The spectral line widths of ClF^+ (**2**) (Figure 1a) are not constant, the outer and high-field lines being broadened.[6] This is a phenomenon characteristic of species with a residual line width due to nonaveraging of the *g* and hyperfine tensors.[7,8]

The Raman spectrum of the chlorine monofluoride radical cation **2** shows in addition to solvent bands a very strong band at 819 cm^{-1}. Unfortunately gas-phase spectra of ClF^+ have not been reported, but comparison with the vibrational frequencies of the isoelectronic species ClO (ground state $\omega_e = 868\ cm^{-1}$)[9] and with the vibrational frequency of ClF (758 cm^{-1})[10] is possible. Since the vibrational frequency of ClO should be lowered on passing from the gas phase into solution[11] and since a π^*-antibonding electron is removed from ClF to form ClF^+, the observed vibrational frequency of ClF^+ would seem to be consonant with those of ClF and ClO.[12]

When solutions of the chlorine molecule cation **1** are heated to 60°, the chlorine monofluoride molecule cation **2** is formed, and when solutions containing **1** and **2** are heated and cooled between the temperatures −80 to +60°, the relative amounts of **1** and **2** change reversibly with **1** predominating at low temperature and **2** predominating at high temperature.[13] Thus Cl_2^+ (**1**) can be

$$\underset{\mathbf{1}}{Cl_2^+} \rightleftarrows \underset{\mathbf{2}}{ClF^+}$$

formed from chlorine monofluoride[1] at or below room temperature with the complete nonformation of **2**, but

$$ClF \xrightarrow{SbF_5} Cl_2^+$$

once any of the radical cation **2** is formed by heating the sample to +60°, the equilibrium is rapidly established. So far we have only been able to obtain the chlorine monofluoride radical cation **2** in the absence of **1** by the reaction of chlorine pentafluoride with SbF_5

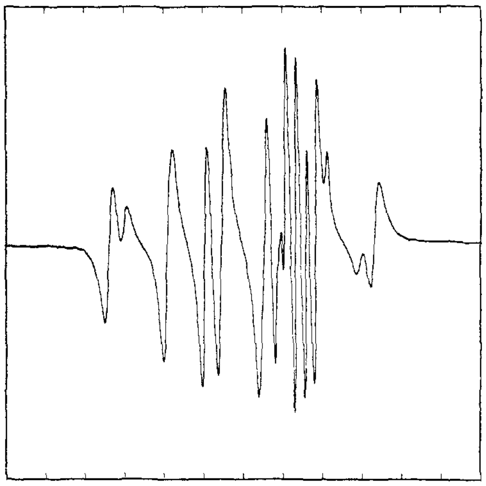

Figure 2. Epr spectrum of an equilibrium mixture of ClF^+ (**2**) and Cl_2^+ (**1**) at −40°. The marker spacing is 10 G.

$$ClF_5 \xrightarrow{SbF_5} ClF^+$$

the reaction of chlorine trifluoride always yielding the equilibrium mixture of **1** and **2**.

$$ClF_3 \xrightarrow{SbF_5} ClF^+ \rightleftarrows Cl_2^+$$

Figure 2 is a typical spectrum of the equilibrium mixture at −40°.

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[5] (a) Since ClF^+ would be expected to have a $^2\pi$ ground state, the *g* value near that of the free-spin value indicates that strong quenching of the orbital angular momentum in ClF^+ is present. This could be due to a strong (bonding) interaction with the solvent.[5b] Thus it is a somewhat moot point if the observed paramagnetic species should be called ClF^+. Similar comments apply to Cl_2^+. In solution, of course, any ion strongly interacts with its solvent environment. (b) The averaged *g* value for chlorine atoms adsorbed on silica is 2.009 and the isotopic coupling is about 10 G: C. L. Gardner, *J. Chem. Phys.*, **45**, 2991 (1967).

[6] The line widths in Figure 1a are approximately 3.25 G (central), 4.00 G (low field), and 4.50 G (high field).

[7] G. E. Pake, "Paramagnetic Resonances," W. A. Benjamin, Inc., New York, N. Y., 1962, p 110.

[8] The line widths for typical Cl_2^+ spectra monotonically increase from high field to low field. Matching of experimental spectra with simulated spectra for Cl_2^+ yields coupling constants of $a(^{35}Cl) = 2.59$ G and $a(^{37}Cl) = 2.15$ G. The highest resolution spectra we have as yet obtained for Cl_2^+ have maximum line widths (low field) of about 1.5 G. The previously published spectrum of Cl_2^+ (Figure 1 of ref 1) has a maximum line width of about 2.5 G.

[9] G. Porter, *Discussions Faraday Soc.*, **9**, 60 (1950).

[10] E. A. Jones, T. F. Parkinson, and T. G. Burke, *J. Chem. Phys.*, **18**, 235 (1950).

[11] H. Stammreich, P. Forneris, and Y. Taveres, *Spectrochim. Acta*, **17**, 1173 (1967).

[12] (a) Assuming the stretching frequencies of ClO would be about 20 cm^{-1} lower in solution than in the gas phase still leaves a difference of 30 cm^{-1} between the vibrational frequencies of ClO and ClF^+. This difference is consonant with strong interaction with the solvent mentioned in footnote 5 which would weaken the (formally bond and a half) Cl–F bond. (b) It has been reported [K. O. Christe and W. Sawodny, *Inorg. Chem.*, **6**, 313 (1967)] that ClF_2^+ possesses a Raman band at 818 cm^{-1}. While the presence of the diamagnetic species ClF_2^+ in the solutions described in present work must be considered, the band at 819 cm^{-1} can also be assigned to ClF^+ based on the above discussion.

[13] At −80° the equilibrium contains about 90% **1** and 10% **2**, and at +60° the equilibrium mixture contains about 5% **1** and 95% **2**.

A Three-Carbon Carborane Analog. 1-Stanna-2,3-dicarba-*closo*-dodecaborane(11)

Sir:

Molecular orbital calculations originally suggested that the $B_{12}H_{12}^{2-}$ ion would be stable[1] and that the icosahedral framework was held together by 26 electrons. The formal substitution of two electronically equivalent carbon atoms for two boron atoms in $B_{12}H_{12}^{2-}$ produces $B_{10}C_2H_{12}$, carborane. A further substitution of carbon for boron so as to maintain 26 electrons in the icosahedral framework would yield the unknown cation $[B_9C_3H_{12}]^+$, or if the species lost a proton, $B_9C_3H_{11}$. We would like to report the preparation and characterization of $B_9C_2SnH_{11}$ (I), a species related to $B_9C_3H_{11}$ by the formal replacement of C by another main-group IV element, Sn.

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[1] H. C. Longuet-Higgins and M. de V. Roberts, *Proc. Roy. Soc.* (London), **A230**, 110 (1955).

Recently, there has been much interest in carbametallic boranes,[2] but the vast majority of those reported are derived from transition metals. The one exception is $B_9BeC_2H_{11} \cdot N(CH_3)_3$ in which a beryllium atom is believed to occupy an icosahedral position.[3]

Synthesis of I was effected in a manner similar to that reported for the "marriage" of transition metals and $B_9C_2H_{11}$,[2-4] except that the dicarbollide ion was generated in refluxing benzene and the reaction was run on a 3-5-mmole scale with a 5% excess of $SnCl_2$. After refluxing for 24 hr the heterogeneous reaction mixture was placed in a Soxhlet thimble and extracted with benzene for 24 hr. Evaporation of the benzene gave a 75% yield of crude product which could be purified by recrystallization from dry benzene or sublimation *in vacuo* at 140°. The white crystals did not melt up to 400° (sealed tube) but discolored at 210° and charred at 265°. *Anal.* Calcd for $B_9C_2SnH_{11}$: B, 38.75; C, 9.56; H, 4.42; Sn, 47.27. Found: B, 38.35; C, 10.40; H, 4.53; Sn, 48.51. The molecular weight (isopiestic in benzene) of I was 251 ± 10 (theory 251.1). The mass spectrum displayed a parent ion cutoff at m/e 258, corresponding to $^{11}B_9{}^{12}C_2{}^{124}Sn^1H_{11}$. The ^1H nmr spectrum in acetonitrile-d_3 showed a broad singlet at δ -2.70 ppm (cage CH) relative to tetramethylsilane. The ^{11}B nmr spectrum (32.1 MHz) consisted of two doublets (J_{BH} = 141 Hz) at +24.8 and +31.8 ppm (relative to external $B(OCH_3)_3$) superpositioned on a broad unresolved signal which peaked at ~30 ppm. The ir spectrum (Figure 1) displayed the following absorptions in the 4000–300-cm^{-1} region (KBr disk): 3041, 2597, 2560, 2515, 1234, 1086, 1043, 1022, 1000, 962, 946, 915, 893, 871, 858, 840, 762, 739, 723, 703, 673, 611, 557, 478 cm^{-1}.

The only hydrogen stretching vibrations were at 3041 and 2597, 2560, 2515 cm^{-1}, C–H and B–H motions, respectively. The notable absence of absorption in the 1900–1800-cm^{-1} region and the presence of only a singlet in the proton nmr spectrum eliminates the possibility of a Sn–H bond in I.

Degradation of I with methanolic KOH gave $B_9C_2H_{12}^-$,[2] which was isolated as the white trimethylammonium salt and identified by its characteristic nmr and ir spectra.

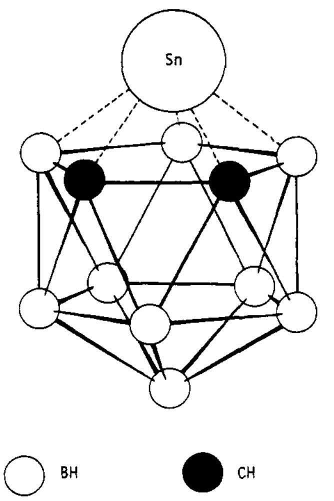

Figure 2. Proposed schematic structure of $B_9C_2SnH_{11}$.

Preliminary work shows that Pb and Ge also form carbametallic boranes analogous to I. Surprisingly, I can also be formed from bis(organo)tin dichlorides and $B_9C_2H_{11}^{2-}$.

The structure shown for I in Figure 2 is intuitively favored on the basis of other carbametallic borane structures and is consistent with the data presented above. The proposed structure represents a "bare" tin atom occupying an apex of the icosahedron. The analogous metallocene, bis(cyclopentadienyl)tin, also contains a "bare" tin as the rings of the sandwich are inclined toward each other to enclose an angle of 55°.[5] The structure of I is being investigated by X-ray crystallography.

Acknowledgment. The authors gratefully acknowledge the use of University of Colorado facilities for the determination of the ^{11}B nmr spectrum and the mass spectrum.

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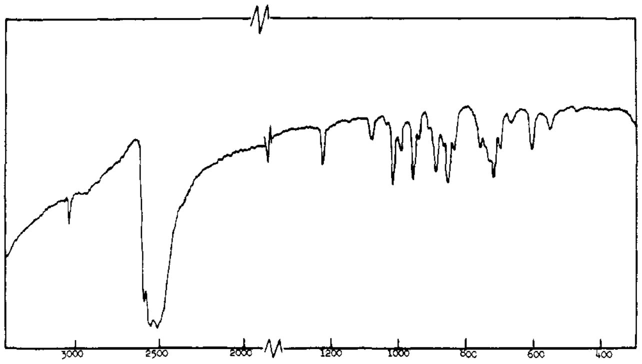

Figure 1. The infrared spectrum (KBr disk) of $B_9C_2SnH_{11}$.

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(2) M. F. Hawthorne, *Accounts Chem. Res.*, **1**, 281 (1968).

(3) G. Popp and M. F. Hawthorne, *J. Am. Chem. Soc.*, **90**, 6553 (1968).

(4) M. F. Hawthorne, *et al.*, *ibid.*, **90**, 879 (1968); M. F. Hawthorne, *et al.*, *Inorg. Syn.*, **10**, 91 (1967).

(5) A. Almenningen, A. Haaland, and T. Motzfeldt, *J. Organometal. Chem.*, **7**, 97 (1967).

One-Electron Oxidation of the $W_2Cl_9^{3-}$ Anion

Sir:

Metal-to-metal bonding is apparently responsible for a large measure of the stability of the metal cluster compounds.[1] Since oxidation reactions will result in either the partial or complete loss of the electrons which are extensively involved in the metal-to-metal bonding, a knowledge of such reactions is then necessary for a complete understanding. The importance of such bonds in the $W_2Cl_9^{3-}$ anion has been indicated by structural, chemical, magnetic, and spectroscopic studies.[2-4] A

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(1) F. A. Cotton, *Rev. Pure Appl. Chem.*, **17**, 25 (1967), and references contained therein.

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(3) R. Saillant and R. A. D. Wentworth, *Inorg. Chem.*, **7**, 1606 (1968).