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

Received: 22 April 2005 / Accepted: 26 July 2005 / Published online: 29 October 2005 © Springer-Verlag 2005

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, [Het5k(1) and Het5k(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

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 (Einc) were determined by statistical fitting to a large number of structures. This procedure gives accurate values but requires extensive computations. Estimated energy penalties (Einc'), 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 and 7,9-C2B9H11 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 (Erel') for 11-vertex nido-sila-, germana-, stanna-, arsa-, stiba-, thia-, selena- and tellura(carba)boranes and -borates, phosphathiaboranes and -borates and selenathiaboranes produced by Einc', 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.

**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.

**Het5k(1) and Het5k(2)**

A heteroatom at a 5k position (1–6) rather than a 4k position (7–11) is indicated by the structural feature Het5k [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., Het5k(1), as compared to positions 2 through 6, i.e.,

**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 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].

![Fig. 1 Numbering scheme for the 11-vertex nido-cluster](image-url)
Het₅k(2) [57]. Estimated Het₅k(1) energy penalties for a given heteroatom were obtained by comparing the 7- and 1-isomers of [HetB₁₀H₁₀]⁶⁻⁻ and that of Het₅k(2) by comparing 7- and 2-isomers of [HetB₁₀H₁₀]⁶⁻⁻ (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. Einc'[Het₅k(1)] and Einc'[Het₅k(2)] for different heteroatoms are listed in Table 1. For the carbon atom at a 5k position in heterocarbaboranes, 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-[C₂B₉H₁₀]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 [HetB₉H₉]⁸⁻⁻ (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 (∑n = 6), the structures to be compared are diamions, 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

| HetHet | \(E_{nido}^\text{C} \) \(\text{pm}^{-1}\) | Group 15 (bare) | Group 15 (Exo-Substituted) | Group 16 |
|--------|----------------|----------------|------------------|---------|
| C      | 2.55          | 3.04           | 3.04             | 3.44    |
| 16.0   | 28.0          | 40.7           | 44.3             | 65.6    |
| 16.0   | 2.2           | 23.4           | 0.5              | 6.7     |
| Si     | 1.9           | 2.19           | 2.19             | 2.58    |
| 8.7    | 45.0          | 12.0           | 31.5             | 56.7    |
| 8.5    | 33.6          | 14.7           | 27.8             | 43.1    |
| Ge     | 2.0           | 2.18           | 2.15             | 2.35    |
| 4.2    | 54.2          | 6.9            | 32.3             | 79.7    |
| 7.7    | 44.2          | 16.0           | 28.5             | 40.7    |
| Sn     | 1.96          | 3.8            | 31.8             | 29.0    |
| 3.1    | 69.7          | 15.7           | 4.5              | 12.5    |
| Te     | 2.4           | 1.7            | 5.7              | 1.2     |

\(\text{HetHet}^1\) is the structural feature for a heteroatom adjacent to a carbon atom in the 11-vertex nido-cluster

\(\text{HetHet}^2\) is the structural feature for a heteroatom at vertices 2 through 6 rather than at the ideal 4k open face positions

\(\text{HetHet}^3\) is the structural feature for a heteroatom at vertices 2 through 6 rather than at the ideal 4k open face positions

\(\text{HetHet}^4\) is the structural feature for a heteroatom adjacent to a hydrogen bridge.

\(\text{HetHet}^5\) denotes the amount of destabilization caused by a heteroatom adjacent to a bridged hydrogen atom.

\(\text{HetHet}^6\) is estimated by comparing two suitable reference structures which differ with respect to one structural feature.

\(\text{HetHet}^7\) is the starting 11-vertex nido-oxaborane geometries.

\(\text{HetHet}^8\) is not accurately obtained as the structure rearranged.

\(\text{HetHet}^9\) is the rough energy penalty derived by fixing N7-B2 and N8-B2 distances to be 1.775 Å was even higher.

\(\text{HetHet}^{10}\) is the 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.

\(\text{HetHet}^{11}\) and \(\text{HetHet}^{12}\) 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] (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] (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] (HetP) and to an exo-substituted phosphorus atom (HetP^R\) are listed in Table 2.

Energy penalties as periodic properties of heteroatoms in 11-vertex nido-clusters. In this section, the general trends of HetHet', HetHet^1\) and HetHet^2\) energy penalties will be discussed.

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

| HetHet | \(R_{Het} \) \(\text{pm}^{-1}\) | \(E_{inc}^\prime \) [kcal mol\(^{-1}\)] | HetP^R | HetP |
|--------|----------------|----------------|--------|-----|
| NP     | 71             | 18.8           | CP     | 77   |
| PP     | 93             | 10.7           | N^RPR  | 71   |
| PP^R   | 93             | 36.9           | S^R    | 104  |
| SeP^R  | 117            | 35.8           |

and thiacarbaboranes (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.

\(\text{Het}(H)\)

This structural feature presents the amount of destabilization caused by a heteroatom (Het) adjacent to a hydrogen bridge. Comparing \(nido\)-7-[HetB\(_{10}\)H\(_{11}\)]\(^{(5-n)}\)-isomers, \(n = \text{number of electrons donated by Het}\) with \(\mu-H-8,9\) and \(\mu-H-9,10\) hydrogen positions, directly gives an estimated energy penalty for the structural feature \(\text{Het}(H)\) (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 \(\text{Het}(H)\) energy penalty (9.4 kcal mol\(^{-1}\)) is observed for the four-electron-donating \(R^P\) 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.

\(\text{Het}^R\)

This structural feature allows to compare bare (three-electron donating) and exo-substituted (four-electron donating) group 14 heteroatoms. \(nido\)-7-[HetB\(_{10}\)H\(_{11}\)]\(^{(5-n)}\)-isomers, \(n = \text{number of electrons donated by Het}\) and \(\mu-H-9,10\) hydrogen positions, directly gives a direct estimate of the energy penalty of \(\text{Het}^R\) 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 (\(R^P\) 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).
HetHet and HetC energy penalties decrease along group 14 (C → Sn), 15 (N → Sb) and 16 (S → Te) and increase along the periods (C → N, Si → S, Ge → Se, Sn → 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)-B2 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-heteroboranes 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 HetPR and HetP energy penalties, where one heteroatom is a phosphorus atom.

Energy penalties for Het₅k(1) and Het₅k(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).
The importance of geometric consequences also becomes clear by the pronounced preference for open-face positions for larger heteroatoms. Larger heteroatoms have much larger Het₅k(1) and Het₅k(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 (\(E_\text{inc}^\mu\)), estimated relative energies (\(E_\text{rel}^\mu\)) and computed relative energies for thia(carba)boranes and -borates. All values are in kcal mol\(^{-1}\).

| Compound | \(\mu\)-H- | C\(\text{S}_5\) | C(H) | CC | S\(\text{S}_5(1)\)' | S\(\text{S}_5(2)\)' | S(H)' | SC' | \(\sum E_\text{inc}^\mu\) | \(E_\text{rel}^\mu\) | \(E_\text{calc}\) | \(\Delta E^\mu\) |
|----------|----------|-----------|------|----|----------------|----------------|-------|------|-----------|-----------|----------|--------|
| AA\(^a\) | 7-SB\(10\)H\(_{12}\) | 8.9; 9,10 | 28.0 | 2.1 | 1 | 1 | 1 | 31.2 | 12.4 | 0.0 | 0.0 | 0.0 |
| AB | 2-SB\(10\)H\(_{12}\) | 7.8; 9,10 | 1 | 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\(^b\) | 7-SB\(10\)H\(_{11}\) | 8.9 | | | | | | | 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\(_{10}\) | – | | | | | | | 0.0 | 0.0 | 0.0 | 0.0 |
| CB | 2-SB\(10\)H\(_{10}\) | – | 1 | 43.8 | 43.8 | 43.8 | 0.0 |
| CC | 1-SB\(10\)H\(_{10}\) | – | 1 | 52.2 | 52.2 | 52.2 | 0.0 |
| DA\(^b\) | 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\(^b\) | 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\(_9\)H\(_{10}\) | – | | 1 | 17.0 | 0.0 | 0.0 | 0.0 |
| GB\(^a\) | 7,8-10-SC\(_2\)B\(_9\)H\(_{10}\) | – | 1 | 31.2 | 14.2 | 13.1 | 1.1 |
| GC\(^b\) | 8,2-10-SC\(_2\)B\(_9\)H\(_{10}\) | – | 1 | 28.0 | 11.0 | 13.6 | -2.6 |
| GD\(^b\) | 7,1-9-SC\(_2\)B\(_9\)H\(_{10}\) | – | 1 | 28.0 | 11.0 | 17.5 | -6.5 |
| GE\(^b\) | 7,8-9-SC\(_2\)B\(_9\)H\(_{10}\) | – | 1 | 48.2 | 31.2 | 32.3 | -1.7 |
| GF | 7,8-11-SC\(_2\)B\(_9\)H\(_{10}\) | – | 2 | 62.4 | 45.4 | 48.8 | -3.4 |

\(^a\)Experimentally known isomers
\(^b\)Only metal derivatives are experimentally known
\(^c\)Strong candidates
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 ($E_{\text{inc}}^{\text{rel}}$) derived from estimated energy penalties ($E_{\text{inc}}'$) with DFT computed values ($E_{\text{calc}}$) for the 11-vertex nido-hetero(carba)boranes and -borates

Estimated ($E_{\text{inc}}'$) and statistically fitted ($E_{\text{inc}}$) energy penalties as well as $E_{\text{inc}}$ 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 ($E_{\text{inc}}^{\text{rel}}$) are compared with the DFT-computed relative energies ($E_{\text{calc}}$) for thia(carba)boranes and -borates, phosphathiaboranes and -borates, selena-, and tellura(carba)boranes.

Fig. 5 Most stable thia(carba)borane and -borate isomers. White, black and pink balls represent boron, carbon and sulfur atoms, respectively. AA, BA, DA–GA are experimentally known. Metal complexes of CA are also experimentally known.
and -borates, and selenathiaboranes and -borates. $\Delta E'$ is the difference between $E_{\text{inc}}^{\text{rel}}$ and $E_{\text{calc}}$.

**Thia(carba)boranes and -borates**

Twenty-five isomers of thia(carba)boranes and -borates from nido-$\text{SB}_{10}H_{12}$ to nido-$\text{SC}_{2}B_{8}H_{10}$ are considered in this study. The estimated energy penalties for $\text{S}_{5k}(1)$, $\text{S}_{5k}(2)$, 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-$\text{SB}_{10}H_{12}$ and -borates, and nido-$\text{SC}_{2}B_{8}H_{10}$ (this paper) along with phosphathiaboranes are compared in Table 4. The estimated relative energies ($E_{\text{inc}}^{\text{rel}}$) for phosphathiaboranes (derived this paper) along with energy penalties for PS (derived by comparing nido-7,9-[$\text{PSB}_{9}H_{10}$]$^\text{--}$ with nido-7,8-[$\text{PSB}_{9}H_{10}$]$^\text{--}$) and P$^{\text{PS}}$ (derived by comparing nido-7,9-(PH)$\text{SB}_{9}H_{9}$ with nido-7,8-(PH)$\text{SB}_{9}H_{9}$ can be used to estimate the relative stabilities of phosphathiaboranes. The estimated relative energies of four nido-$\text{PSB}_{9}H_{10}$ 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-$\text{PSB}_{9}H_{10}$ $\mu$-H-10,11 (HA) with the structural features P(H) and S(H) has the least $\sum E_{\text{inc}}^{\text{rel}}$, $E_{\text{inc}}^{\text{rel}}$, and $E_{\text{calc}}$ values but is still experimentally unknown. nido-7,9-$\text{PSB}_{9}H_{10}$ with an exo-substituted phosphorus atom (HB) is computed to be 3.4 kcal mol$^{-1}$ higher in

| Compound | $\mu$-$H$ | P(H) | P$^R$ | S(H)$'$ | P$^S$ | P$^{R,S}$ | $\sum E_{\text{inc}}^{\text{rel}}$ | $E_{\text{inc}}^{\text{rel}}$ | $E_{\text{calc}}$ | $\Delta E'$ |
|----------|----------|------|-------|--------|-------|---------|----------------|----------------|--------------|----------|
| HA$^a$   | 7.9-$\text{PSB}_{9}H_{10}$ | 10,11 | 1     | 1      | 6.1   | 21.4    | 38.8           | 8.3             | 0.0          | 0.0       | 0.0      |
| HB$^b$   | 7.9-(HP)$\text{SB}_{9}H_{10}$ | 10,11 | 1     | 1      | 6.1   | 21.4    | 38.8           | 13.3            | 5.0          | 3.4       | 1.6      |
| HC       | 7.8-$\text{PSB}_{9}H_{10}$ | 10,11 | 1     | 1      | 6.1   | 21.4    | 38.8           | 23.6            | 15.3         | 13.8      | 1.5      |
| HD       | 7.8-(HP)$\text{SB}_{9}H_{10}$ | 10,11 | 1     | 1      | 6.1   | 21.4    | 38.8           | 52.1            | 43.8         | 42.2      | 1.6      |
| IA       | 7.9-$\text{PSB}_{9}H_{9}$ |       |       |       |       |         |                 | 21.4            | 21.4         | 21.4      | 0.0      |
| IB       | 7.8-$\text{PSB}_{9}H_{9}$ |       |       |       |       |         |                 | 21.4            | 21.4         | 21.4      | 0.0      |

$^a$Strong candidate for synthesis
$^b$7-Ph–HB, i.e., 7-Ph derivative of 7.9-$\text{PSB}_{9}H_{10}$ is experimentally known.
energy than the former and its phenyl derivative i.e., \textit{nido-7-Ph-7,9-PSB}_{3}H_{9} was experimentally characterized [3].

\textit{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 \(E^\text{rel}\) and \(E^\text{calc}\)) is larger for \(\text{SeC}_{2}B_{3}H_{10}\) isomers (up to 9.8 kcal mol\(^{-1}\) for PB).

The most stable \(\text{SeB}_{10}H_{12}\) isomer i.e., \textit{nido-7-SeB}_{10}H_{12} (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., \textit{nido-7-[SeB}_{10}H_{11}\) [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 \textit{nido-7-[(PH)B}_{10}H_{12}\) [59]. \textit{nido-7-[SeB}_{10}H_{12}\) \(\text{LA}\) was reported as a ligand in complexes with different metal fragments [35–38, 42, 43, 71, 72]. The geometry of \textit{nido-7,8-SeC}_{2}B_{3}H_{9} (MB) [73–76] unlike that of \textit{nido-7,8-S}_{2}B_{3}H_{9} 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 \textit{nido-7,9-SeC}_{2}B_{3}H_{11} (NA), the most stable \(\text{SeC}_{2}B_{3}H_{11}\) isomer, is

\begin{table}[h]
\centering
\begin{tabular}{|l|l|l|l|l|l|l|l|l|l|l|}
\hline
Compound & \(\mu\)-H- & \(\text{Se}_{3k}(1)^\prime\) & \(\text{Se}_{3k}(2)^\prime\) & \(\text{Se}(H)^\prime\) & \(\text{SeC}^\prime\) & \(\sum F^\text{inc}\) & \(E^\text{rel}\) & \(E^\text{calc}\) & \(\Delta E\) \\
\hline
JA & \(\text{7-SeB}_{10}H_{12}\) & 8.9; 10.11 & 48.2 & 61 & 35.1 & 12.2 & 0.0 & 0.0 & 0.0 \\
JB & \(\text{7-SeB}_{10}H_{12}\) & 7.8; 9.10 & 1 & 1 & 46.8 & 34.6 & 39.5 & -4.9 \\
KA & \(\text{7-SeB}_{10}H_{12}\) & 9.10 & 1 & 1 & 6.1 & 6.1 & 6.1 & 0.0 \\
KB & \(\text{7-SeB}_{10}H_{12}\) & 8.9 & 1 & 1 & 48.2 & 48.2 & 52.6 & -4.4 \\
KC & \(\text{1-SeB}_{10}H_{12}\) & 7.8 & 1 & 1 & 36.4 & 34.6 & 39.5 & -4.9 \\
LA & \(\text{7-SeB}_{10}H_{12}\) & 9.10 & 1 & 1 & 40.7 & 40.7 & 40.7 & 0.0 \\
LB & \(\text{7-SeB}_{10}H_{12}\) & 9.10 & 1 & 1 & 40.7 & 40.7 & 40.7 & 0.0 \\
MA & \(\text{7,9-SeC}_{2}B_{3}H_{9}\) & 0.0 & 0.0 & 0.0 & 0.0 & 0.0 & 0.0 \\
MB & \(\text{7,8-SeC}_{2}B_{3}H_{9}\) & 1 & 35.1 & 35.1 & 35.1 & 0.0 & 0.0 \\
\hline
\end{tabular}
\caption{Estimated energy penalties (\(E^\text{inc}\)), estimated relative energies (\(E^\text{rel}\)) for selenaboranes and -borates. DFT computed relative energies are also reported for some structures. All values are in kcal mol\(^{-1}\).}
\end{table}

\begin{table}[h]
\centering
\begin{tabular}{|l|l|l|l|l|l|l|l|l|l|l|}
\hline
Compound & \(\mu\)-H- & \(C_{3k}\) & \(C(H)\) & \(C(C)\) & \(\text{Se}_{3k}(1)^\prime\) & \(\text{Se}_{3k}(2)^\prime\) & \(\text{Se}(H)^\prime\) & \(\text{SeC}^\prime\) & \(\sum F^\text{inc}\) & \(E^\text{rel}\) & \(E^\text{calc}\) & \(\Delta E\) \\
\hline
NA & \(\text{7,9-SeC}_{2}B_{3}H_{11}\) & 10.11 & 1 & 1 & 8.2 & 0.0 & 0.0 & 0.0 \\
NB & \(\text{7,8-SeC}_{2}B_{3}H_{11}\) & 9.10 & 1 & 1 & 32.4 & 24.2 & 24.8 & -0.6 \\
NC & \(\text{7,8-SeC}_{2}B_{3}H_{11}\) & 10.11 & 1 & 1 & 36.4 & 28.2 & 26.5 & 1.7 \\
ND & \(\text{1,7-SeC}_{2}B_{3}H_{11}\) & 9.10 & 1 & 1 & 42.8 & 34.6 & 32.8 & 1.8 \\
NE & \(\text{1,7-SeC}_{2}B_{3}H_{11}\) & 8.9 & 1 & 1 & 50.3 & 42.1 & 46.7 & -4.6 \\
NF & \(\text{2,4-SeC}_{2}B_{3}H_{11}\) & 9.10 & 1 & 1 & 70.8 & 62.6 & 65.0 & -2.4 \\
OA & \(\text{7,9-SeC}_{2}B_{3}H_{10}\) & 0.0 & 0.0 & 0.0 & 0.0 \\
OB & \(\text{7,8-SeC}_{2}B_{3}H_{10}\) & 1 & 30.3 & 30.3 & 30.3 & 0.0 \\
OC & \(\text{7,1-SeC}_{2}B_{3}H_{10}\) & 1 & 28.0 & 28.0 & 32.6 & -4.6 \\
PA & \(\text{7,9,10-SeC}_{2}B_{3}H_{10}\) & 1 & 17.0 & 0.0 & 0.0 & 0.0 \\
PB & \(\text{7,8,10-SeC}_{2}B_{3}H_{10}\) & 1 & 30.3 & 13.3 & 2.5 & 9.8 \\
PC & \(\text{7,1,9-SeC}_{2}B_{3}H_{10}\) & 1 & 28.0 & 11.0 & 7.6 & 3.4 \\
PD & \(\text{7,8,9-SeC}_{2}B_{3}H_{10}\) & 1 & 47.3 & 30.3 & 22.5 & 8.8 \\
PE & \(\text{7,8,11-SeC}_{2}B_{3}H_{10}\) & 2 & 60.6 & 42.6 & 37.4 & 5.2 \\
\hline
\end{tabular}
\caption{Estimated energy penalties (\(E^\text{inc}\)), estimated relative energies (\(E^\text{rel}\)) for selencarboraboranes and -borates. DFT computed relative energies are also reported for some structures. All values are in kcal mol\(^{-1}\).}
\end{table}

\begin{table}[h]
\centering
\begin{tabular}{|l|l|l|l|l|}
\hline
Compound & \(E^\text{rel}\) & \(E^\text{calc}\) & \(\Delta E\) & Structural feature \\
\hline
7,9-SeB_{10}H_{9} & 0.0 & 0.0 & None \\
7,8-SeB_{10}H_{9} & 40.2 & 40.2 & 0.0 & SS_{2} \\
2,9-SeB_{10}H_{9} & 40.7 & 36.0 & 4.7 & Se_{3k}(2)^\prime \\
9,2-SeB_{10}H_{9} & 43.8 & 38.3 & 5.5 & S_{2}(2)^\prime \\
1,7-SeB_{10}H_{9} & 48.1 & 51.9 & -3.8 & Se_{3k}(1)^\prime \\
7,1-SeB_{10}H_{9} & 52.2 & 54.7 & -2.5 & S_{3k}(1)^\prime \\
\hline
\end{tabular}
\caption{Estimated energy penalties (\(E^\text{inc}\)), estimated relative energies (\(E^\text{rel}\)) for selenathiaboranes. All values are in kcal mol\(^{-1}\).}
\end{table}
Table 8  Estimated relative energies (kcal mol\(^{-1}\)) of 7,9,10-, 7,8,10-, 7,8,9- and 7,8,11-isomers in \([\text{HetC}_2\text{B}_8\text{H}_{10}]^{(4-n)}\) \(^{a,b}\)

| Heteroatom (cluster charge) | 7,9,10- | 7,8,10- | 7,8,9- | 7,8,11- |
|-----------------------------|---------|---------|---------|---------|
| Het = H-Si (-1)             | \(E_{\text{rel}} = 7.5\) | \(E_{\text{rel}} = 0.0\) | \(E_{\text{rel}} = 17.0\) | \(E_{\text{rel}} = 8.5\) |
| Het = H-Ge (-1)             | \(E_{\text{rel}} = 9.3\) | \(E_{\text{rel}} = 0.0\) | \(E_{\text{rel}} = 17.0\) | \(E_{\text{rel}} = 7.7\) |
| Het = H-Sn (-1)             | \(E_{\text{rel}} = 14.6\) | \(E_{\text{rel}} = 0.0\) | \(E_{\text{rel}} = 17.0\) | \(E_{\text{rel}} = 2.4\) |
| Het = N (-1)                | \(E_{\text{rel}} = 0.0\) (0.0) | \(E_{\text{rel}} = 11.4\) (6.1) | \(E_{\text{rel}} = 23.0\) | \(E_{\text{rel}} = 39.8\) |
| Het = P (-1)                | \(E_{\text{rel}} = 1.9\) (3.0) | \(E_{\text{rel}} = 0.0\) (0.0) | \(E_{\text{rel}} = 17.0\) (17.9) | \(E_{\text{rel}} = 15.1\) (18.1) |
| Het = As (-1)               | \(E_{\text{rel}} = 1.0\) | \(E_{\text{rel}} = 0.0\) | \(E_{\text{rel}} = 17.0\) | \(E_{\text{rel}} = 16.0\) |
| Het = Sb (-1)               | \(E_{\text{rel}} = 1.3\) | \(E_{\text{rel}} = 0.0\) | \(E_{\text{rel}} = 17.0\) | \(E_{\text{rel}} = 15.7\) |
| Het = H-N (0)               | \(E_{\text{rel}} = 0.0\) (0.0) | \(E_{\text{rel}} = 20.2\) (18.8) | \(E_{\text{rel}} = 37.2\) (41.3) | \(E_{\text{rel}} = 57.4\) (58.8) |
| Het = H-P (0)               | \(E_{\text{rel}} = 0.0\) (0.0) | \(E_{\text{rel}} = 7.3\) (5.2) | \(E_{\text{rel}} = 23.6\) (24.9) | \(E_{\text{rel}} = 31.6\) (29.5) |
| Het = H-As (0)              | \(E_{\text{rel}} = 0.0\) | \(E_{\text{rel}} = 0.3\) | \(E_{\text{rel}} = 17.3\) | \(E_{\text{rel}} = 17.6\) |
| Het = H-Sb (0)              | \(E_{\text{rel}} = 4.5\) | \(E_{\text{rel}} = 0.0\) | \(E_{\text{rel}} = 17.0\) | \(E_{\text{rel}} = 12.5\) |
| Het = S (0)                 | \(E_{\text{rel}} = 0.0\) (0.0) | \(E_{\text{rel}} = 15.0\) (13.1) | \(E_{\text{rel}} = 32.0\) (32.9) | \(E_{\text{rel}} = 47.0\) (48.8) |
| Het = Se (0)                | \(E_{\text{rel}} = 0.0\) (0.0) | \(E_{\text{rel}} = 12.7\) (2.5) | \(E_{\text{rel}} = 30.3\) (22.5) | \(E_{\text{rel}} = 43.6\) (37.4) |
| Het = Te (0)                | \(E_{\text{rel}} = 0.0\) | \(E_{\text{rel}} = 11.6\) | \(E_{\text{rel}} = 28.6\) | \(E_{\text{rel}} = 40.2\) |

\(^{a}\)Het may be a three- or four-electron-donating heteroatom. \(n\) corresponds to the number of electrons donated by a given heteroatom
\(^{b}\)B3LYP/6-311 + G(d,p)/B3LYP/6-31G(d) + ZPE computed relative stabilities of various \([\text{HetC}_2\text{B}_8\text{H}_{10}]^{(4-n)}\) isomers are listed in parenthesis for various heteroatoms. These values are usually very close to the values predicted by estimated energy penalties
\(^{c}\)\(7,9,10-[\text{NC}_2\text{B}_8\text{H}_{10}]\), \(7,10,9-(\text{HN})\text{C}_2\text{B}_8\text{H}_{10}\), \(7,9,10-\text{SC}_2\text{B}_8\text{H}_{10}\), 7,9,10-\text{SeC}_2\text{B}_8\text{H}_{10}\) are experimentally known
\(^{d}\)7,8,10-\text{SC}_2\text{B}_8\text{H}_{10}\) is experimentally known
\(^{e}\)7,8,9-\([\text{NC}_2\text{B}_8\text{H}_{10}]\) and 7-Me and 7-Ph derivatives of 7,8,9-(\text{HP})\text{C}_2\text{B}_8\text{H}_{10}\) are experimentally known
\(^{f}\)7-Ph derivatives of 7,8,11-(\text{HP})\text{C}_2\text{B}_8\text{H}_{10}\) 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-SeSB8H9. The latter is more stable and is
Estimated energy penalties ($E_{\text{inc}}$) and corresponding estimated relative stabilities ($E_{\text{rel}}$) for other 11-vertex nido-hetero(carba)boranes and -borates

Estimated energy penalties for sila-, germa-, stanna-, and exo-substituted arsa- and stiba(carba)boranes and -borates are reported in Table 1, which can be used to produce the $E_{\text{inc}}$ 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, [C$_2$B$_8$H$_{11}$]– [57], P$_2$B$_8$H$_{11}$ [59], Se$_2$B$_8$H$_9$ or that of heteroboranes with two different heteroatoms, e.g., 7,8- and 7,9-isomers of [PSB$_9$H$_9$] and PSB$_9$H$_{10}$, SeSB$_9$H$_9$ etc. However, it is complex to predict the thermodynamically most stable isomer in mixed heteroboranes with three open-face heteroatoms, e.g., [P$_2$CB$_8$H$_{10}$]– [78], [PC$_2$B$_8$H$_{10}$]– [79, 80], SC$_2$B$_8$H$_{10}$ [3], SeC$_2$B$_8$H$_{10}$ [73], NC$_2$B$_8$H$_{11}$ [81], [NC$_2$B$_8$H$_{10}$]– [81]. Here we present only [HetC$_2$B$_8$H$_{10}$]($^{4-n}$) 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 [HetC$_2$B$_8$H$_{10}$]($^{4-n}$) structures with open face heteroatoms, i.e., 7,9,10-, 7,8,10-, 7,8,9- and 7,8,11-[HetC$_2$B$_8$H$_{10}$]($^{4-n}$) will be discussed.

Both 7,9,10- and 7,8,10-isomers of [HetC$_2$B$_8$H$_{10}$]– have one structural feature each, i.e., CC and HetC, respectively. However, 7,8,9- and 7,8,11-isomers of [HetC$_2$B$_8$H$_{10}$]– have two structural features each, i.e., HetC+CC and 2HetC, 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 SnC$_2$B$_8$H$_{10}$ 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 [PC$_2$B$_8$H$_{10}$]–, [AsC$_2$B$_8$H$_{10}$]–, [SbC$_2$B$_8$H$_{10}$]–.

The estimated relative stabilities for HetC$_2$B$_8$H$_{10}$ structures for four-electron-donating heteroatoms are listed in Table 8. H–N and H–P have HetC energy penalties ($E_{\text{inc}}[\text{NRC}]$ = 36.0 kcal mol$^{-1}$ and $E_{\text{inc}}[\text{PRC}]$ = 23.6 kcal mol$^{-1}$) much larger than CC ($E_{\text{inc}}[\text{CC}]$ = 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-AsC$_2$B$_8$H$_{11}$ (with structural feature As$^8$C ($E_{\text{inc}}[\text{AsRC}]$ = 17.3 kcal mol$^{-1}$) and 7,9,10-AsC$_2$B$_8$H$_{11}$ with the structural feature CC ($E_{\text{inc}}[\text{CC}]$ = 17.0 kcal mol$^{-1}$) are very similar in energy. Since HetHet energy penalties decrease down the group, the HetC energy penalty (Sb$^8$C) for a four-electron-donating antimony atom (Sb$^8$C) is 4.8 kcal mol$^{-1}$ less than that of As$^8$C and therefore the 7,8,10-isomer is more stable for (HSb)C$_2$B$_8$H$_{10}$ as compared to the 7,9,10-isomer (7,9,10-isomer has structural feature CC and $E_{\text{inc}}[\text{CC}] > E_{\text{inc}}[\text{SbRC}]$).

HetC energy penalties for all four-electron-donating group 16 heteroatoms are much higher than CC and therefore 7,9,10-HetC$_2$B$_8$H$_{10}$ isomers are thermodynamically more stable than 7,8,10-isomers. 7,8,10- and 7,8,11-isomers have more than one structural feature, i.e., HetHet + HetC and 2HetC, 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$_{3k}$ (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.
Acknowledgement Financial support by DFG is gratefully acknowledged.

References

1. Stibor B (2002) Collec Czech Chem Commun and references therein 67:843–868
2. Haubold W, Keller W, Sawitzki G (1988) Angew Chem Int Ed Engl 27:925–926
3. Shedlow AM, Sneddon LG (1998) Inorg Chem 37:5269–5277
4. Todd LJ, Little JL, Silverstein HT (1969) Inorg Chem 8:1698–1703
5. Little JL, Whitesell MA, Chapman RW, Kester JG, Huffman JC, Todd LJ (1993) Inorg Chem 32:3369–3372
6. Williams RE (1992) Chem Rev and references therein 92:177–207
7. Fox MA, Goeta AE, Hughes AK, Johnson AL (2002) J Chem Soc Dalton Trans 9:2009–2019
8. Fox MA, Gireaitis S, Brain PT, Picton MJ, Rankin DH (1998) Coord Chem Rev 170:207
9. Dirk W, Paetzold P, Radacki K (2001) Z Anorg Allg Chem 627:2615–2618
10. Dopke JA, Bridges AN, Schmidt MR, Gaines DF (1996) Inorg Chem 35:7186–7187
11. Wesemann L, Englert U, Seyferth D (1995) Angew Chem 107:2345–2436
12. Wesemann L, Englert U, Seyferth D (1995) Angew Chem Int Ed Engl 34:2236–2238
13. Dopke JA, Powel DR, Hayashi RK, Gaines DF (1998) Inorg Chem 37:4160–4161
14. Loffredo RE, Norman AD (1971) J Am Chem Soc 93:5587–5588
15. Wesemann L, Trinkaus M, Ruck M (1999) Angew Chem Int Ed 38:2375–2377
16. Wesemann L, Ramjoie Y, Trinkaus M, Spaniol TP (1998) Eur J Inorg Chem 9:1263–1268
17. Wesemann L, Ramjoie Y, Trinkaus M, Heilbronner H (1997) Inorg Chem 36:5192–5197
18. Greenwood NN, Youll B (1975) J Chem Soc Dalton Trans 2:158–162
19. Dupont TJ, Loffredo RE, Haltiwanger RC, Turner CA, Norman AD (1978) Inorg Chem 17:2062–2067
20. Loffredo RE, Dupont TJ, Haltiwanger RC, Norman AD (1977) J Chem Soc Chem Commun 4:121–122
21. Loffredo RE, Drullinger LF, Sluter JA, Turner CA, Norman AD (1976) Inorg Chem 15:478–480
22. Todd LJ, Burke AR, Garber AR, Silverstein HT, Storhoff BN (1970) Inorg Chem 9:2175–2179
23. Bould J, Kennedy JD, Ferguson G, Tony D, O’Riordan GM, Spalding TR (2003) Dalton Trans 23:4557–4564
24. 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 Chem Dalton Trans 4:121–122
25. Fontaine XLR, Kennedy JD, McGrath M, Spalding TR (1991) Magn Reson Chem 29:711–720
26. Wright WF, Garber AR, Todd LJ (1978) J Magn Reson 30:595–602
27. Little JL, Pao SS (1978) Inorg Chem 17:584–587
28. Little JL, Pao SS, Sugathan KK (1974) Inorg Chem 13:1752–1756
29. Hanusa TP, Roig de Parisi N, Kester JG, Arafat A, Todd LJ (1987) Inorg Chem 26:4100–4102
30. Little JL (1979) Inorg Chem 18:1598–1600
31. Yamamoto T, Todd LJ (1974) J Organomet Chem 67:75–80
32. Colquhoun HM, Greenough TJ, Wallbridge MGH (1979) J Chem Research 7:248
33. Valton JY (1978) Synthesis 8:590–592
34. Pretzer WR, Rudolph RW (1976) J Am Chem Soc 98:1441–1447
35. Ferguson G, Gallagher JF, McGrath M, Sheahan JP, Spalding TR, Kennedy JD (1993) J Chem Soc Dalton Trans 1:27–34
36. Ferguson G, Parvez M, MacCurtain JA, Dhubhghaill ON, Spalding TR, Reed D (1987) J Chem Soc Dalton Trans 4:699–704
37. Little JL, Friesen GD, Todd LJ (1977) Inorg Chem 16:869–872
38. Faridoon, Dhubhghaill ON, Spalding TR, Ferguson G, Kaitner B, Fontaine XLR, Kennedy JD (1989) J Chem Soc Dalton Trans 9:1657–1668
39. Ferguson G, Hampden-Smith MJ, Dhubhghaill ON, Spalding TR (1988) Polyhedron 7:187–193
40. Barriola AM, Hanusa TP, Todd LJ (1980) Inorg Chem 19:2801–2802
41. Reed D, Ferguson G, Ruhl BL, Dhubhghaill ON, Spalding TR (1988) Polyhedron 7:17–23
42. Faridoon S, Trevor R, Ferguson G, Kennedy JD, Fontaine XLR (1989) J Chem Soc Chem Commun 14:906–908
43. Faridoon O, Dhubhghaill ON, Spalding TR, Ferguson G, Kaitner B, Fontaine XLR, Kennedy JD (1988) J Chem Soc Dalton Trans 11:2739–2745
44. Thornton-Pett M, Kennedy JD, Spalding F, Spalding TR (1995) Act Cryst C51:840–843
45. Ferguson G, O’Connell D, Spalding TR (1994) Act Cryst C50:1432–1434
46. Ferguson G, Gallagher JF, Sheenan JP, Spalding TR, Kennedy JD, Macias R (1993) J Chem Soc Dalton Trans 20:3147–3148
47. Sheenan JP, Spalding TR, Ferguson G, Gallagher JF, Kaitner B, Kennedy JD (1993) J Chem Soc Dalton Trans 1:35–42
48. Faridoon, McGrath M, Spalding TR, Fontaine XLR, Kennedy JD, Thornton-Pett M (1990) J Chem Soc Dalton Trans 6:1819–1829
49. Ferguson G, Lough AJ, Faridoon, McGrath MN, Spalding TR, Kennedy JD, Fontaine XLR (1990) J Chem Soc Dalton Trans 6:1831–1839
50. Ferguson G, Gallagher JF, Sheean JP, Spalding TR (1998) J Organomet Chem 559:477–480
51. Ferguson G, Kennedy JD, Fontaine XLR, Faridoon, Spalding TR (1988) J Chem Soc Dalton Trans 10:2555–2564
52. Mceneaney PA, Spalding, Ferguson G (1997) J Chem Soc Dalton Trans 2:145–147
53. Ferguson G, Kennedy JD, Fontaine XLR, Faridoon, Spalding TR (1988) J Chem Soc Dalton Trans 10:2555–2564
54. Williams RE (1965) J Am Chem Soc 87:3513–3515
55. Williams RE (1970) Carbaboranes. In: Brotherton RJ, Steinberg RE (eds) Progress in Boron Chemistry, Vol 2, Chapter 2. Pergamon Press, Oxford, England, p 57
56. Hofmann M, Fox MA, Grearet R, Schleyer PVR, Williams RE (2001) Inorg Chem 40:1790–1801
57. Kiani FA, Hofmann M (2004) Inorg Chem 43:8561–8571
58. Kiani FA, Hofmann M (2005) Eur J Inorg Chem 12:2545–2553
59. Kiani FA, Hofmann M (2005) Inorg Chem 44:3746–3754
60. 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, Petersons GA, Ayala PY, Cui Q, Morokuma K, Malick DK, Rabuck AD, Scuseria GE, Piskorz P, Komaromi I, Gomperts R, Martin, RL, Fox DJ, Ogliaro F, Petersson GA, Nakai Y, Loos L, Replogle ES, Gomperts R, Martin RJ, Martin W, Fox DJ, Williams PW, Farkas O,Tomasi J, Mennucci B, Cossi M, Scalmani G, Rega N, Petersson GA, Ochterski J, Ayala PY, Cui Q, Morokuma K, Malick DK, Rabuck AD, Scu,
61. Huzinaga S, Andzelm J (1984) Gaussian basis sets for molecules. Elsevier, Amsterdam, pp 23–25
62. These values were optimized for the atomic ground state anion, using ROHF with a flexible ECP basis set, by Ted Packwood at NDSU.
63. These values were optimized for the atomic ground state anion, using ROHF with a flexible ECP basis set, by Ted Packwood at NDSU.
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, Jelinek T, Stibr B (1994) Inorg Chem 8:1317–1323
71. Ferguson G, Faridoon, Spalding TR (1988) Acta Cryst C44:1368–1371
72. Ferguson G, Ruhl BL, Ni DO, Spalding TR (1987) Acta Cryst C43:1250–1253
73. Base K, Štibr 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, Štibr B, Hnyk D, Wrackmeyer B (2005) Inorg Chem DOI 10.1021/ic048232c
79. Štibr 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, Štibr B (2000) Inorg Chem Commun 3:178–181
81. Plesek J, Štibr B, Hnyk D, Jelinek T, Hefmánek S, Kennedy JD, Hofmann M, Schleyer PvR (1998) Inorg Chem 37:3902–3909