The enhanced stability of this compound,[8] probably due to the additional π-type interaction, is clearly demonstrated by the temperature dependence of the 60-MHz nmr spectra shown in Figure 3. Rapid exchange on the nmr time scale does not occur until a temperature of ~70° is reached, which implies that the exchange process in this system proceeds with a higher activation energy than that observed for any other system studied so far.

Further study of this system should lead to a better understanding of cyclopropyl π-type interactions and the nature of the electron-deficient bridge bond. To this end the exact analysis of the nmr spectrum is continuing and the crystal structure and optical spectra are currently under investigation.

Acknowledgment. We gratefully acknowledge the support of this research by National Science Foundation Grants GP-3908, GP-6762, and GP-8323.

(8) H. H. Jaffé, *Z. Elektrochem.*, **59**, 823 (1955).

David A. Sanders, John P. Oliver
Department of Chemistry, Wayne State University
Detroit, Michigan 48202
Received June 12, 1968

Comment on the Thermal Decomposition of Triphenylthallium

Sir:

In a recent interesting publication[1] concerned with thallium in organic synthesis is the statement: "Contrary to the suggestion of Gilman and Jones, we have shown that triphenylthallium does *not* disproportionate to biphenyl and thallium."[2] In the earlier experiments described by us[3] we obtained biphenyl when triphenylthallium dissolved in xylene was refluxed under nitrogen. Also, in two check experiments, a solution of triphenylthallium in xylene was refluxed while a slow stream of dry carbon dioxide was admitted over the surface of the boiling solution. Subsequent to cooling and hydrolysis, there was obtained biphenyl and benzoic acid. It may be relevant to remark that Birch[4] stated after heating what was presumably only a small quantity of solid triphenylthallium: "When heated it decomposes suddenly to give metallic thallium and a vapor possessing an odor of biphenyl."

We now confirm that biphenyl is indeed formed by thermal decomposition of triphenylthallium under our reported conditions which are more vigorous than those employed in ref 1. Thus, biphenyl is formed by thermal decomposition in xylene of freshly prepared triphenylthallium. These experiments were carried out with newly prepared materials. As in our earlier work the identity of the biphenyl was confirmed by the method of mixture melting points with an authentic specimen, and in the present work also by comparison of infrared spectra.

The following item may have some significance. An interesting and important aspect of the coupling reactions[1] is that they take place in the presence of excess TlBr (see footnote 4 of ref 1). In the reference to our experiment in which some biphenyl was obtained when phenyllithium was added to thallous chloride at −15° (see ref 3) it is of interest that the TlCl was present in excess because the phenyllithium was added to it slowly. Ordinarily, in the preparation of organothallium compounds, the thallous chloride or bromide is added slowly to the RMgX or RLi compound so that thallous halide is not present in excess. This suggests that a key step in the coupling reaction may be expressed in eq 2 of ref 1.

$$\mathrm{RTl + 2TlBr \longrightarrow RTlBr_2 + 2Tl}$$

There would then be little opportunity for this reaction to take place when TlBr is added to excess RMgX or RLi.

H. Gilman, I. Haiduc
Department of Chemistry, Iowa State University
Ames, Iowa 50010
Received June 19, 1968

---

(1) A. McKillop, L. F. Elsom, and E. C. Taylor, *J. Am. Chem. Soc.*, **90**, 2423 (1968).

(2) The authors[1] have informed us that this observation was made under the conditions of their coupling reaction, *i.e.*, in refluxing tetrahydrofuran–benzene (1:1), thus indicating that triphenylthallium was not an intermediate in the coupling.

(3) H. Gilman and R. G. Jones, *J. Am. Chem. Soc.*, **62**, 2357 (1940).

(4) S. F. Birch, *J. Chem. Soc.*, 1132 (1934).

Synthesis of Novel Substituted (3)-1,7-Dicarbaundecaborate(12) Ions from 1,8-Dicarba-*closo*-undecaborane(11) and Carbanions

Sir:

Recently, the Lewis acid behavior of 1,8-dicarba-*closo*-undecaborane(11)[1-3] and the properties of some of its Lewis base adducts[4] have been reported. We now report the synthesis of a group of analogous ions, including two novel two-cage systems.

The previously described 1,8-$B_9C_2H_{11}$ carborane reacts with 1 mole of methyllithium in diethyl ether–hexane to produce a new $B_9C_2H_{11}CH_3^-$ ion I, which is isolated as its tetramethylammonium salt in 62% yield. Recrystallization from pure acetone yields white air-sensitive crystals. The infrared spectrum of a Nujol mull of I exhibits absorptions at 4.01 (s), 7.73 (w), 9.10 (m), 9.89 (w), 10.24 (m), 10.62 (s), 12.12 (w), and 13.79 μ (s). *Anal.* Calcd for $[(CH_3)_4N][B_9C_2H_{11}CH_3]$: C, 34.40; H, 12.51; B, 46.41; N, 6.63; equiv wt, 209.8. Found: C, 35.02; H, 11.29; B, 46.78; N, 6.57; mol wt (osmometric in acetonitrile), 207.

The 60-Mc/sec ^{1}H nmr spectrum of the tetramethylammonium salt of I in deuterioacetone exhibited a sharp singlet of intensity 12 at τ 6.64, a broad singlet of intensity 2 at τ 8.55, and a broad singlet of intensity 3 at τ 9.65. The intensity 12 resonance was assigned to the cation methyl protons, and the intensity 2 and 3 resonances were assigned to the carborane protons and to the cage methyl protons, respectively. The 32.1-Mc/sec ^{11}B nmr spectrum of I is complex, with a high-field doublet of intensity 2, a set of overlapping doublets of intensity 3, a singlet of intensity 1, and a low-field set of overlapping doublets of intensity 3. This spectrum, except for the aforementioned singlet, bears a striking resemblance to the spectrum of the previously reported (3)-1,7-$B_9C_2H_{12}^-$ ion,[5] which can now be obtained in

---

(1) F. N. Tebbe, P. M. Garrett, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **86**, 4222 (1964).

(2) C. D. Tsai and W. E. Streib, *ibid.*, **88**, 4513 (1966).

(3) T. E. Berry, F. N. Tebbe, and M. F. Hawthorne, *Tetrahedron Letters*, 715 (1965).

(4) F. N. Tebbe, P. M. Garrett, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **90**, 869 (1968).

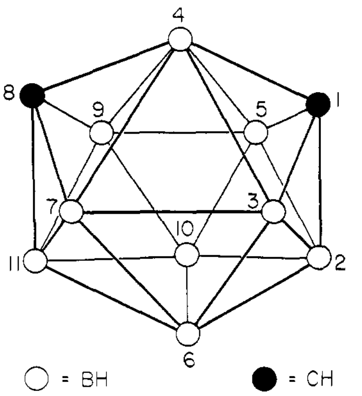

Figure 1. Structure of 1,8-dicarba-*closo*-undecaborane.

80% yield by the reaction of $1,8-B_9C_2H_{11}$ with 1 mole of $NaBH_4$ in 1,2-dimethoxyethane.

The $1,8-B_9C_2H_{11}$ carborane also reacts with a solution of $Li-1,2-B_{10}C_2H_{10}CH_3$[6] in diethyl ether to form a corresponding $B_9C_2H_{11}B_{10}C_2H_{10}CH_3^-$ ion II, which can be isolated as its tetramethylammonium salt in 72% yield. Recrystallization from water–ethanol yields white, air-stable needles which do not melt to 320°. The infrared spectrum of a Nujol mull of II exhibits absorptions at 3.94 (s), 7.09 (m), 7.82 (w), 8.46 (m), 8.87 (m), 9.09 (m), 9.84 (m), 10.16 (m), 10.57 (s), 11.50 (w), 12.49 (w), and 13.69 μ (s). *Anal.* Calcd for $[(CH_3)_4N][B_9C_2H_{11}B_{10}C_2H_{10}CH_3]$: C, 29.70; H, 9.97; B, 56.47; N, 3.86; equiv wt, 364. Found: C, 30.09; H, 10.09; B, 56.23; N, 3.96; mol wt (cryoscopic in ethanol), 363.

The 60-Mc/sec ^1H nmr spectrum of the tetramethylammonium salt of II in pyridine exhibited a sharp singlet of intensity 12 at τ 6.91, a sharp singlet of intensity 3 at τ 7.89, and a broad singlet of intensity 2 at τ 8.32. The resonances were assigned, as before, to cation methyl, carborane proton, and carborane methyl. The 32.1-Mc/sec ^{11}B nmr spectrum is complex, with the high-field doublet reminiscent of the high-field doublet in I and in the aforementioned $(3)-1,7-B_9C_2H_{12}^-$. This doublet has intensity 2:17 relative to the remainder of the resonances which features a large "doublet" very reminiscent of $1,2-B_{10}C_2H_{10}R_2$ systems.[7]

The $1,8-B_9C_2H_{11}$ carborane also reacts with the similarly formed $Li-1,10-B_8C_2H_8C_6H_5$ in diethyl ether–benzene to produce an analogous $B_9C_2H_{11}B_8C_2H_8C_6H_5^-$ ion III, which is isolated as the tetramethylammonium salt in 52% yield. Recrystallization from acetone–water yields air-stable white crystals. The infrared spectrum of a Nujol mull of III exhibited absorptions at 4.03 (s), 7.79 (w), 8.02 (w), 8.54 (w), 9.11 (m), 9.27 (w), 9.72 (m), 10.19 (m), 10.58 (s), 10.85 (w), 11.54 (w), 12.01 (m), 13.08 (s), 13.58 (w), and 14.35 μ (s). *Anal.* Calcd for $[(CH_3)_4N][B_9C_2H_{11}B_8C_2H_8C_6H_5]$: C, 41.88; H, 9.02; B, 45.63; N, 3.49; equiv wt, 402.4. Found: C, 39.88; H, 8.94; B, 45.63; N, 3.42; mol wt (cryoscopic in ethanol), 414.

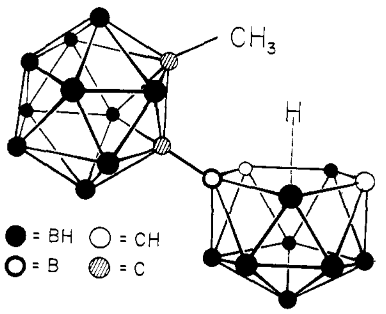

Figure 2. Proposed structure of the $B_9C_2H_{11}B_{10}C_2H_{10}CH_3^-$ ion.

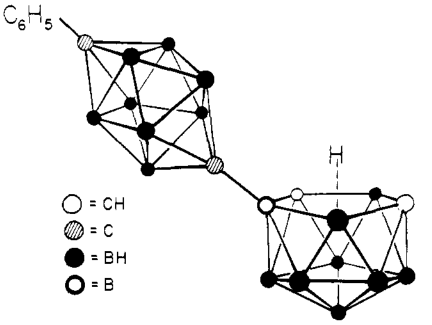

Figure 3. Proposed structure of the $B_9C_2H_{11}B_8C_2H_8C_6H_5^-$ ion.

The 60-Mc/sec ^1H nmr of the tetramethylammonium salt of III exhibits a sharp singlet of intensity 12 at τ 6.64, a broad singlet of intensity 2 centered at τ 8.70, and two multiplets of total intensity 5 centered at τ 2.45. These resonances were assigned to cation methyl, carborane protons, and phenyl protons, respectively. The 32.1-Mc/sec ^{11}B nmr exhibited the familiar high-field doublet of intensity 2, a multiplet of intensity 3, and a low-field multiplet of intensity 12, which was marked by the characteristic doublet exhibited in $1,10-B_8C_2H_8R_2$ systems.[4]

The nmr results indicated that the compounds formed were boron-substituted $(3)-1,7-B_9C_2H_{11}R$ ions. Since there is considerably more complexity in the 32.1-Mc/sec ^{11}B spectrum of I compared with the spectrum of $(3)-1,7-B_9C_2H_{12}^-$, we tentatively propose that the various R groups are substituted in the chemically equivalent but asymmetric 4 or 8 positions. This would be the point of substitution resulting from nucleophilic attack by the Lewis base at boron atoms 3, 5, 7, or 9 on $1,8-B_9C_2H_{11}$ (Figure 1). Since the 60-Mc/sec ^1H spectra of II and III exhibited no other carborane proton resonances other than those expected from a $(3)-1,7-B_9C_2H_{12}^-$ ion, it is suggested that the point of substitution on the B_{10} and B_8 cages is C-1 in each case. This led us to propose the structures shown in Figures 2 and 3 for ions II and III.

Further preliminary work suggests that similar ions of this type may be prepared and that transition metal complexes[8] incorporating this basic unit may be formed.

Acknowledgment. This research was supported in part by the Office of Naval Research.

---

(5) M. F. Hawthorne, D. C. Young, P. M. Garrett, D. A. Owen, S. G. Schwerin, F. N. Tebbe, and P. A. Wegner, *J. Am. Chem. Soc.*, **90**, 862 (1968).

(6) M. M. Fein, D. Grafstein, J. E. Paustian, I. Bobinski, B. M. Lichstein, N. Mayes, N. N. Schwartz, and M. S. Cohen, *Inorg. Chem.*, **2**, 1115 (1963).

(7) R. L. Pilling, F. N. Tebbe, M. F. Hawthorne, and E. G. Pier, *Proc. Chem. Soc.*, 402 (1964).

(8) M. F. Hawthorne, D. C. Young, T. D. Andrews, D. V. Howe, R. L. Pilling, A. D. Pitts, M. Reintjes, L. F. Warren, Jr., and P. A. Wegner, *J. Am. Chem. Soc.*, **90**, 879 (1968).

(9) NASA Fellow, 1966–1968.

M. Frederick Hawthorne, David A. Owen[9]
Department of Chemistry, The University of California
Riverside, California 92502

Received August 2, 1968