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Structures and Energetics of $Al_nH_n^{2-}$ ($5 \leq n \leq 12$) and Al_nH_{n+2} ($4 \leq n \leq 12$): Are Alanes the Borane Analogues?

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In this work, we report the first comparative study directly between $Al_nH_n^{2-}$ and $B_nH_n^{2-}$ ($5 \leq n \leq 12$), Al_nH_{n+2} and B_nH_{n+2} ($4 \leq n \leq 12$) covering diverse structural forms. It was shown that $Al_nH_n^{2-}$ each have a closo ground structure as $B_nH_n^{2-}$, nicely consistent with the Wade−Mingos rule. However, Al_nH_{n+2} adopt the closo-nido ground structures following the even−odd alternation in the number of Al atoms, showing distinct violation of the Wade−Mingos rule for the odd-numbered Al-atoms. Interestingly, the corresponding B_nH_{n+2} also have similar closo (even)-nido (odd) alternation. Therefore, our direct comparison showed that $Al_nH_n^{2-}$ ($5 \leq n \leq 12$) and Al_nH_{n+2} ($4 \leq n \leq 12$) can be viewed as the borane analogues, though not all Al_nH_{n+2} have the ability of being explained by Wade−Mingos rule. So, the analogy between alanes and boranes in form of X_nH_{n+2} should not be simply judged by the Wade−Mingos rule because of the significant influence of the additional two hydrogen atoms on the closo-structure.

1. Introduction

Boron is well-known to have a rich chemistry in its hydrides (boranes). Yet, aluminum has much fewer hydrides than boron, though being in the same group as boron in the periodic table.[1,2] Luckily, the very recent combined anion photoelectron spectroscopy and density functional theory study by Grubisic et al. showed that a series of Al_nH_{n+2} ($n = 4-8$) possess unique stability.[3] The ground structure of each Al_nH_{n+2} ($4 \leq n \leq 8$) was found to adopt a n-vertex polyhedral closo-skeleton in agreement with the Wade−Mingos ($n + 1$) rule. Therefore, in view of the ability of being explained by the Wade−Mingos rule, Grubisic et al. claimed that Al_nH_{n+2} are borane analogues. Their excellent work has marked "the opening of a new chapter in aluminum hydride chemistry".[3] As optimistically described in Grubisic et al.'s work,[4] alanes might find applications in hydrogen-storage and energetic materials.

Very recently, Martínez et al. [5] calculated the structures of a series of Al_nH_{n+2} ($n = 4-11$) clusters. They found that five clusters with $n = 4, 5, 6, 7, 10$ have dihydrogen-bridged closo-structures and thus indeed fulfill the Wade−Mingos rule. However, the remaining species with $n = 8, 9, 11$ do not accord to this rule since each of the ground structures contains more than two hydrogen bridges (i.e., 4, 5, and 5 H-bridges for Al_8H_{10}, Al_9H_{11}, and $Al_{11}H_{13}$, respectively). Moreover, there have been rare reports of the existence of low-lying multi-hydrogen bridged structures in boranes. Martínez et al.'s results are very attractive because they make us (1) question the analogy between alanes and boranes, and (2) question the applicability of the well-known Wade−Mingos rule to alanes.

For further understanding of the alane chemistry including its potential application, a detailed structural and energetic exploration is indispensable. Yet, the sharp discrepancies between the results of Grubisic et al. and those of Martínez et al. bring us to the question: Are Al_nH_{n+2} the borane analogues? We are aware that there has been no direct comparison between Al_nH_{n+2} and B_nH_{n+2} in the work of both Grubisic et al. and Martínez et al. In principle, the most rational and convincing way to show whether or not these aluminum hydrides can be classified as the borane analogues should be the direct comparison between Al_nH_{n+2} and B_nH_{n+2}, and between $Al_nH_n^{2-}$ and $B_nH_n^{2-}$ species. Therefore, a detailed theoretical study on diverse structures including multi-hydrogen bridges along with a direct comparison of Al_nH_{n+2}/B_nH_{n+2} and $Al_nH_n^{2-}/B_nH_n^{2-}$ are highly desired

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and will be reported in this paper. The first direct comparative study made in our work will show that alanes in form of $Al_nH_n^{2-}$ ($5 \le n \le 12$) and Al_nH_{n+2} ($4 \le n \le 12$) can be viewed as the borane analogues, though the odd-numbered Al_nH_{n+2} cannot be interpreted by the Wade−Mingos rule.

2. Theoretical methods

All the geometries of the alanes studied in our work are fully optimized at the B3PW91/TZVP level. After geometrical optimization, vibrational analysis is performed to check whether the obtained structure is a true minimum point with all real frequencies. For selected structures, the more costly calculations are performed at the 6-311++G(d,p)-MP2, QCISD, and CCSD(T) levels. All calculations are carried out with the Gaussian-03 program package.[6]

3. Results and Discussions

Diverse structural forms are considered starting from a large number of configurations without any symmetry restriction to obtain the most stable structure of $Al_nH_n^{2-}$ (n = 5−12) and Al_nH_{n+2} (n = 4−12). A total of 70 isomeric forms are obtained, which can be found in the Supporting Information. For simplicity and for ease of comparison, only the lowest closo and nido structures are shown in Figure 1 (for each $Al_nH_n^{2-}$) and Figure 2 (for each Al_nH_{n+2}).

3.1. $Al_nH_n^{2-}$ ($5 \le n \le 12$). We first consider $Al_nH_n^{2-}$ (n = 5−12) because the corresponding borane dianions $B_nH_n^{2-}$ ($5 \le n \le 12$) have been well understood by chemists in various aspects (i.e., unique bonding, aromaticity, and unusual stability).[7,8] Moreover, it has been generally taken as granted that Al_nH_{n+2} is a result of the di-protonation of $Al_nH_n^{2-}$. So, the direct structural and energetic information of $Al_nH_n^{2-}$ is very necessary for comparison with Al_nH_{n+2} to show how many features can be inherited from $Al_nH_n^{2-}$ to Al_nH_{n+2} upon protonation. To our knowledge, the known reports on $Al_nH_n^{2-}$ are only limited to $Al_6H_6^{2-}$ and $Al_{12}H_{12}^{2-}$, whose closo-structures were recently studied by Charkin et al.[9] As shown in Figure 1, the ground structure of each $Al_nH_n^{2-}$ (n = 5−12) is associated with an n vertex closo-skeleton, closely akin to the corresponding borane $B_nH_n^{2-}$. Thus, all the alanes $Al_nH_n^{2-}$ (n = 5−12) can be viewed as the borane analogues, both of which can be explained by Wade's (n + 1) rule. We should note that attempts to locate a nido-like form of $Al_nH_n^{2-}$ always lead to the corresponding closo-form.

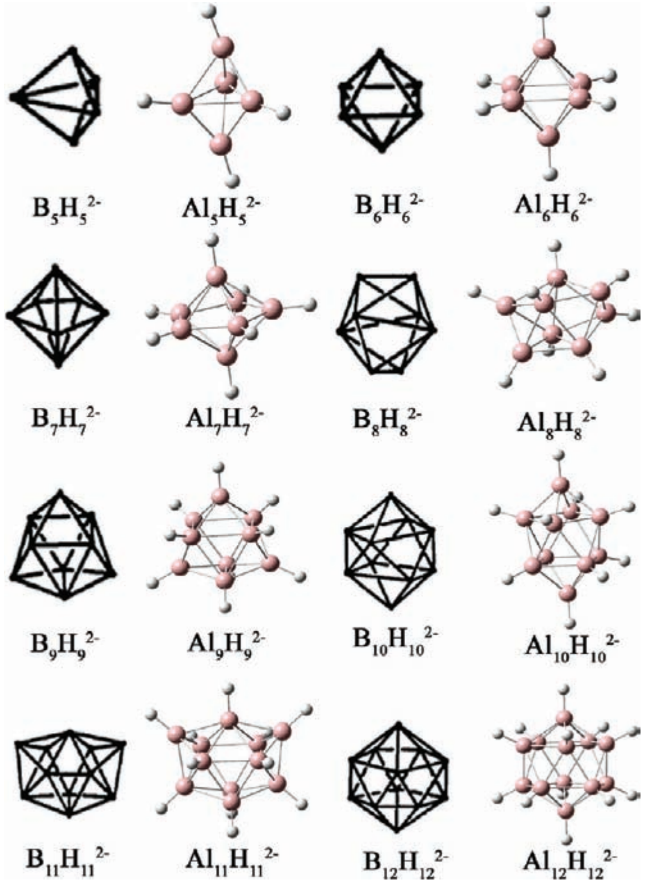

Figure 1. Ground state structures of $Al_nH_n^{2-}$ ($5 \le n \le 12$) at the B3PW91/TZVP level. The ground state structures of $B_nH_n^{2-}$ ($5 \le n \le 12$) from ref 8 (a) is shown for comparison.

3.2. Al_nH_{n+2} ($4 \le n \le 12$). As depicted in Figure 2, the ground structure of five even-numbered alanes Al_nH_{n+2} (n = 4, 6, 8, 10, 12) each adopt a low-lying n vertex closo-form with two additional hydrogen-atoms bridging to either the Al−Al side or the Al_3 face. So we can easily find that Al_nH_{n+2} (n = 6, 8, 10, 12) have the ability of being explained by the Wade−Mingos rule. The closo ground structure of Al_4H_6 seems not to be in accord with Wade−Mingos rule, yet it is consistent with the polyhedral skeletal electron pair theory (PSEPT). In fact, as discussed by Grubisic et al.[3], taking into consideration of the $T_d \rightarrow D_{2d}$ distortion, the Wade's (n + 1) rule can also be extended to Al_4H_6. For comparison, we can find in Figure 3 that generally each of the even-numbered boron species (i.e., B_nH_{n+2}) have closo-structures. The exception is $B_{10}H_{12}$, for which the nido-form is slightly more competitive in energetics than the closo-form by 1.18 kcal/mol. This might originate from the di-protonation effect at the B−B bonds. Because the B−B single bond distance (ca., 1.8 Å) is much shorter than the Al−Al bond distance (ca., 2.6 Å), protonation should pose a much greater strain in the B_3-ring than in the Al_3-ring. Accordingly, one B−B bond would be significantly elongated to relax the strain and results in a nido-like form.

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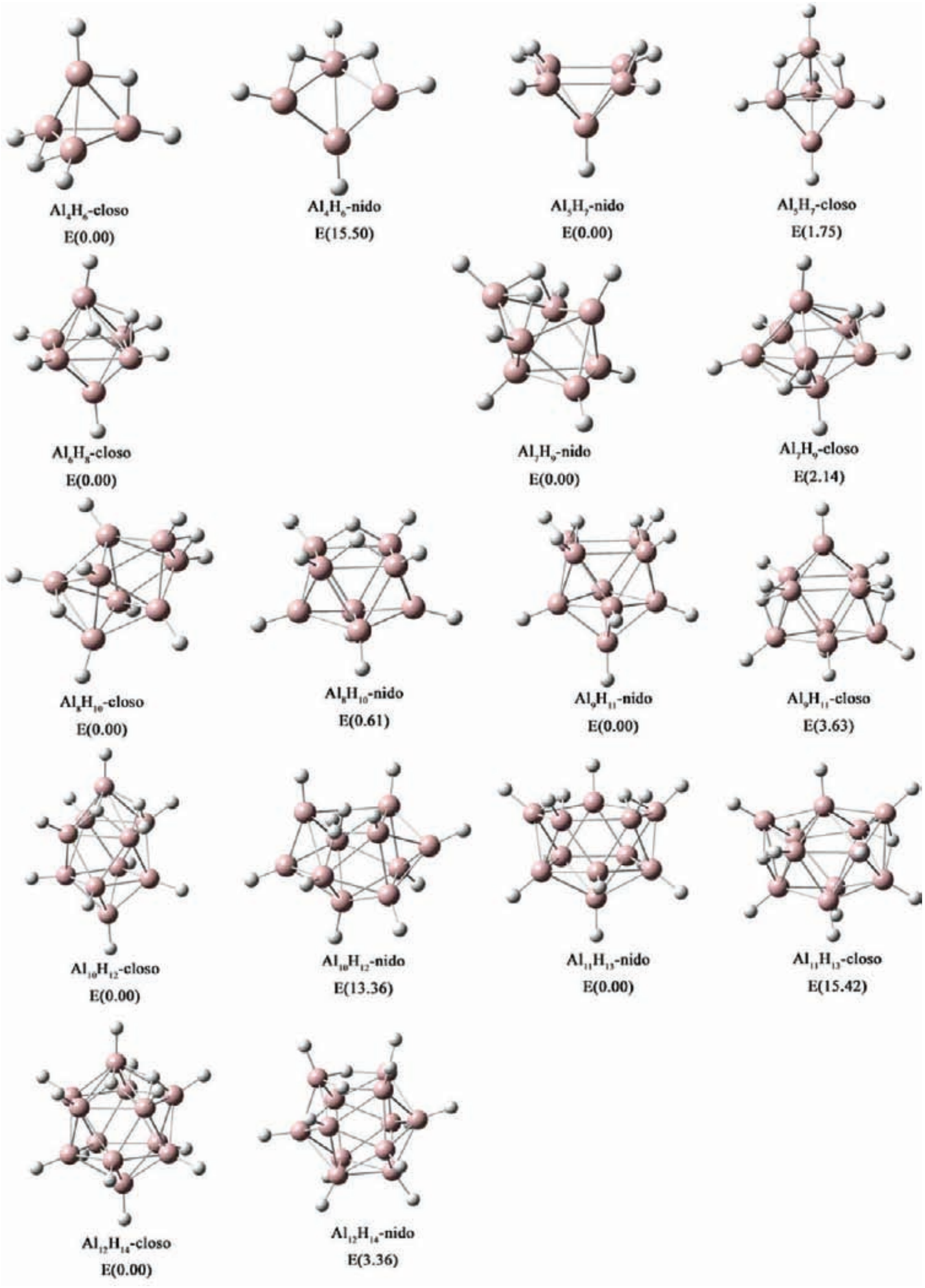

Figure 2. Closo- and nido- structures and relative energies (in kcal/mol) of Al_nH_{n+2} ($4 \le n \le 12$) at the B3PW91/TZVP level.

The situation of the odd-numbered Al_nH_{n+2} (n = 5, 7, 9, 11) becomes much different from the even-numbered species, in contrast to our expectation. Each has a nido ground structure rather than the closo-form. So, these odd-numbered neutral alanes clearly violate the Wade–Mingos rule. Since the Wade–Mingos rule was initially deduced from the borane series, it would be reasonable for one to speculate that the odd-numbered alanes do not mimic boranes. However, and to our great surprise, the odd-numbered boranes B_nH_{n+2} also have the ground open-structures (see Figure 3).[10] In this regard, we can still say that the odd-numbered alanes Al_nH_{n+2} are also the borane analogues, though neither follow the Wade–Mingos rule.

The above direct comparison between $Al_nH_n^{2-}$ and $B_nH_n^{2-}$ (n = 5–12), Al_nH_{n+2} and B_nH_{n+2} (n = 4–12) shows that the studied alanes can generally be considered as the borane analogues, though the odd-numbered Al_nH_{n+2} and B_nH_{n+2} neither obey the Wade–Mingos rule.

At a first glance, the violation of Al_nH_{n+2} (n = 5, 7, 9, 11) from the Wade–Mingos rule could be ascribed to the additional two H-atoms. We are aware that in studying polyhedron boranes (i.e., $B_nH_n^{2-}$, B_nH_{n+4}, B_nH_{n+6}), King has proposed the idea of defective vertices, that is,

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[10] The systematic study on B_nH_{n+2} will be published elsewhere.

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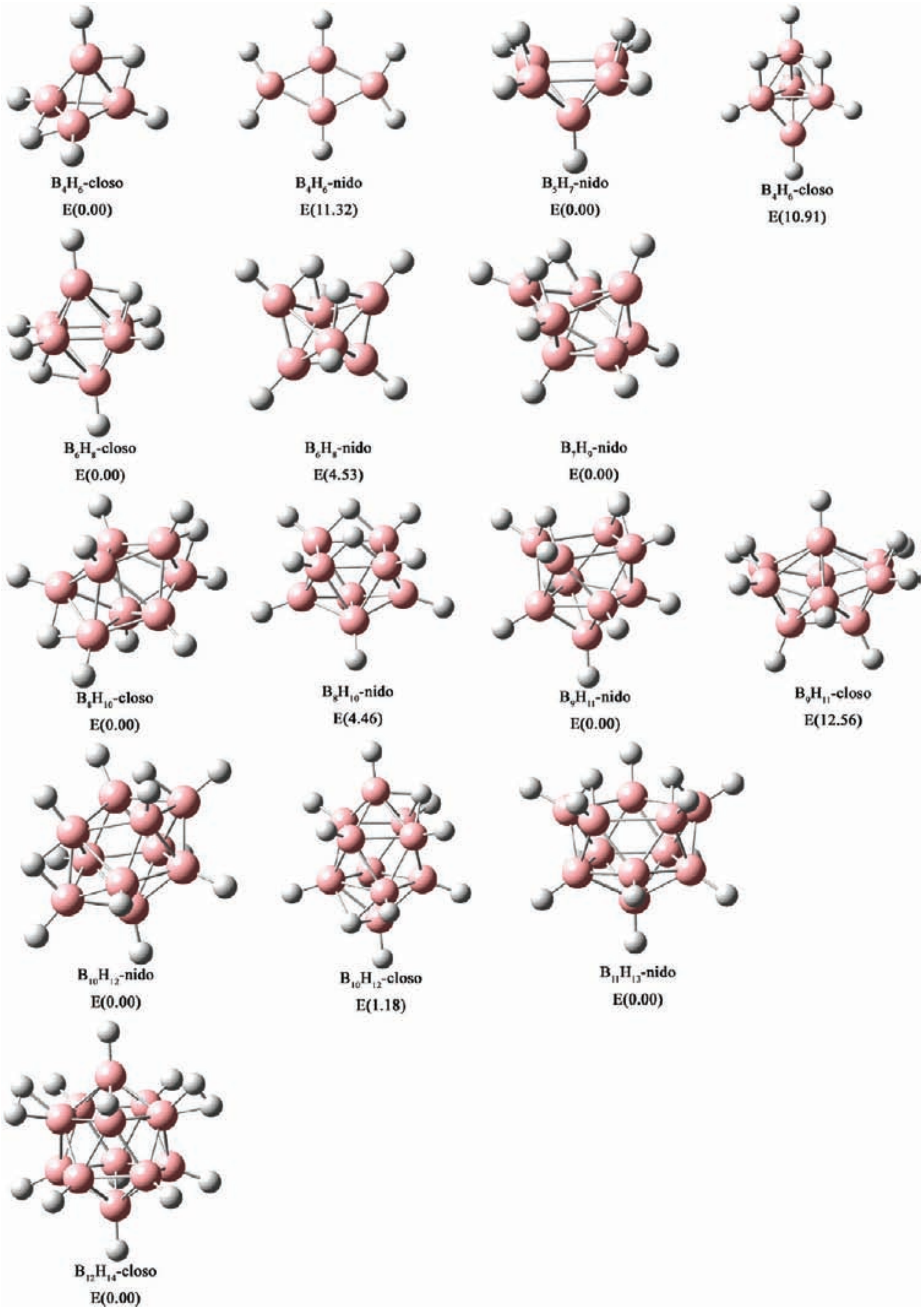

Figure 3. Closo- and nido- structures and relative energies (in kcal/mol) of B_nH_{n+2} ($4 \leq n \leq 12$) at the B3PW91/TZVP level.

vertices of degrees other than 5 can be considered as defective vertices, where the degree of a vertex is defined as the number of edges meeting at that vertex.[13,14] King also suggested that the most favorable structures for borane polyhedra are those in which the defective vertices are isolated as much as possible.[13] For the presently studied Al_nH_{n+2} (n = 7, 9, 11), the number of defective vertices for nido-forms of Al_nH_{n+2} (n = 7,9,11) are three V4 (denote as degree 4 vertex), one V4, and one V4, respectively, whereas for closo-forms, the number of defective vertices are two V6 (denote as degree 6 vertex), four V6 with one V4, and five V6, respectively. In addition, there only have degree 4 or 5 vertices in the deltahedral borane anions $B_nH_n^{2-}$ (n = 6−12), except for $B_{11}H_{11}^{2-}$ which is topologically required to have at least one degree 6 vertex. So Al_7H_9 tends to have three V4 rather than two V6. Then, King's scheme can reasonably account for the preference of nido-form over closo-form for Al_nH_{n+2} (n = 7, 9, 11) since each nido-form has less defective vertices than the corresponding closo-form.

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(12) (a) Corminboeuf et al. found that from $B_8H_8^{2-}$ to $B_8F_8^{2-}$, the multiple fluorine substituents cause a deviation from the Wade−Mingos skeletal electron rules, that is, a distortion from the expected D_{2d} bisdisphenoid to a C_{2v} nido type bicapped trigonal prism.(b) Corminboeuf, C.; Wodrich, M. D.; King, R. B.; Schleyer, P. von R. *Dalton Trans.* **2008**, 1745.

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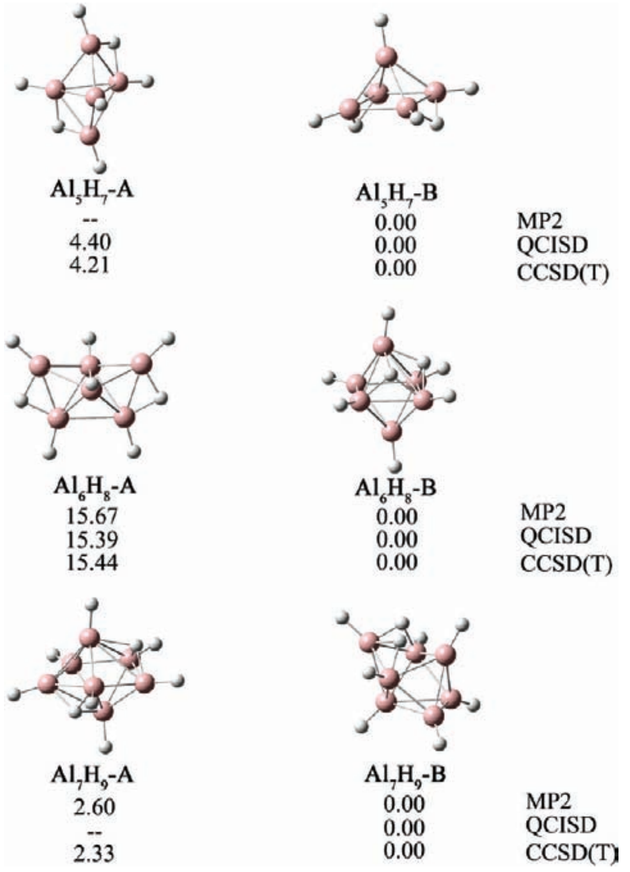

Figure 4. Optimized structures and relative energies (in kcal/mol) of Al_5H_7, Al_6H_8, and Al_7H_9 at the 6-311++G(d,p)-MP2 and QCISD optimization levels and the single-point CCSD(T)/6-311++G(d,p)//B3PW91/TZVP level. "A" is the lowest energy structure predicted in ref 3, and "B" is the lowest energy structure predicted in our work. Note that at the MP2/6-311++G(d,p) level, the structure "A" of Al_5H_7 cannot exist and would collapse to the lower-energy "B". The structure "B" can also be found at the QCISD/6-311++G(d,p) level. The structure "A" of Al_7H_9 does not exist at the QCISD/6-311++G(d,p) level, and would collapse to another nido-like structure.

3.3. Comparison with Previous Results. It is of great interest to compare our results with previous theoretical studies. In the pioneering work of Grubisic et al., the Al_nH_{n+2} (n = 4−8) alanes were all optimized to possess the closo ground structures at the B3PW91/TZVP level. Moreover, their predicted Al_6H_8 has a bicapped tetrahedron structure (see Figure 4. Al_6H_8 - A), whereas we predict a perfect octahedral structure (see Figure 4. Al_6H_8 - B). Clearly, Grubisic et al.'s results of n = 5, 6, and 7 show marked contrast from ours. For confirmation, we perform the more costly 6-311++G(d,p)-MP2, QCISD and CCSD(T) (single-point) calculations on Al_nH_{n+2} (n = 5, 6, 7). Their optimized structures and relative energies are shown in Figures 4. We can find that all the three testifying calculations support the B3PW91/TZVP results, that is, Al_5H_7 and Al_7H_9 have nido-like ground structures, whereas Al_6H_8 has a closo-structure (octahedral). It should be noted that the adiabatic electron affinity (EAa) and vertical detachment energy (VDE) values of Al_6H_8, Al_5H_7, and Al_7H_9 using our newly obtained ground structures are all in good agreement with Grubisic et al.'s experimental measurements (see Table 1).

Table 1. Adiabatic Electron Affinities (EAa) and Vertical Detachment Energies (VDE) of Al_nH_{n+2} ($4 \le n \le 12$) from Experiments [Ref [3]] and our Calculations

	EAa (in eV)		VDE (in eV)	
	experiment	theory	experiment	theory
Al_4H_6	1.25 ± 0.15	1.36	1.35 ± 0.05	1.49
Al_5H_7	1.9 ± 0.1	2.03	2.20 ± 0.05	2.19
Al_6H_8	2.4 ± 0.3	1.97	2.65 ± 0.05	2.83
Al_7H_9	2.2 ± 0.2	2.24	2.6 ± 0.1	2.70
Al_8H_{10}	2.3 ± 0.2	2.03	2.8 ± 0.1	2.78
Al_9H_{11}		2.58		2.79
$Al_{10}H_{12}$		2.61		3.18
$Al_{11}H_{13}$		3.05		3.60
$Al_{12}H_{14}$		2.68		3.43

It should be pointed out that although the general conclusion in Grubisic et al.'s work and in ours is the same (i.e., "*Al_nH_{n+2} can be viewed as the borane analogues*"), the criteria to draw the conclusion are quite different. Grubisic et al. reached the conclusion based on the applicability of the Wade−Mingos rule to Al_nH_{n+2}, whereas we arrived at the conclusion by directly comparing Al_nH_{n+2} and B_nH_{n+2}. Neglect of the lowest-energy structures (nido-like) of Al_5H_7 and Al_7H_9 and application of the unsuitable criteria (Wade−Mingos rule) in Grubisic et al.'s work coincidentally resulted in the right conclusion, since the corresponding boranes B_5H_7 and B_7H_9 also violate the Wade−Mingos rule as the corresponding Al_5H_7 and Al_7H_9, as shown in our work.

On the other hand, very recently, Martínez et al. reported at the density functional theory (DFT) level that some Al_nH_{n+2} species do not have the classic dihydrogen bridged structures, that is, Al_8H_{10}, Al_9H_{11}, and $Al_{11}H_{13}$ have 4, 5, and 5 hydrogen bridges, respectively. In our work, we have made a careful search for the multi-hydrogen bridged structures. We find that the classic dihydrogen bridged structures are still more stable than the multi-hydrogen bridged structures. The bias of Martínez et al.'s work from ours can be easily understood as follows. As stated in Martínez et al.'s paper, Al_nH_{n+2} species were designed based on the corresponding pure aluminum (Al_n) clusters by adding $n + 2$ hydrogen atoms. Yet, their referenced Al_n (n = 7, 8, 9, 11) ground structures do not correspond to the lowest energy forms that were reported very recently by Truhlar and coworkers.[11] Therefore, for alanes with the Al_nH_{n+2} form, the classic dihydrogen structures still dominate and have the greatest importance.

For larger Al_nH_{n+2} ($9 \le n \le 12$) species, there is no experimental data available at present. Our predicted adiabatic electron affinity and vertical detachment energy values at the B3PW91/TZVP level (see Table 1) are expected to provide reliable information and await future experimental verification.

3.4. Chemical Implications. The recent theoretical studies by Grubisic et al. and by Martínez et al.[3,5] have led to the confusing uncertainty—"Are Al_nH_{n+2} the borane analogues?" Clearly, the first systematic comparative study on both $Al_nH_n^{2-}$ ($5 \le n \le 12$) and Al_nH_{n+2} ($4 \le n \le 12$) reported in our work has clarified the confusion. The answer is as inspiring as "Yes"! While Grubisic et al.'s excellent experimental work has opened "a new chapter in aluminum hydride chemistry",[3] our systematic studies would further our understanding of the novel class of alanes. Being structurally (static) akin in various aspects between boranes and alanes with (n + 1) skeletal electrons, an interesting question is surely to ask to what degree these alanes can mimic boranes in kinetics. Comparison of the reactivity behavior of alanes with boranes is underway in our group.

The present work also shows that the odd-numbered alanes Al_nH_{n+2} do not have the ability of being explained by the Wade−Mingos rule. The analogy between alanes and boranes in the form of X_nH_{n+2} should not be simply be judged by the Wade−Mingos rule because the additional two hydrogen atoms have significant influence on the closo-structure. We are aware that such Wade−Mingos deviation was also very recently revealed in $B_8F_8^{2-}$.[12] In applying the Wade−Mingos rules, the protonation or substitution effects need to be considered.

4. Conclusion

In light of the recent confusion of whether alanes are the borane analogues or not, we present the detailed structural and energetic characterization of alane $Al_nH_n^{2-}$ ($5 \leq n \leq 12$) and Al_nH_{n+2} ($4 \leq n \leq 12$), as well as the comparison with the corresponding boranes. The calculated results illuminate the following:

(1) All the studied $Al_nH_n^{2-}$ ($5 \leq n \leq 12$) have closo ground structures as have the corresponding $B_nH_n^{2-}$, in accordance with the well-known Wade−Mingos rule.

(2) The alanes with the general formula Al_nH_{n+2} interestingly have a closo-nido alternation in the ground structure with respect to the even−odd number of Al-atoms. Though these odd-numbered alanes obviously show distinct violation from Wade−Mingos rule for the odd-numbered Al-atoms, they are generally similar to boranes. The deviation of the Wade−Mingos rule can be ascribed to the effect of diprotonation.

In all, the first direct comparative study between the alanes and boranes with (n + 1) skeletal electrons clearly reveal that alanes can be viewed as the borane analogues, though not all alanes have the ability of being explained by the Wade−Mingos rule.

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Supporting Information Available: Additional information as noted in the text. This material is available free of charge via the Internet at http://pubs.acs.org.