The Hexahydro-*closo*-hexaborate Dianion $[B_6H_6]^{2-}$ and Its Derivatives

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$[B_6H_6]^{2-}$ as the smallest known hydro-*closo*-borate is only moderately stable, and therefore its reaction chemistry remained unexplored for quite a long time. Since the mid 1980s some progress has been made in this field, and a considerable number of derivatives has been prepared. The provided structural and spectroscopic data together with the results of more sophisticated theoretical investigations by high level ab initio methods are a good basis for a systematic review on this class of compounds, and may encourage further synthetic and theoretical work. This is the aim of the present article giving a comprehensive survey up to the beginning of 1999.

Introduction

The story of the polyhedral *closo*-borates is characterized as an interplay of theoretical and synthetic progress. Based on theoretical studies of the valence structures of boron hydrides the existence of closed-shell hydro-*closo*-borate anions of the type $[B_nH_n]^{2-}$, $n = 5-12$, had been predicted in 1954.[1−3] Even some years later, in 1959 and 1960 salts of the exceptionally stable species $[B_{10}H_{10}]^{2-}$ [4] and $[B_{12}H_{12}]^{2-}$ [5] could be synthesized. The until now smallest known member of this series $[B_6H_6]^{2-}$, which is merely moderately stable, evaded preparation until 1964[6] − a decade after its prediction.

While for $[B_{10}H_{10}]^{2-}$ and $[B_{12}H_{12}]^{2-}$ an extensive derivative chemistry had been established very soon after their discovery,[7][8] for $[B_6H_6]^{2-}$ until 1984 the unique descendant remained $[B_6Br_6]^{2-}$, which only has been mentioned in a footnote.[9] The reason for this hiatus may lie in the initially complicated synthesis using the dangerous diborane, the small yield, and the instability of $[B_6H_6]^{2-}$ in acidic media. Therefore, a more vigorous study of its reaction chemistry was difficult, and demanded better synthetic routes to

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MICROREVIEWS: This feature introduces the readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

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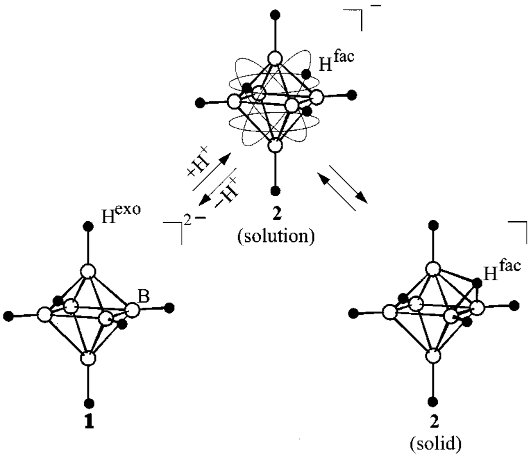
its preparation. Stimulated by our findings in the fields of classical octahedral mixed-ligand complexes of the transition metals and of the hexanuclear clusters of Mo, W, Nb, and Ta[10] with respect to the interrelation between symmetry and structural and spectroscopic properties, the octahedral B_6 cage with its terminally bonded or *exopolyhedral* substituents seemed to be a worthwhile investigation object, in order to study these interrelations in this field, too.

In this review we report on the parent compound $[B_6H_6]^{2-}$ (**1**) and its derivatives resulting by replacement of the *exopolyhedral* H atoms against inorganic and organic substituents. The cluster anion is a regular octahedral cage of 6 B atoms surrounded by a larger octahedron of 6 radially disposed *exopolyhedral* H atoms. Special attention is drawn to the property of $[B_6H_6]^{2-}$ to react as a Brønsted base, and to attach an additional proton H^{fac} giving $[B_6H_6H^{fac}]^-$ (**2**). In solution in a nonrigid structure H^{fac} fluctuates across the octahedron's surface via the edges, and in the solid state it is fixed above one of the octahedron's facets, as is shown in Equation 1.



(1)

The protolysis equilibrium in Equation 1 is exemplary, and it will be of crucial importance for the chemistry of the *closo*-hexaborates and their substitution processes. Furthermore, $[B_6H_6]^{2-}$ is discussed as a ligand in metal complexes, and some reactions modifying the B_6 core are included, while the carbaboranes are excluded. The literature for the title subject is covered up to the beginning of 1999.

The structures of most of the compounds have been solved by single-crystal X-ray structure analyses, and, in general, ^{11}B-NMR spectroscopy is used for the characterization of the derivatives, accompanied by the respective hetero-nucleus NMR spectroscopy in case of suitable substituent nuclei such as ^{1}H, ^{13}C, ^{19}F, ^{29}Si, ^{77}Se, ^{113}Cd, and ^{199}Hg. Further, the vibrational spectra, IR and Raman, have been measured and for sure assignment accompanied by normal coordinate analyses.

The influence of the different substituents on the kinetics, the molecular parameters and the spectral properties is discussed in detail. In some special cases ab initio calculations have been performed to obtain insight into the electronic and molecular structures, and to affirm the assignment of spectral data by frequency analysis and by calculated NMR chemical shifts.

Whenever possible, the pK_a values of the protolysis equilibria determined by potentiometric titration are reported, and for redox active species electrochemical data are added. UV/Vis and ESR spectroscopy have been applied to the colored radical anions obtained by oxidation processes.

Syntheses, Structure, and Properties of $[B_6H_6]^{2-}$

Starting with commercially available materials diborane is generated in a first step as formulated in Equation 2.

$$3\,NaBH_4 + 4\,BF_3\cdot O(C_2H_5)_2 \xrightarrow{20\,°C,\ Diglyme} 2\,B_2H_6\uparrow + 3\,NaBF_4 + 4\,(C_2H_5)_2O \quad (2)$$

B_2H_6 is passed through a diglyme solution of tetrahydroborate, and octahydrotriborate $[B_3H_8]^-$ is formed as an intermediate product according to Equation 3.

$$B_2H_6 + NaBH_4 \xrightarrow{90\,°C,\ Diglyme} Na[B_3H_8] + H_2\uparrow \quad (3)$$

On boiling, the colorless reaction mixture turns to yellow, and in parallel reactions the following clusters are produced as given in Equations 4−6.

$$2\,Na[B_3H_8] \xrightarrow{162\,°C,\ Diglyme} Na_2[B_6H_6] + 5\,H_2\uparrow \quad (4)$$

$$4\,Na[B_3H_8] \xrightarrow{162\,°C,\ Diglyme} Na_2[B_{10}H_{10}] + 2\,NaBH_4 + 7\,H_2\uparrow \quad (5)$$

$$5\,Na[B_3H_8] \xrightarrow{162\,°C,\ Diglyme} Na_2[B_{12}H_{12}] + 3\,NaBH_4 + 8\,H_2\uparrow \quad (6)$$

The ratio of $[B_6H_6]^{2-}/[B_{10}H_{10}]^{2-}/[B_{12}H_{12}]^{2-}$ is 2:1:15, and the total amount of $[B_6H_6]^{2-}$ is 5% at most. In a recently published one-pot synthesis[11] the liberation of large and dangerous amounts of B_2H_6 is avoided, and yield of $[B_6H_6]^{2-}$ is raised to 25%. Boron trifluoride−diethyl ether is treated in diglyme at 100° C with an excess of tetrahydroborate according to Equation 7 to give $Na[B_3H_8]$,[12] which is transformed by subsequent refluxing for 36 h into a mixture of the *closo*-borate clusters.[11]

$$5\,NaBH_4 + 4\,BF_3\cdot O(C_2H_5)_2 \xrightarrow{100\,°C,\ Diglyme} 2\,Na[B_3H_8] + 2\,H_2\uparrow + 3\,NaBF_4 + 4\,(C_2H_5)_2O \quad (7)$$

Fortunately, from the always resulting product mixtures of all synthetic routes a crude separation of $[B_6H_6]^{2-}$ from $[B_{10}H_{10}]^{2-}$ and $[B_{12}H_{12}]^{2-}$ is possible on the basis of the protolysis equilibrium of $[B_6H_6]^{2-}$ and the pH dependence of the solubility of the tetra-*n*-butylammonium $[n\mathrm{Bu}_4N]^+$ salts in water.[13][14] While $[B_{10}H_{10}]^{2-}$ and $[B_{12}H_{12}]^{2-}$ are precipitated in basic media, $[B_6H_6]^{2-}$ remains in solution, from which after separation and following cautious acidification $[n\mathrm{Bu}_4N][B_6H_6H^{fac}]$ is obtained as a scarcely soluble compound. Dissolution in dichloromethane and addition of an aliquot amount of $[n\mathrm{Bu}_4N]OH$ yields the deprotonated $[n\mathrm{Bu}_4N]_2[B_6H_6]$, which in aqueous solution is converted into the scarcely soluble Cs salt according to Equation 8.

$$[nBu_4N]_2[B_6H_6] + 2\ CsOH \rightarrow Cs_2[B_6H_6]\downarrow + 2\ [nBu_4N]OH \qquad (8)$$

Protonation to the well-soluble $Cs[B_6H_6H^{fac}]$ is accomplished by addition of an aliquot amount of hydrochloric acid.

As another synthetic route, however with small yields only, the reaction of iodine with tetrahydroborate may be mentioned as described by Equation 9.[15−17]

$$6\ NaBH_4 + 2\ I_2 \rightarrow Na_2[B_6H_6] + 4\ NaI + 9\ H_2\uparrow \qquad (9)$$

As in the preceding reactions the intermediate formation of $[B_3H_8]^-$ as formulated in Equations 3 and 7 is decisive, and also in the solid small amounts of $[B_6H_6]^{2-}$ are produced from salts of $[B_3H_8]^-$ on tempering them above 200° C.[18] Anhydrous $Na_2[B_6H_6]$ is conveniently prepared by reaction of $Na[B(C_5H_6)_4]$ and $[nBu_4N]_2[B_6H_6]$ in methanol.[19]

$[B_6H_6]^{2-}$ (**1**) has a regular octahedral cage of 6 B atoms surrounded by a larger octahedron of 6 radially disposed *exopolyhedral* H atoms. This octahedral structure of $[B_6H_6]^{2-}$ had been postulated already in 1954,[1][3] and could be confirmed for the solid state by X-ray structure analyses on the $[Me_4N]^+$,[20] K^+ and Cs^+ salts,[21] and for the solution state by NMR spectroscopy.[22][23] The B−B and B−H distances are 169, 172.1, 172.2 pm and 111, 107, 109 pm, respectively. On polycrystalline $Cs_2[B_6H_6]$ a solid-state ^{11}B-, ^{133}Cs-, and ^1H-NMR study at 1.88 T has been performed revealing fine structure due to ^{11}B-^1H and ^{10}B-^1H quadrupolar and dipolar interactions, which has allowed the calculation of the B−H distance to 119 pm. The accuracy of the determination of distances by NMR spectroscopy, X-ray, and neutron diffraction has been discussed.[24]

As the Brønsted base $[B_6H_6]^{2-}$ has a pK_a value of 7 the protonated form $[B_6H_6H^{fac}]^-$ (**2**) is present already in weak acidic solutions.[14] The localization of H^{fac} above one of the facets of the octahedron in a face-capped structure had been predicted on the basis of theoretical calculations,[25−29] and was confirmed by X-ray analyses on $[Ph_4P][B_6H_6H^{fac}]$, $[Ni(bipy)_3][B_6H_6H^{fac}]_2$, and $[Ni(phen)_3][B_6H_6H^{fac}]_2$.[30] The observed decomposition of $[B_6H_6H^{fac}]^-$ in stronger acidic media is explained by the instability of the twofold protonated species, the hypothetical *closo*-borane $[B_6H_8]$, which should better be written as $[B_6H_6(H^{fac})_2]$. This also follows from theoretical investigations, and corresponds to experimental results on $[H_2Os_6(CO)_{18}]$.[25,28,31,32]

A more profound understanding of the Brønsted base behavior of $[B_6H_6]^{2-}$ is provided by calculations of the electron density. An instructive idea is given by the electron localization function (ELF)[33][34] of the three-center, two-electron (3c2e) bonds of the B_3 faces. The maxima of electron density are centered above the eight faces resulting in the geometrical arrangement of a cube, the dual polyhedron to the octahedron. For this reason the faces of the octahedron are the favored regions for the addition of H^{fac} or the attack of other electrophilic reactants, and because of their Lewis basicity they can act as donating centers to Lewis acidic metal ions.

In principle, ^1H-NMR solution spectroscopy as the quick method of choice allows the reliable identification of H^{fac}, and provides slightly solvent- and cation-dependent high-field signals with unresolved ^{11}B couplings at $\delta(^1H) = -5.6$ for H^{fac}, while the signal of the *exopolyhedral* protons is a quadruplet with the typical pattern due to quadrupolar coupling to ^{11}B ($I = 3/2$) at $\delta(^1H) = 1.2$. The ^1H-coupled ^{11}B spectra of both $[B_6H_6]^{2-}$ and $[B_6H_6H^{fac}]^-$ show markedly solvent- and cation-dependent single doublets, each, with coupling constants $^1J(^{11}B,^1H^{exo}) = 140-150$ Hz. Table 1 gives an overview of the solvent and cation dependence.

In solutions of both $[B_6H_6]^{2-}$ and $[B_6H_6H^{fac}]^-$ the 6 B core atoms as well as the 6 terminal H atoms are chemically and magnetically equivalent at room temperature, and therefore H^{fac} must fluctuate across all faces with the same residence time. The migration is intramolecular, and takes place chiefly via the edges across the surface of the octahedron with a migration barrier in the order of 10 $kcal\cdot mol^{-1}$.[22] This way is favored energetically in comparison to that across the vertices by 21 $kcal\cdot mol^{-1}$.[36] From studies on different salts a cation−anion interaction must be taken into consideration,[22][36] and from relaxation considerations with respect to quadrupolar coupling and electric field gradient interactions $^1J(^{11}B,^1H^{fac})$ scalar coupling constants of 13 and 16 Hz for $[nBu_4N][B_6H_6H^{fac}]$ and $[Ni(bipy)_3][B_6H_6H^{fac}]_2$ in acetone have been derived, respectively.[22] Only after cooling of solutions containing $[B_6H_6H^{fac}]^-$ below the coalescence temperature the ^{11}B resonance is split into two signals with $\delta(^{11}B)$ shifted downfield for the uncapped facet and upfield for the facet capped by H^{fac} [22] (see Table 1). The coalescence points have been determined to 196 K at 1.88 T for $[Ni(bipy)_3][B_6H_6H^{fac}]_2$ in acetone[22] and to 227 K at 9.35 T for $[Ph_4As][B_6H_6H^{fac}]$ in CD_2Cl_2.[35] Because of the great interest in the fluxional behavior of the additional proton H^{fac} different calculations with regard to the barrier of movement across the octahedron facets have been done. From the temperature dependence of the ^{11}B-NMR spectra of $[nBu_4N][B_6H_6H^{fac}]$ and $[Ni(bipy)_3][B_6H_6H^{fac}]_2$ in acetone values of 10 and 11.5 $kcal\cdot mol^{-1}$ have been determined,[22] which are in good agreement with theoretical investigations resulting in 10.4 $kcal\cdot mol^{-1}$ with an SCF/DEHD approach,[36] 12.1 $kcal\cdot mol^{-1}$ at the MP2/6-31G* level,[37] and in 8.3 $kcal\cdot mol^{-1}$ at the B3LYP/6-311+G** level.[38] This low energetic barrier is attributed to the three-dimensional aromaticity[39][40] of *closo*-borates, which may be described as the tendency of the molecule anions to realize equal electronic conditions at all boron atoms by a "cluster current". In several theoretical studies the migration barrier of H^{fac} in $[B_6H_6H^{fac}]^-$ has been compared to those in $[B_{10}H_{10}H^{fac}]^-$ [41] and $[B_7H_7H^{fac}]^-$, $[B_9H_9H^{fac}]^-$, $[B_{12}H_{12}H^{fac}]^-$.[38,42−44] The cluster bond enthalpies have been calculated for $[B_nH_n]^{2-}$, $n = 6, 8-10$.[45]

$[B_6H_6]^{2-}$ can be deuteriated completely by treatment with D_2O.[46] Kinetic investigations have shown, that the reaction rate is proportional to the ratio of the protonated form, so that the deuteriation proceeds very fast in neutral or acidic media, while in basic media it runs not at all or very

Table 1. Chemical shifts δ(^{1}H) and δ(^{11}B) [ppm] and coupling constants $^1J(^1H,^{11}B)$ [Hz] of $[B_6H_6]^{2-}$ (a) and $[B_6H_6H^{fac}]^-$ (b) in different solvents, at different temperatures and with different cations and of $[B_6D_6D^{fac}]^-$ (c)

Cation		*T* [K]	Solvent	δ(^{1}H)		δ(^{11}B)	$^1J(^1H,^{11}B)$		Ref.
				exo	*fac*		*exo*	*fac*	
$[Ni(bipy)_3]^{2+}$	b	190	acetone	1.2	−5.6	−6.7, −15.3	150	13	[22]
	b	300	acetone	1.2	−5.6	−14.7	146	–	
$[nBu_4N]^+$	b	190	acetone	–	−5.6	−9.9, −17.8	146	16	[22]
	b	300	acetone	–	−5.6	−14.2	144	–	
$[nBu_4N]^+$	b	297	CD_3CN	–	–	−13.6	147	–	[23]
	a	297	CD_3CN	–	–	−13.2	133	–	
$[nBu_4N]^+$	c	297	CD_3CN	–	–	−13.9	–	–	[23]
$[nBu_4N]^+$	b	297	CD_3CN[a]	–	−5.6	−14.6	145	–	[35]
	a	297	CD_3CN[b]	–	–	−14.8	133	–	
$[nBu_4N]^+$	b	297	CD_2Cl_2	–	−5.4	−18.0	145	–	[35]
	a	297	CD_2Cl_2[b]	–	–	−18.0	132	–	
$[Ph_4As]^+$	b	297	CD_2Cl_2	1.1	−5.5	−18.0	147	–	[35]
	b	223	CD_2Cl_2	1.1	−5.5	−14.1, −21.7	–	–	
	a	297	CD_2Cl_2	1.1	–	−18.0	133	–	
Cs^+	b	297	H_2O	1.2	−3.9	−17.7	146	–	[35]
	a	297	H_2O[c]	1.2	–	−18.1	123	–	
Cs^+	c	297	D_2O[d]	–	–	−17.9	–	–	[35]
$[Me_4N]^+$	a	not reported	–	–	−13.0	122	–	–	[6]

[a] = + citric acid. – [b] = + DBU. – [c] = + OH^-. – [d] = + NaH_2PO_4.

slow.[14] Although the movement of H^{fac} across the octahedral surface proceeds from face to face via the edges and not via the corners, the decisive step is the intramolecular exchange of H^{fac} or D^{fac} respectively against one of the terminally bonded H atoms. The activation energy of this process has been determined to be 18 kcal·mol^{-1}.[14]

As $[B_6H_6]^{2-}$ may serve as a paradigm of the class of doubly octahedral structured systems, its vibrational spectra have been examined and interpreted repeatedly.[47–49] The octahedral structure of $[B_6H_6]^{2-}$, which has been proven by X-ray structure analysis and by NMR spectroscopy, is clearly derived from the vibrational spectra, too. For a 12-atomic *homoleptic* molecule $[B_6X_6]^{2-}$ with point group O_h the normal modes of vibration transform as given by Equation 10.

$$\Gamma_{\tilde{\nu}} = 2\,A_{1g} + 2\,E_g + T_{1g} + 3\,T_{1u} + 2\,T_{2g} + 2\,T_{2u} \qquad (10)$$

For systems with a center of symmetry the rule of mutual exclusion is valid, and according to the group-theoretical selection rules the vibrations with symmetries A_{1g}, E_g, and T_{2g} are Raman-active, those with symmetry T_{1u} are IR-active and those with T_{1g} and T_{2u} are inactive. The B_6 cage and the X_6 octahedra, put into each other, perform coherent vibrations, which are subdivided in two groups[50]:
1. Vibrations with equidirectional movement of the two spheres (in phase) transform as given in Equation 11.

$$\Gamma_{\text{in phase}} = A_{1g} + E_g + T_{1u} + T_{2g} + T_{2u} \qquad (11)$$

2. Vibrations with a counter-directional movement of the two spheres (anti phase) transform as given in Equation 12.

$$\Gamma_{\text{anti phase}} = A_{1g} + E_g + T_{1g} + 2T_{1u} + T_{2g} + T_{2u} \qquad (12)$$

The normal vibrations are presented in Figure 1. The highest spectral resolution on the parent compound has been achieved by measurement at low temperature.[51] As the isotopic ratio of boron at natural abundance is 80.22% ^{11}B and 19.78% ^{10}B, $[B_6H_6]^{2-}$ is in fact an isotopomeric series $[^{11}B_n{}^{10}B_{(6-n)}H_6]^{2-}$, $n = 0-6$, and this is observed in the 10 K Raman spectra with very sharp lines for the respective isotopomers having a half-width of 1.5 cm^{-1}, only. An unambiguous assignment of the normal vibrations has become possible by measurement of the final members $[^{11}B_6H_6]^{2-}$ (96% ^{11}B) and $[^{10}B_6H_6]^{2-}$ (92% ^{10}B), which have been prepared in high isotopic enrichment.[52] The Raman-active cage vibrations $\tilde{\nu}_1$, $\tilde{\nu}_2$, and $\tilde{\nu}_3$ are shifting with increasing *n* in steps of 7 cm^{-1} to lower frequencies. From the fine-structure of the signals even the geometrical isomers of the isotopomers, existing for $n = 2$, 3, and 4, are recognizable. Normal coordinate analysis has been carried out on the basis of a modified valence force field with the Wilson GF matrix method utilizing a set of 6 force constants (Table 2), and an excellent adaptation of the computed values to the observed frequencies has been achieved (Table 3).[50] This is true also for the deuteriated compounds $Cs_2[^{11}B_6D_6]$ and $Cs_2[^{10}B_6D_6]$.[50] Due to the markedly different masses of the boron isotopes ^{10}B and ^{11}B the isotopic effect on the degeneracy is observed.[53] Only for the pure final members of the series with $n = 0$ and $n = 6$ O_h point symmetry is valid. For the members with $n = 1-5$ symmetry is descending to D_{4h}, C_{4v}, C_{3v}, and C_{2v}, with the result that normal vibrations derived from the degenerate modes with symmetry T and E become less or nondegenerate, and the corresponding lines are split. By restriction of the rule of mutual exclusion certain lines of the IR spectrum are recognizable with weak intensity also in the Raman spectrum.[50] Calculations of the potential energy distribution (PED) show that $\tilde{\nu}_1$ and $\tilde{\nu}_3$ with PED values of 98% are nearly genuine modes of the B_6 core, while the same is right for the B–H fundamentals $\tilde{\nu}_2$ and $\tilde{\nu}_4$. The other vibrations exhibit with 10% and 90%, respectively, pronounced couplings between the core modes and the boron-substituent modes.[50] The influence of protonation has been studied by vibrational spectroscopy on the pair $Cs_2[B_6H_6]$ and $Cs[B_6H_6H^{fac}]$.[14] The symmetric and antisymmetric vibrations of H^{fac} against the B_3 facet could not be observed, but have been calculated to lie in the range of 1800 and 1280 cm^{-1}, respectively.[54] A characteristic shift of B−H stretching modes by about 100 cm^{-1} to higher frequencies is observed on protonation, viz. the Raman lines at 2414 and 2460 cm^{-1} to 2522 and 2574 cm^{-1}, and the broad IR band at 2432 cm^{-1} to 2518−2545 cm^{-1}. In the range of the skeletal vibrations beyond 1100 cm^{-1} many additional bands are exhibited for the protonated compound if compared to the deprotonated one.[14] These observed higher B−H frequencies of the protonated cluster in comparison to the deprotonated could be verified by ab initio frequency analyses.[54]

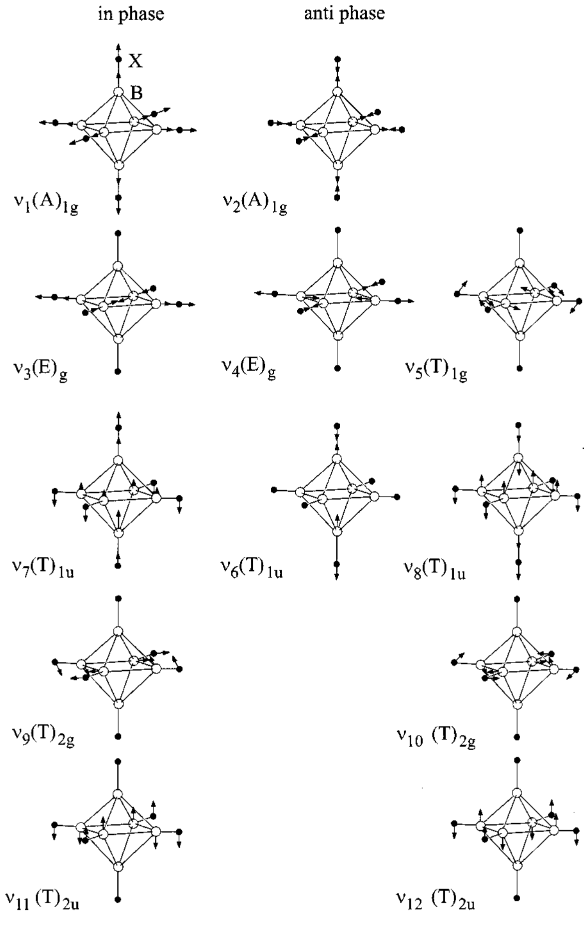


Figure 1. In-phase and anti-phase normal vibrations of a $[B_6X_6]^{2-}$ molecule

Table 2. Averaged bond lengths d [pm] and calculated force constants f [10^2 $N{\cdot}m^{-1}$] of the cluster anions $[B_6X_6]^{n-}$ (X = H, Cl, Br, I; n = 1, 2)

	n	X=H	Cl	Br	I
d_1(B−B)	1		173	173	173
	2	172	172	168	165
d_2(B−X)	1		176	191	212
	2	109	182	199	219
f_d(BB)	1		1.17	1.18	1.18
	2	1.78	1.40	1.43	1.49
f_d(BX)	1		4.17	3.34	2.60
	2	3.19	3.99	3.28	2.35
$d_1^2f_\alpha$(BBB)	1		0.15	0.17	0.25
	2	0.64	0.29	0.27	0.29
$d_1d_2f_\alpha$(BBX)	1		0.39	0.34	0.51
	2	0.18	0.49	0.51	0.54
$f_{dd'}$(BB/BB)	1		0.30	0.24	0.40
	2	0	0.10	0.15	0.15
f_{dd}(BB/BB)	1		−0.08	−0.02	−0.03
	2	0	−0.07	−0.05	−0.02
f_{dd}(BB/BX)	1		0.05	−0.03	0
	2	0	0.03	0	0
$d_1f_{d\alpha}$(BX/BBB)[a]	1		−0.39	−0.32	−0.41
	2	−0.21	−0.61	−0.45	−0.31
$d_1f_{d\alpha}$(BX/BBB)[b]	1		0	0	0
	2	0.08	0	0	0
$d_2f_{d\alpha}$(BX/BBX)	1		0	0	0.20
	2	0	0.25	0.18	0.08
$d_1^2f_{\alpha\alpha}$(BBB/BBB)	1		0.20	0.30	0
	2	0	0	0	0

[a] X at the middle B atom. − [b] Bond as part of the angle.

Concerning the fluxional behavior of H^{fac} the monosubstitution products of $[B_6H_6]^{2-}$ are particularly interesting, because as a consequence of substitution the octahedron is built up from two energetically different square pyramids: an upper one topped by the substituted boron atom, which is called the *ipso* boron atom, and a lower one topped by the *antipodal* boron atom. Accordingly, protonation may happen either in the *antipodal* or the *ipso* sphere (see Figure 2), and this may be influenced by the nature of the substituent. Therefore, systematic efforts have been made in preparing and characterizing such $[B_6H_5H^{fac}X]^-$/$[B_6H_5H^{fac}R]^-$ species. Details on this subject will be discussed in the derivatives section beyond.

Derivatives

Halogeno Substituents

The derivative chemistry of $[B_6H_6]^{2-}$ started in 1984 with the syntheses of the hexahalo-*closo*-hexaborates $[B_6X_6]^{2-}$, X = Cl, Br, and I,[55], and their characterization by ^{11}B-NMR[56] and vibrational spectroscopy.[57] They are formed in a series of substitution steps by reaction of $[B_6H_6]^{2-}$ with the free halogens in strong basic aqueous solution according to Equation 13.

$$[B_6H_6]^{2-} + n\,X_2 + n\,OH^- \rightarrow [B_6H_{(6-n)}X_n]^{2-} + n\,X^- + n\,H_2O \quad (n = 1{-}6) \qquad (13)$$

The pH dependence of the reaction of $[B_6H_6]^{2-}$ with iodine in aqueous solution has been studied by potentiometry showing an almost instantaneous stoichiometric course without gas evolution.[58] The partially halogenated derivatives are obtained as intermediates by moderate application of the halogens,[59] or better by reaction with the *N*-halosuccinimides NXS, X = Cl, Br, and I.[60] However, mixtures with several components always result. As the rate of halogenation is very fast for the first steps, the mono- and the disubstituted products are accessible in small yields only, while the 3- to 5-fold substituted species are produced in

Table 3. Assignment of calculated (c) and observed (o) frequencies [cm^{-1}] of the cluster anions [$^{11}B_6X_6]^{n-}$ (X = H, Cl, Br, I; n = 1, 2); i.a. = inactive, n. o. = not observed

$\tilde{\nu}_i$	N	$[^{11}B_6H_6]^{n-}$ o	c	$[^{11}B_6Cl_6]^{n-}$ o	c	$[^{11}B_6Br_6]^{n-}$ o	c	$[^{11}B_6I_6]^{n-}$ o	c
$\tilde{\nu}_1$	1			1206	1206	1206	1204	1162	1163
	2	988	989	1217	1219	1202	1202	1165	1167
$\tilde{\nu}_2$	1			334	334	201	204	156	159
	2	2455	2453	333	329	209	210	151	153
$\tilde{\nu}_3$	1			n.o.	981	961	960	895	894
	2	816	816	979	981	945	944	901	901
$\tilde{\nu}_4$	1			324	324	211	212	152	152
	2	2414	2410	319	320	206	207	152	151
$\tilde{\nu}_5$	1			i.a.	493	i.a.	442	i.a.	516
	2	i.a.	838	i.a.	547	i.a.	536	i.a.	537
$\tilde{\nu}_6$	1			950	954	916	909	943	940
	2	2421	2421	1125	1125	1090	1091	1058	1060
$\tilde{\nu}_7$	1			521	518	425	432	364	367
	2	1044	1039	536	536	439	439	386	385
$\tilde{\nu}_8$	1			n.o.	127	n.o.	73	n.o.	69
	2	729	729	141	139	96	96	74	73
$\tilde{\nu}_9$	1			738	737	686	689	736	737
	2	763	767	744	743	749	747	744	746
$\tilde{\nu}_{10}$	1			n.o.	105	n.o.	55	n.o.	53
	2	697	695	111	114	74	71	53	58
$\tilde{\nu}_{11}$	1			i.a.	540	i.a.	482	i.a.	545
	2	i.a.	538	i.a.	634	i.a.	624	i.a.	633
$\tilde{\nu}_{12}$	1			i.a.	82	i.a.	46	i.a.	42
	i.a.	813	i.a.	95	i.a.	59	i.a.	45	

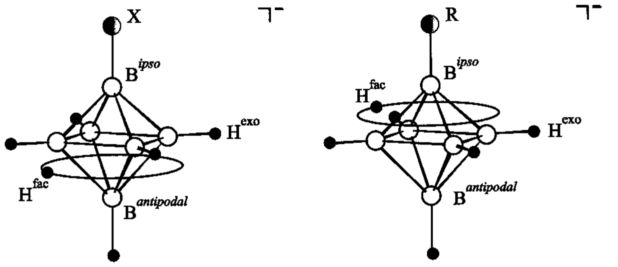


Figure 2. Fluctuation of H^{fac} in monosubstituted $[B_6H_5H^{fac}X]^-$ and$[B_6H_5H^{fac}R]^-$

high concentrations. For the isolation of pure compounds on a preparative scale ion exchange column chromatography with diethylaminoethylcellulose as a stationary phase and molar aqueous salt solutions as mobile phases has proven a well-tried method.[59−61] The rate of elution decreases strongly in the series Cl > Br > I, and additionally with increasing degree of halogenation. While the differences in mobility for higher halogenated compounds are more than 100%, those within the pairs of geometrical isomers are merely 5−15%. Therefore, their separation is very difficult, and can be overcome only by repeated ion exchange procedures with careful work up of the separated front and final sections of the corresponding chromatographic zones. The tendency towards formation of the *cis*/*fac* isomers decreases within the series Cl, Br, I, and with increasing degree of halogenation. While in the Cl and Br series for n = 2, 3, and 4 the pairs of geometrical isomers are formed in different ratios, in the I series the pure *trans* and *mer* isomers are found exclusively. As a result *trans*-$[B_6H_4I_2]^{2-}$, *mer*-$[B_6H_3I_3]^{2-}$, and *trans*-$[B_6H_2I_4]^{2-}$ are prepared in a stereomeric pure form very easily and with highest yields.[59] Unlike compounds with a low degree of halogenation the tetra-, penta-, and hexahalohydro-*closo*-hexaborates are stable against dilute mineral acids for reasonably long times. With respect to Equation 1 only the monohalo derivatives can be protonated without difficulties, and a crystal structure of $[Ph_4P][B_6H_5H^{fac}I]$ may serve as an example.[62] Utilizing a glass electrode for potentiometric titration with 0.1 N NaOH the pk_a values have been determined for the acid-base pairs $[B_6H_5H^{fac}X]^-/[B_6H_5X]^{2-}$ to be 5.35, 5.00, and 4.65 for X = Cl, Br, and I, respectively.[14] Because of their decomposition in stronger acidic media the protonation of the dihalo derivatives and even more of the compounds with higher degree of halogenation is no longer measurable by titration. The pk_a values are < 2.5, decreasing with increasing degree of halogenation. On the protonated monosubstituted derivatives $[B_6H_5H^{fac}X]^-$ and $[B_6H_5H^{fac}R]^-$, X = Cl, Br, I, SCN, R = CH_3, C_2H_5, n-C_3H_7, n-C_4H_9,

n-C_8H_{17}, variable-temperature ^{11}B-NMR studies have been performed, and revealed the migration of H^{fac} to occur in the *ipso* sphere of the B_6 octahedron for the alkyl derivatives and in the *antipodal* sphere in case of the halogens and SCN in these series[63] (see Figure 2).

Studies on the deuteriation of the halohydro-*closo*-hexaborates have shown that the H/D exchange rate decreases in agreement with their increasing basic character in the series Cl > Br > I, and in particular with increasing degree of halogenation. Accordingly, the H/D exchange must occur via the protonated forms. Since protonation is strongly impeded with increasing degree of substitution, and further is limited by decomposition on increasing acidification, the iodo-*closo*-hexaborates with 3 or more I substituents cannot be deuteriated. Thus, to obtain the species $[B_6D_nI_{(6-n)}]^{2-}$ ($n = 1-3$) iodination of $[B_6D_6]^{2-}$ is the exclusive synthetic route.[14]

A special feature of the kinetics of deuteriation is that the H atoms are exchanged at different rates with respect to the geometrical arrangement of the substituents. For example, the H atoms in *antipodal* position to the halogen substituents in $[B_6ClH_5]^{2-}$ and $[B_6Cl_3H_3]^{2-}$ are exchanged at about the 100-fold rate in comparison to the other *exopolyhedral* H atoms. This *antipodal effect*[64] may be regarded as an analogue to the *trans effect* of the coordination compounds.[10] An impressive example of the *antipodal influence* is discussed below on the series of mixed hexahalo-*closo*-hexaborates.

The preparation of the bis-*heteroleptic* halo derivatives $[B_6X_nY_{(6-n)}]^{2-}$ ($n = 1-5$, $X \neq Y$ = Cl, Br, I) is achieved by reaction of the pure partially halogenated $[B_6H_nY_{(6-n)}]^{2-}$ with the corresponding halogen or *N*-halosuccinimide in aqueous basic solution.[60][65] However, in each case successive halogenation is only possible with the respective heavier halogen, in other words: in a synthetic route the more electronegative substituent must be introduced at first, and then the less electronegative substituent as the second. The reaction Equations 14a−14c are valid.

$$[B_6Cl_nH_{(6-n)}]^{2-} + (6-n)\ Br_2 \rightarrow [B_6Cl_nBr_{(6-n)}]^{2-} + (6-n)\ HBr\ (n = 1-5) \quad (14a)$$

$$[B_6Cl_nH_{(6-n)}]^{2-} + (6-n)\ I_2 \rightarrow [B_6Cl_nI_{(6-n)}]^{2-} + (6-n)\ HI\ (n = 1-5) \quad (14b)$$

$$[B_6Br_nH_{(6-n)}]^{2-} + (6-n)\ I_2 \rightarrow [B_6Br_nI_{(6-n)}]^{2-} + (6-n)\ HI\ (n = 1-5) \quad (14c)$$

The course of substitution in these series cannot be influenced by any changes in the reaction conditions, and it is impossible to unlink halogen atoms attached to the B_6 cluster, at least, if the B_6 core has to be retained. Therefore, the possibility of chlorinating or brominating some readily available partially iodinated geometric isomers in order to synthesize the respective chloro- or bromohydro-*closo*-hexaborates from the iodohydro-*closo*-hexaborates is ruled out.

On treatment of dichloromethane solutions of the hexahalo-*closo*-hexaborates with Br_2, $(SCN)_2$, BrF_3, or $K[BrF_4]$ intense colors can be observed due to the formation of the radical anions $[B_6X_6]^{\bullet-}$. The half-wave potentials $E_{1/2}$ were determined by cyclic voltammetry to be 0.58, 0.77, and 0.88 V for X = Cl, Br, I, respectively.[66][67] In case of the partially halogenated compounds $E_{1/2}$ is shifted to less positive potentials without exception, for example to 0.28 V for *fac*- and *mer*-$[B_6Cl_3H_3]^{2-}$, 0.29 V for $[B_6BrH_5]^{2-}$, and 0.19 V for $[B_6H_5I]^{2-}$. The parent compound $[B_6H_6]^{2-}$ is oxidized at a half-wave potential $E_{1/2}$ = 0.86 V, however, under the experimental conditions (CH_3CN, $[nBu_4N]ClO_4$, Pt working electrode, Pt auxiliary electrode vs. Ag/AgCl/LiCl sat. in EtOH) the electrochemical process is irreversible.[66] For $Cs_2[B_6H_6]$ in water at a Pt electrode vs. saturated calomel electrode a value of −0.3 V has been reported.[68] On the preparative scale chemical oxidation with Ce^{IV} according to Equation 15 is suitable.

$$[nBu_4N]_2[B_6X_6] + [NH_4]_2[Ce(NO_3)_6] \rightarrow [nBu_4N][B_6X_6] + [nBu_4N]NO_3 + 2\ [NH_4]NO_3 + Ce(NO_3)_3\ (X = Cl, Br, I) \quad (15)$$

In this way deep blue $[B_6I_6]^{\bullet-}$, orange $[B_6Br_6]^{\bullet-}$and yellowish-green $[B_6Cl_6]^{\bullet-}$ are generated. The X-ray structures of the $[nBu_4N]^+$ and the bis(triphenylphosphanyl)imminium $[Ph_3P{=}N{=}PPh_3]^+$ salts have been solved.[66][67] Because of the paramagnetism ^{11}B-NMR spectra could not be recorded. The characteristic transitions in the UV/Vis spectra with extinction coefficients in the order of 1000−6000 $cm^2 \cdot mol^{-1}$ are shifted systematically to lower energies in the series Cl, Br, I. The radical anions and some mixed congeners of the type $[B_6X_nY_{(6-n)}]^{\bullet-}$ ($X \neq Y$ = Cl, Br, I), dissolved in dichloromethane, exhibit intense ESR signals in the X-band spectra, which in some cases are observable only on frozen solutions down to 4 K. The expected hyperfine couplings due to the isotopes ^{11}B and ^{10}B could not be resolved. A strongly increasing g anisotropy on replacing Cl by Br and especially by I with $g_1 = 2.04$, $g_2 = 1.66$, $g_3 = 1.15$ is interpreted by increasing participation of the halide orbitals in the singly occupied molecular orbitals (SOMOs) of the clusters.[69] The 10 K IR and Raman spectra of $[B_6X_6]^{2-}$, like the parent compound $[B_6H_6]^{2-}$, exhibit patterns of sharp lines reflecting the isotopomeric series $[^{10}B_n{}^{11}B_{(6-n)}X_6]^{2-}$ (X = Cl, Br, I, H; $n = 0-6$). Using the molecular parameters of X-ray structure analyses the vibrations of $[B_6X_6]^{2-}$ and the radical anions $[B_6X_6]^{\bullet-}$ have been assigned by normal coordinate analyses.[70][71] With sets of 8 force constants (Table 2) a good agreement of observed and calculated frequencies has been achieved (Table 3).

On the chemical shifts $\delta(^{11}B)$ of the series of mixed hexahalo-*closo*-hexaborates $[B_6X_nY_{(6-n)}]^{2-}$ ($X \neq Y$ =Cl, Br, I; $n = 5-2$) a linear regression analysis has been performed. Depending on the geometric position of the substituents in symmetric X−B···B−X and Y−B···B−Y and asymmetric X−B···B−Y arrangements of the cluster anions and their mutual influences on the electron density at the substituted ^{11}B nuclei the *antipodal influence* AI has been calculated as the difference between the ^{11}B shifts of the corresponding asymmetric and the symmetric arrangements for a given n according to Equation 16a.

$$AI = \delta(^{11}B)_{asym} - \delta(^{11}B)_{sym} \quad (16a)$$

The *antipodal shift constant* ASC[10] of a series is obtained as the difference of the *antipodal influences* of two successive compounds according to Equation 16b. The results are given in Table 4.

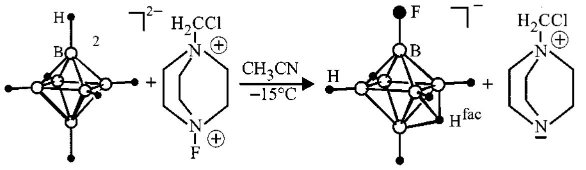
$$\mathrm{ASC} = \mathrm{AI}_{(n+1)} - \mathrm{AI}_{(n)} \quad (16b)$$

Table 4. *Antipodal Influence* AI [ppm] and *Antipodal Shift Constants* ASC [ppm] of the series *closo*-$[B_6X_nY_{(6-n)}]^{2-}$ (X ≠ Y = Cl, Br, I; n = 5−2), derived from the chemical shifts $\delta(^{11}B)$ [ppm] for symmetric X−B···B−X or Y−B···B−Y and asymmetric X−B···B−Y arrangements

Compounds[a]	$\delta(^{11}B)$ sym.	asym	AI	ASC
$[B_6\mathbf{Cl}_5Br]^{2-}$	−17.00	−17.18	−0.18	+0.34
$[B_6\mathbf{Cl}_4Br_2]^{2-}$	−16.54	−16.38	+0.16	+0.34
$[B_6\mathbf{Cl}_3Br_3]^{2-}$	−16.08	−15.58	+0.50	+0.34
$[B_6\mathbf{Cl}_2Br_4]^{2-}$	−15.62	−14.78	+0.84	
$[B_6Cl\mathbf{Br}_5]^{2-}$	−19.31	−19.42	−0.11	+0.03
$[B_6Cl_2\mathbf{Br}_4]^{2-}$	−19.96	−20.04	−0.08	+0.03
$[B_6Cl_3\mathbf{Br}_3]^{2-}$	−20.61	−20.66	−0.05	+0.03
$[B_6Cl_4\mathbf{Br}_2]^{2-}$	−21.26	−21.28	−0.02	
$[B_6\mathbf{Cl}_5I]^{2-}$	−15.97	−13.82	+2.15	+0.36
$[B_6\mathbf{Cl}_4I_2]^{2-}$	−14.50	−11.99	+2.51	+0.36
$[B_6\mathbf{Cl}_3I_3]^{2-}$	−13.03	−10.16	+2.87	+0.36
$[B_6\mathbf{Cl}_2I_4]^{2-}$	−11.57	−8.33	+3.24	
$[B_6Cl\mathbf{I}_5]^{2-}$	−26.57	−27.28	−0.71	−0.02
$[B_6Cl_2\mathbf{I}_4]^{2-}$	−28.58	−29.31	−0.73	−0.02
$[B_6Cl_3\mathbf{I}_3]^{2-}$	−30.59	−31.34	−0.75	−0.02
$[B_6C_{14}\mathbf{I}_2]^{2-}$	−32.60	−33.37	−0.77	
$[B_6\mathbf{Br}_5I]^{2-}$	−17.50	−16.78	+0.72	−0.53
$[B_6\mathbf{Br}_4I_2]^{2-}$	−16.57	−16.38	+0.19	−0.52
$[B_6\mathbf{Br}_3I_3]^{2-}$	−15.65	−15.98	−0.33	−0.53
$[B_6\mathbf{Br}_2I_4]^{2-}$	−14.72	−15.58	−0.86	
$[B_6Br\mathbf{I}_5]^{2-}$	−26.00	−25.86	+0.14	−0.22
$[B_6Br_2\mathbf{I}_4]^{2-}$	−27.26	−27.34	−0.08	−0.22
$[B_6Br_3\mathbf{I}_3]^{2-}$	−28.52	−28.82	−0.30	−0.22
$[B_6Br_4\mathbf{I}_2]^{2-}$	−29.78	−30.30	−0.52	

[a] The respective ^{11}B nuclei under consideration are bonded to the substituents typed with bold letters.

The synthesis of the up to now unique fluoro compounds $[B_6FH_5H^{fac}]^-$ and $[B_6FH_5]^{2-}$ has succeeded only recently. Various experiments with the common fluorination agents had failed because of their acidic character or their too strong oxidation power. However, the desired fluorination product is formed with XeF_2 in dichloromethane at −60° C, even if yield is very low. Decisive progress was made with the commercially available 1-(chloromethyl)-4-fluoro-1,4-diazabicyclo[2.2.2]octane bis(tetrafluoroborate) (abbr.: F-TEDA-$[BF_4]_2$),[72] which has tailor-made properties for this application, and thus enables synthesis of $[B_6FH_5H^{fac}]^-$ (**3a**) (see Figure 3) in 50% yield according to Equation 17. This synthesis concept has successfully applied to prepare fluorine derivatives of $[B_{10}H_{10}]^{2-}$ [73][74] and $[B_{12}H_{12}]^{2-}$.[72]



(17)

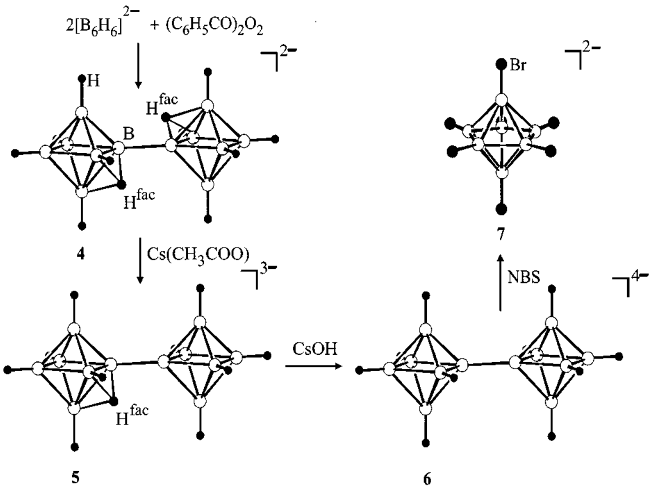
3a

$[nBu_4N][B_6FH_5H^{fac}]$, dissolved in dichloromethane, is deprotonated by $[nBu_4N]OH$, and upon addition of cesium acetate $Cs_2[B_6FH_5]$ is precipitated. The ^{19}F resonances are observed as typical quadrupolar coupled quadruplets due to $I = 3/2$ of ^{11}B with $\delta(^{19}F) = -212.8$, $^1J(^{19}F,^{11}B) = 63$ Hz and $\delta = -209.5$ for the protonated and deprotonated compound, respectively.[72] $^1J(^{11}B,^{19}F)$ coupling is not resolved in the ^{11}B spectra, but is attained from the ^{19}F spectra in the order of 60 Hz. The X-ray structure determination on single crystals of $K_2[B_6FH_5]$ failed because of the orientation disorder of the nearly spherical cluster anions in the unit cell. Therefore, the structural parameters of *closo*-$[B_6FH_5]^{2-}$ have been derived from ab initio calculations on the basis of C_{4v} symmetry at the MP2/6-31G* level revealing B−F and B−B bond lengths of 143.4 and 172.5−173.9 pm, respectively. The results of the ab initio frequency analysis correspond with the assignments and values obtained from normal coordinate analysis, and a good agreement of observed and calculated frequencies is achieved. The valence force constants are $f_d(BB) = 1.92 \cdot 10^2$ and $f_d(BF) = 5.25 \cdot 10^2$ N·m^{-1}.[75]

In resemblance to the iodination reactions (Equations 14b and 14c) $[B_6FH_5]^-$, prepared according to Equation 17, reacts with I_2 in aqueous solution at pH = 9 to give $[B_6FI_5]^{2-}$ {$\delta(^{11}B) = +3.8$ (*ipso*), −30.1 (equatorial), −33.3 (*antipodal*); $\delta(^{19}F) = -247.6$, $^1J(^{19}F,^{11}B) = 54$ Hz} as described by Equation 18.[76]

$$[B_6FH_5]^{2-} + 5\,I_2 \rightarrow [B_6FI_5]^{2-} + 5\,HI \quad (18)$$

In contrast to the perhalogenated *closo*-hexaborates oxidation of $[B_6H_6]^{2-}$ takes a surprising course. In dichloromethane with dibenzoyl peroxide two cluster units are joined by a σ bond with a B−B distance of 170 pm to the novel *conjuncto*-cluster $[H^{fac}H_5B_6{-}B_6H_5H^{fac}]^{2-}$ (**4**). The deprotonation of the dianion proceeds in two steps, first with cesium acetate to the trivalent $[H^{fac}H_5B_6{-}B_6H_5]^{3-}$ (**5**) with pK_a = 9.6, and secondly with CsOH to $Cs_4[H_5B_6{-}B_6H_5]^{4-}$ (**6**).[77] By single-crystal structure analysis of $[Ph_4P]_2[H^{fac}H_5B_6{-}B_6H_5H^{fac}]$ the H^{fac} atoms could not be refined, but their location above the *ipso* spheres is clearly indicated by a 6% expansion of the respective faces adjacent to the B−B bridge. Based on averaged crystallographic data and adopting idealized D_{4h} symmetry a normal coordinate analysis has been performed. With a set of eleven force constants [e.g. $f_d(BB)_{conjuncto} = 2.9 \cdot 10^2$ and $f_d(BB)_{cage} = 1.6 \cdot 10^2$ N·m^{-1}] a very good agreement of observed and calculated frequencies has been achieved.[77] Even more surprising oxidation of **6** with *N*-bromosuccinimide at pH > 9 takes place under expansion of the octahedral core, and heptabromo-*closo*-heptaborate $[B_7Br_7]^{2-}$ (**7**)[78] as the first structurally secured derivative of the parent heptahydro-*closo*-heptaborate $[B_7H_7]^{2-}$ [68][79] is obtained. A single-crystal structure determination has succeeded on its $[(C_5H_5N)_2CH_2]^{2+}$ salt revealing the pentagonal-bipyramidal arrangement of 7 boron atoms.[78] An illustration of these reactions is presented by Scheme 1.



Scheme 1. Oxidation of $[B_6H_6]^{2-}$

Pseudohalo and Chalcogeno Substituents

During reaction of $[B_6H_6]^{2-}$ with the pseudohalogens $(SCN)_2$ or $(SeCN)_2$ in dichloromethane the protonated compounds $[B_6H_5H^{fac}(SCN)]^-$ and $[B_6H_5H^{fac}(SeCN)]^-$ are formed, respectively,[80][81] which can be precipitated on addition of an ethanol solution of cesium acetate as the deprotonated salts $Cs_2[B_6H_5(SCN)]$ and $Cs_2[B_6H_5(SeCN)]$. A crystal structure of $Cs_2[B_6H_5(SCN)]$ with a B−S−C angle of 99.8° clearly indicates S bonding of the thiocyanate.[82] Reaction of $[B_6H_5(SCN)]^{2-}$ with Na in liquid NH_3 yields $[B_6H_5S]^{3-}$, while the analogous Se compound $[B_6H_5Se]^{3-}$ is prepared from $[B_6H_5(SeCN)]^{2-}$ already by treatment with CsOH in dichloromethane/methanol, indicating the less stability of the SeCN group. On $[Ph_4P][B_6H_5H^{fac}(SH)]$ a crystal structure determination has been performed.[83] The protonation of $[B_6H_5S]^{3-}$ is especially interesting, because the following compounds are to be assumed: $[B_6H_5H^{fac}S]^{2-}$, $[B_6H_5(SH)]^{2-}$, $[B_6H_5H^{fac}(SH)]^-$, and $[B_6H_5(SH_2)]^-$. $[B_6H_6(H^{fac})_2S]^-$, $[B_6H_5H^{fac}(SH)_2]$, and $[B_6H_6(H^{fac})_2(SH)]$ are not very likely because of their too strong acidity. Up to now the protolysis equilibria according to Eqations 19a, 19b have been established.[83]

$$[B_6H_5S]^{3-} + H^+ \rightleftharpoons [B_6H_5H^{fac}S]^{2-} \qquad (19a)$$

$$[B_6H_5H^{fac}S]^{2-} + H^+ \rightleftharpoons [B_6H_5H^{fac}(SH)]^- \qquad (19b)$$

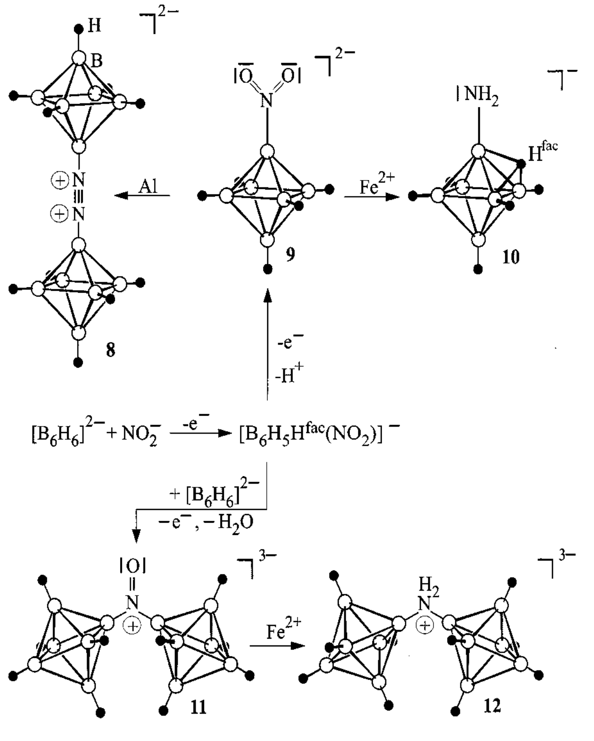
The expected reaction to completely substituted derivatives in analogy to Equation 13 with an excess of $(SCN)_2$ or $(SeCN)_2$ in the presence of a base has been proven to be false.[84] Virtually, the cluster is degraded, and beside the long-known $[B(NCS)_4]^-$ [85] as a main product the novel compound $[B_2(NCS)_6]^{2-}$ is formed.[86] NCS stands for *N*-bonded thiocyanate, while SCN has the meaning of *S*-bonded thiocyanate. In contrast to the well-known boron trihalides this boron tripseudohalide is dimerized. By X-ray structure analysis on the $[Ph_3P{=}N{=}PPh_3]^+$ salt the B−B bond length has been determined to be 173 pm. An extensive vibrational spectroscopic study including ^{10}B and ^{11}B isotopic labeling accompanied by normal coordinate analysis has been performed resulting in the remarkably high force constant $f_d(BB) = 3.62 \cdot 10^2\ N \cdot m^{-1}$.[86] As an interesting feature *N*-bonding has been clearly confirmed by X-ray structure determination for these compounds in contrast to the *closo* clusters, where *S*-bonding prevails without exceptions up to now. The same is found in case of the SeCN compounds $[BH_n(NCSe)_{(4-n)}]^-$ ($n = 0-4$),[87] which has been proven by crystal structures on $[BH(NCSe)_3]^-$ and $[B_3H_7(NCSe)]^-$ [88] in comparison to $[B_6H_5(SeCN)]^{2-}$.[81] Here ^{77}Se-NMR spectroscopy is a valuable tool to distinguish the bonding mode of the selenocyanate: Signals of *N*-bonded substituents are found in the high-field region around $\delta(^{77}Se) = -300$, while *Se*-bonded species resonate in the downfield region between $\delta = 0$ and -100, viz. at $\delta = -72.8$ for $[B_6H_5(SeCN)]^{2-}$, at $\delta = -68.2$ for $[B_{10}H_9(SeCN)]^{2-}$, and even more deshielded at $\delta = -22.6$ for $[B_{12}H_{11}(SeCN)]^{2-}$.[81] During reaction of $[B_6H_6]^{2-}$ with cyanogen $(CN)_2$, which is generated from KCN and $CuSO_4$ in aqueous basic medium, the cyano derivatives $[B_6(CN)H_5]^{2-}$ and *cis*-$[B_6(CN)_2H_4]^{2-}$ are formed, and confirmed by X-ray structure determination.[89]

N-Bonded Substituents

On irradiation of an aqueous alkaline solution of $[B_6H_6]^{2-}$ and nitrite ions with a mercury vapor lamp the color turns to intense blue. From this solution a blue and a yellow product have been isolated by ion exchange chromatography on diethylaminoethylcellulose. On the basis of spectroscopic data these compounds have been assigned erroneously.[90] Both species are also obtainable, however in very low yields, from $[nBu_4N]_2[B_6H_6]$ in acetonitrile by addition of isopentyl nitrite. The highest yields of 8% for both of the compounds are attained during electrolysis of a dichloromethane solution containing $[nBu_4N][B_6H_6H^{fac}]$, $[nBu_4N]NO_2$, and 8-diazabicyclo[5.4.0]undec-7-ene (abbr.: DBU) as a base at a platinum electrode in the separated anodic room of an electrolysis cell with a carbon cathode. The single-crystal X-ray analysis revealed, that the yellow compound is the mononitro derivative $[B_6H_5(NO_2)]^{2-}$ (**9**),[91] and the blue compound is the dimeric bridged species $[H_5B_6{-}(NO){-}B_6H_5]^{3-}$ (**11**).[92] *Caution! Both compounds are stable as Cs salts, however, they explode if only are touched. By anodic oxidation of* $[B_6H_5(NO_2)]^{2-}$*, the yellow, highly explosive cis-*$[B_6H_4(NO_2)_2]^{2-}$ *has become feasible.*[93] The mononitro compound $[B_6H_5(NO_2)]^{2-}$ (**9**) is reduced with Fe^{2+} in aqueous alkaline solution to the amine derivative $[B_6H_5H^{fac}(NH_2)]^-$ (**10**) analogous to aniline. Although H^{fac} could not be refined by X-ray structure analysis, it is likely positioned between a B_3 facet and the free electron pair of the NH_2 group.[94] If aluminum is used as a reducing agent in place of Fe^{2+}, the reduction process is ceased at the state of zero-valent nitrogen, and two cluster units are bridged by a triply bonded dinitrogen molecule according to Equation 20.

$$2\,[B_6H_5(NO_2)]^{2-} + 2\,Al + 4\,H_2O \rightarrow [H_5B_6{-}N{\equiv}N{-}B_6H_5]^{2-} + 2\,[Al(OH)_4]^- \quad (20)$$

The X-ray structure analysis of μ-dinitrogenbis(pentahydro-*closo*-hexaborate) (**8**) succeeded on single crystals of the tetraphenylarsonium $[Ph_4As]^+$ salt.[95] In the same way as for $[B_6H_5(NO_2)]^{2-}$ reduction with Fe^{2+} in alkaline solution is applicable to $[H_5B_6{-}(NO){-}B_6H_5]^{3-}$ (**11**), and yields the amido-bridged derivative $[H_5B_6{-}(NH_2){-}B_6H_5]^{3-}$ (**12**).[96] According to its Brønsted base character two protons are added in neutral aqueous solution to give $[H^{fac}H_5B_6{-}(NH_2){-}B_6H_5H^{fac}]^-$, and the X-ray structure has been solved, however without refinement of H^{fac}.[96] The reactions and connections between the derivatives with N-substituents are shown in Scheme 2. Furthermore *cis*-$[B_6(CN)H_4(NO_2)]^{2-}$ and *cis*-$[(CN)H_4B_6{-}(NO){-}B_6H_4(CN)]^{3-}$ have been prepared and structurally characterized.[97] A highly interesting arrangement of B_6 in a cyclic structure has been found for hexakis(diethylamino)-*cyclo*-hexaborane $[B_6\{N(C_2H_5)_2\}_6]$,[98] however, the claimed interconversion of the *cyclo* structure to the octahedral structure could not be verified by X-ray structure determination.



Scheme 2. Derivatives of $[B_6H_6]^{2-}$ with N substituents

Organic Substituents

As already discussed in detail *closo*-$[B_6H_6]^{2-}$ is a Brønsted base with a pK_a value of 7.0. This fact will be of crucial importance during the following substitution reactions, because all protonated *closo*-hexaborates are inaccessible to substitution. This subject has already been discussed in the sections on the halogens and *pseudo*-halogens, and the same is true for the alkylation reactions. It is also the reason for the quite different alkylation conditions observed for the *closo*-borates. While the higher members $[B_{10}H_{10}]^{2-}$ and $[B_{12}H_{12}]^{2-}$ react under acidic conditions,[99] $[B_6H_6]^{2-}$ demands at least neutral solutions for the first substitution step and strong basic media for subsequent substitutions. In this way *mono*-, *di*-, and *tri*-alkyl-*closo*-hexaborates have been synthesized utilizing alkyl halides as alkylation agents.[100][101] On principle, all organic solvents must be dried accurately prior to use in order to maintain $[B_6H_6]^{2-}$ really in its deprotonated state.

For introduction of alkyl substituents $[nBu_4N]_2[B_6H_6]$ is dissolved in dichloromethane or acetonitrile and treated with alkyl halides.[101] According to common organic concepts the alkyl carbon atom attached to the halogen atom is more positive through the −I effect of the halogen according to $R{-}C^{\delta+}{-}X^{\delta-}$, and an electrophilic attack on the region of maximum electron density above the octahedron facets is to be assumed. The resulting transitory state with a four-center, two-electron (4c2e) $C^{\delta+}{-}B_3$ interaction is stabilized by displacement of an *exopolyhedral* H atom from a vertex onto a facet of the B_6 cluster giving a more favorable 4c2e $H^{fac}{-}B_3$ bond and a common 2c2e B−C σ-bond under liberation of the respective halide ion. The course of alkylation reactions is exemplified by Equation 21.

$$[nBu_4N]_2[B_6H_6] + RX \rightarrow [nBu_4N][B_6H_5H^{fac}R] + [nBu_4N]X\ (R = CH_3, C_2H_5, n\text{-}C_3H_7, n\text{-}C_4H_9, n\text{-}C_8H_{17}) \quad (21)$$

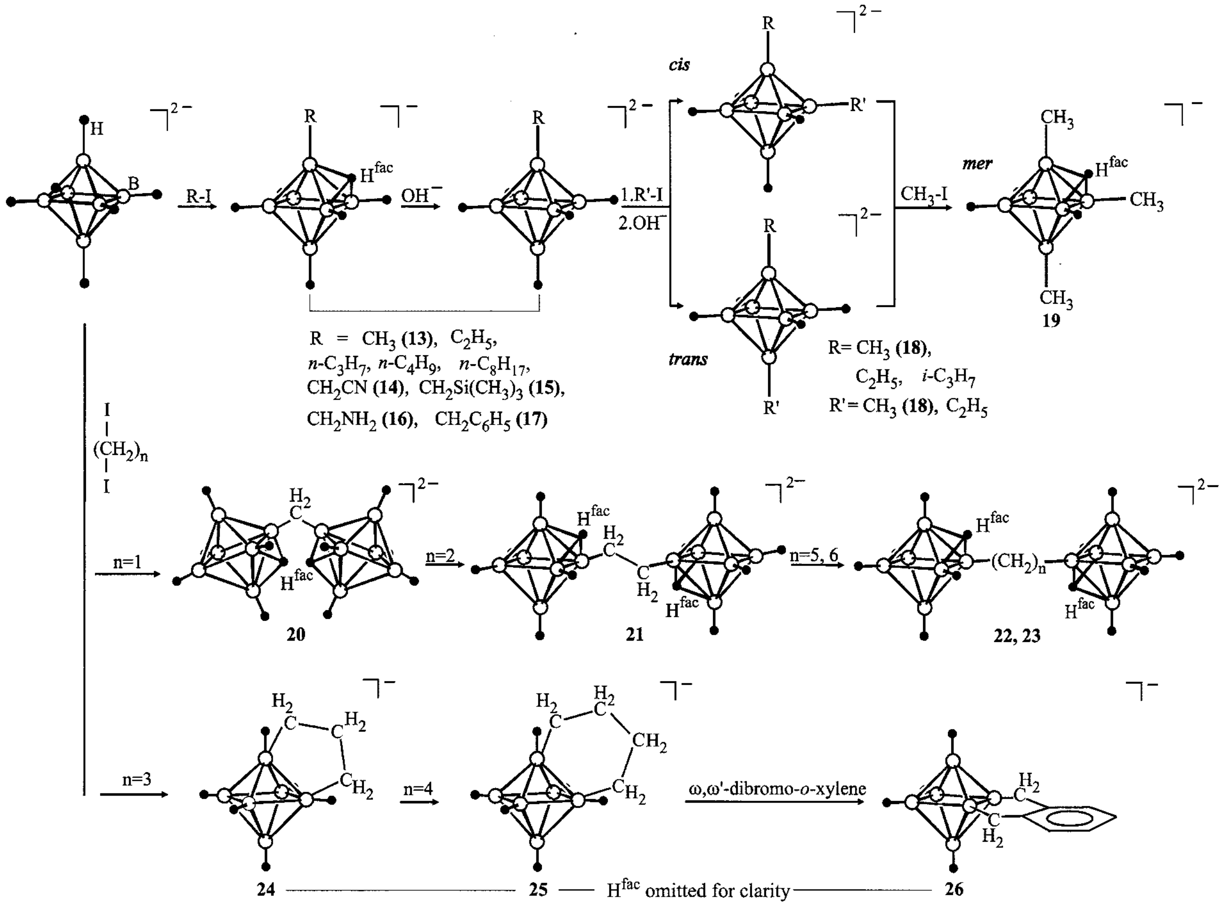
Alkyl iodides have proven as the most suitable agents, but as reactivity generally decreases with increasing chain length, *n*-octyl iodide, for example, must be applied in large excess and at 80° C to obtain $[B_6(n\text{-}C_8H_{17})H_5H^{fac}]^-$.[80] In the series of alkyl derivatives the Brønsted base character increases with increasing chain length, as is demonstrated by the pk_a values: 8.85 for CH_3, 9.50 for C_2H_5, 9.55 for n-C_3H_7 and 9.60 for both n-C_4H_9 and n-C_8H_{17}.[80] Deprotonation and precipitation as Cs salts is accomplished by addition of CsOH, dissolved in ethanol, to the dichloromethane solutions of $[nBu_4N][B_6H_5H^{fac}R]$ as given by Equation 22.

$$[nBu_4N][B_6H_5H^{fac}R] + 2\,CsOH \rightarrow Cs_2[B_6H_5R] + [nBu_4N]OH + H_2O \quad (22)$$

The Cs salts are soluble in water, but show markedly basic reactions due to protolysis according to Equation 23.

$$[B_6H_5R]^{2-} + H_2O \rightleftharpoons [B_6H_5H^{fac}R]^- + OH^- \quad (23)$$

As to be seen from Equation 21 the formation of the protonated compounds is unavoidable, and reaction is stopped at the monosubstituted state. For further substitution well-considered deprotonation procedures are required, which may be exemplified in the following substitution series: The $[Ph_4As]^+$ salt of the protonated compound of choice is suspended in strong basic aqueous solution. In this way colorless $[Ph_4As][B_6H_5H^{fac}R]$ (**13−17**) is transformed to yellow $[Ph_4As]_2[B_6H_5R]$. The isolated deprotonated monoalkyl derivative is treated with the neat alkyl iodide of choice, whereupon the solid is decolorized. The colorless product $[Ph_4As][B_6H_4H^{fac}RR']$ (**18**) is dissolved in acetonitrile, and on addition of CsOH in 2-propanol *cis*- and *trans*-$Cs_2[B_6H_4RR']$ are obtained (R = CH_3, C_2H_5, *i*-C_3H_7; R′ = CH_3, C_2H_5).[102] With the up to now highest degree of alkylation the threefold methylated compound *mer*-$[B_6(CH_3)_3H_3H^{fac}]^-$ (**19**) has been synthesized, which refuses deprotonation, and thus further substitution. It is prepared from *cis*- or *trans*-$[Ph_4As]_2[B_6(CH_3)_2H_4]$ (**18**), which is obtained in the manner described above, on digestion with CH_3I (see Scheme 3, 1st row).



Scheme 3. Alkylation of $[B_6H_6]^{2-}$

Additionally, the derivatives $[B_6(CH_2CN)H_5H^{fac}]^-$ (**14**) $pK_a = 5.85$,[103] $[B_6\{CH_2{-}Si(CH_3)_3\}H_5H^{fac}]^-$ (**15**), $\delta(^{29}Si) = 2.25$,[104] $[B_6(CH_2NH_2)H_5H^{fac}]^-$ (**16**),[105] and $[B_6\{CH_2(C_6H_5)\}H_5H^{fac}]^-$ (**17**)[106] are to be mentioned for the sake of completeness, which have been synthesized from $[nBu_4N]_2[B_6H_6]$ by reaction with chloroacetonitrile, trimethyliodomethylsilane, *N*-(chloromethyl)phthalimide, and benzyl bromide, respectively.

By reaction of $[B_6H_6]^{2-}$ with ω,ω′-diiodoalkanes $I{-}(CH_2)_n{-}I$ (n = 1, 2, 5, and 6) dicluster anions $[H^{fac}H_5B_6{-}(CH_2)_n{-}B_6H_5H^{fac}]^-$ are formed, which are built up from two protonated cluster anions bridged by methylene or a methylene chain. $[H^{fac}H_5B_6{-}(CH_2){-}B_6H_5H^{fac}]^-$ (**20**) has a bent structure and two ionizable protons with $pK_{a1} = 6.0$ and $pK_{a2} = 10.9$[107]. For $[H^{fac}H_5B_6{-}(CH_2)_2{-}B_6H_5H^{fac}]^-$ (**21**)[108] only a single pK_a value = 10.9 has been found, and the same applies to the μ-pentamethylene (**22**) and μ-hexamethylene (**23**) derivatives with $pK_a = 8.8$ and $pK_a = 9.1$,[109] respectively. (see Scheme 3, 2nd row).

Interestingly, alkylation with 1,3-diiodopropane or 1,4-diiodobutane prefers an intramolecular route, and the two boron atoms of an edge of the octahedron are substituted resulting in *ansa*-like species with five- or six-membered anellated rings, respectively.[100] Both compounds are isolated in their protonated form $[B_6({-}CH_2{-}CH_2{-}H_2C{-})H_4H^{fac}]^-$ (**24**) and $[B_6({-}CH_2{-}CH_2{-}CH_2{-}H_2C{-})H_4H^{fac}]^-$ (**25**) (see Scheme 3, 3rd row). Although H^{fac} could not be refined during X-ray structure analysis, its location is clearly indicated by markedly expanded B_3 facets.[100] Another six-membered anellated ring system featuring the interesting connection of a two- and a three-dimensional aromatic system is provided by *cis*-$[B_6$(*o*-xylene)$H_4H^{fac}]^-$ (**26**, see Scheme 3, 3rd row), which is obtained with ω,ω′-dibromo-*ortho*-xylene as alkylating agent. Structures have been solved of single crystals of the tetraphenylphosphonium $[Ph_4P]^+$ salt and the $[nBu_4N]^+$ salt.

Refinement of H^{fac} failed in the former case, but succeeded in the latter with $B-H^{fac}$ distances ranging from 111 pm to 148 pm and an expansion of the corresponding B_3 facet by about 7%.[110] A selection of the essentials of alkylation reactions is given by Scheme 3.

Very recently, the first aryl derivative the $[B_6(p\text{-}C_6H_4-NO_2)H_5H^{fac}]^-$ has been obtained by reaction of $[B_6H_6]^{2-}$ with *para*-bromonitrobenzene in acetonitrile and isolated in its deprotonated form as the red salt $Cs_2[B_6(p\text{-}C_6H_4-NO_2)H_5H^{fac}]$. After complete chlorination with *N*-chlorosuccinimide an X-ray structure determination succeeded on single crystals of $[(C_5H_5N)_2CH_2][B_6(p\text{-}C_6H_4-NO_2)Cl_5]$.[111] The reduction of $[B_6(p\text{-}C_6H_4-NO_2)H_5H^{fac}]^-$ with Fe^{II}, Al, and Raney-Ni in the presence of N_2H_4 results in a deep blue compound, which in all probability is the diazo compound $[H_5B_6-C_6H_4-N{\equiv}N-C_6H_4-B_6H_5]^{2-}$, as derived from ^{11}B- and ^{14}N-NMR data.[112]

Additionally, the following explosive alkylnitro derivatives have been synthesized and characterized by X-ray structure determination: *cis*-$[B_6(CH_3)H_4(NO_2)]^{2-}$, *fac*- and *mer*-$[B_6(CH_3)H_3(NO_2)_2]^{2-}$,[113] and *cis*-$[B_6(C_2H_5)H_4(NO_2)]^{2-}$.[114] From the structural data is to be seen, that the B_6 cage is expanded in direction towards the substituents in case of alkyl,[101][102] while it is compressed in case of cyano,[89] nitro,[91] and halo[62][115] substituents with shortening of the cage B···B diagonal distances in the order of 5−10%.

In an effort to obtain more insight into the influence of the localization of H^{fac}, and to calculate the energetic barrier of movement of H^{fac}, ab initio calculations have been performed with the GAUSSIAN 94[116] program. Structure optimization has been done according to standard methods on HF/6-31G*-basis, and the hyper face minimum has been confirmed by analytical frequency analysis.[117] The refinement of geometry and the calculation of the total energies is performed on MP2/6-31G* level assuming C_{4v} symmetry for $[B_6FH_5]^{2-}$ (**3**) and $[B_6(CH_3)H_5]^{2-}$ (**13**) and their respective protonated derivatives both for localization of H^{fac} above an *antipodal* facet (**3a** and **13a**) and an *ipso* facet (**3b** and **13b**) (see Figure 3). Similar to $[B_6H_6]^{2-}$ an energy of approx. 450 kcal·mol^{-1} is gained by protonation. This corresponds to the property of the monosubstituted derivatives to act as Brønsted bases. The relative energetic differences between *ipso* and *antipodal* protonation are indeed small, however, they are in agreement with the results of the ^{11}B-NMR investigations.[54] The fluorine compound is more stable by about 1 kcal·mol^{-1} in case of *antipodal* protonation (**3a**) as compared to *ipso* protonation (**3b**). For the methyl compound the opposite behavior is observed, and an even smaller gain in stability of merely 0.06 kcal·mol^{-1} results with *ipso* protonation (**13c**) in comparison to *antipodal* protonation (**13a**). However, the *ipso* localization of H^{fac} (**13b**) is affirmed by NMR investigations[54] and X-ray structure analysis.[101]

Between H^{fac} and the H atoms of the methyl group in $[B_6H_5H^{fac}(CH_3)]^-$ distances of 258, 279, and 320 pm have been obtained from X-ray structure. As a consequence an assumed nuclear Overhauser interaction could be proven by 2D-^1H-NOESY NMR spectroscopy. This may be the reason for the decreased tendency of $[B_6H_5H^{fac}(CH_3)]^-$ with $pK_a = 8.85$[80] to dissociate in comparison to $[B_6H_6H^{fac}]^-$ with $pK_a = 7$[14] and $[B_6H_5H^{fac}F]^-$ with $pK_a = 5$.[72] Further, the obtained structure parameters served as a basis for calculation of the NMR shifts making use of the RHF/GIAO method[118] with an Ahlrichs tzp basis set.[119] In order to eliminate the solvent influence on the chemical shift referencing was done by use of signals of the respective deprotonated parent compounds in the same solvent as secondary standards. The ^1H-, ^{11}B-, ^{13}C-, and ^{19}F-NMR shifts have been calculated and found in good agreement with experimental data.[120] Furthermore, former results of vibrational spectroscopic assignments and the results of normal coordinate analyses could be verified by the ab initio frequency analyses. In good agreement with the experimental data[14] the ab initio calculations result in shifts of the terminal B−H valence modes by about 100 to 200 cm^{-1} to higher frequencies for the protonated cluster anions. This is consistent with the calculated shortening of the B−H distances. An effect of the protonation is also observed on the vibrational frequencies of polyatomic substituents. Accordingly, the C−H valence vibration of $[B_6(CH_3)H_5H^{fac}]^-$ is shifted to higher energy by about 150 cm^{-1} in comparison to $[B_6(CH_3)H_5]^{2-}$.[54] The symmetric and antisymmetric vibration of H^{fac} against the B_3 facet have not been observed, but are calculated to 1820 and 1295 cm^{-1} for *antipodal*-localized H^{fac}, and to 1791 and 1275 cm^{-1} for *ipso*-localized H^{fac}, respectively.[54]

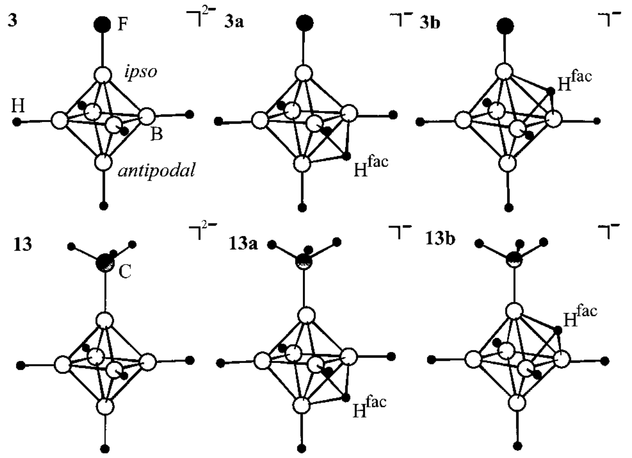


Figure 3. Localization of H^{fac} in monosubstituted $[B_6H_6]^{2-}$

The chemical shift of the nonequivalent ^{11}B nuclei in monosubstituted derivatives of $[B_6H_6]^{2-}$ and the mutual influence of substitution on the *ipso* and the *antipodal* B atoms depends on the electronegativity, the polarizability, and the spin orbit coupling of that atom bound to the cluster. While the signals of the equatorial B atoms are found nearly uninfluenced around $\delta = -15$, the resonances of the *ipso*- and *antipodal*-B are shifted increasingly with decreasing electronegativity or with increasing polarizability and spin orbit coupling, namely to high field for the *ipso*-B and downfield for the *antipodal*-B. These qualitative trends are visualized by Figure 4.

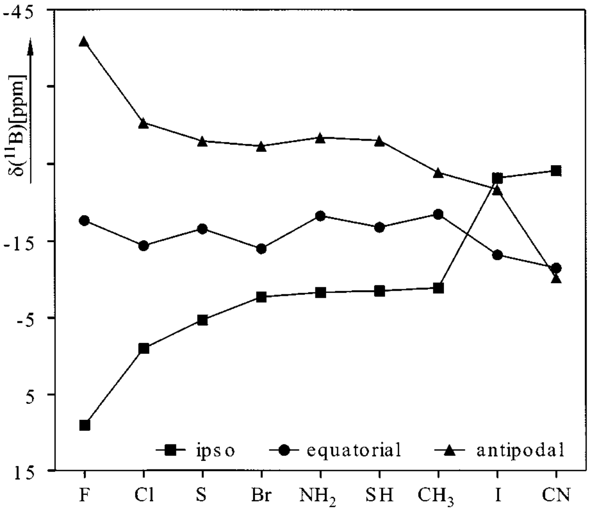


Figure 4. ^{11}B-NMR shifts of monosubstituted derivatives $[B_6H_6]^{2-}$

$[B_6H_6]^{2-}$ as a Ligand in Metal Complexes

In contrast to the higher *closo*-borates only a few metal derivatives are known for *closo*-$[B_6H_6]^{2-}$. By reaction of the nucleophilic nickelocene with $[B_6H_6]^{2-}$ two electrons are donated to the boron cluster, reducing it to the hypothetical $[B_6H_6]^{4-}$,[11] and induce cage opening. By elimination of a cyclopentadienyl ligand from Ni and oxidative addition of the borate moiety Ni atoms are built into the boron core, and under expansion of the octahedron the *closo*-metallaborates $[(\eta^5\text{-}C_5H_5)NiB_6H_6]^-$ [11][121] and $[(\eta^5\text{-}C_5H_5)_3Ni_3B_6H_6]^-$ [122] are formed, which correspond to the parent *closo*-borates $[B_7H_7]^{2-}$ [68][79] and $[B_9H_9]^{2-}$.[123] In contrast to the reaction of nickelocene with $[B_6H_6]^{2-}$ from cobaltocene and $[B_6H_6H^{fac}]^-$ the molecule compound $[(\eta^5\text{-}C_5H_5)Co(\eta^5\text{-}C_5H_4)B_6H_5H^{fac}]$ is formed with a normal σ(B−C) bond from one of the cyclopentadienyl groups C atoms to a vertex of the B_6 cluster having a bond length of 157.5 pm.[124]

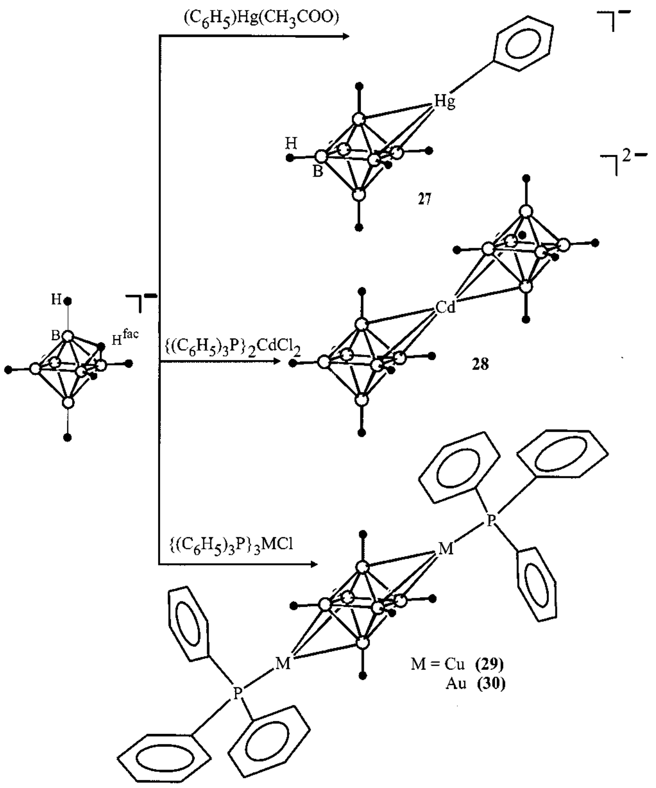
In accordance with the high electron density above the octahedral B_3 facets $[B_6H_6]^{2-}$ can act as a Lewis base and coordinate in a 4c2e bond to the metal atom of a complex. In this way $[(C_6H_5)Hg(\eta^3\text{-}B_6H_6)]^-$ (**27**) was synthesized from phenylmercury acetate, and its structure was solved on the $[Ph_4P]^+$ salt with B−Hg distances from 240 to 243 pm indicating the localization above one facet, the edges of which are markedly elongated to 183 pm.[125] In CD_2Cl_2 at 263 K a singlet has been recorded with $\delta(^{199}Hg) = -74$ vs. $Hg_2(NO_3)_2$ saturated in D_2O. However, the *hapticity* of $[B_6H_6]^{2-}$ must not be inevitably three, but may be two. This has been found in $[(2,2'\text{-bipyridine})Pb(\eta^{2,3}\text{-}B_6H_6)]$, in which $[B_6H_6]^{2-}$ is coordinated via an η^2-B_2 edge as well as via an η^3-B_3 facet,[126] although considerable long Pb−B_3 distances of about 280 pm resulted for the η^3 coordination.

Two η^3-$[B_6H_6]^{2-}$ ligands, which are symmetrically arranged with distances of 218 pm from the Cd^{2+} center to the B_3 planes, are found in $[Cd(\eta^3\text{-}B_6H_6)_2]^{2-}$ (**28**),[127] which has been prepared from $[B_6H_6]^{2-}$ and $[\{(C_6H_5)_3P\}_2CdCl_2]$. The ^{113}Cd resonance of **28** in CD_2Cl_2 is found in the low-field region at $\delta(^{113}Cd) = 117$ vs. 3 M $Cd(NO_3)_2$ in D_2O at $\delta = -692.1$. From a view on the structure the term of a Cd^{2+} sandwich complex with the two B_6 clusters as three-dimensional aromatic systems seems to be justified.

During the reactions of $[\{(C_6H_5)_3P\}_3MCl]$, M = Cu and Au, with $[B_6H_6]^{2-}$ the binuclear complexes $[\{(C_6H_5)_3P\}_2M_2(\mu\text{-bis-}\eta^3\text{-}B_6H_6)]$ (**29**, **30**) are formed, containing $[B_6H_6]^{2-}$ as a bridging ligand in a bis(tri-*hapto*) mode of two opposite B_3 facets.[128] The metal centers in **29** and **30** are found in remarkably short distances of about 210 pm above the B_3 planes. The Au compound **30** has been obtained in two polymorphous forms in dependence of the crystallization conditions. While from dichloromethane solutions on slow diffusion of methylbutane, isopentane, or petroleum ether large cubic crystals (form A, space group *Pa*3bar) are precipitated, the same procedure with diethyl ether or *n*-pentane yields needles (form B, space group *Pccn*).[129] The coordinating B_3 facets are markedly expanded in both cases, viz. by 6% in A and 8% in B. However, packing in the elementary cells is different. The molecules in A are stacked loosely against one another, whereas in form B compact infinite stacking is to be seen. Therefore, the difference of about 40% in the calculated densities $\rho(A) = 1.326$ and $\rho(B) = 1.885\ g\cdot cm^{-3}$ (B) is surprising. In analogy to the reactions of Cu and Au $[\{(C_6H_5)_3P\}_3AgCl]$ forms with $[B_6H_6]^{2-}$ in a first step $[\{(C_6H_5)_3P\}_2Ag_2\{\mu\text{-bis}(\eta^3\text{-}B_6H_6)\}]$. However, this complex is very instable, and due to the lack of suitable single crystals structural proof by X-ray analysis has not yet been done. The ^{11}B-NMR spectra agree with those of the respective Cu and Au complexes. During decomposition of the initial product metallic silver is precipitated, and from the remnants a dichloromethane adduct of *hypho*-decahydrohexaborane $[\{(C_6H_5)_3P\}_2B_6H_{10}]\cdot CH_2Cl_2$ could be crystallized, and its structure could be solved.[130] This is the first documented example for the opening of a *closo*-B_6 cluster to a *hypho*-hexaborane. An illustration of the versatile ligating capabilities of $[B_6H_6]^{2-}$ is given in Scheme 4.

Concluding Remarks

Systematically synthesized derivatives of the hexahydro-*closo*-hexaborate $[B_6H_6]^{2-}$ with classical inorganic and organic substituents were characterized structurally and spectroscopically. In this way, a better insight into the chemical and physical properties of this class of compounds was gained, and strong mutual support of the ab initio results and the experimental data could be achieved. As a central point of the reaction chemistry the protolysis behavior and its special importance during substitution reactions was discussed. The localization of the additional proton H^{fac}, bound in the solid state above one of the facets of the octa-



Scheme 4. $[B_6H_6]^{2-}$ as a tri-*hapto* ligand in metal complexes

hedron via a 4c2e bond, could be refined in several X-ray structures. In the solution state clear evidence of H^{fac} was given by ^{1}H-NMR spectroscopy. The dynamic behavior due to the fluctuation of H^{fac} across the octahedron facets in the parent compound $[B_6H_6H^{fac}]^-$ and the $[B_6H_5H^{fac}X]^-$ species was elucidated by variable-temperature ^{11}B-NMR spectroscopy and determination of the coalescence points. The interrelations between symmetry, electronic and geometrical structure, and spectroscopic properties could be demonstrated by the monosubstituted derivatives as instructive examples for the energetic difference between the *ipso* and the *antipodal* sphere arising through substitution. The effect of this imbalance depends on the nature of the substituent. This has been proven by single-crystal X-ray structure determinations and different NMR-spectroscopic techniques, and has been affirmed by ab initio calculations with the GAUSSIAN 94 program on the MP2/6-31G* level resulting in a consistent discussion of the experimental and theoretical data with strong mutual support. From the empirical data the following facts could be manifested:

- $pK_a < 7$ for X = halogen, pseudohalogen or NO_2,$pK_a > 7$ for X = alkyl
- In solid salts and in solution below the coalescence temperature H^{fac} is fixed above one of the *antipodal* facets in the case of halogen and pseudohalogen substituents, while it resides above one of the *ipso* facets in the case of alkyl substituents. The B_3 facets capped by H^{fac} are generally expanded by 5−8%.
- On substitution the octahedral B_6 cage is deformed with changes of the diagonal cage B···B distances up to 5−10%. It is compressed in direction towards the substituents in the case of halogen, pseudohalogen or N-substituents and expanded in direction towards substituents in the case of alkyl.
- The synthesis of bis(heteroleptic) derivatives $[B_6X_nY_{(6-n)}]^{2-}$ ($n = 1-5$, $X \neq Y$ = Cl, Br, I) requires that in a synthetic route the more electronegative substituent must be introduced at first, and then the less electronegative substituent as the second.
- During repeated substitution further substituents are directed in *trans*/*mer* position by I^- and in *cis* positions by NO_2^- and CN^-.
- A systematic *antipodal* influence within the complete series of persubstituted mixed halo-*closo*-hexaborates $[B_6Cl_nBr_{(6-n)}]^{2-}$, $[B_6Cl_nI_{(6-n)}]^{2-}$, and $[B_6Br_nI_{(6-n)}]^{2-}$ ($n = 1-5$) has been found, and therefrom for each series a characteristic *antipodal* shift constant (ASC) has been derived.

Besides this subsumption of the results of systematic synthetic work, which is already a good justification to pursue derivative chemistry, some reactions of the *closo*-B_6 parent compound have led unintentionally into new directions: Under formation of a B−B bond the *conjuncto* compounds $[H^{fac}H_5B_6{-}B_6H_5H^{fac}]^{2-}$ and $[H_5B_6{-}B_6H_5]^{4-}$ were formed, and therefrom by expansion the first structurally characterized *closo*-heptaborate $[B_7Br_7]^{2-}$ was established. Another new field of research is the introduction of $[B_6H_6]^{2-}$ as a ligand in coordination compounds, bound in an η^3 fashion to metal centers like Pb^{2+}, Cd^{2+}, Hg^+, Cu^+, Ag^+, and Au^+. For the first time opening to a *hypho*-borane of a ligated $[B_6H_6]^{2-}$ to Ag^+, the decahydrohexaborane B_6H_{10}, has been realized. Last, but not least the planned expansion of the octahedral cage by metal atoms to form hydro-*closo*-metallaborates with some examples of Ni is in its beginning, and promises interesting new pathways.

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