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Carbon, nitrogen, and oxygen hypercoordination in half-sandwich and sandwich structures

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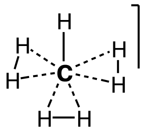
The structures and stabilities of a number of neutral and charged half-sandwich (pyramidal) and sandwich compounds, which obey the "electron octet" rule and contain hypercoordinate carbon, nitrogen, and oxygen atoms, were studied by *ab initio* MP2(full)/6-311+G** and density functional B3LYP/6-311+G** methods. Introduction of lithium counterions or bridging hydrogen atoms can provide an additional stabilization of non-classical systems with hypercoordinate centers.

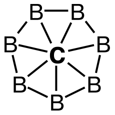
Key words: hypercoordinate carbon, nitrogen, and oxygen atoms; lithium counterions; bridging hydrogen atoms; half-sandwich compounds; sandwich compounds; quantum chemical calculations, *ab initio* quantum chemical calculations.

The last decade is characterized by dramatic intensification of research in the field of design of novel systems containing hypercoordinate atoms of the main group elements.[1—9] The key problems in chemistry of compounds with hypercoordinate atoms include establishment of (i) a maximum number of ligands that can be arranged at a valence distance from the atom of a main-subgroup element and (ii) stereoelectronic conditions for stabilization of such a system. Quite recently, quantum chemical calculations revealed stable compounds of penta-, hexa-, and heptacoordinate carbon in both planar[10—13] and nonplanar environments including atoms of the main-group elements[14—19] as well as stable lithium derivatives CLi_6,[20—22] CLi_8,[21] and CLi_{10};[21] conditions for stabilization of these systems were also studied. The existence of compound with the CLi_6 stoichiometry was confirmed by mass spectroscopy.[23]

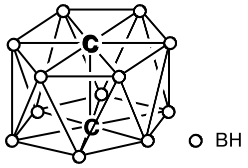
Pentacoordination and hexacoordination of carbon atoms in the Masamune cation,[24] Hogeveen cation,[25] and carboranes[2,26,27] was detected by NMR spectroscopy and X-ray analysis.[7] The theoretically predicted maximum coordination of carbon atom in organoelement compounds containing atoms of the main-group elements as ligands occurs in trication **1**,[6,14] planar system **2**,[15] carborane **3** [18] (coordination number is six), and in CLi_{12} compound (coordination number is eight) with C_{4v} symmetry.[21]



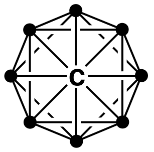
1, C_{3v}



2, C_s



3, D_{6d}



$C \cdot Ni_8(CO)_{16}^{2-}$ (**4**)
$C \cdot Co_8(CO)_{16}^{2-}$

According to X-ray studies,[28,29] the coordination number of carbon in metal clusters **4** is also as high as eight. At present, this is the record high value among all theoretically predicted and experimentally known compounds. The higher coordination number of carbon with the main-group element atoms in environment is still questionable, although stable sandwich structures **5—7** with hypercoordinate carbon atom (formally, the coordination number of carbon in structure **7** is as high as twelve) have recently been predicted.[17]

Hypercoordination of nitrogen was investigated in line with the hypercoordination of carbon, although less intensively. As far as we know, systematic studies of pentacoordinate and hexacoordinate nitrogen began with two reports[30,31] in which structural and electronic stability of nitrogen fluorides NF_5 (**8**) and NF_6^- (**9**) was predicted based on the results of *ab initio* MP2/6-31+G* calculations.

Further detailed higher-level (CCSD/DZP) *ab initio* calculations[32] confirmed the local stability of NF_5, but showed that its decomposition into components, $NF_5 \rightarrow NF_3 + F_2$, is a highly exothermic reaction

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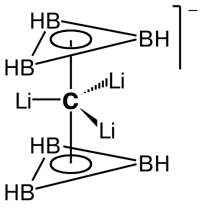
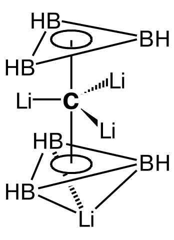
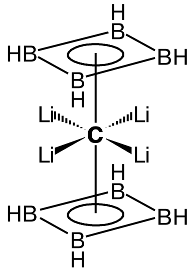


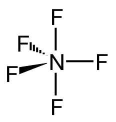
5, D_{3h}



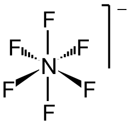
6, C_{3v}



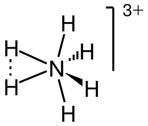
7, D_{4h}



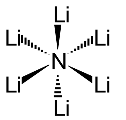
8, D_{3h}



9, O_h



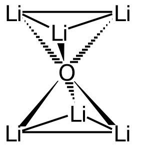
10, D_{3h}



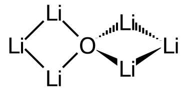
11, D_{3d}

(42 kcal mol^{-1}), which thus provides an explanation for unsuccessful attempts to detect molecule **8**.[33] Using the isolobal analogy[34] with the known gold complexes $\{[(C_6H_5)_3PAu]_5N\}^{2+}$ [35] and *ab initio* calculations, a local structural stability of pentacoordinate nitrogen in NH_5^{2+} cation[36] and NH_6^{3+} cation (**10**)[37] was shown. However, these hydrides, as well as compound **8**, are thermodynamically highly unstable and decompose into fragments as follows: $NH_5^{2+} \rightarrow NH_4^+ + H^+$ (99.0 kcal mol^{-1}) and $NH_6^{3+} \rightarrow NH_5^{2+} + H^+$ (280.6 kcal mol^{-1}). The stability of different configurations of the NLi_6 system was studied by the BLYP/6-31G* method; structure **11** with D_{3d} symmetry was found to be the most stable.[38] Besides, hypercoordinate nitrogen in planar environment was also studied.[39–41] At present, the maximum theoretically predicted coordination number of nitrogen is six, as in structures **9**—**11**; a hot discussion about the possibility for compounds with higher coordination of nitrogen to exist is being conducted in the literature.[1–10]

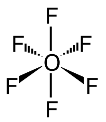
Hypercoordination of oxygen has been the subject of a few studies.[22,42–45] If, according to modern concepts, hypercoordination of carbon and nitrogen begins with a coordination number of five, oxygen atoms are treated as hypercoordinate starting from a coordination number of four, although the structure of such systems can be quite correctly described using the classical scheme of sp^2-hybridized atom of a second-row element. Stable tetrahedral structure of a lithium derivative, OLi_4, predicted by *ab initio* calculations[43] was more recently confirmed by mass spectrometry.[44] Recently, tetracoordination of oxygen atom in stable oxahexaborane was shown by *ab initio* (MP2/6-311+G**) and DFT (B3LYP/6-311+G**) calculations.[45] Calculations[38,42] predicted the possibility of stabilization of hexacoordinate oxygen atom in the OLi_6 system (**12**, D_{3d} symmetry); however, structure **13** (D_{2d} symmetry) with a tetracoordinate O atom was found to be more thermodynamically stable.



12, D_{3d}



13, D_{2d}



14, O_h

Analysis of the electronic structure and molecular geometry of compound **12** shows that the structure of this compound best corresponds to a sandwich system in which two three-membered lithium rings donate an electron each to the central O atom. System **12** is stable because it obeys the "electron octet" rule (the total count of the valence electrons of the central atom and of the π-electrons in the two rings must be equal to eight),[1,8,46] the more so the stability of the Li_3^+ cyclic cation is well known.[42,47,48] Structural stability (*i.e.*, correspondence to the energy minimum on the potential energy surface (PES)) of oxygen hexafluoride **14** was reported,[31] but the electron shell of this system possesses a Hartree—Fock instability (RHF→UHF), which requires higher-level theoretical studies.

Hypercoordination of atoms of the main-subgroup elements in organic and organoelement systems is a direct consequence of obeying the principles of stabilization of non-classical structures with unusual stereochemistry of tetracoordinate carbon (planar, pyramidal and inverted or, "umbrella", carbon),[8–10] which were intensively investigated by V. I. Minkin and his collaborators[1,2,8,12,15–17,39,40,45] over the last two decades. The present work is a next step of evolution of the ideas by V. I. Minkin in the field of research on non-classical structures of organic compounds. Here we report the results of our studies of the electronic and molecular structure of previously unknown hypothetical non-classical half-sandwich and sandwich systems containing hypercoordinate carbon, nitrogen and oxygen atoms. The main goal of this work is to evaluate new approaches to directed design of non-classical organic systems with hypercoordinate atoms of the main-subgroup elements using various examples. These strategies offer great prospects for prediction of novel organoelement compounds.

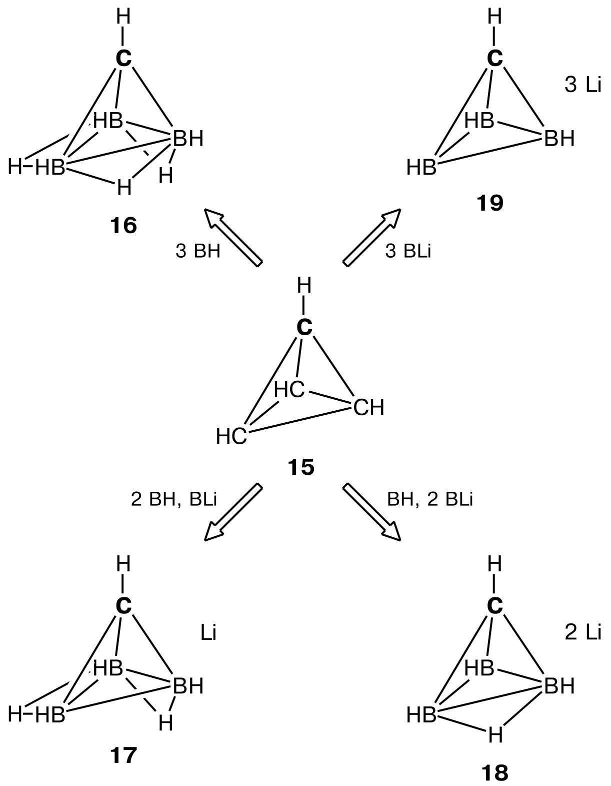
Calculation Procedure

Quantum-chemical calculations were carried out by the restricted Hartree—Fock (RHF) method with inclusion of all (valence and core) electrons at the second-order Møller—Plesset level (MP2(full)) of perturbation theory and by the density functional theory (DFT) approach with the B3LYP three-parameter potential in the split valence basis set 6-311+G** using the GAUSSIAN-98 [49] and GAMESS [50] program packages. Full optimization of the geometry of the molecular structures corresponding to the energy minima (λ* = 0) and to the saddle points (λ = 1) on the PES was carried out using the "tight" optimization criterion (GAUSSIAN-98) or conducted to a gradient value of 10^{-5} hartree Bohr^{-1} (GAMESS). The structures corresponding to the energy minima on the PES were found by the steepest descent method (movement along the gradient line) from a saddle point to the neighboring stationary point (a saddle point or a minimum). The initial direction of the gradient line was specified by minor displacement (1/10 of the length of the normalized transition vector) along the transition vector. Molecular structure images (see Figs 1, 2, 4—8, 10) were obtained using the GaussView program,[51] for which the corresponding Cartesian atomic coordinates taken from the results of *ab initio* calculations served as input parameters.

Results and Discussion

Half-sandwich or pyramidal systems. It is convenient to design systems with hypervalent centers using stable pyramidal hydrocarbon structures as frames. Indeed, replacement of basal carbon atoms by isoelectronic BH or BLi fragments allows new non-classical systems to be obtained and their electronic structure to be varied. Recently, this strategy has become very popular. It was successfully implemented in the calculations of novel non-classical boron hydrides, hydrocarbons, and organoelement systems.[8,9,19,27,52,53] In the present work we used this approach for the design of novel structures containing hypercoordinate carbon (nitrogen, oxygen) starting from tetrahedrane **15**.

Pyramidal systems containing hypercoordinate carbon atoms. Replacement of three carbon atoms in the basal plane of molecule **15** by three BH groups leads to the system **16**. Replacement of the same atoms by (i) two BH groups and one BLi group, (ii) one BH group and two BLi groups, and (iii) three BLi groups gives systems **17**, **18**, and **19**, respectively.



According to our B3LYP/6-311+G** and MP2(full)/6-311+G** calculations (hereafter denoted as DFT and MP2 calculations, respectively), structures **15—19** correspond to the energy minima on the PESs of these systems. The calculated geometric parameters of systems **15—19** are presented in Fig. 1 and their energy characteristics are listed in Table 1.

According to our and previous[54] calculations, the carbon—carbon bonds (~1.48 Å) in stable tetrahedrane structure **15** are much shorter than in less strained molecules, *e.g.*, cubane (~1.57 Å)[55—57] or prismane (~1.52—1.56 Å); this can be explained by three-dimensional σ-aromaticity of compound **15**.[8,9,58] In carborane **16**, the boron—carbon bonds are shorter than typical single B—C bonds (~1.58 Å in BMe_3),[59] whereas the B—B and B—H bond lengths fall in the range of standard bond length values for boranes and carboranes.[26,59,60] It should be noted that if the H atom in the BH substituent always is in the bridging position, the Li atom in the lithium-containing systems is coordinated to the BBB (BBC) face, which can lead to an increase in the coordination number of the apical atom. Involvement of the apical carbon atoms in systems **17—19** in additional coordination and an increase in their coordination numbers up to a value of five (structure **17**), six (structures **18** and **19a**), and seven (structure **19b**) is accompanied by elongation of the C—B bond by more than 0.5 Å compared to system **16**. The isomers of systems **17** and **18**, in which the Li atom is coordinated to the BBB face, are less energetically favorable (their energies are 30

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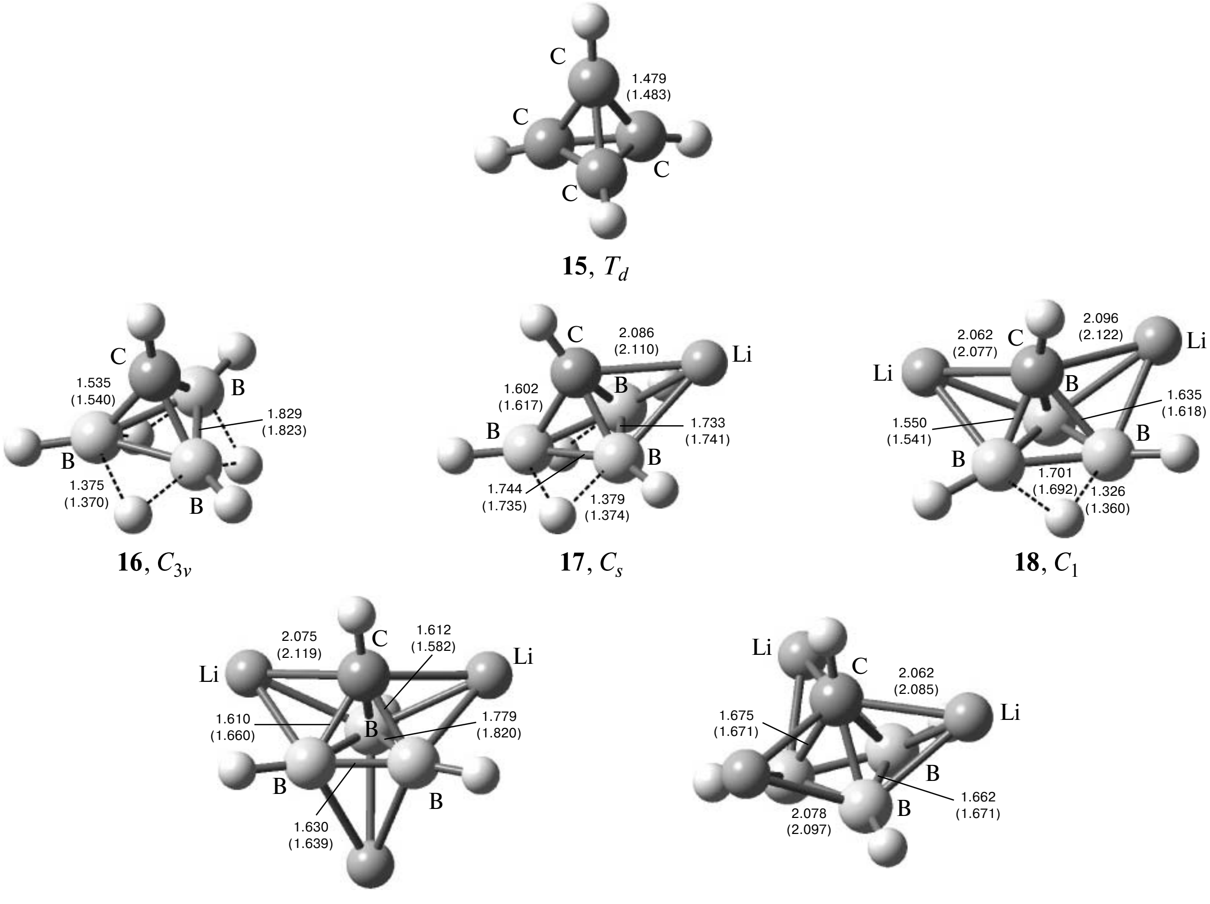
* The stationary point index equal to the number of negative eigenvalues of the Hessian at a given stationary point.



15, T_d

16, C_{3v} **17**, C_s **18**, C_1

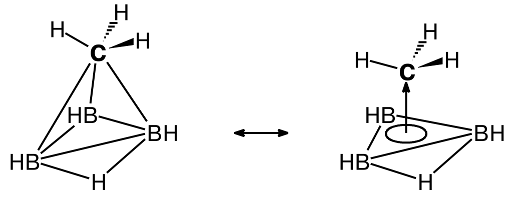
19a, C_s (C_1) **19b**, C_{3v}

Fig. 1. Geometric parameters of pyramidal structures **15—19** corresponding to energy minima on the PES (λ = 0) obtained from B3LYP/6-311+G** (DFT) and MP2/6-311+G** (MP2, figures in parentheses) calculations. Here and in Figs 2, 4—8, and 10, the bond lengths are given in Å.

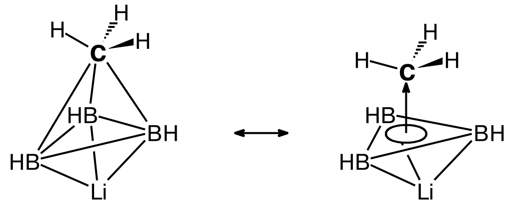
and more kcal mol^{-1} higher); they are left out of consideration. According to calculations, structure **19a** is 6.8 (DFT) and 7.1 kcal mol^{-1} (MP2) more energetically favorable than a more symmetric structure **19b**. The carbon—lithium bond lengths (~2.10 Å) lie in the range of experimental bond length values for ordinary covalent C—Li bonds in MeLi (1.96—2.10 Å).[61] The electron density distribution in systems **17—19** also corresponds to covalent rather than zwitter-ionic type of bonding, as is usually assumed, because the degree of electron density transfer to each lithium center is at most 0.4 e.

It is interesting to compare the energy stabilities of structures **16** and **17** and isomeric structures **20** and **21** containing an apical Me group (see Table 1 and Fig. 2).

Structures **20** and **21** also correspond to energy minima on the PES, but the former is 27.9 (DFT) and 30.0 kcal mol^{-1} (MP2) while the latter is 30.5 (DFT) and 31.2 kcal mol^{-1} (MP2) less energetically favorable than structures **16** and **17**, respectively. Structurally, systems **20** and **21** are best described as π-complexes **20a** and **21a** with a relatively weak bonding between the Me group and the boron ring. This is indicated by the boron—carbon bond lengths (1.8—2.0 Å), which exceed the upper bound



20 **20a**



21 **21a**

Table 1. Energy characteristics of compounds **15—21** obtained from B3LYP/6-311+G** (DFT) and MP2(full)/6-311+G** (MP2) calculations

Structure	Symmetry	Method	$-E_{\text{total}}$	$-(E_{\text{total}}$ + ZPE)	$\omega_1/i\omega$ /cm^{-1}
			a.u.		
15	T_d	DFT	154.681097	154.621814	564.9
		MP2	154.272358	154.213141	483.0
16	C_{3v}	DFT	116.855255	116.774448	274.7
		MP2	116.475478	116.392310	287.1
17	C_s	DFT	123.782105	123.710050	99.9
		MP2	123.366987	123.293251	139.5
18	C_1	DFT	130.712929	130.650167	127.5
		MP2	130.263454	130.199302	115.1
19a	C_s	DFT	137.656009	137.600971	93.3
		MP2	137.171795	137.116153	106.3
19b	C_{3v}	DFT	137.645212	137.591853	49.5
		MP2	137.160512	137.106870	76.0
20	C_s	DFT	116.810746	116.727459	246.4
		MP2	116.427626	116.393715	258.6
21	C_{3v}	DFT	123.733455	123.659272	122.4
		MP2	123.317315	123.241651	151.1

Note: E_{total} is the total energy (1 a.u. = 627.5095 kcal mol^{-1}); E_{total} + ZPE is the total energy with inclusion of zero-point vibrational energy correction; the number of negative eigenvalues of the Hessian $\lambda = 0$; and $\omega_1/i\omega$ is the lowest (or imaginary) harmonic frequencies.

of the range of standard bond length values for ordinary B—C bonds. It should be noted that, although the Me group in structure **20** is displaced toward the B—B bond with the bridging H atom, the displacement is small (*cf.* the geometric parameters of systems **20** and **22**), being an indication of a three-center interaction between the Me group and the basal ring.

Decompositions of systems **17—19** into fragments are highly endothermic reactions, which also confirms that these compounds are thermally stable.

$$\textbf{17} \rightarrow \text{MeLi} + \text{B}_3\text{H}_3 \qquad (Q_1)$$

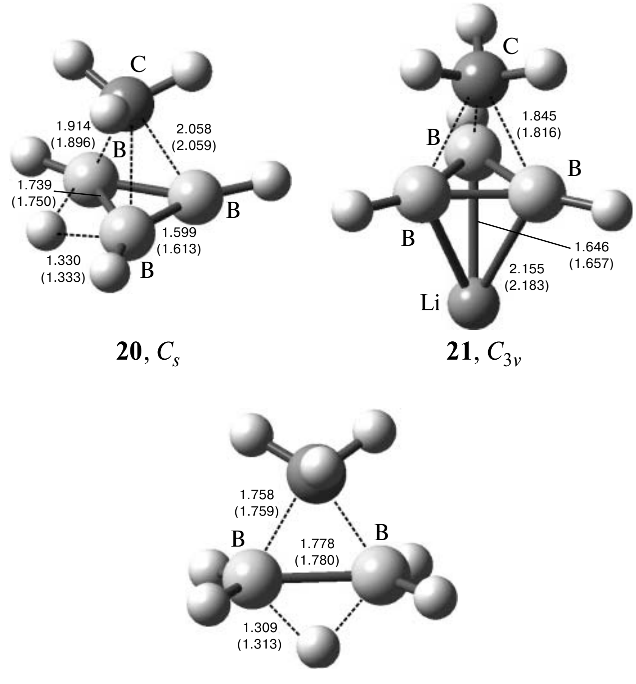
$$\textbf{18} \rightarrow \text{CH}_2\text{Li}_2 + \text{B}_3\text{H}_3 \qquad (Q_2)$$

$$\textbf{19a} \rightarrow \text{CHLi}_3 + \text{B}_3\text{H} \qquad (Q_3)$$

$$\textbf{19b} \rightarrow \text{CHLi}_3 + \text{B}_3\text{H}_3 \qquad (Q_4)$$

Method	Q_1	Q_2	Q_3	Q_4
	kcal mol^{-1}			
MP2	77.4	109.6	133.1	126.0
DFT	66.3	95.9	121.3	114.5

Taking tetrahedrane **15** as an example, we show here how the bonding π-MOs of pyramidal compounds of the second-row elements are composed of fragment orbitals and how the MOs formed are transformed on going to



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

22, C_s

Fig. 2. Geometric parameters of pyramidal structures **20—22** corresponding to energy minima on the PES ($\lambda = 0$) obtained from B3LYP/6-311+G** (DFT) and MP2/6-311+G** (MP2, figures in parentheses) calculations.

isoelectronic boron-containing systems with lithium ligands or bridging H atoms. Analysis of the MOs of tetrahedrane **15** and other pyramidal systems shows[8] that stabilization of the pyramidal structure is mainly due to the interaction of p-orbitals of the apical center with the basal ring π-system (Fig. 3).

Passage from the $\text{HCB}_3\text{H}_3^{3-}$ anionic carborane system obeying the "electron octet" rule to neutral lithium derivatives causes no changes in the pattern of orbital filling and MO shapes; however, the energies of all π- and σ-orbitals decrease markedly (see Fig. 3), thus stabilizing the corresponding structures. A similar stabilization mechanism was also found for the systems with bridging H atoms. Introduction of such atoms also causes no changes in the shape and relative order of the MOs but leads to a marked decrease in their energies compared to the initial anionic system. Thus, bridging H atoms can act as counterions providing an additional stabilization of systems with hypervalent centers.

Pyramidal systems with hypercoordinate N and O atoms. As in hypercoordinate carbon compounds, replacement of carbon atoms by BH and BLi groups in the molecule of azatetrahedrane **23** leads to systems **24—26** (Fig. 4, Table 2). According to calculations, they correspond to minima on the corresponding PES.

Azatriborane **24** was not experimentally detected as yet. The calculated geometric parameters of this system

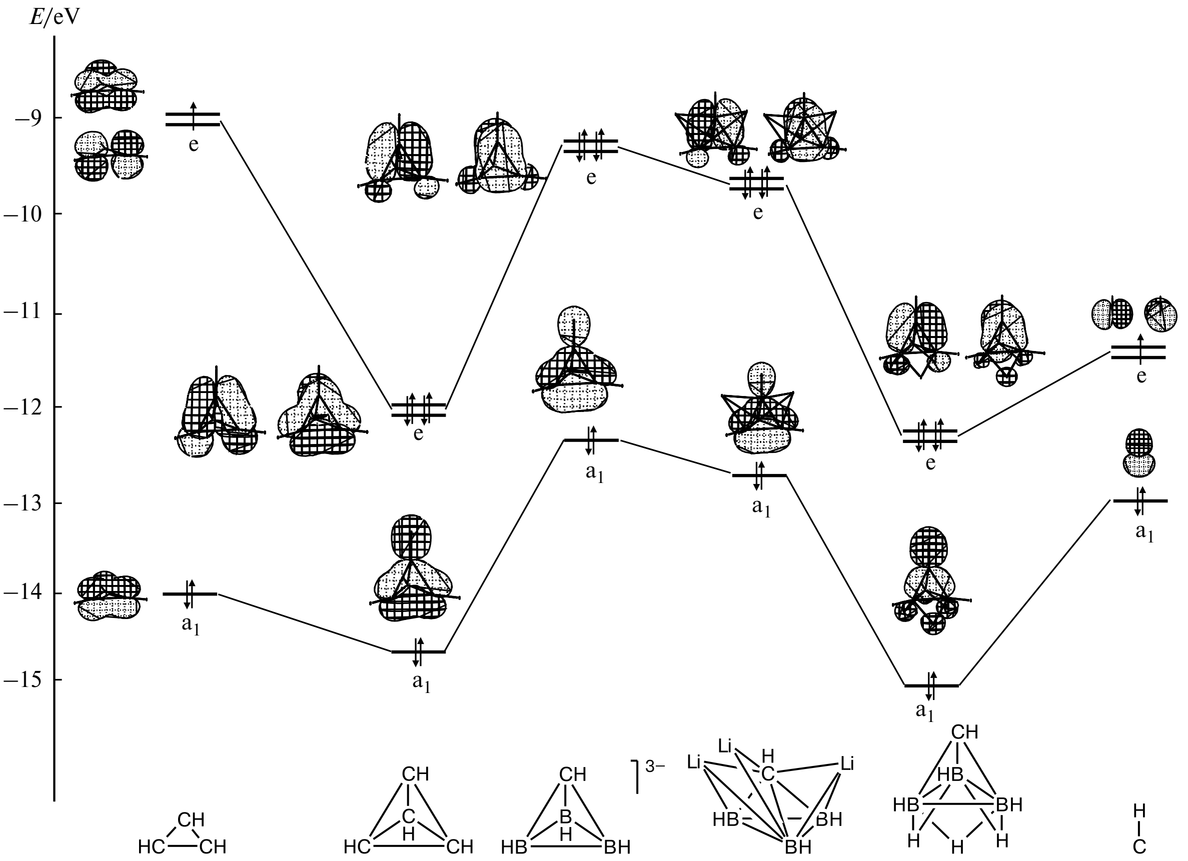


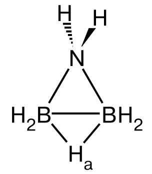
Fig. 3. Composition diagram of tetrahedrane (**15**) bonding π-MOs from fragment orbitals (dark contour) and transformation of the MOs formed as a result of transformation of system **15**.

Table 2. Energy characteristics* of compounds **23**—**26**, **29**, **32**, and **33** obtained from B3LYP/6-311+G** and MP2(full)/6-311+G** calculations

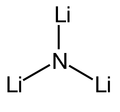
Structure	Symmetry	Method	$-E_{\text{total}}$ (a.u.)	$-(E_{\text{total}}$ + ZPE) (a.u.)	ω_1 /cm^{-1}
23	C_{3v}	DFT	170.736564	170.687964	672.4
		MP2	170.317053	170.268636	584.0
24	C_{3v}	DFT	132.940163	132.869976	408.7
		MP2	132.547144	132.474749	448.7
25	C_s	DFT	153.756341	153.710760	150.0
		MP2	153.256796	153.210691	167.9
26	C_{3v}	DFT	153.755095	153.709849	129.7
		MP2	153.253938	153.208274	118.3
29	C_{3v}	DFT	190.905655	190.857100	584.0
		MP2	190.461694	190.412480	607.3
32	C_s	DFT	178.002943	177.957687	336.8
		MP2	177.565990	177.519966	392.8
33	C_s	DFT	166.683719	166.641545	108.2
		MP2	166.188696	166.145626	165.1

* See note to Table 1.

are in good agreement with those of aminodiborane $H_2NB_2H_5$ (**27**) well-studied[59] by gas-phase electron diffraction. On going from structure **24** to structures **25** and **26** the boron—nitrogen bond length monotonically increases while (to the contrary) the boron—boron bond is monotonically shortened owing to an increase in the coordination number of nitrogen and weakening of its bonding with the boron ring. The electron density transfer from each Li atom to the N atom is at most 0.2 e. The boron—lithium bond order is rather high (>0.2), thus indi-

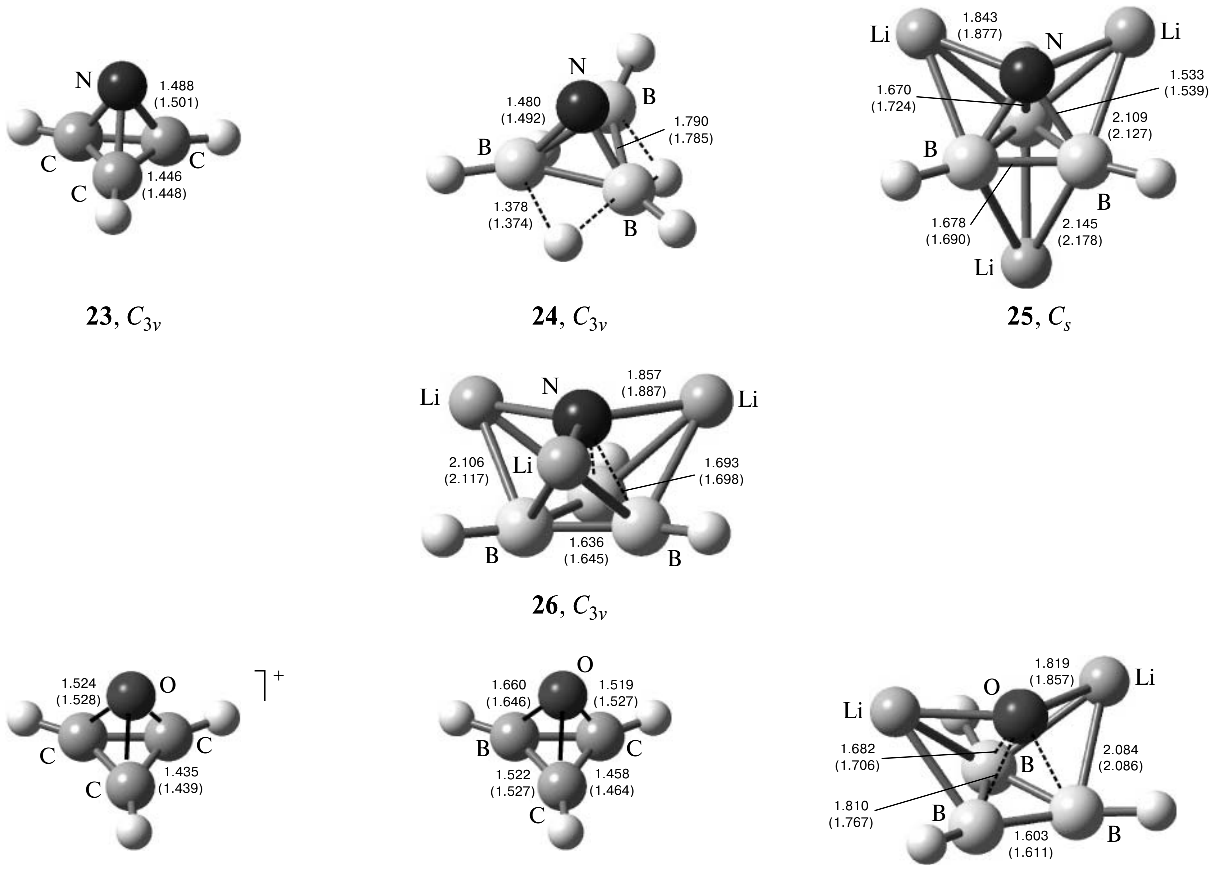


27, C_{2v}



28, D_{3h}

Compound	Bond	Experiment[62]	Calculations DFT	Calculations MP2
27	B—H_a	1.35±0.09	1.344	1.339
	B—N	1.504±0.026	1.561	1.560
28	N—Li	—	1.722	1.764



23, C_{3v} **24**, C_{3v} **25**, C_s

26, C_{3v}

29, C_{3v} **32**, C_{3v} **33**, C_s

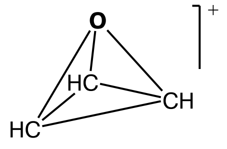
Fig. 4. Geometric parameters of pyramidal structures **23—26**, **29**, **32** and **33** corresponding to energy minima on the PES ($\lambda = 0$) obtained from B3LYP/6-311+G** (DFT) and MP2/6-311+G** (MP2, figures in parentheses) calculations.

cating a large contribution of covalent bonding between the counterion and the pyramidal fragment. At the same time the N—Li bonds in structures **25** and **26** are much weaker than in the simplest system **28**, which can be explained by hypervalence of nitrogen in these molecules.

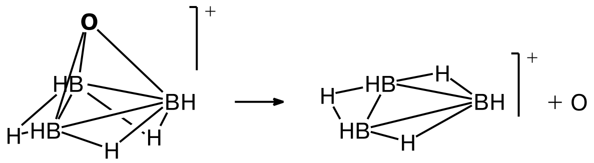
According to our calculations, it is impossible for a boron-containing analog of oxatetrahedrane cation **29** to exist. System **30** barrierlessly decomposes into cation **31** (an aromatic analog of the cyclopropenyl cation[62] with two π-electrons) and a singlet O atom.

Destabilization of system **30** can be explained by inefficient interaction between orbitals of the apical atom and the boron ring π-system due to the high electronegativity of oxygen leading to a decrease in the p-orbital energies (and an increase in the energy gap between the interacting orbitals of the basal and apical fragments), and to a decrease in their diffuseness.

At the same time, structure **32** containing one B atom in the three-membered ring is rather stable and replacement of carbon atoms by BLi groups leads to a stable structure **33** ($\lambda = 0$). The calculated geometric parameters of structures **29**, **32**, and **33** are shown in Fig. 4 and their energy characteristics are listed in Table 2.



29, C_{3v}



30, C_{3v} **31**, C_{3v}

In system **33** the pentacoordinate O atom is distant from the boron ring. Owing to hypercoordination of this atom, all boron—oxygen bonds exceed the upper bound of the range of standard ordinary B—O bond length values (~1.38—1.61 Å) for the known compounds,[63] the oxygen—lithium bond being ~0.2 Å longer than in the simplest molecule **34**.

Li—O—Li

34, $C_{\infty v}$

Method	d(Li—O)/Å
Experiment[64]	1.60±0.02
DFT	1.621
MP2	1.647

Decompositions of systems **25**, **26** and **33** into fragments are highly endothermic reactions, which also confirms that these compounds are thermally stable.

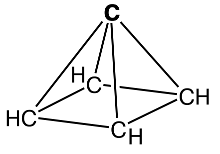
25 $\rightarrow NLi_3 + B_3H_3$ (Q_5)

26 $\rightarrow NLi_3 + B_3H_3$ (Q_6)

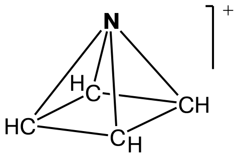
33 $\rightarrow OLi_2 + B_3H_3$ (Q_7)

Method	Q_5	Q_6	Q_7
	kcal mol^{-1}		
MP2	117.9	116.1	58.0
DFT	109.0	108.2	51.9

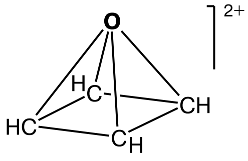
Systems with extended basal rings can be designed analogously to the molecules containing three basal atoms. This is accompanied by a further increase in the coordination number of the hypercoordinate apical center. As in the case of cation **30**, replacement of basal carbon atoms by BH groups in the pyramidane molecule **35** and in azapyramidane and oxapyramidane cations (**36** and **37**, respectively) does not lead to corresponding stable heteroboranes, whereas replacement of the same atoms by BLi groups gives stable systems **38—40** (Fig. 5, Table 3).



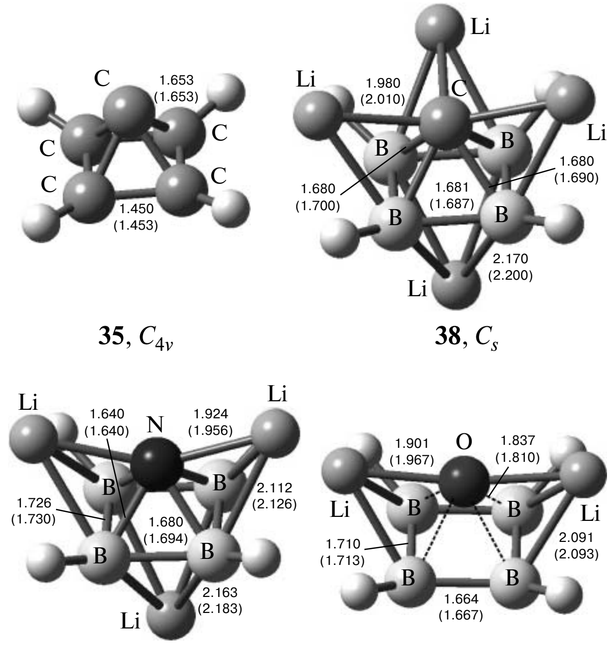
35, C_{4v}



36, C_{4v}



37, C_{4v}



35, C_{4v} **38**, C_s

39, C_{2v} **40**, C_{2v}

Fig. 5. Geometric parameters of pyramidal structures **35**, **38—40** corresponding to energy minima on the PES ($\lambda = 0$) obtained from B3LYP/6-311+G** (DFT) and MP2/6-311+G** (MP2, figures in parentheses) calculations.

Table 3. Energy characteristics* of compounds **35** and **38—40** obtained from B3LYP/6-311+G** and MP2(full)/6-311+G** calculations

Structure	Symmetry	Method	$-E_{\text{total}}$	$-(E_{\text{total}}$ + ZPE)	ω_1 /cm^{-1}
			a.u.		
35	C_{4v}	DFT	192.781074	192.714358	407.4
		MP2	192.309904	192.242659	422.6
38	C_s	DFT	170.089963	170.027867	69.1
		MP2	169.505135	169.441833	126.3
39	C_{2v}	DFT	179.242246	179.181312	208.0
		MP2	178.670047	178.608245	215.1
40	C_{2v}	DFT	192.118946	192.063233	201.3
		MP2	191.547485	191.490155	221.9

* See note to Table 1.

System **38** contains a heptacoordinate carbon atom. The boron—carbon and carbon—lithium bond lengths lie in the ranges of standard bond length values for ordinary covalent bonds.[59—63] The electron density transfer from each Li atom to the pyramidal fragment is at most 0.3 e. A similar situation was found for the systems **39** and **40** with hexacoordinate atoms N and O, respectively. A change in the arrangement of Li atoms in structures **38—40** can result in other stable ($\lambda = 0$) isomeric systems, which are less energetically favorable (>20 kcal mol^{-1}) and therefore left out of consideration. Similarly to the systems discussed above, decompositions of pyramidal systems **38—40** into fragments are highly endothermic reactions, which can indicate thermal stability of these compounds.

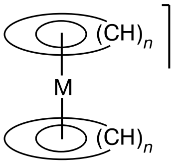
38 $\rightarrow CLi_4 + B_4H_4$ (Q_8)

39 $\rightarrow NLi_3 + B_4H_4$ (Q_9)

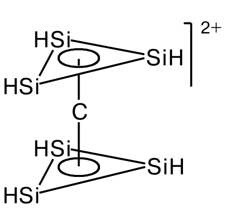
40 $\rightarrow OLi_2 + B_4H_4$ (Q_{10})

Method	Q_8	Q_9	Q_{10}
	kcal mol^{-1}		
MP2	151.3	121.1	27.0
DFT	143.1	113.7	24.8

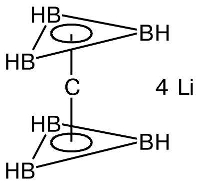
Sandwich systems. Using pyramidal systems, one can design hydrocarbon or boron hydride derivatives, but this is not the case for sandwich systems. Sandwich systems with nitrogen or oxygen central atoms are also unknown. At the same time, chemistry of transition-metal sandwich compounds, metallocenes **41** (M = Fe, Mn, Ni...; *n* = 3—7), is one of the most intensively developing fields of organometallic chemistry.[65] Analogous derivatives of η^5-cyclopentadienyl (*n* = 5) sandwich compounds of Group I (M = Li, Na)[66—70] and Group II (M = Mg, Ca, Ba) elements[68—71] are also well studied. Recently, the first decamethyl-substituted beryllocenes (M = Be, *n* = 5) were synthesized,[72] although decamethyl-substituted silicocene (M = Si, *n* = 5)[73] has rather long been known.



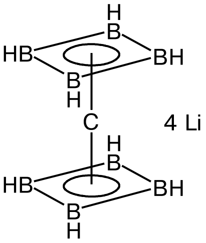
41, D_{nh} (D_{nd})



42, D_{nh}



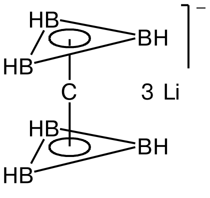
43, D_{3h}



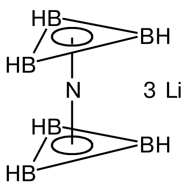
7, D_{4h}

However, it should be noted that (i) both beryllocene[74] and silicocene[75] structures with D_{5d} symmetry are energetically less favorable than isomeric η^1,η^5-half-sandwich and η^2,η^5-bent sandwich systems and (ii) the existence of the η^5-D_{5d}-conformation in solids is governed solely by the crystal packing effects.

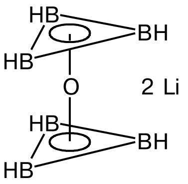
Unlike transition-metal atoms, the bonding of atoms of the main-subgroup elements involves their s- and p- valence orbitals. In stable sandwich compounds of the main-subgroup elements **41**, this limits the number of the bonding MOs composed of the basal ring π- and π*-MOs and the valence orbitals of M atoms to four and the number of core electrons to eight. Obeying these restrictions ("electron octet" rule[1,2,8,76]), one can expect that the simplest stable carbocenes **41** (M = C) with a structure of D_{nh} or D_{nd} symmetry must bear a positive charge *m* = 2 at *n* = 3 and *m* = 4 at *n* = 4. Recently, this assumption was confirmed by the results of B3LYP/6-311++G** calculations of silicon-containing analogs, $C[(SiH)_3]_2^{2+}$, of carbocene **42** (*n* = 3)[77] and lithium derivatives of carborane systems **7**, **43**.[17] According to calculations, the approach to the design of non-classical pyramidal systems with hypercoordinate atoms of the main-subgroup elements based on replacement of carbon atoms in the basal rings by the corresponding number of BLi groups (see above) can also be successfully employed for the design of novel types of sandwich compounds. We present here the results of calculations of a stable sandwich compound of carbon (**44**) and the first stable sandwich systems **45** and **46** containing heteroatoms N and O, respectively.



44



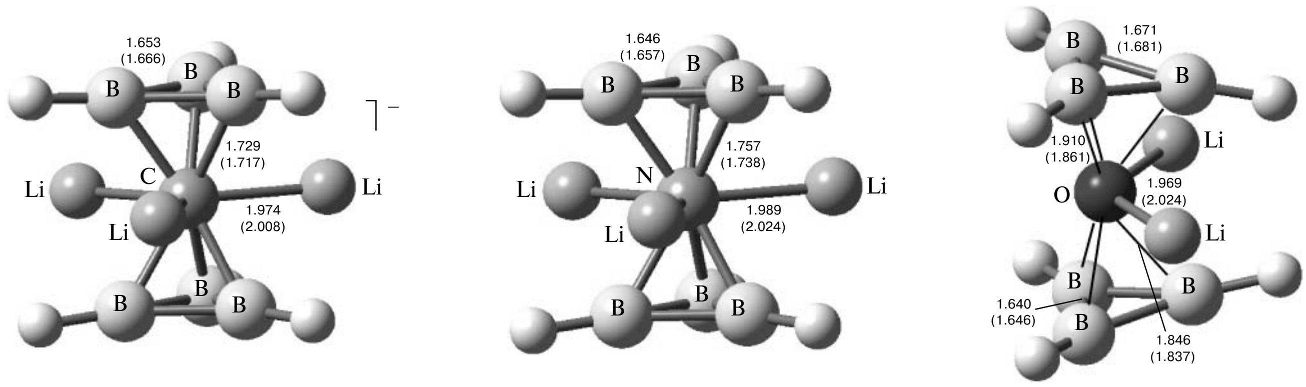
45



46

According to calculations, the structures of ionic clusters **44—46** correspond to rather deep energy minima on the PES. The optimized geometric parameters of these systems are presented in Fig. 6 and their energy characteristics are listed in Table 4. The ring boron—boron bond lengths in clusters **44—46** lie in the range of standard bond length values for ordinary B—B bonds, whereas the distances between B atoms and the central atom monotonically increase on going from carbon to nitrogen atom and then to oxygen. The C—Li, N—Li, and O—Li distances are similar to the corresponding covalent bond lengths.[61,63,64] The B—Li bond lengths are also close to the sum of the covalent radii of B and Li (2.03 Å).[78] These structural characteristics indicate an important role of covalent bonding as a factor which favors stabilization of lithium carborane sandwich structures. Isomers of systems **44—46** with other types of Li coordination are much less energetically favorable and therefore not shown here. The central atoms in structures **44—46** bear large positive Mulliken charges (+2.0 e). This provides a decrease in the effective size of the central atom and weakens the steric strain due to arrangement of the central atom in the rigid lithium—boron cage.

To estimate the thermal stability of neutral sandwich clusters **45** and **46** with respect to decompositon into components, we calculated the heats of the following reactions.



44, D_{3h} **45**, D_{3h} **46**, C_{2v}

Fig. 6. Geometric parameters of sandwich structures **44—46** corresponding to energy minima on the PES (λ = 0) obtained from B3LYP/6-311+G** (DFT) and MP2/6-311+G** (MP2, figures in parentheses) calculations.

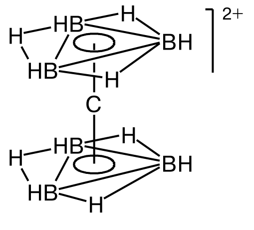
45 → $NLi_3 + 2\,B_3H_3$ (Q_{11})

46 → $OLi_2 + 2\,B_3H_3$ (Q_{12})

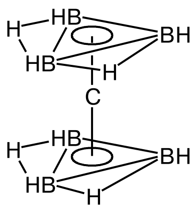
Method	Q_{11}	Q_{12}
	kcal mol^{-1}	
MP2	170.5	55.3
DFT	150.9	45.9

High endothermicity of these dissociation reactions suggests stability of the sandwich structures of lithium-containing heteroboranes.

Replacement of Li atoms in system **44** by bridging hydrogen atoms (the system thus obtained is isoelectronic to the initial system) leads to different structural types of stable carborane sandwich systems. According to calculations, the structures of dication **47** and neutral carboranes **48** and **49** correspond to rather deep energy minima on the corresponding PES.



47



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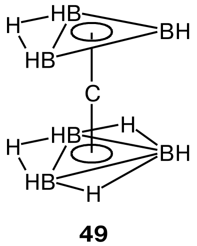


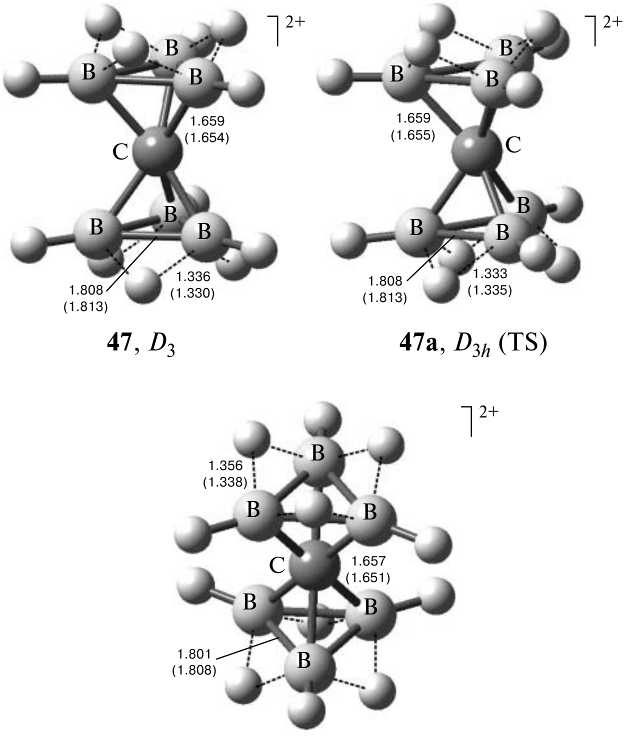
49

Table 4. Energy characteristics* of compounds **44—48**, **50**, and **51** obtained from B3LYP/6-311+G** and MP2(full)/6-311+G** calculations

Structure	Symmetry	Method	$-E_{total}$	$-(E_{total} + ZPE)$	λ	$\omega_1/i\omega$ /cm^{-1}
			a.u.			
44	D_{3h}	DFT	213.462666	213.379937	0	162.1
		MP2	212.761208	212.677490	0	161.1
45	D_{3h}	DFT	230.079609	229.997324	0	158.3
		MP2	229.341579	229.257704	0	161.9
46	C_{2v}	DFT	242.930512	242.853066	0	71.6
		MP2	242.185359	242.105863	0	105.9
47	D_3	DFT	193.672451	193.528085	0	46.0
		MP2	193.054288	192.906718	0	24.9
47a	D_{3h}	DFT	193.672440	193.528181	1	i13.5
		MP2	193.054275	192.906668	1	i18.5
47b	D_{3d}	DFT	193.669694	193.526284	1	i78.1
		MP2	193.053021	192.906340	1	i57.9
48a	C_2	DFT	193.154719	193.034193	0	108.7
		MP2	192.539745	192.416324	0	108.8
48b	C_s	DFT	193.154109	193.033268	0	99.6
		MP2	192.539864	192.416520	0	97.6
48c	C_{2h}	DFT	193.142479	193.023070	1	i123.0
		MP2	192.528488	192.406148	1	i114.8
50	C_s	DFT	193.146784	193.026964	0	68.0
		MP2	192.529141	192.406188	0	80.5
51	D_{3d}	DFT	209.650405	209.511428	0	52.9
		MP2	209.009208	208.866950	0	43.0
51a	D_{3h}	DFT	209.648427	209.509283	1	i72.1
		MP2	209.005907	208.863167	1	i72.8

* See note to Table 1.

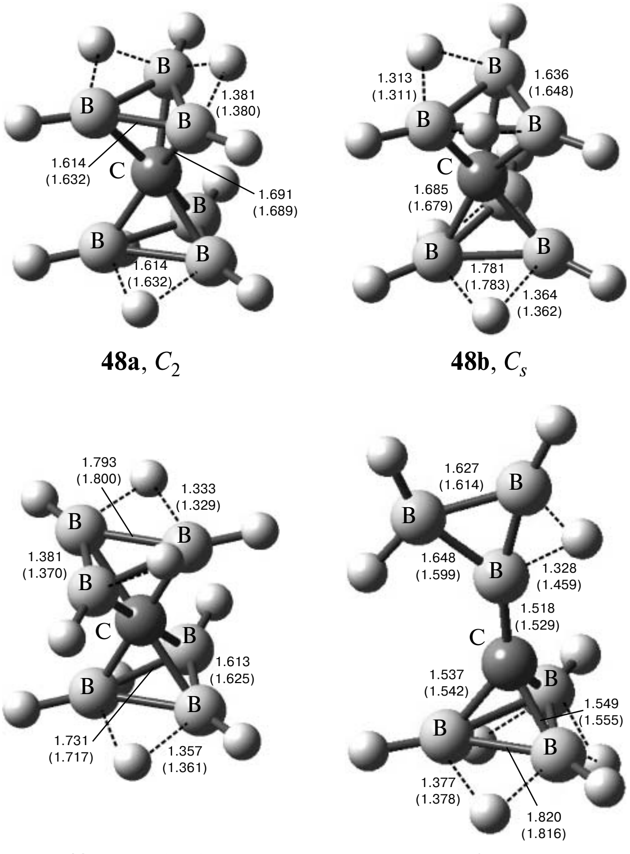
The bridging H atoms act as counterions and can be used for charge control in the system. For instance, by abstracting two bridging H atoms from dication **47** it is possible to obtain neutral systems **48** and **49**. Indeed, according to calculations, neutral systems **48a** and **48b** retain their sandwich structures. A neutral sandwich system **49** with differently arranged bridging H atoms is 5.0 (DFT) and 6.7 kcal mol^{-1} (MP2) less stable than **48a**. The geometric parameters of systems **47** and **48** are pre-



47, D_3 **47a**, D_{3h} (TS)

47b, D_{3d} (TS)

Fig. 7. Geometric parameters of sandwich structure **47** corresponding to a minimum on the PES ($\lambda = 0$) and of structures **47a** and **47b** corresponding to saddle points ($\lambda = 1$) obtained from B3LYP/6-311+G** (DFT) and MP2/6-311+G** (MP2, figures in parentheses) calculations.



48a, C_2 **48b**, C_s

48c, C_{2h} (TS) **50**, C_s

Fig. 8. Geometric parameters of sandwich structures **48a** and **48b** and pyramidal structure **50** corresponding to energy minima on the PES ($\lambda = 0$) and of structure **48c** corresponding to a saddle point ($\lambda = 1$) obtained from B3LYP/6-311+G** (DFT) and MP2/6-311+G** (MP2, figures in parentheses) calculations.

sented in Figs 7 and 8, respectively, and their energy characteristics are given in Table 4.

The most stable form of dication **47** is **47a**. Structure **47a** with D_3 symmetry is stereochemically nonrigid because of a fast internal rotation of one ring relative to the other with a barrier of 1.7 (DFT) and 0.8 kcal mol^{-1} (MP2), which is comparable with the barriers to internal rotation in ferrocene and related metallocene systems.[65] It is noteworthy that internal rotation in system **47a** involves two transition states (TS), **47b** and **47c**. We failed to locate stable ($\lambda = 0$) η^1,η^3- or η^1,η^1-isomers of system **47**. Asymmetric system **48** is characterized by two energy minima corresponding to structures **48a** (C_2 symmetry) and **48b** (C_s symmetry) and one TS **48c** corresponding to internal rotation of one ring relative to the other with a barrier of 7.7 (DFT) and 7.1 kcal mol^{-1} (MP2). In contrast to dication **47a**, we succeeded in locating a classical η^1,η^3-isomer **50** of neutral system **48a** (see Fig. 8). The energy of isomer **50** is 28.8 (DFT) and 21.4 kcal mol^{-1} (MP2) lower than the energy of structure **48**.

The B—B bond lengths in the $(BH)_n$ rings of carboranes **47** and **48** with bridging B—H—B bonds lie in the range of standard bond length values for this type of boranes and carboranes[9,26] and for the pyramidal system **16** considered above (see Figs 7 and 8). The distances between the central carbon atom and B atoms in structures **47** and **48** are amazingly short for these systems and lie in the range of standard bond length values for ordinary B—C bonds.

Taking the $C(B_3H_3)_2^{4-}$ tetraanion obeying the "electron octet" rule as an example, the diagram presented in Fig. 9 shows how the bonding π-MOs of sandwich compounds of the second-row elements are composed of fragment orbitals and how the MOs formed are transformed on going to isoelectronic systems with lithium ligands or bridging H atoms acting as counterions (systems **44** and **47**, respectively). As in the case of pyramidal systems (see above), stabilization of sandwich structures is due to the interaction between p-orbitals of the carbon center and the π-orbitals of two basal rings. Replacement of carbon atom by nitrogen and oxygen atoms makes the p-orbitals of the central atom less diffuse and decreases their energies, thus increasing the energy gap between fragment

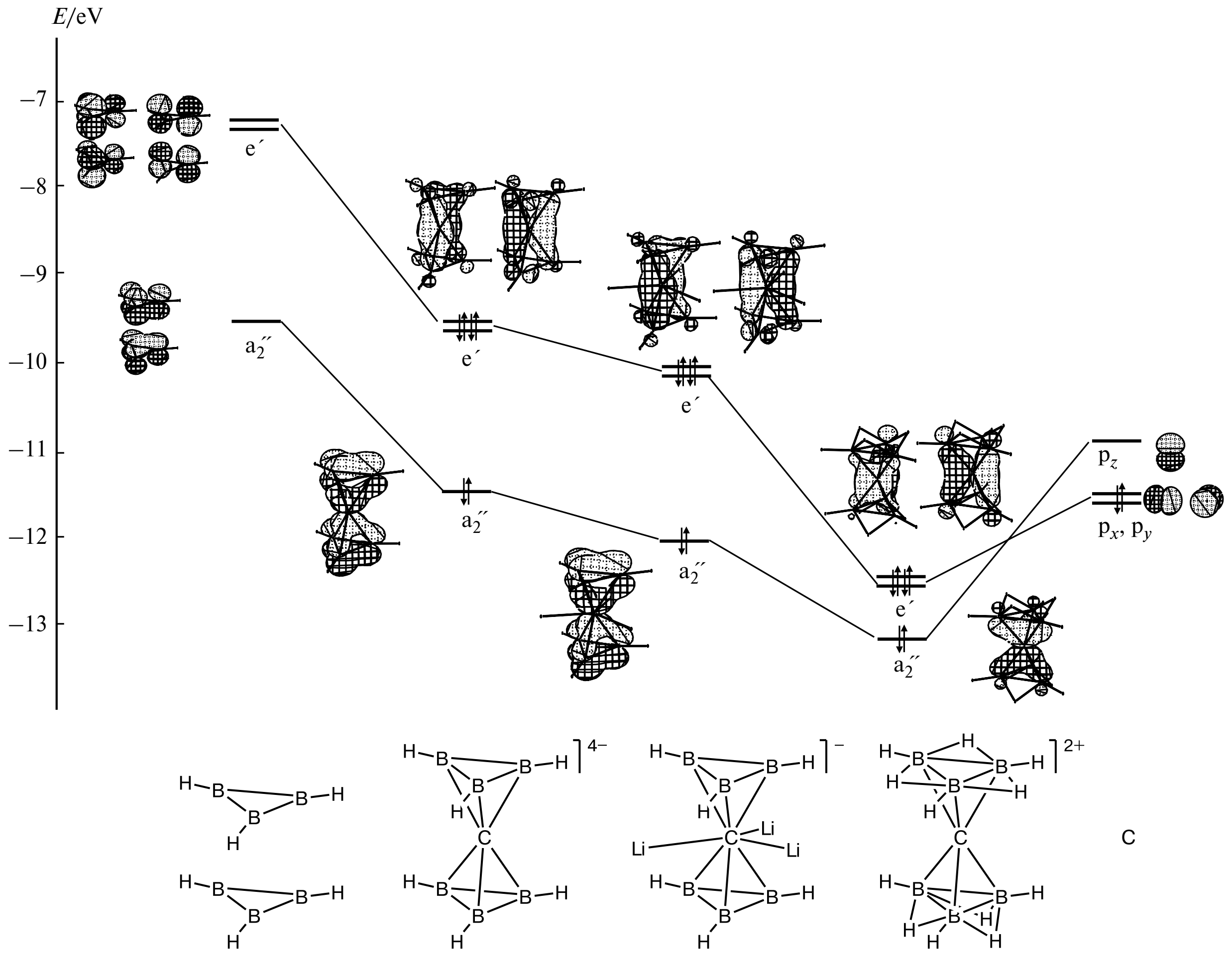
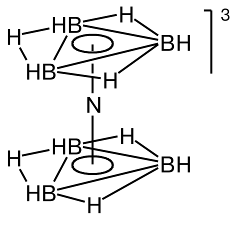


Fig. 9. Composition diagram of bonding π-MOs of $C(B_3H_3)_2{}^{4-}$ tetraanion from fragment orbitals (dark contour) and transformation of the MO formed as a result of incorporation of lithium counterions or bridging hydrogen atoms.

orbitals and reducing the stability of the sandwich system. Weakening of the orbital interaction on going from carbon compounds to the nitrogen and oxygen compounds is accompanied by monotonic elongation of the bonds between the central atom and the boron rings in systems **44—46** (see Fig. 6). Introduction of lithium counterions or bridging H atoms causes no changes in the shape and relative order of the MO energy levels, but leads to a marked decrease in the energy, thus providing an additional stabilization compared to the initial anionic system.

Our study of heteroborane systems isoelectronic to carborane **47** revealed only nitrogen trications **51** corresponding to energy minima on the PES. Calculations of the PES of the sandwich system **52** with the central O atom revealed no corresponding stationary points.

According to calculations, the structure of heteroborane trication **51** (D_{3d} symmetry) corresponds to the energy minimum and structure **51a** with D_{3h} symmetry corresponds to the transition state of internal rotation of one ring relative to the other. The barrier height is 1.3 (DFT) and 2.1 kcal mol^{-1} (MP2), being comparable with the barriers to internal rotation in metallocene systems[65] (see Table 4, Fig. 10).



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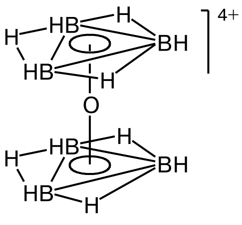
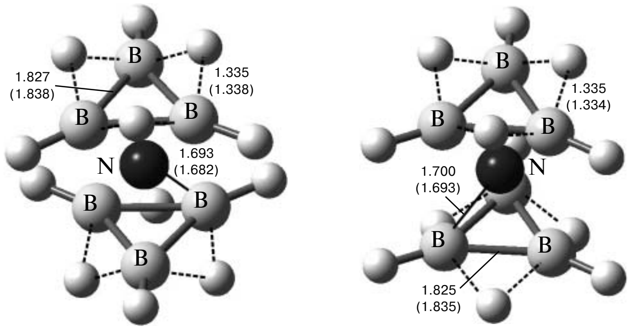


52

Similarly to compounds **16**, **47**, and **48** considered above, the B—B bond lengths in the $(BH)_n$ rings of azaborane **51** (see Fig. 10) lie in the range of standard bond length values for this type of bonds in boranes and carboranes.[9,26] The distances from the central N atom to B atoms in system **51** (~1.7 Å) are longer than all known lengths of covalent ordinary B—N bonds, being very similar to the length of the N→B coordination bond in trimethylaminoborane $Me_3N \cdot BH_3$ (~1.609—1.655 Å).[59] High second normal-mode harmonic frequency (the first



51, D_{3d} **51a**, D_{3h} (TS)

Fig. 10. Geometric parameters of sandwich structure **51** corresponding to minimum on the PES (λ = 0) and of structure **51a** corresponding to a saddle point (λ = 1) obtained from B3LYP/6-311+G** (DFT) and MP2/6-311+G** (MP2, figures in parentheses) calculations.

frequency corresponds to internal rotation) indicates a sufficiently deep energy minimum.

We estimated the thermal stabilities of the dication (**47**) and neutral (**48**) sandwich systems with respect to their decomposition into components. Similarly to the compounds studied above, endothermicity of the decomposition of these systems can serve as an additional confirmation of their stability.

$\mathbf{47a} \rightarrow \mathrm{C} + 2\,\mathrm{B_3H_6}^+$ (Q_{13})

$\mathbf{48a} \rightarrow \mathbf{16} + \mathrm{B_3H_3}$ (Q_{14})

Method	Q_{13}	Q_{14}
	kcal mol^{-1}	
MP2	152.9	39.7
DFT	125.6	27.0

The thermal stabilities of tricationic compounds can hardly be evaluated.

Thus, the results of our calculations show the efficiency of the method considered for the design of novel types of pyramidal and sandwich systems containing hypercoordinate atoms of the second-row elements. The approach is based on the introduction of lithium counterions or bridging H atoms into an initial anionic system. This ensures a pronounced stabilization and allows the electronic structure of a non-classical system to be varied without loss of stability. In addition, the introduction of lithium counterions provides a way for varying the coordination number of the central atom.

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