Tricarbahexaborane(7)

Sir:

We have isolated and structurally characterized three major volatile products from the room-temperature vapor-phase reaction of tetraborane(10) and acetylene. These compounds have been identified as C-methyl derivatives of tricarbahexaborane(7), which is the first three-carbon carborane to be reported. A fourth product is believed to be the parent compound, $C_3B_3H_7$, for which the structure 2,3,4-tricarbahexaborane(7) is proposed (Figure 1).

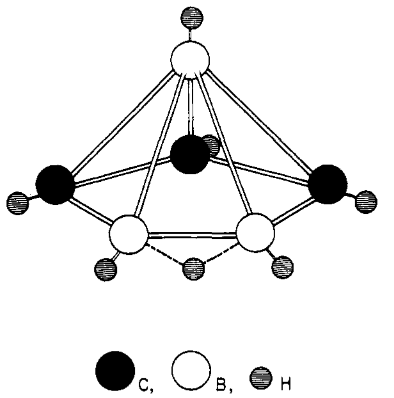

Figure 1. Structure of 2,3,4-tricarbahexaborane(7).

In a typical experiment the reaction between 3.1 mmoles of purified B_4H_{10} and 3.3 mmoles of C_2H_2 was allowed to proceed 7 days in a sealed Pyrex flask, at the end of which time 1.7 mmoles of B_4H_{10} and only a trace of C_2H_2 remained. During the reaction a white solid continually formed in the flask and settled to the bottom. After removal of unreacted starting materials by repeated fractionation through a $-95°$ trap, the volatile products were separated by vapor phase chromatography (9.8 ft × 0.25 in. column of 30% Kel-F on Chromosorb W). Retention times (B_5H_9 = 1) are: 2-CH_3-2,3,4-$C_3B_3H_6$ (I), 2.4; 2,3-$(CH_3)_2$-2,3,4-$C_3B_3H_5$ (II), 4.1; 2,4-$(CH_3)_2$-2,3,4-$C_3B_3H_5$ (III), 5.6; $C_3B_3H_7$ (?) (IV), 2.0. Approximately 0.01 mmole each of I, II, and III, 0.001 mmole of IV, and 0.006 mmole of B_5H_9 were produced per mmole of B_4H_{10} consumed. When excess C_2H_2 was used, 3.5 mmoles of C_2H_2 reacted per mmole of B_4H_{10}.

The structures of I, II, and III were assigned from the infrared spectra, mass spectra, and ^{11}B and ^1H nmr spectra of the pure compounds. Parent mass peaks of 90, 104, and 104 were obtained for I, II, and III, respectively, as indicated by very sharp high-mass cutoffs, and the nearly identical mass spectra of II and III are suggestive of isomers.

The ^{11}B nmr spectra of I, II, and III (Figure 2) indicate the presence of three boron atoms in each, and the high-field doublet of unit area appearing in all three spectra is reasonably assigned to an apical B–H group. Consistent with the proposed structure, B(5) and B(6) in the spectrum of III are equivalent, and the fine splitting caused by coupling of B(5) and B(6) to a common bridge hydrogen is apparent. It is clear that each boron in all of the compounds is bonded to one terminal proton, so that B-alkylated products are excluded.

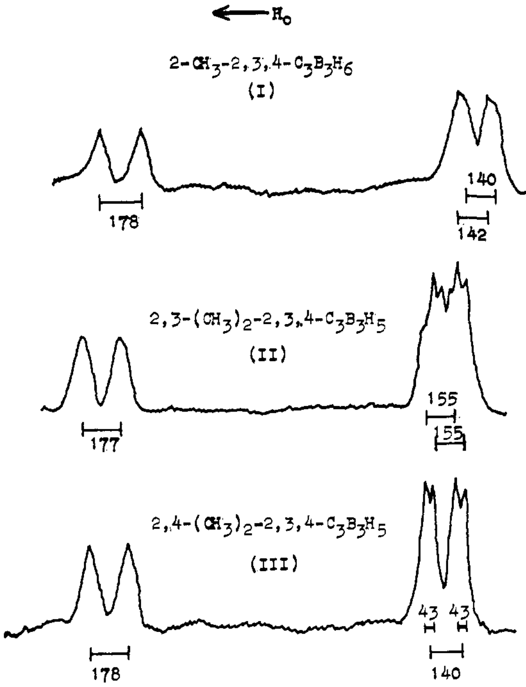

Figure 2. ^{11}B nmr spectra (32.2 Mc) of pure 2,3,4-$C_3B_3H_7$ methyl derivatives. Coupling constants are given in cycles per second. Exact chemical shifts relative to a standard were not determined, but in each spectrum the low-field doublet is centered at approximately δ 0 ($BF_3 \cdot O(C_2H_5)_2$ reference). The chemical shift (ppm) between the lowest field doublet and the high-field doublet is 49.2 in I, 46.9 in II, and 46.9 in III.

The infrared spectra of I, II, and III resemble that of 2,3-dicarbahexaborane(8)[1] and suggest an open-cage carborane structure. Bridge hydrogen atoms are indicated by absorptions near 1900 and 1500 cm^{-1} in all three compounds, and the relative weakness of these bands is consistent with the presence of only one such bridge. There are no strong bands near 1320 cm^{-1}, indicating a lack of B-methyl groups, but the bands at ~1450 cm^{-1} are characteristic of C-methyl deformations. Similarly, the relative intensities of the CH_3 (~2900 cm^{-1}) and BH (~2500 cm^{-1}) stretching bands are consistent with the assignment of I as a monomethyl derivative and II and III as dimethyl derivatives. A single, sharp band near 3020 cm^{-1} is characteristic of the cage C–H stretch[1] and is strongest in I, as expected when two such groups are present.

The proton nmr spectra of the pure compounds support the suggested structures. In addition to the broad B–H multiplets, the spectrum of I has three strong singlets in a 3:1:1 area ratio, at τ 8.63, 5.84, and 4.33, respectively, corresponding to the methyl group and two nonequivalent cage C–H groups. The spectrum of II shows single peaks at τ 9.95, 8.53, and 5.08 with relative intensities 3:3:1, while III has two singlets at τ 9.55 and 4.82 with a 6:1 area ratio. Assigning the peaks near τ 5.0 to cage C–H resonance and the higher field peaks to methyl groups, the assignments of II and III as asymmetrical and symmetrical derivatives, respectively, are clearly supported.

A fourth volatile product (IV) has an infrared spectrum similar to those of I–III minus the CH_3 stretching bands and may be the parent compound. This material

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(1) T. Onak and G. B. Dunks, *Inorg. Chem.*, 5, 439 (1966).

is about as volatile as hexaborane(10) but is highly unstable at room temperature. It is to be noted that $C_3B_3H_7$ is related to known molecules in the isoelectronic series: B_6H_{10} (four bridge protons), CB_5H_9 (three bridges),[2] $C_2B_4H_8$ (two bridges),[3] $C_3B_3H_7$ (one bridge), and the hypothetical molecule[4] $C_4B_2H_6$ (no bridges).

The mechanisms operating in this reaction system are at present a matter for speculation, but it seems likely that hydroboration reactions are involved at early stages.[5] The observed formation of methylated species fits the pattern noted in other recent studies of borane–acetylene reactions,[2,5,6] but its occurrence at ambient temperature is novel. A detailed investigation of the B_4H_{10}–C_2H_2 reaction and the chemistry of the tricarbahexaborane(7) derivatives is in progress.

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(2) T. P. Onak, G. B. Dunks, J. R. Spielman, F. J. Gerhart, and R. E. Williams, *J. Am. Chem. Soc.*, **88**, 2061 (1966).

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Electron-Deficient Bonding Involving Sulfur Atoms. II. The Crystal Structure of $Cu_4[SC(NH_2)_2]_9(NO_3)_4$

Sir:

In a previous communication[1] we described a new type of bridge bond in the structure of bis(thiourea)silver(I) chloride in which a thiourea S–C $p\pi$ molecular orbital was used to form a three-center bridge bond with $\sigma(sp^3)$ Ag(I) orbitals. During the course of structure investigations of a number of metal–thiourea complexes we prepared a complex of thiourea with cuprous ion with the unusual formula of $Cu_4[SC(NH_2)_2]_9(NO_3)_4$, hereafter referred to as $Cu_4(tu)_9(NO_3)_4$. The crystal structure revealed no less than five different types of metal–sulfur bonds, at least one of which is a completely new type of three-center electron-deficient bridge bond involving a sulfur sp^2 nonbonding orbital.

Stoichiometric amounts of cupric nitrate and thiourea were caused to react in aqueous solution and the solution was allowed to cool and evaporate to grow single crystals of $Cu_4(tu)_9(NO_3)_4$. The crystals were found to be orthorhombic; with Cu K($\alpha_1 = 1.505$, $\alpha_2 = 1.544$ A), the cell constants are $a = 14.94$, $b = 21.76$, and $c = 14.63$ A, all ±0.01 A. Four $Cu_4(tu)_9(NO_3)_4$ entities per cell gave a calculated density of 1.71 g cm^{-3} in good agreement with the 1.75 g cm^{-3} observed. Systematic absences indicated the possible space groups to be $Pbc2_1$ or Pbcm; the structure analysis confirmed the latter (*vide infra*). A single crystal 0.1 × 0.2 × 0.3 mm was mounted with the long dimension vertical on a G.E. single-crystal orienter seated on a Picker diffractometer for the collection of 1099 independent *hkl* intensity data by a scanning technique.

The structure was solved by conventional three-dimensional Patterson and Fourier techniques.[2] Refinement was carried out by complete matrix least squares including anisotropic temperature factors[3] with observations weighted as the inverse of their variances.[4] The final disagreement index, R ($R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$), was found to be 0.108. A final three-dimensional difference map did not indicate any unusual features.

The structure may be described as made up of a rectangle of Cu atoms (Cu_1,Cu_2,Cu_1',Cu_2'; Figures 1 and 2) which are connected by bridging sulfur atoms of thiourea groups. These rectangles are, in turn, interconnected by other sulfur bridges to form an infinite polymer of sulfur-bridged Cu atoms propagating in the *c* direction. By this means each Cu is surrounded by four S atoms to give Cu(I) its most common tetrahedral coordination. The only functions of the nitrate groups, other than that of perhaps participation in some hydrogen bonding, are to fill "holes" left by the polymer and balance charge.

There exist in the structure no less than five distinctly different types of metal–sulfur bonds (see roman numerals in Figure 1). Of course, molecular packing may well be important in such a complex structure, and it is difficult to determine its magnitude. However, we wish to describe and discuss each of these types of metal–sulfur bonds in turn.

The four-membered ring defined by Cu_1,Cu_2,S_1,S_2 contains sulfur bridges of type I and has a particularly interesting geometry: (1) the Cu_1–Cu_2 distance is only 2.707 ± 0.005 A; (2) the Cu–S–Cu angles are only 69°; (3) the dihedral angle between normals of the planes defined by Cu_1–$S_1(S_2)$–Cu_2 and the $S_1(S_2)$ thiourea plane is 86°; (4) the angle between a line formed by the intersection of the plane defined by the $S_1(S_2)$ thiourea group and the Cu_1–$S_1(S_2)$–Cu_2 plane with the S_1–C_1(S_2–C_2) bond is 110°.[5] Further, individually, each thiourea group is planar within experimental error.

This short metal–metal distance and the accompanying sharp bridge angle are strikingly similar to the electron-deficient bridges in polymeric dimethylberyllium[6] and dimeric trimethylaluminum[7,8] where the metal–metal distances are approximately equal to the sum of the covalent radii and the bridge angles are 66 and 74.3°, respectively. If the reasonable assumption is made that the sulfur atom in thiourea is sp^2 hybridized

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(1) E. A. Vizzini and E. L. Amma, *J. Am. Chem. Soc.*, **88**, 2872 (1966).

(2) Sly–Shoemaker–Van den Hende Fourier program for the IBM 7090.

(3) W. Busing, K. O. Martin, and H. Levy, OR FLS program for least squares and OR FFE program for distances, angles, and errors.

(4) S. W. Peterson and H. A. Levy, *Acta Cryst.*, **10**, 70 (1957).

(5) The notation Cu_1–$S_1(S_2)$–Cu_2 refers to either the Cu_1–S_1–Cu_2 plane or the Cu_1–S_2–Cu_2 plane and, in similar fashion, $S_1(S_2)$ refers to S_1 or S_2. Items 2, 3, and 4 are average values, but the differences are at most three standard deviations. However, the four-membered ring (Cu_1,Cu_2,S_1,S_2) has two sets of distinctly different Cu–S distances: Cu–S_1, 2.469; Cu_2–S_1, 2.291; Cu_1–S_2, 2.326; Cu_2–S_2, 2.472 A (all ±0.008 A). The Cu_1,S_1,Cu_2,S_2 unit is also not quite planar with Cu_1,Cu_2,S_1,S_2 displaced +0.042, + 0.043, −0.155, and −0.134 A, respectively, from the best least-squares plane through the four atoms. These details can be understood in terms of refinements of the postulated model, but space limits the discussion.

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