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 $\pm$ 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 $\sim$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.

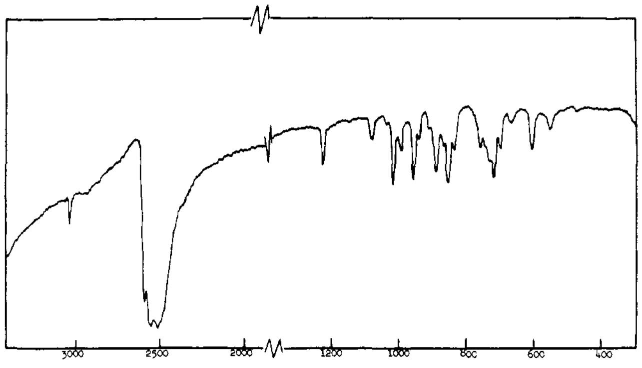

Figure 1. The infrared spectrum (KBr disk) of $B_9C_2SnH_{11}$.

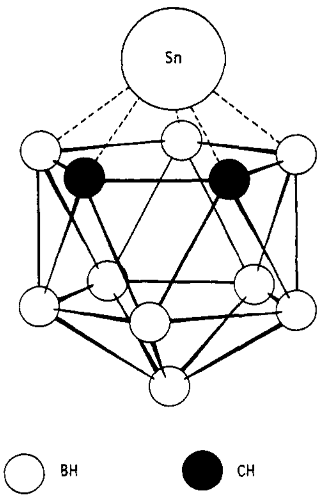

Figure 2. Proposed schematic structure of $B_9C_2SnH_{11}$.

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.

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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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crude formulation of the metal-to-metal molecular orbitals arises from the overlap of the t_{2g} orbitals on the adjacent metal atoms. From a consideration of the appropriate overlap integrals, the order of molecular orbitals with increasing energy is $a_1' < e' < e'' < a_2''$, where the a_1' and a_2'' orbitals result from the symmetric and antisymmetric combinations of the trigonally directed d_{z^2} orbitals, and the e' and e'' orbitals are derived from similar combinations of the $t_\pm$ orbitals.[5,6] In the case of the $W_2Cl_9^{3-}$ anion, the electronic configuration is then $(a_1')^2(e')^4$. From the limited evidence available in the literature, it would appear that the $(a_1')^2(e')^2$ configuration obtained from a two-electron oxidation is relatively unstable, and subsequent reactions lead to mononuclear W(IV) species.[7] Thus, the reaction of the anion with CN^- leads[8] to $W(CN)_8^{4-}$, while the pyrolysis in the presence of 8-hydroxyquinoline yields[9] the eight-coordinate, tetrakis derivative of W(IV).

We have now initiated an investigation of the $(a_1')^2(e')^3$ configuration. One-electron oxidation of the anion in dichloromethane occurs according to the equation

$$2W_2Cl_9^{3-} + X_2 \rightarrow 2W_2Cl_9^{2-} + 2X^-$$

$$X = Cl, Br, \text{ and } I$$

and without the incorporation of the oxidant into the anion. The compound has been isolated as the violet $[(n\text{-}C_4H_9)_4N]_2W_2Cl_9$ with an effective magnetic moment of 1.87 BM per formula unit. *Anal.* Calcd for $[(n\text{-}C_4H_9)_4N]_2W_2Cl_9$: C, 32.80; H, 6.19; N, 2.39; Cl, 27.23; W, 31.38. Found: C, 33.11; H, 6.25; N, 2.38; Cl, 26.90; W, 30.86. The molar conductance of a solution of this compound in acetonitrile (4.41×10^{-4} *M*) at 25° is 315 ohm^{-1} cm^2 $mole^{-1}$, which compares favorably with the molar conductivities of $Re_2Cl_9^{2-}$, $Re_2Br_9^{2-}$, and $Re_2Cl_8^{2-}$ with the same cation.[10] The oxidation was easily followed spectrophotometrically by the disappearance of the intense band at 4640 Å which was complete upon the addition of 1 equiv of the halogen. The stoichiometry of the reaction was rigorously proven from the equation

$$\frac{A}{C_w} = \varepsilon_{3,3} - n\Delta\varepsilon\left(\frac{C_x}{C_w}\right)$$

where A is the absorbance at 4640 Å, C_w is the initial concentration of $W_2Cl_9^{3-}$, C_x is the number of moles of added halogen divided by the total volume, $\varepsilon_{3,3}$ and $\varepsilon_{3,4}$ are the molar extinction coefficients of $W_2Cl_9^{3-}$ and $W_2Cl_9^{2-}$, respectively, and $\Delta\varepsilon = \varepsilon_{3,3} - \varepsilon_{3,4}$. Using I_2 as the oxidant, a plot of the variables gave an intercept of 4370 for $\varepsilon_{3,3}$ (4390 observed) and a slope of 8080. From the assumed stoichiometry, $n = 2$ and therefore $\Delta\varepsilon = 4040$ (4070 observed). The final spectrum consisted of bands at 13,530 cm^{-1} (ε 1040) and 17,200 cm^{-1} (ε 1700) with a shoulder at 25,600 cm^{-1} ($\varepsilon \sim 618$). Further addition of halogen simply caused the intensity of the spectrum of the $W_2Cl_9^{2-}$ anion to decrease, until finally a colorless solution was obtained.

While the dinuclear nature of the anion is clear, the actual structure remains in some doubt. The far-infrared spectrum of $[(n\text{-}C_4H_9)_4N]_2W_2Cl_9$ has a band at 295 cm^{-1} and a shoulder at 306 cm^{-1}, while that of $[(n\text{-}C_4H_9)_4N]_3W_2Cl_9$ has a shoulder at 270 cm^{-1} and resolved bands at 280 and 300 cm^{-1}. It is possible that the bioctahedron structure has been retained, but other structures are also possible. For example, the oxidized species may have a structure derived from that of $Re_2Cl_8^{2-}$ by the attachment of a Cl atom along one end of the fourfold axis. A similar structure was included as a possibility for the $Re_2Cl_9^-$ anion.[10] However, $W_2Cl_9^{2-}$ is not isoelectronic with any known rhenium dinuclear species, so that corresponding structures are not necessarily expected.

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Pentacoordinate Sulfur Compounds as Intermediates in Organic Reactions

Sir:

Much work has been performed on the mechanism of displacement reactions at sulfur.[1] One major question that remains unanswered is whether the pentacoordinate sulfur species represents an intermediate or a transition state. Earlier work[2-4] suggested the possibility of these types of intermediates in reactions of organolithium compounds with electron-deficient sulfur compounds, although this mode of reaction has been questioned.[4] We wish to report evidence strongly implicating pentacoordinate sulfur species as reaction intermediates as well as to establish a new synthetic method to effect coupling of two unsaturated fragments and to generate sulfur ylides, a versatile class of synthetic intermediates.

The reaction of triphenylsulfonium fluoroborate (I) with vinyllithium (II) generates diphenyl sulfide and styrene in quantitative yields (see Scheme I). Of the various reaction pathways, the most likely are (1) elimina-

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