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Sandwich Compounds with Central Hypercoordinate Carbon, Nitrogen, and Oxygen: A Quantum-Chemical Study

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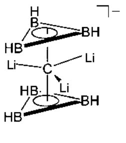
ABSTRACT: *Ab initio (MP2(fu)/6-311+G**) and DFT (B3LYP/6-311+G**) calculations predict stable structures of sandwich compounds with the central carbon, nitrogen, and oxygen atoms surrounding lithium counterions between three-membered* $(BH)_3$ *rings. The lithium counterions play a crucial role in the stabilization of these systems. The topological Bader analysis performed for these sandwich systems demonstrates that the central atom is linked to the ligands by nine-bond paths and, consequently, should be regarded as a nine-coordinated atom. Such a coordination number of carbon is the highest for all known main group organoelement compounds.* © 2006 Wiley Periodicals, Inc. Heteroatom Chem 17:464–474, 2006; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20268

INTRODUCTION

The quest for nonclassical structures of organic compounds has been started by the seminal experimental discovery of the methonium cation as the first hypercoordinate carbon species [1,2] and the theoretical prediction of the ways of stabilization of planar tetracoordinate carbon [3]. Since then, the research in both directions has been intensively developed and extended to other main group element compounds with unusual coordination and/or configuration of their bonds [4–11]. Apart from protonated methanes in which the coordination number of carbon has been shown to be increased up to seven [9], a variety of new rather unusual structures with planar penta- [12,13], hexa- [14,15], hepta- [16], and octacoordinate [17] carbon and heptacoordinate nitrogen [18], hepta- and octacoordinate boron [19], silicon [17], and phosphorus [17] have been computationally discovered. A representative recent example is the carborane sandwich systems **1–3**, in which the central carbon forms multicenter bonds with up to 12 neighboring ligands, as in **3** [20].



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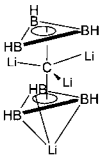

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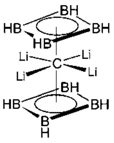

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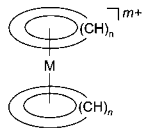

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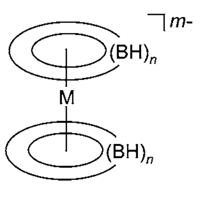
Whereas transition metal sandwich compounds, metallocenes **4** (M = Fe, Mn, Ni..., $n = 3$–7) constitute one of the most amply studied domain of organometallic chemistry [21], their main group element analogues are represented by rare examples of the η^5-cyclopentadienyl sandwiches ($n = 5$) of the alkaline (M = Li, Na) [22–24] and alkaline-earth metals (Mg, Ca, Ba) [24,25]. In contrast with transition metals, the bonding schemes of main group elements are confined to the use of their valence s- and p-orbitals, which limit the number of bonding MOs, formed in main group element sandwich compounds **4** by π- and π^*-MOs of the basal rings and the valence orbitals of M, to four and, hence, the number of the "interstitial" electrons in a stable main group element sandwich structure to eight. According to these requirements (eight electron count rule [5,11,26]), one may expect that the simplest stable carbocenes (M = C) possessing a D_{nh} or a D_{nd} structure must have large positive charges: $m = 2$ for the cyclopropenyl (**4**, $n = 3$), and $m = 4$ for the cyclobutadiene (**4**, $n = 4$) sandwiches.

The validity of this expectation has been recently demonstrated by the B3LYP/6-311++G** calculations [27] of a silicon analogue, $\mathrm{C[(SiH)_3]_2^{2+}}$, of the carbocene **4** ($n = 3$). It is also possible to explore another way to match the requirements of the 8*e* rule in the carborane sandwich systems **5**, in which carbons in the basal rings of **4** are substituted by more electropositive boron atoms and the electron-deficient $\mathrm{(BH)}_n$ rings leave more vacancies for electrons of the central carbon. The efficiency of this approach to the adjustment of main group element polyhedral structures to the rigid requirements, imposed by the electron count rules on the number of interstitial electrons in the closed shells, has been recently additionally demonstrated by computational findings of boron wheels containing hypercoordinated carbon and other main group element centers [4,5].

The orbital interaction diagram (Fig. 1), which is built up by analogy with the metal-sandwich orbital diagrams, shows the formation of the MOs of a sandwich **6**. The completely similar bonding schemes are characteristic of other members of this structural family. Filling all bonding MOs of the sandwiches **5** $\mathrm{C[(BH)_4]_2}$ with electrons provides for a typical three-dimensional aromatic closed shell but gives rise to the tetraanions **6**, which are, apparently, destabilized because of the strong electrostatic repulsion between four extra charges even though delocalized over the ligands. Indeed, according to the B3LYP/6-311G** calculations, the sandwich structure **5** ($n = 3$, $m = -4$, with D_{3h} and D_{3d} symmetries) with the closed electron shell corresponds not to a minimum, but a two-dimensional hill-top (two negative force constants) on the respective potential energy surface (PES). At the same time, a less compact sandwich structure **6** (D_{4h}) corresponds, according to the B3LYP/6-311G** calculations, to a very flat minimum ($\omega_1 = 14\ \mathrm{cm}^{-1}$).



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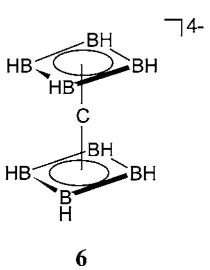

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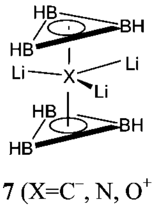
The experimentally observed main group element sandwiches are stabilized as the solvated and ate-type complexes with the environment of solvent molecules and counterions, which provide for delocalization of the electric charge at the central ion [21–24]. In order to fully or partially neutralize the excessive negative charge in the anions **5**, they may be surrounded by the appropriate number of counterions, e.g., $\mathrm{Li^+}$. We have previously shown that in the complexes with π-ligands, the role of such counterions is not reduced to the electrostatic stabilization, but applies also to charge–transfer effects leading to the formation of a closed electron shell of the complex (induced aromaticity [28]).

In the present work, we report on quantum chemical computational study of the first thermodynamically stable lithioheteroboranes **7** ($\mathrm{X = C^-}$, N, $\mathrm{O^+}$) and their closest isomers exemplifying a novel structural type of sandwich compounds containing highly hypercoordinate central carbon, nitrogen, and oxygen atoms. We are also considering the bonding nature of hypercoordinate central main group element centers with surrounding ligands in the compounds **7** in the context of the "atoms in molecules" theory [29].



7 ($\mathrm{X{=}C^-}$, N, $\mathrm{O^+}$)

COMPUTATIONAL METHODS

The ab initio (MP2(full)) and density functional theory (DFT) calculations were carried out using the Gaussian 98 [30] and Gamess [31]

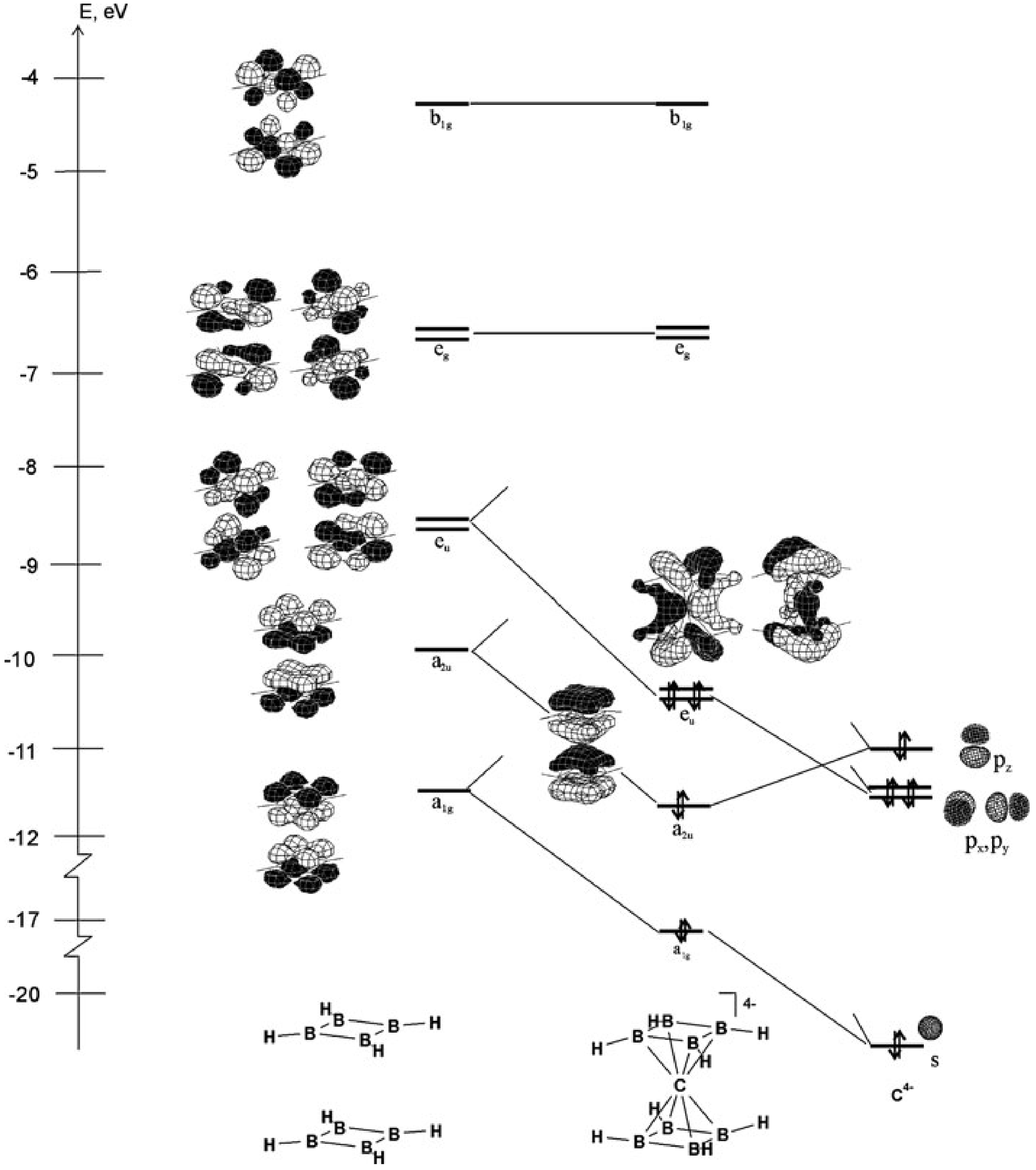


FIGURE 1 Correlation diagram of interaction of the carbon s- and p-valence orbitals with π- and π^*-molecular orbitals of the four-membered boron ring in the sandwich structure **6**.

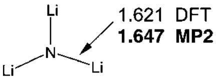
systems of programs with 6-311+G(d,p) basis set. The ab initio calculations were carried out by the restricted Hartree–Fock method including electron correlation energy of all electrons according to the Moller–Plesset perturbation theory scheme. The Becke-3 parameter density functional with the Lee–Yang–Parr correlation functional (B3LYP) [32,33] was used in the DFT calculations. All the structures were fully optimized using key word “tight.” Analytic harmonic frequencies at the same level of approximation were used to characterize the nature of the structures under study and to evaluate zero-point energy corrections (ZPE). The Bader topological analysis [29,34] of total electronic density distribution as obtained in the DFT calculations was performed using original AIMPAC program package [35]. The distributions of all critical points obtained in the DFT calculations were compared with those obtained in the MP2 calculations and found to be fully identical. Thus, the molecular graphs given in the figures correspond to the results of DFT calculations. The orbital interaction diagram and shape of MOs have been constructed using CACAO [36,37] program. Molecular structure images presented in the figures are obtained using the program package GaussView [38], with the final Cartesian coordinates of atoms obtained in the DFT optimization process as the input.

RESULTS AND DISCUSSION

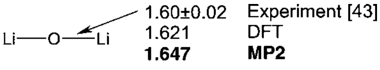
Isoelectronic Sandwich Heteroboranes

According to the DFT and MP2 calculations, the D_{3h} structures of the sandwich isoelectronic clusters **1, 8**, and **9** correspond to the energy minima ($\lambda = 0$, hereafter λ designates the number of negative Hessian eigenvalues) on the respective PESs. The optimized geometries of these molecules and ions found by the calculations are shown in Fig. 2 along with their Bader molecular graphs **1a, 8a**, and **9a** obtained by the analysis of the topology of the electron density distribution [34,35]. The energy characteristics are listed in Table 1.

As seen from Fig. 2, the B—B bond lengths in the $(BH)_3$ rings of all lithioheteroboranes fall into the range of typical single bonds of this type, whereas the C—B, N—B, and O—B distances are longer than the normal covalent X—B bonds (~1.6 Å for C—B bonds [39,40], ~1.61–1.55 Å for N—B bonds in pyrazaboles [40], and ~1.37–1.47 Å for O(2)—B(3) bonds [40]). Of special interest is the C—Li distances, which are of the same value as the covalent C—Li bond in CH_3Li (1.959–2.10 Å [41]). The N–Li and O–Li distances are considerably longer then respective bonds in the molecules NLi_3 **10** and OLi_2 **11** [42] and are close to the sum of covalent N (O) and Li radii (1.93 and 1.89 Å), correspondingly [43].



10, D_{3h}



11, $D_{\infty v}$

The B–Li distances are also close to the sum of covalent B and Li radii (2.03 Å) [43]. The covalent bonding of the central atom with all the neighboring ligating atoms in **1, 8**, and **9** is confirmed by the

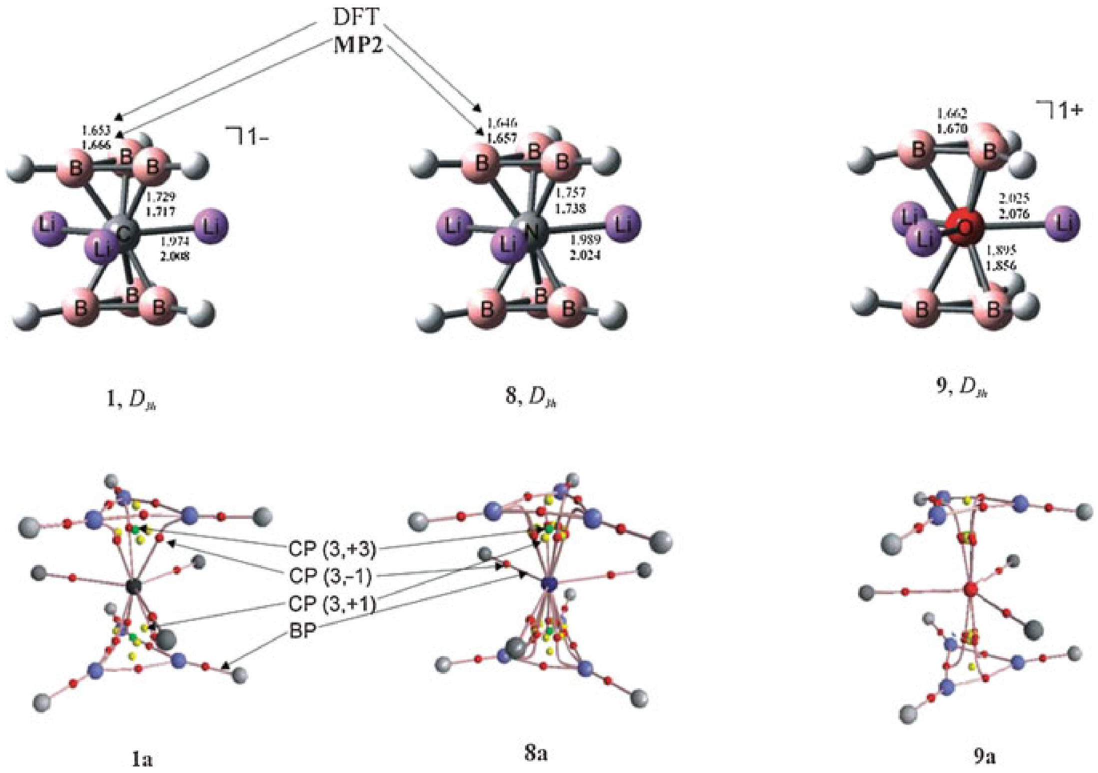


FIGURE 2 Geometry parameters of sandwich compounds **1, 8**, and **9** calculated by the DFT (B3LYP/6-311+G**) and ab initio (MP2(full)/6-311+G**) methods. Here and in other figures, the bond lengths are indicated in angström. The Bader molecular graph **1a, 8a**, and **9a** of structures **1, 8**, and **9** are given at the bottom of the figure; BP designates the Bader bond path, CP (3,−1) is the bond path critical point, CP (3,+1) is the ring critical, and CP (3,+3) is the cage critical point.

TABLE 1 Ab initio (MP2(full)/6-311+G**) and DFT (B3LYP/6-311+G*) Data for Carbon Sandwich Structures **1, 8, 9, 12–15**[a]

Structure	*Method*	E_{tot}	λ	ΔE	ΔE_{ZPE}	$\omega_1/i\omega_1$
1, D_{3h}	DFT	−213.4627	0	0	0	162 (E')
	MP2	−212.7612	0	0	0	161 (E')
8, D_{3h}	DFT	−230.0796	0	0	0	158 (E')
	MP2	−229.3416	0	0	0	162 (E')
9, D_{3h}	DFT	−250.3038	0	0	0	108 (E')
	MP2	− 249.5220	0	0	0	122 (E')
12, C_{3v}	DFT	−220.9813	0	0	0	131 (E)
	MP2	−220.2391	0	0	0	133 (E)
13, C_{2v}	DFT	−220.9551	0	16.5	16.5	107
	MP2	−220.2122	0	16.9	16.7	90
14, C_{2v}, C_s	DFT	−220.9646	0	10.5	10.8	14
	MP2	−220.2226	0	10.4	10.8	107
15, C_{2v}	DFT	−220.9615	1	12.4	12.9	i123
	MP2	−220.2180	1	13.2	13.7	i163

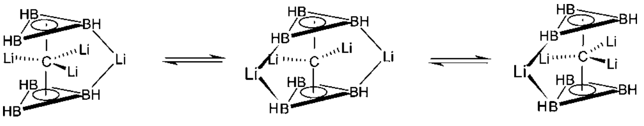
[a] E_{tot} (in a.u.) and ΔE are total and relative energies (1 a.u. = 627.5095 kcal mol^{-1}); λ is the number of negative Hessian eigenvalues; ΔE_{ZPE} (in kcal mol^{-1}) is relative energy with the account for harmonic zero-point corrections; $\omega_1/i\omega_1$ (in cm^{-1}) are the lowest or imaginary harmonic vibration frequencies.

formation of the bond paths [34] connecting atoms C, N, and O with the six boron (the "banana"-like type) and three lithium atoms. This finding leads to the conclusion that the central atoms in **1**, **8**, and **9** form nine covalent bonds which correspond to the coordination number 9. It is worth noting that the same type of σ-bonding of metallic centers with all basal carbons was recently found in a number of neutral 3d metal metallocenes [44]. In contrast with the structures **1** and **8**, the bond paths in **9** link the central oxygen to the BB bond path critical points and not to the boron atoms. Such a molecular graph indicates the π-bonding between the oxygen and BB-bonds in the boron rings.

Neutral Lithiocarborane Systems

The ionic clusters **1** and **9** are important for the comparison of bonding schemes in the isoelectronic series of **1, 8**, and **9** having the same symmetry and satisfying the 8*e*-rule [11,26]. More realistic are the neutral structures in which a negative charge is compensated by additional lithium counterions. For the carborane **1**, such isomeric systems are given by the structures **12–14** and the optimized geometries and molecular graphs are shown in Figs. 3 and 4. The energy characteristics are listed in Table 1.

Structure **12** is energy preferred to other isomeric forms. In **12**, the C—Li distances are slightly longer than those in **1**, whereas the averaged C—B distance in **12** matches well with those in **1**. System **15** is the transition state structure for the intramolecular rearrangement **14a** ⇆ **15** ⇆ **14b** ⇆ . . . , redistributing the C—Li bonds within a molecule through overcoming a very small activation barrier (~2 kcal mol^{-1}).



14a **15, TS** **14b**

The central carbon atoms in the cage structures **1, 12–14** bear large Mulliken positive charges amounting to +2.0e. This provides for the decrease in the effective size of the central atom and for the reduction of the steric strain caused by its encapsulation into the rigid lithioboron framework. The Bader molecular graphs of **12a** and **14a** shown in Fig. 4 are similar to the graph of **1a**. Therefore, the sandwiches **12** and **14** may be regarded as the compounds with highly hypercoordinate (nine-coordinate) carbon atoms in the electrically neutral cluster systems.

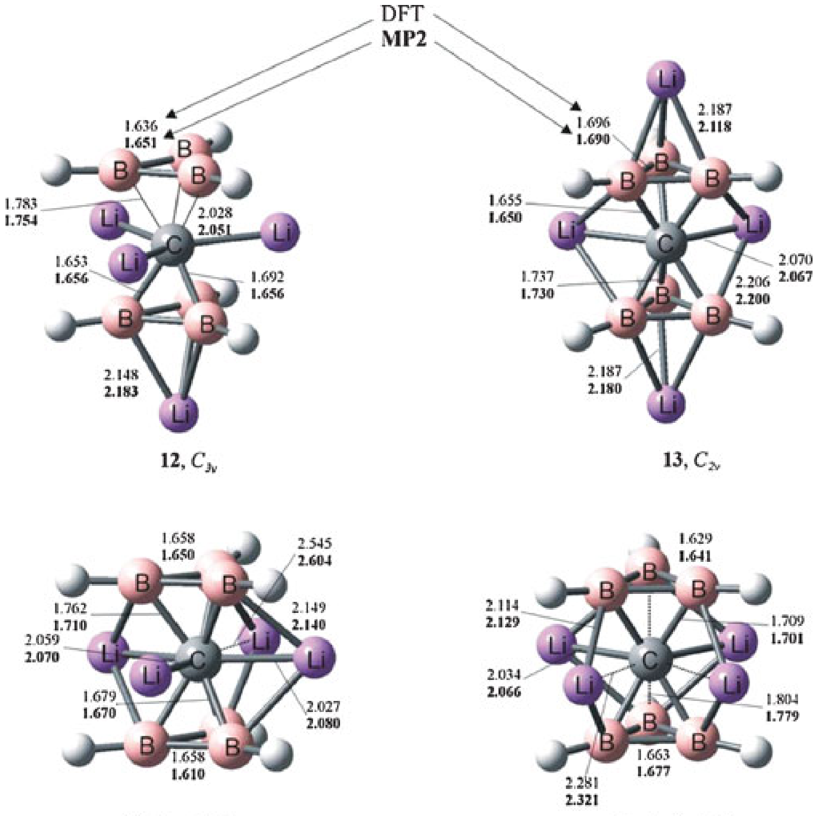
To assess the relative thermodynamic stability of the most stable electrically neutral sandwich **12** with respect to their decay to the fragments **16–19**—well studied both experimentally and by calculations for various borane and carborane cluster systems [39,45]—we have calculated heats of the following reactions:

12 $\rightarrow CLi_4 + 2B_3H_3$ 239.9 (MP2) or 214.2 (DFT) kcal mol^{-1}

12 $\rightarrow CLi_2 + B_6H_6 \cdot Li_2$ (**17**) 110.5 (MP2) or 96.6 (DFT) kcal mol^{-1}

12 $\rightarrow B_3H_3CLi_4$ (**20**) $+ B_3H_3$ 100.7 (MP2) or 84.1 (DFT) kcal mol^{-1}

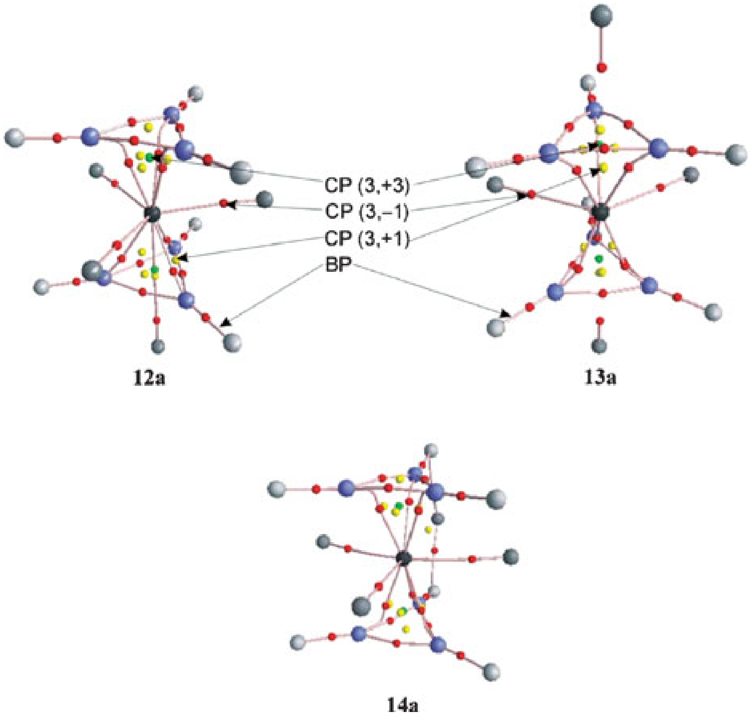
Here we use the total energies without including zero-point energy (ZPE) of the systems **14–19**



12, C_{3v} **13**, C_{2v}

14, C_{2v}, (C_s) **15**, C_{2v}(λ=1,1)

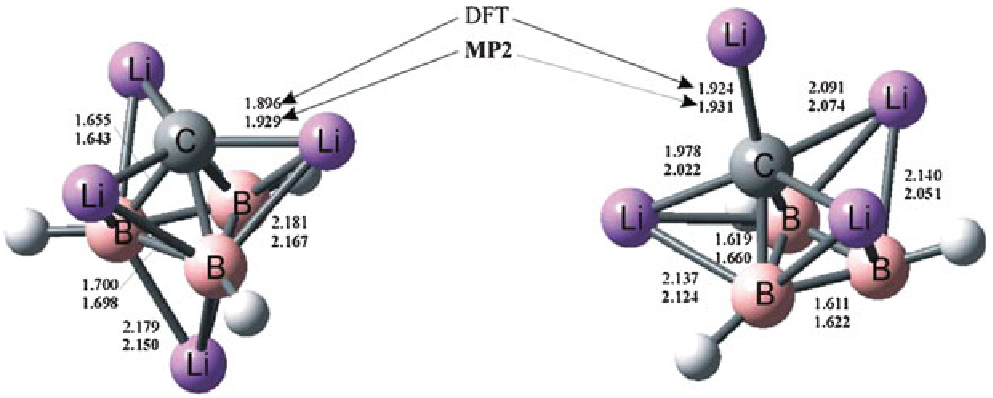
FIGURE 3 Geometry parameters of sandwich compounds **12–14**, corresponding to the minima, and **15** corresponding to the saddle point calculated by DFT (B3LYP/6-311+G**) and ab initio (MP2(full)/6-311+G**) methods.



12a **13a**

14a

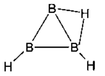
FIGURE 4 The Bader molecular graph **12a, 13a**, and **14a** of structures **12, 13**, and **14**. BP designates the Bader bond path, CP (3,−1) is the bond path critical point, CP (3,+1) is the ring critical point, and CP (3,+3) is the cage critical point.



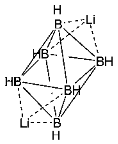
20, C_{3v} **21**, C_s

FIGURE 5 Geometry parameters of semisandwich compounds **20** and **21** calculated by DFT (B3LYP/6-311+G**) and ab initio (MP2(full)/6-311+G**) methods.

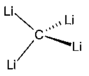
because including ZPE almost does not affect the values of heats of these reactions. For the systems $B_6H_6 \cdot Li_2$ and $B_3H_3CLi_4$, the calculations were performed for the most stable isomers **17** and **20** (see Fig. 5).



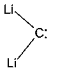
16, C_s



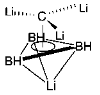
17, D_{3d}



18, T_d



19, C_{2v}



20, C_{3v}

Table 2 contains some data on the energy characteristics of the components of these reactions. The high endothermicity of the above dissociation reactions points to the significant stability of the sandwich structures of the lithiocarboranes.

Neutral Lithioaza- and Lithiooxa-borane Systems

The sandwich azaboranes **22, 23** and oxaboranes **26, 28** correspond to minima on the respective PESs. The optimized geometries of these systems are shown in Figs. 6 and 7 along with the most stable pyramidal fragments **24, 25**, and **28**. The energy characteristics are listed in Table 3.

As seen from Fig. 6, the bond lengths and the nature of the stationary points on the PES corresponding to the azaborane structures **22** and **23** predicted by the DFT and MP2 methods are notably different, especially for **23** for which even the symmetries differ. A possible explanation may be associated with the incomplete account for long-range π–π interactions by the DFT methods [46]. All geometrical parameters in aza- and oxa-boranes are close to the respective values in the carboranes considered

TABLE 2 Ab initio (MP2(full)/6-311+G**) and DFT (B3LYP/6-311+G**) Data^a for the Structures **16–21** Appeared in the Equations for the Estimation of Thermodynamic Stability of the Sandwich **12**

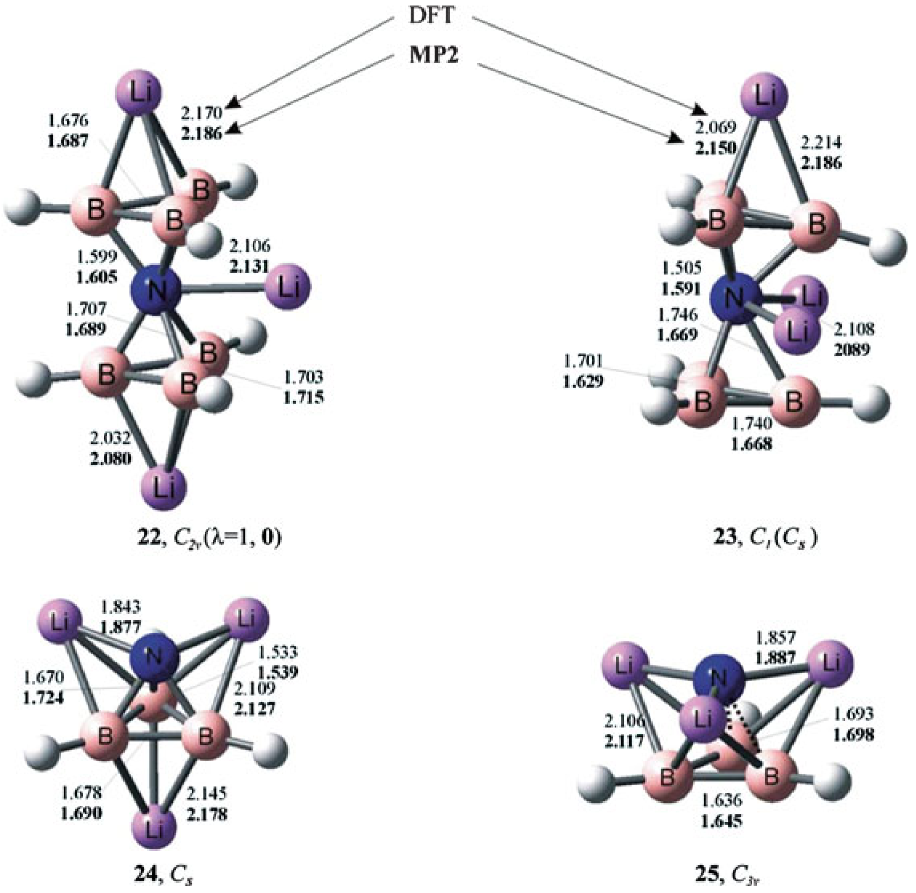
Structure	*Method*	E_{tot}	E_{ZPE}	ω_1
16, B_3H_3, C_s	DFT	−76.2564	−76.2211	306
	MP2	−76.0010	−75.9651	286
17, $B_6H_6Li_2$, D_{3h}	DFT	−167.9114	−167.8305	123 (E_u)
	MP2	−167.3512	−167.2694	139 (E_u)
18, CLi_4, T_d	DFT	−68.1271	−68.1188	170 (T_2)
	MP2	−67.8549	−67.8473	136 (T_2)
19, CLi_2, C_{2v}	DFT	−52.9160	−52.9113	300
	MP2	−52.7118	−52.7067	288
20, C_{3v}	DFT	−144.5908	−144.5441	109 (E)
	MP2	−144.0777	−144.0309	102 (E)
21, C_s	DFT	−144.5688	−144.5222	84
	MP2	−144.0515	−144.0043	120

$^a E_{tot}$ are total energies (1 a.u. = 627.5095 kcal mol^{-1}); E_{ZPE} (in a.u.) are total energies with the account for harmonic zero-point corrections; ω_1 (in cm^{-1}) are the lowest harmonic vibration frequencies.

TABLE 3 Ab initio (MP2(full)/6-311+G**) and DFT (B3LYP/6-311+G**) Data[a] for Nitrogen Sandwich Structures **22–28**

Structure	*Method*	E_{tot}	λ	ΔE	ΔE_{ZPE}	$\omega_1/i\omega_1$
22, C_{2v}	DFT	−230.0191	1	37.9	38.3	*i* 41
	MP2	−229.2799	0	38.4	38.9	77
23, C_1, C_s	DFT	−230.0973	0	−11.1	−9.8	94
	MP2	−229.3107	0	19.4	19.4	121
24, C_s	DFT	−153.7563	0	0	0	150
	MP2	−153.2568	0	0	0	168
25, C_{3v}	DFT	−153.7551	0	0.8	0.6	130 (*E*)
	MP2	−153.2539	0	1.8	1.5	118 (*E*)
26, C_{2v}	DFT	−242.9305	0	0	0	72
	MP2	−242.1854	0	0	0	106
27, D_{3h}	DFT	−242.8417	2	55.7	56.0	*i* 106 (*E*)
	MP2	−242.0988	2	54.3	54.6	*i* 37 (*E*)
28, C_s	DFT	−166.6837	0	0	0	108
	MP2	−166.1887	0	0	0	165

[a] E_{tot} (in a.u.) and ΔE are total and relative energies (1 a.u. = 627.5095 kcal mol^{-1}); λ is the number of negative Hessian eigenvalues; ΔE_{ZPE} (in kcal mol^{-1}) is relative energy with the account for harmonic zero-point corrections; $\omega_1/i\omega_1$ (in cm^{-1}) are the lowest or imaginary harmonic vibration frequencies.



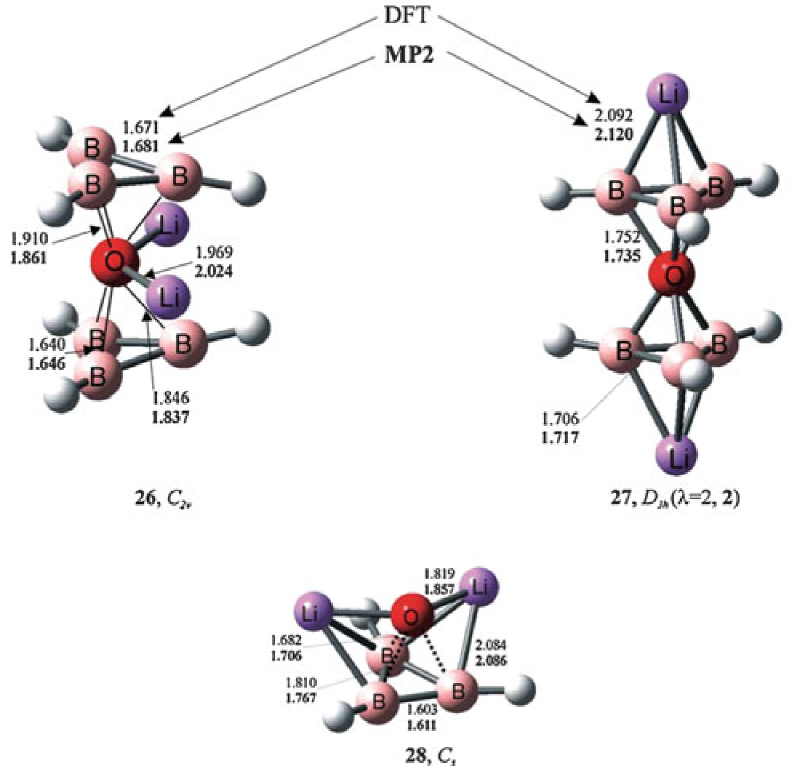
22, C_{2v}(λ=1, **0**)

23, C_1(C_s)

24, C_s

25, C_{3v}

FIGURE 6 Geometry parameters of azasandwich compounds **22, 23** and azasemi-sandwich compounds **24** and **25** corresponding to the minima, calculated by the DFT (B3LYP/6-311+G**) and ab initio (MP2(full)/6-311+G**) methods.



26, C_{2v} **27**, $D_{3h}(\lambda=2, 2)$

28, C_s

FIGURE 7 Geometry parameters of oxasandwich compound **26**, corresponding to the minima, and **27**, corresponding to the second-order saddle point and lithium oxaborane **28** corresponding to the minima calculated by the DFT (B3LYP/6-311+G**) and ab initio (MP2(full)/6-311+G**) methods.

above. According to the molecular graphs **22a** and **26a** depicted in Fig. 8, the central nitrogen in **22** is dicoordinated and the oxygen in **26** is tetracoordinated.

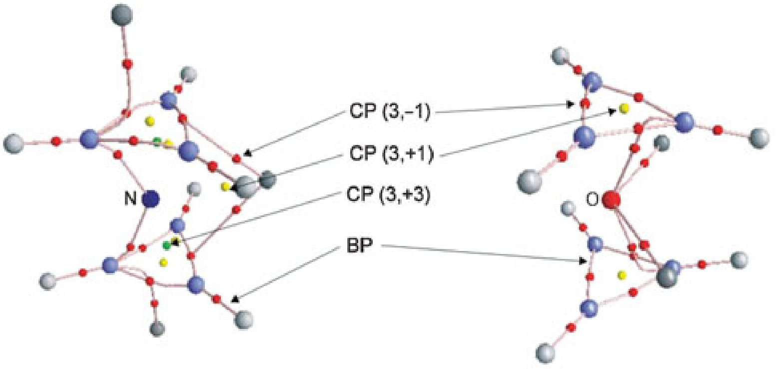
To evaluate thermodynamic stability of the electrically neutral heterosandwich clusters **8** and **24** with respect to their decay to the fragments, we have calculated heats of the following reactions:

8 $\rightarrow$ $NLi_3 + 2B_3H_3$ 170.5 (MP2) or 150.9 (DFT) kcal mol^{-1}

8 $\rightarrow NB_3H_3Li_3$ (**24**) $+ B_3H_3$ 28.9 (MP2) or 18.9 (DFT) kcal mol^{-1}

26 $\rightarrow OLi_2 + 2B_3H_3$ 55.3 (MP2) or 45.9 (DFT) kcal mol^{-1}

26 $\rightarrow OB_3H_3Li_2$ (**28**) $+ B_3H_3 + 2.7$ (MP2) or 6.1 (DFT) kcal mol^{-1}



22a, C_{2v} **26a**, C_{2v}

FIGURE 8 The Bader molecular graph **22a**, and **26a** of structures **22**, and **26**. BP designates the Bader bond path, CP (3,−1) is the bond path critical point, CP (3,+1) is the ring critical point, and CP (3,+3) is the cage critical point.

Here we also use total energy without including zero-point energy of the systems **8, 24, 26**, and **28**. For the systems $B_3H_3NLi_3$and $B_3H_3OLi_2$, we choose the most stable isomers **24** and **28** (see Figs. 6 and 7), respectively. Including ZPE does not change the principal results of the calculations. With the exception of the last reaction, the high endothermicity of these dissociations points to the sufficiently high stability of the sandwich structures of the lithioheteroboranes.

In conclusion, the calculations performed have shown that the clusters **1, 8–9, 14**, and **26** represent a new structural type of stable sandwich compounds containing highly hypercoordinate carbon, nitrogen, and oxygen atoms centered between two hydroboron rings and closely surrounded by lithium counterions. The topological Bader analysis demonstrates that the central atom in the compounds **1** and **8–9** is linked to the ligating atoms by nine-bond paths and, consequently, should be regarded as a nine-coordinated atom.

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