corresponds to that of a ternary electrolyte[7]) indicate that, besides the NO_2^- anion, another anion must be present in the first coordination sphere of platinum. However, the mild conditions used in the preparation of the parent nitrito isomer from $[Pt(NH_3)_5(H_2O)]Cl_4$ should prevent NH_3 substitution. Moreover, the elemental analysis shows that NH_3 substitution by NO_2^- or Cl^- (which were the only anions available in the reaction medium) did not occur. Therefore, the only reasonable hypothesis is that our compound contains an amido group (presumably, trans to the NO_2^- group), *i.e.*, that its formulation is $[Pt(NH_3)_4(NH_2)(NO_2)]Cl_2$. The per cent composition calculated for this formula gives 49.26% Pt, 17.89% Cl, 21.20% N, and 3.56% H. These values are in good agreement with those experimentally found (see above). The complex cation maintains the above formulation also in solution. In fact, if a proton associates to the NH_2^- ligand, the molar conductivity should correspond to that expected for a quaternary electrolyte, contrary to what we have found; moreover, the aqueous solutions of the complex should result strongly basic, whereas they are practically neutral.

The acid–base equilibria of other complexes of the $Pt(NH_3)_5X^{3+}$ type have already been investigated.[9] For example, it has been found that the pK_a values of $Pt(NH_3)_5Cl^{3+}$, $Pt(NH_3)_5Br^{3+}$, and $Pt(NH_3)_5OH^{3+}$ are 8.4, 8.3, and 9.5, respectively. It is also known[10] that the electronic absorption bands of the amido forms are displaced toward longer wavelengths in comparison with the bands of the ammine complexes. Therefore, we have carried out potentiometric titrations and spectrophotometric measurements in solutions of various acidities for establishing the pH range in which the nitro- and nitritotetraammineamidoplatinum(IV) complexes exist.

As far as the *nitro* isomer is concerned, the titration of a 10^{-2} *M* solution (which was near the solubility limit of the complex) with standard acid and base proved to be reversible and did not show any acid–base equilibrium below pH 9 (at higher pH values, the progressive acid dissociation of the other NH_3 ligands occurred). Moreover, the absorption spectrum of the complex did not undergo any change in the pH range from 9 to 0 and even in concentrated H_2SO_4. Thus, one must conclude that the pentaamminenitro complex, $Pt(NH_3)_5(NO_2)^{3+}$, is such a strong acid that it cannot exist in aqueous solutions.

As far as the *nitrito* isomer is concerned (which, as previously mentioned, cannot be obtained as a pure salt), no acid–base equilibrium was found between pH 4 and 9. Moreover, the spectra of freshly prepared solutions at pH 4 and 9 were practically identical. Unfortunately, at pH lower than 4 the complex undergoes isomerization and decomposition reactions, so that its acid–base behavior cannot be investigated at any lower acid level. Thus, from the available data, it can be only concluded that the pK_a of the pentaamminenitrito form is lower than 4. This result is a rather surprising one, considering the much higher pK_a values of the other $Pt(NH_3)_5X^{3+}$ complexes (see above), but it is consistent with the fact that the nitrito complex is isolated in its tetraammineamido form from acid solutions.

Acknowledgment.—The authors are indebted to Professor V. Carassiti for his interest in this work.

---

[9] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, p 33.

[10] C. K. Jørgensen, *Acta Chem. Scand.*, **10**, 518 (1956).

[11] Centro di Studio di Fotochimica e Reattività degli Stati Eccitati dei Composti di Coordinazione del CNR, Istituto Chimico dell'Università, Ferrara, Italy.

[12] Laboratorio di Fotochimica e Radiazioni d'Alta Energia del CNR, Istituto Chimico dell'Università, Bologna, Italy.

* To whom correspondence should be addressed.

ISTITUTO CHIMICO DELL'UNIVERSITÀ N. SABBATINI[11]
FERRARA, ITALY

ISTITUTO CHIMICO DELL'UNIVERSITÀ V. BALZANI*,[12]
BOLOGNA, ITALY

RECEIVED APRIL 13, 1970

Carboranes and Boranes; Polyhedra and Polyhedral Fragments

Sir:

Because the *nido*-boranes B_6H_{10} and $B_{10}H_{14}$ and the *arachno*-boranes B_4H_{10} and B_5H_{11} were discovered and structurally characterized as icosahedral fragments before the *closo*-carboranes were discovered, a dominant thesis during the evolution of boron chemistry has been the characterization of borane structures as icosahedral fragments. B_5H_9 has been the only exception. The more recently discovered species B_6H_{12}, B_8H_{14}, and two isomers of B_9H_{15}, all presumably icosahedral fragment structures, would also appear to augment and confirm the icosahedral fragment thesis. If the reverse had been true, that is, had the *closo*-carboranes been discovered first, then possibly the entire series of *closo*-carborane polyhedral structures would have been accepted as a set of standard structures for subsequent comparison. We believe the tacit acceptance of the icosahedral fragment thesis was somewhat unfortunate because, as we will illustrate below, it is demonstrable that all of the known borane and carborane structures can more clearly be derived from the *closo*-carborane series of polyhedral structures in a simplistic fashion with few if any exceptions (Figure 1). Even if our preferred "polyhedral-series" thesis is found to have no theoretical basis and is simply the unlikely result of quite a number of coincidences, it should at least serve as a convenient memory aid in the teaching of this subject. Additionally, the polyhedral-series thesis predicts a different set of nonicosahedral structures for yet to be discovered *nido*-carboranes and, we believe, rationalizes the lack of stability for such hypothetical species as B_7H_{11}, B_9H_{13}, and perhaps B_7H_{13}.

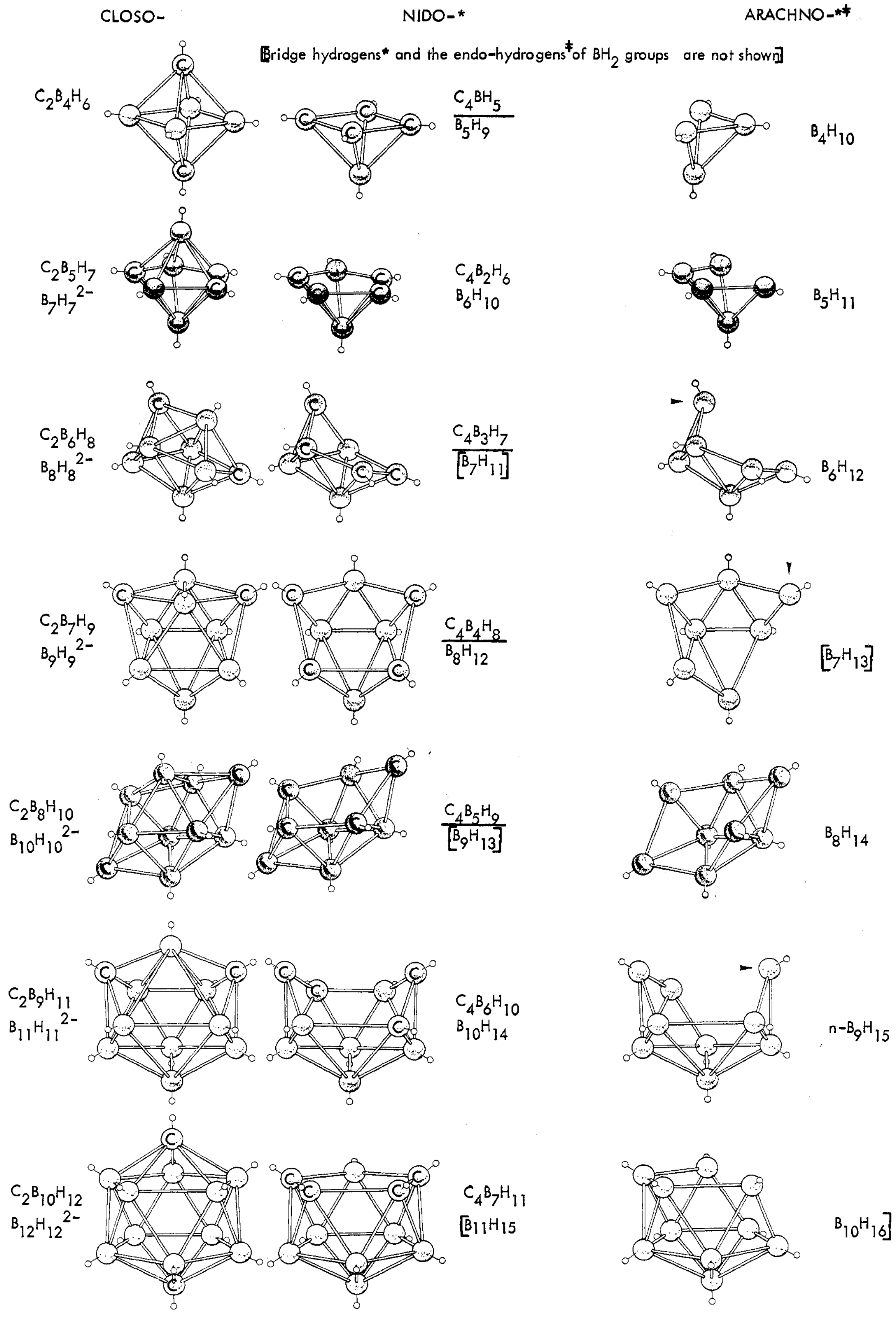


Figure 1.—Structures of carboranes and related compounds. Species underlined are predicted; those in brackets are expected to be unstable if they can be isolated.

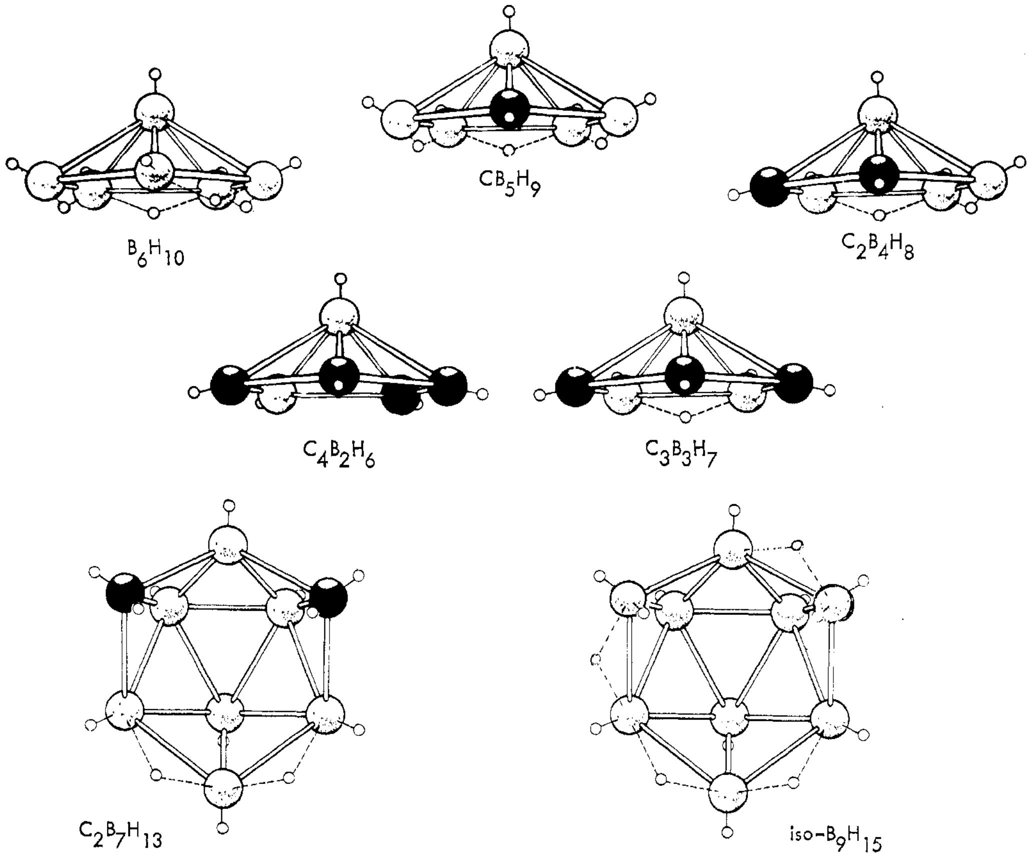


Figure 2.—A series of *nido*-carboranes (top) and related *arachno*-carboranes (below).

For bookkeeping purposes[1,2] all carborane–borane chemistry may be divided into three categories: (1) *closo*-carboranes, $C_{0-2}B_nH_{n+2}$; examples include $C_2B_5H_7$, $C_2B_8H_{10}$, $C_2B_{10}H_{12}$, etc.;[3] (2) *nido*-carboranes, $C_{0-4}B_nH_{n+4}$; examples include the series B_6H_{10}, CB_5H_9, $C_2B_4H_8$, $C_3B_3H_7$, and $C_4B_2H_6$ (Figure 2) as well as the $C_2B_9H_{13}$ isomers and the so-called stable boranes B_5H_9, B_8H_{12}, and $B_{10}H_{14}$;[4] (3) *arachno*-carboranes, $C_{0-6}B_nH_{n+6}$; examples are B_4H_{10}, B_5H_{11}, B_6H_{12}, B_8H_{14}, the B_9H_{15} isomers and $C_2B_7H_{13}$ (Figure 2).

All of the last group, *i.e.*, the *arachno*-boranes or *arachno*-carboranes, *may* be considered as having structures wherein the borons and/or carbons are disposed about the vertices of a fragment of an icosahedron. Almost all of the presently known *nido*-boranes and *nido*-carboranes (group 2 above) have structures that may be considered as derived from icosahedral fragments, all but B_5H_9, that is,[5] and it is the purpose of this communication to suggest that in the future many more *nido*-carboranes that are not icosahedral fragments will be discovered. In contrast, within the first group (*closo*-carbaranes) only the $C_2B_{10}H_{12}$ isomers and the isoelectronic species $B_{12}H_{12}^{2-}$ and $CB_{11}H_{12}^{-}$ have icosahedral symmetry.

The left-hand column in Figure 1 illustrates the series of polyhedra[6] characteristic of the *closo*-carboranes $C_2B_nH_{n+2}$ and/or the *closo*-borane anions $B_nH_n^{2-}$; the large circles containing "C" in the structures may be either boron or carbon, depending upon whether boranes or carboranes are being discussed, while the other large circles represent boron only. It is illuminating to note that the simple removal of one highest coordination vertex in any member of the closo polyhedral series generates the boron skeleton (bridge hydrogens are not shown) of a related *nido*-borane B_nH_{n+4} or the boron–carbon skeleton of a related *nido*-carborane $C_{0-4}B_nH_{n+4}$. The results of this manipulation are displayed in the middle column of Figure 1. For example, in the B_6H_{10} family, which includes CB_5H_9, $C_2B_4H_8$, $C_3B_3H_7$, and $C_4B_2H_6$ (Figure 2), the formal skeletal structure is simply that of the *closo*-$C_2B_5H_7$ polyhedron minus one of the high coordination positions. Similarly B_5H_9 has the skeletal structure of $C_2B_4H_6$ minus one vertex, and on the same premise one would also expect a related C_4BH_5 to have a "B_5H_9" structure.[7]

It is interesting to note further that the largest *nido*-borane species $B_{10}H_{14}$ and the "reported" $B_{11}H_{15}$[8] may both be pictured simply as structural derivatives of the

---

(1) R. E. Williams, "Progress in Boron Chemistry," Vol. 2, Pergamon Press, Oxford, England, 1970, Chapter 2, p 51.

(2) R. E. Williams, "The 1970 McGraw-Hill Yearbook of Science and Technology," McGraw-Hill, New York, N. Y., 1970, p 133.

(3) When one considers B^- as equivalent to neutral C, then the well-known *closo*-borane dianions are also representative examples, *e.g.*, $B_{10}H_{10}^{2-}$, $B_{12}H_{12}^{2-}$, etc.

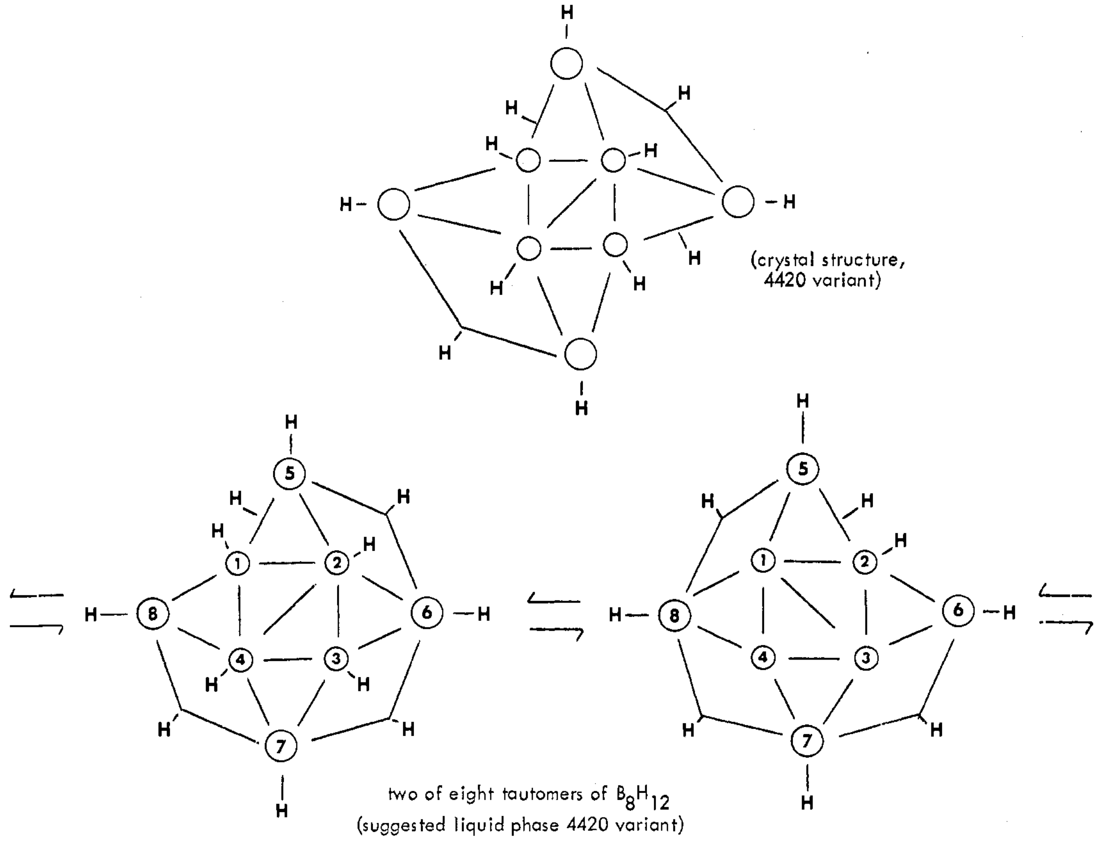
(4) Many isoelectronic anions ($B^- = C^0$) are also of this group, *e.g.*, $C_2B_9H_{11}^{2-}$, $C_2B_4H_7^-$, etc.

(5) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, New York, N. Y., 1963.

(6) See ref 1, pp 38–45.

(7) See ref 1, p 61; a similar structure would be predicted for the isoelectronic carbonium ion $C_6H_5^+$.

(8) J. L. Edwards and J. M. Makhlouf, *J. Amer. Chem. Soc.*, **88**, 4728 (1966).



(crystal structure, 4420 variant)

two of eight tautomers of B_8H_{12} (suggested liquid phase 4420 variant)

Figure 3.—Known crystal[5] 4420 structure and liquid 4420 structures for B_8H_{12}.

related closo compounds, generated by removing one high coordination vertex each (middle column in Figure 1).

Digressing for the moment, the placement of carbons in the carboranes in Figure 1 is assisted by two empirical observations. First of all (rule 1) the carbons seek the low-coordination positions when a choice exists.[9] This is true for the entire series of *closo*-carboranes (left column in Figure 1) and for the nido series (middle column in Figure 1) wherein the low-coordination positions are around the open "mouth." A second observation (rule 2) is that the carbons tend to assume nonadjacent positions, all other things being equal,[9] as illustrated for 1,2-$C_2B_4H_6$ which rearranges to 1,6-$C_2B_4H_6$ and for 1,2-$C_2B_{10}H_{12}$ which rearranges to 1,7-$C_2B_{10}H_{12}$.

We are confident that one of the compounds reported by Köster (m/e 348; $^{12}C_{20}{}^{11}B_6{}^{1}H_{42}$)[10] is actually an alkyl derivative of $C_4B_6H_{10}$ (middle row, Figure 1) which in turn is related to $B_{10}H_{14}$; that is, by placing methyl groups on the four carbons and ethyl groups on the six borons (in the parent $C_4B_6H_{10}$) one arrives at $(CH_3)_4C_4B_6(C_2H_5)_6$, which has exactly the same empirical formula, $C_{20}B_6H_{42}$, as does Köster's compound. *All of* Köster's *"other carboranes"* have been shown to be *B*-ethyl,*C*-methyl derivatives of our known parent carboranes, *i.e.*, $C_2B_5H_7$, CB_5H_9, $C_2B_3H_5$.[10] One and only one pair of *dl*-carbon-position isomers of $C_4B_6H_{10}$ (middle column of Figure 1) should be most stable (rules 1 and 2), and, not surprisingly, Köster found a single compound with this empirical formula was formed in high yield.

Another compound of this type is $C_4B_7H_{11}$, and a mass spectrum corresponding to this formula (cutoff peak m/e 136) has been observed in unexpected abundance by Ditter[11] among the products of the high-temperature copyrolysis of $C_2B_4H_8$ and B_2H_6. Its most probable structure, which contains no bridge hydrogens, is displayed in the middle column of Figure 1 and is analogous to the presumed $B_{11}H_{15}$.[8] $B_{11}H_{15}$, in contrast, would have to pack four additional bridge hydrogens around the open mouth, and the probable steric interactions would explain the lack of stability of the "presumed" $B_{11}H_{15}$.[12] Structurally similar isoelectronic species, such as $B_{11}H_{14}^-$ (three bridge hydrogens),[13]

---

(9) (a) See ref 1, pp 55, 58. (b) Recently it has been noted that both empirical carbon placement rules are "overruled" by bridge-hydrogen placement considerations thus, for $C_2B_3H_7$ (isoelectronic with B_5H_9) to place the bridge hydrogens about the open face, one carbon assumes the highest coordination apex position and the carbons are adjacent (overriding both rules 1 and 2): D. A. Franz and R. N. Grimes, *J. Amer. Chem. Soc.*, **92**, 1438 (1970). It is noteworthy that this compound is much less stable than B_5H_9; *all other carboranes are more thermally stable than their bridge hydrogen containing borane analogs.* The anomalous "second" isomer of $C_2B_9H_{13}$ (derived from 1,7-$C_2B_{10}H_{12}$) possibly accommodates its two bridge hydrogens by "moving" one carbon away from the low-coordination open-mouth positions into a high-coordination skeletal position (ref 1, p 60).

(10) See ref 1, pp 87–89, and R. Köster and G. W. Rotermund, *Tetrahedron Lett.*, **No. 12,** 777 (1965).

(11) J. F. Ditter and R. E. Williams, to be submitted for publication.

(12) Lipscomb[5] suggested that, to a first approximation, the borons and bridge hydrogens lie on the surface of an inner sphere while the terminal hydrogens lie on the surface of an outer sphere. In the case of $B_{11}H_{15}$ the four bridge hydrogens would be very crowded.

(13) W. R. Hertler, F. Klanberg, and E. L. Muetterties, *Inorg. Chem.*, **6**, 1696 (1967).

$C_2B_9H_{13}$ (two bridge hydrogens),[14] $C_2B_9H_{12}^-$ (one bridge hydrogen),[15] and $C_2B_9H_{11}^{2-}$ [16] (no bridge hydrogens and isoelectronic to $C_4B_7H_{11}$), exist and are known to be progressively more stable as the number of bridge hydrogens diminishes.

In the $C_4B_nH_{n+4}$ series[17] we have discussed both the two smallest species C_4BH_5 (possible) and $C_4B_2H_6$ (known as the alkyl derivative)[18] as well as the two largest species $C_4B_6H_{10}$ (Köster's alkyl derivative) and $C_4B_7H_{11}$. However, what of the other potential species of intermediate size, $C_4B_3H_7$, $C_4B_4H_8$, and $C_4B_5H_9$? Such compounds would be related to B_7H_{11} (unknown), B_8H_{12} (known), and B_9H_{13} (unknown) as shown in the middle column of Figure 1. Based upon our assumption that the related polyhedron minus a high-coordination vertex would define the most probable structure we would predict the nonicosahedral carborane structures that are shown in the middle column in Figure 1. The related parent borane species, B_7H_{11} and B_9H_{13}, with four bridge hydrogens around the open mouth, would encounter special structural problems. Note that *only* these two species in the B_nH_{n+4} series have *never* been observed, and among our suggested structures *only* those same two species would have an open face puckered in such a fashion that there could be *insufficient room* for the placement of four bridge hydrogens. The carborane analogs, with three or less bridge hydrogens, should have correspondingly less steric interactions, and we predict they will have the nonicosahedral structures displayed in Figure 1.

The suggested B_8H_{12} structure (Figure 1) has ample room to accommodate four bridge hydrogens and is reproduced as a series of tautomers (bottom, Figure 3). Expected tautomerism[19] of bridge hydrogens about the "open face" of such a structure would account for the observed two sets of four equivalent borons in the ^{11}B nmr spectrum. A slight structural adjustment caused by crystalline phase packing considerations could well favor the slightly different structure determined by Lipscomb[5] (top of Figure 3).

This tautomerism should not occur when carbons replace boron (with the concurrent loss of bridge hydrogens), and the series $C_4B_nH_{n+4}$ (*i.e.*, $C_4B_3H_7$, $C_4B_4H_8$, and $C_4B_5H_9$, middle column of Figure 1) structurally derived from the closo polyhedra minus a high-coordination atom (not icosahedral fragments) should be given very serious consideration before being discarded in favor of simplistic icosahedral fragment structures.[20]

Having dispensed with the closo series wherein only one structure is icosahedral and having suggested that many *nido*-carboranes will join B_5H_9 in not having icosahedral fragment structures (*caveat emptor*), what of the hydrogen-rich boranes B_4H_{10}, B_5H_{11}, B_6H_{12}, B_8H_{14}, and B_9H_{15} (right column of Figure 1), all of which would seem to have icosahedral fragment structures?[5] We point out only that without exception all these structures may also be derived from the parent polyhedral series by a similar repetition of the process by which the nido structures (middle column of Figure 1) were generated from the closo structures (left column of Figure 1). An additional skeletal atom is removed from the open face of the nido structures (middle column of Figure 1). As in the closo to nido manipulation, the highest coördination skeletal atom is chosen where a choice exists and in every case the known arachno structure[5] (see right column of Figure 1) is generated. Of the many icosahedral fragment arachno structures which may be imagined the simple removal of a high-coordination vertex from the open face of the related nido structure empirically yields the correct or presumed to be correct structure in every case. The one revealing exception, the generation of an "unexpected" isomer of B_9H_{15} (Figure 2), is obtained by the removal of a lower coordination boron from the $B_{10}H_{14}$ nido structure, which produces *i*-B_9H_{15}.[21] Interestingly this isomer, though it has higher symmetry than *n*-B_9H_{15}, is kinetically less stable.

Two *arachno*-boranes (right row of Figure 1) are known to lose a BH_3 group with ease, *i.e.*, *n*-$B_9H_{15} \rightarrow B_8H_{12}$[22] and $B_6H_{12} \rightarrow B_5H_9$.[23] Perhaps the suggested *arachno*-borane structure for a B_7H_{13} will remain unobserved since the formation of B_6H_{10} by the loss of a BH_3 group may be favored.

In summary we have shown that there is a rational alternative to considering carborane–borane structures as icosahedral fragments which has fewer structural exceptions to date, which should serve as a teaching aid, and which predicts a new and different set of structures for the $C_{0-4}B_nH_{n+4}$ carboranes.

Acknowledgment.—This work was supported by the Office of Naval Research, and the author is grateful to Dr. J. F. Ditter for his critical review.

CHEMICAL SYSTEMS INC.
SANTA ANA, CALIFORNIA 92705
ROBERT E. WILLIAMS

RECEIVED JUNE 23, 1970

---

(14) R. A. Weisboeck and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **86**, 1642 (1964).

(15) M. F. Hawthorne, P. A. Wegner, and R. C. Stafford, *Inorg. Chem.*, **4**, 1675 (1965).

(16) T. E. Berry, F. N. Tebbe, and M. F. Hawthorne, *Tetrahedron Lett.*, **No. 12**, 715 (1965).

(17) The $C_2B_nH_{n-2}$ series of *closo*-carboranes is presently accepted as the most stable carboranes because of (a) their closed-cage structures and (b) the absence of bridge hydrogens. The $C_4B_nH_{n+4}$ series of *nido*-carboranes is also very stable (prepared under very energetic or high-temperature conditions—they also lack bridge hydrogens which we feel is the overriding prerequisite for stability).

(18) P. Binger, *Tetrahedron Lett.*, **No. 24**, 2657 (1966).

(19) R. E. Williams, *J. Inorg. Nucl. Chem.*, **20**, 198 (1961).

(20) W. N. Lipscomb, *Inorg. Chem.*, **3**, 1683 (1964).

(21) J. Dobson, P. C. Keller, and R. Schaeffer, *J. Amer. Chem. Soc.*, **87**, 3522 (1965).

(22) J. F. Ditter, J. R. Spielman, and R. E. Williams, *Inorg. Chem.*, **5**, 118 (1966).

(23) D. F. Gaines and R. Schaeffer, *ibid.*, **3**, 438 (1964).