central and ligand atoms and is weakly antibonding.[8] As might be anticipated from the discussion of AB_2 molecules by Walsh,[9] this band shifts to lower ionization potential as the ionization potential of the central atom decreases in the series O_3, SO_2, and SiF_2.[10]

The second and third bands of SiF_2 are partly hidden by the bands of SiF_4. However, both the bandwidths and relative intensities of the second and third bands with apparent vertical ionization potentials of 15.6 and 17.1 eV indicate that they result from ionization from at least two molecular orbitals each. This is reasonable as the splittings of the $1a_2$, $4b_2$ and $1b_1$, $5a_1$ pairs is small for O_3, SO_2, and NO_2.[10] These orbital pairs correlate with the π_g and π_u orbitals in linear AB_2 molecules and, as they are expected to be somewhat localized on B,[9] will appear at higher ionization energies than similar orbitals in SO_2.[3,7] The spectrum of SiH_2F_2 has two fairly narrow bands at 12.85 and 15.20 eV assigned to ionization from molecular orbitals associated with the SiH bonding and two broad and more intense bands between 15.5-16.5 and 17-19 eV assigned to the $1a_2$, $4b_2$ and $1b_1$, $5a_1$, $3b_2$ orbital groups, respectively.[11] These broad bands are very similar to the second and third bands observed for SiF_2. SiH_3F exhibits a band at 16.1 eV which has been assigned to fluorine "lone pair" ionization[12] and NSF also has two bands between 15.5 and 16.5.[13] Thus, one is tempted to assign the second band in SiF_2 to the $1a_2$, $4b_2$ pair and the third band to the $1b_1$, $5a_1$ pair.

It is of interest to compare this orbital assignment based on Koopmans' theorem with the information available from ultraviolet emission and absorption spectra of SiF_2. There is substantial evidence[14,15] that the ultraviolet absorption with a vibrationless transition at 44,109 cm^{-1} corresponds to the transition

$$\ldots(4b_2)^2(1a_2)^2(6a_1)(2b_1),\ {}^1B_1 \leftarrow \ldots(4b_2)^2(1a_2)^2(6a_1)^2,\ {}^1A_1$$

Recently,[16] absorption in the vacuum ultraviolet with a vibrationless transition at 62,214 cm^{-1} has been assigned to the transition

$$\cdots(4b_a)^2(1a_2)(6a_1)^2(2b_1),\ {}^1B_2 \leftarrow \cdots(4b_2)^2(1a_2)_2^2(6a_1)^2,\ {}^1A_1$$

This suggests that the spacing between the $6a_1$ and $1a_2$ orbitals should be 18,105 cm^{-1} (2.24 eV) and, thus, there should be a band in the photoelectron spectrum at $11.08 + 2.24 = 13.32$ eV. Clearly no such band is present. The photoelectron and ultraviolet absorption data are compatible if the vacuum ultraviolet absorption at 62,214 cm^{-1} is reassigned to ${}^3B_2 \leftarrow {}^1A_1$ as a near ultraviolet system with a vibrationless transition at 26,310 cm^{-1} has been observed and assigned to ${}^3B_1 \leftarrow {}^1A_1$.[17] This revised assignment leads to a splitting of the $6a_1$ and $1a_2$ orbitals of 35,904 cm^{-1} (4.45 eV) which compares well with the difference in ionization energies of the first two bands in the photoelectron spectrum (4.49 eV). The ${}^1B_2 \leftarrow {}^1A_1$ transition would then be predicted to lie at *ca.* 80,000 cm^{-1}.[18]

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Registry No. SiF_2, 13966-66-0.

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Synthesis of *closo*-1,7-$B_{10}C_2H_{12}$ from *nido*-2-B_5CH_9

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Until now, direct routes to two-carbon carboranes have involved treating boron hydrides with acetylenes, alkenes, and atomic carbon species.[1] Many other two-carbon carboranes have been discovered by subjecting known two-carbon carboranes to chemical oxidation, hydroboration, pyrolysis, photolysis, or electrical discharge.[1,2] We now report a unique synthesis of a closed two-carbon carborane accomplished by joining two units of a one-carbon carborane.

Experimental Section

Techniques for the preparation and purification of 2-B_5CH_9 have been described elsewhere.[3,4]

In a typical pyrolysis, 0.0968 g of 2-B_5CH_9 (1.29 mmol) was sealed in a 100-cm^3 Pyrex bomb and heated to 250° for 84 hr. A total of 2.32 mmol of hydrogen was generated. The volatile borane products (0.040 g, 41.5 wt % conversion to two-carbon carboranes) were separated on a 25 ft × $^1/_4$ in. glass vpc column at 210° (10% Apiezon L on firebrick). The products (see Table I) were identified by their characteristic R_f values, mass spectra, and ^{11}B nmr spectra. The 1,7-$B_{10}C_2H_{12}$ derivative was also identified by comparison of its melting point and ir spectrum with those of an authentic sample. Neither the 1,2- nor 1,12-$B_{10}C_2H_{12}$ isomer was detected.

In a separate experiment, 0.0707 g of 3-$CH_3B_5CH_8$[3,4] (0.794 mmol) was pyrolyzed for 2 days at 250°. The only product was 0.0093 g of a clear liquid. Boron-11 nmr, proton nmr, and mass spectra showed this liquid to be a B-methylated 1,6-$B_8C_2H_8(CH_3)_2$ species (0.063 mmol, 16% conversion). No B-methylated $B_{10}C_2H_{10}(CH_3)_2$ species were detected.

Results and Discussion

The gas-phase pyrolysis of 2-B_5CH_9 at 250° proceeds in two identifiable directions. In one pathway, two molecules of *nido*-2-carbahexaborane(9) apparently fuse, face to face, to

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Table I. Carboranes Formed in the Gas-Phase Pyrolysis of $2\text{-}B_5CH_9$

	$R_f{}^a$	Yield mmol	Yield $\%^b$
$1,7\text{-}B_6C_2H_8$	2.3	0.033	5
$1,6\text{-}B_8C_2H_{10}$	5.1	Trace	1
$1,7\text{-}B_{10}C_2H_{12}$	13.4	0.105	16
$1,3\text{-}B_7C_2H_{13}$	14.0	0.196	30

[a] Relative to *n*-pentane = 1.00. [b] Based on conversion of 2 mol of $2\text{-}B_5CH_9$/1 mol of product.

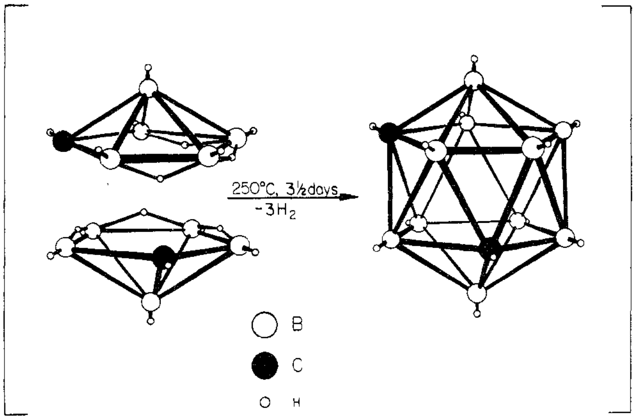

Figure 1. Schematic representation of the fusion of two B_5C skeletons to produce the $1,7\text{-}B_{10}C_2$ skeleton.

form one molecule of *closo*-1,7-dicarbadodecaborane(12). We find unusual the fact that the two nido B_5C cages do not come together with bridge hydrogens apart, thereby generating the $1,12\text{-}B_{10}C_2H_{12}$ species.

One reviewer has proposed the idea that the reacting species may not be $2\text{-}B_5CH_9$ but a nido isomer of B_5CH_7.[5] At the temperature of the pyrolysis reaction simple bridge hydrogen loss from *nido*-$2\text{-}B_5CH_9$ would generate the *nido*-B_5CH_7 isomer. This isomer would retain one bridge hydrogen on the open B_5C skeleton. The area from which the two bridge hydrogens were removed would now have a high electron density and would serve as a center to attack the most electrophilic area (*i.e.*, the carbon atom) on *nido*-$2\text{-}B_5CH_9$ or another *nido*-B_5CH_7. Assuming the lone bridge hydrogen on a *nido*-B_5CH_7 lies opposite the carbon atom, the $1,7\text{-}B_{10}C_2$ skeleton would be uniquely generated. We find this proposal interesting but must add that one might also expect the known *closo*-B_5CH_7[5] to be generated from a *nido*-B_5CH_7. No *closo*-B_5CH_7 is observed, although nido → closo conversions are well known for two-carbon carboranes.[1,2]

A second pathway for decomposition is suggested by the high yield of $1,3\text{-}B_7C_2H_{13}$ and its pyrolysis products $1,7\text{-}B_6C_2H_8$ and $1,6\text{-}B_8C_2H_{10}$.[6] The exact nature of this mechanism is unclear at this time, but it, too, represents a monocarbon to dicarbon carborane conversion. This latter mechanism is apparently the only pathway followed in the pyrolysis of $3\text{-}CH_3B_5CH_8$ (see Experimental Section). Examination of the ^{11}B nmr spectrum of the $1,6\text{-}B_8C_2H_8(CH_3)_2$ recovered revealed only that the two *B*-methyl units were in equatorial positions.

At the present time, few other systems exist to test whether this "fusing" reaction is a general one in boron chemistry. We suggest that $2,3\text{-}B_4C_2H_8$ and B_6H_{10} might fuse to form $1,2\text{-}B_{10}C_2H_{12}$. We also point out that the isostructural molecules, $2,3,4\text{-}B_3C_3H_7$[1] and $2,3,4,5\text{-}B_2C_4H_6$,[7] may prove interesting candidates for future reactions of this kind.

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Registry No. $2\text{-}B_5CH_9$, 12385-35-2; $1,7\text{-}B_6C_2H_8$, 23732-90-3; $1,6\text{-}B_8C_2H_{10}$, 23704-81-6; $1,7\text{-}B_{10}C_2H_{12}$, 16986-24-6; $1,3\text{-}B_7C_2H_{13}$, 49547-48-0; $3\text{-}CH_3B_5CH_8$, 23087-40-3; $1,6\text{-}B_8C_2H_8(CH_3)_2$, 17731-50-9.

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Single-Crystal Magnetic Susceptibility Measurements on Tris(ethylenediamine)cobalt(III) Di-μ-chloro-bis[trichlorocuprate(II)] Dichloride Dihydrate. A Compound Which Contains the Dimeric $Cu_2Cl_8{}^{4-}$ Anion

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The preparation of a complex having the empirical formula $Co(en)_3CuCl_5{\cdot}H_2O$ (en is ethylenediamine) was reported by Kurnakow[1] in 1898. Recently,[2,3] this compound was found to be structurally unique and consequently it is of unusual chemical interest. The X-ray crystal structure analysis[2] revealed the expected tris(ethylenediamine)cobalt(III) cation, an unexpected $[Cu_2Cl_8]^{4-}$ dimeric anion, along with uncoordinated chloride ions and water molecules. Preliminary magnetic susceptibility measurements[3] on a powdered sample revealed the presence of an exchange interaction between the copper(II) ions. In order to more precisely characterize the exchange interaction and to accurately determine the associated magnetic parameters for this compound, we have undertaken magnetic susceptibility measurements on a single crystal of $[Co(en)_3]_2[Cu_2Cl_8]Cl_2{\cdot}2H_2O$, and the results are reported herein along with additional high-temperature magnetic susceptibility data on a powdered sample.

Experimental Section

Preparation. Reasonably large single crystals of $[Co(en)_3]_2[Cu_2Cl_8]Cl_2{\cdot}2H_2O$ were grown from an aqueous solution containing 3.5 g of $[Co(en)_3]Cl_3$, 1.5 g of $CuCl_2{\cdot}2H_2O$, and 1-2% HCl. In most instances, some starting material ($[Co(en)_3]Cl_3$) recrystallized and was removed before the desired crystals formed.

Anal. Calcd for $[Co(C_2N_2H_8)_3][Cu_2Cl_8]Cl_2{\cdot}2H_2O$: C, 14.47; H, 5.26; N, 16.87. Found (powdered sample): C, 14.56; H, 5.28; N, 16.65. Found (single crystal): C, 14.65; H, 5.40; N, 17.12.

The crystals form as hexagonal prisms whose morphology has been described elsewhere.[2] The hexagonal faces are bounded by the (100) and $(\bar{1}00)$ planes, and the rectangular faces are bounded by the $(01\bar{1})$, $(0\bar{1}1)$, (001), $(00\bar{1})$, (011), and $(0\bar{1}\bar{1})$ planes. The crystals were found to cleave in the *bc* plane.

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