Potential Applications of the Boron Cluster Compounds

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I. Introduction

Boron cluster compounds represent distinctive covalent species with a unique molecular architecture, nonconventional cluster bonding, and unusual chemistry. Consequently they exhibit rather specific properties not encountered in other types of compounds. This is apparent from all articles in this issue of the *Chemical Reviews*.

Bearing in mind the profound impact of organic chemistry on our civilization one wonders why such special compounds have not yet found wider application so far. However, it is not wise to compare incomparable subjects. Organic chemistry is based on essentially limitless resources of raw materials with preformed C–C and C–H bonds in fossil fuels and in the biomass all around. The man-made chemistry of boron cluster compounds, however, has to start out with limited quantities of boric oxide derivatives and to create all B–B and B–H bonds in sequence.

Consequently, boron cluster species are, and always will be, very expensive and find practical applications only in some exclusive areas where no alternative exists. In this respect, the situation is similar to the applications of the precious metals.

Jaromír Plešek was born in 1927. He graduated in organic chemistry from the Institute of Chemical Technology in Prague (1950) and received his Ph.D. equivalent (1952) from the same institution. He was an Assistant Professor in organic chemistry from 1952 to 1958 and a research chemist (1958–1961) at Dental working on polymers for human medicine, e.g. edible carboxylic cation exchangers, flexible water-permeable membranes and artificial veins, and plastic coatings, applied as sprays, for the treatment of damaged skin (i.e. severe burns). During the period 1950 to 1961 he published 20 papers on organic syntheses and co-authored a book on Aldol-type condensations. Since 1961, he has been a member of the Institute of Inorganic Chemistry, Czechoslovak Academy of Sciences and a co-founder of its Boron Department. He is active in the syntheses of boranes and heteroboranes including practical applications and has published around 130 papers, received about 40 patents, and co-authored a book on sodium hydride in practical chemistry. He was a co-founder of the IMEBORON conferences and the chairman of the organizing committee of the first one in 1971. He never had the opportunity to work in a laboratory outside of Czechoslovakia.

A few of the boron cluster species have been produced on a multiton per year scale in the heroic era of boron chemistry aimed at advanced jet and rocket propulsion systems.[1] Since this era ended in the early 1960s no pentaborane, decaborane, or icosahedral carboranes have been produced in any substantial quantity. Supply of these raw materials is very limited, lasting only until still existing stocks are exhausted completely. At present, the current price of *o*-carborane is comparable to that of gold. Decarborane is about half as expensive while pentaborane can be purchased for about one tenth of this price. However, the supply of the latter two boron hydrides is strictly limited, another obstacle for interested chemists.

A revival in industrial production can be expected only after the development of some important applications for these species yet only a few specialists are active in the area due to the present unavailability of the raw materials. Will this "circulus vitiosus" ever be broken? Hopefully!

In the 3rd edition of the *Kirk-Othmer Encyclopedia of Chemical Technology* (1978)[2] essentially no commercial importance was ascribed to the boron cluster compounds and very few applications were mentioned.

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Although the commercial aspects of boron cluster species remain quite limited, some progress toward applications is apparent.

In this article we shall discuss some unique properties of the boron cluster compounds which might provoke practical uses. Established applications as well as some suggestions will be presented in order to challenge the creative specialist. Emphasis will be given to applications recorded in *Chemical Abstracts* within the last decade. Whereever a review on a particular subject has been published, it is considered here as covering earlier knowledge in this area. Older papers will be cited selectively in order to elucidate the history of the respective application. For practical reasons papers and reviews appearing in generally available scientific journals and written in English are preferentially cited.

Only deltahedral boron compounds will be considered with the exception of elementary boron and of the refractory borides (although these species are undoubtedly based on cluster arrangement of boron atoms). The latter subject has been reviewed many times,[3-6] and the readers are well informed in this area of boron chemistry. Also excluded are all monoborane derivatives such as polyalkylboranes, amine boranes, tetrahydroborates, etc.

The currently claimed applications for boron cluster compounds are based either on the unique properties of the molecules or on specific properties of the basic element itself. Let us briefly mention some of them: the extreme acidity of acids conjugated to the polyhedral ions combined with a unique hydrophobicity of these anions; the exceptional stability of the polyhedral species associated with the virtual three-dimensional "aromacity" of these systems; and the unexpected ability of nearly all open-cage deltahedral boron hydride derivatives to function as very strong sandwich-forming ligands. So far these properties have been only reported rather than exploited. Nevertheless several heavy-duty polymers, solvent extraction of radionuclides, electrolytes for nonaqueous solvents, and homogeneous catalysts of hydrogenations have been developed.

Applications associated with the properties of boron as the element within the deltahedral species primarily exploit the unusually high cross section of the ^{10}B isotope for neutron capture (20% natural abundance). This led to the development of light-weight neutron shields and in particular to the boron neutron capture therapy (BNCT) of tumors.

In some new applications the boron cluster species serves as an expensive, but nevertheless very convenient and easily modifiable, source of boron, e.g. for advanced boron-based ceramics and for doping the semiconducting E^{IV} elements where B^{III} behaves as an electron hole.

In spite of this, the enormous potential use of deltahedral boron compounds in modifying physiologically active organic species has not been generally recognized. The transparency to UV light down to about 200 nm of the *closo*-polyheteroboranes along with the chemical and optical stability of these compounds has so far not found application. All the colors of the rainbow can be precisely tuned by using a variety of sandwich complexes based on borane derivative ligands—one wonders therefore why no color filters or wave length transformers have been developed using these very stable compounds which are soluble in plastics. The use of deltahedral boron cluster anions as stable electrolytes in nonaqueous solvents cannot be excelled, yet few electrochemists are aware of this. With the exception of some rhodacarboranes, which are effective homogeneous catalysts in hydrogenations, hydrosilylations, and isomerization of unsaturated organic species, there is little ongoing research in the application of metallaheteroboranes to potential catalysis of other reactions. The area possesses enormous potential, and the future looks brighter than the present state would suggest.

II. Applications Based on Specific Properties of the Deltahedral Borane Clusters

A. Peculiar Solubilities of the Salts

It is common knowledge that an overwhelming majority of the salts of organic and inorganic acids do not dissolve in organic solvents or at least cannot be extracted form water solutions into organic phases. In this respect the deltahedral polyborate ions are truly exceptional. Essentially all salts of the deltahedral polyborate monoacids readily dissolve in electron-donating organic solvents, and the water-soluble salts can be easily extracted into the organic phase. Good extractants are alcohols, ethers, esters, ketones, nitriles, nitro compounds, and other electron-donating solvents.

This unique feature of the deltahedral ions was recognized as a general one in our Institute over two decades ago. Our general practice was to separate deltahedral ions from other ions by ether extraction and to exchange the counterions via solvent extraction instead of the generally recommended application of ion exchange resins.[7-9]

Our observations led us to the conclusion that this curious extractability is associated with the distinctly hydridic character of the terminal hydrogens enhanced by the delocalized negative charge of the ion spread over the surface of the deltahedral cage. If the negative charge is localized outside of the framework, the extractability vanishes.

Thus the salts with the $[7\text{-HS-}7,8\text{-}C_2B_9H_{11}]^-$ ion are extractable from water using diethyl ether, while those with the $[1,2\text{-}C_2B_{10}H_{11}\text{-}1\text{-}S]^-$ ion are not (negative charge at the –S group). The same applies to the related pair $[8,8'\text{-}\mu\text{-S-}(1,2\text{-}C_2B_9H_{10})_2\text{-}3\text{-Co}]^-$ and $[8,8'\text{-}\mu\text{-OOCCH}_2\text{S-}(1,2\text{-}C_2B_9H_{10})\text{-}3\text{-Co}]^-$ (negative charge at the carboxy group). The former is easily extractable from water, and the latter prefers the aqueous environment like other substituted acetic acids.

The extractability increases with the size of the deltahedral cage $B_3H_8^- < B_9H_{14}^- < CB_{11}H_{12}^- < [(C_2B_9H_{11})_2Co]^-$ and is independent of the acid strength; for instance the *nido*-$7,8\text{-}C_2B_9H_{12}^-$ ($pK = 2.15$) and *closo*-$CB_{11}H_{12}^-$ (conjugated acid is unmeasurably strong) are easily extractable from water to diethyl ether despite the enormous difference in acid strength of the respective conjugated acids.

This unusual property is especially pronounced with the bulky peanut-shaped sandwich ions $[(C_2B_9H_{11})_2\text{-}3\text{-}M^{III})]^-$. These prototypes of the metallacarborane world were discovered in 1965.[10] The authors coined a semitrivial name bis(dicarbollide)metalates(1-) for these species instead of the more correct *commo*-3,3′-metallabis(1,2-dicarba-*closo*-dodecabor)ate(1-). Thus for M

= Co the semitrivial name will be bis(dicarbollide)cobaltate (BDCCo). This convention will be applied throught this article.

Although the BDCCo-Na salt is as strong an electrolyte as is sodium chloride[9,11] mild shaking of a 0.5 M water solution with an equal volume of diethyl ether transfers the salt completely to the organic layer.

The salts of di- and polybasic deltahedral polyborate acids seem to be too "inorganic" for extraction from water to diethyl ether. In this case usually a three-layer system is obtained with most of the respective salt accumulated in the intermediate layer. Some further information may be found in the following paragraphs and in the references cited therein.

Chemical reactivity and general physicochemical properties of the BDCM were extensively investigated in our Institute since their discovery and our observations triggered some important applications.

1. Solvent Extraction of Radionuclides

The first application of the BDCCo for solvent extraction of radionuclides was patented in 1974[12a] and was soon followed by the first scientific communication.[13] These events triggered an extensive activity in this field. The principally new extraction reagent has been investigated regarding all aspects of solvent extraction and up to now about 100 papers and patents have been published on the subject. The results including technological aspects have been reviewed.[14-16]

The essence of this application is to use BDCCo and especially its hexachloro derivative BDCCO-Cl_6[12b] as the extraction reagent, nitrobenzene with various modifiers as the organic phase and eventually some additives to shift the conventional specificity from M^{1+} to M^{2+} and M^{3+} ion, respectively.

Chlorination of BDCCo to BDCCo-Cl_6 dramatically improves the stability of the reagent toward strongly oxidizing 3 M nitric acid,[12b] which is essential for routine engineering scale recovery of ^{137}Cs and ^{90}Sr. Without additives, the BDCCo reagents extract and separate mainly the heavy alkali metal cations.[13] Addition of some polyethylene glycol derivatives shifts the specificity toward the M^{2+} ions[17] and with organic phosphonates even the actinides and lanthanides may be recovered.[18]

The process seems to be suited for analytical monitoring of milk, various body fluids, and excrements[19-21] as well as for an engineering scale recovery of several radionuclides from the spent nuclear fuels.[15,16]

A variety of other nuclides, both radioactive and stable, can be successfully separated and isolated using BDCCo-type reagents,[14] e.g. Li^+, Na^+, K^+, Rb^+, Cs^+, Tl^+; Ca^{2+}, Sr^{2+}, Ba^{2+}, Ra^{2+}, Pd^{2+}, Pb^{2+}; M^{3+}, lanthanides, actinides, ^{99m}Tc from ^{95}Zr and ^{95}Nd etc. This review covers other generally useful BDCCo data.[14]

The fact that the parent BDCCo undergoes B substitution relatively easily, as well as their general similarity to other polyhedral ions with respect to solubility, are assets which can be used in tailoring this new class of extraction reagents for use in specific cases.

2. Electrolytes for Nonaqueous Solvents, Interphase Transfer of Cations, and Storage Batteries

All deltahedral borane derivatives are somewhat acidic if their number of hydrogen atoms exceeds that of skeletal atoms. In most cases the acidities are rather weak (usual pK_a values over 2). On the other hand the polyhedral polyborate ions $B_nH_n^{2-}$ are essentially nonprotonizable—the hypothetical conjugated acids are extremely strong, comparable to and probably surpassing such acids as hydrochloric, sulfuric, or even perchloric. The same applies to the heteroatomic polyhedral ions, e.g. $CB_nH_{n+1}^-$, BDCCo etc.

These closed-shell polyhedral ions simply cannot accomodate an external proton or any other cation without loss of their superaromaticity. Consequently the conjugated acids (with hydrated hydroxonium ion as the balancing counterion), as well as their salts, are 100% dissociated in any solvent.[9,11] As has already been mentioned above, the polyhedral acids and their salts readily dissolve in almost any weakly electron donating organic solvent even when anhydrous. The same is true for many dibasic acids and their salts if the polarity of the solvent is slightly enhanced, e.g. they dissolve in polyethers, alcohols, nitriles, and especially in nitro compounds. This is why such salts are ideally suited as electrolytes for nonaqueous solvents. The solubility can be further enhanced by bulky counterions, e.g. tetrabutylammonium. The electrochemical stability of the ions can be substantially increased by substitution of the terminal hydrogens (by Cl or Br) at the most reactive vertices. Moreover one has the opportunity to choose between species transparent in the UV/vis range, or highly colored, e.g. BDCCo is intensively orange yellow with a strong absorption band around 290 nm, whereas the *closo*-$[1\text{-}CB_{11}H_6Br_6]^-$ ion is colorless and transparent to UV down to about 210 nm. The BDCCo-NBu_4 was first used in an electrochemical study as early as 1977[22] and has been found to be appreciably more suitable than tetraphenylborate ion for interphase transfer of cations from water to nitrobenzene[23] as well as to other solvents[24] and across lipid membranes.[25] Experiments with BDCCo salts as ion-selective electrodes[26] and even as a dropping electrode[22] have been carried out. Further information on this subject is found in part of the review on solvent extraction.[14]

Application of the perchloro closo ions $B_nCl_n^{2-}$ as nonaqueous electrolytes for advanced rechargeable Li batteries was suggested in early 1980s.[27-29] The latter communication is especially informative, describing synthesis and purification of the $Li_2B_{10}Cl_{10}$ and $Li_2B_{12}Cl_{12}$ salts, their interesting solubility diagrams in a synergistic binary solvent system of glycol dimethyl ether/1,3-dioxolane, electrochemical properties of these solutions and some other properties important for practical heavy-duty electrochemistry. A more recent addition to this subject appeared in Japan in 1986.[30] The application has been patented several times, e.g. see refs 31–33 eventually for electrochromic displays.[34] Several types of polyethers and some weakly donating plastics seem to be the solvents of choice for these electrolytes.

3. Isolation, Separation, and Characterization of Organic Bases, Introduction of Cations into Organic Solvents and Polymers

Essentially all salts involving BDCCo or BDCCo-Br_6 and bulky organic cations are water insoluble[9] but dissolve readily in acetone, acetonitrile, and other donating solvents. Because of the intense color of the sandwich anions a quantitative colorimetric determination of such bases is conveniently possible. (The threshold perception by naked eye for BDCCo is about 3×10^{-4} mol/dm^3.[9]) Moreover the strong ^{1}H NMR signal of the four equivalent C–H protons at 3.89 ppm {$(CD_3)_2CO$) may serve as an internal standard for identification of the ^{1}H NMR active cations. In this respect the more colorful BDCFe and BDCNi are inferior due to their paramagnetism; TLC on silica gel may be used as an auxiliary tool for rapid qualitative monitoring of mixtures of organic bases.[9]

BDCCo, its derivatives, and analogues precipitate almost quantitatively even such hydrophilic bases as diethanolamine,[9] diamino acids,[9] dimethyl sulfoxide,[35] and acid amides like dimethylformamide or caprolactam[36] etc. The salts with protonated amines, tetraalkylammonium ions, and its analogues, $[Me_3S]^+$, $[R_4P]^+$, etc., contain 1 mol of BDCCo per unit charge of the counterion, whereas weak bases like Me_2SO and acid amides in general precipitate as complex cations of the $[L_2H]^+$ type.[9]

These properties of BDCM are potentially useful in the isolation, separation, and characterization of organic bases including various natural substances such as alkaloids, basic vitamins, and diamino acids.[9] Quantitative determination (based on colorimetry and ^{1}H NMR of the BDCCo component) of total bases and of the ratio nonquarternary:quarternary has been described. Isolation of cinchonine from a 3.4×10^{-4} M solution in water has been demonstrated.[9]

Typically hydrophilic cations, e.g. $[Me_3NCH_2COOH]^+$, $[(Me_2SO)_2H]^+$, $[(HOCH_2CH_2)_2NH_2]^+$, [ornithine·H]$^+$, etc., can be introduced into organic solvents such as acetone, acetonitrile, alcohols etc. for investigation of their behavior in an entirely foreign environment.

Hydrophilic basic dyes can be rendered soluble in aprotic solvents including polymers such as polyvinylacetate and polymethacrylates on addition of an equivalent amount of any deltahedral ion. For example crystal violet, malachite green, methylene blue, safranines etc. dissolve readily in polymethacrylate prepolymers if BDCCo$^-$ or, even better, the colorless $[CB_{11}H_6Br_6]^-$ are used as counterions.[37] Affinity of the BDCCo for generally basic and lipid substances along with its relatively heavy central ion led to the suggestion to "dye" biological samples for the transmission electron microscopy. Unfortunately the relevant paper appeared only in Czech.[38]

This is an area of application which is relevant today and is open to further creative development.

B. High Thermal and Chemical Stability of the *closo*-Dicarbaboranes, Exclusive Polymers

An extraordinary thermal stability of the *closo*-dicarbaboranes $C_2B_nH_{n+2}$ (n = 3–10) is one of the most exciting properties of this large class of deltahedral heteroboranes.[39] It generally increases with the size of the framework and with increasing mutual distance of both carbon atoms within the structure. The species with an even number of skeletal atoms are usually more stable than the less symmetric counterparts with an odd number of vertices. (But $C_2B_5H_7$ is more stable than its congeners $C_2B_4H_6$ and $C_2B_6H_8$.) Apparently the most stable *closo*-dicarbaboranes are the three members of the icosahedral family, the 1,2-, 1,7-, and 1,12-dicarba-*closo*-dodecaboranes better known under the more popular names *o*-, *m*- and *p*-carborane, respectively.

In an inert atmosphere *o*-carborane begins to isomerize irreversibly to the meta isomer above 425 °C (48 h to completion) and at 600 °C in a gas flow reactor the isomerization is nearly quantitative after residence time < 1 min; at 700 °C under the same conditions an equilibrium mixture of *m*- and *p*-carborane is obtained containing approximately 25% of the latter.[39] At this high temperature, however, some degradation of the carborane cage is apparent, manifested by a brown-black deposit of a boron/boron carbide mirror. A comparable thermal stability of the family of dicarba-*closo*-decarboranes $C_2B_8H_{10}$ may be inferred from the published data;[39] again the stability increases with increasing mutual distance of both carbon atoms, i.e. in the series 1,2 < 1,6 < 1,10 isomers, respectively.

The closed-shell structures of the *closo*-dicarbaboranes also contribute to their astonishing chemical inertness as well. Thus, icosahedral carboranes are not attacked by hot sulfuric acid and are essentially inert to the conventional mixture of nitric and sulfuric acid, smoothly nitrating the aromatic organic species.

On the other hand, the weak point of carboranes is their susceptibility to alkaline degradation. But again, this weakness applies practically only to the species with adjacent carbon atoms. Thus, *o*-carborane is quantitatively converted to the *nido*-$[7,8\text{-}C_2B_9H_{12}]^-$ ion within a few hours by sodium methoxide in methanol or by sodium (potassium) hydroxide in ethanol.[40] With *m*-carborane the same type of degradation proceeds at least 100 times more slowly and a temperature of at least 70 °C is required for any practical effect;[41] the first observed degradation of the para isomer could only be forced using a 30% solution of potassium hydroxide in propylene glycol at 180 °C.[42]

The remarkable thermal and chemical stability of the *closo*-dicarbaboranes provoked the interest of polymer chemists immediately after these compounds were discovered in early 1960s.[43–46] It is virtually impossible to compile all relevant papers and patents, and the following paragraph will be considered more as an informative index than a comprehensive review.

In the mid 1960s several groups of polymer scientist investigated the effect of incorporation of the *closo*-dicarbaborane units into chains and networks of almost any known type of polymers.[47] It was soon recognized that the carborane units attached to the otherwise organic backbone of the polymer brought no practical advantage. However, if the carborane became a part of the polymeric chain, e.g. regularly interspersed among repeating $-Si(R)_2O-$ units they induced an appreciable thermal stability in the product. In this respect, the *o*-carborane is far inferior to its meta and para congeners because it tends to form stable monomeric or at best dimeric cyclic species of no use in polymer formation. An excellent discussion of various aspects of early research in this area was given in the famous book on carboranes.[48]

The best results have been achieved with the family of poly-*m*-carborane–siloxanes)[49,50] which became renowned under the trade name DEXSIL.[49,50] Some of these polymers with appropriate fillers retain their rubberlike properties even around 500 °C and when applied as a liquid phase for GLC columns they made an effective separation of gaseous substances possible up to 375 °C.[47] Tubings, insulation jackets, gaskets, membranes, coatings, etc. have all been made of such polymers.[48,51] Scores of Sn, Ge, and Pb analogues instead of Si were investigated, as well as polymers with –Hg–, –S–, –PR–, etc. linking units between the carborane moieties. This area has been comprehensively reviewed.[51] Another review on this subject[47] quoted all types of polymers described earlier and emphasized incorporation of the 2,4-$C_2B_5H_7$ and 1,10-$C_2B_8H_{10}$ carboranes into the poly(carborane–siloxane) chains. Other authors reviewed the carborane–siloxane rubbers in 1971[52] and in 1979.[53]

A systematic research program on all aspects of carborane-modified polymers has operated for decades in the Soviet Union. The published results have been reviewed in two local publications.[54,55] This research is still under way. Flammability of the carborane–siloxane polymers was investigated,[56] stabilization of the polyarene polymers by incorporation of carborane units was the subject of a recent paper,[57] and carborane modified polybenzimidazoles were discussed.[58]

The most recent review on polycarboranes and polydecaboranes appeared in 1990 in a Polish journal.[59] Applications of the carborane–siloxane polymers in glass coatings[60] and as insulation for multilayer integrated circuits[61] are claimed in two recent Japanese patent applications.

C. Metallaheteroboranes as Homogeneous Catalysts in Hydrogenation, Hydrosilylation, and Isomerization of Unsaturated Species

Essentially any open cage borane or heteroborane is prone to afford a wide variety of sandwich type complexes involving a majority of elements of the periodical system. This propensity of deltahedral borane derivatives was discovered in 1965[10] and has been reviewed many times since.

In this vast realm of complexes those of the platinum metals derivatives deserve special attention with respect to their potential in promoting hydrogenation of unsaturated species and hydrogen transfer in general. In the case of the Rh complexes the relationship to the homogeneous catalysts of the Wilkinson type should also be noted.

A long series of papers starting in 1974 systematically reported on investigations of the catalytic activity of the *closo*-[3,3′-$(PPh_3)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$] complex in hydrogenation, hydrosilylation, and isomerization of unsaturated organic compounds. A variety of substituted derivatives of the parent species, its isomers, homologues, and analogues have been synthesized and characterized. It has been found that in fact no icosahedral Rh^{III} species is catalytically active, but the observed effect is due to the presence of a small equilibrium concentration of the formally 16-electron Rh^I tautomer, the [*exo*-*nido*-{$(PPh_3)_2Rh$-μ-4,9-$(H)_2$-7,8-$C_2B_9H_{10}$}]. Detailed mechanisms of the hydrogenation and isomerization processes mediated by this species has been elucidated. The principal author published a condensed account of this research in 1988.[62]

It seems that the clue to the true nature of the active moieties $[(PPh_3)_3Rh]^+$ and $[(PPh_3)_3RuH]^+$ had been found already in 1974[63] when an unusually rapid exchange of deuterium for terminal hydrogens in the icosahedral *o*-carborane had been observed as proceeding preferentially at the most positive vertices $B_{(3,6)}$. New additions to present research have been published recently.[64,65] The rhodacarborane catalysts may be immobilized by attachment to the polystyrene network without loss of the catalytic activity.[66]

An apparently parallel research program seems to have been proceeding in the Soviet Union since 1977. It is, however, difficult to comment on the results because nearly all the findings have been published only as short notes without experimental details. The interested reader may find further information in one of the more recent papers[67] and in references cited therein.

Potent catalytic activity has been observed also with a different kind of metallo complex of the icosahedral carboranes, e.g. with [Cl·Rh^I(CO)-1,2-$(Ph_2P)_2$-1,2-$C_2B_{10}H_{10}$][68] and with the [1-Ir(CO)(PhCN)-7-Ph-1,7-$C_2B_{10}H_{10}$] complex.[69] In the former the phosphino derivative of *o*-carborane serves only as a bidentate ligand for the [Rh^I(CO)Cl] moiety. In the latter the catalytically active metal is σ-bonded to the carbon atom of the substituted *m*-carborane.

The scope of the catalytically active species involving platinum metals and the deltahedral heteroboranes is potentially endless.

Precise tuning of the electron density donated to the metal is feasible by appropriate substitution of the deltahedral ligand. The number of metal orbitals available for catalytic activity may be varied by selection of the bond type between the metal and the attached cluster (e.g. E–M σ-bonds, B–H–M three center bonds, η^x-coordination).

Investigation of such versatile systems may contribute not only to better understanding of hydrogen transfer but also to wider applications of these metallaheteroboranes in practical chemistry. Metallaheteroboranes with other metal centers might be found to be active in a variety of other catalytical processes, e.g. oxidations, polymerizations, etc.

III. Applications Based on Properties of Elemental Boron

Boron is a nonmetallic refractory element with a melting point of 2300 °C that is prone to combine with most other elements with the formation of highly refractory borides of extreme structural diversity and with a variety of unusual properties. As the fifth element of the periodical table it possesses only three valence electrons and interspersed in an E^{IV} environment it behaves as a local electron hole. The element consists of two stable isotopes ^{10}B (19.8%) and ^{11}B (80.2%). The former nuclide has an extremely high cross section for thermal neutron capture [3.840×10^{-28} m^2 (barns)], giving rise to the nuclear reaction:

$$^{10}_{5}B + n = {}^{4}_{2}He + {}^{7}_{3}Li \ (-2.79 \text{ MeV})$$

Several important applications of the deltahedral borane derivatives are based on these elemental features.

A. Doping of Semiconductors

Decaborane(14), octadecaborane(22), and some of their halogeno derivatives have been recommended as boron sources for doping silicon to form the p-type semiconductor using the chemical vapor deposition process.[70,71] The deltahedral species are easily purifiable to the necessary degree and their vapor pressure can be controlled within a wide range by tempering the containers and tubing. At the heated wafer of the semiconductor substrate the boron carrier decomposes to the element and essentially innocuous gasses. This simple philosophy led to the development of a very reliable fool-proof procedure for the manufacture of p-type semiconductors which has been in operation in Czechoslovakia for two decades. Recently the same principle has been applied elsewhere in the chemical vapor deposition of boron nitride layers.[72]

If boric oxide is to be deposited, the deltahedral boron carriers should withstand the slightly oxidizing environment as long as possible in order to minimize its losses before reaching the target area; icosahedral carboranes in general and *m*-carborane in particular have been found ideal for this purpose.[73,74]

B. Precursors to the Advanced Boron-Based Ceramics and Pure Borides

Although elemental boron and its refractory binary compounds of the B–E type are not the subject of this article one can not overlook the newest trends linking deltahedral boranes with the chemistry of binary refractories. At first glance any deliberate pyrolytic destruction of expensive deltahedral species would appear to be foolish but many recent papers seriously describe such experiments. The approach opens up new horizons into the field of advanced boron-based ceramics.

Many deltahedral compounds including polymers are quite soluble in organic solvents. Treatment of various substrates with such solutions leaves a coating of the boron-rich species at its surface or within its pores. After pyrolysis in an appropriate atmosphere various refractory borides remain firmly bound to the substrate. Hitherto unknown composites and coatings can be prepared in this way. In principle the same trick has been used in the production of essentially poreless graphite products for decades.

Refractory coatings of boron carbide/silicide have been produced through pyrolysis of carborane–siloxane polymers.[75–77] Boron carbide coatings may be obtained through pyrolysis of polymeric Lewis base adducts of the decaborane(12)[78] or of the vinylpentaborane polymers.[79] If fired in a NH_3 stream the same precursors afford boron nitride or boron carbonitride coatings.[80–82] Boron phosphide and boron carbophosphide coatings have been deposited with polymeric dialkylphosphine derivatives of decaborane(12) as precursors.[83,84]

Synthesis of boron nitride from triammonia decaborane and hydrazine under pressure has been investigated;[85] the cerium and gadolinium borides were prepared by pyrolysis of the respective *closo*-decahydrodecaborate salts.[86] A general preparation of pure borides in this way has been recently reported.[87] A review of polymeric precursors for boron-based ceramics was presented at the 7th IMEBORON conference in 1990.[81]

The technical importance of this rapidly growing field seems to be reflected in the increasing number of patent applications.[82,88–90]

C. Boron Neutron Capture Therapy of Tumors

Among the many weapons against deadly tumors this one is of special interest, albeit it is still in the early stages of development. Nevertheless, the basic strategy was probably conceived in 1936[94]—only four years after the discovery of the neutron. Choose a harmless species rich in ^{10}B, functionalize it in order to bind preferentialy to the target cells without contamination of the benign tissue, and irradiate the target area with a stream of thermal neutrons. According to the reaction $^{10}_{5}B + n = ^{4}_{2}He + ^{7}_{3}Li$ (−2.79 MeV) the energetic fragments will destroy any material within their flight distance (around 10 μm). The labeled cells will disintegrate, whereas the nonlabeled ones will remain intact even if located in close vicinity to the target. In principle dangerous isolated single cells of metastases could also be destroyed using this approach.

The practical realization of this strategy is, however, extremely difficult, and the task has not yet been satisfactorily solved.[91] But promising results were reported mainly in the last two decades in the treatment of malignant brain tumors and of some forms of melanoma. Specialized international conferences on this application of the deltahedral borane derivatives were held in succession: USA (1983), Japan (1987), Germany (1989), and Australia (1990).

Extensive cooperation of chemists, biochemists, surgerons, nuclear physicists, and technicians is a primary condition of success. So far, however, each group of specialists faces very difficult problems in their respective areas. Here only some of the chemical aspects will be discussed.

It is not easy to choose a potentially applicable borane derivative, to synthesize it, and to squeeze it through the bottleneck of all the prescribed tests for compounds for human medicine. The compound ought not to be too toxic, it should bind preferentially to the target cells avoiding contamination of the healthy tissue, and its ^{10}B content ought to be as high as possible—this means that the chemist must start with the essentially pure $^{10}B(OH)_3$—and the compound should still be available in multigram quantities. These are only several of the many imperatives for developing a suitable species.

According to increasing tumor specificity three major classes of potentially applicable borane derivatives can be distinguished: (1) functionalized deltahedral boranes (FDB)—non specific, (2) boronated organic species (BOS)—area seeking, and (3) boronated monoclonal antibodies (BMA)—tumor seeking.

1. Functionalized Deltahedral Boranes

Many polyhedral boranes are essentially nontoxic due to their inertness to biochemical reactions, e.g. L_{D50} for the $B_{12}H_{12}^{2-}$ for oral administration to rats has been estimated as 7g/kg![92] This is the main reason why they became so popular in the early stages of development of the BNCT concept.

In order to attach the polyhedral boranes to the target cells one has to functionalize them with some groups capable of interaction with the biochemical system, e.g. through –SH groups which become preferentially bound to the –SH and –S–S– moieties within peptides. This type of functionalization can not be too target specific. Such species accumulate in the malignant cells mainly due to an enhanced metabolism of those cells.

The main representative of the FBD family is the *closo*-HS-$B_{12}H_{11}^{2-}$ ion better known as "mercaptoborate".[93] It is far more toxic than the parent ion, but still less harmful than penicillin.[94] Dozens of papers have been devoted to various aspects of the use of this species in BNCT and the subject has been reviewed several times,[95–98] most recently in 1991.[94]

Several other functionalized deltahedral boranes and carboranes have been suggested for the same purpose, e.g. both isomeric HS-$B_{10}H_9^{2-}$ ions,[99] B-mono and B,B′-dithiols of the *closo*-carboranes[100–102] and a variety of the icosahedral *closo*-$[CB_{11}H_{12}]^-$ ion derivatives with –SH, –SMe, –NH_xR_{3-x}, –COOH, etc. functional groups.[103,104] However, so far none of these species seems to have been applied in clinical trials so far.

2. Boronated Organic Species

A variety of physiologically active organic compounds tend to accumulate in specific body areas, e.g. promazine shows a distinct affinity for melanin pigments, porphyrine derivatives prefer the brain tissue and steroidal sex hormones address the sexual glands in man or breast tissue in woman. After appropriate boronation such compounds may concentrate in these specific areas and eventually accumulate in the malignant tissue localized there.

In 1964 the application of boronated steroidal hormones for BNCT of breast cancer was suggested.[105] However, the investigation of three boronated estrogens in 1981 revealed a serious problem—deactivation of the hormones. Thus, the 1-*o*-carboranylmethoxy group in position 3β dramatically decreased the hormonal activity, 60-fold in one case. On the other hand the 1-*o*-carboranylmethyl group at $C_{17\alpha}$ did not deactivate the hormone.[106]

Recently six other carboranylmethoxylated steroids have been synthesized[107] but their elementary biochemical properties are not known yet.

Boronated promazines have been synthesized and suggested for BNCT treatment of melanoma.[108] An extensive study of boronated porphyrins is currently under way[109–112] and is aimed at the BNCT of brain tumors. The recently synthesized (1-carboranylmethyl)uridine[113] is expected to show a rather general tumor seeking propensity.

Reviews on boronated porphyrins,[114,115] boronated promazines,[116] and BNCT of melanoma[117] were presented at the 2nd International Symposium on BNCT in Japan 1987.

3. Boronated Monoclonal Antibodies

In principle, monoclonal antibodies to any kind of tumor can be cultured and isolated. These species bind specifically to the respective tumor cells and represent the most sophisticated and precise vehicles for any kind of antitumor reagents.

In the BNCT concept they can be viewed as molecular guided missiles charged with a warhead rich in ^{10}B. However, since only a few antibody molecules become bound to an individual target cell, their ^{10}B load should be very heavy in order to deliver a sufficient quantity of the nuclide to the target. Thus, only the largest deltahedral cages are suitable for this task and as many as possible ought to be attached to each antibody molecule, avoiding any essential damage to the complex biomolecule.

Essentially any type of deltahedral borane derivative might be suitable; however, their lipophility/hydrophility balance may be critical. Toxicity, sufficient stability, and other factors should also be considered. Applications of $[HS\text{-}B_{12}H_{11}]^{2-}$,[118] $[7,8\text{-}C_2B_9H_{12}]^-$ ion derivatives,[119] glucosyl-carboranes,[120] $[CB_{11}H_{12}]^-$ ion derivatives,[121] and other species have been suggested and tested.

The linking units between the borane derivative and the antibody are various reactive groups commonly known from organic chemistry, e.g. the SCN- group.[119] Carboxylic groups are preferred presently because they can be routinely activated for bonding to the NH_2- and HO- groups by the "reactive ester" technique elaborated to perfection by peptide specialists; derivatives of the substituted *N*-hydroxysuccinimide are frequently exploited as the "reactive esters". If direct functionalization of the deltahedral species is not possible, intervening phenylene groups or other organic junctions may help. Advances in this field have been reviewed several times in succession.[116,122,124,125]

To overcome the difficulty of the desired heavy load of a boron compound without inactivation of the antibody Hawthorne[125] suggested the strategy of the "^{10}B trailers". The borane units are linked together in sequence and the whole "trailer" is then coupled to the antibody by a single link. Artificial polypeptides based on repeating 2-amino-5-(1-methyl-*o*-carborane-2-yl)-pentanoic acid and polyamides with both components containing carborane units were synthetized as trailers. These were eventually hydrophilized by subsequent degradation of the original *o*-carborane units to the respective $[7,8\text{-}C_2B_9H_{12}]^-$ ion derivatives. Radioactive or fluorescent tracers may be attached to the trailers. A still more advanced strategy involving the "bispecific antibody" concept is currently being investigated.[125] The outcome of this approach might very well become the highlight of some future conferences on BNCT.

A popular review on the general features of the BNCT appeared in 1990,[97] and a book on clinical aspects of the NCT has been edited in 1989.[126]

4. Related Applications

In 1990 a very interesting approach to tumor imaging and eventual destruction has been reported.[127] The substituted BDCCo labeled with ^{57}Co (halftime 271 days) was constructed through condensation of the 4-(methoxycarbonyl)pyrazolide ion with two molecules of the $[7,8\text{-}C_2B_9H_{12}]^-$ ion followed by insertion of the Co^{3+} ion under formation of the BDCCo complex with a pyrazolecarboxylic acid bridging the positions 8,8′ via the respective nitrogen atoms. After esterification of the carboxy group using *N*-hydroxysulfosuccinimide, the complex could then be coupled to the selected antibody. Excellent long duration tumor imaging in mice was observed.[127]

The long life of the radionuclide might eventually contribute to the destruction of the labeled cells, on the other hand it may be found to be prohibitive in human medicine. It remains, however, another pioneering venture in the struggle against disease.

D. Other Neutron Capture Applications

Although usually not explicitly emphasized, all carborane-based polymers mentioned in section II.B. should be efficient light-weight neutron shields. This application is explicitly claimed in a Japanese patent.[128] Of course boron carbide as a filler would further augment the neutron shielding.

Polyhedral carborane derivatives have been recommended as effective inhibitors of the dangerous spontaneous fission occurring during the solvent extraction of fissionable nuclides.[123]

IV. Conclusion and Challenge

Deltahedral boron derivatives are and always will be quite expensive substances. Any reasonable applications may be expected to occur only in exclusive areas where no other compounds compete. Thus, applications involving only minute quantities of deltahedral species or processes permitting complete recycling will have to be developed. Catalytic effects, BNCT, optical and electrochemical applications, as well as solvent extraction of valuable cations seem to be in accord with this strategy.

The author predicts increasing biochemical and medicinal applications using deltahedral clusters even though, with the exception of the impressive BNCT concept, so far no systematic study of their basic biochemical properties has been published—even toxicity studies are scarce. The same is true for biochemically active organic species modified by deltahedral boranes—except the pioneering research of the Swiss group concerning several naturally occurring oligopeptides modified by substitution of L-*o*-carboranylalanine for L-phenylalanine.[129–132] Bearing in mind observed substitution effects of adamantanyl groups for phenyl groups in some drugs one wonders why analogous substitution studies involving the countless promising *closo*-heteroboranes has not been found to be worthy of studying.

Since all deltahedral boranes were created by human beings and have never existed in nature it could be expected that there are no enzymes capable of modifying or destroying such moieties. The possibility of an antibiotic based on a deltahedral cage compound, with the chance that no bacterium or virus could get accustomed to it, is an exciting speculation. For instance the hitherto unknown *closo*-1-HOCO-*p*-NH_2-$C_2B_nH_n$ ($n = 8, 10$) analogues of *p*-aminobenzoic acid could conceivably deceive bacteria. Such compounds could very well become the advanced analogues of drugs such as the sulfamides.

Fundamental research on deltahedral borane derivatives opened a wide access to specifically tailored substances but now the time is ripe for exploitation of the accumulated knowledge. Hopefully, this review will be the inspiration for scientists to enter this exciting and challenging area of chemistry.

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