

herently weaker than the Cu-P bond, which is consistent with the expected relative polarizing capability of the two metals, one might expect the trend to be $L_3AgBH_4 > L_3AgH_3BCOOC_2H_5 > L_3CuBH_4 > L_3CuH_3BCOOC_2H_5$. Transposition of the L_3CuBH_4 to the position of greatest dissociation to give the observed trend is reasonable if BH_4^- interacts much more strongly with copper(I) than with silver(I) and thus forms a significantly more stable bidentate complex with copper than with silver. The results are that the (ethoxycarbonyl)tri-hydroborate interaction is sufficiently weaker that it does not affect dissociation to the extent that BH_4^- does and the difference in stability between bidentate copper and silver (ethoxycarbonyl)tri-hydroborate complexes is not great enough to

be the determining factor in ligand dissociation for these two complexes.

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Registry No. $(MePh_2P)_3CuBH_4$, 63371-86-8; $(MePh_2P)_3AgBH_4$, 72347-03-6; $(MePh_2P)_3CuBD_4$, 72347-04-7; $(MePh_2P)_3-CuH_3BCO_2C_2H_5$, 72347-05-8; $(MePh_2P)_3AgH_3BCO_2C_2H_5$, 72347-06-9; $(Ph_3P)_2CuBH_4$, 16903-61-0; $(Ph_3P)_2AgBH_4$, 16902-95-7.

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Relative Proton Affinities of 1,6- $C_2B_4H_6$ and 2,4- $C_2B_3H_7$

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The ion-molecule reactions of the *closo*-carboranes 1,6- $C_2B_4H_6$ and 2,4- $C_2B_3H_7$ have been investigated by using pulsed ion cyclotron resonance (ICR) methods. Condensation reactions of the parent ion with itself are observed with loss of H_2 for both molecules. Condensation of 1,6- $C_2B_4H_6$ with protonated acetone is observed again with loss of H_2 . Proton affinities (PA) of the two carboranes were determined by bracketing techniques giving $PA(1,6-C_2B_4H_6) = 208 \pm 4$ kcal/mol and $PA(2,4-C_2B_3H_7) = 173 \pm 1$ kcal/mol. The large difference in proton affinities is attributed to the fact that the molecule CB_3H_7 which is isoelectronic to $C_2B_4H_7^+$ is known while the molecule CB_6H_8 which is isoelectronic to $C_2B_3H_8^+$ is not known.

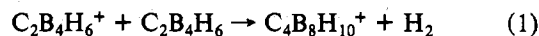
The chemistry of electron-deficient compounds has provided many insights into systems that contain novel bonding features.¹ The best characterized compounds of this type are the boranes and the carboranes.² The *closo*-dicarboranes belong to this class of compounds and form neutral closed polyhedra. A variety of experimental² and theoretical studies³ have been made on these systems including mass spectral studies on both the positive⁴ and negative ions⁵ created by electron impact. The positive ion spectra for the carboranes have been compared to the spectra obtained for similar boranes.⁴ We present in this paper a study of some of the gas-phase ion chemistry of the *closo*-carboranes 1,6- $C_2B_4H_6$ and 2,4- $C_2B_3H_7$. A number of ion cyclotron resonance (ICR) studies⁶ and chemical ionization mass spectral studies⁷ of small boranes have previously been carried out but this study represents the first study of closed polyhedral systems.

The ICR studies were carried out on the trapped ion ICR apparatus at the California Institute of Technology by using experimental techniques that have previously been discussed in detail.⁸ The carboranes were obtained in purified form from Professor T. Onak (California State College at Los Angeles). The carboranes and the other chemicals which were readily available reagent grade materials were subjected to freeze-pump-thaw cycles to remove noncondensable impurities.

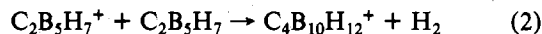
The mass spectra for the carboranes are in good agreement with those published in the literature.⁴ Complications due to the presence of two boron isotopes ($^{11}B/^{10}B = 4.0$) have previously been discussed.⁴ For compounds with four borons, the peaks containing the $^{11}B_4$ and $^{11}B_3^{10}B$ moieties are the most intense and are of comparable height while, for compounds with five borons, the peak containing the $^{11}B_4^{10}B$ moiety is the most intense with the peak containing the $^{11}B_5$ moiety having the second highest intensity. Thus, it is relatively straight-

forward to observe the $P + 1$ peaks associated with the $^{11}B_4$ and $^{11}B_5$ parent ion peaks. The previous positive ion mass spectra have been analyzed in terms of the isotopic content of the ion and it was shown that the dominant ion in the 2,4- $C_2B_3H_7$ spectrum is the parent ion while the $P - 1$ ion is the dominant ion for the 1,6- $C_2B_4H_6$ spectrum; the parent ion for this latter compound still has considerable intensity.

A general feature of the mass spectrum taken at long reaction time is the observation of condensation reactions. The isotopic patterns for eight borons make it more difficult to unravel the data but the general reaction for the 1,6- $C_2B_4H_6$ system is condensation with loss of H_2



This reaction has been confirmed by double resonance studies. For the 2,4- $C_2B_3H_7$ system a similar condensation reaction, again with loss of H_2 , is also observed



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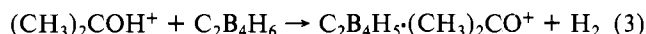
[†] A. P. Sloan Foundation Fellow.

Table I. Proton-Transfer Reactions Used in Determining the Relative Basicities of the Carboranes

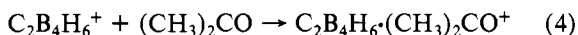
reaction	PA(carborane) ^a
$\text{NH}_4^+ + \text{C}_2\text{B}_4\text{H}_6 \rightarrow \text{NH}_3 + \text{C}_2\text{B}_4\text{H}_7^+$	>203.6
$\text{C}_2\text{B}_4\text{H}_7^+ + \text{C}_6\text{H}_5\text{NH}_2 \rightarrow \text{C}_2\text{B}_4\text{H}_6 + \text{C}_6\text{H}_5\text{NH}_3^+$	<210.1 ^b
$\text{C}_2\text{B}_4\text{H}_7^+ + \text{As}(\text{CH}_3)_3 \rightarrow \text{C}_2\text{B}_4\text{H}_6 + \text{As}(\text{CH}_3)_3\text{H}^+$	<211.9 ^c
$\text{H}_3\text{O}^+ + \text{C}_2\text{B}_5\text{H}_7 \rightarrow \text{H}_2\text{O} + \text{C}_2\text{B}_5\text{H}_8^+$	>171.6 ^d
$\text{C}_2\text{B}_5\text{H}_8^+ + \text{CF}_3\text{CH}_2\text{OH} \rightarrow \text{C}_2\text{B}_5\text{H}_7 + \text{CF}_3\text{CH}_2\text{OH}_2^+$	<173.5 ^d

^a Proton affinity of the carborane in kcal/mol. All proton affinities are based on the value of NH_3 given in ref 11. ^b Reference 13; although the double resonance signals were quite weak. ^c Reference 12. ^d Reference 14.

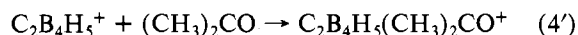
and confirmed by double resonance measurements. Condensation reactions similar to this have been observed⁹ for the neutral borane B_3H_9 to form $\text{B}_{10}\text{H}_{16}$ where a B-B bond is formed between the apical borons and in thermal studies on the C_2B_4 and C_2B_5 ¹⁰ carboranes again with formation of B-B bonds. Condensation reactions of 1,6- $\text{C}_2\text{B}_4\text{H}_6$ with acetone have also been observed with a product being formed from the reaction of protonated acetone (*m/e* 59) with the carborane



This sequence was verified by double resonance. The product ion in this case probably contains a B-O-C linkage and a tertiary carbonium ion. The following condensation starting from a carborane ion was also observed



but for certain mass combinations we cannot exclude the possibility that the following reaction is also occurring:



Proton-transfer reactions of 1,6- $\text{C}_2\text{B}_4\text{H}_6$ with the reagents CH_4 , H_2S , $\text{CF}_2\text{HCH}_2\text{OH}$, $\text{CFH}_2\text{CH}_2\text{OH}$, CH_3OH , $\text{CH}_3\text{C}-\text{H}_2\text{OH}$, $(\text{CH}_3)_2\text{S}$, and NH_3 were investigated. All showed proton transfer from the $\text{P} + 1$ ion of the respective reagent and these reactions were checked by double resonance. The protonated carborane was observed to transfer a proton to $\text{As}(\text{CH}_3)_3$ as evidenced by the temporal dependence of the ion intensity and by double resonance. Proton transfer reactions with aniline showed no proton transfer from protonated aniline to the carborane and only a weak double resonance from the protonated carborane to the aniline. The proton affinity of 1,6- $\text{C}_2\text{B}_4\text{H}_6$ definitely falls between those of NH_3 ¹¹ and $\text{As}(\text{CH}_3)_3$ ¹² (see Table I) and is most likely less than that of aniline.¹³ Using a value of 203.6 kcal/mol for the proton affinity of NH_3 ,¹¹ we find the proton affinity of 1,6- $\text{C}_2\text{B}_4\text{H}_6$ to be 208 ± 4 kcal/mol.

Proton-transfer reactions of 2,4- $\text{C}_2\text{B}_5\text{H}_7$ with the reagents $\text{CH}_3\text{CH}_2\text{OH}$, $\text{CFH}_2\text{CH}_2\text{OH}$, CH_3OH , $\text{CF}_3\text{CH}_2\text{OH}$, and H_2O were investigated. The ion H_3O^+ definitely protonates the carborane. Double resonance and temporal dependence studies of ion intensities of the alcohols except for $\text{CF}_3\text{CH}_2\text{OH}$ show that the protonated carborane donates its proton to the alcohol. Double resonance which was somewhat weak shows that the carborane $\text{P} + 1$ ion protonates $\text{CF}_3\text{CH}_2\text{OH}$, but double resonance showing proton donation from the protonated al-

Table II. Proton Affinities (PA) of Boranes and Carboranes

molecule	PA, kcal/mol	molecule	PA, kcal/mol
B_2H_5^a	146 ± 5	$\text{B}_2\text{H}_{10}^a$	195 ± 8
$\text{B}_4\text{H}_{10}^a$	144 ± 5	1,6- $\text{C}_2\text{B}_4\text{H}_6^b$	208 ± 4
B_5H_9^a	167 ± 6	2,4- $\text{C}_2\text{B}_5\text{H}_7^b$	173 ± 1
$\text{B}_5\text{H}_{11}^a$	≤ 173		

^a Reference 7b. ^b This work.

cohol to the carborane was not observed. The proton affinity thus falls between that of H_2O ¹⁴ and $\text{CF}_3\text{CH}_2\text{OH}$ ¹⁴ (see Table I), and with the value for $\text{PA}(\text{NH}_3)$ given previously, the proton affinity of 2,4- $\text{C}_2\text{B}_5\text{H}_7$ is 173 ± 1 kcal/mol.

The remarkable feature of these results is the large difference (~ 35 kcal/mol) in proton affinities for the two carboranes with the smaller polyhedron having the greater proton affinity. From thermochemical considerations, the proton affinity of X is defined as

$$\text{PA}(\text{X}) = \text{HA}(\text{X}^+) + \text{IP}(\text{H}) - \text{IP}(\text{X}) \quad (5)$$

where $\text{HA}(\text{X}^+)$ is the hydrogen affinity of X^+ (the $\text{X}-\text{H}^+$ bond strength) and IP corresponds to the appropriate ionization potential. The values of the adiabatic ionization potentials for these two carboranes are 9.77 eV (1,6- $\text{C}_2\text{B}_4\text{H}_6$) and 10.54 eV (2,4- $\text{C}_2\text{B}_5\text{H}_7$) as determined by photoelectron spectroscopy.¹⁵ These numbers together with our proton affinities yield the values $\text{HA}(1,6\text{-C}_2\text{B}_4\text{H}_6) = 120$ kcal/mol and $\text{HA}(2,4\text{-C}_2\text{B}_5\text{H}_7) = 102$ kcal/mol. The difference in bond strengths is 18 kcal/mol favoring the smaller carborane and, thus, about 50% of the difference in proton affinities is due to the difference in the bond strengths. This large difference in bond strengths is somewhat surprising until we note that a protonated dicarbaborane $\text{C}_2\text{B}_{n-2}\text{H}_{n+1}^+$ is isoelectronic to a neutral monocarbaborane $\text{CB}_{n-1}\text{H}_{n+1}$. Isoelectronic equivalence is prevalent in carborane and borane chemistry with the best example being the equivalence for the closo compounds $\text{C}_2\text{B}_{n-2}\text{H}_n \leftrightarrow \text{B}_n\text{H}_n^{2-}$. The ion $\text{C}_2\text{B}_4\text{H}_7^+$ is isoelectronic to the neutral molecule CB_5H_7 which has been characterized and where the extra hydrogen is found to be fluxional in a bridge position between equatorial borons.^{16,17} No stable structure for the CB_5H_8 molecule which is isoelectronic to $\text{C}_2\text{B}_5\text{H}_8^+$ has been identified. Thus the smaller carborane can more easily add a proton to its cage, giving a more stable ion and a corresponding higher proton affinity; it is likely that the proton is in a bridge position between equatorial borons in analogy with the neutral CB_5H_7 molecule.¹⁷ We compare the proton affinities of these carboranes with the proton affinities for some open polyhedral boranes in Table II. The boranes all have lower proton affinities than that for 1,6- $\text{C}_2\text{B}_4\text{H}_6$ while the proton affinity of 2,4- $\text{C}_2\text{B}_5\text{H}_7$ is similar to those of B_5H_9 and B_5H_{11} . Further studies of the ion-molecule reactions of carboranes will provide new insights into their structure and into the bonding of protons to electron-deficient polyhedra. Formation of extremely stable ions could lead to the prediction of new stable carboranes.

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Registry No. 1,6- $\text{C}_2\text{B}_4\text{H}_6$, 20693-67-8; 2,4- $\text{C}_2\text{B}_5\text{H}_7$, 20693-69-0.

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