Table I. Initial Rate Data[a] on the Formation of $B_{10}H_9COHC_6H_5^-$

No.	$B_{10}H_{10}^{2-}$ [b]	C_6H_5COCl	CF_3CO_2H	10^6k_i, M sec^{-1}	10^4k, M^{-1} sec^{-1}
1	0.075	0.45		17.32	4.99
2	0.075	0.225		8.67	5.13
3	0.075	0.075		2.92	5.19
4	0.075	0.045		1.69	5.01
5	0.075	0.0075		0.267	4.75
6	0.0375	0.045		0.832	4.93
7	0.0375	0.225		4.26	5.05
8	0.0075	0.045		0.0165	4.89
9	0.0075	0.225		0.816	4.84
10	0.075	0.45	0.05	12.87	
11	0.075	0.45	0.10	11.59	
12	0.075	0.45	0.20	9.25	
13	0.075	0.45	0.30	7.64	
14	0.075	0.45	0.40	6.27	
15	0.075	0.45	0.50	5.20	
16	0.075	0.45	0.60	4.63	
17	0.075	0.45	0.70	3.93	

[a] At 308°K, CH_3CN solvent. [b] $(C_4H_9)_4N^+$ salt.

nature of the acid effect was examined by 80.5-MHz ^{11}B nmr and was shown to be a consequence of the equilibrium protonation of $B_{10}H_{10}^{2-}$ to yield a new species, probably $B_{10}H_{11}^-$.[5] In Figure 1B both $B_{10}H_{10}^{2-}$ and $B_{10}H_{11}^-$ are present in the initial reaction mixture, and substantial formation of I occurs within 2 min after addition of C_6H_5COBr. However, some $B_{10}H_{10}^{2-}$ and $B_{10}H_{11}^-$ clearly remain. After 16 min, the reaction is essentially complete and the spectrum is principally that of I. In the absence of acid the reaction would be complete in less than 3 min. In Figure 1C all the $B_{10}H_{10}^{2-}$ is initially present as $B_{10}H_{11}^-$ and after 15 min, within the limits of nmr detection, little reaction has occurred with C_6H_5COBr. The apparent inertness of $B_{10}H_{11}^-$ to benzoylation is even more striking in the case of the less reactive benzoyl chloride. Under conditions equivalent to those of Figure 1C, the nmr spectrum of the acid form is unchanged even after 1 hr. This evidence is supported by the 40% recovery of $B_{10}H_{10}^{2-}$ from reaction mixtures of C_6H_5COCl and $B_{10}H_{11}^-$ after a 1-hr reaction period. In the absence of acid the same reaction mixture proceeds to greater than 80% yield.

A mechanism consisting of eq 4 and 5 yields an initial

$$B_{10}H_{10}^{2-} + H^+ \overset{K}{\rightleftharpoons} B_{10}H_{11}^- \qquad (4)$$

$$B_{10}H_{10}^{2-} + C_6H_5COCl \xrightarrow{k_2} B_{10}H_9COHC_6H_5^- + Cl^- \qquad (5)$$

rate law which agrees with both the kinetic and spectroscopic data (eq 6). In the absence of acid eq 6 reduces to the observed rate law (eq 3). With acid present eq 6

$$\left(\frac{d[I]}{dt}\right)_0 = k_i = \frac{k_2[B_{10}H_{10}^{2-}]_0[C_6H_5COCl]_0}{1 + K[H^+]} \qquad (6)$$

requires a plot of $[B_{10}H_{10}^{2-}]_0[C_6H_6COCl]_0/k_i$ *vs.* $[H^+]$ to be linear with an intercept equal to $1/k_2$ and a slope equal to K/k_2. Using the kinetic results of Table I, the expected linear plot was obtained and from this plot a value of $K = 4.6 \pm 0.5$ M was extracted. An independent evaluation[5] of K from ^{11}B nmr data yields a value of $K = 0.8 \pm 0.2$ M. Closer agreement between the independently determined values is unlikely because of the nonideality of the solutions for all determinations of K and the absence of C_6H_5COX in the ^{11}B nmr determinations.[5]

The substitution chemistry of $B_{10}H_{10}^{2-}$ [6] is not well understood and the results reported here suggest that some of the complexity may be due to the presence of two species of different reactivity: $B_{10}H_{10}^{2-}$ and a protonated form $B_{10}H_{11}^-$. This is especially relevant since the preponderance of the synthetic studies of $B_{10}H_{10}^{2-}$ was carried out under strongly acidic conditions. Moreover, the apparent inertness of $B_{10}H_{11}^-$ toward electrophilic attack coupled with the electrophilic properties of the proton may imply an intermediate in electrophilic substitution at $B_{10}H_{10}^{2-}$ which resembles $B_{10}H_{11}^-$. An electrophile (E) may attack $B_{10}H_{10}^{2-}$ to produce $B_{10}H_{10}E^{2-}$ where E takes the place of the additional proton in $B_{10}H_{11}^-$. We are examining this possibility.

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(5) P. A. Wegner, R. Unger, R. Wiersema, M. F. Hawthorne, unpublished results. The equilibrium formation of $B_{10}H_{11}^-$ from $B_{10}H_{10}^{2-}$ and CF_3CO_2H in acetonitrile has been studied quantitatively using ^{11}B nmr spectroscopy. These studies regarding the structure and reactivity of $B_{10}H_{11}^-$ will be reported later.

(6) E. L. Muetterties and W. Knoth, "Polyhedral Boranes," Marcel Dekker, New York, N. Y., 1968, includes an extensive discussion of the substitution chemistry of $B_{10}H_{10}^{2-}$.

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$C_2B_6H_{10}$, a New *nido*-Carborane

Sir:

The heretofore unknown *nido*-carborane, $C_2B_6H_{10}$, has been synthesized,[1] isolated, and identified from the reaction between $C_2B_3H_5$ and B_2H_6 in a heated stainless steel flow reactor. Yields of <5% based upon the stoichiometric equation (1) were obtained.[2]

$$C_2B_3H_5 + {}^3/_2B_2H_6 \longrightarrow C_2B_6H_{10} + 4H_2 \qquad (1)$$

The product $C_2B_6H_{10}$ is an air-sensitive clear liquid which is relatively unstable in the liquid phase, decomposing at ambient temperatures primarily to $C_2B_6H_8$ and $C_2B_5H_7$; it can be stored in the gas phase for extended periods of time with no apparent decomposition.

Reaction conditions consisted of a flow system (~20 sec nominal residence time) of equimolar quantities of diborane and $C_2B_3H_5$ (preparation reported previously[3]) at 0.5 atm in a 0.75 in. × 12 in. stainless steel tube reactor heated to 300°. The effluent from the

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(1) J. F. Ditter, J. D. Oakes, and E. B. Klusmann, Abstracts of the 160th National Meeting of the American Chemical Society, Chicago, Ill., 1970.

(2) For general information on carborane structures, properties, and reactions see (a) R. E. Williams, "Progress in Boron Chemistry," Vol. 2, Pergamon Press, Oxford, England, 1970, Chapter 2; (b) R. N. Grimes, "Carboranes," Academic Press, N. Y., 1970.

(3) J. F. Ditter, E. B. Klusmann, J. D. Oakes, and R. E. Williams, *Inorg. Chem.*, 9, 889 (1970).

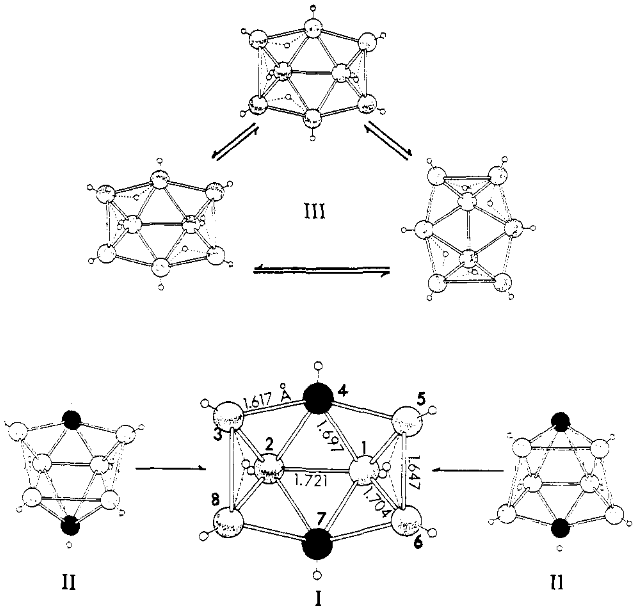

Figure 1. Eight-vertex *nido*-carboranes of the $C_2B_6H_{10}$–B_8H_{12} family: III, *nido*-B_8H_{12} tautomers, arachno structures dominant; II, nido structure; I, *nido*-$C_2B_6H_{10}$ (bond distances estimated from ADD theory), arachno structure; II′, nido structure.

reactor was sampled intermittently and analyzed by a gas chromatograph coupled to a mass spectrometer. The condensable products were collected in a liquid nitrogen trap and subsequently purified on a 2 in. diameter × 15 ft long gas chromatographic column of Apiezon N on Chromosorb P. Approximately 1.9 g of gc-pure $C_2B_6H_{10}$ was obtained in this manner.

The polyisotopic mass spectrum of the envelope of the parent peaks of $C_2B_6H_{10}$ has a cut off at *m/e* 100, corresponding to the ion $^{12}C_2{}^{11}B_6H_{10}{}^+$, and has its maximum intensity peak at *m/e* 96. The calculated monoisotopic spectrum indicates that $C_2B_6H_8{}^+$ (closo fragment) is the most stable ion species, as one would expect from a comparison of the stabilities of the closo and nido structures.[4] The mass spectral profile[4] is typically that of a *nido*-carborane.

Infrared absorption bands (cm^{-1}) are as follows: 1351 (vb), 1412 (m), 1446 (m), 1449 (m), 1457 (m), 1466 (m), 1508 (w), 1580 (w), 1710 (w), 1725 (w), 1732 (w), 1952 (w), 2608 (s), 2865 (s), 2878 (w), 2965 (w), and 2975 (w).

The most probable static structure for $C_2B_6H_{10}$ (I) is depicted in Figure 1 along with the less likely II and II′ valence bond tautomers which may not be ruled out. From the apparent 4:2 doublet patterns in the ^{11}B nmr spectra obtained at −80 and −30° (b and c in Figure 2) the doublet of area 2 at higher field is attributed to the higher coordinated boron atoms in the cage, while the doublet at lower field is due to the four lower coordinated edge borons for reasons illustrated previously.[2a]

The ^1H nmr spectrum was then obtained for comparison with the ^{11}B nmr spectrum as a test for structural compatibility. The requisite quartets representing two kinds of BH groups in equal quantity with appropriate chemical shift values and exact spin coupling values as well as a singlet (power saturated) representing the two identical CH groups were observed. Most interesting was the highly resolved bridge hydrogen septet which can only be rationalized in terms of identical bridge hydrogens identically spin coupled to identical borons. In previous cases ^{11}B nmr spectra rather than ^1H nmr spectra revealed boron to bridge hydrogen spin coupling most readily.

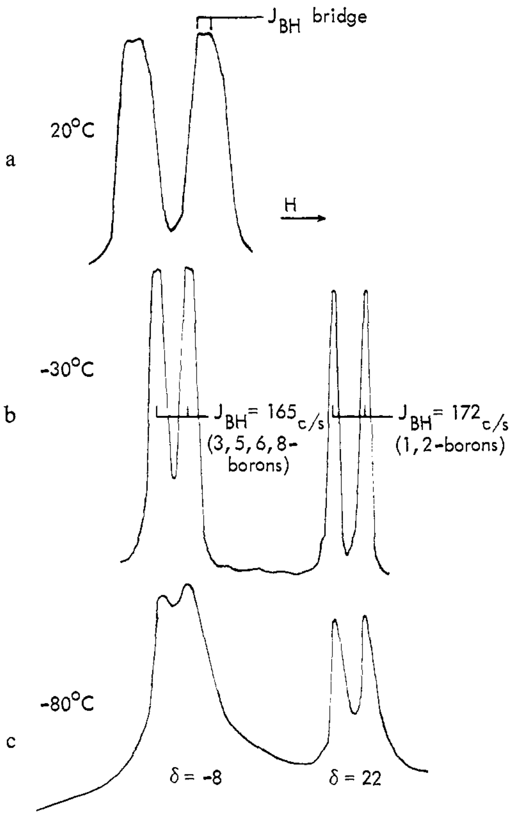

Figure 2. The 32.1-MHz ^{11}B nmr spectra of 4,7-$C_2B_6H_{10}$ relative to BF_3–etherate. These data compare almost exactly with δ −6.8 (J = 168 Hz) and 20.5 (J = 153 Hz), which must respectively represent the 3,5, 6,8, and 1,2,4,7 sets of borons in the parent B_8H_{12} reported previously.[5]

Accordingly the ^{11}B nmr spectrum of $C_2B_6H_{10}$ was obtained at 20° (a in Figure 2) whereupon the requisite same spin coupling was observed accompanied by slow decomposition of our sample.

In the desirable but unlikely event that the tautomer pair II and II′ were correct, then we would have discovered the first example of a species isoelectronic with *nido*-B_8H_{12}[5] which would have assumed the "predicted"[6] nido eight-vertex structure.

The structures of all the known *nido*-carboranes and boranes have been depicted as polyhedral fragments derived by the formal removal of a high coordination vertex from the appropriate closo carborane;[6] however, in one case (*i.e.*, B_8H_{12})[5] the nido fragment opens into an arachno structure (at least in the crystalline phase) by the breaking of one additional bond.

As is evident, our preferred structure of $C_2B_6H_{10}$ (I) would also deviate from the "norm" in that it is not a true *nido*-carborane but is instead an open or pseudo-arachno type.[7] Hence, it resembles its isoelectronic borane counterpart, B_8H_{12} (III in Figure 1), which, even

[4] J. F. Ditter, F. J. Gerhart, and R. E. Williams, *Advan. Chem. Ser.*, No. 72, 191 (1968).

[5] J. Dobson and R. Schaeffer, *Inorg. Chem.*, 7, 402 (1968).

[6] R. E. Williams, *Inorg. Chem.*, 10, 210 (1971).

[7] Bond distances and bond angles were derived from the ADD Bond Theory (to be published by A. J. Gotcher).

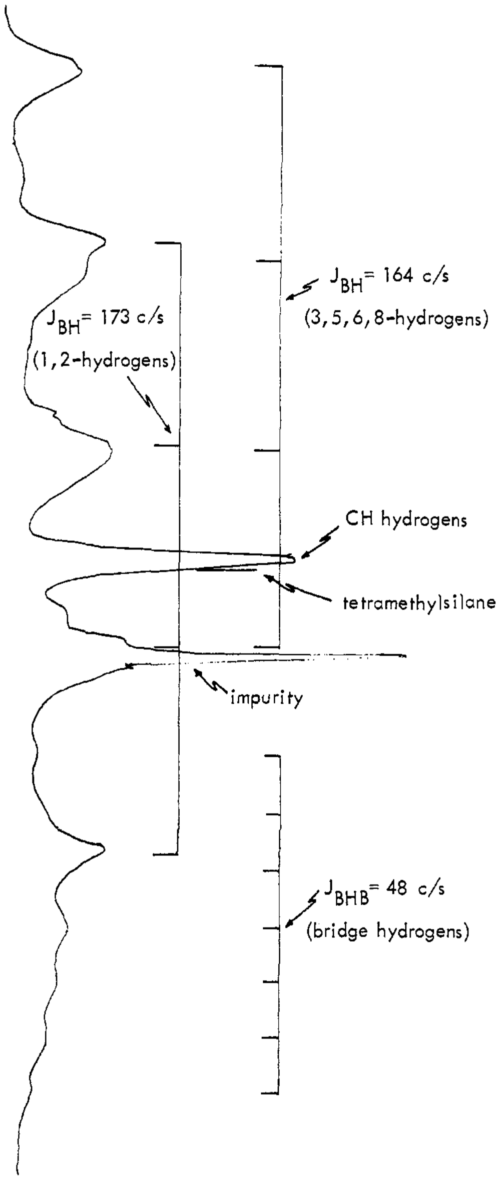

Figure 3. The 60-MHz ^1H nmr spectrum of 4,7-$C_2B_6H_{10}$.

though it is a *nido*-borane according to its empirical formula,[6] and/or equivalent electron counting scheme,[8,9] has an open arachno structure.

A tentative reaction mechanism which may account for the production of $C_2B_6H_{10}$ and its by-products follows. In the thermal decomposition of diborane one of the transient products is generally conceded to be $[B_3H_7]$, present in pseudoequilibrium with B_2H_6,[10] and since diborane is thermally less stable than $C_2B_3H_5$, a plausible mechanism for formation of $C_2B_6H_{10}$ is the reaction

$$C_2B_3H_5 + [B_3H_7] \longrightarrow C_2B_6H_{10} + H_2 \qquad (2)$$

$C_2B_6H_8$ is produced as a by-product, and at slightly higher reaction temperatures the ratio of $C_2B_6H_8$ to $C_2B_6H_{10}$ increases proportionately with the temperature increase, suggesting that $C_2B_6H_8$ evolves from $C_2B_6H_{10}$ by simple loss of hydrogen, *i.e.*

$$C_2B_6H_{10} \longrightarrow C_2B_6H_8 + H_2 \qquad (3)$$

$C_2B_5H_7$ and $CH_3CB_5H_8$, other major by-products in the diborane–$C_2B_3H_5$ reaction, are possibly formed by direct assimilation of B_2H_6 by $C_2B_3H_5$, *i.e.*

$$C_2B_3H_5 + B_2H_6 \longrightarrow CH_3CB_5H_8 \qquad (4)$$

$$C_2B_3H_5 + B_2H_6 \longrightarrow C_2B_5H_7 + 2H_2 \qquad (5)$$

Alternatively, $C_2B_5H_7$ might arise by loss of BH_3 from $C_2B_6H_{10}$.

$$C_2B_6H_{10} \longrightarrow C_2B_5H_7 + BH_3 \qquad (6)$$

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(8) K. Wade, *Chem. Commun.*, 792 (1971).

(9) R. W. Rudolph and W. R. Pretzer, *Inorg. Chem.*, 11, 1974 (1972).

(10) R. P. Clarke and R. N. Pease, *J. Amer. Chem. Soc.*, 73, 2132 (1951).

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Chemistry of Thiocarbonyl Complexes of Chromium, Molybdenum, and Tungsten

Sir:

Several metal thiocarbonyl complexes have previously been prepared,[1-3] but little is known about the chemistry of the thiocarbonyl ligand. We now report the preparation of the first group VI metal thiocarbonyl complexes and some novel reactions of these compounds.

Anions of Cr, Mo, and W were prepared by stirring the hexacarbonyls, $M(CO)_6$, with excess sodium amalgam in refluxing tetrahydrofuran for 12 hr. Studies of Hayter[4] and Kaska[5] indicate that $M_2(CO)_{10}{}^{2-}$ and possibly some $M(CO)_5{}^{2-}$ are produced in these reductions. These solutions were cooled to room temperature and added rapidly to a tetrahydrofuran solution of thiophosgene (Cl_2CS). After stirring the mixture several minutes, it was evaporated to dryness under reduced pressure. Sublimation of the residue at 50–60° under high vacuum yielded a mixture of $M(CO)_6$ and $M(CO)_5(CS)$. The $M(CO)_6$ complexes were removed from the mixtures by repeated crystallization at −20° from pentane or hexane solutions, in which the thiocarbonyl complexes were appreciably more soluble. Chromatography of the thiocarbonyl-containing solutions on Florisil with pentane followed by sublimation yielded the pure air- and moisture-stable yellow $M(CO)_5(CS)$ complexes.[6]

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(1) I. S. Butler and A. E. Fenster, *J. Chem. Soc. D*, 933 (1970), and references therein.

(2) A. E. Fenster and I. S. Butler, *Can. J. Chem.*, 50, 598 (1972).

(3) M. J. Mays and F. P. Stefanini, *J. Chem. Soc. A*, 2747 (1971).

(4) R. G. Hayter, *J. Amer. Chem. Soc.*, 88, 4376 (1966).

(5) W. C. Kaska, *J. Amer. Chem. Soc.*, 90, 6340 (1968).

(6) Analytical data for $Cr(CO)_5(CS)$. Calcd: C, 30.51; H, 0.00; S, 13.56. Found: C, 30.14; H, <0.01; S, 13.59. $W(CO)_5(CS)$. Calcd: C, 19.55; H, 0.00; S, 8.70. Found: C, 18.93; H, <0.01; S, 8.36. Satisfactory elemental analyses have also been performed on all other new compounds reported here except $Mo(CO)_5(CS)$.