Synthesis of the Tridecahydro-1-carba-*nido*-undecaborate(1—) Ion

By D. C. Beer, A. R. Burke, T. R. Engelmann, B. N. Storhoff, and L. J. Todd*
(*Department of Chemistry, Indiana University, Bloomington, Indiana* 47401)

Summary Acid hydrolysis of 1,2-, 1,7-, and 1,12-$B_{10}H_{10}$-CHE^{2-} (E = P or As) gave 7-$B_{10}H_{12}CH^-$, 7,8-B_9H_{10}-CHE^-, and 1-$B_{10}H_{12}CH^-$, respectively as major products.

The icosahedral carboranes can be reduced with sodium metal in liquid ammonia to form dianion derivatives,[1,2] and the dianions can be reoxidized with a variety of reagents to form neutral icosahedral carboranes once again. We have observed that 1,7- and 1,12-$B_{10}H_{10}CHE$ (E = P or As) undergo the same type of rearrangement in the reduction–oxidation procedure as do the corresponding isomers of the isoelectronic system, $B_{10}H_{10}C_2H_2$.[3]

When 1,2-$B_{10}H_{10}CHE^{2-}$ (E = P of As) was treated with aqueous acid, the phosphorus or arsenic atom was removed from the cage and the known tridecahydro-7-carba-*nido*-undecaborate(1 −) ion[4] was obtained as the major product. Treatment of the reduced product of 1,7-$B_{10}H_{10}CHE$ with aqueous acid led to boron atom abstraction and the formation of 7,8-$B_9H_{10}CHE^-$ as the major product.[5]

Sodium (2 equiv.) in liquid ammonia was treated with 1,12-$B_{10}H_{10}CHAs$ for 40 min at reflux and then the liquid ammonia was allowed to boil off. After acid hydrolysis of the products, a salt (I) of the composition $(CH_3)_4N(B_{10}H_{12}CH)$ was isolated in 30% yield. The i.r. and ^{11}B n.m.r. spectra of (I) were quite different from the corresponding spectra of tetramethylammonium tridecahydro-7-carba-*nido*-undecaborate-(1−). The ^{11}B n.m.r. spectrum of (I) at 70·6 MHz externally referenced to $BF_3{\cdot}O(C_2H_5)_2$ contained two doublets of equal intensity at +17·0 and +20·0 p.p.m. The simplicity of this n.m.r. spectrum suggests that the carbon atom in the new carborane anion (I) is located on the opposite side of the cage to the empty vertex (see Figure). This structure was further confirmed by deprotonation of (I) with sodium hydride in tetrahydrofuran and subsequent reaction with phosphorus trichloride to form 1,12-$B_{10}H_{10}CHP$ in good yield. These results suggest that the second known isomer with the composition $B_{10}H_{12}CH^-$ is the tridecahydro-1-carba-*nido*-undecaborate(1−) ion. This new carborane anion can also be obtained from 1,12-$B_{10}H_{10}CHP$ in a similar manner. Transition-metal complexes of the type $[(B_{10}H_{10}CH)_2M]^n$ derived from this new carborane ion would be of considerable value in carbollyl–metal bonding studies due to the high symmetry of the complex.

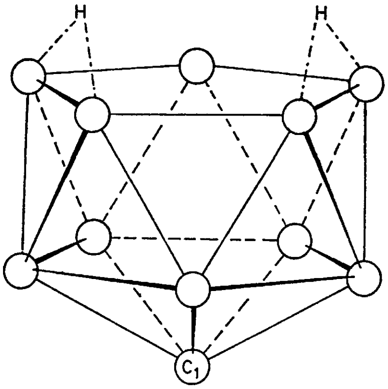

FIGURE. *Suggested structure of the tridecahydro-*1*-carba-*nido*-undecaborate*(1−) *ion.*

This work was supported by the Office of Naval Research.

(*Received, October 4th,* 1971; *Com.* 1731.)

[1] M. M. Fein, J. Bobinski, N. Mayes, N. Schwartz, and M. S. Cohen, *Inorg. Chem.*, 1963, **2**, 1111.

[2] L. I. Zakharkin, V. N. Kalinin, and L. S. Podvisotskaya, *Izvest. Akad. Nauk SSSR, Ser Khim.*, 1966, 1495.

[3] V. I. Stanko, Yu. V. Gol'tyapin, and V. A. Brattsev, *Zhur. obshchei Khim.*, 1969, **39**, 1175.

[4] D. E. Hyatt, F. R. Scholer, L. J. Todd, and J. L. Warner, *Inorg. Chem.*, 1967, **6**, 2229.

[5] L. J. Todd, J. L. Little, and H. T. Silverstein, *Inorg. Chem.*, 1969, **8**, 1698.

[6] D. E. Hyatt, J. L. Little, J. T. Moran, F. R. Scholer, and L. J. Todd, *J. Amer. Chem. Soc.*, 1967, **89**, 3342.