C.; Tierny, P. A. *J. Am. Chem. Soc.* **1958**, *80*, 1552.

[2] We define a molecule having an unsupported X–H–X bond as one that is held together solely by that one unique bond. Thus, a molecule such as B_2H_6, which has two B–H–B bridge bonds, is excluded by this definition.

[3] (a) Gaines, D. F. *Inorg. Chem.* **1963**, *2*, 523. (b) Matsui, Y.; Taylor, R. C. *J. Am. Chem. Soc.* **1968**, *90*, 1363. (c) Evans, W. G.; Holloway, C. E.; Sukumarabandhu, K.; McDaniel, D. H. *Inorg. Chem.* **1968**, *7*, 1747. (d) Hertz, R. K.; Johnson, H. D., II; Shore, S. G. *Inorg. Chem.* **1973**, *12*, 1875.

[4] (a) Hall, J. H., Jr.; Marynick, D. S.; Lipscomb, W. N. *Inorg. Chem.* **1972**, *11*, 3126. (b) Hoheisel, C.; Kutzelnigg, W. *J. Am. Chem. Soc.* **1975**, *97*, 6970. (c) Bigot, B.; Lequan, R. M.; Devaquet, A. *Nouv. J. Chim.* **1978**, *2*, 449.

[5] (a) Lathan, W. A.; Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 808. (b) Raghavachari, K.; Whiteside, R. A.: Pople, J. A.; Schleyer, P. v. R. *Ibid.* **1981**, *103*, 5649.

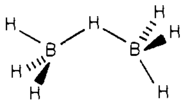
[6] (a) Clayton, W. R.; Saturnino, D. J.; Corfield, P. W. R.; Shore, S. G. *J. Chem. Soc., Chem. Commun.* **1973**, 377. (b) Saturnino, D. J.; Yamauchi, M.; Clayton, W. R.; Nelson, R. W.; Shore, S. G. *J. Am. Chem. Soc.* **1975**, *97*, 6063.

[7] Hertz, R. K.; Johnson, H. D., II; Shore, S. G. *Inorg. Synth.* **1977**, *17*, 24.

[8] MULTAN: a system of computer programs for the automatic solution of crystal structures from X-ray diffraction data [Germain, G.; Main, P.; Woolfson, M. M., *Acta Crystallogr., Sect. A*, **1971**, *A27*, 368].

R factor of 0.056. After calculated H positions of the phenyl groups and solvent molecule were added to the atomic coordinate list, a subsequent difference-Fourier map revealed the seven H positions of the $[B_2H_7]^-$ anion. Exhaustive least-squares refinement (in which the H coordinates of the anion were also varied) resulted in a final R factor of 0.049 for 3569 nonzero reflections $[I > 3\sigma(I)]$.[9]

A plot of the $[B_2H_7]^-$ anion is shown in Figure 1, and selected distances and angles are given in Table I. Other results of the structural analysis are available.[10] The single-H-bridged model is confirmed, with a bent B–H–B linkage [136 (4)°]. The terminal H atoms are found in staggered arrangement, and the molecular conformation has C_s symmetry, as depicted in I. (This conformation can be seen in Figure 1: note the approximate mirror plane defined by the atoms H_3, B_1, H_1, B_2, H_5, which are coplanar within ±0.03 Å). As expected for an X-ray analysis, the individual B–H distances show considerable scatter (Table I), but the average terminal B–H distance (1.03 Å) is appreciably shorter than the average bridging B–H distance (1.14 Å), as anticipated. The apparent asymmetrical positioning of the bridging H atom [$B_1 - H_1$ = 1.27 (5) Å, $B_2 - H_1$ = 1.00 (5) Å] may reflect some sort of donor–acceptor interaction (i.e., $BH_4^- \rightarrow BH_3$), but until more accurate H positions are available (hopefully, from a neutron diffraction analysis[11]), we cannot be sure if this phenomenon is real. The B···B distance of 2.107 (7) Å is very much shorter than the corresponding distance found in $[B_2(C_4H_8)_2H_3]^-$ (B···B = 2.43 Å), and this is probably a consequence of the removal of steric constraints (i.e., the two C_4H_8 bridges) in going from $[B_2(C_4H_8)_2H_3]^-$ to $[B_2H_7]^-$.



I

We have now completed the structural analysis of the entire sequence of compounds having unsupported X–H–X bonds,[2] i.e., compounds having M–H–M, M–H–B, and B–H–B linkages. The M–H–M class is represented by our neutron diffraction studies of several compounds having single W–H–W bridges,[12] and the M–H–B class by our recent neutron analysis of $(Ph_2MeP)_3Cu(BH_4)$.[13] All these investigations have shown the existence of bent 3-center two-electron linkages, consistent with the present structural results on $[B_2H_7]^-$. On the other hand, a recent X-ray study of $[Me_3Al(\mu\text{-}H)AlMe_3]^-$ revealed a linear Al–H–Al bond.[14] In order to check out the possibility that the conformation of $[B_2H_7]^-$ might be sensitive to crystal lattice effects,[15] we are planning to carry out the structure analyses of other salts of this anion.[16]

Acknowledgment. This work has been supported by National Science Foundation Grant CHE-81-01122 to R.B. and by Army Research Office Grant DAAG 29-78-G-0112 to S.G.S.

Registry No. $[(Ph_3P)_2N]^+[BzH_7]^-\cdot CH_2Cl_2$, 83731-71-9.

Supplementary Material Available: Final atomic coordinates (Table II), torsion angles (Table III), and a least-squares plane calculation (Table IV) of the $[B_2H_7]^-$ anion (4 pages). Ordering information is given on any current masthead page.

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[9] Major computations in this work were performed on the USC IBM 370/158 computer using CRYM, an amalgamated set of crystallographic programs developed by R. E. Marsh's group at the California Institute of Technology.

[10] See supplementary material paragraph at end of paper.

[11] A neutron diffraction analysis was in fact attempted on $[(Ph_3P)_2N]^+[B_2H_7]^-\cdot CH_2Cl_2$ very recently (Chiang, M.; Koetzle, T. F.; Bau, R.; Shore, S. G.; Lawrence, S. H., July 1982), but the size of the crystal used in that work was not large enough to yield a satisfactory data set. Efforts are continuing.

[12] (a) $HW_2(CO)_9(NO)$: Olsen, J. P.; Koetzle, T. F.; Kirtley, S. W.; Andrews, M. A.; Tipton, D. L.; Bau, R. *J. Am. Chem. Soc.* **1974**, *96*, 6621. (b) $HW_2(CO)_8(NO)P(OMe)_3$: Love, R. A.; Chin, H. B.; Koetzle, T. F.; Kirtley, S. W.; Whittlesey, B. R.; Bau, R. *J. Am. Chem. Soc.* **1976**, *98*, 4491. (c) $[Et_4N]^+[NW_2(CO)_{10}]^-$ and $[Ph_4P]^+[HW_2(CO)_{10}]^-$: Bau, R.; Teller, R. G.; Kirtley, S. W.; Koetzle, T. F. *Acc. Chem. Res.* **1979**, *12*, 176.

[13] Takusagawa, F.; Fumagalli, A.; Koetzle, T. F.; Shore, S. G.; Schmitkons, T.; Fratini, A. V.; Morse, K. W.; Wei, C. Y.; Bau, R. *J. Am. Chem. Soc.* **1981**, *103*, 5165.

[14] Atwood, J. L.; Hrncir, D. C.; Rogers, R. D.; Howard, J. A. K. *J. Am. Chem. Soc.* **1981**, *103*, 6787.

[15] In this regard, it should be noted that there is some precedence for conformational changes due to crystal packing forces. For example, the non-hydrogen skeleton of the $[HW_2(CO)_{10}]^-$ anion is linear and eclipsed in $[Et_4N]^+[HW_2(CO)_{10}]^-$ but bent and staggered in $[(Ph_3P)_2N]^+[HW_2(CO)_{10}]^-$ (Wilson, R. D.; Graham, S. A.; Bau, R. *J. Organomet. Chem.* **1975**, *91*, C49). Nevertheless, the W–H–W core is bent in all salts of $[HW_2(CO)_{10}]^-$ investigated so far, including $[Et_4N]^+[HW_2(CO)_{10}]^-$ (see Figure 4 in ref 12c).

[16] The X-ray diffraction analysis of $[Ph_3MeP]^+[B_2H_7]^-$ is currently, being attempted (Chiang, M.; Bau, R.; Lawrence, S. H.; Shore, S. G.).

A [4 + 4] Annulation Approach to Eight-Membered Carbocyclic Compounds[1a]

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Although cyclooctane derivatives have been the subject of extensive physical-organic investigations, relatively little progress has been made toward the development of general synthetic approaches to this system. The recent isolation of a number of biologically important natural products whose structures incorporate eight-membered rings has lent further importance to the search for new methodology for the synthesis of cyclooctane derivatives. Cyclooctane derivatives are most commonly prepared either by cyclization methods, via the ring expansion of cycloheptanes, or by the cleavage (or fragmentation) of bi- and polycyclic systems that already incorporate eight-membered rings. Few general annulation[2] approaches to cyclooctanes have been described previously. 1,5-Cyclooctadienes can be prepared via the thermal,[3] photochemical,[4] or nickel(0)-catalyzed[5] dimerization of 1,3-dienes, followed by Cope rearrangement of the intermediate 1,2-vinylcyclobutanes. Unfortunately this [4 + 4] annulation process generally proceeds in low yield and is both nonstereoselective and regiochemically ambiguous.

In this communication we describe a new [4 + 4] annulation approach to eight-membered carbocycles that is applicable to the synthesis of unsymmetrically substituted and highly functionalized cyclooctane derivatives. As outlined in Scheme I, 1,3-dienes serve as one four-carbon component in this annulation. The second four-carbon unit is a vinylketene derivative, generated either by electrocyclic opening of a cyclobutenone or via the 1,4-dehydrohalogenation of an α,β-unsaturated acid chloride.

The cyclobutenone version of the annulation simply involves heating the enone and 1,3-diene in an inert solvent and proceeds via a cascade of well-precedented pericyclic reactions (one representing each major class of pericyclic process!). Electrocyclic opening of the cyclobutenone[6] generates a vinylketene derivative

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[1] (a) Presented at the 183rd National Meeting of the American Chemical Society, March 30, 1982; (b) Alfred P. Sloan Research Fellow, 1981–1983.

[2] We define as annulations those ring-forming processes in which *two* molecular fragments are united with the formation of *two* new bonds.

[3] (a) Cope, A. C.; Schmitz, W. R. *J. Am. Chem. Soc.* **1950**, *72*, 3056. (b) Vogel, E. *Justus Liebigs Ann. Chem.* **1958** *615*, 1. (c) Sartori, G.; Turba, V.; Valvassori, A.; Riva, M. *Tetrahedron* Lett. **1966**, 4777. (d) Stewart, C. A. *J. Am. Chem. Soc.* **1971**, *93*, 4815. (e) Berson, J. A.; Dervan, P. B.; Malherbe, R.; Jenkins, J. A. *Ibid.* **1976**, *98*, 5937 and references cited therein.

[4] (a) Hammond, G. S.; De Boer, C. D. *J. Am. Chem. Soc.* **1964**, *86*, 899. (b) Trecker, D. J.; Henry, J. P. *Ibid.* **1964**, *86*, 902 and references cited therein.

[5] For a review, see: Jolly, P. W.; Wilke, G. "The Organic Chemistry of Nickel"; Wiley: New York, 1975; Vol. II, Chapter 4.

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