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Periodic trends and easy estimation of relative stabilities in 11-vertex *nido-p*-block-heteroboranes and -borates

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Abstract Density functional theory computations were carried out for 11-vertex *nido-p*-block-hetero(carba)boranes and -borates containing silicon, germanium, tin, arsenic, antimony, sulfur, selenium and tellurium heteroatoms. A set of quantitative values called “estimated energy penalties” was derived by comparing the energies of two reference structures that differ with respect to one structural feature only. These energy penalties behave additively, i.e., they allow us to reproduce the DFT-computed relative stabilities of 11-vertex *nido*-heteroboranes in general with good accuracy and to predict the thermodynamic stabilities of unknown structures easily. Energy penalties for neighboring heteroatoms (HetHet and HetHet′) decrease down the group and increase along the period (indirectly proportional to covalent radii). Energy penalties for a five- rather than four-coordinate heteroatom, [Het_{5k}(1) and Het_{5k}(2)], generally, increase down group 14 but decrease down group 16, while there are mixed trends for group 15 heteroatoms. The sum of HetHet′ energy penalties results in different but easily predictable open-face heteroatom positions in the thermodynamically most stable mixed heterocarbaboranes and -borates with more than two heteroatoms.

Keywords Structural features · Structural increments · Energy penalties · Density functional theory · 11-Vertex *nido*-heteroboranes and heteroborates · 11-Vertex *nido*-heterocarbaboranes and heterocarbaborates

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Dedicated to Professor Dr. Paul von Ragué Schleyer on the occasion of his 75th birthday

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Introduction

The 11-vertex *nido*-cluster represents the most diverse family of heteroboranes and -borates. Many reactions are known [1–3] to incorporate a hetero-fragment into a smaller *nido*- or *arachno*-cluster, leading to 11-vertex *nido*-heteroboranes. Removal of one vertex from a 12-vertex *closo*-heteroborane cluster also leads to 11-vertex *nido*-heteroboranes and -borates [2, 4, 5]. Experimentally known 11-vertex *nido*-heteroborane and -borate clusters include: group 14 heteroatoms, i.e., carbon [6–9], silicon [10–13], germanium [14–17] and tin [6–8, 18–21]; group 15 heteroatoms, i.e., nitrogen, phosphorus [1, 2], arsenic [5, 22–32] and antimony [33]; group 16 heteroatoms, i.e., sulfur [34], selenium [35–41] and tellurium [35–37, 42, 53]. Williams’ qualitative rules predict isomers with low-coordinate heteroatoms and separated heteroatoms to be preferred [6, 54, 55]. While these rules suffice to select the most stable *closo*-heteroboranes, the presence of additional endo-hydrogen atoms, the large number of isomers and possibly irresolvable conflicts ask for more sophisticated rules to predict the most favorable isomer in the case of *nido*-clusters.

A set of quantitative rules was presented that reproduced the stability order of 6-vertex *nido*-carboranes on the basis of 15 structural increments [56]. Disfavoring structural features, e.g., neighboring carbon atoms, were identified and the so-called energy penalties were derived by a statistical fitting procedure. Applying these energy penalties additively, the stability order of isomeric 6-vertex *nido*-(carba)boranes and -borates can easily be derived by a paper-and-pencil approach. With only nine such fitted quantitative rules, the relative stability order of numerous 11-vertex *nido*-(carba)boranes and -borates [57] was reproduced successfully. The approach was applied to the 10-vertex *nido*-(carba)boranes and -borates [58], and to the 11-vertex *nido*-mixed hetero(carba)boranes and -borates [59] with H–C, P, H–P, N and H–N heteromoieties. Our work [56–59] quantified Williams’ rules [6, 54, 55] by corresponding

energy penalties for each heteroatom and introduced some more rules due to open-face hydrogen characteristics of the *nido*-cluster. These quantitative rules allow us not only to predict the thermodynamically most stable isomer but also to estimate a stability order of various isomers easily [56–59]. Furthermore, these energy penalties successfully elaborate which two heteroatoms are more favorable choices for adjacent positions in the thermodynamically most stable mixed *nido*-heteroboranes. For example, quantitative rules indicate 7,8,10- rather than 7,8,9-, 7,9,10- and 7,9,8-positions for the heteroatoms in *nido*-[P₂CB₈H₉][−] to be thermodynamically most stable [59].

In our previous work [56–59], energy penalties (E_{inc}) were determined by statistical fitting to a large number of structures. This procedure gives accurate values but requires extensive computations. Estimated energy penalties, (E_{inc}'), which are the energy difference of two suitable reference structures differing with respect to one structural feature only, are usually very close to the energy penalties arising from statistical fitting to a large number of isomers [59]. This is to be expected when structural features behave additively. For instance, the estimated energy penalty for adjacent carbon atoms, i.e., the energy difference of 7,8-C₂B₉H₁₁^{2−} and 7,9-C₂B₉H₁₁^{2−} is 16.3 kcal mol^{−1}, very close to the statistically fitted value (16.0 kcal mol^{−1}) derived from 20 carboranes [57–59]. Here, we present the relative stability order ($E_{\text{inc}}^{\text{rel}'}$) for 11-vertex *nido*-sila-, germana-, stanna-, arsa-, stiba-, thia-, seleno- and tellura(carba)boranes and -borates, phosphathiaboranes and -borates and selenathiaboranes produced by E_{inc}' , which are more approximate but easier to determine and are accurate enough for the interpretation of general trends which we wish to investigate in the present study.

The numbering scheme for the 11-vertex *nido*-cluster is shown in Fig. 1. The apical position is numbered as 1. The vertices next to the apex (middle belt) are given numbers 2–6, while the vertices of the open face are numbered from 7 to 11 where 7 is connected to 2 and 3. There are six cage vertices with connections to five other cluster atoms, $k_c=5$ and five peripheral vertices with $k_p=4$, where, c and p denote cage and peripheral vertices, respectively. In the literature, different numbering patterns have been used for mixed heteroboranes.

Computational details

For all hetero(carba)boranes and -borates except stanna, stiba and tellura(carba)boranes and -borates, geometries were consecutively optimized at B3LYP/3-21G and B3LYP/6-31G(d) using the *Gaussian 98* program [60]. The structures presented in this paper are local minima at B3LYP/6-31G(d). Single point energies were computed at B3LYP/6-311+G(d,p). Zero point vibrational energies from B3LYP/6-31G(d) frequency calculations were included to derive the relative energies for all the isomers.

For stanna, stiba and telluraboranes, geometries were optimized at the B3LYP/LANL2DZ level with additional d-polarization functions [61] for Sn, Sb, Te, B and C atoms ($\zeta=0.183, 0.211, 0.237, 0.388, 0.600$, respectively). Single point energies were determined at B3LYP/SDD together with p-polarization function for H ($\zeta=1.000$) and d-polarization function for Sn, Sb, Te, B and C [61] along with an sp set of diffuse functions for Sn, Sb, Te ($\zeta=0.0231, 0.0259, 0.0306$, respectively) [62] as well as for B and C ($\zeta=0.0315$ and 0.0438 , respectively) [63].

Results and discussion

Structural features for hetero(carba)boranes and -borates

Different structural features for hetero(carba)boranes and -borates are shown in Fig. 2 and their energy penalties are listed in Table 1. Energy penalties for carbon in Table 1 are statistically fitted values taken from our previous work [57, 59]. For all other heteroatoms, the energy penalties are estimated as the energy difference of two structures that differ with respect to one structural feature only.

$Het_{5k}(1)$ and $Het_{5k}(2)$

A heteroatom at a 5k position (1–6) rather than a 4k position (7–11) is indicated by the structural feature Het_{5k} [57]. The apical position (number 1) differs from positions 2–6: the former has only 5k neighbors, the latter has two 4k and three 5k neighbors. Hence, higher energy penalties are observed for position 1, i.e., $Het_{5k}(1)$, as compared to positions 2 through 6, i.e.,

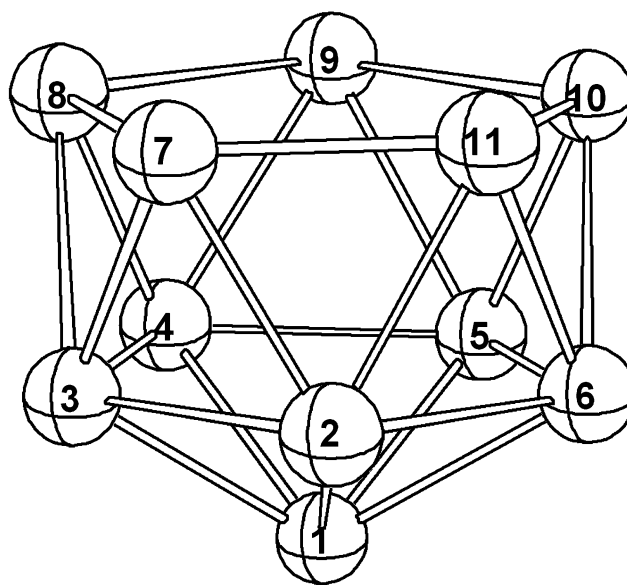
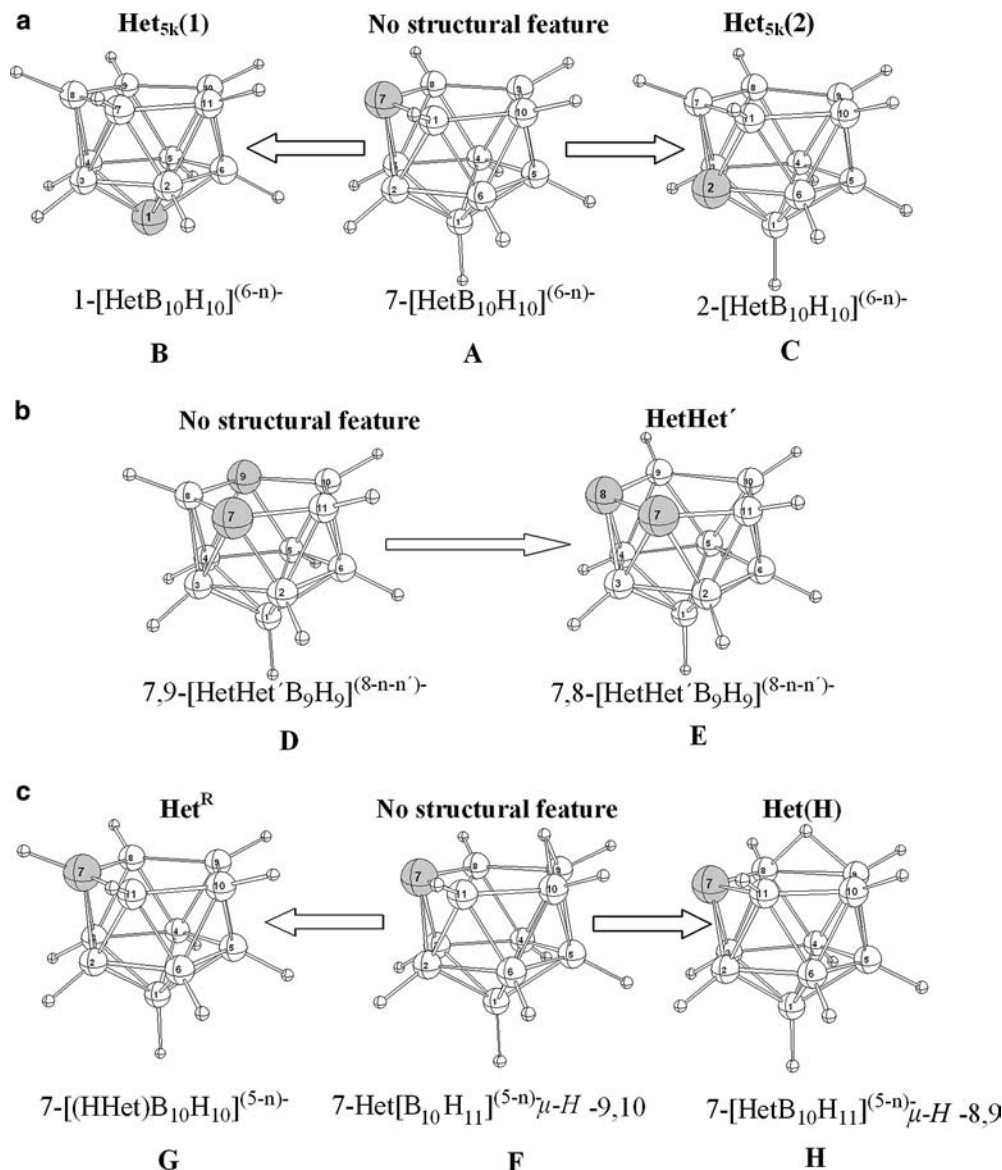


Fig. 1 Numbering scheme for the 11-vertex *nido*-cluster

Fig. 2 a A heteroatom (Het) at a 5 k apical position (vertex number 1, structure *B*) or in the middle belt (positions 2 through 6, structure *C*) rather than at the open face (positions 7 through 11, structure *A*) represent the structural features $\text{Het}_{5k}(1)$ and $\text{Het}_{5k}(2)$, respectively. **b** Heteroatom adjacent (*E*) rather than heteroatom apart isomer (*D*) represent the structural feature HetHet' , where Het and Het' may be equal or different heteroatoms. *n* and *n'* are the number of electrons donated by two heteroatoms (Het and Het')

c μ -*H*-8,9 (hydrogen bridge adjacent to heteroatom, *H*) rather than μ -*H*-9,10 (hydrogen bridge far away from heteroatom, *F*) in *nido*-7- $[\text{HetB}_{10}\text{H}_{11}]^{(4-n)-}$, represent the structural feature Het^R . Hydrogen as an exo-substituent (*G*) rather than bridged between positions 9 and 10 (*F*) produces the structural feature Het^R



$\text{Het}_{5k}(2)$ [57]. Estimated $\text{Het}_{5k}(1)$ energy penalties for a given heteroatom were obtained by comparing the 7- and 1-isomers of $[\text{HetB}_{10}\text{H}_{10}]^{(6-n)-}$ and that of $\text{Het}_{5k}(2)$ by comparing 7- and 2-isomers of $[\text{HetB}_{10}\text{H}_{10}]^{(6-n)-}$ (Fig. 2a), where Het = H-C, H-Si, N, H-N, P or H-P etc. and *n* = number of electrons donated by a given hetero group. $E_{\text{inc}}'[\text{Het}_{5k}(1)]$ and $E_{\text{inc}}'[\text{Het}_{5k}(2)]$ for different heteroatoms are listed in Table 1. For the carbon atom at a 5k position in heterocarboranes, the statistically fitted energy penalty of 28.0 kcal mol⁻¹ obtained originally from 11-vertex *nido*-carboranes will be used [57].

HetHet'

Heteroatom-apart isomers are generally more favorable than heteroatom-adjacent isomers in heteroboranes and -borates [6, 54–59]. The structural feature HetHet' gives the amount of destabilization caused by two adjacent

heteroatoms. For example $7,8-[\text{C}_2\text{B}_8\text{H}_{10}]^{2-}$ with two adjacent carbon atoms (CC) is 16.3 kcal mol⁻¹ less stable than carbon apart 7,9-isomer [57, 59]. The estimated energy penalties for HetHet' were obtained by comparing the 7,8- and 7,9-isomers of $[\text{HetHet}'\text{B}_9\text{H}_9]^{(8-n-n')-}$ (Fig. 2b), where Het or Het' may be equal or different heteroatoms and *n* and *n'* are the number of electrons donated by Het and Het'. When Het and Het' are three-electron-donating heteroatoms ($\sum n = 6$), the structures to be compared are dianions, but they are neutral and monoanionic for two four-electron-donating heteroatoms ($n + n' = 8$) and one three and one four-electron-donating heteroatom ($n + n' = 7$), respectively. HetHet' energy penalties for two adjacent carbon atoms, CC [57], and two adjacent phosphorus atoms, PP [59], are 16.0 and 10.7 kcal mol⁻¹, respectively. HetHet' energy penalties for Het' = Het and for Het' = C are listed in Table 1. The energy penalties for a heteroatom adjacent to a bare phosphorus atom

Table 1 Relative trends of energy penalties [kcal mol⁻¹] for different features in 11-vertex *nido*-hetero(carba)boranes and -borates

Het _a ^a r [pm] ^c		Het _{5k(1)} ^f		Het _{5k(2)} ^g		Het(H) ^h	
Group 14		Group 15 (bare)		Group 15 (Exo-Substituted)		Group 16	
C	2.55 ⁱ 77	N	3.04 75	N^R	3.04 75	O	3.44 ^j 73
16.0	28.0	40.7	44.3	63.6^k	65.6	---	---
16.0	28.0	23.4	41.1	36.9	49.9	---	---
	2.2		0.5		6.7		
Si	1.90 111	P	2.19 106	P^R	2.19 106	S	2.58 102
8.7	45.0	12.0	31.5	36.9	56.7	45.0^l	52.2
8.5	33.6	14.7	27.8	20.1	43.1	31.2	43.8
	4.9		4.3		6.8		6.2
Ge	2.01 122	As	2.18 119	As^R	2.18 119	Se	2.55 116
4.2	54.2	6.9	32.3	26.8	79.7	35.1	48.2
7.7	44.2	16.0	28.5	17.3	---	30.3	40.7
	4.2		3.8		3.4		6.1
Sn	1.96 141	Sb	2.05 138	Sb^R	2.05 138	Te	2.1 135
3.1	69.7	3.8	31.8	15.8	92.6	29.3	45.0
2.4	---	15.7	29.0	12.5	26.2	28.6	34.8
	-1.7		4.5		1.2		6.3

^aHeteroatom^bElectronegativity values, see Pauling, L. *The Nature of the Chemical Bond*. Cornell University Press: Ithaca, New York, 1960^cCovalent radii in pico meter, see Huheey, J.E.; Keiter, E.A.; Keiter, R.L. *Inorganic chemistry: Principles of structure and reactivity*, 4th edition, HarperCollins, New York, USA, 1993^dEnergy penalty for two identical adjacent heteroatoms in the 11-vertex *nido*-cluster^eEnergy penalty for a heteroatom adjacent to a carbon atom in the 11-vertex *nido*-cluster^fHet_{5k(1)} is the structural feature for a heteroatom at a 5k apical position (vertex number 1) rather than the ideal 4k open face positions^gHet_{5k(2)} is the structural feature for a heteroatom at vertices 2 through 6 rather than at the ideal 4k open face positions^hStructural feature Het(H) denotes the amount of destabilization caused by a heteroatom adjacent to a bridged hydrogen atomⁱStatistically fitted values taken from ref. 31. For all other heteroatoms, energy penalties are estimated by comparing two suitable reference structures which differ with respect to one structural feature^jInitial starting 11-vertex *nido*-oxaborane geometries did not survive geometry optimizations due to the expected very high energy penalties of the oxygen atom^kThe N^RN^R energy penalty could not be accurately obtained as the structure rearranged. The rough energy penalty derived by fixing N7-B2 and N8-B2 distances to be 1.775 Å was even higher (76.5 kcal mol⁻¹)^lThe energy penalty for SS (45 kcal mol⁻¹) also needed to be derived by fixing the S(7)-S(8) bond distance to be 2.34 Å

(HetP) and to an exo-substituted phosphorus atom (HetP^R) are listed in Table 2.

Very similar energy penalties were derived for CC (i.e., two adjacent carbon atoms) in carboranes (16.0 kcal mol⁻¹) [57], phosphacarbaboranes (18.3 kcal mol⁻¹) [59], exo-substituted azacarbaboranes (15.4 kcal mol⁻¹) [59]

Table 2 Energy penalties [kcal mol⁻¹] for HetP^R and HetP together with covalent radius of heteroatom (Het)

HetHet'	R _{Het} [pm]	E _{inc'} [kcal mol ⁻¹]
NP	71	18.8
CP	77	15.1
PP	93	10.7
N ^R P ^R	71	42.5
P ^R P ^R	93	36.9
SP ^R	104	38.8
SeP ^R	117	35.8

and thiacarboranes (17.7 kcal mol⁻¹). Hence, we use an average value of 17.0 kcal mol⁻¹ for E_{inc}[CC] in all heterocarbaboranes considered in this work.

Het(H)

This structural feature presents the amount of destabilization caused by a heteroatom (Het) adjacent to a hydrogen bridge. Comparing *nido*-7-[HetB₁₀H₁₁]⁽⁵⁻ⁿ⁾⁻ isomers, (*n* = number of electrons donated by Het) with μ -*H*-8,9 and μ -*H*-9,10 hydrogen positions, directly gives an estimated energy penalty for the structural feature Het(H) (Fig. 2c). This structural feature has a relatively small destabilizing effect. For example, the energy penalty for C(H) was determined to be 2.2 kcal mol⁻¹ for carboranes [57]. The energy penalties of other heteroatoms adjacent to a hydrogen bridge are listed in Table 1. The largest Het(H) energy penalty (9.4 kcal mol⁻¹) is observed for the four-electron-donating P^R heterogroup, while tin has the smallest (even negative) energy penalty E_{inc'}[Sn(H)] = -1.7 kcal mol⁻¹. It is the only negative energy penalty observed for any heteroatom structural feature in 11-vertex *nido*-heteroboranes.

Het^R

This structural feature allows to compare bare (three-electron donating) and exo-substituted (four-electron donating) group 14 heteroatoms. *nido*-7-[HetB₁₀H₁₁]²⁻ (μ -*H*-9,10) and *nido*-7-[(HHet)B₁₀H₁₀]²⁻ (Fig. 2c) give a direct estimate of the energy penalty of Het^R for group 15 heteroatoms. Generally, three-electron-donating nitrogen and phosphorus atoms (N and P) have smaller energy penalties as compared to four electron donating exo-substituted nitrogen and phosphorus (N^R and P^R) atoms [59]. The same is true for bare arsenic (As) and antimony (Sb) atoms in the 11-vertex *nido*-cluster which have generally smaller energy penalties as compared to exo-substituted arsenic (As^R) and antimony (Sb^R) atoms (see Table 1).

Energy penalties as periodic properties of heteroatoms in 11-vertex *nido*-clusters

In this section, the general trends of HetHet', Het_{5k(1)} and Het_{5k(2)} energy penalties will be discussed.

HetHet and HetC energy penalties decrease along group 14 (C \rightarrow Sn), 15 (N \rightarrow Sb) and 16 (S \rightarrow Te) and increase along the periods (C \rightarrow N, Si \rightarrow S, Ge \rightarrow Se, Sn \rightarrow Te, see Table 1). The magnitude of energy penalties depends largely upon the extent of electron localization, which is determined primarily by the number of electrons donated by a heteroatom and secondarily by the electronegativity of the heteroatom. All the heteroatoms in Table 1 formally donate more than two electrons (two electrons are donated by a BH vertex) to the total of 26 skeletal electrons required in an 11-vertex *nido*-cluster and hence cause stronger electron localization as compared to a BH vertex. Two adjacent heteroatoms result in a larger degree of electron localization on two adjacent vertices and hence a positive HetHet energy penalty. This HetHet energy penalty is more positive for three-electron-donating group 15 heteroatoms as compared to the three-electron-donating group 14 heteroatoms. This is due to the larger electronegativity of three-electron-donating group 15 members. Four-electron-donating group 15 members have even higher electron localization due to four rather than three electrons localized at one vertex. Group 16 heteroatoms have even higher energy penalties as compared to group 15 heteroatoms due to larger electronegativity of the group 15 heteroatoms. It is interesting to note that neighboring NH groups have such a large destabilizing effect that the energy penalty could only be estimated by fixing the N(7)-B(2) and N(8)-B(2) distances as the cluster shape was destroyed upon free geometry optimization [59]. Considering the general trends, the energy penalties for oxygen should be the largest but none of the five structural features for 11-vertex *nido*-oxaboranes could

be determined as none of the oxaborane starting geometries optimized to a *nido*-11-vertex cluster geometry. Among the heteroatoms in Table 1, oxygen is the only one for which no experimentally known 11-vertex *nido*-heteroborane exists. The smallest HetHet energy penalty (3.1 kcal mol⁻¹) is found for tin (on the left bottom of Table 1).

Geometric consequences also seem to be important. Incorporation of one large heteroatom requires geometric distortion of the cluster. Incorporating another large heteroatom next to the first enhances the geometric distortion but to a lesser extent as compared to placing it at a yet undistorted site. Although this effect is overruled by the opposing electronic effects, it considerably reduces the energy penalties for two adjacent larger heteroatoms. When there is a significant electronegativity difference between boron and the heteroatoms, the electronic effect dominates. However, when the electronegativity of the heteroatom is very close to that of boron, the relative position of hetero-groups does not influence the electronic situation much and the geometric consequences are important.

Figure 3 shows such general trends for HetHet' and HetC energy penalties, which are indirectly proportional to the covalent radii (directly proportional to electronegativity) within one group. Table 2 also shows very similar effects for HetP^R and HetP energy penalties, where one heteroatom is a phosphorus atom.

Energy penalties for Het_{5k}(1) and Het_{5k}(2) increase down group 14 but decrease down group 16. For both three- as well as four-electron-donating heteroatoms in group 15, however, they show mixed trends (Fig. 4).

Fig. 3 Covalent radii, HetHet and HetC energy penalties for group 14, group 15 and group 16 heteroatoms. HetHet and HetC energy penalties for heteroatoms increase with decrease in covalent radii

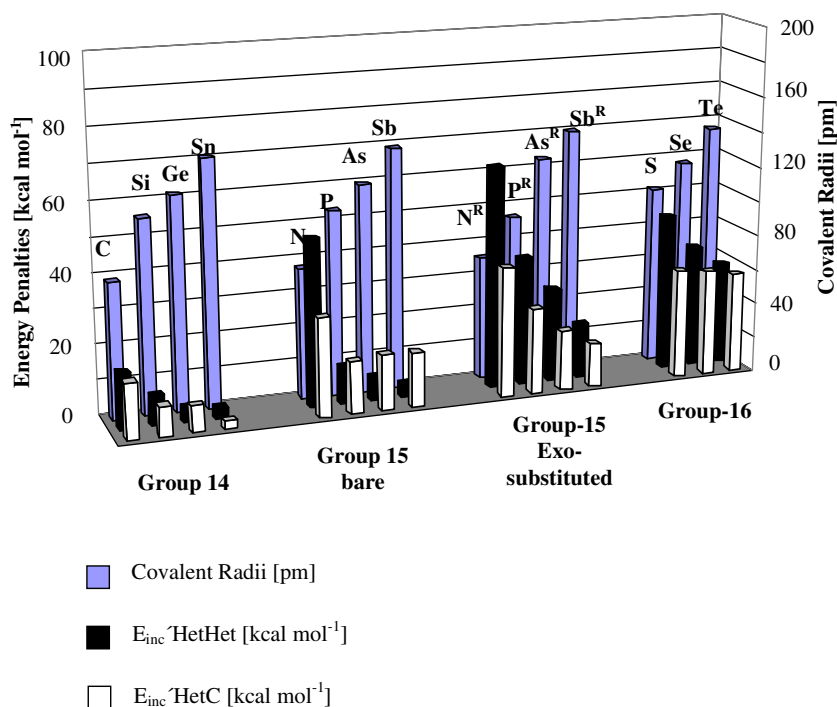
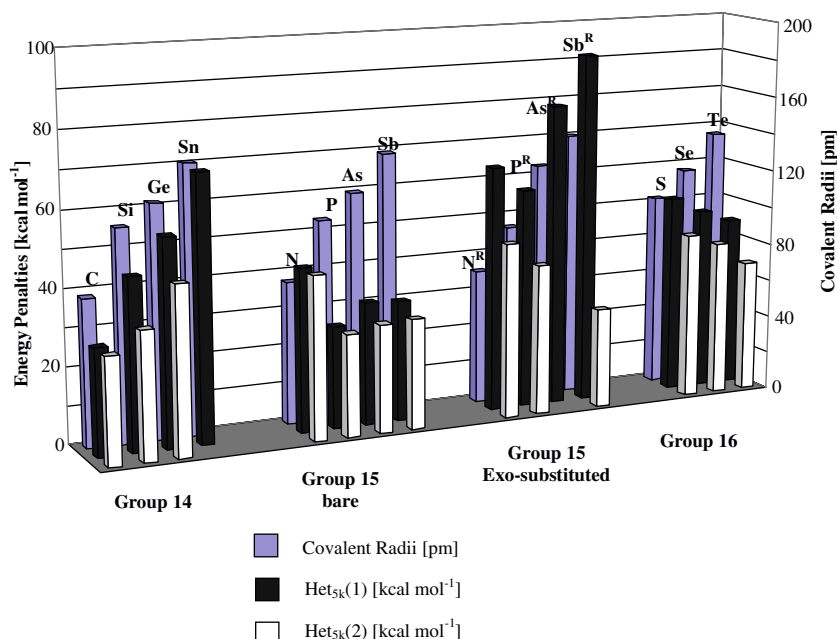


Fig. 4 $\text{Het}_{5k}(1)$ and $\text{Het}_{5k}(2)$ energy penalties for group 14 heteroatoms decrease with decreasing covalent radii but increase for group 16 heteroatoms. Group 15 heteroatoms have mixed trends



The importance of geometric consequences also becomes clear by the pronounced preference for open-face positions for larger heteroatoms. Larger heteroatoms have much larger $\text{Het}_{5k}(1)$ and $\text{Het}_{5k}(2)$ energy penalties. The larger heteroatoms cause more

geometric distortion when connected to five cage vertices (at apical position or in the middle belt), and hence larger energy penalties as compared to the smaller heteroatoms which are closer to a BH vertex in size. In the open face, larger heteroatoms are

Table 3 Estimated energy penalties (E_{inc}'), estimated relative energies ($E_{\text{inc}}^{\text{rel}'}$) and computed relative energies for thia(carba)boranes and -borates. All values are in kcal mol⁻¹

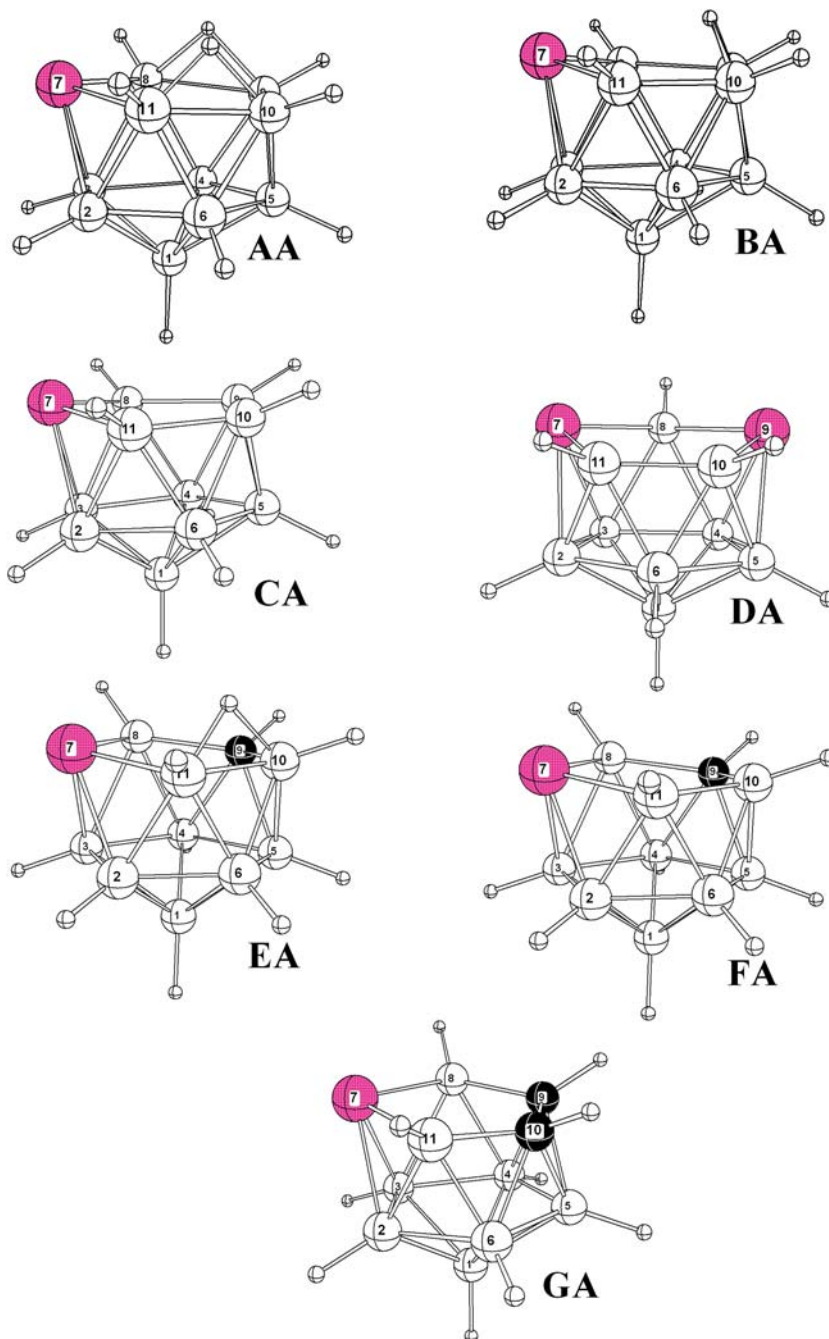
Compound	$\mu\text{-H-}$	C_{5k} 28.0	C(H) 2.1	CC 17.0	$S_{5k}(1)'$ 52.2	$S_{5k}(2)'$ 43.8	S(H) 6.2	SC 31.2	$\sum E_{\text{inc}}'$	$E_{\text{inc}}^{\text{rel}'}$	E_{calc}	$\Delta E'$
AA ^a	7-SB ₁₀ H ₁₂	8,9; 9,10					2		12.4	0.0	0.0	0.0
AB	2-SB ₁₀ H ₁₂	7,8; 9,10				1	1		50.0	37.6	39.8	-2.2
AC	1-SB ₁₀ H ₁₂	7,8; 9,10			1				52.2	39.8	43.8	-4.0
BA ^a	7-SB ₁₀ H ₁₁ ⁻	9,10							0.0	0.0	0.0	0.0
BB ^a	7-SB ₁₀ H ₁₁ ⁻	8,9					1		6.2	6.2	6.2	0.0
BC	2-SB ₁₀ H ₁₁ ⁻	8,9				1			43.8	43.8	44.3	-0.5
CA ^b	7-SB ₁₀ H ₁₀ ²⁻	–							0.0	0.0	0.0	0.0
CB	2-SB ₁₀ H ₁₀ ²⁻	–				1			43.8	43.8	43.8	0.0
CC	1-SB ₁₀ H ₁₀ ²⁻	–			1				52.2	52.2	52.2	0.0
DA ^a	7,9-S ₂ B ₉ H ₉	–							0.0	0.0	0.0	0.0
DB	1,7-S ₂ B ₉ H ₉	–			1				52.2	52.2	55.5	-3.3
EA ^a	7,9-SCB ₉ H ₁₁	10,11	1				1		8.3	0.0	0.0	0.0
EB	7,8-SCB ₉ H ₁₁	9,10	1					1	33.3	25.0	25.6	-0.6
EC	7,8-SCB ₉ H ₁₁	10,11					1	1	37.4	29.1	27.9	1.2
ED	2,8-SCB ₉ H ₁₁	9,10		1		1			45.9	37.6	35.0	2.6
FA ^a	7,9-SCB ₉ H ₁₀ ⁻	–							0.0	0.0	0.0	0.0
FB	7,8-SCB ₉ H ₁₀ ⁻	–						1	31.2	31.2	31.2	0.0
FC	7,1-SCB ₉ H ₁₀ ⁻	–	1						28.0	28.0	33.3	-5.3
FD	1,7-SCB ₉ H ₁₀ ⁻	–			1				52.2	52.2	54.4	-2.2
GA ^a	7,9,10-SC ₂ B ₈ H ₁₀	–		1					17.0	0.0	0.0	0.0
GB ^a	7,8,10-SC ₂ B ₈ H ₁₀	–						1	31.2	14.2	13.1	1.1
GC ^c	8,2,10-SC ₂ B ₈ H ₁₀	–	1						28.0	11.0	13.6	-2.6
GD ^c	7,1,9-SC ₂ B ₈ H ₁₀	–	1						28.0	11.0	17.5	-6.5
GE ^a	7,8,9-SC ₂ B ₈ H ₁₀	–		1				1	48.2	31.2	32.9	-1.7
GF	7,8,11-SC ₂ B ₈ H ₁₀	–						2	62.4	45.4	48.8	-3.4

^aExperimentally known isomers

^bOnly metal derivatives are experimentally known

^cStrong candidates

Fig. 5 Most stable thia(carba)borane and -borate isomers. *White, black and pink balls* represent boron, carbon and sulfur atoms, respectively. **AA**, **BA**, **CA**, **DA**–**GA** are experimentally known. Metal complexes of **CA** are also experimentally known



connected to four cluster vertices and hence are more suitable.

The structural feature Het(H) has very similar energy penalties for four-electron-donating group 16 heteroatoms (S, Se and Te have energy penalties of 6.2, 6.1 and 6.3 kcal mol⁻¹, respectively), however, Het(H) energy penalties do not follow any specific general trend for group 14 and -15 heteroatoms. Moreover, Het(H) energy penalties have a small disfavoring effect (~5 kcal mol⁻¹ in many cases) and can be considered as a fine-tuning increment for two structural isomers differing with respect to open face hydrogen positions only.

Comparisons of the estimated relative stabilities (E_{inc}^{rel}) derived from estimated energy penalties (E_{inc}) with DFT computed values (E_{calc}) for the 11-vertex *nido*-hetero(carba)boranes and -borates

Estimated (E_{inc}) and statistically fitted (E_{inc}) energy penalties as well as E_{inc}^{rel} were reported for 11-vertex *nido*-(carba)boranes and -borates, phospho(carba)boranes and -borates, and aza(carba)boranes and -borates [59]. In this section, the estimated relative stabilities (E_{inc}^{rel}) are compared with the DFT-computed relative energies (E_{calc}) for thia(carba)boranes and -borates, phosphathiaboranes and -borates, seleno-, and telluro(carba)boranes

and -borates, and selenathiaboranes and -borates. $\Delta E'$ is the difference between $E_{\text{inc}}^{\text{rel}'}$ and E_{calc} .

Thia(carba)boranes and -borates

Twenty-five isomers of thia(carba)boranes and -borates from *nido*-SB₁₀H₁₂ to *nido*-SC₂B₈H₁₀ are considered in this study. The estimated energy penalties for S_{5k}(1), S_{5k}(2), SS, SC, CC and S(H) were obtained as explained in the [Structural features for hetero\(carba\)boranes and -borates](#) section. A total of nine 11-vertex *nido*-thia(carba)borane and -borate clusters is experimentally known (labeled by “a” in Table 3, also see Fig. 5). Metal complexes of *nido*-[SB₁₀H₁₀]²⁻ (**CA**) were also reported [64–67]. Two experimentally unknown SC₂B₈H₁₀ isomers, **GC** and **GD** (see Table 3) are predicted as strong candidates for synthesis because of their competitive thermodynamic stabilities.

The experimentally known [3, 34, 68] most stable *nido*-SB₁₀H₁₂ isomer, i.e., *nido*-7-SB₁₀H₁₂ (**AA**) has a sulfur atom at the open face with two bridged hydrogen atoms adjacent to the sulfur atom (structural feature S(H), twice). Both $E_{\text{inc}}^{\text{rel}'}$ and E_{calc} have very similar relative energy values for **AA** (*nido*-2-SB₁₀H₁₂), **AB** (*nido*-2-SB₁₀H₁₂) and **AC** (*nido*-1-SB₁₀H₁₂) (Table 3).

One extra hydrogen atom in *nido*-7-[SB₁₀H₁₁]⁻ (**BA**) [3] bridges positions 9 and 10, resulting in no disfavoring structural feature but is adjacent to the sulfur atom in isomer **BB**, resulting in $E_{\text{inc}}'[\text{S(H)}] = 6.2 \text{ kcal mol}^{-1}$. **BC**, i.e., *nido*-2-[SB₁₀H₁₁]⁻ has a sulfur atom at position number 2 ($E_{\text{inc}}'[\text{S}_{5k}(2)] = 43.8 \text{ kcal mol}^{-1}$) and hence the structure is higher in energy than both **BA** and **BB**.

The absence of hydrogen bridges in *nido*-[SB₁₀H₁₀]²⁻ results in only three possible isomers, i.e., *nido*-7-[SB₁₀H₁₀]²⁻ (**CA**), *nido*-2-[SB₁₀H₁₀]²⁻ (**CB**) and *nido*-1-[SB₁₀H₁₀]²⁻ (**CC**), used to derive $E_{\text{inc}}'[\text{S}_{5k}(2)] = 43.8 \text{ kcal mol}^{-1}$ and $E_{\text{inc}}'[\text{S}_{5k}(1)] = 52.2 \text{ kcal mol}^{-1}$.

The experimentally known [69] *nido*-7,9-S₂B₉H₉ (**DA**) is the most stable isomer as it lacks any structural feature. None of the dithiaborane starting geometries with two adjacent sulfur atoms optimized successfully but converged to rearranged structures. However, a rough estimate for the SS feature was obtained by fixing the S(7)-S(8) distance in 7,8-S₂B₉H₉ to be 2.34 Å (45.5 kcal

mol⁻¹). Obviously, the SS feature, like N^RN^R [59], is incompatible with the *nido*-11-vertex cluster due to too large destabilization.

nido-7,9-SCB₉H₁₁ with μ -*H*-10,11 (**EA**) [70], the most stable SCB₉H₁₁ isomer, has non-adjacent carbon and sulfur atoms. Isomers **EB** through **ED** are at least 25 kcal mol⁻¹ less stable than **EA**. A similar profound preference is found for the heteroatom apart *nido*-7,9-isomer (**FA**) [70] among [SCB₉H₁₀]⁻ structures.

The experimentally known *nido*-7,9,10-SC₂B₈H₁₀ (**GA**) [3] is the most stable of the seven computed isomers. *nido*-7,8,9-SC₂B₈H₁₀ (**GE**) [3] and *nido*-7,8,10-SC₂B₈H₁₀ (**GB**) [3] with $E_{\text{calc}} = 32.9$ and 14.2 kcal mol⁻¹, respectively are also experimentally known. 8,2,10- (**GC**) and 7,1,9-SC₂B₈H₁₀ (**GD**) are thermodynamically more stable than 7,8,9-SC₂B₈H₁₀ (**GE**) [3], but are still experimentally unknown.

Phosphathiaboranes and -borates

The relative stabilities as determined from DFT computations and from structural increments for a few phosphathiaboranes are compared in Table 4. [PSB₉H₉]⁻ structures lack extra hydrogen atoms and possess bare-phosphorus atom/s only. For *nido*-PSB₉H₁₀, however, both bare and exo-substituted phosphorus atoms are considered. The energy penalties derived for a phosphorus atom in phospho(carba)boranes and -borates [59] and for a sulfur atom in thia(carba)boranes and -borates (this paper) along with energy penalties for PS (derived by comparing *nido*-7,9-[PSB₉H₉]⁻ with *nido*-7,8-[PSB₉H₉]⁻) and P^RS (derived by comparing *nido*-7,9-(PH)SB₉H₉ with *nido*-7,8-(PH)SB₉H₉) can be used to estimate the relative stabilities of phosphathiaboranes. The estimated relative energies of four *nido*-PSB₉H₁₀ isomers (i.e., **HA**–**HD** that differ in more than one feature) were found to be in good agreement with the relative energies computed at B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) (see Table 4, **HA**–**HD**). 7,9-PSB₉H₁₀ μ -*H*-10,11 (**HA**) with the structural features P(H) and S(H) has the least $\sum E_{\text{inc}}'$, $E_{\text{inc}}^{\text{rel}'}$ and E_{calc} values but is still experimentally unknown. *nido*-7,9-PSB₉H₁₀ with an exo-substituted phosphorus atom (**HB**) is computed to be 3.4 kcal mol⁻¹ higher in

Table 4 Estimated energy penalties (E_{inc}'), estimated relative energies ($E_{\text{inc}}^{\text{rel}'}$) for phosphathiaboranes. DFT computed relative energies are also reported for **HA** to **HD**. All values are in kcal mol⁻¹

Compound	μ - <i>H</i> -	P(H) 2.2	P ^R 13.3	S(H)' 6.1	PS' 21.4	P ^R S' 38.8	$\sum E_{\text{inc}}'$	$E_{\text{inc}}^{\text{rel}'}$	E_{calc}	$\Delta E'$
HA ^a	7,9-PSB ₉ H ₁₀	10,11	1	1			8.3	0.0	0.0	0.0
HB ^b	7,9-(HP)SB ₉ H ₁₀		1				13.3	5.0	3.4	1.6
HC	7,8-PSB ₉ H ₁₀	10,11	1		1		23.6	15.3	13.8	1.5
HD	7,8-(HP)SB ₉ H ₁₀			1		1	52.1	43.8	42.2	1.6
IA	7,9-PSB ₉ H ₉ ⁻						0.0	0.0	0.0	0.0
IB	7,8-PSB ₉ H ₉ ⁻				1		21.4	21.4	21.4	0.0

^aStrong candidate for synthesis

^b7-Ph-**HB**, i.e., 7-Ph derivative of 7,9-PSB₉H₁₀ is experimentally known

Table 5 Estimated energy penalties (E_{inc}'), estimated relative energies ($E_{\text{inc}}^{\text{rel}'}$) for selenaboranes and -borates. DFT computed relative energies are also reported for some structures. All values are in kcal mol⁻¹

Compound	μ -H-	Se _{5k} (1)'	Se _{5k} (2)'	Se(H)'	SeSe'	$\sum E_{\text{inc}}'$	$E_{\text{inc}}^{\text{rel}'}$	E_{calc}	$\Delta E'$
		48.2	40.7	6.1	35.1				
JA ^a	7-SeB ₁₀ H ₁₂	8,9; 10,11		2		12.2	0.0	0.0	0.0
JB	2-SeB ₁₀ H ₁₂	7,8; 9,10	1	1		46.8	34.6	39.5	-4.9
KA ^a	7-SeB ₁₀ H ₁₁ ⁻	9,10				0.0	0.0	0.0	0.0
KB	7-SeB ₁₀ H ₁₁ ⁻	8,9		1		6.1	6.1	6.1	0.0
KC	1-SeB ₁₀ H ₁₁ ⁻	7,8	1			48.2	48.2	52.6	-4.4
LA ^b	7-SeB ₁₀ H ₁₀ ²⁻					0.0	0.0	0.0	0.0
LB	2-SeB ₁₀ H ₁₀ ²⁻		1			40.7	40.7	40.7	0.0
MA	7,9-Se ₂ B ₉ H ₉					0.0	0.0	0.0	0.0
MB ^a	7,8-Se ₂ B ₉ H ₉				1	35.1	35.1	35.1	0.0

^aExperimentally known isomers^bCyclopentadienyl metal derivatives are experimentally known**Table 6** Estimated energy penalties (E_{inc}'), estimated relative energies ($E_{\text{inc}}^{\text{rel}'}$) for selenacarbaboranes and -borates. DFT computed relative energies are also reported for some structures. All values are in kcal mol⁻¹

Compound	μ -H-	C _{5k}	C(H)	CC	Se _{5k} (1)'	Se _{5k} (2)'	Se(H)'	SeC'	$\sum E_{\text{inc}}'$	$E_{\text{inc}}^{\text{rel}'}$	E_{calc}	$\Delta E'$
		28.0	2.1	17.0	48.2	40.7	6.1	30.3				
NA ^a	7,9-SeCB ₉ H ₁₁	10,11	1				1		8.2	0.0	0.0	0.0
NB ^b	7,8-SeCB ₉ H ₁₁	9,10	1					1	32.4	24.2	24.8	-0.6
NC	7,8-SeCB ₉ H ₁₁	10,11					1	1	36.4	28.2	26.5	1.7
ND	1,7-SeCB ₉ H ₁₁	9,10	1			1			42.8	34.6	32.8	1.8
NE	1,7-SeCB ₉ H ₁₁	8,9	1		1				50.3	42.1	46.7	-4.6
NF	2,4-SeCB ₉ H ₁₁	9,10	1	1		1			70.8	62.6	65.0	-2.4
OA	7,9-SeCB ₉ H ₁₀								0.0	0.0	0.0	0.0
OB	7,8-SeCB ₉ H ₁₀							1	30.3	30.3	30.3	0.0
OC	7,1-SeCB ₉ H ₁₀	1							28.0	28.0	32.6	-4.6
PA ^c	7,9,10-SeC ₂ B ₈ H ₁₀			1					17.0	0.0	0.0	0.0
PB	7,8,10-SeC ₂ B ₈ H ₁₀							1	30.3	13.3	2.5	9.8
PC	7,1,9-SeC ₂ B ₈ H ₁₀	1							28.0	11.0	7.6	3.4
PD	7,8,9-SeC ₂ B ₈ H ₁₀			1				1	47.3	30.3	22.5	8.8
PE	7,8,11-SeC ₂ B ₈ H ₁₀							2	60.6	42.6	37.4	5.2

^aStrong candidate^b7-Cycloheptamine derivative is experimentally known^cExperimentally known isomer

energy than the former and its phenyl derivative i.e., *nido*-7-Ph-7,9-PSB₉H₉ was experimentally characterized [3].

Selena(carba)boranes and -borates

Estimated energy penalties were used to give the relative stability order of 25 selena(carba)boranes and -borates (Tables 5 and 6). The relative stability order is correctly reproduced in most cases, yet $\Delta E'$ (the difference of $E_{\text{inc}}^{\text{rel}'}$ and E_{calc}) is larger for SeC₂B₈H₁₀ isomers (up to 9.8 kcal mol⁻¹ for **PB**).





The most stable SeB₁₀H₁₂ isomer i.e., *nido*-7-SeB₁₀H₁₂ (**JA**) [39] has the selenium atom at vertex number seven with hydrogens bridging between 8/9 and 10/11 positions (structural feature Se(H) twice). The increment system suggests the deprotonated species, i.e., *nido*-7-[SeB₁₀H₁₁]⁻ [35–41], with a hydrogen bridging positions 9/10 (**KA**) rather than positions 8/9 (**KB**) to be the most stable as in the case of exo-substituted

nido-7-[(PH)B₁₀H₁₂]⁻ [59]. *nido*-7-[SeB₁₀H₁₀]²⁻ (**LA**) was reported as a ligand in complexes with different metal fragments [35–38, 42, 43, 71, 72]. The geometry of *nido*-7,8-Se₂B₉H₉ (**MB**) [73–76] unlike that of *nido*-7,8-S₂B₉H₉ could successfully be optimized and is 35.1 kcal mol⁻¹ higher in energy than the experimentally still unknown but energetically more favorable 7,9-isomer (**MA**). Similarly, the heteroatom apart *nido*-7,9-SeCB₉H₁₁ (**NA**), the most stable SeCB₉H₁₁ isomer, is

Table 7 Estimated energy penalties (E_{inc}'), estimated relative energies ($E_{\text{inc}}^{\text{rel}'}$) for selenathiaboranes. All values are in kcal mol⁻¹

Compound	$E_{\text{inc}}^{\text{rel}'}$	E_{calc}	ΔE	Structural feature
7,9-SeSB ₉ H ₉	0.0	0.0	0.0	None
QB	40.2	40.2	0.0	SSe'
QC	40.7	36.0	4.7	Se _{5k} (2)'
QD	43.8	38.3	5.5	S _{5k} (2)'
QE	48.1	51.9	-3.8	Se _{5k} (1)'
QF	52.2	54.7	-2.5	S _{5k} (1)'

Table 8 Estimated relative energies (kcal mol⁻¹) of 7,9,10-, 7,8,10-, 7,8,9- and 7,8,11-isomers in [HetC₂B₈H₁₀]⁽⁴⁻ⁿ⁾⁻ a,b

Heteroatom (cluster charge)	 7,9,10- ^c	 7,8,10- ^d	 7,8,9- ^e	 7,8,11- ^f
Het = H-Si (-1)	CC = 17.0 <i>E</i> _{rel} = 7.5	SiC = 8.5 <i>E</i> _{rel} = 0.0	SiC + CC = 25.5 <i>E</i> _{rel} = 17.0	2*SiC = 17.0 <i>E</i> _{rel} = 8.5
Het = H-Ge (-1)	CC = 17.0 <i>E</i> _{rel} = 9.3	GeC = 7.7 <i>E</i> _{rel} = 0.0	GeC + CC = 24.7 <i>E</i> _{rel} = 17.0	2*GeC = 15.4 <i>E</i> _{rel} = 7.7
Het = H-Sn (-1)	CC = 17.0 <i>E</i> _{rel} = 14.6	SnC = 2.4 <i>E</i> _{rel} = 0.0	SnC + CC = 19.4 <i>E</i> _{rel} = 17.0	2*SnC = 4.8 <i>E</i> _{rel} = 2.4
Het = N (-1)	CC = 17.0 <i>E</i> _{rel} = 0.0 (0.0)	NC = 28.4 <i>E</i> _{rel} = 11.4 (6.1)	NC + CC = 40.0 <i>E</i> _{rel} = 23.0	2*NC = 56.8 <i>E</i> _{rel} = 39.8
Het = P (-1)	CC = 17.0 <i>E</i> _{rel} = 1.9 (3.0)	PC = 15.1 <i>E</i> _{rel} = 0.0 (0.0)	PC + CC = 32.1 <i>E</i> _{rel} = 17.0 (17.9)	2*PC = 31.2 <i>E</i> _{rel} = 15.1 (18.1)
Het = As (-1)	CC = 17.0 <i>E</i> _{rel} = 1.0	AsC = 16.0 <i>E</i> _{rel} = 0.0	AsC + CC = 33.0 <i>E</i> _{rel} = 17.0	2*AsC = 32.0 <i>E</i> _{rel} = 16.0
Het = Sb (-1)	CC = 17.0 <i>E</i> _{rel} = 1.3	SbC = 15.7 <i>E</i> _{rel} = 0.0	SbC + CC = 32.7 <i>E</i> _{rel} = 17.0	2*SbC = 31.4 <i>E</i> _{rel} = 15.7
Het = H-N (0)	CC = 17.0 <i>E</i> _{rel} = 0.0 (0.0)	N ^R C = 37.2 <i>E</i> _{rel} = 20.2 (18.8)	N ^R C + CC = 44.2 <i>E</i> _{rel} = 37.2 (41.3)	2*N ^R C = 74.4 <i>E</i> _{rel} = 57.4 (58.8)
Het = H-P (0)	CC = 17.0 <i>E</i> _{rel} = 0.0 (0.0)	P ^R C = 24.3 <i>E</i> _{rel} = 7.3 (5.2)	P ^R C + CC = 43.6 <i>E</i> _{rel} = 23.6 (24.9)	2*P ^R C = 48.6 <i>E</i> _{rel} = 31.6 (29.5)
Het = H-As (0)	CC = 17.0 <i>E</i> _{rel} = 0.0	As ^R C = 17.3 <i>E</i> _{rel} = 0.3	As ^R C + CC = 34.3 <i>E</i> _{rel} = 17.3	2*As ^R C = 34.6 <i>E</i> _{rel} = 17.6
Het = H-Sb (0)	CC = 17.0 <i>E</i> _{rel} = 4.5	Sb ^R C = 12.5 <i>E</i> _{rel} = 0.0	Sb ^R C + CC = 29.5 <i>E</i> _{rel} = 17.0	2*Sb ^R C = 25.0 <i>E</i> _{rel} = 12.5
Het = S (0)	CC = 17.0 <i>E</i> _{rel} = 0 (0.0)	SC = 32.0 <i>E</i> _{rel} = 15.0 (13.1)	SC + CC = 49.0 <i>E</i> _{rel} = 32.0 (32.9)	2*SC = 64.0 <i>E</i> _{rel} = 47.0 (48.8)
Het = Se (0)	CC = 17.0 <i>E</i> _{rel} = 0 (0.0)	SeC = 30.3 <i>E</i> _{rel} = 12.7 (2.5)	SeC + CC = 47.3 <i>E</i> _{rel} = 30.3 (22.5)	2*SeC = 60.6 <i>E</i> _{rel} = 43.6 (37.4)
Het = Te (0)	CC = 17.0 <i>E</i> _{rel} = 0	TeC = 28.6 <i>E</i> _{rel} = 11.6	TeC + CC = 45.6 <i>E</i> _{rel} = 28.6	2*TeC = 57.2 <i>E</i> _{rel} = 40.2

^aHet may be a three- or four-electron-donating heteroatom. *n* corresponds to the number of electrons donated by a given heteroatom

^bB3LYP/6-311+G(d,p)//B3LYP/6-31G(d)+ZPE computed relative stabilities of various [HetC₂B₈H₁₀]⁽⁴⁻ⁿ⁾⁻ isomers are listed in parenthesis for various heteroatoms. These values are usually very close to the values predicted by estimated energy penalties

^c7,9,10-[NC₂B₈H₁₀]⁻, 7,9,10-(HN)C₂B₈H₁₀, 7,9,10-SC₂B₈H₁₀, 7,9,10-SeC₂B₈H₁₀ are experimentally known

^d7,8,10-SC₂B₈H₁₀ is experimentally known

^e7,8,9-[NC₂B₈H₁₀]⁻ and 7-Me and 7-Ph derivatives of 7,8,9-(HP)C₂B₈H₁₀ are experimentally known

^f7-Ph derivatives of 7,8,11-(HP)C₂B₈H₁₀ is experimentally known

still experimentally unknown although the 7-cyclohexanamine derivative of the 7,8-isomer (**NB**) is experimentally known [77]. *nido*-7,9,10-SeC₂B₈H₁₀ (**PA**) is experimentally known [73] and other computed SeC₂B₈H₁₀ structures (**PB–PE**) are thermodynamically less stable (Table 6).

Selenathiaboranes

The energy penalty (40.2 kcal mol⁻¹) for the structural feature SSe was obtained as the energy difference of 7,8- and 7,9-SeSB₉H₉. The latter is more stable and is

experimentally known [69]. Relative energies of five SeSB₉H₉ isomers are given in Table 7.

Estimated energy penalties (E_{inc}^{\prime}) and corresponding estimated relative stabilities ($E_{\text{inc}}^{\text{rel}}$) for other 11-vertex nido-hetero(carba)boranes and -borates

Estimated energy penalties for sila-, germa-, stanna-, bare and exo-substituted arsa- and stiba(carba)boranes and -borates are reported in Table 1, which can be used to produce the $E_{\text{inc}}^{\text{rel}}$ for the 11-vertex nido-hetero(carba)boranes and -borates with H–Si, H–Ge, H–Sn, As, H–As, Sb and H–Sb heterogroups, respectively.

Prediction of thermodynamically most stable mixed heteroboranes and -borates with three open face heteroatoms

Energy penalties for the HetHet' structural features describe the relative energies of open-face heteroboranes with two equal heteroatoms, for example, [C₂B₉H₁₁]²⁻ [57], P₂B₉H₁₁ [59], Se₂B₉H₉ or that of heteroboranes with two different heteroatoms, e.g., 7,8- and 7,9-isomers of [PSB₉H₉]⁻ and PSB₉H₁₀, SeSB₉H₉ etc. However, it is complex to predict the thermodynamically most stable isomer in mixed heteroboranes with three open-face heteroatoms, e.g., [P₂CB₈H₉]⁻ [78], [PC₂B₈H₁₀]⁻ [79, 80], SC₂B₈H₁₀ [3], SeC₂B₈H₁₀ [73], NC₂B₈H₁₁ [81], [NC₂B₈H₁₀]⁻ [81]. Here we present only [HetC₂B₈H₁₀]⁽⁴⁻ⁿ⁾⁻ examples, (where n = number of electrons donated by a heterogroup, and Het may be a three-electron-donating heteroatom/group, i.e., H–C, H–Si, H–Ge, H–Sn, N, P, As, Sb, or a four-electron-donating heteroatom/group, i.e., H–N, H–P, H–As, H–Sb, S, Se, Te (Table 8). All four possibilities for [HetC₂B₈H₁₀]⁽⁴⁻ⁿ⁾⁻ structures with open face heteroatoms, i.e., 7,9,10-, 7,8,10-, 7,8,9- and 7,8,11-[HetC₂B₈H₁₀]⁽⁴⁻ⁿ⁾⁻ will be discussed.

Both 7,9,10- and 7,8,10-isomers of [HetC₂B₈H₁₀]⁻ have one structural feature each, i.e., CC and HetC, respectively. However, 7,8,9- and 7,8,11-isomers of [HetC₂B₈H₁₀]⁻ have two structural features each, i.e., HetC+CC and 2-HetC, respectively. For group 14 heteroatoms, i.e., H–Si, H–Ge and H–Sn, the HetC, i.e., SiC, GeC and SnC energy penalties are smaller than that of CC and therefore 7,8,10-isomers (i.e., isomers with the HetC structural feature) are more stable. The 7,8,11-isomers with twice the structural feature HetC for three-electron-donating group 14 heteroatoms is not a too high energy option. HetC is very small for group 14 heteroatoms and therefore the 7,8,11-isomers of SnC₂B₈H₁₀ is only 2.4 kcal mol⁻¹ higher in energy than the 7,8,10-isomer (see Table 8). In the case of three-electron-donating bare nitrogen atom (N), however, the NC structural feature has a larger disfavoring effect than CC, and therefore the 7,9,10-isomer (with structural feature CC) is more stable than the 7,8,10-isomer (with

structural feature NC). But for other three-electron-donating group 15 heteroatoms, i.e., P, As, Sb, HetC has less disfavoring effect than CC and therefore the 7,8,10-isomer is more favorable for [PC₂B₈H₁₀]⁻, [AsC₂B₈H₁₀]⁻, [SbC₂B₈H₁₀]⁻.

The estimated relative stabilities for HetC₂B₈H₁₀ structures for four-electron-donating heteroatoms are listed in Table 8. H–N and H–P have HetC energy penalties ($E_{\text{inc}}^{\prime}[\text{N}^{\text{RC}}] = 36.0$ kcal mol⁻¹ and $E_{\text{inc}}^{\prime}[\text{P}^{\text{RC}}] = 23.6$ kcal mol⁻¹) much larger than CC ($E_{\text{inc}}^{\prime}[\text{CC}] = 17.0$ kcal mol⁻¹) and hence 7,9,10-isomers with structural feature CC are more favorable than the 7,8,10-isomers. For H–As, however, 7,8,10-AsC₂B₈H₁₁ (with structural feature As^{RC}C ($E_{\text{inc}}^{\prime}[\text{As}^{\text{RC}}] = 17.3$ kcal mol⁻¹) and 7,9,10-AsC₂B₈H₁₁ with the structural feature CC ($E_{\text{inc}}^{\prime}[\text{CC}] = 17.0$ kcal mol⁻¹) are very similar in energy. Since HetHet' energy penalties decrease down the group, the HetC energy penalty (Sb^{RC}C) for a four-electron-donating antimony atom (Sb^{RC}C) is 4.8 kcal mol⁻¹ less than that of As^{RC}C and therefore the 7,8,10-isomer is more stable for (HSb)C₂B₈H₁₀ as compared to the 7,9,10-isomer (7,9,10-isomer has structural feature CC and $E_{\text{inc}}^{\prime}[\text{CC}] > E_{\text{inc}}^{\prime}[\text{Sb}^{\text{RC}}]$).

HetC energy penalties for all four-electron-donating group 16 heteroatoms are much higher than CC and therefore 7,9,10-HetC₂B₈H₁₀ isomers are thermodynamically more stable than 7,8,10-isomers. 7,8,9- and 7,8,11-isomers have more than one structural feature, i.e., HetHet+HetC and 2-HetC, respectively, and therefore have even larger disfavoring effects for four-electron-donating heteroatoms.

Conclusions

Estimated energy penalties present a convenient method to predict the relative stabilities of 11-vertex nido-heteroboranes and -borates. Energy penalties for adjacent heteroatoms increase along the period and decrease down the group. Four-electron-donating heteroatoms generally have larger energy penalties than those of three-electron-donating heteroatoms. Larger heteroatoms usually have larger Het_{5k}(1) and Het_{5k}(2) energy penalties and smaller HetHet' energy penalties, indicating that they prefer open-face vertices and that the destabilizing effect of adjacent heteroatoms is smaller for larger heteroatoms. Most stable mixed heteroboranes with more than two open-face heteroatoms have different but easily predictable heteroatom positions in the thermodynamically most stable 11-vertex nido-heteroborane isomers. Energy penalties are likely to have periodic trends in other polyborane clusters.

Supplementary material

Cartesian coordinates of the optimized geometries of 11-vertex nido-heterocarbaboranes and -borates considered in this paper are listed in Appendices I through V.

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References

- Štibr B (2002) *Collec Czech Chem Commun* and references therein 67:843–868
- Haubold W, Keller W, Sawitzki G (1988) *Angew Chem Int Ed Engl* 27:925–926
- Shedlow AM, Sneddon LG (1998) *Inorg Chem* 37:5269–5277
- Todd LJ, Little JL, Silverstein HT (1969) *Inorg Chem* 8:1698–1703
- Little JL, Whitesell MA, Chapman RW, Kester JG, Huffman JC, Todd LJ (1993) *Inorg Chem* 32:3369–3372
- Williams RE (1992) *Chem Rev* and references therein 92:177–207
- Fox MA, Goeta AE, Hughes AK, Johnson AL (2002) *J Chem Soc Dalton Trans* 9:2009–2019
- Fox MA, Greatrex R, Nikrahi A, Brain PT, Picton MJ, Rankin DWH, Robertson HE, Bühl M, Li L, Beaudet RA (1998) *Inorg Chem* 37:2166–2176
- Dirk W, Paetzold P, Radacki K (2001) *Z Anorg Allg Chem* 627:2615–2618
- Dopke JA, Bridges AN, Schmidt MR, Gaines DF (1996) *Inorg Chem* 35:7186–7187
- Wesemann L, Englert U, Seyferth D (1995) *Angew Chem* 107:2345–2436
- Wesemann L, Englert U, Seyferth D (1995) *Angew Chem Int Ed Engl* 34:2236–2238
- Dopke JA, Powel DR, Hayashi RK, Gaines DF (1998) *Inorg Chem* 37:4160–4161
- Loffredo RE, Norman AD (1971) *J Am Chem Soc* 93:5587–5588
- Wesemann L, Trinkaus M, Ruck M (1999) *Angew Chem Int Ed* 38:2375–2377
- Wesemann L, Ramjoie Y, Trinkaus M, Spaniol TP (1998) *Eur J Inorg Chem* 9:1263–1268
- Wesemann L, Ramjoie Y, Trinkaus M, Ganter B (1997) *Inorg Chem* 36:5192–5197
- Greenwood NN, Youll B (1975) *J Chem Soc Dalton Trans* 2:158–162
- Dupont TJ, Loffredo RE, Haltiwanger RC, Turner CA, Norman AD, (1978) *Inorg Chem* 17:2062–2067
- Loffredo RE, Dupont TJ, Haltiwanger RC, Norman AD (1977) *J Chem Soc Chem Commun* 4:121–122
- Loffredo RE, Drullinger LF, Slater JA, Turner CA, Norman AD (1976) *Inorg Chem* 15:478–480
- Todd LJ, Burke AR, Garber AR, Silverstein HT, Storhoff BN (1970) *Inorg Chem* 9:2175–2179
- Bould J, Kennedy JD, Ferguson G, Tony DF, O’Riordan GM, Spalding TR (2003) *Dalton Trans* 23:4557–4564
- O’Connell D, Patterson JC, Spalding TR, Ferguson G, Gallagher JF, Li Y, Kennedy JD, Macias R, Thornton-Pett M, Holub J (1996) *J Chem Soc Dalton Trans* 15:3323–3333
- Fontaine XLR, Kennedy JD, McGrath M, Spalding TR (1991) *Magn Reson Chem* 29:711–720
- Wright WF, Garber AR, Todd LJ (1978) *J Magn Reson* 30:595–602
- Little JL, Pao SS (1978) *Inorg Chem* 17:584–587
- Little JL, Pao SS, Sugathan KK (1974) *Inorg Chem* 13:1752–1756
- Hanusa TP, Roig de Parisi N, Kester JG, Arafat A, Todd LJ (1987) *Inorg Chem* 26:4100–4102
- Little JL (1979) *Inorg Chem* 18:1598–1600
- Yamamoto T, Todd LJ (1974) *J Organomet Chem* 67:75–80
- Colquhoun HM, Greenhough TJ, Wallbridge MGH (1979) *J Chem Research* 7:248
- Valnot JY (1978) *Synthesis* 8:590–592
- Pretzer WR, Rudolph RW (1976) *J Am Chem Soc* 98:1441–1447
- Ferguson G, Gallagher JF, McGrath M, Sheehan JP, Spalding TR, Kennedy JD (1993) *J Chem Soc Dalton Trans* 1:27–34
- Ferguson G, Parvez M, MacCurtain JA, Dhuhghaill ON, Spalding TR, Reed D (1987) *J Chem Soc Dalton Trans* 4:699–704
- Little JL, Friesen GD, Todd LJ (1977) *Inorg Chem* 16:869–872
- Faridoon, Dhuhghaill ON, Spalding TR, Ferguson G, Kaitner B, Fontaine XLR, Kennedy JD (1989) *J Chem Soc Dalton Trans* 9:1657–1668
- Ferguson G, Hampden-Smith MJ, Dhuhghaill ON, Spalding TR (1988) *Polyhedron* 7:187–193
- Barriola AM, Hanusa TP, Todd LJ (1980) *Inorg Chem* 19:2801–2802
- Reed D, Ferguson G, Ruhl BL, Dhuhghaill ON, Spalding TR (1988) *Polyhedron* 7:17–23
- Faridoon S, Trevor R, Ferguson G, Kennedy JD, Fontaine XLR (1989) *J Chem Soc Chem Commun* 14:906–908
- Faridoon O, Dhuhghaill ON, Spalding TR, Ferguson G, Kaitner B, Fontaine XLR, Kennedy JD (1988) *J Chem Soc Dalton Trans* 11:2739–2745
- Thornton-Pett M, Kennedy JD, Spalding F, Spalding TR (1995) *Act Cryst C51*:840–843
- Ferguson G, O’Connell D, Spalding TR (1994) *Act Cryst C50*:1432–1434
- Ferguson G, Gallagher JF, Sheehan JP, Spalding TR, Kennedy JD, Macias R (1993) *J Chem Soc Dalton Trans* 20:3147–3148
- Sheehan JP, Spalding TR, Ferguson G, Gallagher JF, Kaitner B, Kennedy JD (1993) *J Chem Soc Dalton Trans* 1:35–42
- Faridoon, McGrath M, Spalding TR, Fontaine XLR, Kennedy JD, Thornton-Pett M (1990) *J Chem Soc Dalton Trans* 6:1819–1829
- Ferguson G, Lough AJ, Faridoon, McGrath MN, Spalding TR, Kennedy JD, Fontaine XLR (1990) *J Chem Soc Dalton Trans* 6:1831–1839
- Ferguson G, Gallagher JF, Sheehan JP, Spalding TR (1998) *J Organomet Chem* 550:477–480
- Ferguson G, Kennedy JD, Fontaine XLR, Faridoon, Spalding TR (1988) *J Chem Soc Dalton Trans* 10:2555–2564
- Mcneaney PA, Spalding TR, Ferguson G (1997) *J Chem Soc Dalton Trans* 2:145–147
- Ferguson G, Kennedy JD, Fontaine XLR, Faridoon, Spalding TR (1988) *J Chem Soc Dalton Trans* 10:2555–2564
- Williams RE (1965) *J Am Chem Soc* 87:3513–3515
- Williams RE (1970) *Carboranes*. In: Brotherton RJ, Steinberg H (eds) *Progress in Boron Chemistry*, Vol 2, Chapter 2. Pergamon Press, Oxford, England, p 57
- Hofmann M, Fox MA, Greatrex R, Schleyer PvR, Williams RE (2001) *Inorg Chem* 40:1790–1801
- Kiani FA, Hofmann M (2004) *Inorg Chem* 43:8561–8571
- Kiani FA, Hofmann M (2005) *Eur J Inorg Chem* 12:2545–2553
- Kiani FA, Hofmann M (2005) *Inorg Chem* 44:3746–3754
- Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Zakrzewski VG, Montgomery JA, Stratmann RE, Burant JC, Dapprich S, Millam JM, Daniels AD, Kudin KN, Strain MC, Farkas O, Tomasi J, Barone V, Cossi M, Cammi R, Mennucci B, Pomelli C, Adamo C, Clifford S, Ochterski J, Petersson GA, Ayala PY, Cui Q, Morokuma K, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Cioslowski J, Ortiz JV, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Gomperts R, Martin, RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Gonzalez C, Challacombe M, Gill PMW, Johnson BG, Chen W, Wong MW, Andres JL, Head-Gordon M, Replogle ES, Pople JA (1998) *Gaussian 98*. Gaussian Inc, Pittsburgh, PA
- Huzinaga S, Andzelm J (1984) *Gaussian basis sets for molecular calculations*. Elsevier, Amsterdam, pp 23–25
- These values were optimized for the atomic ground state anion, using ROHF with a flexible ECP basis set, by Ted Packwood at NDSU. Diffuse functions for these and other heteroatoms may be found at the website: <http://phoenix.liu.edu/~nmatuna/gamess/refs/basis.refs.html>

63. Clark T, Chandrasekhar J, Spitznagel GW, Schleyer PvR (1983) *J Comput Chem* 4:294–301
64. Kang SO, Carroll PJ, Sneddon LG (1989) *Inorg Chem* 28:961–964
65. Kang SO, Carroll PJ, Sneddon LG (1988) *Organometallics* 7:772–776
66. Zimmerman GJ, Sneddon LG (1981) *J Am Chem Soc* 103:1102–1111
67. Thompson DA, Rudolph RW (1976) *J Chem Soc Chem Commun* 19:770–771
68. Kang SO, Sneddon LG (1988) *Inorg Chem* 27:3298–3300
69. Friesen GD, Barriola A, Daluga P, Ragatz P, Huffman JC, Todd LJ (1980) *Inorg Chem* 19:458–462
70. Holub J, Kennedy J D, Jelínek T, Štíbr B (1994) *Inorg Chem* 8:1317–1323
71. Ferguson G, Faridooon, Spalding TR (1988) *Acta Cryst C* 44:1368–1371
72. Ferguson G, Ruhl BL, Ni DO, Spalding TR (1987) *Acta Cryst C* 43:1250–1253
73. Base K, Štíbr B (1977) *Chem Ind* 22:919–920
74. Friesen GD, Barriola A, Todd LJ (1978) *Chem Ind* 16:631
75. Base K (1983) *Collect Czech Chem Commun* 48:2593–2603
76. Schultz RV, Huffman JC, Todd LJ (1979) *Inorg Chem* 18:2883–2886
77. Arafat A, Friesen GD, Todd LJ (1983) *Inorg Chem* 22:3721–3724
78. Bakardjiev M, Holub J, Štíbr B, Hnyk D, Wrackmeyer B (2005) *Inorg Chem* DOI 10.1021/ic048232c
79. Štíbr B, Holub J, Bakardjiev M, Hnyk D, Tok OL, Milius W, Wrackmeyer B (2002) *Eur J Inorg Chem* 9:2320–2326
80. Holub J, Ormsby DL, Kennedy J D, Greatrex R, Štíbr B (2000) *Inorg Chem Commun* 3:178–181
81. Plešek J, Štíbr B, Hnyk D, Jelínek T, Heřmánek S, Kennedy JD, Hofmann M, Schleyer PvR (1998) *Inorg Chem* 37:3902–3909