to PEt_3 at +4.1 ppm and a doublet at +40.3 ppm due to P(1,2). Each resonance has satellites due to coupling to ^{195}Pt (^{1}J(Pt-P) = 3906 Hz, ^{2}J(Pt-P) = 301 Hz). When the temperature is reduced, the low-field resonance broadens and at about −55 °C splits into two resonances assignable to the P(1) and P(2) atoms of the solid-state structure. Clearly, at higher temperatures a rapid dynamic interchange occurs between the coordinated and noncoordinated sulfur atoms, which in turn renders the phosphorus atoms equivalent on the NMR time scale. The unusual pivotal nature of the process has been pointed out above, and it is also noteworthy that the complex is chiral at C(0) and the dynamic interchange inverts the configuration. This occurs by interchange of the roles of the two sulfur atoms despite the fact that the actual motion is simply a rotation about the Pt-C(0) bond.

The lability of the Pt-S(2) bond in **5** (X = Y = S) may be attributed in part to the trans influence of the **4**, PEt_3 ligand. It is thus interesting that isomer **4** (X = Y = S), in which the sulfur is trans to Cl, exhibits an ambient-temperature $^{31}P\{^{1}H\}$ NMR spectrum assignable to a static structure. The resonances of P_a and P_b at +61.9 and +39.9 ppm are both doublets, due to coupling to P_c (^{3}J(P-P) = 11.4 and 9.5 Hz, respectively), with platinum satellites (^{2}J(Pt-P) = 451 and 84 Hz, respectively). The P_c resonance at +5.4 ppm is an overlapping doublet of doublets with platinum satellites (^{1}J(Pt-P) = 2949 Hz). When the temperature is raised, isomerization to **5** begins but there is also evidence for dynamic interchange of the P_a and P_b atoms of **4**, with a coalescence temperature of about +50 °C.

Our research into the various coordination modes exemplified by Scheme I is continuing, and full details will be published at a later date.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada and the University of Victoria for research grants and K. Beveridge for technical assistance during the crystal structure determination. A.P. thanks the University of Sussex for a leave of absence and the University of Victoria for a visiting appointment.

Registry No. **4** (X = Y = S), 85957-01-3; **4** (X = S, Y = O), 85957-02-4; **4** (X = Y = Se), 85957-03-5; **5** (X = Y = S), 85994-29-2; **5** (X = Y = Se), 85994-30-5; **6** (X = Y = S), 85957-04-6; **6** (X = S, Y = O), 85957-05-7; **6** (X = Y = Se), 85957-06-8; **7** (X = Y = S), 85976-64-3; $CH_2(PPh_2S)(PPh_2S)$, 14633-92-2; $Li(CH(PPh_2S)_2)$, 85976-65-4; $Pt_2Cl_4(PEt_3)_2$, 15692-96-3; PEt_3, 554-70-1.

Supplementary Material Available: Tables of fractional atomic coordinates, interatomic distances, bond angles, selected intermolecular distances, anisotropic temperature parameters, and structure factors (27 pages). Ordering information is given on any current masthead page.

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Structural Nomenclature for Polyboron Hydrides and Related Compounds. 1. Closed and Capped Polyhedral Structures

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Received November 11, 1982

The method for uniquely describing closed, fully triangulated boron polyhedra developed previously is used for naming closed polyboron hydrides and their replacement analogues and derivatives. A descriptor system for uniquely describing capped closed polyboron polyhedra is proposed.

Introduction

Polyboron hydrides and their replacement analogues and derivatives have been described in the past by a stoichiometric nomenclature[2a-d,3a-c] that provides information only on the number and type of skeletal atoms and exopolyhedral hydrogen atoms, substituents, or ligands. Except for recognition of "closed" structures by the prefix *closo*-,[2b,e,3d,e,4] the specific polyhedral structure of a polyboron hydride was not provided by its name. A knowledge of boron hydride chemistry was necessary in order to know the structure. Even this has not been sufficient in an increasing number of cases, where structures could not be inferred from previous chemistry.[7] Recently, we reported a method for definitively describing structures of closed polyhedral compounds.[8] This report

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[2] American Chemical Society. "The Nomenclature of Boron Compounds", *Inorg. Chem.* **1968**, *7* (10), 1945–1964: (a) Rules 1.3 and 1.4, pp 1946–1947; (b) Rule 4.1, pp 1950–1951; (c) Rules 7.3 and 7.4, p 1953; (d) Rule 7.5, p 1953; (e) Rule 1.6, p 1947, and Rule 7.4, p 1953; (f) Rule 1.6, Comment, p 1947; (g) Rule 2.3234, p 1949; (h) Rules 3.2–3.4, p 1950; (i) Rule 6, p 1952; (j) Rule 4.2, p 1951.

[3] International Union of Pure and Applied Chemistry. "Nomenclature of Inorganic Boron Compounds", *Pure Appl. Chem.* **1972**, *30* (3–4), 683–710: (a) Rules 2.2 and 2.3, pp 685–686; (b) Rules 5.3 and 5.4, p 694; (c) Rules 7.1 and 7.5, pp 697–699; (d) Rule 2.4, p 686, and Rule 5.4, p 694; (e) Rule 7.1, pp 696–698; (f) Rule 7.5, p 699; (g) Rule 3.24, p 689; (h) Rules 4.2 and 4.3, pp 690–693; (i) Rule 8, pp 699–700; (j) Rule 7.2, p 698.

[4] The descriptor *closo* was first proposed as "clovo" for describing "cage" phosphorus compounds,[5] which was later adapted for closed polyboron hydrides.[2f,6]

[5] Van Wazer, J. "Phosphorus and Its Compounds"; Interscience: New York, 1958; Vol. I., p 89.

[6] Adams, R. *Inorg. Chem.* **1963**, *2* (6), 1087–1088.

[7] For example, see: Hewes, J. D.; Knobler, C. B.; Hawthorne, M. F. *J. Chem. Soc., Chem. Commun.* **1981**, 206–207; Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* **1974**, *13* (6), 1411–1418. Compare with: Dustin, D. F.; Evans, W. J.; Jones, C. J.; Wiersema, R. J.; Gong H.; Chan, S.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1974**, *96* (10), 3085–3090; Dustin, D. F.; Dunks, G. B.; Hawthorne, M. F. *Ibid.* **1973**, *95* (4), 1109–1115.

incorporates that descriptor system into polyboron hydride names to provide for recognition of the polyhedral structure.

A discussion of names for closed polyboron hydride systems must include consideration of some of the special problems associated with polyboron hydride nomenclature. Three of these are discussed in this and the following paragraphs. One problem involves modification of organic replacement nomenclature[9a] and its merger with the principles of coordination nomenclature[10a] used to name ionic ~~polyboron~~ hydrides.[2c,3b] In organic replacement nomenclature, carbon atoms of a parent structure are replaced by other atoms (for example, a carbon atom by a nitrogen or oxygen atom) as indicated by prefixes attached to the name of the parent structure. Hence, in a replacement name, some atoms expressed by the parent name are not, in fact, present in the actual hetero compound. Further, the replacing atom often carries implied hydrogen atoms consistent with the standard valence of the atom and the structure of the parent compound; these hydrogen atoms may be substituted by other atoms or groups also indicated by prefixes. Such operations are foreign to coordination nomenclature, which is based on additive principles where all atoms or groups are expressed in the name. In coordination nomenclature, exclusive of organic ligands, there are no atoms implied in the name that are not present in the actual compound; hence, there is neither replacement of atoms nor substitution of hydrogen atoms of a parent structure.

Another special problem of polyboron hydride nomenclature involves the phenomenon of "extra" hydrogen, i.e., BH_2 skeletal groups and bridging hydrogen atoms, in neutral polyboranes. Although this phenomenon occurs primarily in nonclosed systems, bridging hydrogen has been observed in closed polyboranes.[11] Two methods for specifying positions of "extra" hydrogens in polyboranes will be described in this report, one of which is an adaptation of the principle of "indicated hydrogen" used in organic nomenclature[9b] and the other is a method which has been used in *Chemical Abstracts* index names to distinguish between isomeric polyboranes.[13]

A third special problem of polyboron hydride nomenclature involves neutral groups attached to skeletal atoms of neutral polyboranes and heteropolyboranes. In the past, neutral polyboranes have been named by substitutive (organic) techniques and ionic polyboron hydrides by coordination principles. The use of a different nomenclature system depending on charge is obviously quite artificial but has been quite successful with polyboron hydrides. However, it is not so easy to deal with heteropolyboron hydrides, especially metallopolyboron hydrides, and their derivatives with such an arbitrary differentiation, and de facto naming procedures have already partially merged the two systems. In this report we suggest specific ways in which principles of substitutive and coordination nomenclature can be merged to provide a more structurally definitive general nomenclature system for polyboron hydrides and related compounds.

Closed Polyboron Hydrides

Polyhedral boron ions are usually named by principles of coordination nomenclature.[2c,3b,10a] Anions are named by attaching the general anionic suffix "-ate" to the stem "bor" and indicating the total charge by means of a Ewens–Bassett number,[10b] i.e., an Arabic number equal to the amount of charge followed by a minus sign, all enclosed in parentheses. The number of boron atoms in the anion is given by an appropriate numerical prefix, and the total number of hydrogen atoms is denoted by a numerical prefix attached to the ligand prefix hydro. Thus, $[B_{10}H_{10}]^{2-}$ is named decahydrodecaborate(2−). Cations are named similarly except that the element name "boron" is used instead of "borate" and the plus sign is used in the Ewens–Bassett number.

These names for polyboron hydride ions are only stoichiometric, giving neither the skeletal structure of the boron atoms nor the position of hydro ligands. This information can only be inferred by those with a knowledge of the chemistry. With the rapid advance of polyboron hydride chemistry, especially heteropolyboron hydride chemistry, there are polyboron hydride ions having the same stoichiometry but different geometry. To designate a ~~specific~~ polyhedral structure, we suggest that the appropriate descriptor, described previously,[8] be added to the name just before the prefix denoting the number of boron atoms in the skeleton. Secondly, to be complete, locants should be used to indicate the position of each hydro ligand. However, in the interest of simplicity, we suggest the following principle: *When, in a closed polyhedral polyboron hydride ion, each boron atom of the skeleton that is not attached to other ligands has one and only one attached hydrogen atom, locants for these hydro ligands may be omitted.* Thus, $[B_{10}H_{10}]^{2-}$, a bicapped square antiprism, would be named: decahydro[D_{4d}-($1v^44v^54v^51v^4$)-Δ^{16}-*closo*]decaborate(2−). The structure of the boron skeleton is unambiguously specified by the descriptor enclosed in brackets, and it is understood that each boron atom is attached to one hydrogen atom. Using the slightly modified descriptor as suggested previously,[8a] whereby vertices having the common skeletal connectivity of five need not be fully specified, this name would be decahydro[D_{4d}-($1v^441v^4$)-Δ^{16}-*closo*]decaborate(2−). The descriptor may be shortened even further as suggested earlier[8a] for the common polyhedra with twelve or fewer vertices, giving the name decahydro[D_{4d}-(1441)-Δ^{16}-*closo*]decaborate(2−). Obviously, if there is no need or desire to convey structural information, the original stoichiometric name decahydrodecaborate(2−), or the formula, $[B_{10}H_{10}]^{2-}$, could be used.

Neutral closed polyboron hydrides, B_nH_n, are considered here even though they are not yet known, at least to our knowledge, because they are used formally as parents for naming alkyl[14a] and halo[14b] derivatives and heteropolyboranes; the latter are considered in detail later. If *closed* polyboranes are reported, they would be named stoichiometrically according to the existing rules,[2a,3a] i.e., by citing a prefix giving the number of boron atoms in the polyhedral structure to the generic name borane followed by a parenthetical Arabic number giving the number of exopolyhedral hydrogen atoms. Specific polyhedral structures of neutral closed polyboranes may be described by

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(8) (a) Casey, J. B.; Evans, W. J.; Powell, W. H. *Inorg. Chem.* **1981**, *20* (5), 1333–1341. (b) *Ibid.* **1981**, *20* (10), 3556–3561.

(9) International Union of Pure and Applied Chemistry. "Nomenclature of Organic Chemistry, Sections A, B, C, D, E, F, and H"; Pergamon Press: Oxford, 1979: (a) Rule B-4, pp 68–70, and Subsection C-0.6, pp 123–127; (b) Rule A-21.6, p 25; (c) Section D, Table I, Appendix, pp 459–460; (d) Rule C-41.2, pp 115–116; (e) Rule C-16.11, p 108; (f) Rule B-1.53, p 55, and Rule B-4.1, p 68; (g) Rule C-13.11(e), footnote; (h) Rule A-34, pp 35–37, and Rule B-15, pp 75–76.

(10) Internation Union of Pure and Applied Chemistry. "Nomenclature of Inorganic Chemistry (1970)", 2nd ed.; Butterworths: London, 1971: (a) Chapter 7, pp 39–83; (b) Rule 2.252, p 17; (c) Rules 7.611 and 7.612, pp 65–67; (d) Rule 7.421, pp 49–50.

(11) (a) McKown, G. L.; Don, B. P.; Beaudet, R. A.; Vergamini, P. J.; Jones, L. H. *J. Chem. Soc., Chem. Commun.* **1974**, 765–766; *J. Am. Chem. Soc.* **1976**, *98* (22), 6909–6912. (b) Brint, P.; Healy, E. F.; Spalding, T. R.; Whelan, T. *J. Chem. Soc., Dalton Trans.* **1981**, 2515–2522. An edge-bridged structure was favored by a theoretical calculation,[12] which would be described structurally by the proposals in this paper as follows: (i) (2,3-μH)-1-carba[O_h-(141)-Δ^8-*closo*]hexaborane(7) or (ii) 1-carba-[O_h-(141)-Δ^8-*closo*]hexaborane(7)-2,3-μH.

(12) Lambiris, S. K.; Marynick, D. S.; Lipscomb, W. N. *Inorg. Chem.* **1978**, *17* (12), 3706–3707.

(13) Chemical Abstracts Service. "Parent Compound Handbook"; American Chemical Society: Columbus, OH, 1977; Cage Parent Section, pp 5CP and 7CP.

(14) (a) Davan, T.; Morrison, J. A. *J. Chem. Soc., Chem. Commun.* **1981**, 250–251. (b) See, for example: Saulys, D. A.; Kutz, N. A.; Morrison, J. A. *Inorg. Chem.* **1983**, *22* (12), 1821–1824. Kutz, N. A.; Morrison, J. A. *Ibid.* **1980**, *19* (11), 3295–3299. Davan, T.; Morrison, J. A. *Ibid.* **1979**, *18* (11), 3194–3197.

an appropriate descriptor,[8] added immediately in front of the stoichiometric name. For example, if B_9H_9 had the structure of a tricapped trigonal prism, it would be named [D_{3h}-($33v^{4}3$)-Δ^{14}-*closo*]nonaborane(9). If it had the C_{2v} structure,[8a] it would be named [C_{2v}-($1v^{6}4v^{4}22$)-Δ^{14}-*closo*]nonaborane(9).

Closed Heteropolyboron Hydrides

Although the known closed polyboron hydrides are almost always anionic, heteropolyboron hydrides may be anionic, neutral, or even cationic depending on the electronic nature of replacing atoms: for example, $[B_{11}CH_{12}]^-$, $B_{10}C_2H_{12}$, $B_{11}PH_{12}$, and $[B_{11}SH_{12}]^+$ all have an icosahedral structure and are isoelectronic with $[B_{12}H_{12}]^{2-}$. Substitutive nomenclature principles that name compounds as derivatives of parent hydrides seem most convenient for neutral heteropolyboron hydride derivatives such as $(CH_3)_2C_2B_{10}H_{10}$. Coordination nomenclature is almost always used for ionic polyboron hydrides such as $[B_{12}H_{12}]^{2-}$. Replacement techniques must be incorporated into both systems to permit the full range of heteropolyboron hydrides to be named. The rapidly developing field of metallopolyboron hydrides has provided a strong motivation for incorporating metallic elements into the replacement nomenclature system. However, the unique characteristics of the polyboron hydrides require modification of some of the principles of organic replacement nomenclature, as will be explained in following sections.

Neutral heteropolyboron hydrides, i.e., heteropolyboranes with closed polyhedral structures, are named conveniently on the basis of a neutral polyboron hydride (usually hypothetical) discussed above. Atoms replacing boron atoms of the polyhedral skeleton are indicated by replacement prefixes listed in Table I,[9c] which, together with appropriate locants for positions in the polyhedral structure, are cited immediately in front of the structural descriptor:[8] for example, 1-carba[O_h-(141)-Δ^{8}-*closo*]hexaborane(7). Two or more of the same replacing heteroatoms are indicated by the usual prefixes such as di-, tri-, etc.: for example, 1,2-dicarba[I_h-(1551)-Δ^{20}-*closo*]dodecaborane(12). Different replacement prefixes are cited in decreasing order of their seniority, i.e., in the order of their appearance in the list of prefix names as given in Table I: for example, 1-thia-10-carba[D_{4d}-(1441)-Δ^{16}-*closo*]decaborane(9).

In the adaptation of organic replacement nomenclature to heteropolyboron hydrides, it must be clearly understood that the replacement prefixes do not imply a specific bonding capacity for a heteroatom nor do they imply any attached hydrogen atoms, except for carbon as noted below.[15] This fundamental difference from traditional organic replacement nomenclature is necessary because the skeletal atoms in the polyboron hydrides and their hetero analogues do not exhibit constant bonding capacity. The number of skeletal neighbors of both boron and heteroatoms varies from 4 (occasionally even 3) to 6 and even 7, and the number of hydrogen atoms associated with each polyhedral structure does not seem to have a simple relationship to the number of skeletal atoms. Therefore, just as for polyboranes,[2a,3a] the total number of hydrogen atoms of a neutral heteropolyborane must be indicated by a parenthetical Arabic number attached directly to the end of the heteropolyborane name.[2b,3e] For example, the icosahedral $B_{11}PH_{12}$ would be named 1-phospha[I_h-(1551)-Δ^{20}-*closo*]dodecaborane(12). It is very important to remember that this parenthetical number represents the total number of hydrogen atoms of the heteropolyborane and not the number of hydrogen atoms of the parent polyborane (see earlier discussion).

Table I. Replacement ("a") Prefixes[9c]

element[a]	"a" prefix	element	"a" prefix	element	"a" prefix
F	fluora	Au	aura	Eu	europa
Cl	chlora	Ni	nickela	Gd	gadolina
Br	broma	Pd	pallada	Tb	terba
I	ioda	Pt	platina	Dy	dysprosa
At	astata	Co	cobalta	Ho	holma
O	oxa	Rh	rhoda	Er	erba
S	thia	Ir	irida	Tm	thula
Se	selena	Fe	ferra	Yb	ytterba
Te	tellura	Ru	ruthena	Lu	luteta
Po	polona	Os	osma	Ac	actina
N	aza	Mn	mangana	Th	thora
P	phospha	Tc	techneta	Pa	protactina
As	arsa	Re	rhena	U	urana
Sb	stiba	Cr	chroma	Np	neptuna
Bi	bisma	Mo	molybda	Pu	plutona
C	carba	W	tungsta	Am	america
Si	sila	V	vanada	Cm	cura
Ge	germa	Nb	nioba	Bk	berkela
Sn	stanna	Ta	tantala	Cf	californa
Pb	plumba	Ti	titana	Es	einsteina
B	bora	Zr	zircona	Fm	ferma
Al	alumina	Hf	hafna	Md	mendeleva
Ga	galla	Sc	scanda	No	nobela
In	inda	Y	yttra	Lr	lawrenca
Tl	thalla	La	lanthana	Be	berylla
Zn	zinca	Ce	cera	Mg	magnesa
Cd	cadma	Pr	praseodyma	Ca	calca
Hg	mercura	Nd	neodyma	Sr	stronta
Cu	cupra	Pm	prometha	Ba	bara
Ag	argenta	Sm	samara	Ra	rada

[a] Replacement ("a") prefixes for 90 elements are included in this list, which are given *in order of seniority*; i.e., a prefix occurring earlier in the list is senior (preferred). Prefixes for the alkali metal elements have not been officially approved. Seniority order of prefixes for hydrogen and the inert (rare, noble) gases has not been officially established.

Specification of Hydrogen Atoms. The name above for $B_{11}PH_{12}$ still does not specify the location of hydrogen atoms, which becomes very important when, as frequently happens in heteropolyboranes other than carbaboranes, there is not a one-to-one correspondence between the number of skeletal atoms and the number of hydrogen atoms. Therefore, we suggest the following guidelines for specifying the location of hydrogen atoms in closed heteropolyboranes:

(1) One nonbridging hydrogen atom is assumed to be attached to each skeletal boron and carbon atom. For example, the icosahedral 1,2-$C_2B_{10}H_{12}$ is named 1,2-dicarba[I_h-(1551)-Δ^{20}-*closo*]dodecaborane(12). Thus, except for the addition of a structural descriptor,[8] names of most closed carbaboranes will be the same as they are now.

(2) All other hydrogen atoms must be specified to provide a structurally definitive name; this includes (a) hydrogen atoms on boron or carbon skeletal atoms in addition to the one assumed in (1) above, (b) all hydrogen atoms on other skeletal atoms, and (c) all bridging hydrogen atoms. We suggest two possible methods for specifying the positions of these hydrogen atoms:

(i)[18] In front of the name of the heteropolyborane cite the capital italic letter *H*, prefixed (without an intervening hyphen) by the appropriate locant or set of locants for each additional nonbridging hydrogen atom to be specified and the symbol for indicating bridging, i.e., "μ", "μ_3", etc.[10c] for each bridging

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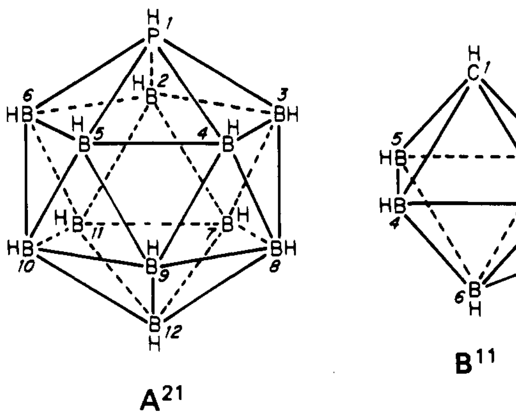
(15) The first official boron rules noted that a BH group of a polyborane was replaced by an EH group, where E is the replacing atom.[2b] However, this was not carried along into later rules,[3e] because heteropolyboranes were being reported without hydrogen atoms on the heteroatoms: for example, $B_{10}CPH_{11}$[16] and $B_9C_2SnH_{11}$.[17]

(16) Todd, L. J.; Little, J. L.; Silverstein, H. T. *Inorg. Chem.* **1969**, *8* (8), 1698–1703.

(17) Rudolph, R. W.; Voorhees, R. L.; Cochoy, R. E. *J. Am. Chem. Soc.* **1970**, *92* (11), 3351–3354.

(18) This technique is an adaption of the "indicated hydrogen" technique used in organic nomenclature to specify isomers or organic rings containing the maximum number of noncumulative double bonds.[9b]



A (i): 1H-1-phospha[I_h-(1551)-Δ^{20}-*closo*]dodecaborane(12)
(ii): 1-phospha[I_h-(1551)-Δ^{20}-*closo*]dodecaborane(12)-1-*H*
B (i): (2,3,6-μ_3H)-1-carba[O_h-(141)-Δ^{8}-*closo*]hexaborane(7)
(ii): 1-carba[O_h-(141)-Δ^{8}-*closo*]hexaborane(7)-2,3,6-μ_3H

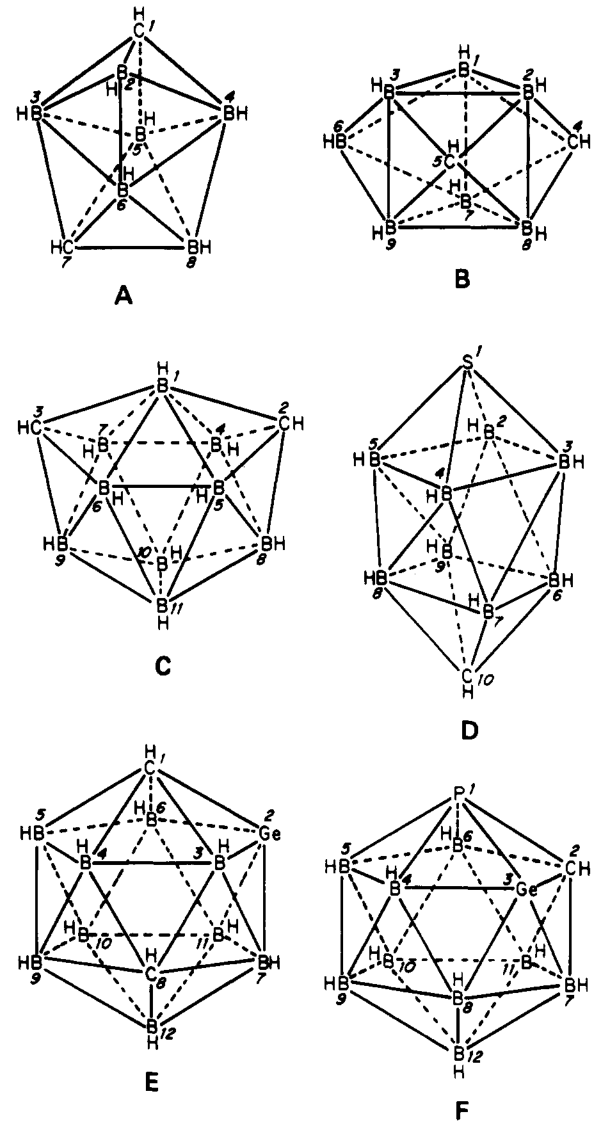
Figure 1. Specification of "extra" hydrogen atoms in heteropolyboranes.

hydrogen atom. To facilitate comprehension, we have enclosed the symbolism for bridging hydrogen atoms in parentheses, e.g., (1,2-μH), (1,2,3-μ_3H). We suggest also that the symbolism for bridging hydrogen be placed after that for the additional nonbridging hydrogen atoms, regardless of the numerical value of the respective locants.

(ii)[19] After the name of the heteropolyborane, append a symbol H_n for additional nonbridging and for bridging hydrogen atoms, where *n* is the sum of the respective kind of "extra" hydrogen atoms if greater than 1, prefixed (with an intervening hyphen) by the appropriate locants *or* sets of locants for each hydrogen atom to be specified and the traditional symbolism for bridging, i.e., "μ", "μ_3", etc.,[10c] for the bridging hydrogen atoms. Locants within locant sets for bridging hydrogen atoms are separated by commas; locant sets are separated from each other by the colon, e.g., 2,4:2,5:3,6-μH_3.

The presence of additional nonbridging hydrogen atoms on boron and carbon atoms occurs more commonly in nonclosed polyborane systems, which are discussed in the following paper.[20] Figure 1 illustrates the specification of hydrogen atoms on skeletal atoms other than boron and carbon and of bridging hydrogen atoms by both methods. We prefer method i because the end of the name is much less complicated with this method when the polyborane name is modified for use as a prefix or when a suffix is added.

(3) The lack of a hydrogen atom on a skeletal boron or carbon atom must be indicated by the prefix "dehydro" and an appropriate locant.[22] We recommend that the prefix "dehydro" be attached directly to the front of the name of the polyborane or heteropolyborane, i.e., just before the replacement prefixes, if any, where it would immediately precede the polyhedral descriptor or heteroatom replacement prefixes. As such, it becomes part of the name of a modified parent polyborane or heteropolyborane, and the hydrogen removed is not included in the parenthetical Arabic number appended to the name that gives the number of hydrogen atoms in the parent polyborane. For example, one of the isomers of $C_2B_{10}H_{11}$ would be named [3-dehydro-1,2-dicarba[I_h-(1551)-Δ^{20}-*closo*]dodecaborane](11). We have used brackets in this name to emphasize the dehydro prefix as a part of the parent heteropolyborane name.[23]



A: 1,7-dicarba[D_{2d}-(2222)-Δ^{12}-*closo*]octaborane(8)
B: 4,5-dicarba[D_{3h}-(333)-Δ^{14}-*closo*]nonaborane(9)
C: 2,3-dicarba[C_{2v}-(1$v^6$2$v^4$422)-Δ^{18}-*closo*]undecaborane(11)
D: 1-thia-10-carba[D_{4d}-(1441)-Δ^{16}-*closo*]decaborane(9) (thia preferred to carba for locant "1" (see Table I))
E: 1,8-dicarba-2-germa[I_h-(1551)-Δ^{20}-*closo*]dodecaborane(11) (carba preferred to germa for locant "1" (see Table I); the locant set 1,2,8 is lower than 1,4,7 and therefore preferred)
F: 1-phospha-2-carba-3-germa[I_h-(1551)-Δ^{20}-*closo*]dodecaborane(10) (phospha preferred to carba or germa for locant "1"; carba preferred to germa for lower locant (see Table I))

Figure 2. Numbering of some heteropolyboranes.

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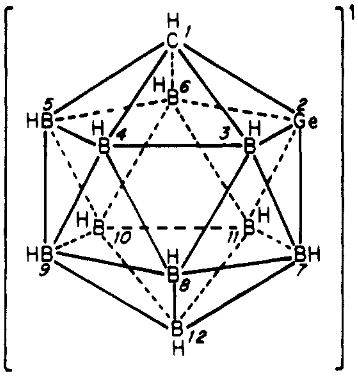
(19) This technique is based on that used in the Chemical Abstracts "Parent Compound Handbook"[13] to distinguish between isomeric polyboranes.

(20) Casey, J. B.; Evans, W. J.; Powell, W. H. *Inorg. Chem.*, following paper in this issue.

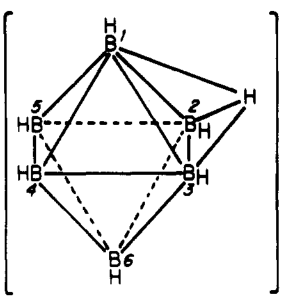
(21) A hypothetical parent heteropolyborane used when atoms or groups attached to the phosphorus atom are named by substitutive nomenclature (see discussion on derivatives of polyboranes and heteropolyboranes).

(22) This technique, needed for treating certain derivatives of heteropolyboranes and polyboranes, is an adaptation of a principle used in organic nomenclature.[9d]

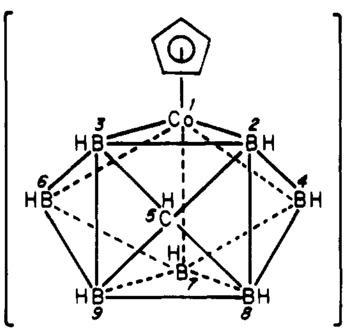
(23) The prefix "dehydro" used in this manner is classified in the current organic nomenclature rules as a nondetachable prefix.[9c] If it were detachable, it would be alphabetized along with other substitutive prefixes, and the name of the parent structure would have to include the hydrogen atom(s) removed by its use in the parenthetical Arabic numbers appended to the name. For the $C_2B_{10}H_{11}$ example, the name would thus be 3-dehydro[1,2-dicarba[I_h-(1551)-Δ^{20}-*closo*]dodecaborane(12)]. Again, the brackets have been used here to define precisely the name of the parent polyborane. It should be noted here that the detachability of the prefix "dehydro" is much more crucial to the nomenclature of polyboranes than in organic nomenclature, because the number of exopolyhedral hydrogen atoms is explicitly stated in polyborane names. For a discussion of a similar problem, see the descriptor method in the section on naming capped closed polyhedral polyboron hydrides.



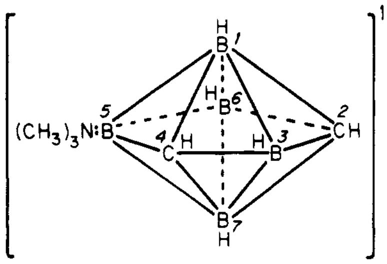
A^{28}



B^{11b}



C^{29}



D^{30}

A: undecahydro-1-carba-2-germa[I_h-(1551)-Δ^{20}-*closo*]dodecaborate(1−) (carba preferred to germa for locant "1" (see Table I))

B: μ_3-hydro-hexahydro[O_h-(141)-Δ^8-*closo*]hexaborate(1−)

C: 1-(η^5-cyclopentadienyl)octahydro-5-carba-1-cobalta[D_{3h}-(333)-Δ^{14}-*closo*]nonaborate(1−)[26] (cobalta must be numbered "1"; even though carba is preferred in Table I, it is not considered first for numbering unless it occupies a vertex that can be numbered "1")

D: 5-(trimethylamine)hexahydro-2,4-dicarba[D_{5h}-(151)-Δ^{10}-*closo*]heptaboron(1+)

Figure 3. Heteropolyboron hydride ions.

Numbering of Heteropolyboranes. The position of a heteroatom in a polyhedral structure is indicated by the lowest locant consistent with the numbering rules for polyhedra as given in the Appendix to our previous report.[8b] It should be emphasized strongly that, except for the chiral D_n and T polyhedra, the numbering of a polyhedron may be in either direction, whichever gives lower locants to the heteroatoms. Numbering for three dicarbapolyboranes is shown in Figure 2A–C. When the rules for numbering the polyhedral structure itself[8b] permit a further choice for assigning locants to heteroatoms of a heteropolyborane, locant numbers are assigned according to the following criteria, applied in sequence, until a decision is attained:

(1) If more than one heteroatom can be assigned locant "1", the senior heteroatom, i.e., a heteroatom whose replacement prefix occurs earliest in the list of prefixes given in Table I, is preferred[24] (see Figures 2D–F, 3A, and 5D).

(2) Lowest locants are then assigned: (a) to the set of heteroatoms, regardless of the nature of the heteroatoms[25] (see Figures 2E and 5D,F); (b) to the heteroatoms in their order of seniority, i.e., their order of appearance in the list of replacement prefixes given in Table I (see Figure 2F).

Closed Heteropolyboron Hydride Ions. As noted above, polyhedral boron ions are usually named by principles of coordination nomenclature. Combining the operation of replacement with principles of coordination nomenclature has been the method of choice for naming heteropolyboron ions.[2d,3f] A heteropolyboron ion such as $[CB_{11}H_{12}]^-$ is described as a polyhedral framework of boron atoms, which for this example is an icosahedral framework of 12 boron atoms named as described in the section on closed polyboron hydride ions. Replacement of one or more of the boron atoms in this polyhedral framework by an atom other than boron is indicated by a replacement prefix (see Table I); the charge on the ion is given by the Ewens–Bassett number in the usual manner; hydrogen atoms are denoted by the ligand prefix name hydro as described above for polyboron hydride ions; and other attached atoms or groups are described by ligand names of coordination nomenclature.[10a,26] Thus, a structurally descriptive name for $[CB_{11}H_{12}]^-$ is dodecahydro-1-carba[I_h-(1551)-Δ^{20}-*closo*]dodecaborate(1−). Examples of heteropolyboron ions and their derivatives are given in Figure 3.

Derivatives of Polyboranes and Heteropolyboranes

Neutral compounds that may be derived from a parent heteropolyborane (or polyborane) by substitution of the hydrogen atoms attached to skeletal atoms by other atoms or groups are conveniently named by the principles of substitutive (organic) nomenclature.[9] Substitution of bridging hydrogen atoms may be indicated by the prefix "μ" together with locants of the bridged skeletal atoms, if needed.[2g,3g] The latter operation occurs more commonly with nonclosed heteropolyboranes and thus is illustrated more fully in the following paper.[20] Prefixes for expressing heteropolyboranes (or polyboranes) as substituents to other parent hydrides are derived according to the current rules.[2h,3h] However, with the addition of our proposed descriptor, we would suggest one minor modification: placing the locant for the free valence position just ahead of the appropriate suffix. Examples of nonmetal

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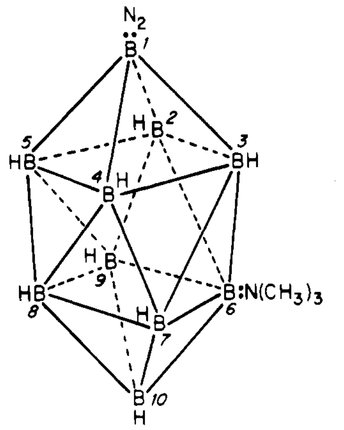
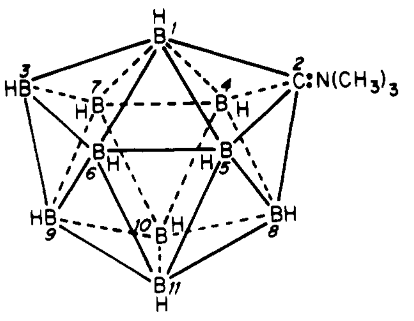
[24] This criterion for numbering is quite analogous to the first rule for numbering organic heteromonocycles[9f] and is used mainly to reduce the number of alternative numberings to be considered by subsequent criteria. The criterion could be applied to vertex positions other than "1" by requiring simply that a senior heteroatom have the lowest locant. We feel that any improvement by such a generalization would be quite marginal, as may be illustrated by the structure shown in Figure 3C.

[25] This is a common numbering principle[9g] and is really quite simple to apply. For each possible alternative numbering, the locants for all heteroatoms, regardless of what element the heteroatom is, are arranged in ascending numerical order and compared locant by locant. Since the lowest set of locants is the set with the lowest locant *at the first point of difference*, it is usually not necessary to consider the full locant set for all possibilities.

[26] A superscript number to the η symbol, e.g., η^5, is used for ligands even where all atoms in a chain or ring are associated with the coordination center. This procedure is consistent with the practice in CAS index names[27a] and much of the literature; however, the IUPAC Inorganic Nomenclature Rules do not use it.[10d]



A



B

A: 1-(dinitrogen)-6-(trimethylamine)[1,6-didehydro[D_{4d}-(1441)-Δ^{16}-*closo*]decaborane](8)
B: 2-(trimethylamine)[2-dehydro-2-carba[C_{2v}-($1v^6 2v^4 422$)-Δ^{18}-*closo*]undecaborane](10)

Figure 4. Dehydro polyborane and carbapolyborane derivatives.

heteropolyborane derivatives are included as supplementary material (Figure A).

Neutral polyboron hydrides that have neutral, nonradical atoms or groups attached to skeletal atoms have been difficult situations for structural nomenclature for a long time. Such compounds can be named by the coordination nomenclature principles used for ionic polyboron hydrides:[2c,3b] for example, $B_{10}H_8[CH_3C(O)NH_2)_2$ can be named bis(acetamide)octahydrodecaboron. Such compounds may also be named as addition compounds between a hypothetical polyborane and an electron donor:[2i,3i] for example, $B_{10}H_8[CH_3C(O)NH_2]_2$ would be named decaborane(8)–bis(acetamide). Until 1977, the latter method was used for *Chemical Abstracts* index names,[27b] although a slightly different format was followed, for example decaborane(8) compound with acetamide (1:2). However, such names do not provide specific structural information. By use of polyhedral descriptors and numbering procedures as described in this and in earlier reports,[8] coordination names for these compounds are structurally definitive, as shown by the name 1,10-bis(acetamide)octahydro[D_{4d}-(1441)-Δ^{16}-*closo*]decaboron for the 1,10-isomer of $B_{10}H_8[CH_3C(O)NH_2]_2$.

The nomenclature problem of neutral nonradical groups attached to skeletal atoms of polyboron hydrides broadened with the development of metallopolyborane chemistry. Metallopolyboranes, i.e., neutral heteropolyboron hydrides in which at least one heteroatom is a metal, have been named by adapting the principles for carbapolyboranes or the principles of coordination nomenclature in which the polyboron hydride fragment is expressed as a ligand of the metal.[2j,3j] For example, 3-(η^5-C_5H_5)-1,2-C_2-3-FeB_9H_{11} can be named 3-(η^5-cyclopentadienyl)-1,2-dicarba-3-ferradodecaborane(11) or (η^5-cyclopentadienyl)(7,8,9,10,11-η)-[undecahydro-7,8-dicarbaundecaborato(2−)]iron;[26] the descriptors *closo* and *nido* have often been used in these names. Although the coordination method is used for *Chemical Abstracts* index names,[27b] but without the descriptor *closo* or *nido*, neither of these methods provides adequate structural information. With procedures described in this report and in the following report,[20] both of these methods for naming metallopolyboranes become more satisfactory.

These problems can be handled very satisfactorily, in our opinion, for *neutral polyboron compounds* by combining some principles of coordination nomenclature with substitutive nomenclature principles normally used for naming heteropolyborane derivatives. Specifically, in addition to using the substitutive (radical) prefixes of organic nomenclature to describe atoms or groups substituting exopolyhedral hydrogen atoms, we suggest that the ligand prefixes of coordination nomenclature be used to describe neutral nonradical groups attached to any skeletal atom of the polyhedron and to indicate any atom or group attached to a heteroatom that does not have exopolyhedral hydrogen atoms present for substitution in the neutral parent polyborane. Of course, hydrogen as needed for substitution may be "indicated" on any skeletal atom, as discussed above; however, it is very likely that this technique for indicating exopolyhedral hydrogen atoms would be acceptable only for nonmetallic heteroatoms and perhaps a few metals such as germanium, tin, lead, and bismuth. Prefixes denoting attached atoms or groups are listed in alphabetic order regardless of whether they are substitutive or ligand prefixes. When neutral, nonradical groups are attached to boron and carbon skeletal atoms that do not carry an exopolyhedral hydrogen atom, the prefix "dehydro" must be used to indicate removal of the hydrogen atom implied in the neutral polyborane or carbapolyborane name.

Examples of "dehydro" polyborane and carbapolyborane derivatives are given in Figure 4 and examples of a variety of metallopolyborane derivatives are given in Figure 5. Other examples of metallopolyborane derivatives are included as supplementary material (Figure B).

Capped Closed Polyhedral Polyboron Hydrides

For the purpose of this report, we define a capped polyhedral system as a fully triangulated structure with an additional vertex capping one or more faces. In our work, the only exception to this is the trigonal bipyramid, which is considered

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(27) "The Naming and Indexing of Chemical Substances for Chemical Abstracts", Appendix IV in "Chemical Abstracts 1977 Index Guide": (a) § 215, pp 180I–184I; (b) § 182, pp 140I–142I.

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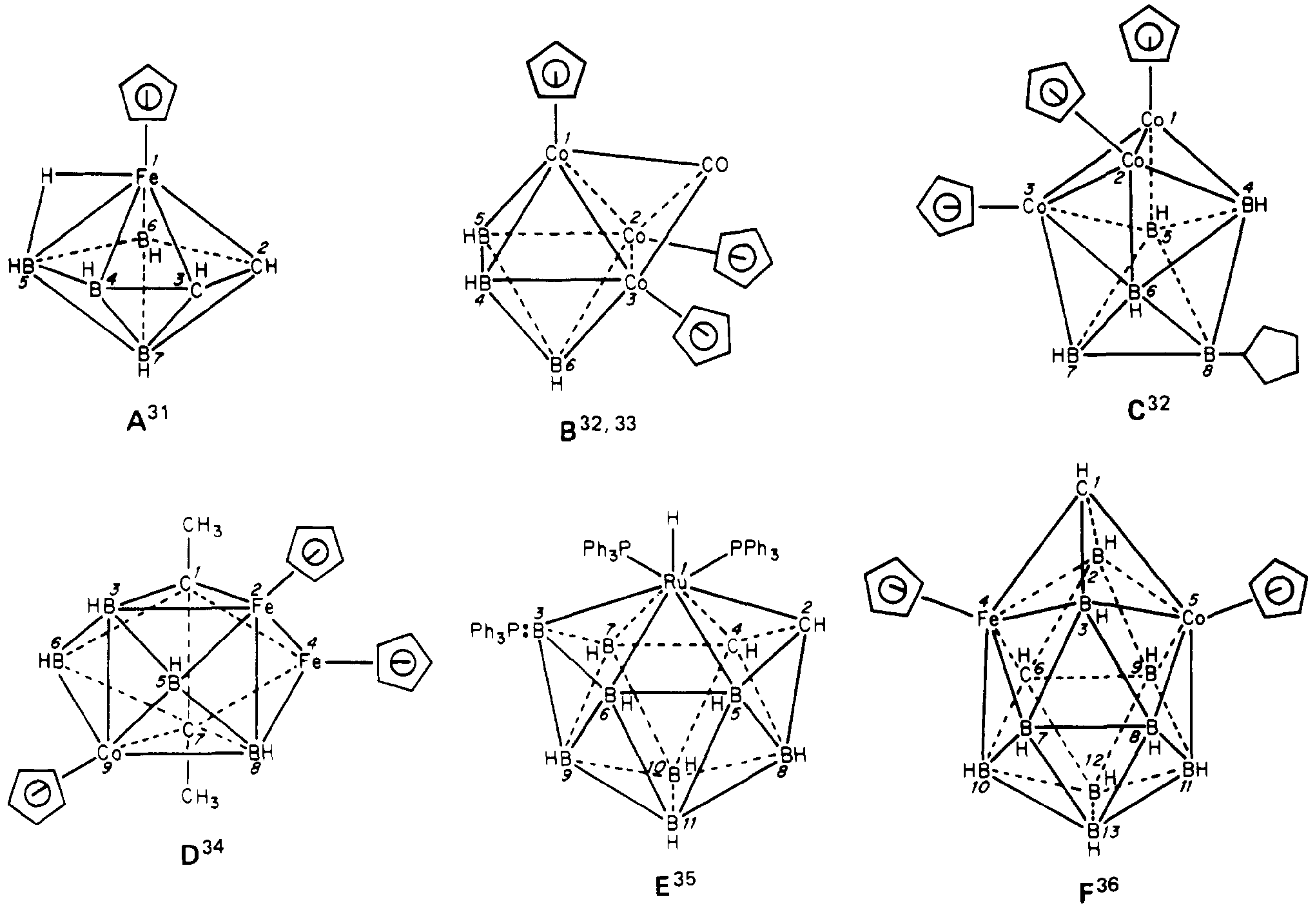


A[31] B[32, 33] C[32] D[34] E[35] F[36]

A (i): 1-(η^5-cyclopentadienyl)(1,5-μH)-2,3-dicarba-1-ferra[D_{5h}-(151)-Δ^{10}-*closo*]heptaborane(7)
(ii): 1-(η^5-cyclopentadienyl)-2,3-dicarba-1-ferra[D_{5h}-(151)-Δ^{10}-*closo*]heptaborane(7)-1,5-μH
B: 1,2,3-μ_3-carbonyl-1,2,3-tris(η^5-cyclopentadienyl)-1,2,3-tricobalta[O_h-(141)-Δ^8-*closo*]hexaborane(3)
C: 1,2,3-tris(η^5-cyclopentadienyl)-8-cyclopentyl-1,2,3-tricobalta[D_{2d}-(2222)-Δ^{12}-*closo*]octaborane(5)
D: 2,4,9-tris(η^5-cyclopentadienyl)-1,7-dimethyl-1,7-dicarba-9-cobalta-2,4-diferra[D_{3h}-(333)-Δ^{14}-*closo*]nonaborane(6) (carba preferred for locant "1" (see Table I); the locant set 1,2,4,7,9 for the C, Fe, Fe, C, Co atoms, respectively, is lower than 1,2,6,7,9 for the C, Co, Fe, C, Fe atoms, respectively, and is therefore preferred even though cobalta is preferred to ferra in Table I)
E: 1-hydrido-1,1,3-tris(triphenylphosphine)[3-dehydro-2,4-dicarba-1-ruthena[C_{2v}-(1$v^6$2$v^4$422)-Δ^{18}-*closo*]undecaborane](9)
F: 4,5-bis(η^5-cyclopentadienyl)-1,6-dicarba-5-cobalta-4-ferra[C_{2v}-(1$v^4$22$v^6$422)-Δ^{22}-*closo*]tridecaborane(11) (locant set 1,4,5,6 for the C, Fe, Co, C atoms, respectively, is preferred to 1,4,5,9 for the C, Co, Fe, C atoms, respectively, even though cobalta is preferred to ferra in Table I)

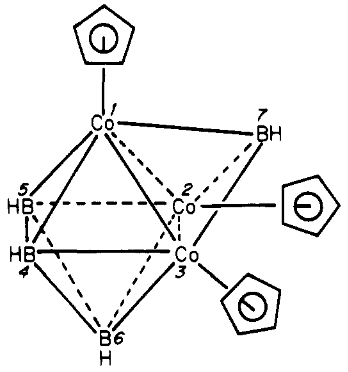
Figure 5. Metallopolyborane derivatives.[26]

to be a closed polyhedral structure rather than a capped tetrahedron. Although there are only a few examples of capped polyhedral polyboron hydrides, there are a number of metal cluster systems having such capped structures, and, as the number of metal atoms in metallopolyboron hydrides increases, it sems reasonable to expect that the number of capped systems will increase.

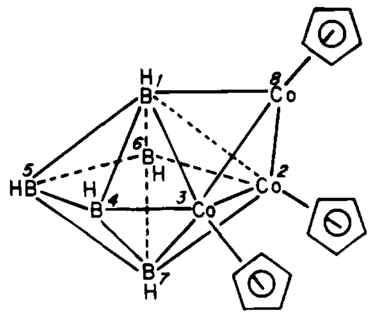
In addition to the trigonal bipyramid, a few capped systems such as the monocapped and symmetrically bicapped octahedron can be described quite easily by the descriptor system developed in our earlier reports.[8] However, other capped systems have characteristics that make the application of the descriptor system more difficult, particularly when the principal symmetry axis does not pass through a cap. For example, an octahedron capped on two adjacent faces has four planes of vertices, i.e., $2v^3 2v^6 2v^5 2v^5$, but in the preferred terminal plane[8a] the vertices are not connected, leading to possible difficulties in constructing the polyhedron from its descriptor. One of the important aspects of our proposed descriptor system[8] is its assistance in building polyhedra. In addition, two structurally different polyhedra having the same descriptor can be generated from the tricapped trigonal prism ([D_{3h}-(333)-Δ^{14}-*closo*] polyhedron) by adding caps to opposite pairs of faces of one of the caps. Therefore, we believe that it will be much easier, in general, to treat capped systems as derivatives of more symmetrical, more easily visualized parent polyhedral systems.

In this report, two methods are proposed for describing capped polyhedral polyboron hydride systems. The first, based on traditional organic nomenclature techniques for naming bridged fused ring systems,[9h] describes capping vertices as additions to a parent closed polyboron hydride whose polyhedral structure is given by a descriptor as proposed in our earlier reports.[8] The second method proposes a technique that incorporates the capping operation into the descriptor for the closed parent polyhedral structure.

Bridging Method. A capped polyhedral polyboron hydride may be described by indicating the addition of a "B" vertex by the prefix "bor-" attached to the name of the polyboron hydride as discussed above. The position of the added "B" vertex is given by a locant set consisting of the three locants for the vertices of the face that is capped. Two or more capping "B" vertices are described by an appropriate numerical prefix, such as "di-", "tri-", etc.; the locant sets for the positions



A[37]



B[38]

A (1): 1,2,3-tris(η^5-cyclopentadienyl)-1,2,3-tricobalta-1,2,3-bor[O_h-(141)-Δ^8-*closo*]hexaborane(4)
(2): 1,2,3-tris(η^5-cyclopentadienyl)-1,2,3-tricobalta[O_h-(141)-Δ^8-*closo*(+1*v*)^{1,2,3}]heptaborane(4)
B (1): 2,3,8-tris(η^5-cyclopentadienyl)-2,3,8-tricobalta-1,2,3-bor[D_{5h}-(151)-Δ^{10}-*closo*]heptaborane(5)
(2): 2,3,8-tris(η^5-cyclopentadienyl)-2,3,8-tricobalta[D_{5h}-(151)-Δ^{10}-*closo*(+1*v*)^{1,2,3}]octaborane(5)

Figure 6. Capped closed polyhedral polyboron hydrides.[26]

of two or more vertices are separated by a colon. The added vertices are assigned the next available numbers after the parent polyhedron has been numbered.[8b] When necessary, added vertices are numbered in the order of increasing value of the locants for the vertices of the faces that are capped. Replacement of skeletal boron atoms and derivatives are named in the same manner as described earlier in this paper. Two examples of capped systems named by the bridging method are given in Figure 6 as A(1) and B(1) names.

Descriptor Method. The bridging method just discussed is an additive approach based on the name of a parent closed polyhedral polyboron hydride to which one or more vertices, i.e., "B" groups, are added by the prefix "bor". An important disadvantage of this approach is that the actual capped polyboron hydride contains more skeletal atoms than are described by the name of the parent closed polyboron hydride system. For example, the name 1,2,3-bor[O_h-(141)-Δ^8-*closo*]hexaborate would describe a seven-vertex polyboron anion derived from the closed six-vertex octahedral polyboron structure clearly given by the descriptor and the numerical prefix "hexa-". The concept of adding skeletal atoms by prefixes is not new. It has been used for a very long time to name bridged fused ring systems in organic nomenclature.[9h] In fact, in addition to single skeletal atoms, both carbon atoms and heteroatoms, chains, and even rings may be added. For example, the names 9,10-methanoanthracene, 9,10-epoxyanthracene, and 9,10-*o*-benzenoanthracene describe the addition of a $-CH_2-$, a $-O-$, and a $-C_6H_4-$ group, respectively, across the middle ring of anthracene. However, it is not nearly as obvious in such names that the number of skeletal atoms in the actual compounds is more than the number in the parent structure as it is in the names of capped polyboron hydride systems given above: in the latter case, the number of boron atoms in the parent structure is given explicitly by a numerical prefix.

Therefore, it may be quite desirable in naming capped polyboron hydrides to include the addition of vertices as part of a descriptor that would precede the name of a capped polyboron hydride that states the actual number of boron atoms in the skeletal structure. We propose that capping vertices of a capped polyhedral structure be indicated by an additional symbol added after the term *closo* in the descriptor of the appropriate closed uncapped polyhedral structure developed in our earlier reports.[8] The symbol we suggest consists of an Arabic number equal to the number of vertices added, preceded by the plus sign indicating addition and followed by the italic letter *v* standing for vertex, all enclosed in parentheses. For example, the name for a monocapped octahedral polyborate skeleton would be [O_h-(141)-Δ^8-*closo*(+1*v*)]heptaborate. The positions of the additional vertices are given by appropriate locants for the vertices of the face that is capped cited as superscripts outside the parentheses. Alternatively, the faces of the parent polyhedron could be assigned letters, which could be used as superscript locants. As for the bridging method, locants for designating added vertices in the numbering of the capped polyhedral structure are the next available numbers after the uncapped parent polyhedron has been numbered. Two examples of capped systems named by the descriptor method are given in Figure 6 as A(2) and B(2) names.

Summary

The method for uniquely describing closed polyhedral polyboron structures developed previously[8] has been extended to include capped polyhedral systems and incorporated into names for specific polyboron hydrides. Techniques developed for naming organic compounds such as replacement nomenclature, bridging prefixes, and subtractive nomenclature have been combined with basic principles of coordination nomenclature to name the broad range of polyboron compounds.

Supplementary Material Available: Figures A and B, showing examples of nonmetallic heteropolyborane and metallopolyborane derivatives (2 pages). Ordering information is given on any current masthead page.