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Published on Web 04/06/2002

Gas-Phase Stability of Derivatives of the *closo*-Hexaborate Dianion $B_6H_6^{2-}$

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Received December 10, 2001. Revised Manuscript Received February 4, 2002

Abstract: $B_6H_6^{2-}$ does not represent a stable gas-phase dianion, but emits spontaneously one of its excess electrons in the gas phase. In this work we address the question whether *small* stable gas-phase dianions can be constructed from the parent $B_6H_6^{2-}$ dianion by substitution of the hydrogens with appropriate ligands. Various hexa-, tetra-, and disubstituted derivatives $B_6L_6^{2-}$, $B_6H_2L_4^{2-}$, and $B_6H_4L_2^{2-}$ (L = F, Cl, CN, NC, or BO) are investigated with ab initio methods in detail. Four stable hexasubstituted $B_6L_6^{2-}$ (L = Cl, CN, NC, or BO) and three stable $B_6H_2L_4^{2-}$ (L = CN, NC, or BO) gas-phase dianions could be identified and predicted to be observable in the gas phase. The trends in the electron-detachment energies depending on various ligands are discussed and understood in the underlying electrostatic pattern and the electronegativities of the involved elements.

1. Introduction

The study of boron hydrides is a classic field in inorganic chemistry, and its development was, and still is, characterized by an interplay of theoretical and synthetic progress. After the pioneering works of Alfred Stock, who managed to prepare boron hydrides,[1] the description of the bonding in these electron-defficient molecules has been a problem in theoretical chemistry for many years. The bonding situation in the boron hydrides can be explained with the existence of three-center two-electron bonds, a concept which led Lipscomb to the formulation of the so-called styx-code, which allows description and prediction of the topology of the boron hydrides.[2,3] Further theoretical and experimental progress made the detailed investigation of the relationship between structure and electron number possible, and provided the foundation for the generalized electron count schemes known as Wade's rules.[4−6] According to Wade's rules, the boron hydrides can be placed into groups according to the number of electron pairs associated with cage bonding. The designations are *closo*, *nido*, and *arachno* for cages with $n + 1$, $n + 2$, and $n + 3$ electron pairs, respectively, where n is the number of vertices. In general, as the number of electron pairs increases for a cage with a constant number of vertices, the structure becomes more open.

The most structurally appealing boron hydrides are the hydro-*closo*-borates $B_nH_n^{2-}$, the structures of which are based on regular polyhedra with triangular faces, sometimes called deltahedra.[7] The existence of the dianionic species $B_nH_n^{2-}$ ($n = 5-12$) was predicted theoretically in 1954,[8−10] but it took another five years before salts of the exceptionally stable $B_{10}H_{10}^{2-}$ [11] and $B_{12}H_{12}^{2-}$ [12] could be synthesized in 1959. Until today, the smallest member of the hydro-*closo*-borate family that has been synthesized is $B_6H_6^{2-}$, which is only moderately stable in condensed phases.[13] Its octahedral structure has been confirmed by X-ray analysis of its $[Me_4N]^+$,[14] K^+, and Cs^+ salts,[15] as well as by NMR[16,17] and vibrational spectroscopy[18] for the solution state. Soon after their detection, a broad derivative chemistry was been established for $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$.[19] In contrast, the only derivative of $B_6H_6^{2-}$ known until 1984 was $B_6Br_6^{2-}$,[20] and a derivative chemistry started with the syntheses of the hexahalo-*closo*-borates $B_6X_6^{2-}$ (X = Cl, Br, or I)[21] and their spectroscopic characterization.[22,23] Today, several derivatives of $B_6H_6^{2-}$ have been prepared and

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10.1021/ja012681j CCC: $22.00

analyzed,[24] for example, bis-*heteroleptic* halo derivates $B_6X_nY_{(6-n)}^{2-}$ ($n = 1-5$, $X \neq Y = Cl, Br, or I$)[25] and pseudohalogeno- and chalcogeno-substituted species, like $B_6H_5(SCN)^{2-}$,[26] $B_6H_5(CN)^{2-}$, and *cis*-$B_6H_4(CN)_2^{2-}$.[27]

Although $B_6H_6^{2-}$ is now well-known in the chemistry of condensed phases, it has been shown theoretically that $B_6H_6^{2-}$ does not exist in the gas phase but spontanously emits one of its excess electrons.[28] Furthermore, calculations on a series of hydro-*closo*-borates $B_nH_n^{2-}$ ($n = 5-17$) have revealed that all small members with $n = 5-11$ are electronically unstable, while $B_{12}H_{12}^{2-}$ is the first electronically stable hydro-*closo*-borate cluster. $B_{13}H_{13}^{2-}$ is again unstable, but from that size on all larger members of the hydro-*closo*-borate family are stable with respect to electron autodetachment in the gas phase.[29]

Today, it is a well-established fact that most of the multiply charged anions (MCAs) known from condensed phases, such as carbonate CO_3^{2-},[30−32] sulfate SO_4^{2-},[33−35] or phosphate PO_4^{2-},[33] do not represent stable gas-phase entities owing to the strong Coulomb repulsion between the two excess negative charges. In contrast to these examples of electronically unstable MCAs, several small dianions have been found experimentally and theoretically to be long-lived in the gas phase.[36−39] Such small dianions are, for example, LiF_3^{2-},[40] BeF_4^{2-},[41−43] C_7^{2-},[44,45] S_n^{2-},[46] $S_2O_6^{2-}$,[34,35] SiC_6^{2-},[47−49] BeC_4^{2-},[50,51] $PtCl_4^{2-}$,[52,53] ZrF_6^{2-},[54,55] MF_6^{2-} (M = Sc, Y, or La),[56] SeF_8^{2-},[57] and $Mg_2S_3^{2-}$.[58] It is worth mentioning that the theoretical prediction of the dianions BeF_4^{2-} [41] and SiC_6^{2-} [48] encouraged the experimental search for these species, which has culminated in their mass spectrometric detection.[43,49]

Turning back to the *closo*-hexaborate family of dianions, the instability of the hexahydro-*closo*-hexaborate $B_6H_6^{2-}$ gives rise to the question of whether some of the synthesized derivatives, e.g. $B_6Cl_6^{2-}$ or $B_6H_4(CN)_2^{2-}$, could be stable gas-phase dianions. It is more generally asked whether it is possible to generate free, stable *closo*-hexaborate dianions by substitution of the hydrogens of the parent hexahydro-*closo*-hexaborate with appropriate ligands? To answer these questions we have examined the gas-phase stability of hexa-, tetra-, and disubstituted *closo*-hexaborate dianions, $B_6L_6^{2-}$, $B_6H_2L_4^{2-}$, and $B_6H_4L_2^{2-}$ (L = F, Cl, CN, NC, or BO), with standard ab initio quantum chemical methods. We focus on the electronic stability of the dianions in the gas phase and discuss the influence of the different ligands on the geometric and electronic properties of the dianions. The paper is organized as follows. After computational details of our investigation are given in Section 2, we present our results for the derivatives of $B_6H_6^{2-}$ (Section 3). The paper concludes with a brief summary of our main results.

2. Computational Details

The theoretical investigation of the *closo*-hexaborate dianions $B_6L_6^{2-}$, $B_6H_2L_4^{2-}$, and $B_6H_4L_2^{2-}$ (L = H, F, Cl, CN, NC, BO, or CCH) comprises the geometry optimization at the standard self-consistent field (SCF) Hartree−Fock (HF) level of theory. The geometry optimizations within a given symmetry group (O_h for the $B_6L_6^{2-}$ and D_{4h} for the H-substituted systems) were carried out until the geometrical parameters corresponding to a stationary point were found. For all stationary points, the harmonic vibrational frequencies were calculated, and all possess only real values, i.e., all investigated dianions represent minima on the corresponding potential energy surface (PES). Furthermore, the equilibrium geometries of those dianions that were found to be stable at the SCF geometries were reoptimized at the theoretical level of second order Møller−Plesset perturbation theory (MP2) to include electron correlation into the geometry optimization step.

The electronic stability of a given dianion is investigated by calculation of the binding energy of the excess electrons, which is quantified by the electron detachment energy (EDE). The EDE can be computed in two conceptually different ways. The EDE can be calculated with the so-called “direct methods”, of which we have employed Koopmans’ theorem (KT)[59] and the OVGF approach.[60] KT relates the negative of the orbital energy of the highest occupied molecular orbital to the vertical EDE and approximates the vertical EDE in a static orbital approximation, hence overestimating the binding of the excess electrons. In contrast, the OVGF method considers electron correlation and orbital relaxation effects, and, for this reason, OVGF possesses the ability to yield improved EDEs compared with KT. OVGF is a theoretical method to calculate quick, but nonetheless reliable, ionization potentials. A second possibility to obtain the EDE is indirectly by computing the difference of the total energies of the monoanion and dianion. These methods are usually referred to as “Δ methods”. Here, we have used the ΔSCF method to calculate the EDEs of the dianions, where we have employed the restricted open-shell Hartree−Fock (ROHF) method for the open-shell monoanions. Unfortunately, higher correlated methods are out of reach for us at this time due to the computational costs of the calculation of the large substituted *closo*-hexaborate dianions and monoanions.

We have chosen Dunning’s DZP basis set[61] as the standard basis set within our calculations. In the case of the halogen-substituted

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species, the basis set is further augmented with a set of diffuse p-type functions for each atom. This basis set is denoted as the DZP+p basis set, and the exponents used are 0.048 for hydrogen, 0.074 for fluorine, 0.044 for chlorine, 0.034 for carbon, 0.048 for nitrogen, 0.019 for boron, and 0.059 for oxygen. The choice of these DZP basis sets is based on the following grounds: Employment of additional diffuse functions in the basis leads to a stabilization of the dianion versus the monoanion, since the MOs of the dianion are in general more diffuse than the MOs of the monoanion. Consequently, if electronic stability of a dianion is already given using a nondiffuse basis set, the dianion can be considered as an electronically stable gas-phase system. But if the examined dianion lies at the edge of electronic stability, the use of diffuse functions is essential to make a meaningful prediction of its stability, e.g. $B_6Cl_6^{2-}$ is unstable at the ΔSCF and OVGF levels of theory with the nondiffuse DZP basis set, but turns out to be a long-lived gas-phase dianion employing the DZP+p basis (see Section 3.1). From that point of view it is sufficient to use the DZP basis set to establish electronic stability of an examined dianion and to turn to the diffuse DZP+p basis set if necessary. Of course, if one wishes to make quantitative predictions of the EDE one would have to use highly diffuse basis sets. For our purpose, the DZP and DZP+p basis sets seem to be an ideal compromise between accuracy and calculation time. The ab initio programs used within our theoretical investigation stem from the GAUSSIAN 98, GAMESS,[63] and Aces 2[64] packages of programs.

3. Gas-Phase Stability of Derivatives of $B_6H_6^{2-}$

The theoretical investigation of multiply charged anions, in this work dianions, is in general more complex than the study of neutral or cationic systems, since the latter possess an infinite number of bound electronic states. In contrast, electronic stability of a dianion cannot be taken for granted owing to the strong electrostatic repulsion between the excess electrons (see the Introduction). Furthermore, this repulsion energetically supports the fragmentation of the dianions into two monoanionic fragments. Hence, the theoretical investigation of a dianion includes all aspects of a typical study of neutrals and cations, like characterization of the electronic ground state and localization of the energetically lowest minimum on the potential energy surface. But additionally, electronic stability and stability with respect to fragmentations of the investigated dianion needs to be considered as well.

The stability of a given dianion with respect to electron autodetachment is examined by computation of its electron detachment energy (EDE). In principle, the EDE often strongly depends on the geometry of the system, and thus, we distinguish vertical and adiabatic stability, which are quantified by the vertical and adiabatic EDEs, respectively. While the vertical EDE describes the local stability of the system, i.e., at the equilibrium geometry of the dianion, the adiabatic EDE is calculated with respect to a related equilibrium geometry of the monoanion and thus takes account of geometry relaxation effects during the electron detachment process.[48] In this context only monoanions need to be considered which are structurally related to the dianion, since otherwise the Franck−Condon factors vanish and strongly suppress the adiabatic electron emission with respect to a structurally unrelated monoanion. In this work, we have calculated only vertical EDEs, since for none of the investigated *closo*-hexaborates could a structurally related monoanion be identified.

The second property a stable gas-phase dianion must possess, stability with respect to fragmentations, is investigated by comparison of the total energy of the dianion with the sum of the total energies of possible fragments. If the sum of the total energies of the fragmentation products is higher than the total energy of the gas-phase dianion, the investigated dianion is thermodynamically stable with respect to this fragmentation channel. Otherwise the reaction pathway along the dissociation must be calculated explicitly to estimate the height and width of the activation energy barrier that exists due to the Coulomb repulsion of the monoanionic fragmentation products. It has turned out in previous theoretical studies of gas-phase dianions that fragmentations play only minor roles in the dianion's decay, due to broad energy barriers.[42,65,66] Especially for covalent systems, like the investigated *closo*-borates, fragmentations need not be considered as relevant decay channels due to the high binding energies of the involved covalent bonds.[45,48,67]

In the following section the results for several derivatives of $B_6H_6^{2-}$ are presented, and the influence of the ligands on the electronic stability is examined. In the very beginning of our investigation we tested many different ligands in preliminary Hartree−Fock calculations with respect to their ability to stabilize the electronically unstable $B_6H_6^{2-}$. We have tested the halogen ligands F and Cl; pseudohalogenes such as CN, NC, or BO; OH; CC and CCH; methyl CH_3; and even metal atoms such as Li or Be. While the metal atoms and methyl groups strongly destabilize the excess negative charges of the boron cage, substitution of the hydrogens by hydroxy or acetylide groups results in an opening of the *closo*-hexaborate cage and no borane-related minimum structure could be identified. Out of all tested ligands only the halogenes and pseudohalogenes lead to a significant stabilization of the borate cages, and therefore, we restrict our presentation to these dianions.

To give our numerical results some order, we decided to start our presentation with the octahedral *closo*-hexaborate dianion $B_6L_6^{2-}$ systems (L = F, Cl, CN, NC, and BO), in which all hydrogens of the "parent" $B_6H_6^{2-}$ are substituted (Section 3.1). Since we are interested in finding the *smallest* or least electron-rich free stable *closo*-hexaborate system, we reduced the number of ligands to four leading to $B_6H_2L_4^{2-}$ dianions, which are

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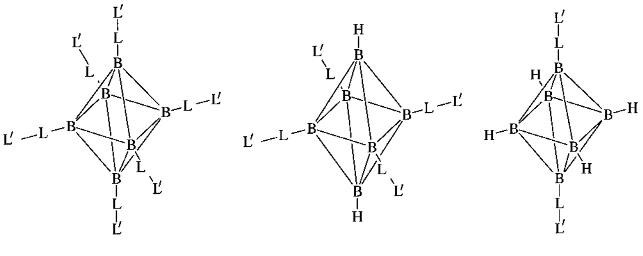

O_h D_{4h} (stretched) D_{4h} (compressed)

Figure 1. Structures of the investigated substituted *closo*-hexaborates are shown. While the hexasubstituted species (left) represent regular octahedra (O_h symmetry), the tetra- and disubstituted clusters (middle and right) correspond to stretched and commpressed octahedra, respectively, having D_{4h} symmetry.

presented in Section 3.2. Finally we present our results for the even smaller $B_6H_4L_2^{2-}$ dianions in Section 3.3.

3.1. Hexasubstituted *closo*-Borates. The geometry optimizations of all studied hexasubstituted *closo*-hexaborate dianions $B_6L_6^{2-}$ (L = F, Cl, CN, NC, and BO) were restricted to octahedral symmetry (O_h) and converged rapidly. All converged geometries were checked by an analysis of the harmonic frequencies, and all obtained O_h symmetric structures possess only real frequencies, i.e., they represent minima on the corresponding potential energy surfaces. This is in agreement with the predicted structures according to Wade's rule and with the experimentally determined structures of $B_6H_6^{2-}$ and its derivatives in condensed phases.[24] The octahedral structure of the *closo*-hexaborates is displayed in Figure 1.

The SCF optimized B−B and B−H bond lengths of the "parent" $B_6H_6^{2-}$ dianion are 1.751 and 1.216 Å (Table 1), respectively, and are in good agreement with other theoretical calculations at higher levels of theory.[68] They differ slightly from the experimentally determined values of 1.72 and 1.10 Å for the B−B and B−H bonds in $B_6H_6^{2-}$, possibly owing to the presence of counterions in the experimental examinations. Another limiting fact is the strong electronic instability of the $B_6H_6^{2-}$ dianion, which puts a question mark onto the results obtained with bound-state ab initio methods. The vertical EDE of the "parent" system has been found to have values of −1.249, −2.332, and −1.646 eV at the theoretical levels of KT, ΔSCF, and OVGF, respectively (Table 2). Although $B_6H_6^{2-}$ has been synthesized and characterized in condensed phases it does not correspond to a stable gas-phase dianion.[28,29]

Table 1. The Optimized Geometrical Parameters of the Examined $B_6L_6^{2-}$, $B_6H_2L_4^{2-}$, and $B_6H_2L_4^{2-}$ Dianions (L = F, Cl, CN, NC, and BO) Are Given at the RHF Level of Theory and MP2 Level of Theory (in brackets)[a]

	B_a–B_e	B_e–B_e	B–L	BH	L–L′
$B_6H_6^{2-}$	1.751			1.216	
$B_6F_6^{2-}$	1.733		1.405		
$B_6H_2F_4^{2-}$	1.745	1.724	1.407	1.212	
$B_6H_4F_2^{2-}$	1.736	1.759	1.410	1.214	
$B_6Cl_6^{2-}$	1.719		1.833		
	(1.721)		(1.809)		
$B_6H_2Cl_4^{2-}$	1.736	1.704	1.858	1.198	
$B_6H_4Cl_2^{2-}$	1.722	1.764	1.894	1.205	
$B_6(CN)_6^{2-}$	1.723		1.562		1.144
	(1.727)		(1.538)		(1.194)
$B_6H_2(CN)_4^{2-}$	1.738	1.713	1.568	1.191	1.147
	(1.738)	(1.720)	(1.543)	(1.190)	(1.195)
$B_6H_4(CN)_2^{2-}$	1.730	1.757	1.575	1.201	1.150
$B_6(NC)_6^{2-}$	1.720		1.480		1.153
	(1.721)		(1.464)		(1.196)
$B_6H_2(NC)_4^{2-}$	1.735	1.708	1.492	1.194	1.152
	(1.735)	(1.708)	(1.474)	(1.189)	(1.196)
$B_6H_4(NC)_2^{2-}$	1.725	1.757	1.506	1.203	1.152
$B_6(BO)_6^{2-}$	1.735		1.666		1.208
	(1.733)		(1.645)		(1.239)
$B_6H_2(BO)_4^{2-}$	1.743	1.731	1.665	1.194	1.213
	(1.740)	(1.731)	(1.643)	(1.192)	(1.243)
$B_6H_4(BO)_2^{2-}$	1.740	1.752	1.664	1.202	1.219

[a] B_a and B_e refer to the axial and equatorial boron atoms in the D_{4h} symmetric tetra- and disubstituted species. L−L′ describes the intraligand bond length of the diatomic pseudohalogen ligands CN, NC, and BO. For the hydrogen- and halogen-substituted borates we used the DZP+P basis set and for the larger systems the standard DZP basis set. The bond lengths are given in Ångstrøms.

Table 2. Vertical Electron Detachment Energies (EDEs) of the Hexasubstituted *closo*-Hexaborates $B_6L_6^{2-}$ Are Given in eV[a]

	L =					
	H	F	Cl	CN	NC	BO
KT	−1.249	−0.828	1.237	3.145	2.098	3.304
			(1.046)	(3.151)	(1.812)	(3.527)
ΔSCF	−2.332	−1.683	0.184	2.120	0.995	2.206
OVGF	−1.646	−1.594	0.154	2.003	1.768	1.953
			(−0.004)	(1.916)	(1.573)	(2.082)

[a] They are computed at the equilibrium geometries obtained at the SCF and MP2 (in brackets) levels of theory. For the hydrogen- and halogen-substituted boranes the DZP+P basis set and for the other dianions the DZP basis set was employed. Note that negative values for the EDEs have no quantitative meaning except that the dianions are electronically unstable.

Turning to the halogen-substituted species $B_6F_6^{2-}$ and $B_6Cl_6^{2-}$, the B−B bond lengths decrease slightly to 1.733 and 1.719 Å (Table 1), respectively, at the SCF level of theory compared to the parent $B_6H_6^{2-}$. The boron−halogen bonds possess lengths of 1.405 and 1.833 Å for the fluorine and chlorine systems and correspond to covalent single bonds. Calculation of the vertical EDEs of both systems reveals that $B_6F_6^{2-}$ is not electronically stable, since the EDE has a value of −0.828V, −1.683, and −1.594 eV at the theoretical levels of KT, ΔSCF, and OVGF, respectively. In contrast, $B_6Cl_6^{2-}$ has only positive values of the EDE at the SCF optimized geometry, indicating its electronic stability. For further corroboration, we have reoptimized the structure of this dianion at the MP2 level of theory and calculated the EDE also for this new geometry. The obtained bond lengths of 1.721 and 1.809 Å for the B−B and B−Cl bonds (Table 1) are in very good agreement with experimental values obtained from the X-ray structure of 1.72 and 1.82 Å, respectively.[24] At the MP2 optimized geometry, the EDE has values of 1.046 eV at the level of KT and −0.004 eV at the OVGF level of theory. Comparing the different geometries obtained at the SCF and MP2 level (Table 1) one realizes that inclusion of correlation leads to a remarkable decrease of the B−Cl single bond from 1.833 Å at the SCF level to 1.809 Å at the MP2 level of theory, while the B−B cage bond length remains unchanged. This reduction of molecular space comes along with an increase of Coulomb repulsion between the excess negative charges and a decrease of electronic stability. In previous examinations we have shown that slightly unstable dianions, e.g. BeC_4^{2-} [51] and C_8^{2-},[69] can have very long lifetimes with respect to electron

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(68) Kalvoda, S.; Paulus, B.; Dolg, M.; Stoll, H.; Werner, H.-J. *Phys. Chem. Chem. Phys.* **2001**, *3*, 514.

(69) Dreuw, A.; Cederbaum, L. S. *Phys. Rev. A* **2001**, *63*, 012501. Due to production errors see Erratum: *Phys. Rev. A* **2001**, *63*, 049904.

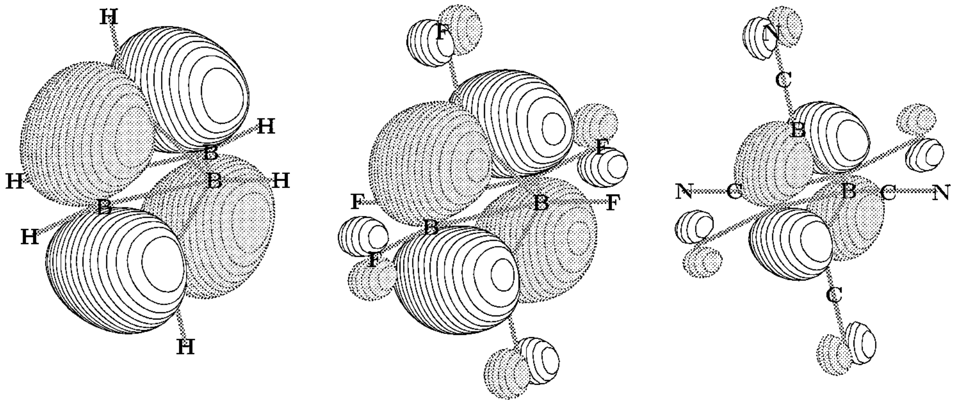

Figure 2. HOMOs of the *closo*-hexaborate dianions $B_6H_6^{2-}$, $B_6F_6^{2-}$, and $B_6(CN)_6^{2-}$. The HOMOs of all examined octahedral borates are triply degenerate t_{2g} orbitals.

emission due to the repulsive Coulomb barrier, and this is also the case for $B_6Cl_6^{2-}$ at its MP2 optimized equilibrium geometry. As already mentioned, fragmentations can be excluded as relevant decay channels due to the highly covalent character of the involved bonds and the resulting high binding energies. On the basis of these grounds we predict the $B_6Cl_6^{2-}$ dianion to be the least electron rich hexahalogen substituted *closo*-hexaborate dianion that is observable in the gas phase. Preliminary calculations at the Hartree−Fock level of theory of the bromine-substituted $B_6Br_6^{2-}$ dianion, which is known in solution,[20,21] indicate that this system represents a stable gas-phase dianion as well.

At first glance it is surprising that the $B_6F_6^{2-}$ dianion is electronically strongly unstable while the $B_6Cl_6^{2-}$ lies at the edge of stability. Since fluorine has the larger electronegativity (EN) one would naively have expected a vice versa trend. But more important than the larger electronegativity of fluorine is the longer B−Cl bond compared to B−F, which provides extended molecular space for the excess electrons to distribute over. Hence, the repulsion of the excess electrons in the $B_6Cl_6^{2-}$ dianion is significantly reduced and the excess negative charge is strongly stabilized. This simple geometric argument explains nicely the increased electronic stability of $B_6Cl_6^{2-}$ compared to $B_6F_6^{2-}$.

Substitution of the hydrogen atoms of the parent $B_6H_6^{2-}$ with the diatomic pseudohalogen ligands CN, NC, and BO leads to the *closo*-hexaborate dianions $B_6(CN)_6^{2-}$, $B_6(NC)_6^{2-}$, and $B_6(BO)_6^{2-}$, respectively. The geometries of these dianions have been optimized at the theoretical level of Hartree−Fock as well as MP2, and the geometrical parameters are given in Table 1. While the B−B cage bond lengths differ only very slightly for these derivatives, the major differences occur for the cage ligand bonds (B−L) and the intraligand bond lengths (L−L′). The boron−ligand bond length increases from the NC- to the CN- and BO-substituted species from 1.480 (1.464) to 1.562 (1.538) and 1.666 (1.645) Å, respectively, at the theoretical level of SCF (MP2) (Table 1). All these lengths have values of typical single bonds.[70] The intraligand bond lengths of the CN and NC species are essentially equal with a value of about 1.15 (1.195) Å at the SCF (MP2) level, while the intraligand B−O bond length of the $B_6(BO)_6^{2-}$ dianion is slightly longer with a length of 1.208 (1.239) Å at the SCF (MP2) level of theory. While the CN and NC bonds of the $B_6(CN)_6^{2-}$ and $B_6(NC)_6^{2-}$ dianions correspond to triple bonds, the BO bond has clearly more double bond character, since the calculated bond length indicates a shortened double bond. The typical value of a BO double bond is about 1.27 Å.[70] Comparison of the geometrical parameters obtained at the SCF and MP2 levels of theory shows that the influence of correlation is only small and only the intraligand bond lengths are clearly prolonged. The elongation of terminal multiple bonds in dianions when correlation is taken into account has been observed previously.[48,51]

Turning to the electronic stability of the pseudohalogen-substituted dianions $B_6(CN)_6^{2-}$, $B_6(NC)_6^{2-}$, and $B_6(BO)_6^{2-}$, all of them are clearly electronically stable. The values of the vertical EDEs of these clusters obtained at the SCF as well as at the MP2 optimized geometries are compiled in Table 2 and are positive throughout. The CN-, NC-, and BO-substituted *closo*-hexaborates have EDEs of 2.003 (1.916), 1.768 (1.573), and 1.953 (2.082) eV, respectively, at the SCF (MP2) optimized geometries, using the OVGF approach for the calculation of the EDE. As mentioned previously, fragmentations of the molecular framework can be excluded due to the covalent character and the high dissociation energies of the involved bonds.[45,48,67] Since the hexasubstituted dianions $B_6(CN)_6^{2-}$, $B_6(NC)_6^{2-}$, and $B_6(BO)_6^{2-}$ are vertically stable with respect to electron emission, all these dianions represent local minima on the corresponding potential energy surfaces, and fragmentations are not relevant decay channels, we predict the hexasubstituted dianions $B_6(CN)_6^{2-}$, $B_6(NC)_6^{2-}$, and $B_6(BO)_6^{2-}$ represent stable gas-phase dianions which are observable in mass spectrometric experiments.

The high electronic stability of these species compared to the halogen-substituted or the parent hydrogen systems is simply explained with the increased molecular size. Through the introduction of diatomic ligands the excess electrons can distribute over more atoms and thus significantly reduce their electrostatic repulsion resulting in an increased electronic stability of the dianion. This trend can be nicely seen out by looking at the highest occupied molecular orbitals (HOMOs) of $B_6H_6^{2-}$, $B_6F_6^{2-}$, and $B_6(CN)_6^{2-}$, which are displayed in Figure 2. The HOMO of all examined octahedral clusters is a triply degenerate t_{2g} orbital, of which only one of each cluster is shown. In the parent $B_6H_6^{2-}$ dianion, the HOMO is a pure cage orbital, i.e., the excess electrons are strictly localized at the boron cage. According to a Mulliken charge analysis, the

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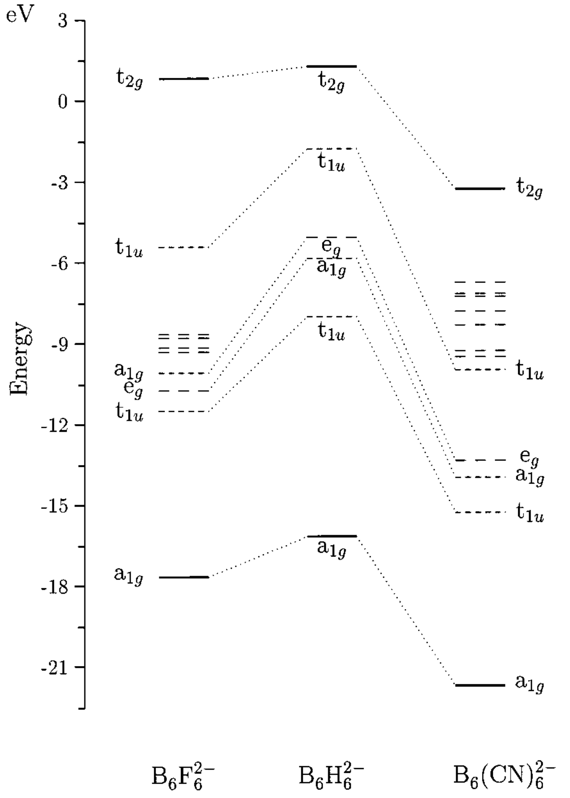

Figure 3. The orbital energies of $B_6H_6^{2-}$ (middle), $B_6F_6^{2-}$ (left), and $B_6(CN)_6^{2-}$ (right) are compared. Solid orbital lines refer to cage orbitals, short-dashed lines to mixed cage-ligand orbitals, and long-dashed lines to pure ligand orbitals. This characterization cannot be strict but rather represents more a guideline, since the HOMO of $B_6(CN)_6^{2-}$ has mostly cage character but also nonnegligible contributions on the ligand atoms (see text).

boron cage atoms have a partial charge of −0.1 and the hydrogens of −0.24, which goes along with a strong electrostatic repulsion between the additional charges. This is the major reason why the $B_6H_6^{2-}$ dianion is electronically unstable and emits spontaneously one of its excess electrons when it is brought into the gas phase.

Going to $B_6F_6^{2-}$, the HOMO already has small coefficients at the fluorine ligands, i.e., the additional electrons are also slightly distributed over the fluorine ligands (Figure 2). Indeed, the negative charge at the fluorine atoms is strongly increased compared to that of the hydrogens of the parent $B_6H_6^{2-}$ dianion. The fluorines have a partial charge of −0.55 while the boron cage atoms are slightly positively charged by +0.21. This corroborates the tendency of the excess electrons to localize at the ligands and thus to minimize their electrostatic repulsion. As can be seen in the orbital scheme (Figure 3), the HOMO and all other orbitals are stabilized when going from $B_6H_6^{2-}$ to $B_6F_6^{2-}$. But the stabilization is not sufficient to make the latter a stable gas-phase dianion, since the energy of the HOMO is clearly positive, i.e., the electrons of the HOMO are unbound.

In the case of the $B_6(CN)_6^{2-}$ dianion, the HOMO has significant coefficients at the nitrogen atoms of the CN ligands, indicating a further charge transfer to the outermost ligand atoms (Figure 2). A Mulliken charge analysis supports this picture, since the cage boron atoms have a charge of +0.2, the ligand carbons a charge of −0.23, and the ligand nitrogens a charge of −0.3. This localization of the excess charges at the outermost nitrogen atoms leads to a vigorous reduction of the electrostatic repulsion and to a significant lowering of all orbital energies (Figure 3). The energy of the HOMO drops clearly below zero, i.e., all electrons are bound, and $B_6(CN)_6^{2-}$ is an electronically stable gas-phase dianion.

Closer inspection of the vertical EDEs of $B_6(CN)_6^{2-}$ and $B_6(NC)_6^{2-}$ reveals that the CN-substituted species is substantially more stable than the NC-substituted one. The vertical EDE of $B_6(CN)_6^{2-}$ is 2.003 (1.916) eV while the EDE of $B_6(NC)_6^{2-}$ is only 1.768 (1.573) eV at the theoretical level of OVGF, using the SCF (MP2) optimized geometries (Table 1). This difference can be nicely explained by the tendency of the excess electrons to localize at the outermost ligand atoms and the EN of the involved elements. In $B_6(CN)_6^{2-}$ the outermost ligand atom is nitrogen, which has a higher EN than carbon, and hence, the EN difference supports the localization of the excess charges at the nitrogen. In contrast, in the $B_6(NC)_6^{2-}$ dianion nitrogen is not in the outermost position but carbon. Thus, the EN difference between nitrogen and carbon acts directly opposed to the tendency of the excess electrons to localize at the outermost position. This is confirmed by the charge distributions of these clusters, since in $B_6(CN)_6^{2-}$ the boron has a charge of +0.2, the carbon a charge of −0.23, and the nitrogen a charge of −0.3, while in $B_6(NC)_6^{2-}$ the boron carries a charge of +0.16, the nitrogen a charge of −0.4, and the carbon a charge of −0.1. Comparing the charge distributions in these clusters, the additional charges of $B_6(NC)_6^{2-}$ are more localized in the inner region, giving rise to more Coulomb repulsion and to less electronic stability.

3.2. Tetrasubstituted *closo*-Borates. One of our intentions in this theoretical investigation is to identify the *smallest* or *least electron rich closo*-hexaborate dianion. Since we have already identified the stable hexasubstituted species $B_6Cl_6^{2-}$, $B_6(CN)_6^{2-}$, $B_6(NC)_6^{2-}$, and $B_6(BO)_6^{2-}$, it is thus natural to reduce the number of ligands from six to four and to examine the resulting $B_6H_2Cl_4^{2-}$, $B_6H_2(CN)_4^{2-}$, $B_6H_2(NC)_4^{2-}$, and $B_6H_2(BO)_4^{2-}$ in the same fashion. We have restricted ourselves to the *trans*-isomers which possess D_{4h} symmetry sketched in Figure 1.

The geometry optimization of the $B_6H_2Cl_4^{2-}$ dianion reveals that the cluster is stretched along the C_4 axis, resulting in a longer boron−boron distance between axial and equatorial atoms than between axial and axial atoms (Table 1). At the SCF level of theory, the involved bonds have typical lengths of single bonds, and are comparable to the values obtained for the hexasubstituted dianion. However, computation of the vertical EDE of the $B_6H_2Cl_4^{2-}$ dianion clearly proves its electronic instability, since the EDE has a value of −0.306 eV at the level of OVGF. Therefore, we can conclude that $B_6Cl_6^{2-}$ is the smallest halogen-substituted *closo*-hexaborate dianion that is long-lived.

Turning to the pseudohalogen tetrasubstituted dianions $B_6H_2(CN)_4^{2-}$, $B_6H_2(NC)_4^{2-}$, and $B_6H_2(BO)_4^{2-}$, their geometry optimizations give analogous results as for $B_6H_2Cl_4^{2-}$. Again, the equilibrium structures correspond to elongated octahedra (Figure 1) and the geometrical parameters are very similar to the parameters obtained for the hexasubstituted species (Table 1). The most important differences to the hexasubstituted dianions occur in the elongation of the axial−equatorial B−B bonds and the shortening of the B−B bonds between two equatorial borons. Note that equatorial borons lie in the plane spanned by the four ligands, while axial borons are perpendicular

Table 3. Vertical Electron Detachment Energies (EDEs) of the Tetrasubstituted $B_6H_2L_4^{2-}$ *closo*-Hexaborate Dianions Obtained at the SCF and MP2 (in brackets) Equilibrium Geometries[a]

	L =				
	F	Cl	CN	NC	BO
KT	−1.135	0.548	1.769 (1.835)	1.132 (0.903)	1.768 (1.929)
ΔSCF	−2.216	−0.551	0.675	−0.029	0.665
OVGF	−1.929	−0.306	0.857 (0.838)	0.707 (0.611)	0.843 (0.892)

[a] For the halogen-substituted borates the DZP+P basis set was employed, for the pseudohalogenes the DZP basis set. The EDEs are given in eV. Negative values for the EDEs have no quantitative meaning except that the dianions are electronically unstable.

Table 4. Vertical Electron Detachment Energies (EDEs) of the Disubstituted $B_6H_4L_2^{2-}$ Dianions Are Given in eV[a]

	L =				
	F	Cl	CN	NC	BO
KT	−1.219	0.305	0.126	−0.077	0.053
ΔSCF	−2.278	−1.465	−1.050	−1.257	−1.117
OVGF	−1.904	−0.913	−0.547	−0.568	−0.637

[a] They have been computed at the equilibrium geometries obtained at the SCF level of theory. For the hydrogen- and halogen-substituted boranes we used a DZP+P basis set and for the other examined systems a DZP basis set was employed. Negative EDEs only prove the electronic instability of the dianion but have no quantitative meaning.

to this plane. For example, in the $B_6(CN)_6^{2-}$ dianion all B−B bonds are identical and have a length of 1.723 (1.727) Å, while the B−B distance between two equatorial boron atoms in $B_6H_2(CN)_4^{2-}$ decreases to 1.713 (1.720) Å and the distance between an axial and an equatorial atom increases to 1.738 (1.738) Å at the theoretical level of SCF (MP2) (Table 1). In contrast, the cage−ligand bonds and intraligand bonds are largely equal for the tetra- and hexasubstituted species. The CN and NC bonds of $B_6H_2(CN)_4^{2-}$ and $B_6H_2(NC)_4^{2-}$ possess, like those of the analogous hexasubstituted borates, typical lengths of triple bonds, while the BO bond of the $B_6H_2(BO)_4^{2-}$ corresponds to a shortened double bond. Inclusion of correlation into the geometry optimization by optimizing the structures at the MP2 level of theory has only negligible effects on the geometrical parameters (Table 1).

In contrast to $B_6H_2Cl_4^{2-}$, the pseudohalogen-substituted species are electronically stable, since the vertical EDEs of $B_6H_2(CN)_4^{2-}$, $B_6H_2(NC)_4^{2-}$, and $B_6H_2(BO)_4^{2-}$ have values of 0.857 (0.838), 0.707 (0.611), and 0.843 (0.892) eV, respectively, at the SCF (MP2) optimized geometries using the OVGF approach for the EDEs (Table 3). Summarizing, the *closo*-hexaborates $B_6H_2(CN)_4^{2-}$, $B_6H_2(NC)_4^{2-}$, and $B_6H_2(BO)_4^{2-}$ are vertically stable with respect to electron emission and represent minima on the corresponding potential energy surfaces, and fragmentations can be excluded due to the covalent nature of the involved bonds. Thus, $B_6H_2(CN)_4^{2-}$, $B_6H_2(NC)_4^{2-}$, and $B_6H_2(BO)_4^{2-}$ represent stable gas-phase dianions and are predicted to be observable in mass spectrometric experiments.

The increase of electronic stability going from the halogen-tetrasubstituted to the pseudohalogen-tetrasubstituted dianions follows the same reasons as outlined for the hexasubstituted borates. The lower electronic stability of the NC derivative compared to the CN-substituted $B_6H_2(CN)_4^{2-}$ dianion can analogously be explained by the electronegativities of carbon and nitrogen as has been done for the derivatives $B_6(NC)_6^{2-}$ and $B_6(CN)_6^{2-}$ in the previous section.

3.3. Disubstituted *closo*-Borates. Further reduction of the number of ligands from four to two leads to the disubsituted *closo*-hexaborates $B_6H_4(CN)_2^{2-}$, $B_6H_4(NC)_2^{2-}$, and $B_6H_4(BO)_2^{2-}$, which are the only possible disubstituted candidates to be stable gas-phase dianions. Again, we have restricted our investigation to the *trans*-isomers, which possess D_{4h} symmetry, since a maximum distance between the electron-withdrawing groups is necessary for their stability. The structure of these dianions is pictured in Figure 1.

The geometry optimizations of all three dianions converged onto equilibrium structures that correspond to compressed octahedra, in which the boron−boron distance between equatorial atoms is prolonged while the distance between axial and equatorial borons is shortened (Table 1). In this case equatorial boron atoms are those lying in the plane spanned by the four hydrogens, while the axial borons are perpendicular (see Figure 1). The geometrical parameters are very similar to those obtained for the hexa- and tetrasubstituted analogues (Table 1).

Calculation of the vertical EDEs of the $B_6H_4(CN)_2^{2-}$, $B_6H_4(NC)_2^{2-}$, and $B_6H_4(BO)_2^{2-}$ dianions reveals that they are all unstable with respect to electron autodetachment, since their EDEs have clearly negative values at the OVGF level of theory of −0.547, −0.568, and −0.637 eV, respectively (Table 4). Therefore, all the investigated disubstituted *closo*-hexaborates $B_6H_4(CN)_2^{2-}$, $B_6H_4(NC)_2^{2-}$, and $B_6H_4(BO)_2^{2-}$ do not correspond to electronically stable dianions and their existence in the gas phase can be excluded.

4. Brief Summary

Although $B_6H_6^{2-}$ is known in condensed phases, it is not stable with respect to electron autodetachment, but emits spontaneously one of its extra electrons in the gas phase. In this paper we address the question whether it is possible to construct a stable gas-phase dianion by starting from $B_6H_6^{2-}$ as the parent system and replacing the hydrogens with appropriate ligands. Our aim is to identify the *smallest* electronically stable derivative of $B_6H_6^{2-}$ using ab initio methods and to understand the influence of different ligands onto the electronic stability of the dianions.

Our calculations have clearly shown that four hexasubstituted *closo*-hexaborates are stable with respect to electron autodetachment and represent stable gas-phase dianions: $B_6Cl_6^{2-}$, $B_6(CN)_6^{2-}$, $B_6(NC)_6^{2-}$, and $B_6(BO)_6^{2-}$. All these dianions have been geometry optimized and their equilibrium structures have O_h symmetry, which is in agreement with the predicted structures according to the electron count scheme known as Wade's rule. While the $B_6Cl_6^{2-}$ dianion lies at the edge of electronic stability, the pseudohalogen-substituted dianions $B_6(CN)_6^{2-}$, $B_6(NC)_6^{2-}$, and $B_6(BO)_6^{2-}$ are clearly electronically stable by about 2 eV. The increase of electronic stability from the halogen- to the pseudohalogen-substituted species can be nicely explained by the larger molecular space provided by the diatomic pseudohalogen ligands. The larger space allows the additional electrons to distribute further and to reduce their electrostatic repulsion significantly. The decrease of electrostatic repulsion within the systems is strongly reflected by the orbital energies of the *closo*-hexaborate dianions.

A reduction of the number of ligands revealed that the *trans*-isomers of the tetrasubstituted species $B_6H_2(CN)_4^{2-}$, $B_6H_2(NC)_4^{2-}$, and $B_6H_2(BO)_4^{2-}$ represent stable gas-phase dianions as well. Their equilibrium structures are D_{4h} symmetric and correspond to stretched octahedra along the C_4 axes of the molecules. Further reduction of the number of pseudohalogen ligands to disubstituted *closo*-hexaborates does not yield stable gas-phase dianions. On the basis of the results of our investigation, we predict the hexasubstituted *closo*-hexaborates $B_6Cl_6^{2-}$, $B_6(CN)_6^{2-}$, $B_6(NC)_6^{2-}$, and $B_6(BO)_6^{2-}$ and the tetrasubstituted dianions $B_6H_2(CN)_4^{2-}$, $B_6H_2(NC)_4^{2-}$, and $B_6H_2(BO)_4^{2-}$ to exist in the gas phase. All these dianions are observable in mass spectrometric experiments as they are typically performed by Wang et al.[71]

Acknowledgment. Dedicated to Prof. Walter Siebert on the Occasion of his 65th Birthday. The authors thank Dr. Cécile Saint-Espès for helpful discussions and preliminary calculations. Financial support by the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

JA012681J

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