Boron Radicals

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Boron Atoms as Spin Carriers in Two- and Three-Dimensional Systems

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boron · cluster compounds · organoboranes · radicals · spin distribution

Paramagnetic compounds with at least partially boron-centered electron spin can be constructed using either the prototypically electron-accepting boron atoms bridged by planar π-conjugated organic systems, or by taking advantage of the three-dimensional delocalized bonding in oligonuclear borane, haloborane, or carborane clusters. The concept of mixed valency can thus be transferred from organic and transition-metal chemistry to main-group-element molecules, and density functional theory is capable of reproducing the variable spin distribution.

1. Introduction

In comparison to nitrogen and carbon, its neighbors in the periodic table, boron is less often considered as an electron-spin-bearing atom associated with radicals, radical properties, and radical reactivity.[1] The reason for this situation may lie in the common (and correct) perception of boron as an electron-deficient acceptor center, leading either to Lewis acidity (Lewis acid/base theory is an electron *pair* concept!) or to the formation of polyborane, carborane, or metallaborane cluster compounds, the stability of which is typically rationalized using even-electron cluster rules.[2]

Given the current surge in the development of novel materials based on carbon[3] and the successful application of mixed-valence concepts for nitrogen-based radical intermediates,[4,5] we will outline herein how both the acceptor behavior of boron and the existence of clusters can actually favor the formation and stabilization of paramagnetic species with partially boron-centered spin, both in the more familiar two-dimensional form of π systems and within three-dimensional cluster frameworks. In a review on main-group-element radicals,[6] Power noted that some such species may be considered "inspired" by analogy to organic counterparts, while others have no organic analogues. The concepts of boron radical formation and stabilization will be presented using selected examples from the literature, and they will be interpreted in the light of less conventional approaches, such as mixed valency, and supported by quantum chemical approaches (DFT). Eventually, these species may become viable components of extended magnetic systems, for example, just as organoboranes have recently found their way into materials with potential for optical and electrochemical (sensor) applications.[7]

In principle, boron is an excellent element for studying the spin distribution in paramagnetic species, because both stable isotopes ^{10}B (19.8 %, $I=3$) and ^{11}B (80.2 %, $I=3/2$) have nuclear spins and reasonable nuclear magnetic moments ($\mu(^{10}\mathrm{B})/\mu(^{11}\mathrm{B})=0.335$).[8] However, the combination of both isotopes with their rather high I values can create very large numbers of hyperfine lines when several boron atoms and other active nuclei participate in the interaction with the electron spin,[9,10] thus partially or totally obscuring the spectral information from EPR spectroscopy. In such cases, other methods such as electron nuclear double resonance (ENDOR) or TRIPLE spectroscopy have proven advantageous (see Figure 3 in Section 2.3).[11,12] In this Minireview, we

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present several representative kinds of stable and persistent[6] boron radicals with different electronic structures and variable spin density on boron.

2. π Radicals Stabilized through Boron as Acceptor Atom

The function of boron as acceptor atom can be used in several ways to stabilize radical species, as detailed in Sections 2.1–2.3.

2.1. R_2B-Substituted Arenes

The acceptance of just one electron ("single spin injection") by boranes BX_3 should lead to diminished electron deficiency. The corresponding radical anions $[BX_3]^{\bullet -}$ are isoelectronic with the much-studied methyl radicals $[CX_3]^{\bullet}$[1,13] and with aminium radical cations $[NX_3]^{\bullet +}$;[5] reactions of triaryl boranes with alkali metals have thus been studied sporadically since the 1920s.[14–19] Reactions subsequent[15] to the electron transfer, such as boron–aryl bond dissociation and association to form borates, can preclude the observation of corresponding radical anions, which may yet be stabilized according to familiar strategies from organic radical chemistry: A) by steric shielding to prevent bimolecular reactivity, often coupled with B) spin delocalization through π conjugation.

It is not surprising, therefore, that 2,4,6-trimethylphenyl (mesityl, Mes) substituents have featured prominently in this area of research.[16–19] The trimesitylborane radical anion was characterized as a fairly stable species with a sizeable ^{11}B hyperfine coupling constant of about 1.0 mT[17] despite a rather negative redox potential.[19] The *ortho*-methyl substituents of the mesityl group shield the empty or half-filled p_z orbital in boranes or their radical anions from external attack, thereby preventing association reactions (Figure 1). At the same time, the partially conjugated aromatic ring systems of Mes and of phenyl in the systems $[BMes_nPh_{3-n}]^{\bullet -}$ ($n = 0$–3) accommodate some of the spin and charge[17,19]—one reason why these compounds were not described as boron(II) systems. Comparative crystal structure analysis of the redox pair $[BMes_3]^{0/\bullet -}$ confirmed this concept by showing relatively

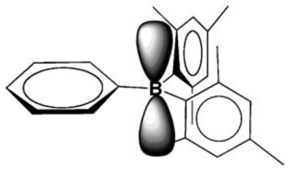


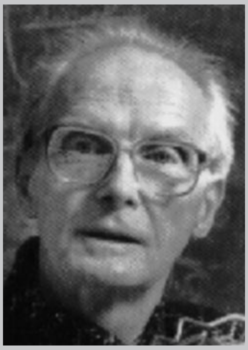
Figure 1. Steric protection of the (partially) unfilled and potentially π-conjugating p_z orbital of boron through dimesityl substitution.

Wolfgang Kaim studied chemistry and physics in Frankfurt/Main and Konstanz, obtained his Ph.D. degree with Hans Bock at the age of 26 and went with a Liebig Fellowship to F. A. Cotton at Texas A&M University. After his habilitation in Frankfurt he moved to Stuttgart in 1987. He has been a Visiting or Adjunct Professor at several universities in Asia and the Americas, and he is the author of more than 500 scientific papers. His research interest focuses on the electron-transfer reactivity of newly synthesized molecules.

Narayan Hosmane obtained a Ph.D. degree in inorganic/organometallic Chemistry in 1974 from the University of Edinburgh. After postdoctoral work with Russell Grimes at the University of Virginia, he joined the faculty at the Virginia Polytechnic Institute and State University in 1979. In 1982 he joined the faculty at the Southern Methodist University, where he became Professor of Chemistry in 1989. In 1998, he moved to Northern Illinois University and is currently a Distinguished Research Professor and Inaugural Board of Trustees' Professor.

Stanislav Záliš obtained a Ph.D. degree in Physical Chemisty in 1977 from the J. Heyrovsky Institute of Physical Chemistry, Prague. After postdoctoral studies with A. A. Vlček he has continued to work at the Heyrovsky Institute of Physical Chemistry, at present as a senior researcher. He has been a Visiting Scientist or Professor at several universities. His main interest lies in theoretical studies of complex compounds using quantum chemical methods.

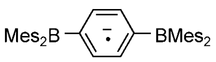
John Maguire received his Ph.D. Degree in Physical Chemistry in 1963 from Northwestern University. He joined the faculty of Southern Methodist University as an Assistant Professor of Chemistry and is now Professor of Chemistry. From 1976–1979 he was Associate Dean of University College at SMU and from 1979–1981 he was Dean of University College and General Education at SMU. In 2002 he was appointed University Distinguished Teaching Professor.



Professor Emeritus William N. Lipscomb, Jr. won the 1976 Nobel Prize in Chemistry in recognition of his outstanding contribution to boron hydride chemistry, with particular emphasis on "his studies on the structure of boranes illuminating problems of chemical bonding". After receiving the Ph.D. degree under L. Pauling in 1946, he became an Assistant Professor of Physical Chemistry at the University of Minnesota. In 1959 he accepted a Professorship at Harvard University and later became Abbott and William James Lawrence Professor of Chemistry.

small changes in the overall structure,[18] implying a rather small reorganization energy.

One possibility to facilitate electron uptake is the conjugative coupling of two dimesitylborane π acceptor groups by a bridging π system. *p*-Phenylene and 4,4′-biphenylene bridges have thus been used to conjugatively connect two Mes_2B groups; two split reduction waves at anodically shifted potentials resulted.[12,19–21] The corresponding radical anion intermediates (**1** and **2**) formed after single spin injection are the "mirror images"[20] of the stable radical cations **I**[22] of *p*-phenylenediamines, the long-known "Wurster's salts" first described in 1879, and of substituted benzidines (**II**) used as hole-transfer components in organic light-emitting diodes.[23] The anion radicals **1** and **2** exhibit long-wavelength absorptions,[21] and EPR/ENDOR spectra indicate spin delocalization to the boron centers, which leaves relatively little unpaired electron density in the bridging carbon rings.[12] In fact, only nitro groups exert a more powerful spin-withdrawing effect from *p*-phenylene radical anions than dimesitylboryl substituents.[19,20]



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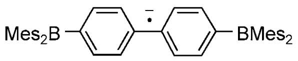

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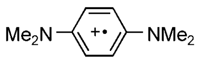
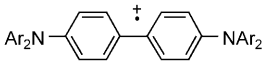


I

Wurster's blue



II

Ar = Aryl

N,*N*,*N'*,*N'*-tetraarylbenzidine radical cation

However, instead of an acceptor-substituted π system, species **1** and **2** may also be referred to as bridged mixed-valent diboron(II,III) compounds.[24] The concept of mixed valency,[25,26] largely associated with transition metals, has been applied recently[4,5] to organic compounds involving coupled hydrazine/hydrazinium, aryl amine/aryl aminium and even triaryl carbon radical functions.[27] Typical phenomena connected with mixed valency are a sizeable splitting of redox processes as quantified by the comproportionation constant K_c ($K_c = [\mathrm{Int}]^2/[\mathrm{Ox}][\mathrm{Red}]$; $RT\ln K_c = nF\Delta E$; $\Delta E = E_1 - E_2$) for the two-step electron transfer [Eq. (1)], and the long-wavelength (low-energy) intervalence charge-transfer (IVCT) transitions of the intermediates [Eq. (2)]).[25,26]

$$\underset{\mathrm{Ox}}{R_xB^n(\mu\text{-L})B^nR_x} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} \underset{\mathrm{Int}}{[R_xB^n(\mu\text{-L})B^{n-1}R_x]^-} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} \underset{\mathrm{Red}}{[R_xB^{n-1}(\mu\text{-L})M^{n-1}R_x]^{2-}} \qquad (E_1) \quad (E_2) \tag{1}$$

$$[R_xB^n(\mu\text{-L})B^{n-1}R_x]^- \underset{\mathrm{IVCT}}{\overset{h\nu}{\rightleftharpoons}} {}^*[R_xB^{n-1}(\mu\text{-L})B^nR_x]^- \tag{2}$$

Ions **1** and **2** may be described as class III species,[25] that is, completely delocalized (symmetrical) mixed-valent $(B^{2.5})_2$ systems bridged by carbanionic donors, which would be compatible with a "hole-transfer mechanism" for the valence exchange.[26] Within the hole-transfer formalism, the electron deficiency ("hole") migrates from the oxidized to the reduced side via a high-lying occupied molecular orbital (MO) of the bridge, resulting in some participation of that bridge in the spin distribution according to MO theory. Large comproportionation constants K_c (e.g. 5×10^{11} for **1**) of the intermediates from Equation (1) and the long-wavelength absorption typical of mixed-valent species[25,26] support the mixed-valence alternative. DFT calculations also confirm this notion, reproducing the low-energy transition between the delocalized singly occupied MO (SOMO) and a mostly boron-centered lowest unoccupied MO (LUMO).[24,28]

The DFT calculations for **1** yield a spin distribution with 30 % on each of the boron centers and only 32 % in the bridge (Figure 2),[24] in agreement with the experimental EPR/ENDOR spectroscopy results.[12] We thus conclude that the conjugatively coupled intermediates **1** and **2** may well be described as mixed-valent diborane(II,III) species, a conclusion which is supported by the fact that related compounds with dialkyl borane substituents, that is, without complete aromatic substitution, show similar effects.[20]

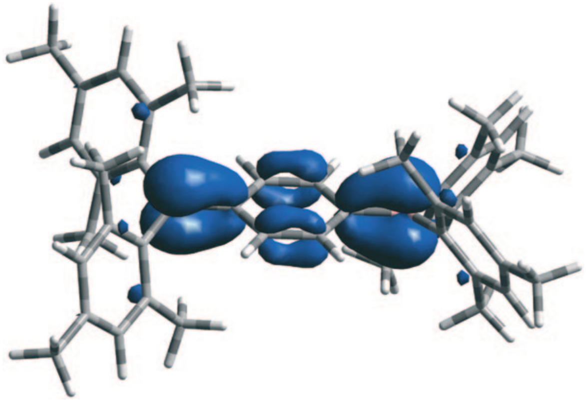
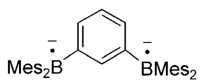


Figure 2. Spin density of compound **1** after energy minimization by DFT. C gray, H white, B pink.

The recognition that *meta* disubstitution on the benzene ring disfavors spin pairing and may thus lead to high-spin materials has prompted the synthesis of a pertinent compound **3** that exhibits corresponding magnetic properties.[29] A related interesting case is the 1,8-disubstituted naphthalene **4**, which shows evidence for B−B interaction arising from the close proximity of the acceptor atoms.[30]



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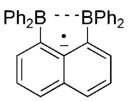
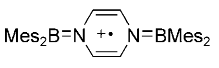


4

As in the hydrazine/hydrazinium versus aryl diamine/aryl diaminium series,[4,22] the organic bridge in species such as **1** or **2** can be omitted to yield directly B−B-bonded diboranes, which can also form stable anion radicals $[R_2BBR_2]^{\bullet-}$.[31] These intermediates with a B−B bond order of 1.5 may be considered equivalent to the cation radicals of olefins, and the hyperfine coupling of the directly connected boron atoms in the EPR spectrum is strongly affected by structural factors, as confirmed by crystallographic studies.[32]

2.2. R_2B-Substituted N-Heterocycles

Modification of systems like **1** or **2** has been achieved by substituting the boron-binding ring carbon atoms by nitrogen atoms (**5, 6**).[12,33] The charge of the radical ions then changes from (−) to (+), and the corresponding neutral precursors may be considered as analogues of Thiele's and Chichibabin's hydrocarbons **III** and **IV**,[34] replacing exocyclic C=C bonds by $^{-}$B=N^{+} units.[35] The spin distribution in **5** and **6**, as evident from EPR and ENDOR spectroscopy,[12] shows that the B–N connection does not favor spin transmission because of the large electronegativity difference and thus diminished delocalization. Obvious manifestations of this difference are the small boron hyperfine coupling constants below 0.1 mT and the increased spin density in the rings.[12] This decreased N–B π conjugation thus lends further credence to arguments used to support the diminished aromaticity of borazines $B_3N_3X_6$.[35]



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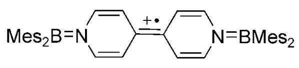

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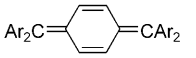
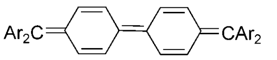


III Ar = Aryl

Thiele's hydrocarbon



IV

Chichibabin's hydrocarbon

2.3. Lewis Acid/Lewis Base Adducts between R_3B and N-Heterocyclic Radicals

There is another, indirect mechanism by which the acceptor effect of boron in boranes, specifically the Lewis acidity, can be exploited to stabilize radical intermediates. Coordination of BX_3 molecules to Lewis basic aromatic nitrogen heterocycles withdraws electron density and thus enhances the reducibility of the π system as well as the stability of the radical intermediates.[36] Again, the effect is most pronounced in symmetrical compounds like **7** and **8**, and the interaction between radical Lewis bases and borane Lewis acids leads to surprisingly large[12] ^{10}B and ^{11}B hyperfine coupling constants of about 0.25 mT for **7** through spin polarization, as demonstrated by EPR, heteroatom ENDOR, and general TRIPLE spectroscopy (Figure 3).[11] As in the previously mentioned cases, there are analogues for **7** and **8** in "conventional" (i.e. non-boron) chemistry, for example, the stable radical cations formed as one-electron reduction products of the 1,4-dialkyl pyrazinium[37,38] and 4,4′-dialkyl 4,4′-bipyridinium (methylviologen, "paraquat") dications.[39,40]

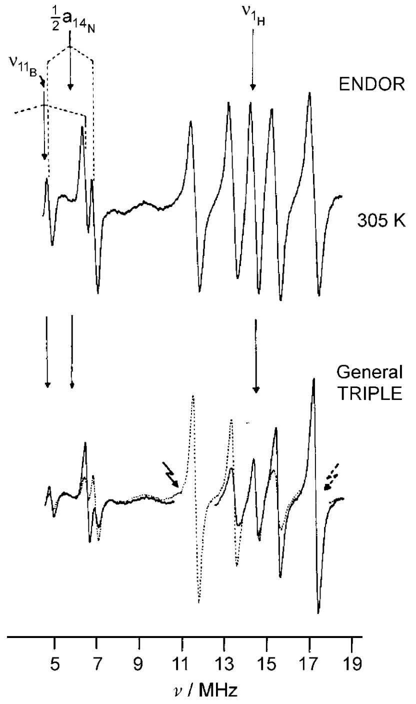
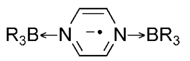


Figure 3. ENDOR and general TRIPLE spectra of radical anion **8** (R = Et) in THF at 305 K, showing ^{1}H, ^{11}B, and ^{14}N resonances (from Ref. [11])



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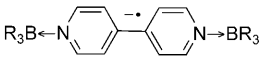

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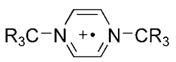
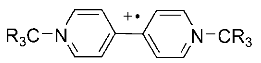


V

1,4-dialkylpyrazinium radical cation



VI

methylviologen radical cation (R = H)

The collection of representative examples for radicals containing B^{III} and B^{II} described in this section is not complete, because databases and more comprehensive reviews[6] are available. Recent developments include more heteroatom-rich systems such as borataverdazyl radical anions[41a] and *cyclo*-$(BR')_2(PR_2)_2$ singlet diradicals.[41b]

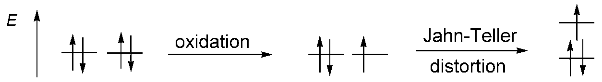
3. Polyborane Cluster Radical Anions $[B_nX_n]^{\bullet-}$

In carbon-based organic chemistry, only a few (generally unstable) "cluster" radicals with three-dimensionally delocalized spin were known[1,42] until the recent explosive development of $(C_n)^{k-}$ chemistry, focused mainly on spherical buckminsterfullerene ($n = 60$) and its reduced forms ($k = 1$–6[3a]). In contrast, several polyhedral cluster anions $[B_nX_n]^{\bullet-}$ were reported as early as 1966 (e.g. X = H, $n = 8$).[43,44] Several theoretical studies appeared later for species with X = H,[45,46] and the attention was also extended to perhalide compounds

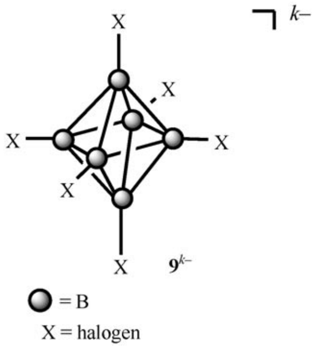
(X = halogen (Hal), $n = 6, 8–10$),[47–54] peralkylated species such as $[B_{12}Me_{12}]^{\bullet-}$,[55] and related OR-substituted derivatives (R = CH_2Ph, H).[56–58] The substituted “*hypercloso*” compounds, often generated by one-electron oxidation from dianionic *closo* precursors but sometimes also available through reduction of B_nX_n, are stabilized with electronegative substituents, because neither Hal^+ nor R^+ nor RO^+ is as good a leaving group as H^+. Our focus herein will be on the more symmetrical cases, on the compound series $[B_6Hal_6]^{\bullet-}$ (Hal = Cl,Br,I), on well-studied ions $[B_9Hal_9]^{\bullet-}$,[52–54] and on the systems $[B_{12}X_{12}]^{\bullet-}$. In most cases, the number of boron nuclei and the resulting extensive hyperfine splitting preclude the observation of resolved EPR spectra; however, the g factor ($h\nu = g\beta H$) and its anisotropy[8] can also provide valuable information on the electronic structure. In keeping with the cluster structure formulation, and in contrast to the organic borane radicals described above, the paramagnetic species described in this section have low (less than 1) non-integer oxidation states.

3.1. $[B_6Hal_6]^{\bullet-}$

The relatively small size and the potentially high (octahedral) symmetry of the clusters $[B_6X_6]^{k-}$ ($\mathbf{9}^{k-}$) has made these systems attractive targets for theory. The *closo* species with $k = 2$ have a molecular orbital arrangement with a doubly degenerate highest occupied MO (HOMO, Scheme 1),[45,46,59] creating an ambiguous situation with likely Jahn–Teller distortion on oxidation to the *hypercloso* form ($k = 1$). Preetz and co-workers have managed to synthesize, isolate, and structurally characterize deeply colored species such as $[B_6I_6]^{\bullet-}$ which, however, show only small signs of cluster distortion beyond counterion and packing effects.[47,48] Small trigonal distortions of the octahedral framework were calculated by DFT for all monoanions $[B_6Hal_6]^{\bullet-}$ (Hal = Cl, Br, I).[24]



Scheme 1. Avoidance of degeneracy by Jahn–Teller distortion after one-electron oxidation.



Yet the unusual electronic structure of such species is evident from EPR spectroscopy.[49] Very rapid relaxation owing to the presence of excited states lying close to the doublet ground state results in severe line broadening, which is particularly pronounced in the presence of the heavier halogens with their large spin–orbit coupling constants; the signal of deep blue $[B_6I_6]^{\bullet-}$ could thus only be observed at 4 K. The line broadening and the vast number of EPR hyperfine lines expected for the coupling of the unpaired electron with six boron and six nuclear-spin-active halogen nuclei (^{35}Cl, ^{37}Cl; ^{79}Br, ^{81}Br; ^{127}I)[8] in the combinations given by their natural abundances precluded the observation of electron–nuclear hyperfine splitting by EPR spectroscopy. However, the close-lying excited states resulting from the partially occupied degenerate MOs[24,45,46,49] are also responsible for the shift of the g tensor components to rather low values, an effect which is further enhanced by the spin–orbit coupling of the significantly participating halogen atoms.[49] In fact, DFT calculations have reasonably reproduced the extraordinary experimental EPR g anisotropy of $g_1 = 2.04$, $g_2 = 1.66$, $g_3 = 1.15$ and indicated a well-averaged spin distribution of about 1/12 for each of the boron and iodine atoms in $[B_6I_6]^{\bullet-}$ (Figure 4).[24] With the lighter halogen substituents bromine and chlorine, the g anisotropy is less pronounced,[49,50] not only due to the much smaller spin–orbit coupling constants of these atoms but also because of diminished spin transfer to the peripheral halides (e.g. 4.5 % to Cl instead of 8.4 % to I).[24]

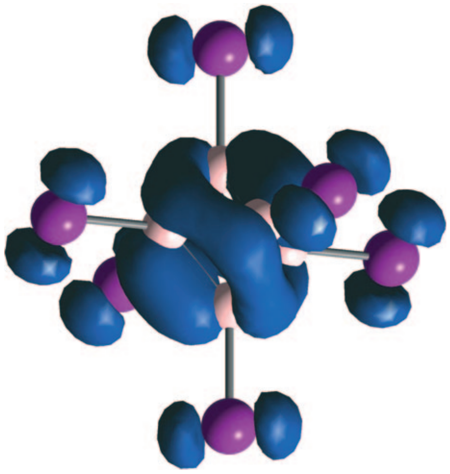
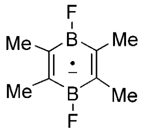


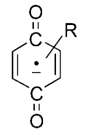
Figure 4. DFT-calculated spin density of compound $\mathbf{9}^{\bullet-}$ ($[B_6I_6]^{\bullet-}$) after energy minimization.

The variation of halides from iodine via bromine to chlorine and the investigation of mixed derivatives $[B_6Hal_nHal'_{6-n}]^{\bullet-}$ in isomeric forms (*cis, trans*) as well as halide/hydride and halide/alkyl species has thus experimentally confirmed the essential contributions from the substituents to the singly occupied cluster orbital.[49,50] The strong substituent effect is surprising at first, considering the high electronegativity difference between halogen and boron atoms. However, free electron pairs of the halogen substituents are involved in the spin accommodation, as confirmed by the calculations for $[B_6I_6]^{\bullet-}$.[24]

While the preparation of $[B_6F_6]^{\bullet-}$ has to date been unsuccessful, there have been radicals reported with the BF group (which is isoelectronic to CO!). The *p*-semiquinone analogue **10** was shown to exhibit rather small spin delocalization onto the BF moiety.[60]



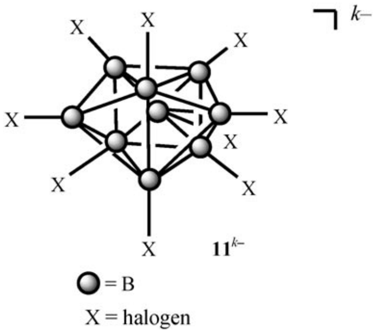
10



p-benzosemiquinone

3.2. $[B_9Hal_9]^{\bullet-}$

The tricapped trigonal prismatic *closo* cluster system $[B_9Hal_9]^{k-}$ ($\mathbf{11}^{k-}$, $k = 0$–2, Hal = Cl, Br, I) has been characterized experimentally and theoretically. Its chemical and electrochemical two-step electron-transfer reactivity with $[B_9Hal_9]^{\bullet-}$ intermediates has been described[52–54] along with the effects of protonation.[54b] The lower symmetry in comparison to $[B_6X_6]^{\bullet-}$ and $[B_{12}X_{12}]^{\bullet-}$ results in a nondegenerate redox-active MO (HOMO of $[B_9X_9]^{2-}$, LUMO of B_9X_9) which is responsible, for instance, for a less unusual *g*-factor anisotropy[54a] in the case of $[B_9Br_9]^{\bullet-}$ ($g > 2$, $g_1 - g_3 = 0.05$) relative to $[B_6Br_6]^{\bullet-}$ ($g < 2$, $g_1 - g_3 = 0.20$). Structural changes during the electron transfer are rather small: the overall tricapped trigonal prismatic cluster arrangement is maintained.[54] The obviously low reorganization energy probably contributes to the stability of the radical intermediate in the redox system $\mathbf{11}^{k-}$.[53,54]



$\mathbf{11}^{k-}$

X = halogen

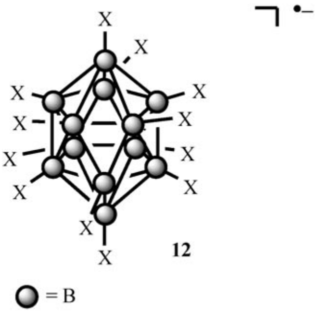
Apart from the stability and the structural characteristics associated within the $[B_9X_9]^{0/\bullet-/2-}$ redox series, two other remarkable features are associated with the $[B_9X_9]^{\bullet-}$ radical anions: They can be obtained in protonated form $[HB_9X_9]^{\bullet}$[54b] and they are conveniently synthesized from B_9X_9 via reduction using iodide or HI [Eqs. (3) and (4)].[54]

$$B_9X_9 + I^- \rightarrow [B_9X_9]^{\bullet-} + \tfrac{1}{2}\, I_2 \tag{3}$$

$$B_9X_9 + HI \rightarrow [HB_9X_9]^{\bullet} + \tfrac{1}{2}\, I_2 \tag{4}$$

3.3. $[B_{12}X_{12}]^{\bullet-}$

Icosahedral *closo*-$[B_{12}X_{12}]^{2-}$ ions are prototypical polyborane clusters with high stability.[2] Similar to the case for $[B_6X_6]^{2-}$, the high symmetry results in a degenerate HOMO.[2a,b,45,46] Although the oxidation of $[B_{12}X_{12}]^{2-}$ (X = Hal) via radical anion intermediates $[B_{12}X_{12}]^{\bullet-}$ **12** has been considered,[46,61] this process is highly irreversible in electrochemical experiments even at low temperatures.[62] UV irradiation of a frozen solution in an EPR spectrometer produces signals with relatively small *g* anisotropy in the frozen state; these were tentatively attributed to distorted $[B_{12}X_{11}]^{\bullet 2-}$ (X = Br, I) arising from the formation of X_2 on prolonged irradiation.[62]



12

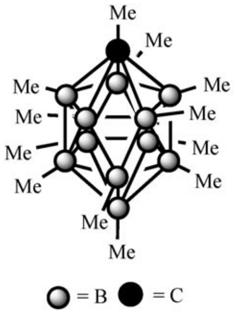
X = halogen, R, OR, OH

For non-halide-substituted derivatives there were several recent reports by Hawthorne and co-workers describing isolated, slightly Jahn–Teller distorted *hypercloso* species $[B_{12}Me_{12}]^{\bullet-}$ ($g = 2.0076$) and purple $[B_{12}(OR)_{12}]^{\bullet-}$ compounds (R = CH_2Ph and other alkyl groups).[55–57] Back-bonding from the electron-rich and lone-pair-providing alkoxy groups to the electron-deficient B_{12} cluster was postulated based on the structural changes, such as shrinking B–O separations on oxidation.[56] The alkoxo derivatives were labeled as discrete nanomolecular ions with tunable pseudometallic properties, such as metal-like redox reactions,[57] that is, two-step reversible one-electron transfer.

Although the diamagnetic $[B_{12}(OH)_{12}]^{2-}$ had been described[58] and used as an example of an "inorganic sugar",[58a] the stable green ion $[B_{12}(OH)_{12}]^{\bullet-}$ was isolated only recently by Schleid and co-workers, structurally analyzed as the Cs^+ salt, and characterized by cyclic voltammetry and EPR spectroscopy ($g = 2.0042$).[58e]

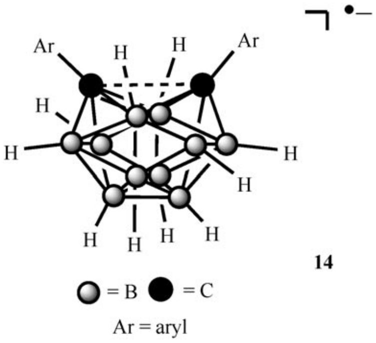
4. Carborane Radicals

Starting from $[B_{12}R_{12}]^{\bullet-}$, the formal replacement of one BR unit by an equivalent $[CR]^+$ function not only removes the symmetry and thus the orbital degeneracy, it also changes the redox potential and leaves a neutral radical species such as $[CB_{11}Me_{12}]^{\bullet}$ **13** ($g = 2.0037$), as described by Michl and co-workers.[63] Compound **13** has been discussed in connection with its synthetic potential as an oxidant.[63b]



13

Related anion radical species $[1,2\text{-}R_2\text{-}1,2\text{-}C_2B_{10}H_{10}]^{\bullet -}$ ($R_2 = Ph_2$[64a] (**14**) or $(CH_2)_3$[64b]) have been reported very recently, along with their structural,[64b] computational,[64a] and (spectro)electrochemical characterization.[64] The C–C distance is calculated to be elongated significantly by about 0.6 Å on reduction from the neutral species to the radical anion **14**, suggesting the absence of a carbon–carbon bond for the radical species.[64a]



14

Higher symmetry was established by EPR spectroscopy for the $[C_4B_8R_4H_8]^{\bullet -}$ radical ion **15** ($R = SiMe_3$),[65] which was obtained by reduction of the neutral cuboctahedral precursor (Figure 5).[66] An unusually well-resolved EPR spectrum ($g = 2.0030$) shows large ^{11}B hyperfine splitting of 1.165 mT ($a(^{10}B) = 0.390$ mT) with only four equivalent boron atoms.[65] The underlying electronic structure has been assessed recently through DFT calculations for the analogous compound with R = H (Figure 6a), which gave spin densities of 7.7 % for each of the carbon atoms, 20.3 % for the separated boron atoms on top and bottom of the cluster, and 0.00 % for the central four boron atoms that lie in a nodal plane of the SOMO (Figure 6b).

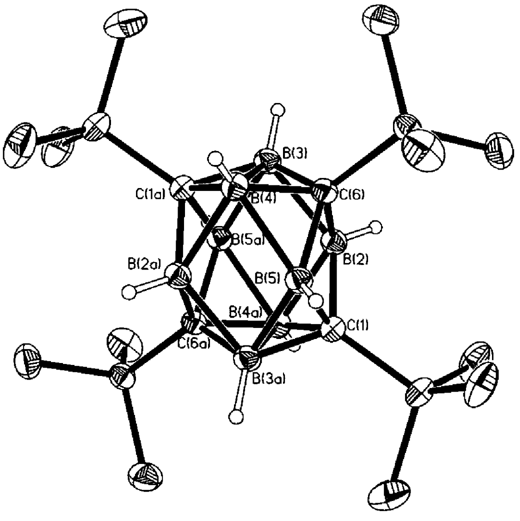


Figure 5. Molecular structure of $[C_4B_8(SiMe_3)_4H_8]$ (**15**; from Ref. [66]).

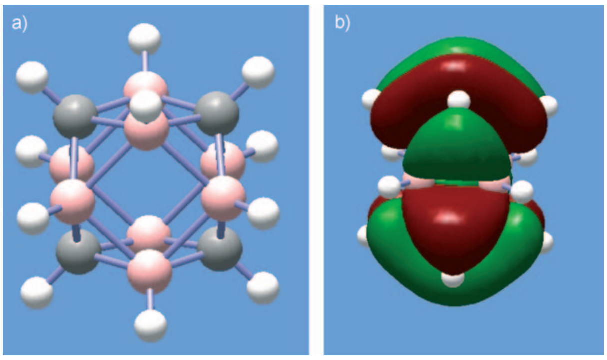
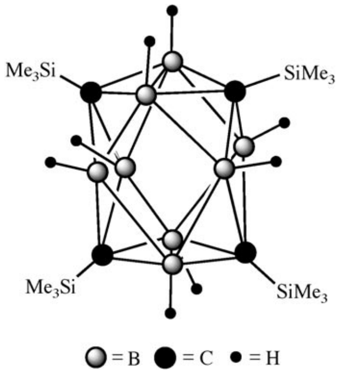


Figure 6. a) Structure and b) DFT-calculated singly occupied molecular orbital of $[C_4B_8H_{12}]$ after energy minimization.



15

Carboranes can be coupled at their B- and C-positions with spin-bearing groups (e.g. conventional radicals), for example, nitronyl nitroxide groups with position-dependent spin–spin interaction.[67] Indirect electron accommodation and thus mediation of electron transfer between coupled organometallic sites has also been described for various species, including $1,12\text{-}C_2B_{10}H_{10}$ connected to two organometallic ruthenium fragments through ethynyl bridges.[68]

For paramagnetic transition-metal carboranes, the spin is also not necessarily restricted to the main-group-element cluster framework, as several examples have shown.[69,70] For instance, the type of nickel carborane involved in electron-transfer-controlled "nanorotary machines" reported by Hawthorne and co-workers[71] was found to contain nickel(IV) or nickel(III), as determined by EPR spectroscopy and spectroelectrochemistry.[70]

5. Perspectives

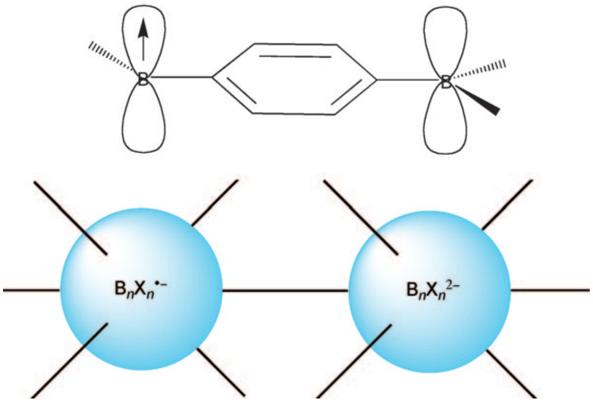


Figure 7. Two kinds of spin accommodation in boron-based radical systems.

The examples presented herein demonstrate that two- and three-dimensional spin accommodation is possible in stable radicals containing boron as an essential constituent (Figure 7). From borane-stabilized one-electron-reduced organic π systems we find a path that leads via boron-centered π radicals with formal mixed valency of boron after single spin injection to halide-, alkyl-, alkoxy-, or trialkyl silyl-substituted polyborane and carborane clusters in which the unpaired electron is distributed three-dimensionally over the cluster framework and the substituents.

The "3D aromaticity"[72] of borane clusters stabilized according to certain rules[2] justifies the extension of 2D spin delocalization to the theoretically and experimentally established 3D spin delocalization, a move beyond the confinements of the otherwise so successful concept of π radical stability. Various aspects of EPR and ENDOR spectroscopy can be employed to analyze the spin distribution, and modern DFT methods now allow a confident assessment of the electronic structure. Still, the application of isoelectronic relationships can guide us in finding suitable paramagnetic structures, with concepts from organic radical chemistry, mixed-valence research, and cluster theory as support. Considering the results summarized herein and the wide use of nitrogen and oxygen atoms in redox- and spin-active components, for example for sensors or molecular magnets,[73] it is apparent that boron-containing materials are also a viable and attractive option, as suggested by Housecroft[74] and also by recent calculations on borafullerenes like B_{80} or B_{84}.[75] Attractive perspectives for this research can also include paramagnetic oligomers or polymers that make use of the *cyclo*-$(BR')_2(PR_2)_2$ diradicals mentioned in Section 2.3[41b,76] or of combinations between organoboranes and transition-metal compounds such as ferrocenes.[77] There is clearly a wide research field open for boron-based spin-carrying systems, and this Minireview has demonstrated various strategies to obtain such materials.

Boron has long been known as an electron-deficient main-group element. By comparison, however, much less is known about its radical-stabilizing facet. Since the discovery of the superconductor properties of MgB_2[78] it has become even more worthwhile to look at those species containing stable boron radicals and to explore their potential applications.

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