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Closo Boron Hydrides with 13 to 24 Boron Atoms

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Structures are proposed for hypothetical closo boron hydrides ranging in size from $B_{13}H_{13}^{2-}$ to $B_{24}H_{24}^{2-}$. The proposed $B_nH_n^{2-}$ structures are deltahedra (polyhedra with triangular faces) having 12 six-coordinate and $n - 12$ seven-coordinate boron atoms for $n > 13$, counting also the external terminal hydrogen. The polyhedra are nearly spherical and have at least C_s symmetry. Several structures have very high symmetry, T_d, T, and D_{6d}, for example, and several exist in enantiomeric forms with D_n or T symmetry. Bond lengths are proposed for these structures. Preliminary SCF calculations are reported for the smaller structures. Unifying structural principles and speculations on synthesis and related chemistry are presented.

I. Introduction

In recent decades the number of known boron hydrides and carboranes has increased dramatically. We believe that in the future a large number of new stable boron hydrides and related molecules will be discovered. The special stabilities[1] of the closed polyhedral class are noteworthy, as is the observation[2] that the historical record led to this most stable class about half of a century after Stock's first discovery of the reactive species of boron hydrides. Recent experimental advances in metallocarborane chemistry[3] have pointed the way to supra-icosahedral boron chemistry.

We have therefore undertaken a survey of possible structures for closo boron hydrides having 13 to 24 boron atoms. Each closo structure should have a number of related open (nido and arachno) relatives,[4] some of which may be stable. Isoelectronic carboranes, $CB_{n-1}H_n^-$ and $C_2B_{n-2}H_n$, should exist for each $B_nH_n^{2-}$ structure. Heteroboranes, including metallocarboranes, may also conform to the proposed closo structures as appears to be the case for $n = 13$ and 14.[3] Fused fragments of the proposed structures may also be stable. As a first step, however, we have limited our survey to the extension of the closo series, for which structures are known for $B_nH_n^{2-}$ for $6 \leq n \leq 12$ and for $C_2B_{n-2}H_n$ for $5 \leq n \leq 12$.[4b,c,5]

II. The Proposed Structures

General Considerations. The proposed structures for $12 < n \leq 24$ are deltahedra, i.e., closed polyhedra with triangular faces. Each face, moreover, is an equilateral or nearly equilateral triangle. The closo boron hydrides are assumed to have a minus two charge and $n + 1$ boron framework electron pairs.[6] Each boron is presumed to have one terminally bonded exo hydrogen. These restrictions are obeyed by the known closo boron hydrides and carboranes and almost constitute a definition of this class of compounds.[4b,c,5]

We propose that the boron atoms in the deltahedra have coordination numbers five, six, and seven (i.e., one exo hydrogen and four, five, and six boron neighbors). These compounds are electron deficient in the sense that their boron atoms have greater numbers of near neighbor contacts than electron pairs available for bonding. As the size of the boron cage increases the coordination numbers of the boron atoms increase (Table I). Boron atoms with coordination numbers of seven and even eight are known. (See Table II.) Calculations by Muetterties et al.[7] indicate that the decrease in boron–boron bond strength with increasing coordination number is less than proportional to the increase in the number of contacts and that therefore there is a net advantage in maximizing the number of near-neighbor contacts.[7] This advantage is tempered by unfavorable second nearest neighbor interactions.[7] Obviously, however, there is a limit to this process. If coordination numbers become too high, the molecule becomes sterically crowded. The high stability of the icosahedral $B_{12}H_{12}^{2-}$ ion indicates that six-coordination may be especially favorable, though the existence of seven- and eight-coordinate boron atoms suggests that six-coordination is by no means an upper limit.

Table I. Coordination in Known Closo Boranes and Carboranes[a]

	Coordination[c]			
V[b]	4	5	6	7
5[d]	2	3		
6		6		
7		5	2	
8		4	4	
9		3	6	
10		2	8	
11		2	8	1
12			12	

[a] See ref 4 and 5. [b] The number of vertices on the polyhedron. [c] Includes one BH (or CH) per vertex. [d] Only the carborane is known.

The following four equations apply to closed deltahedra:[8] (1) $e + 2 = v + f$ (the Euler relation) where e is the number of edges, v the number of vertices, and f the number of faces; (2) $\sum i(v_i) = 2e$ where v_i is the number of vertices of order i (this relation follows from the fact that each edge joins two vertices); (3) $\sum v_i = v$, obviously; and (4) $3f = 2e$ since each edge joins two faces and each face is bounded by three edges.

If i is restricted to four, five, and six, then the maximum value of V_5 consistent with eq 1–4 is 12 for $12 \leq v \leq 24$. Moreover, this maximum value is obtained when $v_4 = 0$ for $13 < v \leq 24$.[9] Oddly enough, for $v = 13$, the $v_5 = 12$, $v_6 = 1$ combination cannot be constructed, though eq 1–4 are satisfied.[8a,b]

The limitation to 12 six-coordinate (v_5 for five boron near neighbors) and $n - 12$ seven-coordinate (v_6) borons does not

Table II. BB Distances for Five-, Six-, Seven-, and Eight-Coordinate Boron Atoms

Molecule	Distance, A	Ref
Five-Coordinate Boron Atoms		
$B_8H_8^{2-}$	1.66	*a*
$B_5H_7(CH_3)_2$	1.67	*b*
B_5H_9	1.68	*c*
$B_6H_6^{2-}$	1.69	*d*
photo-$B_{20}H_{18}$	1.69	*e*
$B_{10}H_7Cl_3^{2-}$	1.70	*f*
$C_2B_7H_7(CH_3)_2$	1.70	*g*
$B_9H_9^{2-}$	1.71	*h*
$B_{20}H_{18}NO^{3-}$	1.72	*i*
$B_{10}H_{10}^{2-}$	1.73	*j*
Av	1.70	
Six-Coordinate Boron Atoms		
n-B_9H_{15}	1.76	*k*
$B_9H_{14}^-$	1.77	*l*
$B_{10}H_{13}^-$	1.77	*m*
$B_{10}H_{14}$	1.77	*n*
$B_{12}H_{12}$	1.77	*o*
B_8H_{12}	1.78	*p*
Av	1.77	
Seven-Coordinate Boron Atoms		
$B_{20}H_{16}$	1.81	*q*
$B_{13}H_{19}$	1.82[r]	*s*
$B_{20}H_{16}(NCCH_3)_2$	1.82	*t*
i-$B_{18}H_{22}$	1.83	*u*
n-$B_{18}H_{22}$	1.84	*v*
$[Ti(C_2B_{10}H_{12})_2]^{2-}$	1.90	*x*
(π-C_5H_5)Co($B_{10}C_2H_{12}$)	1.90	*y*
$C_2B_9H_9(CH_3)_2$	1.94[w]	*z*
Av	1.86[aa]	
Eight-Coordinate Boron Atoms		
$B_{20}H_{16}(NCCH_3)_2$	1.88	*t*

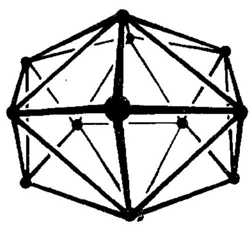
[a] L. J. Guggenberger, *Inorg. Chem.*, 8, 2771 (1969). [b] L. B. Friedman and W. N. Lipscomb, *ibid.*, 5, 1752 (1966). [c] J. C. Huffman, Ph. D. Thesis, Indiana University, 1974, p 464. [d] R. Schaeffer, Q. Johnson, and G. S. Smith, *Inorg. Chem.*, 4, 917 (1965). [e] B. G. DeBoer, A. Zalkin, and D. H. Templeton, *ibid.*, 7, 1085 (1968). [f] F. E. Scarbrough and W. N. Lipscomb, *ibid.*, 11, 369 (1972). [g] T. F. Koetzle, F. E. Scarbrough, and W. N. Lipscomb, *ibid.*, 7, 1076 (1968). [h] L. J. Guggenberger, *ibid.*, 7, 2260 (1968). [i] C. H. Schwalbe and W. N. Lipscomb, *ibid.*, **10**, 160 (1971). [j] R. D. Dobrott and W. N. Lipscomb, *J. Chem. Phys.*, **37**, 1779 (1962). [k] Footnote *c*, p 478. [l] N. N. Greenwood, J. A. McGinnety, and J. D. Owen, *J. Chem. Soc., Dalton Trans.*, 986 (1972). [m] Footnote *c*, p 486. [n] Footnote *c*, p 488; ref 26. [o] J. A. Wunderlich and W. N. Lipscomb, *J. Am. Chem. Soc.*, **82**, 4427 (1960). [p] G. S. Pawley, *Acta Crystallogr.*, **20**, 631 (1966); R. E. Enrione, F. P. Boer, and W. N. Lipscomb, *Inorg. Chem.*, 3, 1659 (1964). [q] Reference 38. [r] Corrected by 0.10 Å for the presence of a bridge hydrogen. See footnote *c*, p 318. [s] J. C. Huffman, D. C. Moody, and R. Schaeffer, *Inorg. Chem.*, **15**, 227 (1976). [t] J. H. Enemark, L. B. Friedman, and W. N. Lipscomb, *ibid.*, **5**, 2165 (1966). [u] P. G. Simpson, K. Folting, R. D. Dobrott, and W. N. Lipscomb, *J. Chem. Phys.*, 39, 2339 (1963). [v] P. G. Simpson and W. N. Lipscomb, *ibid.*, 39, 26 (1963). [w] Including BC bonds corrected by 0.04 Å. See L. Pauling, "The Nature of the Chemical Bond", 3rd ed, Cornell University Press, Ithaca, N.Y., 1960, p 228. [x] M. R. Churchill and B. G. DeBoer, *Inorg. Chem.*, **13**, 1411 (1974). [y] F. Y. Lo, C. E. Strouse, K. P. Callahan, C. B. Knobler, and M. F. Hawthorne, *J. Am. Chem. Soc.*, 97, 428 (1975). [z] C. Tsai and W. E. Streib, *ibid.*, 88, 4513 (1966). [aa] The average is 1.84 if the metallocarboranes are excluded.

completely specify the closo structures. We have found that if the triangular faces are nearly equilateral then the formation of highly symmetric and nearly spherical structures requires that the seven-coordinate borons (the v_6's) must be symmetrically placed on the surface of the deltahedron as far apart as possible. When the ratio of six-coordinate to seven-coordinate borons is high, we therefore eliminate contacts between the seven-coordinate borons.[10] For larger values of *n* the requirement to minimize the number of v_6–v_6 edges is not equivalent to the requirement for nearly spherical shape. (See $B_{22}H_{22}^{2-}$ below.)

The proposed structures have at least a twofold element of symmetry, consistent with the observation that stable boron hydrides have at least that degree of symmetry.[11] Some of the proposed structures have very high symmetry indeed: T_d, T, and D_{6d}, for example. Point groups C_{2v}, D_{3d}, and D_{3h} are common. In some cases more than one structure is proposed, though a preference will be indicated (alphabetically) between competing structures and in Table III. A few alternative structures which we do not prefer are also discussed, though no attempt is made to list all alternative structures. The proposed structures, which will now be discussed in greater detail, are described in Table III.

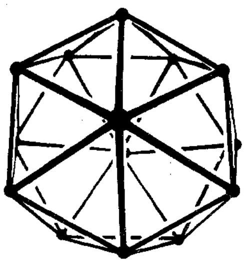
Thirteen Boron Atoms. The proposed $B_{13}H_{13}^{2-}$ structure (I) has C_{2v} symmetry. This structure is unique in our series in that it has eight six-coordinate borons, two seven-coordinate borons, and one five-coordinate boron. This structure may be obtained by adding a vertex of order four (v_4) to any edge of an icosahedron. Precedent for structure I is found in metallocarboranes.[3a–d,f] Capping the hexagonal face of an open 12-vertex boron cage proposed by Lipscomb in considering rearrangements of $C_2B_{10}H_{12}$ also produces structure I.[12]

I

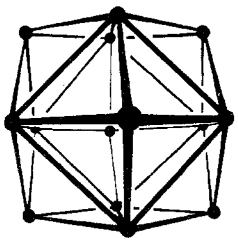


Fourteen Boron Atoms. The $B_{14}H_{14}^{2-}$ proposal (IIa) is a bicapped hexagonal antiprism with D_{6d} symmetry and seven-coordinate borons at opposite ends of the molecule on the sixfold axis. An alternative structure (IIb), an omnicapped cube with O_h symmetry[13] (v_4 = 6, v_6 = 8), was also considered but was found to be inferior to IIa on the basis of SCF calculations (see below). Precedent for structure IIa is found in the structure of 14-coordinate metals in alloys[8b,14] and in metallocarboranes.[3f,g,15]

IIa

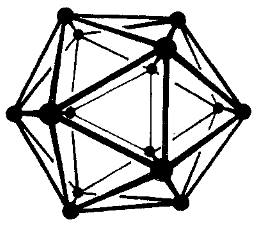


IIb



Fifteen Boron Atoms. The $B_{15}H_{15}^{2-}$ structure (III) has D_{3h} symmetry with three seven-coordinate borons arranged in an equilateral triangle in the plane perpendicular to the threefold

III



IV

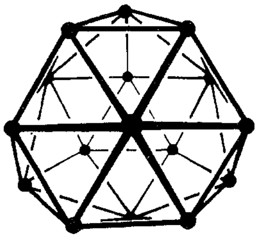
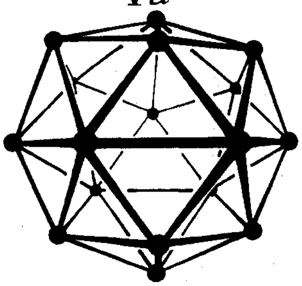


Table III. Selected Polyhedra

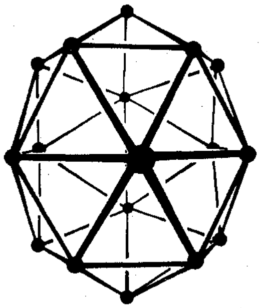
Structure	v	v_4	v_5	v_6	e	e_{45}	e_{46}	e_{55}	e_{56}	e_{66}	f[a]	Symmetry	Arrangement of vertices[b]	Arrangement of v_6's[b]
I	13	1	10	2	33	2	2	19	10	0	22	C_{2v}	1:2:2:4:2:2	2
IIa	14	0	12	2	36	0	0	24	12	0	24	D_{6d}	1:6:6:1	1:1
IIb	14	6	0	8	36	0	24	0	0	12	24	O_h	1:4:4:4:1	4:4[c]
III	15	0	12	3	39	0	0	21	18	0	26	D_{3h}	3:3:3:3:3	3
IV	16	0	12	4	42	0	0	18	24	0	28	T_d	1:6:3:3:3 = 2:2:4:4:2:2	1:3 = 2:2
Va	17	0	12	5	45	0	0	17	26	2	30	C_{2v}	1:4:2:2:4:2:2	1:4
Vb	17	0	12	5	45	0	0	20	20	5	30	D_{5h}	1:5:5:5:1	5
Vc	17	0	12	5	45	0	0	18	24	3	30	C_{2v}	1:4:2:2:4:2:2	1:2:2
VIa	18	0	12	6	48	0	0	15	30	3	32	D_3[f]	3:3:3:3:3:3	3:3
VIb	18	0	12	6	48	0	0	18	24	6	32	D_{3h}	3:3:6:3:3	3:3[d]
VIc	18	0	12	6	48	0	0	18	24	6	32	D_{3d}	3:3:3:3:3:3	3:3[d]
VId	18	6	0	12	48	0	24	0	0	24	32	O_h	1:4:8:4:1	4:4:4[c]
VIIa	19	0	12	7	51	0	0	15	30	6	34	C_{3v}	1:3:3:6:3:3	1:3:3
VIIb	19	0	12	7	51	0	0	15	30	6	34	C_s	3:3:3:2:4:2:2	3:4[e]
VIIc	19	0	12	7	51	0	0	15	30	6	34	C_s	1:6:1:5:1:4:1 (~1:6:6:5:1)	1:5:1
VIIIa	20	0	12	8	54	0	0	12	36	6	36	D_{6h}	1:6:6:6:1	1:6:1
VIIIb	20	0	12	8	54	0	0	15	30	9	36	D_{3h}	1:3:3:6:3:3:1	1:3:3:1
VIIIc	20	0	12	8	54	0	0	14	32	8	36	D_{2d}	2:2:4:2:2:4:2:2	4:4
IXa	21	0	12	9	57	0	0	15	30	12	38	D_3[f]	3:3:3:3:3:3:3	3:3:3
IXb	21	0	12	9	57	0	0	13	34	10	38	C_{2v}	1:6:6:4:2:2	1:6:2
IXc	21	0	12	9	57	0	0	18	24	15	38	D_{3h}	3:3:3:3:3:3:3	3:3:3
Xa	22	0	12	10	60	0	0	12	36	12	40	T_d	1:3:3:6:3:3:3 = 1:4:2:2:4:2:2:4:1	1:3:3:3 = 1:2:4:2:1
Xb	22	0	12	10	60	0	0	10	40	10	40	D_{5d}	1:5:5:5:5:1	5:5
Xc	22	0	12	10	60	0	0	15	30	15	40	C_{2v}	2:2:4:4:8:2	2:4:2:2
XIa	23	0	12	11	63	0	0	9	42	12	42	D_3[f]	1:3:3:3:3:3:3:3:1	1:3:3:3:1
XIb	23	0	12	11	63	0	0	11	38	14	42	C_{2v}	1:4:2:6:2:4:2:2	1:2:2:2:4
XIc	23	0	12	11	63	0	0	13	34	16	42	C_{2v}	1:6:6:2:4:2:2	1:6:4
XIIa	24	0	12	12	66	0	0	12	36	18	44	T[f]	3:3:3:3:3:3:3:3	3:3:3:3
XIIb	24	0	12	12	66	0	0	8	44	14	44	D_2[f]	4:4:4:4:4:4	2:4:4:2
XIIc	24	0	12	12	66	0	0	12	36	18	44	D_{3d}	3:3:6:6:3:3	3:3:3:3[d]
XIId	24	0	12	12	66	0	0	12	36	18	44	D_{3h}	3:3:3:6:3:3:3 (~3:6:6:6:3)	3:6:3[d]
XIIe	24	0	12	12	66	0	0	12	36	18	44	D_{3d}	3:3:3:6:3:3:3 (~3:6:6:6:3)	3:6:3[d]
XIIf	24	0	12	12	66	0	0	18	24	24	44	D_{3d}	3:3:3:3:3:3:3:3	3:3:3:3[c]

[a] The symbols v, e, and f stand for the number of vertices, edges, and faces, respectively. The subscripts denote the coordination number of the vertex, e.g., v_4 denotes a four-coordinate vertex, e_{45} denotes an edge joining a v_4 and v_5. [b] Using Föppl's notation see ref 21. [c] Not a preferred structure. [d] We express no preference between these structures. [e] The base of the triangle (3) is parallel to the base of the quadrilateral (4). [f] Two enantiomers.

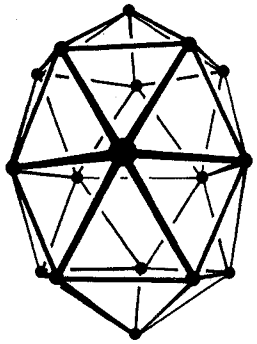
Va



Vc



Vb



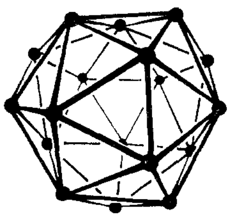
axis, i.e., on the equator of the approximate sphere formed by the polyhedron. Precedent for this structure is also found in metal alloy crystal structures.[8b,14] Capping the open pentagonal face of $(CH_6)_5Fe_2(CH_3)_4C_4B_8H_8$ isomers I and III[3e,g] of Grimes also forms our structure III.

Sixteen Boron Atoms. In $B_{16}H_{16}^{2-}$ (IV) the four seven-coordinate borons are arranged tetrahedrally on the surface of the polyhedron. The overall molecular symmetry is T_d. As is the case for its smaller homologues, there are no near-neighbor contacts between seven-coordinate atoms. Structure IV may be generated by capping the hexagonal faces of a truncated tetrahedron.[16] Precedent for structure IV is also found in metal alloy structures.[8b,14]

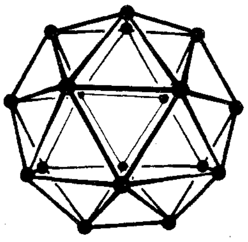
Seventeen Boron Atoms. Three structures are proposed for $B_{17}H_{17}^{2-}$. One (Vb) has D_{5h} symmetry with five seven-coordinate borons arranged in a pentagon perpendicular to the fivefold axis. The 12 six-coordinate borons form pentagonal pyramids above and below the equator of this rather prolate polyhedron. The recently published structure of $B_{14}H_{20}$[17] is related to Vb. Another structure, Va, has C_{2v} symmetry with its five seven-coordinate borons arranged in a rectangular pyramid. Although this structure has lower symmetry than Vb, it is probably more stable since the overall shape is more nearly spherical and the number of near-neighbor contacts between seven-coordinate borons is reduced from five to two. Structures Va and Vb can be interconverted by a double diamond–square–diamond (DSD)[18] mechanism. A single DSD motion creates another C_{2v} structure (Vc) which is less spherical and has three v_6–v_6 contacts.

Eighteen Boron Atoms. The proposed $B_{18}H_{18}^{2-}$ structure (VIa) has D_3 symmetry and therefore may exist in dextro and levo forms. The six seven-coordinate borons are arranged in a twisted trigonal prism (not an antiprism). There are only three near-neighbor contacts between seven-coordinate borons, as compared with two in structure Va, five in structure Vb, and none in structures I, IIa, III, and IV. The structure[19] of $[(1,6\text{-}C_2B_7H_9)_2Co^{III}]^-$ is related to that of VIa. An alternative structure for $B_{18}H_{18}^{2-}$ (VId), a hexacapped cuboctahedron[20] with O_h symmetry ($v_4 = 6$, $v_6 = 12$), was also considered. Preliminary SCF calculations suggest that VIa is a superior structure. A rather oblate (VIb) structure and a rather prolate (VIc) structure with D_{3h} and D_{3d} symmetry respectively can be constructed consistent with the $v_5 = 12$ and $v_6 = 6$ formula but were not considered as stable as VIa as the number of v_6–v_6 edges in both structures is six. No preference is expressed between structures VIb and VIc.

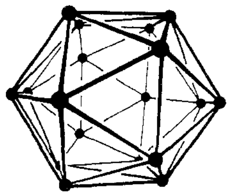
VIa



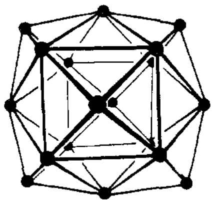
VIb



VIc



VId



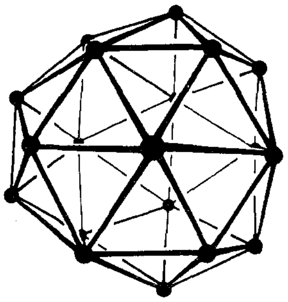
Nineteen Boron Atoms. For $B_{19}H_{19}^{2-}$ the proposed structure VIIa has C_{3v} symmetry. The seven seven-coordinate borons are arranged in a 1:3:3 fashion (using Föppl's[21] notation). There are six v_6–v_6 edges in this deltahedron. Two other structures (VIIb and VIIc) also have six v_6–v_6 edges but only C_s symmetry. In VIIb the seven-coordinate borons (the v_6's) are in a 3:4 arrangement.[22] We prefer VIIa over VIIb because of its higher symmetry. Structure VIIc has a distorted 1:5 arrangement of v_6's and a decidedly nonspherical shape.

Twenty Boron Atoms. Three appealing possibilities, VIIIa, VIIIb, and VIIIc, are available for $B_{20}H_{20}^{2-}$ with D_{6h}, D_{3h}, and D_{2d} symmetry, respectively. Structure VIIIa has two of its eight v_6 vertices at the molecular poles defined by the sixfold symmetry axis and has the remaining six v_6's in a hexagonal ring at the molecular equator. Structure VIIIa is analogous to structure Vb with a sixfold axis and hexagonal rings replacing a fivefold axis and pentagonal rings. The v_6 vertices of VIIIb are arranged in a 1:3:3:1 fashion. Structure VIIIc has its v_6 vertices arranged in a manner similar to the cyclooctatetrene skeleton, i.e., a coincident 4:4 arrangement. We prefer the highly symmetric VIIIa structure as it has only six v_6–v_6 edges. Structure VIIIb has nine such edges and structure VIIIc has eight.

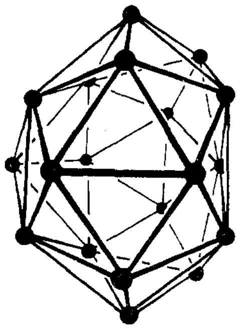
Twenty-One Boron Atoms. For $B_{21}H_{21}^{2-}$ structure IXa belonging to the D_3 point group is proposed. Enantiomeric (optical) isomers are possible. Another structure (IXb) which belongs to the C_{2v} point group has fewer v_6–v_6 edges (ten as compared with twelve for IXa) but is less symmetric and less spherical. We therefore prefer structure IXa over IXb. A third structure (IXc) belonging to the D_{3h} point group has 15 v_6–v_6 edges and is very prolate.

Twenty-Two Boron Atoms. Two highly symmetric structures are available for $B_{22}H_{22}^{2-}$, one with tetrahedral symmetry (Xa) and another rather oblate structure (Xb) with D_{5d} symmetry. The ten seven-coordinate boron atoms in Xa are arranged as are the carbon atoms in adamantane. In Xb they are arranged in a pentagonal antiprism. Despite the higher number of v_6–v_6 edges in Xa (twelve as opposed to ten in Xb)

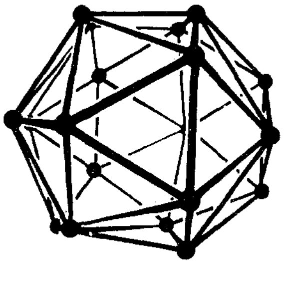
VIIa



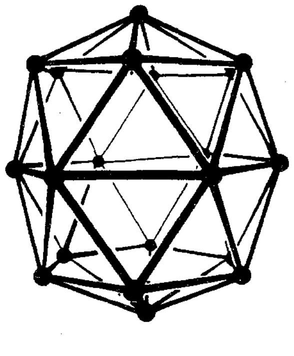
VIIb



VIIc



VIIIa



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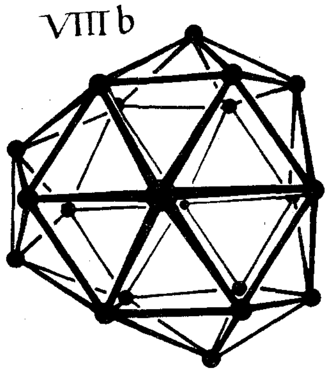
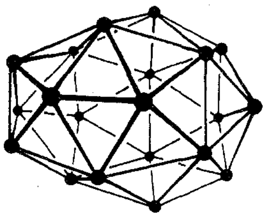
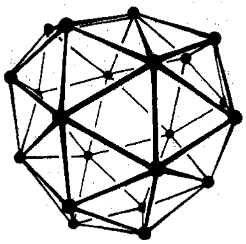


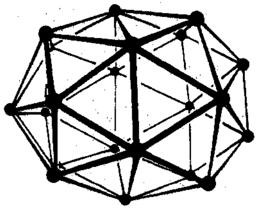
VIIIc



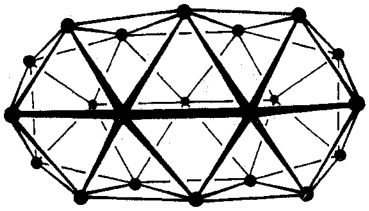
IX a



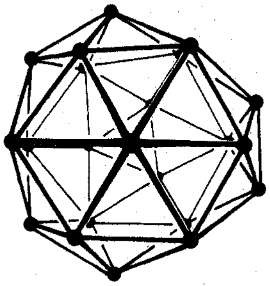
IX b



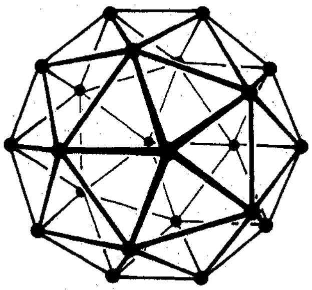
IX c



X a



X b



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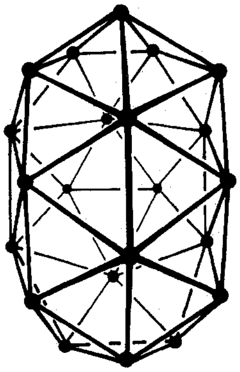

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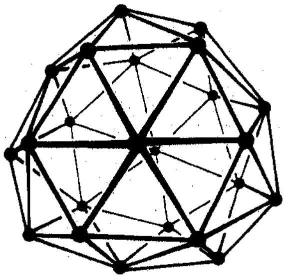
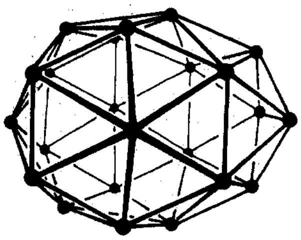
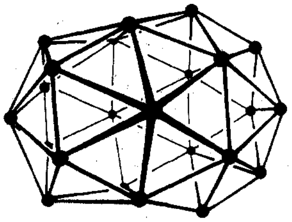


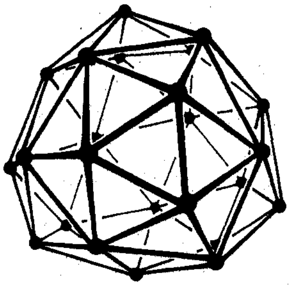
XI b



XI c



XII a



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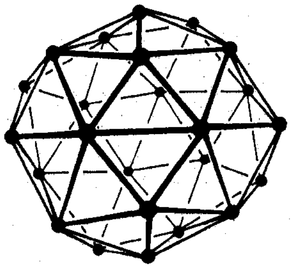

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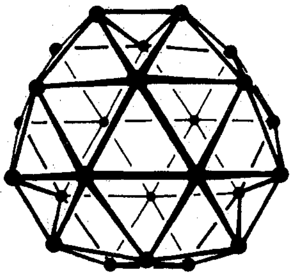
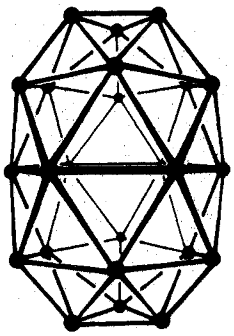
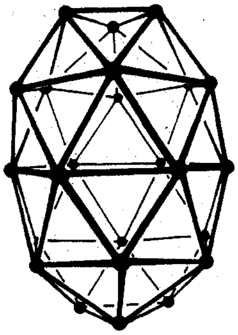


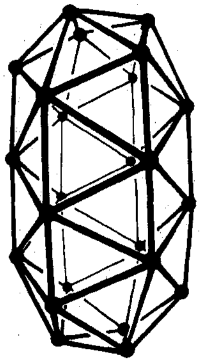
XII d



XII e



XII f



we prefer Xa because of its more spherical shape and greater symmetry. A C_{2v} structure (Xc) with 15 v_6–v_6 edges is possible but is less appealing.

Twenty-Three Boron Atoms. For $B_{23}H_{23}^{2-}$ a structure (XIa) with D_3 symmetry, which is compatible with optical activity, is proposed. Two other structures with C_{2v} symmetry (XIb

Table IV. Proposed Boron Radii and Interatomic Distances

	Boron radii, Å
Five-coordinate[a]	0.815
Six-coordinate[a]	0.885
Seven-coordinate[a]	0.955

BB bonds coordination	Boron distances, Å
7-7	1.91
7-6	1.84
7-5	1.77
6-6	1.77
6-5	1.70
5-5	1.63
BH_t bonds	1.19[b]

[a] Includes coordination to hydrogen. [b] See ref 26.

and XIc) are also shown. These two structures are less spherical than XIa and have 14 and 16 v_6-v_6 edges, respectively, as compared with 12 for XIa.

Twenty-Four Boron Atoms. For $B_{24}H_{24}^{2-}$ an appealing structure (XIIa) belonging to the chemically rare *T* point group is proposed. Structure XIIa can be generated by placing three-atom groups (the v_5's) in each of the four hexagonal faces of a truncated tetrahedron[16] or by closing the square faces of a snub cube.[20b,23] Structure XIIa has 18 v_6-v_6 edges and 12 v_5-v_5 edges. A second 24-vertex structure (XIIb) with D_2 symmetry has 14 v_6-v_6 edges and eight v_5-v_5 edges. Both XIIa and XIIb have enantiomeric forms. Interestingly, three 24-vertex deltahedra, XIIc, XIId, and XIIe, with the same number of v_5-v_5 and v_6-v_6 edges as XIIa can be constructed. Structure XIIc is oblate and has D_{3d} symmetry. Structures XIId and XIIe are both prolate and have D_{3h} and D_{3d} symmetry, respectively. We express no preference among these last three structures. An extremely prolate D_{3d} structure (XIIf) with 24 v_6-v_6 vertices is also possible.

Stabilities. For 14, 15, 16, 18, 20, 22, and 24 vertices very satisfying structures with high symmetry, high sphericity, and a reasonable number of v_6-v_6 edges could be constructed from 12 six-coordinate borons and a complementary number of seven-coordinate borons. For 13, 17, 19, 21, and 23 vertices, the shapes were generally less spherical and the symmetries were generally lower. For 13 vertices only ten six-coordinate borons could be used. Just as $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ are more stable than $B_9H_9^{2-}$ and $B_{11}H_{11}^{2-}$[24] (Table V below), it may be expected that the large closo boranes with even numbers of borons and high symmetry may be more stable than some of their odd-numbered homologues. However, with the assumed bond lengths, structure Vb is more stable than structure IV (Table V), and in any event no structure is more favorable than the $B_{12}H_{12}^{2-}$ icosahedron.

Bond Lengths. On the basis of a survey of known BB bond lengths from x-ray diffraction studies (Table II), radii are proposed for five-, six-, and seven-coordinate borons with one exo hydrogen (Table IV). The resulting bond distances are also shown in Table IV. As indicated in Table II there is considerable variation in the bond lengths for known seven-coordinate borons. It is possible that the exo hydrogen distances are systematically shortened for high-coordinate borons, as suggested by the behavior of exo-bonded carbon substituents in closo boranes and carboranes.[25] Increasing p character in the BH bond, however (see below), would suggest longer BH bonds in the larger polyhedra. In any event, the BH distances for terminally bonded hydrogens probably do not vary much from 1.19 Å.[26]

III. Calculations

Preliminary SCF calculations were carried out using the PRDDO[27] method for structures I, IIa, IIb, III, IV, Va, Vb, VIa, and VId. In all cases a good HOMO–LUMO separation was found, indicating the appropriateness of the 2− charge.[6] However, gaps in the eigenvalues indicate that a 8− charge might be appropriate for structure IIb (e.g., $C_6B_8H_{14}^{2-}$) and that a 4− charge ($B_{16}H_{16}^{4-}$ or $C_4B_{12}H_{16}$) might be appropriate for structure IV.

Table V. PRDDO-SCF Energy per BH Unit in $B_nH_n^{2-}$

Molecule	Energy, au	Molecule	Energy, au
$B_5H_5^{2-}$ [a]	−25.178	$B_{11}H_{11}^{2-}$ [a]	−25.257
$B_6H_6^{2-}$ [a]	−25.215	$B_{12}H_{12}^{2-}$ [a]	−25.276
$B_7H_7^{2-}$ [a]	−25.232	$B_{14}H_{14}^{2-}$ (IIa)	−25.260
$B_8H_8^{2-}$ [a]	−25.238	$B_{16}H_{16}^{2-}$ (IV)	−25.249
$B_9H_9^{2-}$ [a]	−25.249	$B_{17}H_{17}^{2-}$ (Vb)	−25.257
$B_{10}H_{10}^{2-}$ [a]	−25.259		

[a] D. A. Dixon, J. H. Hall, Jr., D. A. Kleier, T. A. Halgren, and W. N. Lipscomb, manuscript in preparation.

Table V indicates that the SCF energy per BH unit for the three highly symmetric IIa, IV, and Vb structures ($B_nH_n^{2-}$) compares favorably with energy per BH unit in smaller closo boron hydrides.

The molecular orbitals in structures I, IIa, III, IV, Vb, and VId were localized by the method of Boys.[28] We here report some preliminary results. A localized structure for $B_{14}H_{14}^{2-}$ (IIa) has three three-center localized molecular orbitals (LMO's) in each hexagonal cap and nine three-center LMO's joining the hexagonal rings. Likewise, in structure Vb the seven-coordinate borons each participate in three three-center LMO's. In a localized structure for Vb ten three-center LMO's join the three pentagonal rings while eight three-center LMO's are employed in the pentagonal caps, three in one cap and five in the other. In structure IV some seven-coordinate borons are associated with four three-center LMO's in addition to the obligatory two-center BH LMO's. We note that in every case examined some borons are associated with five or more valence LMO's in this minimum basis set treatment. Such "fractional bonding"[29] is common in large boron hydrides[28b] and is indicative of an irremovable electronic delocalization.[29] The complexity of the LMO structures casts some doubt on the validity of simple arguments against the stability of boron hydrides which have seven-coordinate borons.[8e]

Our calculations suggest that seven-coordinate borons carry a slightly more negative charge than do the six-coordinate borons.

IV. Discussion

Geometrically the formula of $v_5 = 12$ and $v_6 = n - 12$ may be valid for very large boron hydrides. Highly symmetric figures conforming to this formula include an omnicapped dodecahedron (32 vertices), a pentagonally capped icosidodecahedron (42 vertices), a pentagonally capped snub dodecahedron (72 vertices), and an omnicapped truncated icosahedron (92 vertices).[30] The limiting case is a hexagonal arrangement of v_6's on the surface of a sphere of infinite radius.

As the size of the boron polyhedron increases four factors must be considered. First, the addition of v_6's increases the average coordination number of the borons, which should increase the stability of the molecule.[7] Second, increasing the size of the sphere reduces interactions with borons on the opposite side of the cage, which may reduce the stability. Third, the direction of the atomic orbital hybrids becomes troublesome as the size of the polyhedron increases. If tetrahedral hybrids are used, there will be increased bond-angle strain as the radius of the sphere increases, since the boron–boron hybrids will not be directed toward one another. If trigonal hybrids are used, this problem is eliminated. However, then the hybrid to the exo hydrogen has 100% p character. Adopting Hoffmann and Lipscomb's and Wade's radial sp plus tangential p hybridization scheme[1,4] allows the same problem to be formulated differently. In this model each

Table VI. Common Arrangements of Vertices in Known and Proposed Closo Borane and Carborane Polyhedra

Pattern[a]	V^b	Symmetry	Example	Comments
3:3:3. . .	6	O_h	$B_6H_6^{2-}$	
	9	D_{3h}	$B_9H_9^{2-}$	
	12	I_h	$B_{12}H_{12}^{2-}$	Exceptionally stable
	15	D_{3h}	III	
	18	D_3	VIa	Chiral
	18	D_{3d}	VIc	Prolate
	21	D_3	IXa	Chiral
	21	D_{3h}	IXc	Prolate
	24	T	XIIa	Chiral
	24	D_{3d}	XIIf	Extremely prolate
1:*n*:1	5	D_{3h}	$C_2B_3H_5$	$B_5H_5^{2-}$ not known
	6	O_h	$B_6H_6^{2-}$	Also 3:3
	7	D_{5h}	$B_7H_7^{2-}$	
1:*n*:*n*:1	10	D_{4d}	$B_{10}H_{10}^{2-}$	Exceptionally stable
	12	I_h	$B_{12}H_{12}^{2-}$	Exceptionally stable
	14	D_{6d}	IIa	
1:*n*:*n*:*n*:1	14	O_h	IIb	Not preferred
	17	D_{5h}	Vb	Prolate
	20	D_{6h}	VIIIa	
1:*n*:*n*:*n*:*n*:1	22	D_{5d}	Xb	Oblate

[a] Using Föppl's notation (ref 21) for the arrangement of vertices. [b] The number of vertices in the polyhedron.

BH unit has two radially directed sp hybrids: one directed outward for the BH bonds and one directed inward for boron framework bonding. The remaining p atomic orbitals are oriented tangentially with respect to the pseudospherical surface of the polyhedron.[4c] As the size of the sphere increases the overlap between the tangential p orbitals improves somewhat. However, the overlap of the radial sp hybrid atomic orbitals in the a_1 or a_g bonding molecular orbital becomes poorer with respect to both neighboring borons and borons on the opposite side of the sphere. Parenthetically, this hybridization scheme provides a convenient rationale for our intuitive preference for nearly spherical polyhedra.[4c] Fourth, as the number of boron atoms increases, the charge that must be carried by each boron is reduced. At some point the 2− charge rule for closo boron hydrides[6] may break down, perhaps beyond $B_{24}H_{24}^{2-}$ which has an equal number of v_5's and v_6's. We also note that as the size of the central cavity increases, the possibility of putting the counterion in the center of the sphere becomes more attractive.

The structures proposed resemble solutions to problems of arranging objects which repel one another on the surface of a sphere.[21,31] Föppl[21] in a pre quantum mechanical treatment of electrons in an atom[32] determined stable arrangements for electrons constrained to lie on the surface of a sphere. The solutions to Föppl's problem for $n = 5$–7, 10, and 12[21] are analogous to known closo boranes and carboranes.[5] Structure IIa is Föppl's solution for $n = 14$,[21] and structure VId is Föppl's solution for $n = 18$.[21]

The solutions to Föppl's problem conform to the following generalizations:[21,31]

(1) There may be particles (electrons in Föppl's problem, boron atoms in ours) at a pole or both poles and on latitudinal rings perpendicular to the polar axis.

(2) The latitudinal rings will be twisted so that arrangements of particles are not coincident between neighboring rings.

(3) There will exist special values of *n* corresponding to very stable arrangements.

A similar but more restrictive set of generalizations was made by Gillespie in specifying the arrangement of electron pairs in his VSEPR model.[33] In particular we find Gillespie's restriction that the number of particles on successive circles in passing from the pole to the equator must remain constant or increase by two to be inappropriate for structures Va, VIIa, and Xa among our preferred structures. These three structures show a 3:6 pattern between successive rings or a 4:2 pattern on passing between rings going toward the equator of the sphere. Table VI lists the occurrence of several patterns which appear typical for our structures and for known closo boranes and carboranes.

V. Related Chemistry and Synthesis

Each of the structures proposed should have more open relatives. The B_nH_{n+4} nido boranes and the B_nH_{n+6} arachno boranes have been shown to be related to the closo boranes by the removal of vertices from the closo structure.[4]

Not only are there isomeric possibilities among the proposed structures, but a large number of $C_2B_{n-2}H_2$ isomers are possible in addition. On the basis of previous chemistry[34] we predict that the most stable isomers would have carbon atoms as far apart as possible and in the six- rather than seven-coordinate positions.[35] Carboranes with larger numbers of carbons would be expected to have more open structures than those predicted above. Open hexagonal or pentagonal faces are a distinct possibility.[36]

Four synthetic routes suggest themselves for the proposed structures. The first is to replace the metallic portion of a polyhedral metalloborane with more than 12 vertices with a BH unit (or units). Promising metallocarboranes have been synthesized by Hawthorne[3a–d] and Grimes[3f,g] using a polyhedral expansion and direct insertion reactions. The limits of such reactions remain to be explored. While 13- and 14-vertex metallocarboranes have been synthesized,[3,15] the related boranes, $B_{13}H_{13}^{2-}$ and $B_{14}H_{14}^{2-}$, remain unrealized. The second, already exploited by Grimes,[3f] is to join the two halves of a borane metal sandwich compound by removing the metal atoms. For the largest boranes, triple-decker sandwich compounds[37] might also be considered as precursors. A third synthetic route would be to close the cage of a fused boron polyhedron with cis open faces. To date, only one such compound is known, $B_{14}H_{20}$.[17] However, there is no particular reason to believe that other such compounds cannot be synthesized. A fourth synthetic route would be to add hydrogen to the borons shared between two fused closo polyhedra such as $B_{20}H_{16}$.[38] However, the target borons are so well protected sterically that this alternative looks the least promising.

We have noted the existence of several isomeric structures (e.g., Va and Vb) which presumably would rearrange thermally to the preferred isomer. Thus the initial product of closing a $B_{17}H_{17}^{2-}$ structure might be structure Vb, which would rearrange to Va on heating. Of particular relevance is the observation by Grimes[3f,g] that the cage geometries of the initial products of super-icosahedral metallocarboranes appear to be dominated by kinetic factors. Grimes[3f,g] further observes that thermodynamically the preference by carbon for a low coordination number in supra-icosahedral metallocarboranes appears to be less important than the achievement of mutual separation of carbon atoms, which in turn appears to be less important than the drive to achieve a symmetrical closo structure.

Finally we note that the dual[39] of each of our deltahedra is a possible C_nH_n structure (for $n = 22$ to 44).

Acknowledgment. This work was supported by the Office of Naval Research. We wish to thank R. N. Grimes for helpful comments on the manuscript.

Registry No. $B_{13}H_{13}^{2-}$, 64175-33-3; $B_{14}H_{14}^{2-}$, 12430-58-9; $B_{15}H_{15}^{2-}$, 64175-23-1; $B_{16}H_{16}^{2-}$, 64175-24-2; $B_{17}H_{17}^{2-}$, 64175-25-3; $B_{18}H_{18}^{2-}$, 64175-26-4; $B_{19}H_{19}^{2-}$, 64175-27-5; $B_{20}H_{20}^{2-}$, 64175-28-6; $B_{21}H_{21}^{2-}$, 64175-29-7; $B_{22}H_{22}^{2-}$, 64175-30-0; $B_{23}H_{23}^{2-}$, 64175-31-1; $B_{24}H_{24}^{2-}$, 64175-32-2.

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

(2) E. L. Muetterties, "Boron Hydride Chemistry", Academic Press, New York, N.Y. 1975, p xii.

(3) (a) K. P. Callahan and M. F. Hawthorne, *Adv. Organomet. Chem.*, **14**, 145 (1976); (b) M. F. Hawthorne, *J. Organomet. Chem.*, **100**, 97 (1975); (c) G. B. Dunks and M. F. Hawthorne, ref 2, p 383; (d) C. G. Salentine and M. F. Hawthorne, *Inorg. Chem.*, **15**, 2872 (1976); (e) W. M. Maxwell, E. Sinn, and R. N. Grimes, *J. Chem. Soc., Chem. Commun.*, 389 (1967); (f) W. M. Maxwell, R. F. Bryan, and R. N. Grimes, *J. Am. Chem. Soc.*, **99**, 4008 (1977); (g) W. M. Maxwell, R. Weiss, E. Sinn, and R. N. Grimes, *ibid.*, **99**, 4016 (1977).

(4) (a) Reference 2, pp 12–16; (b) K. Wade, *Chem. Br.*, **11**, 177 (1975); (c) K. Wade, *Adv. Inorg. Chem. Radiochem.*, **18**, 1 (1976).

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(6) For discussions of the 2– charge in closo boron hydrides, see I. R. Epstein and W. N. Lipscomb, *Inorg. Chem.*, **10**, 1921 (1971), and ref 4c.

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(8) (a) A. F. Wells, "Models in Structural Inorganic Chemistry", Oxford University Press, New York, N.Y., 1970, pp 156–161; (b) F. C. Frank and J. S. Kasper, *Acta Crystallogr.*, **11**, 184 (1958); (c) R. B. King, *J. Am. Chem. Soc.*, **91**, 7211 (1969); (d) *ibid.*, **92**, 6460 (1970); (e) *ibid.*, **94**, 95 (1972).

(9) It can easily be shown that the formula $v_5 = 12$, $v_6 = v - 12$ will satisfy eq 1–4 for any $v \geq 12$.

(10) Complete elimination of v_6v_6 edges can only be achieved for $v = 14$, 15, or 16. See ref 8b.

(11) Reference 1, p 52. Hexadecaborane(20) is an exception (L. B. Friedman, R. F. Cook, and M. D. Glick, *Inorg. Chem.*, **9**, 1952 (1970)).

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The Synthesis and Characterization of Methylaminobis(difluorophosphine)–Borane(3), –Bis(borane(3)), and –Triborane(7) Complexes

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The reactions of methylaminobis(difluorophosphine), $F_2PN(CH_3)PF_2$ with diborane(6), borane carbonyl and tetraborane(10) produce the coordination complexes $F_2PN(CH_3)PF_2{\cdot}BH_3$, $F_2PN(CH_3)PF_2{\cdot}2BH_3$ and $F_2PN(CH_3)PF_2{\cdot}B_3H_7$. The new complexes have been characterized by mass, infrared, and NMR spectroscopic techniques. The relative stability of these complexes is discussed with relation to coordination complexes of other related $F_2P{-}X{-}PF_2$ ligands.

Several potentially monodentate, bidentate, and tridentate fluorophosphine ligands of the general type F_2PXPF_2 have been prepared,[1–7] and their coordination chemistry has been partially explored.[2–4,6–12] In the course of investigating the multifunctional coordination properties of F_2PXPF_2 ligands, several investigators have attempted to correlate the variety of steric, inductive, and π-overlap contributions which may be operative and decisive in determining the hapticity of the ligands toward various acceptor sites.[2–4,10,11] An apparently self-consistent bonding model has slowly evolved but new ligands and coordination complexes need to be studied before a complete understanding of the coordination behavior is available. One interesting, potentially tridentate ligand whose coordination properties have been studied little is methylaminobis(difluorophosphine), $F_2PN(CH_3)PF_2$.[5] Johnson and Nixon[8] have reported that this Lewis base can function as a bis ligand toward a single zerovalent metal center. More recently, King and co-workers[12] have shown that the ligand can also act as a biligate ligand toward two metal centers. As part of a study of synthetic routes to small ring systems containing F_2PXPF_2 moieties,[13] we have investigated the coordination chemistry of the same potentially tridentate ligand. This report describes the synthesis and characterization of the mono(borane(3)) complex $F_2PN(CH_3)PF_2{\cdot}BH_3$ (**1**), the bis(borane(3)) complex $F_2PN(CH_3)PF_2{\cdot}2BH_3$ (**2**), and the triborane(7) complex $F_2PN(CH_3)PF_2{\cdot}B_3H_7$ (**3**). A reaction of the ligand with BF_3 is also described. The properties of the new coordination complexes are discussed in the context of