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# Hydrogenation of $B_{12}^{0/-}$ : A Planar-to-Icosahedral Structural Transition in $B_{12}H_n^{0/-}$ (n = 1-6) Boron Hydride Clusters

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Abstract A systematic density functional theory and wave function theory investigation performed in this work reveals a planar-to-icosahedral structural transition between n = 4-5 in the partially hydrogenated  $B_{12}H_n^{0/-}$  clusters (n = 1-6) upon hydrogenation of all-boron  $B_{12}^{0/-}$ . Coupled cluster calculations with triple excitations (CCSD(T)) indicate that a distorted icosahedral  $B_{12}H_6$  cluster with  $C_2$  symmetry is overwhelmingly favored (by 35 kcal/mol) over the recently proposed perfectly planar borozene ( $D_{3h} B_{12}H_6$ ) (Szwacki et al., Nanoscale Res Lett 4:1085, 2009) which proves to be a high-lying local minimum. A similar 2D–3D structural transition occurs to the corresponding boron boronyl analogues of  $B_{12}(BO)_n$  with n –BO terminals. Detailed adaptive natural density partitioning (AdNDP) analyses reveal the bonding patterns of these quasi-planar or cage-like clusters which are characterized with delocalized  $\sigma$  and  $\pi$  molecular orbitals. The electron detachment energies of the concerned anions and excitation energies of the neutrals are also predicted to facilitate their future experimental characterizations.

**Keywords** Boron · Boron hydrides · Density functional theory · Structures · Adaptive natural density partitioning

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## Introduction

It is well-known that boron exhibits a variety of polymorphisms composed of icosahedral  $B_{12}$  cages [1]. In contrast, small boron clusters  $B_n^{-70}$  in the size range between n = 3-20 have been confirmed to possess planar or quasi-planar structures by joint experimental and theoretical investigations in the past decade [2–8], with a 2D–3D transition at the double-ring tubular  $B_{20}$  [5]. Of special interests in these all-boron clusters, the quasi-planar  $C_{3v}$   $B_{12}$  in a triangular motif appears to be unique: it is an all-boron analogue of benzene with six delocalized  $\pi$ -electrons and possesses a large first excitation energy of 2.0 eV [2–4]. Upon hydrogenation of  $C_{3v}$   $B_{12}$  at the six corner positions, Szwacki and coworkers recently presented the possibility of the perfectly planar  $D_{3h}$   $B_{12}H_6$  which they called borozene [9]. Borozene has aroused immediate attention since it was proposed [10, 11] and has been utilized as building blocks to form the nanoscale clusters of  $B_{60}H_{12}$  and  $B_{228}H_{24}$  [10] and boron fullerenes [12]. Typical perfectly planar boron hydride clusters reported also include  $C_{2v}$   $B_7H_2^-$  [13],  $B_4H_n$  (n = 1-3) [14], and  $D_{6h}$   $B_6H_6^{-6-}$  [15].

However,  $B_{12}H_n^+$  cations (n = 0-12) [16] generated in an external quadrupole static attraction ion trap were known to preferentially form planar structures in the size range between n = 0-5, whereas those with more hydrogen atoms (n = 6-12) preferentially formed icosahedral cages similar to the well-known 1:1 hydrogenated  $B_{12}H_{12}^{2-}$  dianion [1]. These results remind us that  $B_{12}H_n$  neutrals and  $B_{12}H_n^-$  anions may take similar geometries with the corresponding  $B_{12}H_n^+$  cations, with a planar-to-icosahedral transition at certain size range. Keeping the inspiration in mind, at both density functional theory (DFT) and wave function theory levels in this work, we performed a systematical investigation on the effects of hydrogenation on both the geometrical and electronic structures of the quasi-planar  $C_{3v} B_{12}$  and  $C_s B_{12}^-$  [2–4]. A planar-toicosahedral structural transition was indeed identified at the coupled cluster level between n = 4-5 for both  $B_{12}H_n$  neutrals and  $B_{12}H_n^-$  anions and distorted icosahedral  $C_2 B_{12}H_6$  and  $C_1 B_{12}H_6^-$  cages were found to be overwhelmingly favored in energy (by 35 and 44 kcal/mol, respectively) over the perfectly planar  $D_{3h}$   $B_{12}H_6$  and the corresponding quasi-planar  $C_2 B_{12}H_6^-$  anion [9]. A similar structural transition was obtained for the corresponding boron boronyls of  $B_{12}(BO)_n^{0/-}$  with *n*-BO radicals (n = 1-6). Detailed adaptive natural density partitioning (AdNDP) [17–19] analyses were performed on these partially hydrogenated species to reveal their bonding patterns which are characterized with delocalized  $\sigma$  and  $\pi$  bonds. The one-electron detachment energies of the anions and excitation energies of the neutrals were also predicted to facilitate their spectroscopic characterizations. This work on  $B_{12}H_n^{0/-}$  clusters parallels the results we recently reported for the partially hydrogenated  $B_{16}H_n$  [20] and  $B_{18}H_n$ [21]. These studies are expected to shed new insight into boron hydride intermediate species and advance the bonding patterns of boron-containing compounds in general.

# **Computational Details**

Starting from initial structures constructed from the corresponding  $B_{12}H_n^+$  cations (n = 0-12) [16] and  $B_{12}H_n$  neutrals (n = 2, 4, 6, and 8) [9], we optimized the

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structures and analyzed the vibrational frequencies of  $B_{12}H_n^{0/-}$  (n = 0-6) clusters using the hybrid DFT method of B3LYP [22, 23] and the second-order Møller-Plesset approach (MP2) [24, 25] with the basis set of 6-311G(d,p). The two methods produced essentially the same geometries with slightly different bond parameters and, in some cases, generated different relative stability orders. The relative energies were further refined using the more accurate coupled cluster method including triple excitations (CCSD(T)) [26–29] at both B3LYP and MP2 structures with zero-point corrections included (with the notations of CCSD(T)//B3LYP and CCSD(T)//MP2 hereafter, respectively). As shown in Figs. 1 and 2, CCSD(T)// B3LYP and CCSD(T)//MP2 methods produced the same stability orders with close relative energies for both the neutral and anion series. The adiabatic detachment energies (ADE) of the anions were calculated as the energy differences between the anions and the corresponding neutrals at their ground-state structures, whereas the vertical detachment energies (VDE) were calculated as the energy differences between the ground states of the anions and the ground states of neutrals at the anionic geometries. AdNDP [17-19] bonding patterns shown in Figs. 3 and 4 were visualized using the MOLDEN 4.1 program [30]. To check the aromaticity of the distorted icosahedral clusters, the widely used nucleus independent chemical shifts (NICS) [31, 32] were calculated at the cage centers using the gauge-independent atomic orbital (GIAO) method [33]. The calculated ADE and VDE values for  $B_{12}H_n^-$  (n = 0-6) anions are summarized in Table 1 and the ionization potentials (IP) and first excitation energies  $(E_{ex})$  of the neutrals are tabulated in Table 2. All the calculations in this work were performed using the Gaussian03 program [34].

# **Results and Discussion**

#### Structures and Stabilities

We start from  $B_{12}H_6$ , the most concerned species in this work. As clearly shown in Fig. 1 at CCSD(T)//B3LYP level, the distorted icosahedral  $C_2 B_{12}H_6(2, {}^{1}A)$  (denoted as  $C_2 B_{12}H_6$  hereafter) is overwhelmingly more stable (34.59 kcal/mol) than the perfect planar  $D_{3h} B_{12}H_6(1, {}^{1}A'_1)$  previously reported in Ref. [9]. CCSD(T)//MP2 method produces essentially the same relative energy (-34.59 kcal/mol) as CCSD(T)//B3LYP, providing further evidence to support the reliability of the theoretical approaches used in this work. With one extra electron, the cage-like  $C_1 B_{12}H_6^{-}(4, {}^{2}A)$  anion also turns out to be strongly favored in energy (by 43.58 kcal/mol) over the quasi-planar  $C_2 B_{12}H_6^{-}(3, {}^{2}A)$  [9]. With such large energy differences, the high-lying planar  $D_{3h} B_{12}H_6(1)$  and quasi-planar  $C_2 B_{12}H_6^{-}(3)$  can be safely ruled out from experiments under normal conditions. As the ground states of the concerned systems,  $C_2 B_{12}H_6(2)$  and  $C_1 B_{12}H_6^{-}(4)$  are expected to be synthesized and characterized in future experiments. Thus, a 1:2 (H:B) hydrogenation of the quasi-planar  $B_{12}^{0/-}$  leads to the formation of the distorted icosahedral  $C_2 B_{12}H_6(2)$  and  $C_1 B_{12}H_6^{-}(4)$ .

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**Fig. 1** Planar and icosahedral isomers optimized for **a**  $B_{12}H_n$  neutrals (n = 0-6) and **b**  $B_{12}H_n^-$  anions (n = 0-6) at B3LYP/6-311G(d,p) level, with relative energies between the two isomers indicated in kcal/ mol at CCSD(T)//B3LYP and CCSD(T)//MP2 (*in parentheses*)

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**Fig. 2** Energy differences between planar and icosahedral isomers for **a**  $B_{12}H_n$  (n = 0-6) neutrals and **b**  $B_{12}H_n^-$  (n = 0-6) anions at CCSD(T)//B3LYP (*squares*) and CCSD(T)//MP2 (*round circles*)

A similar stability order exists in  $B_{12}H_5^{0/-}$  (though the relative energies become smaller than  $B_{12}H_6^{0/-}$ ) for which the distorted icosahedral  $C_1 B_{12}H_5(\mathbf{6}, {}^2A)$  and  $C_s B_{12}H_5^{-}(\mathbf{8}, {}^1A')$  are 26.75(28.13) and 17.30(18.91) kcal/mol more stable than the corresponding quasi-planar  $C_1 B_{12}H_5(\mathbf{5}, {}^2A)$  and  $C_1 B_{12}H_5^{-}(\mathbf{7}, {}^1A)$  at CCSD(T)// B3LYP (CCSD(T)//MP2), respectively.  $B_{12}H_5$  and  $B_{12}H_5^{-}$  favor distorted icosahedral structures over planar geometries for the reason that they possess the same number of valence electrons as the known distorted icosahedral  $B_{12}H_6^+$  and  $B_{12}H_7^+$ [16], respectively.

However, as indicated in Figs. 1 and 2, icosahedral and planar isomers become energetically competitive for  $B_{12}H_4^{0/-}$  clusters, with the distorted  $C_s B_{12}H_4(10, {}^{1}A')$  being only 5.30 (5.53) kcal/mol more stable than  $C_s B_{12}H_4(9, {}^{1}A')$  at CCSD(T)//B3LYP (CCSD(T)//MP2), while  $C_s B_{12}H_4^{-}(12, {}^{2}A')$  having the relative energies of -0.46 kcal/mol at CCSD(T)//B3LYP and +1.84 kcal/mol at CCSD(T)//MP2. Such small energy differences are within the accuracies of the theoretical methods used. The 2D and 3D isomers of  $B_{12}H_4^{-}$  anion can be practically viewed iso-energetic isomers.

A stability conversion actually occurs at  $B_{12}H_3^{0/-}$ , with the quasi-planar  $C_1 B_{12}H_3(13, {}^{2}A)$  and  $C_1 B_{12}H_3^{-}(15, {}^{1}A)$  being 3.23 (7.61) and 12.45 (12.22) kcal/mol more stable than the icosahedral  $C_s B_{12}H_3(14, {}^{2}A')$  and  $C_s B_{12}H_3^{-}(16, {}^{1}A')$ , respectively. Such a tendency develops as the content of the hydrogen atoms decreases, with the quasi-planar isomers (17, 19, 21, 23, 25, and 27) being overwhelmingly favored in energy over the distorted icosahedral ones (18, 20, 22, 24, 26, and 28) for  $B_{12}H_2^{0/-}$ ,  $B_{12}H^{0/-}$ , and bared  $B_{12}^{0/-}$  (convex  $B_{12}^{-0/-}$  were already characterized in previous photoelectron spectroscopy measurements (PES) [2–4]).

The overall stability variation of  $B_{12}H_n$  neutrals can be clearly seen from Fig. 2a, where a planar-to-icosahedral transition occurs at n = 4, well in line with the reported structural transition at  $B_{12}H_5^+$  [16] which is iso-electronic with  $B_{12}H_4$ . A



**Fig. 3** AdNDP bonding patterns obtained for planar  $B_{12}H_n$  neutrals (n = 0, 2, 4, and 6) with occupation numbers (ON) indicated. **a**  $\pi$  and  $\sigma$  bonds of  $D_{3h} B_{12}H_6(1)$ . **b**  $\sigma$  bonds of  $C_s B_{12}H_4(9)$ ,  $C_s B_{12}H_2(17)$ , and  $D_{3h} B_{12}(25)$  (these neutrals also possess *n* similar B–H  $\sigma$  bonds and three similar 5c–2e  $\pi$  bonds with  $D_{3h} B_{12}H_6(1)$ )

similar planar-to-icosahedral transition happens to  $B_{12}H_n^-$  anions at n = 5 as shown in Fig. 2b, where the planar and icosahedral isomers of  $B_{12}H_4^-$  are practically isoenergetic. We conclude that a planar-to-icosahedral structural transition occurs for  $B_{12}H_n^{0/-}$  clusters between n = 4-5.  $B_{12}H_n^{0/-}$  clusters maintain the quasi-planarity of the bared  $B_{12}^{0/-}$  with  $n \le 3$  (H:B  $\le 1:4$ ), but they overwhelmingly favor distorted

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Fig. 4 AdNDP bonding patterns of  $C_2 B_{12}H_6$  (2) with occupation numbers (ON) indicated

Table 1	Calculated	ADE	and	VDE	values	of	$B_{12}H_n^-$	(n = 0-6)	anions	at	CCSD(T)//B3LYP	and
CCSD(T)	//MP2 level	ls										

-	ADE (eV)		VDE (eV)			
	CCSD(T)//B3LYP	CCSD(T)//MP2	CCSD(T)//B3LYP	CCSD(T)//MP2		
<b>4</b> . $C_1 B_{12} H_6^-$	2.15	2.16	2.40	2.50		
<b>8</b> . $C_s B_{12} H_5^-$	2.47	2.41	2.62	2.59		
<b>12</b> . $C_8 B_{12} H_4^-$	1.66	1.64	1.68	1.76		
<b>15</b> . $C_1 B_{12} H_3^-$	2.99	3.01	3.34	3.31		
<b>19</b> . $C_2 B_{12} H_2^-$	2.06	2.04	2.20	2.21		
<b>23</b> . C <sub>1</sub> B <sub>12</sub> H <sup>-</sup>	3.23	3.23	3.39	3.43		
<b>27</b> . $C_s B_{12}^{-}$	1.90	1.83	2.08	2.07		

**Table 2** Calculated first ionization potentials (IP) of  $B_{12}H_n$  (n = 0-6) neutrals at CCSD(T)//B3LYP and CCSD(T)//MP2 and their excitation energies ( $E_{ex}$ ) at TD-B3LYP

	IP (eV)	E <sub>ex</sub> (eV)		
	CCSD(T)//B3LYP	CCSD(T)//MP2	B3LYP	
<b>2</b> . C <sub>2</sub> B <sub>12</sub> H <sub>6</sub>	8.10	8.03	0.91(T)	
<b>6</b> . C <sub>1</sub> B <sub>12</sub> H <sub>5</sub>	7.37	7.45	0.67(D)	
<b>10</b> . C <sub>s</sub> B <sub>12</sub> H <sub>4</sub>	8.10	8.13	0.55(T)	
<b>13</b> . C <sub>1</sub> B <sub>12</sub> H <sub>3</sub>	7.15	7.12	1.05(D)	
<b>17</b> . C <sub>s</sub> B <sub>12</sub> H <sub>2</sub>	8.18	8.17	1.67(T)	
<b>21</b> . C <sub>1</sub> B <sub>12</sub> H	7.62	7.50	1.43(D)	
<b>25</b> . C <sub>3v</sub> B <sub>12</sub>	8.88	8.83	2.32(T)	

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icosahedral structures when the number of hydrogen atoms reaches 5. We also tried  $B_{12}H_8$  which contains two more hydrogen atoms than  $B_{12}H_6$ . At CCSD(T)//B3LYP (CCSD(T)//MP2) level,  $B_{12}H_8$  proves to have a distorted icosahedral  $C_{2v}$   $B_{12}H_8$  (<sup>1</sup>A<sub>1</sub>) ground state similar to the  $B_{12}H_8^+$  cation reported in Ref. [16], It turns out to be 112.53 (114.150) kcal/mol more stable than the quasi-planar  $C_s B_{12}H_8(^1A')$  proposed in Ref. [9].

Orbitals and Aromaticities

AdNDP analyses help to understand the structures and bonding patterns of various compounds [17-19]. As shown in Fig. 3a, D<sub>3h</sub> B<sub>12</sub>H<sub>6</sub>(1) possesses six equivalent 2c-2e B-H  $\sigma$  bonds with the occupation number of ON = 1.97lel, six periphery 2c-2e B-B  $\sigma$  bonds with ON = 1.75lel, six in-plane 3c-2e  $\sigma$  bonds with ON = 1.87 - 1.95 lel, and three 5c-2e  $\pi$  bonds over the B<sub>12</sub> plane with ON = 1.90 lel. Thus, it formally satisfies the 4n + 2 rule for  $\pi$  aromaticity and 4n rule for  $\sigma$  antiaromaticity in electron counts (similar situations were reported for  $B_{16}^{2-}$  [6] and  $B_{19}^{-}$  [7]). However, the globally  $\sigma$  antiaromatic  $D_{3h} B_{12} H_6$  with six delocalized  $\sigma$  bonds covering six B<sub>3</sub> triangles is expected to lead to the formation of islands of  $\sigma$ -aromaticity, as in the case of Li<sub>4</sub> [17–19]. It is true that the in-plane contour plot of NICS(x,y) for D<sub>3h</sub> B<sub>12</sub>H<sub>6</sub> (Fig. 1c (left) in Ref. [9]) possesses six most negative NICS areas which exactly correspond to the six  $3c-2e \sigma$  bonds of the molecule shown in Fig. 3a, indicating that the in-plane flow of the diatropic current mainly originates from the contribution of the six delocalized  $3c-2e \sigma$  bonds. It is also interesting to notice that the central B<sub>3</sub> triangle in D<sub>3h</sub> B<sub>12</sub>H<sub>6</sub> is not covered by either the six 3c-2e  $\sigma$  bonds or the three 5c-2e  $\pi$  bonds in our AdNDP bonding pattern. This agrees with the observation that there exists a spatially localized antiaromatic region with positive NICS values at the center of  $D_{3h} B_{12}H_6(1)$  [9]. This makes borozene  $(D_{3h} B_{12} H_6(1))$  fundamentally different from benzene which is globally aromatic without an antiaromatic area at the center.

Figure 3b compares the bonding patterns of the concerned hydrogenated  $B_{12}$  species. The three delocalized 5c–2e  $\pi$  bonds and the six delocalized 3c–2e  $\sigma$  bonds have been well maintained in  $D_{3h} B_{12}$  (similar to  $C_{3v} B_{12}$ ),  $C_s B_{12}H_2$ ,  $C_s B_{12}H_4$ , and  $D_{3h} B_{12}H_6$ . However, the numbers of 2c–2e B–B  $\sigma$  bonds along the periphery of the  $B_{12}$  core in these species decrease from 9, to 8, to 7, to 6, with one short B–B  $\sigma$  periphery bond at the corner broken as each pair of terminal hydrogen atoms added in. Thus, the size of the outer  $B_9$  ring increases from  $D_{3h} B_{12}$ , to  $C_s B_{12}H_2$ , to  $C_s B_{12}H_4$ , and finally, to  $D_{3h} B_{12}H_6$  which possesses the biggest outer  $B_9$  ring in this series to host the inner  $B_3$  ring in a perfect molecular plane. However, as demonstrated above, the overall stability of the planar structures with respect to their icosahedral counterparts decreases with increasing numbers of hydrogen atoms.

Now we turn to the bonding patterns (Fig. 4) of the distorted icosahedral  $C_2 B_{12}H_6(2)$  which possesses six 2c-2e B-H  $\sigma$  bonds around the  $B_{12}$  cage in  $C_2$  symmetry, twelve 3c-2e  $\sigma$  bonds symmetrically distributed in pairs, one 4c-2e  $\sigma$  bond covering four unterminated boron atoms in a distorted rhombus matching the  $C_2$  symmetry of the molecule, and two 3c-2e  $\pi$  bonds covering three unterminated

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boron atoms each. The thirteen delocalized  $\sigma$  bonds are expected to make major contributions to make C<sub>2</sub> B<sub>12</sub>H<sub>6</sub>(**2**) more table than D<sub>3h</sub> B<sub>12</sub>H<sub>6</sub>(**1**) which has six delocalized  $\sigma$  bonds. The six unterminated boron atoms covered by the two 3c-2e  $\pi$  bonds can be further hydrogenated in radial directions when the number of hydrogen atoms exceeds six (n > 6). We also notice that C<sub>2</sub> B<sub>12</sub>H<sub>6</sub>(**2**) possesses a negative NICS value of -35.82 ppm at the center of the cage, indicating that it is 3D aromatic in nature.

Detachment and Excitation Energies

The calculated ADE values between 1.64 and 3.23 eV and VDE values between 1.68 and 3.43 eV for  $B_{12}H_n^-$  anions (n = 0-6) tabulated in Table 1 may help to facilitate their PES characterizations. CCSD(T)//B3LYP and CCSD(T)//MP2 methods agree well in producing these one-electron detachment energies. There exist a clear even-odd alternation in both ADE and VDE values, with the open-shell  $B_{12}H_n^-$  anions (n = 0, 2, 4, and 6) possessing systematically lower ADE and VDE values than their closed-shell  $B_{12}H_n^-$  neighbors (n = 1, 3, and 5).

Table 2 indicates that  $B_{12}H_n$  neutrals (n = 0-6) possess considerably high first ionization potentials (IP = 7.12–8.88 eV) at CCSD(T). These values also exhibit an even-odd alternation, with IP = 8.10–8.88 eV for the closed-shell  $B_{12}H_n$  neutrals (n = 0, 2, 4, and 6) and IP = 7.12–7.62 eV for the open-shell ones (n = 1, 3, and 5).

As for the first excitation energies of the  $B_{12}H_n$  neutrals at their ground states,  $E_{ex} = 0.91$ , 0.67, and 0.55 eV for the distorted icosahedral  $C_2 B_{12}H_6(2)$ ,  $C_1 B_{12}H_5(6)$ , and  $C_s B_{12}H_4(10)$ , and  $E_{ex} = 1.05$ , 1.67, 1.43, and 2.32 eV for the quasiplanar  $C_1 B_{12}H_3(13)$ ,  $C_s B_{12}H_2(17)$ ,  $C_1 B_{12}H(21)$ , and  $C_{3v} B_{12}(25)$ , respectively. Planar isomers appear to have larger  $E_{ex}$  values than their icosahedral counterparts, but icosahedral isomers prove to be the ground states of the  $B_{12}H_n$  neutrals when the number of hydrogen atoms reaches four ( $n \ge 4$ ).

 $B_{12}(BO)_n$  Boron Boronyls (n = 2, 4, and 6)

The BO/H isolobal relationship recently established in a series of PES experiments [35–37] has built a clear structural link between boron oxide clusters and their boron hydride counterparts. Here we substitute *n* hydrogen atoms in B<sub>12</sub>H<sub>*n*</sub> (*n* = 6, 4, and 2) with *n* BO radicals to form the boron boronyls of B<sub>12</sub>(BO)<sub>6</sub> (D<sub>3</sub> **29** and C<sub>2</sub> **30**), B<sub>12</sub>(BO)<sub>4</sub> (C<sub>s</sub> **31** and C<sub>s</sub> **32**), and B<sub>12</sub>(BO)<sub>2</sub> (C<sub>s</sub> **33** and D<sub>5d</sub> **34**). As shown in Fig. 5, these isomers are all true minima of the systems with similar symmetries and geometries with their parent boron hydride clusters. More importantly, these boron boronyls possess the same stability orders as their B<sub>12</sub>H<sub>*n*</sub> counterparts with similar relative energies (compare Figs. 1 and 5). There exists a similar planar-to-icosahedral transition at *n* = 4 for B<sub>12</sub>(BO)<sub>*n*</sub>, with the distorted icosahedral C<sub>2</sub> B<sub>12</sub>(BO)<sub>6</sub>(**30**) being overwhelmingly more stable than the quasi-planar D<sub>3</sub> B<sub>12</sub>(BO)<sub>6</sub>(**29**). Detailed AdNDP analyses indicate that B<sub>12</sub>(BO)<sub>*n*</sub> neutrals also possess similar bonding patterns with their B<sub>12</sub>H<sub>*n*</sub> counterparts, except the *n* B≡O

Fig. 5 Planar and icosahedral isomers optimized for  $B_{12}(BO)_n$  boron boronyls (n = 2, 4, and 6) at B3LYP, with relative energies indicated in kcal/mol at CCSD(T)//B3LYP



triple bonds (two  $\pi$  and one  $\sigma$ ) involved in *n* BO radicals. A similar situation exists for B<sub>12</sub>(BO)<sup>-</sup><sub>n</sub> anions.

### Summary

Comprehensive theoretical investigations performed in this work indicate that there exists a planar-to-icosahedral structural transition between n = 4-5 in the partially hydrogenated  $B_{12}H_n^{0/-}$  (n = 1-6) clusters and their boron boronyl counterparts. The distorted icosahedral C<sub>2</sub>  $B_{12}H_6(2)$  proves to be overwhelmingly more stable than the perfectly planar borozene ( $D_{3h}$   $B_{12}H_6(1)$ ). Given the fact that  $\alpha$ -sheet boron has proven to be the most stable boron sheet composed of a hybrid of triangular and hexagonal motifs [38, 39], it will be very unlikely that borozene may serve as building blocks to form stable planar boron nanostructures. Instead, icosahedral  $B_{12}$  cages at the centers of the  $B_{12}H_n^{0/-}$  clusters ( $n \ge 5$ ) discussed in this work may serve as the most possible building blocks of novel boron-based nanomaterials.

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