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Structural Increments for 11-Vertex *nido*-Phospha- and Aza(carba)boranes and -borates; Dependence of Energy Penalties on the Extent of Electron Localization

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Relevant structural features and corresponding energy penalties were determined that allow to easily estimate the relative stabilities of 11-vertex *nido*-phospha- and aza-substituted boranes, borates, carbaboranes, and carbaborates. For this purpose, density functional theory computations at the B3LYP/6-311+G(d,p)//B3LYP/6-31G(d)+ZPE level were carried out to determine the relative energies of 95 phospha- and 46 aza(carba)boranes and -borates. Energy penalties assigned to disfavoring structural features show additive behavior and excellent precision with respect to the computed results, as in the case of 6- and 11-vertex *nido*-carboranes and -borates. An unsubstituted phosphorus atom was found to possess energy penalties quite similar to those of the three-electron-donating H–C group. A bare nitrogen atom has energy penalties much larger than those of a bare phosphorus atom. Four-electron-donating RP and RN moieties, however, have even more adverse energy penalties. The disfavoring effects of heteroatoms in a borane cluster are determined by the amount of electron localization, that is, primarily by the number of skeletal electrons that formally originate from the heterogroup and secondarily by the electronegativity. Heteroatom energy penalties are independent of the type of the other heteroatoms present in the same cluster. Some novel phospha(carba)borane geometries with bare and exo-substituted phosphorus atoms in the same cluster have favorable thermodynamic stabilities competitive with those of known isomers.

1. Introduction

Boranes have always attracted attention[1] because of their unusual nonclassical structures, delocalized chemical bonding, multicenter bonds,[2] physiochemical properties with respect to being promising materials for the future,[1f] and for their use in boron neutron capture therapy.[3−5] They are playing a key role in stimulating new concepts and a general picture of chemical bonding. Heteroatoms[2,5−8] can be incorporated to modify the properties. The 11-vertex nido cluster, which can be derived from the icosahedral 12-vertex *closo*-polyborane cluster by the removal of one vertex, features a large number of experimentally known examples for

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phosphorus[9−28] and nitrogen[29,30] substitution in *nido*-boranes. For the sake of simplicity, a single term, hetero(carba)boranes and -borates, is used to refer to heteroboranes, heteroborates, heterocarbaboranes and heterocarbaborates simultaneously, where heteroatom may be a nitrogen or phosphorus atom.

closo-Heteroboranes have been a vast subject of study. Williams' rule[2,31,32] suggests that heteroatoms such as carbon or nitrogen usually occupy the least connected and nonadjacent vertices in the thermodynamically most stable heteroborane isomers. Gimarc and Ott's topological charge stabilization rule suggests that a more electronegative heteroatom should prefer sites of maximum electron density.[33] This rule agrees well with the experimentally observed positional isomer preferences of the *closo*-carboranes[33] and azaboranes.[34] Jemmis and Schleyer[35] extended the planar $(4n + 2)$ Hückel rule to the aromaticity of three-dimensional delocalized systems using the "six interstitial electron" concept. They pointed to the need of orbital overlap compatibility. The radial extension of the π orbitals of the capping atom should optimally match the ring size.[34] Energy-architectural patterns among the 5−12-vertex *closo*-carboranes have been investigated by Williams and Bausch.[36] It was found that the difference between the calculated and established stability values seldom exceeds 6 kcal mol^{-1}. The tight bond with adjacent matrix approach[37] based on bond energies and electronegativities of adjacent atoms can also be used to predict the relative stabilities of various positional isomers in a given heteronuclear closo-icosahedral borane cluster.

However, the placement of both skeletal bridge hydrogens and skeletal endo hydrogens makes the situation more complex in the case of nido-deltahedral fragments.[38] The presence of face hydrogen atoms results in a number of additional rules along with the two basic Williams' rules[2,31,32] if the most stable *nido*-heteroborane is to be predicted. However, in general, not all requirements for the ideal structure can be fulfilled for a given formula. Hence, weights are needed that indicate how severe the violation of a given rule is. We already presented such weights that form a set of quantitative rules called the structural increment system for nido-6-[38] and nido-11-vertex[39] carboranes. It was assumed that a hypothetical perfect structure exists and that (1) deviations from the ideal situation lead to reduced thermodynamic stability of a cluster structure and (2) the amount of destabilization is additive.[39] Hence, a quantitative value (structural increment or energy penalty) may be assigned to each disfavoring structural feature. More than one feature in a single cluster structure results in a total destabilization equal to the sum of the individual contributions. Provided that the above assumptions are valid, an increment system based on a few structural increments (energy penalties) allows for estimating the relative stabilities of isomeric clusters. For 11-vertex *nido*-carboranes, we already showed that this is possible with astonishing accuracy.[39]

There are two different types of phospha(carba)boranes and -borates.[40] Those containing a bare phosphorus atom (P) with an exo-hedral electron pair are referred to as bare phospha(carba)boranes and -borates in this paper. Exo-substituted phospha(carba)boranes and -borates indicate that the P vertex carries an exo substituent and are denoted with a superscript as in P^{R}. Experimentally known 11-vertex nido-nitrogen-containing clusters also include, for example, *nido*-7,9,10-$(\mathrm{NH})\mathrm{C}_2\mathrm{B}_8\mathrm{H}_{10}$ and *nido*-7,9,10-$[\mathrm{NC}_2\mathrm{B}_8\mathrm{H}_{10}]^-$;[30] the former has an exo substituent at the nitrogen atom, whereas the latter incorporates a bare nitrogen atom.

We extend here our previous study of 11-vertex *nido*-carboranes and -borates[39] to 11-vertex *nido*-phospha- and aza(carba)boranes and -borates to investigate the applicability of the increment approach further, to see if the presence of more than one type of heteroatom can be covered as well, and to see how the energy penalties for different heteroatoms compare to each other. Phospha(carba)boranes and -borates were selected for our recent study because of the large number of experimentally known examples and the inherent

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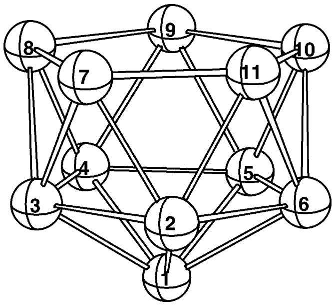

Figure 1. Numbering scheme for the 11-vertex nido cluster.

interest to experimental chemists. Furthermore, phosphorus and carbon atoms are diagonally related to each other, and the electronegativity of phosphorus is very close to that of carbon. The considerably more electronegative nitrogen heteroatom was included for comparison.

The numbering scheme for the 11-vertex nido cluster is shown in Figure 1. The apical position is numbered as 1. The vertexes in the ring directly connected to the apex (middle belt) are given numbers 2−6, and the vertexes of the open face are numbered from 7 to 11, where 7 is connected to both 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.

2. Computational Details

Geometries were optimized at the B3LYP/6-31G(d) level using the Gaussian 98 program.[41] All structures presented in this paper are local minima at the B3LYP/6-31G(d) level. Single-point energies were computed at the B3LYP/6-311+G(d,p) level. Zero-point vibrational energy corrections from B3LYP/6-31G(d) frequency calculations were included to derive the relative energies for all of the isomers. By comparing different isomeric structures, important structural features were identified. These features were given suitable initial energy penalties, which were derived from the relative energies of isomers differing with respect to one structural feature only. The final values were, however, refined through a statistical fitting procedure to reproduce the computed relative energies of all isomers considered as accurately as possible.

3. Results and Discussion

3.1. Structural Features for Hetero(carba)boranes and -borates. Nine structural features and the corresponding energy penalties were already reported for carboranes and carborates.[39] Now, we report six structural features for phospha- and aza(carba)boranes and -borates, five of which have equivalent carborane/carborate structural features. One structural feature, Het^{R}, is a novel one. Energy penalties for the corresponding structural features are listed in Table 1.

Table 1. Structural Features and Corresponding Energy Penalties[a,b] ($\mathrm{kcal\ mol^{-1}}$) for 11-vertex *nido*-Hetero(carba)boranes and -borates

general structural features	heteroatom Het = P^{c}	 Het = P^{Rd}	 Het = N^{c}	 Het = N^{Rd}
	Heteroatom Structural Features			
$\mathrm{Het}_{5k}(1)$	26.9	58.0	43.0	64.7
$\mathrm{Het}_{5k}(2)$	26.9	39.7	43.0	46.3
HetHet	10.7	36.9[e]	48.0	63.6[f]
HetC	15.1	24.3	28.4	37.2
	Hydrogen Structural Features			
HH	19.5		26.3	
Het(H)	2.2	9.6	5.4	7.3
Het^{R}		13.3		0.1
	Carbon Structural Features			
C_{5k}	26.9		30.5	
CC^{g}	18.3		15.3	
C(H)	2.2		3.6	

[a] The RB3LYP/6-311+G(d,p)+RB3LYP/6-31G(d)+ZPE-computed relative stability order of the isomeric clusters was used to select the important disfavoring structural features, each of which was assigned an initial suitable empirical energy penalty. A further refinement was done by a statistical fitting procedure to get more accurate energy penalties. [b] The energy penalties were simultaneously derived for clusters with bare and exo-substituted heteroatoms (e.g., P and P^{R}) but separately for different heteroatoms (e.g., N and P). [c] Three-electron-donating heteroatoms. [d] Four-electron-donating heteroatoms. [e] Only one structure with two adjacent phosphorus atoms was successfully geometry-optimized without rearrangement. [f] This value is based on the relative energy of 7,8-$(NH)_2B_9H_9$ vs 7,9-$(NH)_2B_9H_9$. We note, however, that the former cluster optimized to a distorted structure. A rough energy penalty derived by fixing N7−B2 and N8−B2 distances to 1.775 Å, was even higher (76.5 $\mathrm{kcal\ mol^{-1}}$). [g] The CC energy penalties as derived from phospha(carba)boranes and -borates (18.3 $\mathrm{kcal\ mol^{-1}}$) and aza(carba)boranes and -borates (15.3 $\mathrm{kcal\ mol^{-1}}$) are quite similar to $E_{\mathrm{inc}}[\mathrm{CC}] = 16.0\ \mathrm{kcal\ mol^{-1}}$ derived for carboranes (ref 39).

3.1.1. Structural Features due to the Positions of Heteroatoms. Three structural features, $\mathrm{Het}_{5k}(1)$, $\mathrm{Het}_{5k}(2)$, and HetHet′, are used to describe the positions of heteroatoms in hetero(carba)boranes and -borates.

A heteroatom at a 5k rather than a peripheral 4k position is denoted as Het_{5k}.[42] It occurs as P_{5k}, P^{R}_{5k}, N_{5k}, N^{R}_{5k}, and C_{5k} for different heteroatoms. Positions 2−6 of the 11-vertex nido cluster are slightly preferred over position 1 for carbon atom placement in 11-vertex *nido*-carboranes and carborates; however, this preference is small and a "fine-tuning" increment may be applied where needed to disfavor the 1-isomer.[39] In other words, structural features $C_{5k}(1)$, for a carbon atom at position 1, and $C_{5k}(2)$, for a carbon atom at position 2−6, can be handled together as C_{5k} in carboranes and carborates.[39] The same is true for formally three-electron-donating bare phosphorus and nitrogen atoms (Table 1). In the case of exo-substituted heteroatoms (P^{R} and N^{R}), however, a satisfactory reproduction of computed relative energies by an increment system can only be achieved if the 5k feature is split into $\mathrm{Het}_{5k}(1)$ and $\mathrm{Het}_{5k}(2)$ because they have considerably different energy penalties at different 5k positions. At the apex (position 1, see Figure 1), an exo-substituted phosphorus atom disfavors a structure by

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(42) $\mathrm{Het}_{4k\rightarrow 5k}$ in ref 39 is abbreviated here as Het_{5k} and is identical to the former for the 11-vertex nido cluster.

$E_{inc}[P^R_{5k}(1)] = 58.0$ kcal mol^{-1}, whereas in the middle belt (at positions 2−6), it has a considerably smaller energy penalty of $E_{inc}[P^R_{5k}(2)] = 39.7$ kcal mol^{-1}. For exo-substituted nitrogen structural features, $N^R_{5k}(1)$ and $N^R_{5k}(2)$ energy penalties are 64.7 and 46.3 kcal mol^{-1} at positions 1 and 2−6, respectively.

For hetero(carba)boranes and -borates, heteroatoms next to each other represent an unfavorable structural feature that we describe as HetHet′, where Het = P, P^R, N, or N^R and Het′ may be either equal to Het (i.e., PP, P^RP^R, NN, and N^RN^R) or equal to C (i.e., PC, P^RC, NC, and N^RC) or Het = Het′ = C (i.e., CC).

The energy penalties for the HetHet′ structural features are as follows: For two adjacent bare phosphorus atoms (PP), the energy penalty is 10.7 kcal mol^{-1}, considerably smaller than 36.9 kcal mol^{-1} for P^RP^R (two adjacent exo-substituted phosphorus atoms). The energy penalty for NN (two adjacent bare nitrogen atoms) is 48.0 kcal mol^{-1}. Diazaundecaborane structure with two adjacent exo-substituted nitrogen atoms (structural feature N^RN^R) did not optimize successfully but converged to rearranged structures from which an energy penalty of 63.6 kcal mol^{-1} would be derived. However, a rough estimate for the N^RN^R feature obtained by fixing the B(2)−N(7) and B(2)−N(8) distances in azaboranes was even higher (76.5 kcal mol^{-1}). It can be concluded that the N^RN^R feature is incompatible with the nido-11-vertex cluster because of a too large destabilization.

The energy penalties for HetHet′ when Het′ = C, that is, PC for a bare phosphorus atom, P^RC for an exo-substituted phosphorus atom, NC for a bare nitrogen atom, and N^RC for an exo-substituted nitrogen atom adjacent to a carbon atom, are 15.1, 24.3, 28.4, and 37.2 kcal mol^{-1}, respectively. It is worth pointing out that both bare and exo-substituted phosphorus and nitrogen atoms have HetC energy penalties roughly equal to $^1/_2$(HetHet + CC).

Very similar energy penalties are derived for two adjacent carbon atoms (CC) in carboranes and carborates (16.0 kcal mol^{-1}),[39] phosphacarbaboranes and -carbaborates (18.3 kcal mol^{-1}), and azacarbaboranes and -borates (15.3 kcal mol^{-1}).

3.1.2. Structural Features due to the Positions of Hydrogen Atoms. HH, Het(H), and Het^R are the three structural features in 11-vertex *nido*-hetero(carba)boranes and -borates due to the positions of hydrogen atoms.

The HH feature for two adjacent hydrogen bridges on the open face, has an energy penalty of 25.9 kcal mol^{-1} for 11-vertex *nido*-carboranes and carborates,[39] whereas it is 19.5 kcal mol^{-1} and 26.3 kcal mol^{-1} for bare phospha- and aza(carba)boranes and -borates, respectively (Table 1).

The structural feature of a heteroatom adjacent to a hydrogen bridge, Het(H), was reported as C(H) in 11-vertex *nido*-carboranes and carborates[39] and occurs as P(H), P^R(H), N(H), N^R(H), and C(H) in bare phosphaboranes and -borates, exo-substituted phosphaboranes and -borates, bare azaboranes and -borates, exo-substituted azaboranes and -borates, and carbon-containing heteroboranes and -borates, respectively. For bare phosphacarbaboranes and -borates, the C(H) and P(H) features have very similar effects and, consequently, were finally derived together, giving E_{inc}[P/C(H)] = 2.2 kcal mol^{-1}. Increments for N(H) and C(H) in bare aza(carba)-boranes and -borates were, however, derived separately with E_{inc}[N(H)] = 5.4 kcal mol^{-1} and E_{inc}[C(H)] = 3.6 kcal mol^{-1}. Het(H) features for exo-substituted phosphorus and nitrogen atoms, that is, for P^R(H) and N^R(H), have larger energy penalties (9.6 and 7.3 kcal mol^{-1}, respectively) than those for bare heteroatoms.

The Het^R structural feature allows a comparison of isomers with bare and exo-substituted heteroatoms. An exo-substituted phosphorus atom (P^R) rather than a bare phosphorus atom (P) in an 11-vertex nido-polyhedral borane cluster has an energy penalty of 13.3 kcal mol^{-1}. Unlike P^R, an exo-substituted nitrogen atom, N^R ($E_{inc}[N^R] = 0.1$ kcal mol^{-1}), is generally more favorable than a bare nitrogen atom adjacent to an open-face bridged hydrogen, N(H) (E_{inc}[N(H)] = 5.4 kcal mol^{-1}).

This paper presents five general features for each bare or exo-substituted heteroatom, that is, for P, P^R, N, and N^R, in addition to one Het^R to compare bare and exo-substituted isomers.

3.2. Carbon Structural Features are Largely Independent of Cluster Size and the Types of Other Heteroatoms Present. Energy penalties for carbon structural features such as CC (where two carbon atoms are adjacent to each other) and CH−B (where an endo hydrogen is entrapped between a carbon and boron atom) are similar for 6- and 11-vertex *nido*-carboranes and carborates despite the different cluster sizes.[39] The CC structural feature also has a very similar disfavoring effect on 6-vertex *nido*-carboranes and carborates (15 kcal mol^{-1}),[38] 11-vertex *nido*-carboranes and carborates (16.0 kcal mol^{-1}),[39] phosphacarbaboranes and -borates (18.3 kcal mol^{-1}), and azacarbaboranes and -borates (15.3 kcal mol^{-1}). The energy penalty for the 5k carbon atom (C_{5k}) in 11-vertex *nido*-carbaboranes and -borates (28.0 kcal mol^{-1})[39] is also very similar to that of phosphacarbaboranes and -borates (26.9 kcal mol^{-1}) (Table 1).

3.3. Dependence of Energy Penalties on the Extent of Electron Localization. Energy penalties for $Het_{5k}(1)$ and $Het_{5k}(2)$ are considerably smaller for Het = C, P, or N than for Het = P^R and N^R (see Table 1). A comparison of HetHet′ when Het′ = Het or C also reveals much smaller energy penalties for Het = C, P, and N than for Het = P^R and N^R. We conclude that energy penalties, which are a measure for cluster destabilization, increase with the extent of electron localization in a given cluster. Twenty six skeletal electrons are required by Wade's $2n + 4$ electron count for an 11-vertex nido cluster, where $n = 11$. In 11-vertex bare *nido*-phospha- or aza(carba)boranes and -borates (Table 1), formally three[40] out of 26 skeletal electrons stem from each heteroatom. Exo-substituted phosphorus or nitrogen atoms, however, contribute 4 out of 26 electrons each. Therefore, the energy penalties of N^R and P^R are much larger than those of their respective bare (N and P) isomers (Figure 2). Among the four-electron-donating heterogroups, N^R has energy penalties larger than P^R. The higher electronegativity of nitrogen leads to stronger electron localization and, hence, results in higher energy penalties for $N^R_{5k}(1)$, $N^R_{5k}(2)$, and N^RC. Energy penalties follow the electronegativity trends

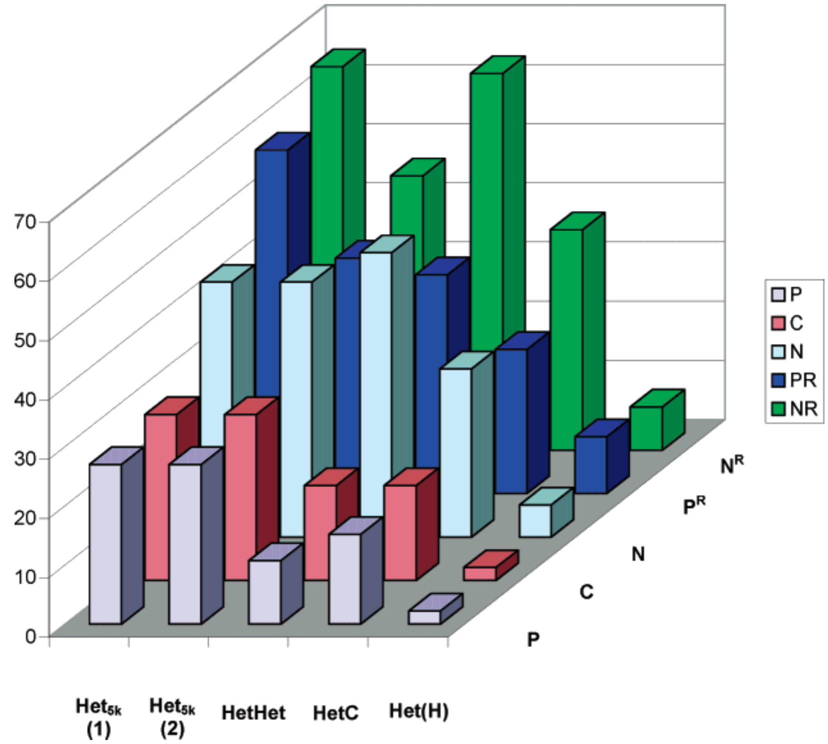

Figure 2. Comparison of energy penalties for 11-vertex *nido*-hetero(carba)boranes and -borates. Energy penalties for four-electron-donating heteroatoms (P^R and N^R) are larger than those for three-electron donors (P, C, N). Energy penalties for structural features $Het_{5k}(1)$, $Het_{5k}(2)$, and HetHet′ (Het′ = Het or C) increase with an increase in electronegativity in both three- and four-electron-donating heteroatoms. Energy penalties for carbon atom structural features are taken from ref 39.

also; in three-electron-donating heteroatoms, for example, P ($\chi = 2.19$), C ($\chi = 2.55$), and N ($\chi = 3.04$)[43] have energy penalties of 10.7, 16.0, and 40.0 kcal mol^{-1} for HetHet (Table 1; Figure 2). In summary, electron localization destabilizes clusters where the number of skeletal electrons formally contributed by a heteroatom is the primary factor and its electronegativity is secondary.

3.4. Comparisons of Relative Stabilities from Empirical Energy Penalties (E_{inc}^{rel}) and from DFT-Computed Values (E_{calc}) for 11-Vertex *nido*-Phospha- and Aza(carba)boranes and -borates. Structural increments have been established separately for 95 phospha- and 46 aza(carba)boranes and -borates. The study reviews thirty 11-vertex *nido*-phospha(carba)boranes and -borates and five 11-vertex *nido*-aza(carba)boranes and -borates, their alkyl/metal derivatives or metal complexes having been reported in the past 40 years. The syntheses of many structures have been reported in the past five years. Corresponding statistically fitted energy penalties for five general structural features along with Het^R can reproduce the relative stabilities of all phospha- and aza(carba)boranes and -borates included in this paper and even more.

Various known and candidate structures are ordered with the lowest energy isomer at the top in Tables 2−5. Different energy penalties in a particular structure are summed up to give $\sum E_{inc}$. The term E_{inc}^{rel} represents the relative energies of a given isomer with respect to the most stable one, as deduced from increments. The term ΔE is the difference between the empirical relative energies (E_{inc}^{rel}) and DFT-computed relative energies (E_{calc}).

3.4.1. Phosphaboranes and -borates. Phosphaboranes and -borates incorporate bare phosphorus (P) as well as exo-substituted phosphorus (P^R) heteroatoms, each behaving independently as a separate heterogroup. Structural features and corresponding energy penalties arising as a result of both heterogroups in fourty-four 11-vertex *nido*-phosphaboranes and -borates are listed in Table 2. This approach can be further applied to many other possible phosphaboranes and -borates. The thermodynamically most stable isomer in each case, from $[PB_{10}H_{10}]^{3-}$ to $P_4B_7H_7$, is included (Table 2).

3.4.1.1. *nido*-$[PB_{10}H_{10+n}]^{(3-n)-}$ (n = 0, 1, 2, 3). The absence of hydrogen atoms in $[PB_{10}H_{10}]^{3-}$ allows one structural feature, P_{5k}, to reproduce the relative stability of all three possible isomers, that is, of *nido*-7-$[PB_{10}H_{10}]^{3-}$ (**AA**), *nido*-2-$[PB_{10}H_{10}]^{3-}$ (**AB**), and *nido*-1-$[PB_{10}H_{10}]^{3-}$ (**AC**). *nido*-7-$[PB_{10}H_{10}]^{3-}$ (**AA**), the most stable isomer, has the phosphorus atom at the open face, whereas **AB** and **AC** have it at vertex numbers 2 and 1, respectively (structural feature P_{5k}). **AC** is slightly higher in energy than **AB**, as a phosphorus atom at the apical position in the former is slightly more disfavoring compared to middle-belt positions (see Table 2 for details).

The presence of one extra hydrogen in $[PB_{10}H_{11}]^{2-}$ can generate one additional structural feature for bare phosphorus atoms, P(H), and three structural features for exo-substituted phosphorus atoms, that is, for P^R, $P^R_{5k}(1)$, and $P^R_{5k}(2)$. Bare phosphorus containing *nido*-7-$[PB_{10}H_{11}]^{2-}$ with *μ-H*-9,10

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[43] Pauling, L. *The Nature of the Chemical Bond*; Cornell University Press: Ithaca, New York, 1960.

Table 2. Structural Increments Accurately Reproduce the Relative Stabilities of Various 11-Vertex *nido*-Phosphaboranes and -borates

	compound	*μ-H*	HH 19.5	P_{5k} 26.9	PP 10.7	P(H) 2.2	P^R 13.3	$P^R_{5k}(1)$ 58.0	$P^R_{5k}(2)$ 39.7	$P^R(H)$ 9.6	PP^R 18.3	P^RP^R 36.9	ΣE_{inc}	E_{inc}^{rel}	E_{calc}	ΔE
AA[a]	$7\text{-}PB_{10}H_{10}^{3-}$												0.0	0.0	0.0	0.0
AB	$2\text{-}PB_{10}H_{10}^{3-}$			1									26.9	26.9	27.8	−0.9
AC	$1\text{-}PB_{10}H_{10}^{3-}$			1									26.9	26.9	31.5	−4.6
BA[b]	$7\text{-}PB_{10}H_{11}^{2-}$	9,10											0.0	0.0	0.0	0.0
BB[b]	$7\text{-}PB_{10}H_{11}^{2-}$	8,9				1							2.2	2.2	4.3	−2.1
BC[c]	$7\text{-}(PH)B_{10}H_{10}^{2-}$						1						13.3	13.3	18.1	−4.8
BD	$2\text{-}PB_{10}H_{11}^{2-}$	8,9		1									26.9	26.9	26.1	0.8
BE	$1\text{-}(PH)B_{10}H_{10}^{2-}$						1	1					71.3	71.3	68.0	3.3
CA[d]	$7\text{-}PB_{10}H_{12}^{1-}$	8,9:10,11				2							4.4	0.0	0.0	0.0
CB[e]	$7\text{-}(PH)B_{10}H_{11}^{1-}$	9,10					1						13.3	8.9	10.9	−2.0
CC	$7\text{-}(PH)B_{10}H_{11}^{1-}$	8,9					1			1			22.9	18.5	17.7	0.8
CD	$2\text{-}PB_{10}H_{12}^{1-}$	7,8:9,10		1		1							29.1	24.7	22.3	2.4
CE	$1\text{-}PB_{10}H_{12}^{1-}$	7,8:9,10		1									26.9	22.5	23.1	−0.6
CF	$2\text{-}(PH)B_{10}H_{11}^{1-}$	8,9					1		1				53.0	48.6	54.0	−5.4
CG	$2\text{-}(PH)B_{10}H_{11}^{1-}$	7,11					1		1	2			72.2	67.8	67.6	0.2
CH	$1\text{-}(PH)B_{10}H_{11}^{1-}$	7,8					1	1					71.3	66.9	70.3	−3.4
DA[f]	$7\text{-}(PH)B_{10}H_{12}$	8,9:10,11					1			2			32.5	0.0	0.0	0.0
DB[b]	$2\text{-}PB_{10}H_{13}$	7,11:8,9:9,10	1	1		2							50.8	18.3	13.2	5.1
DC[b]	$1\text{-}PB_{10}H_{13}$	7,8:8,9:10,11	1	1									46.4	13.9	13.4	0.5
DD[g]	$7\text{-}PB_{10}H_{13}$	8,9:9,10:10,11	2			2							43.4	10.9	13.9	−3.0
DE	$2\text{-}(PH)B_{10}H_{12}$	8,9:9,10	1				1		1				72.5	40.5	38.2	2.3
DF	$1\text{-}(PH)B_{10}H_{12}$	7,8:9,10					1	1					71.3	38.8	42.0	−3.2
EA	$7,9\text{-}P_2B_9H_9^{2-}$												0.0	0.0	0.0	0.0
EB	$7,8\text{-}P_2B_9H_9^{2-}$				1								10.7	10.7	12.0	−1.3
FA[b]	$7,9\text{-}P_2B_9H_{10}^{1-}$	10,11				2							4.4	0.0	0.0	0.0
FB[h]	$7,8\text{-}P_2B_9H_{10}^{1-}$	9,10			1	1							12.9	8.5	6.3	2.2
FC	$7,9\text{-}P(PH)B_9H_9^{1-}$						1						13.3	8.9	8.9	0.0
FD	$1,7\text{-}P_2B_9H_{10}^{1-}$	8,9		1		1							29.1	24.7	27.0	−2.3
FE	$7,8\text{-}P(PH)B_9H_9^{1-}$						1				1		31.6	27.2	27.2	0.0
GA[i]	$7,9\text{-}(PH)_2B_9H_9$						2						26.6	0.0	0.0	0.0
GB	$7,8\text{-}P_2B_9H_{11}$	9,10:10,11	1		1	2							34.6	8.0	7.2	0.8
GC	$2,9\text{-}P_2B_9H_{11}$	7,8:10,11		1		4							35.7	9.1	16.5	−7.4
GD	$2,9\text{-}(PH)_2B_9H_9$						2		1				66.3	39.7	34.5	5.2
GE	$7,8\text{-}(PH)_2B_9H_9$						2					1	63.5	36.9	36.9	0.0
GF	$1,7\text{-}(PH)_2B_9H_9$						2	1					84.6	58.0	54.8	3.2
HA	$7,8,10\text{-}P_3B_8H_8^{1-}$				1								10.7	0.0	0.0	0.0
HB	$7,8,9\text{-}~P_3B_8H_8^{1-}$				2								21.4	10.7	10.9	−0.2
IA	$7,8,10\text{-}P_2(PH)B_8H_8$				1		1						24.0	0.0	0.0	0.0
IB	$7,8,9\text{-}P_3B_8H_9$	10,11			2	2							25.8	1.8	5.5	−3.7
IC	$7,10,8\text{-}P_2(PH)B_8H_8$						1				1		31.6	7.6	7.9	−0.3
ID	$1,7,8\text{-}P_3B_8H_9$	9,10		1	1	1							37.6	13.6	20.8	−7.2
IE	$2,8,9\text{-}P_3B_8H_9$	10,11		1	1	2							39.8	15.8	21.5	−5.7
JA	$7,8,9,10\text{-}P_4B_7H_7$				3								32.3	0.0	0.0	0.0
JB	$1,7,8,10\text{-}P_4B_7H_7$			1	1								37.6	5.3	10.4	−5.1

[a] The cyclopentadienyl cobalt complex of **AA** is experimentally known (ref 18). [b] Still experimentally unknown but more stable than known counterparts and, hence, strong candidates for synthesis. [c] See ref 18 for 7-R−BC, where R = Me, Et, Pr, Ph. [d] ref 9. [e] 7-R-substituted **CB**, *nido*-7-$[RPB_{10}H_{11}]^-$, where R = CH_3, C_2H_5, *n*-C_3H_7, and C_6H_5 (ref 18) are experimentally known. [f] 7-R-substituted **DA**, *nido*-7-$RPB_{10}H_{12}$, where R = CH_3, C_2H_5, *n*-C_3H_7, C_6H_5 (ref 18), CH_3, and Ph (ref 19) are reported. [g] *nido*-7-RC(H)═$PB_{10}H_{13}$ (corresponds to a carbene adduct of **DD**), where R = adamantyl (ref 20a) and tBu (ref 28a,b) are reported. [h] ref 45. [i] The 7,9-diphenyl derivative of **GA**, 7,9-Ph_2-*nido*-7,9-$P_2B_9H_9$, is experimentally known (ref 11).

(**BA**, Figure 3) is the only possible $[PB_{10}H_{11}]^{2-}$ isomer that can prevent the presence of any structural feature (Table 2). Structural feature P(H) emerges when a hydrogen atom is bridged between positions 8 and 9 in **BB**. Computed as well as increment results indicate **BB** to be slightly higher in energy than **BA**. The extra hydrogen atom bound to P as an exo-ligand (**BC**) generates the new structural feature P^R, with $E_{inc}[P^R] = 13.3$ kcal mol^{-1}, which makes **BC** less favorable than **BA** and **BB**. Just like in carboranes and carborates,[39] the closer the extra hydrogen atom is to the open-face heteroatom in phospha(carba)boranes and -borates, the larger the energy penalty. Bare as well as exo-substituted phosphorus atoms at cage vertices generate numerous new isomers with structural features P(H), P_{5k}, $P^R_{5k}(1)$, and $P^R_{5k}(2)$. Two such examples, bare *nido*-2-$[PB_{10}H_{11}]^{2-}$ (**BD**) and exo-substituted *nido*-1-$[(PH)B_{10}H_{10}]^{2-}$ (**BE**), are listed in Table 2.

The $[PB_{10}H_{12}]^-$ and $PB_{10}H_{13}$ isomers require one new structural feature, $P^R(H)$, where an exo-substituted phosphorus atom is adjacent to a hydrogen bridge. The most stable $[PB_{10}H_{12}]^-$ structure, 7-$[PB_{10}H_{12}]^-$ with *μ-H*-8,9:9,10 (**CA**, Figure 3),[9] has a bare phosphorus atom at the open face with both hydrogen bridges adjacent to the phosphorus vertex, producing the structural feature P(H) twice. The most stable $PB_{10}H_{13}$ isomer, *nido*-7-$(PH)B_{10}H_{12}$ (**DA**, Figure 3), has an exo-substituted phosphorus atom rather than the bare phosphorus atom. The order of E_{calc} and E_{inc}^{rel} is reversed in the cases of *nido*-2-$[PB_{10}H_{12}]^-$ (**CD**) and *nido*-1-$[PB_{10}H_{12}]^-$ (**CE**), see Table 2, but the discrepancy can be removed because the apical position for the bare phosphorus atom in **CE** is generally slightly less favorable (energy penalty is slightly larger) than a phosphorus atom at position 2. In the case of isomers **DB**, **DC,** and **DD**, the relative stability order

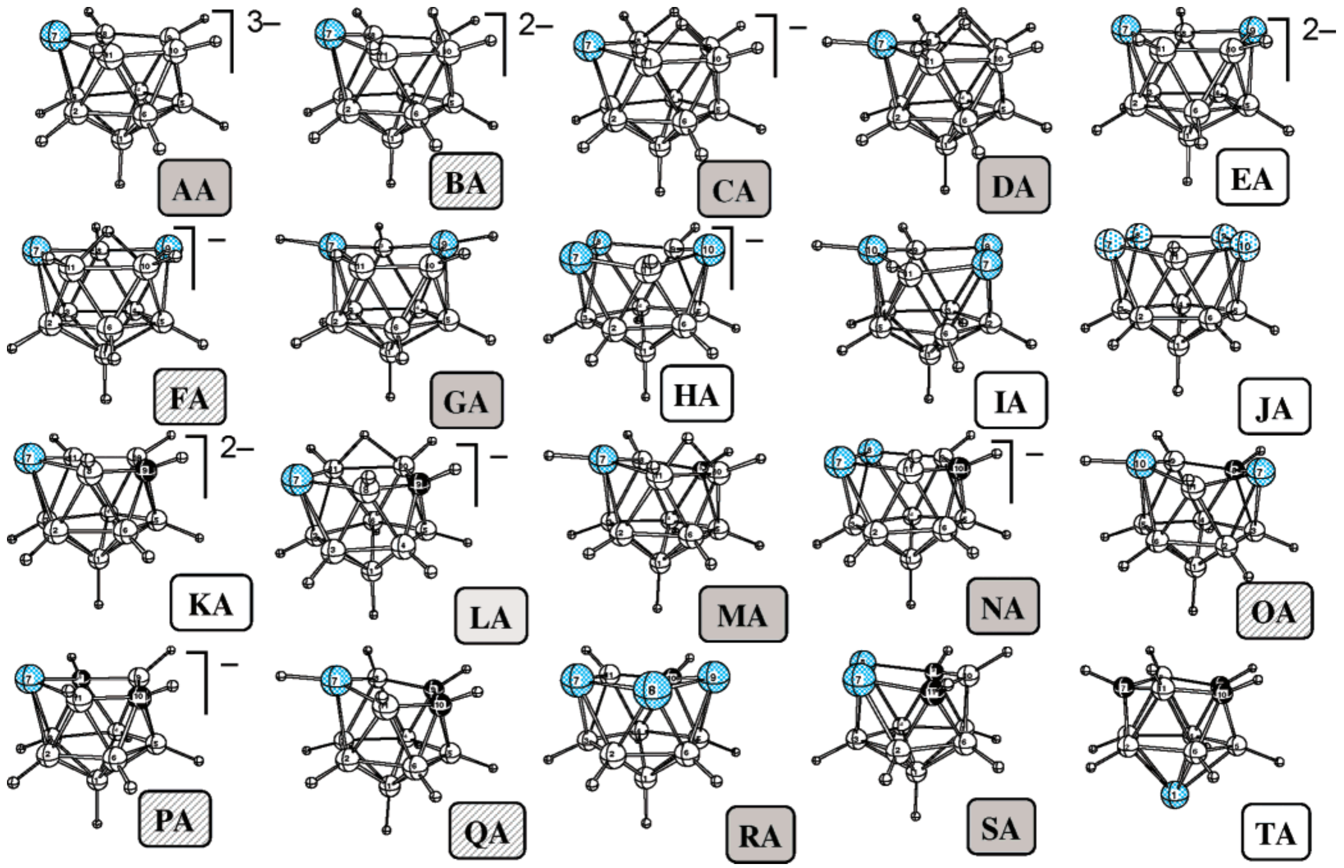

Figure 3. Most stable phospha(carba)borane and -borate isomers. White, black, and blue balls represent boron, carbon, and phosphorus atoms, respectively. Experimentally known structures are labeled with gray boxes; white boxes represent unknown isomers. Lined boxes represent structures that have competitive thermodynamic stabilities compared to their known counterparts.

by our increment system does not strictly match that from the computed relative energies, but ΔE is small in all three cases.

The extra proton in *nido*-7-$[RPB_{10}H_{11}]^-$, where R = CH_3, C_2H_5, *n*-C_3H_7, and C_6H_5,[18] was reported to be either bridging the 9/10 cage positions or rapidly tautomerizing in solution.[9a] DFT-computed as well as increment results point to the former. Comparing measured ^{11}B NMR chemical shifts for 7-$[PB_{10}H_{12}]^-$ to values computed at the B3LYP/6-311+G(d,p) level proves that the hydrogen atom is bridged between boron atoms 9 and 10 rather than tautomerizing on the open face in solution.[44]

3.4.1.2. Oligophosphaboranes and -borates. The presence of more than one phosphorus atom can generate three new structural features (PP, PP^R, and P^RP^R) in oligophoshaboranes and -borates.

nido-7,8-$[P_2B_9H_{10}]^-$ (**FB**)[45] is the only experimentally known representative of a single 11-vertex nido cluster with two bare phosphorus atoms. The binding of one extra hydrogen atom to any of the two bare phosphorus atoms in $[P_2B_9H_{10}]^-$ (rather than to the open face) results in $[P(PH)B_9H_{10}]^-$ structures with one bare phosphorus atom (P) and one exo-substituted phosphorus atom (P^R) in the same cluster. Such a situation is hitherto unknown in phospha(carba)borane chemistry. The relative energies of two such isomers, 7,9-$[P(PH)B_9H_9]^-$ (**FC**) and 7,8-$[P(PH)B_9H_9]^-$ (**FE**), are 8.9 and 27.2 kcal mol^{-1}, respectively, as compared to that of bare 7,9-$[P_2B_9H_{10}]^-$ (**FA**). The energy difference of 7,8-$[P(PH)B_9H_9]^-$ and 7,9-$[P(PH)B_9H_9]^-$ gives an estimate of the energy penalty for PP^R of 18.3 kcal mol^{-1}. This value for PP^R is somewhat smaller than what results from $^1/_2(E_{inc}[PP] + E_{inc}[P^RP^R])$, that is, 23.8 kcal mol^{-1}. PP^R, along with PP, P_{5k}, P^R, $P^R{}_{5k}(1)$, and $P^R{}_{5k}(2)$, can be used to derive the relative energies of all possible (bare + exo)-oligophosphaboranes and -borates.

Neutral $P_2B_9H_{11}$ has two additional hydrogen atoms compared to $[P_2B_9H_9]^{2-}$. The sum of the energy penalties for different structural features shows that the thermodynamic stability is larger for exo-substituted phosphorus atoms than for bare phosphorus atoms (see **GA**, *nido*-7,9-$(PH)_2B_9H_9$, Figure 3; Table 2).

The $E_{inc}{}^{rel}$ and E_{calc} values of various $[P_3B_8H_8]^-$, $P_3B_8H_9$, and $P_4B_7H_7$ isomers are listed in Table 2. The most stable $P_3B_8H_9$ isomer, (bare + exo)-7,8,10-$P_2(PH)B_8H_8$ (**IA**), has a P^R (exo-substituted phosphorus atom) at vertex number 10 and two bare phosphorus atoms at positions 7 and 8.

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(44) The experimental data shows a 2:4:2:1:1 distribution of doublets with chemical shifts of −11.6, −21.5, −22.5, −28.3, and −37.2 ppm for the ethylated derivative. Theoretical results for the C_s symmetric structure are −11.6 (B4, 6), −23.0 (B8, 11), −24.3 (B9, 10), −26.2 (B2, 3), −26.0 (B5), and −41.4 (B1) ppm. Assuming that the hydrogen bridge tautomerizes on the open face from positions 8/9 to positions 10/11, the averaged theoretical chemical shifts are −10.9 (B9, 10), −15.6 (B8, 11), −18.1 (B2, B3), −23.4 (B4, 6), −2.8 (B5), and −31.0 (B1) ppm.

(45) Little, J. L.; Whitesell, M. A.; Chapman, R. W.; Kester, J. G.; Huffman, J. C.; Todd, L. J. *Inorg. Chem.* **1993**, *32*, 3369−3372.

3.4.2. Phosphacarbaboranes and -borates. Phosphacarbaboranes and -borates include one more heteroatom, that is, a carbon in addition to P or P^R. A detailed study of phosphacarbaboranes and -borates from $[PCB_9H_{10}]^{2-}$ to $PC_3B_7H_{10}$ is included in the next section, and their structural features and energy penalties are listed in Appendix 1 (Supporting Information).

3.4.2.1. *nido*-$[PCB_9H_{10+n}]^{(2-n)-}$ ($n = 0, 1, 2$). Three structural features (PP, PC, and P/C_{5k}) are required to give the relative stability of any possible bare $[PCB_9H_{10}]^{2-}$ isomer. $[PCB_9H_{11}]^-$ and PCB_9H_{12} can realize both bare and exo-substituted structures. The relative stabilities of various *nido*-$[PCB_9H_{10+n}]^{(2-n)-}$
($n = 0, 1, 2$) isomers are listed in Appendix 1 (Supporting Information). *nido*-7,9-$(PH)CB_9H_{11}$ (**MA**, Figure 3)[26] is the only experimentally known phosphaborane that has a hydrogen atom rather than an alkyl group as an exo-substituent.

3.4.2.2. *nido*-$[P_2CB_8H_9]^-$ and *nido*-$P_2CB_8H_{10}$. MP2/6-31G(d)+ZPE(RHF/6-31G(d)) computations indicate that the relative energy increases along 7,8,10- (**NA**, Figure 3) < 7,10,8- (**NB**) < 7,9,8- (**ND**) < 7,8,9-$[P_2CB_8H_9]^-$ (**NC**).[12] We computed these isomers at various levels and conclude that, using these methods, the relative energy order comes out to be **NA** < **NB** < **NC** < **ND**. The latter results are also reproduced by the increment system (Appendix 2, Supporting Information).

3.4.2.3. *nido*-$[PC_2B_8H_{10}]^-$ and *nido*-$PC_2B_8H_{11}$. The 7,8,10 positions in the most stable $[PC_2B_8H_{10}]^-$ isomer, **PA** (Figure 3), generate structural feature PC, which is less disfavoring than CC. Three more $[PC_2B_8H_{10}]^-$ isomers that have open-face heteroatoms {7,9,10-$[PC_2B_8H_{10}]^-$ (**PB**), 7,8,9-$[PC_2B_8H_{10}]^-$ (**PF**),[10] and 7,8,11-$[PC_2B_8H_{10}]^-$ (**PG**)}[46] are less favorable options because they possess CC, CC + PC, and 2·CC features, respectively. Any of the heteroatoms at a 5k position causes thermodynamic instability as compared to 7,8,10-$[PC_2B_8H_{10}]^-$ (**PA**, Figure 3). The relative energies estimated from structural increments (E_{inc}^{rel}) of 2,8,10-$[PC_2B_8H_{10}]^-$ (**PC**), 8,2,10-$[PC_2B_8H_{10}]^-$ (**PD**), and 1,7,9-$[PC_2B_8H_{10}]^-$ (**PE**) have the same value. However, **PC** and **PD** can be distinguished from each other because the energy penalty of C_{5k} in **PD** should be slightly higher than that of P_{5k} in **PC** because of the larger electronegativity of carbon as compared to that of phosphorus. 5k splitting[39] applies to **PD** and **PE** because position 1 (**PE**) is slightly more disfavoring as compared to positions 2−6 (**PD**).

Six situations of the three heteroatoms (C, P, and P^R) on the open face of *nido*-$PC_2B_8H_{11}$ are listed in Appendix 1 (Supporting Information).

3.4.2.4. *nido*-$P_xC_{4-x}B_7H_{11-x}$ ($x = 1, 2, 3$). Various *nido*-$P_xC_{4-x}B_7H_{11-x}$ structures (**RA** to **TD**) are listed in Appendix 1 (Supporting Information). Structural feature PP is less disfavoring than PC and CC; therefore, $P_3CB_7H_8$ and $P_2C_2B_7H_9$ can accommodate all heteroatoms at the open face in the thermodynamically most stable isomers (**RA** and **SA**, each with 1·PP + 2·PC; Figure 3). One heteroatom moves to a 5k position in the most stable $PC_3B_7H_{10}$ isomer, 1,7,9,-10-$PC_3B_7H_{10}$ (**TA**, Figure 3), because the open-face configuration 7,8,9,10-$PC_3B_7H_{10}$ (**TB**) exhibits two PC features and one CC feature. Both **TA** and **TD** have one heteroatom at the apical 5k position, but **TD** has the more electronegative carbon atom at the apical position 1 (C_{5k}) and is slightly more disfavored than **TA** with a phosphorus atom at the same position (P_{5k}).

3.4.3. 11-Vertex *nido*-Aza(carba)boranes and -borates. The relative stabilities produced from the increment system (E_{inc}^{rel}) and the computed relative stabilities (E_{calc}) for various 11-vertex *nido*-aza(carba)boranes and -borates are listed in Appendices 3 and 4 (Supporting Information). *nido*-7-$(NH)B_{10}H_{10}$ (**VC**),[47] *nido*-7-$[NB_{10}H_{12}]^-$ (**WC**),[29] and *nido*-7-$(NH)B_{10}H_{12}$ (**XA**)[29] represent the experimentally known *nido*-$[NB_{10}H_{10+n}]^{(3-n)-}$ ($n = 0, 1, 2, 3$) structures.

Adjacent bare nitrogen atoms in *nido*-7,8-$[N_2B_9H_9]^{2-}$ do not cause major geometry distortions, and the relative energy of 7,8-$[N_2B_9H_9]^{2-}$ (**YB**) versus that of 7,9-$[N_2B_9H_9]^{2-}$ (**YA**, Figure 4) (40.7 kcal mol^{-1}) is considerably less than 63.6 kcal mol^{-1} (the energy difference of 7,8-$(NH)_2B_9H_9$ and 7,9-$(NH)_2B_9H_9$, which bear exo-substituted nitrogen atoms). None of the *nido*-$(NH)_2B_9H_9$ isomers is known experimentally. The geometry optimized for 7,8-$(NH)_2B_9H_9$ with adjacent exo-substituted nitrogen atoms was distorted and was 63.6 kcal mol^{-1} higher in energy than 7,9-$(NH)_2B_9H_9$. The energy penalties obtained by fixing N(7)−B(2) and N(8)−B(2) distances at 1.775 Å resulted in an even higher energy penalty of 76.5 kcal mol^{-1}.

nido-7,9,10-$[NC_2B_8H_{10}]^-$ (**ADA**, Figure 4)[30] and *nido*-7,9,10-$(NH)C_2B_8H_{10}$ (**AEA**, Figure 4)[30,48−52] represent the two experimentally known 11-vertex *nido*-clusters with nitrogen and carbon atoms present in the same cluster. The relative stability of various 11-vertex *nido*-aza(carba)boranes and -borates are listed in Appendix 4 (Supporting Information).

3.5. Energy Penalties for Hetero(carba)boranes and -borates Derived by Comparing Two Isomers that Differ with Respect to One Feature. Once the general validity of energy penalties for important structural features is proven, the energy penalties can be estimated as the energy differences of two structures that differ with respect to a single structural feature. For instance, the energy penalty for CC arising from a statistical refinement based on 20 carborane structures[39] is 16.0 kcal mol^{-1}, whereas the relative energy of 7,8-$[C_2B_9H_{11}]^{2-}$ versus 7,9-$[C_2B_9H_{11}]^{2-}$ (both isomers differ only by the presence or absence of CC) is 16.3 kcal mol^{-1}. The N^RC energy penalty (35.6 kcal mol^{-1}) obtained by comparing 7,8-$[(NH)CB_9H_{10}]^-$ with 7,9-$[(NH)CB_9H_{10}]^-$ is very close to the 37.2 kcal mol^{-1} obtained from five

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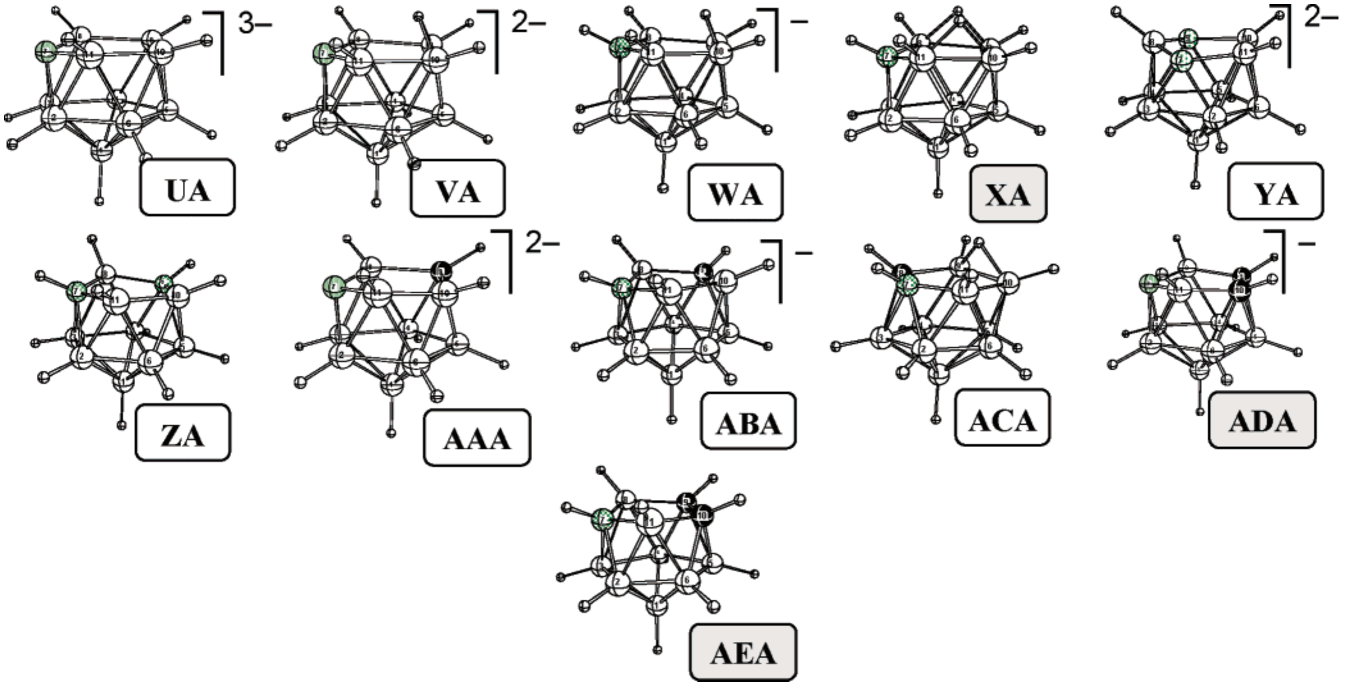

Figure 4. Most stable aza(carba)borane and -borate isomers. White, black, and green balls represent boron, carbon, and nitrogen atoms, respectively. **XA**, **ADA**, and **AEA** represent experimentally known cluster structures. For the relative energies of isomers, consult Appendices 3 and 4 in the Supporting Information.

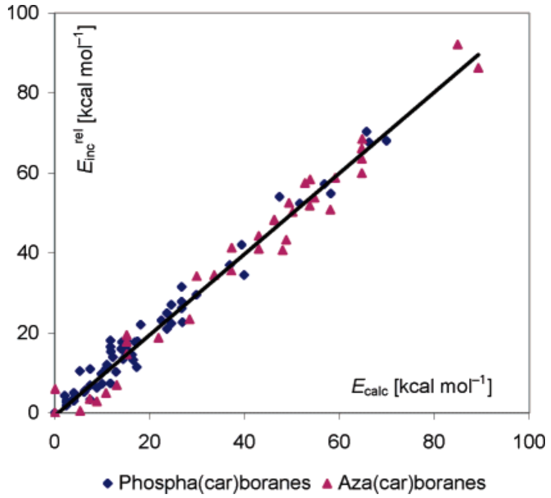

Figure 5. Structural increments (E_{inc}^{rel}) accurately reproduce the relative energies of 11-vertex *nido*-phospha- and aza(carba)boranes and -borates computed by DFT methods (E_{calc}).

structures. Other "statistically established" energy penalties and corresponding "estimated" energy penalties for carboranes and carborates and bare and exo-substituted phospha- and aza(carba)boranes and -borates are listed in Appendix 5 (Supporting Information). Values derived from just two structures are rough estimations that give relative energies with larger errors but are obtained much faster and are accurate enough for the interpretation of general trends.

3.6. Conclusions. Relative energies estimated by applying the increment system presented in this work are plotted against DFT-computed values for 11-vertex bare and exo-substituted *nido*-phospha- and aza(carba)boranes and -borates in Figure 5. Relative energies of 95 (and even more) 11-vertex *nido*-phospha(carba)boranes and -borates and 46 (and even more) 11-vertex *nido*-aza(carba)boranes and -borates can be predicted quite accurately with energy penalties for a few structural features. Energy penalties follow the same relative trends in carboranes and carborates, phospha(carba)boranes and -borates, and aza(carba)boranes and -borates. A heteroatom adjacent to a hydrogen bridge has the least disfavoring effect. Energy penalties depend primarily on the number of electrons donated by a heterogroup and secondarily on the electronegativity (Figure 2). Carbon energy penalties are quite independent of the cluster size and the type of the other heteroatom present in the same cluster (Table 1). Such increments can also be established for other 11-vertex *nido*-hetero(carba)boranes and -borates.

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Supporting Information Available: The DFT-computed relative stabilities as well as those from the increment system for 11-vertex *nido*-phosphacarbaboranes and -borates (Appendix 1), 11-vertex *nido*-azaboranes and -borates (Appendix 3), and 11-vertex *nido*-azacarbaboranes and -borates (Appendix 4); relative energies of $[P_2CB_8H_9]^-$ isomers computed at different levels of theory (Appendix 2); energy penalties derived from statistical fitting and from a comparison of two appropriate structures (Appendix 5); and a list with Cartesian coordinates and absolute energies from B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) computations of all phospha- and aza(carba)boranes and -borates included in this paper (Appendix 6). This material is available free of charge via the Internet at http://pubs.acs.org.

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