**5276** *Inorg. Chem.* **2010**, *49*, 5276–5284
DOI: 10.1021/ic100429b

Inorganic Chemistry
Article

# Understanding the Borane Analogy in $Al_nH_{n+4}$ ($n = 5-19$): Unprecedented Stability of a Non-Wade−Mingos Cluster $Al_8H_{12}$ Fused by Two $T_d$-like $Al_4H_6$

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Received March 3, 2010

Contrasting the boranes $B_nH_{n+4}$ with rich chemistry, the alanes $Al_nH_{n+4}$ remain largely unknown in laboratory, except for the simplest $Al_2H_6$. Though recent experimental and theoretical studies have proved $Al_nH_{n+2}$ to be the borane analogues, whether or not the borane analogy can exist for the more complicated $Al_nH_{n+4}$ is still unclear. In this paper, we find that at the B3PW91/TZVP level, $Al_nH_{n+4}$ each has a *nido*-single cluster ground structure as $B_nH_{n+4}$ for $n < 12$. For $n \geq 12$, the fusion cluster becomes energetically more competitive than the single cluster also as $B_nH_{n+4}$. Thus, concerning the ground structures, the alanes $Al_nH_{n+4}$ ($n = 5-19$) could be considered as the borane analogues. Remarkably, $Al_8H_{12}$ has a novel *closo*(4)−*closo*(4) cluster fused by two $T_d$-like subunits $Al_4H_6$, lying only 0.49 kcal/mol above the single cluster. The Born−Oppenheimer molecular dynamic simulation shows that the *closo*(4)−*closo*(4) fusion cluster intrinsically has high kinetic stability, which can be ascribed to the rigidity of the $T_d$-$Al_4H_6$ subunit. Since $T_d$-$Al_4H_6$ has been experimentally characterized in a gas phase very recently, we strongly recommend that the unprecedented non-Wade−Mingos alane $Al_8H_{12}$ can be effectively formed via the direct dimerization between two $T_d$-$Al_4H_6$, with the reaction energy (−39.65 kcal/mol) very similar to that of the known dialane ($2AlH_3 \rightarrow Al_2H_6$, −35.27 kcal/mol).

## 1. Introduction

The boron hydrides (ranging from simple to polyhedral boranes) have a rather rich chemistry.[1] Exploration on the bonding patterns of various kinds of polyhedral boranes has led to many conceptual treatments in theory.[2,3] Among the most well-known, the Wade−Mingos rule might be one due to its easy applicability to single cluster boranes by simply counting the vertexes and skeletal electrons.[2a] The Wade−Mingos rule predicts that the species with $(n + 1)$, $(n + 2)$, and $(n + 3)$ skeletal electron pairs should adopt the *closo*, *nido*, and *arachno* topologies, respectively. Yet, the Wade−Mingos rule might fail for larger polyhedral boranes for which, in addition to the single clusters, fused clusters become possible, which can be discussed by Jemmis' "mno" and King's "defective vertexes" rules.[2b,3]

Since aluminum has the same number of valence electrons as boron, it is quite natural for one to wonder that aluminum hydrides could behave similarly to boranes in many aspects. However, contrasting to the ample boron hydrides, the aluminum hydride chemistry could be viewed as still in the shade.[4] The polymeric alanes in form of $(AlH_3)_n$ as well as $AlH_4^-$ and $AlH_6^{3-}$ in alkali metal salts (e.g., $LiAlH_4$) were quite familiar.[5] However, the number of gas-phase aluminum hydrides has grown rather slowly. Up to 2006, the known aluminum hydrides have been limited to the mono- ($AlH$,[6] $AlH_2$,[6] $AlH_3$),[6,7] di- ($Al_2H_4$,[6,8] $Al_2H_6$),[6,8] and $Al_{13}H^-$,[9] with no analogues to the higher boranes. In 2007, the combined anion photoelectron spectroscopy and density functional theory studies by Grubisic et al disclosed the existence of $Al_4H_4$ and $Al_nH_{n+2}$ ($n = 4-8$) and claimed their analogy to boranes.[10]

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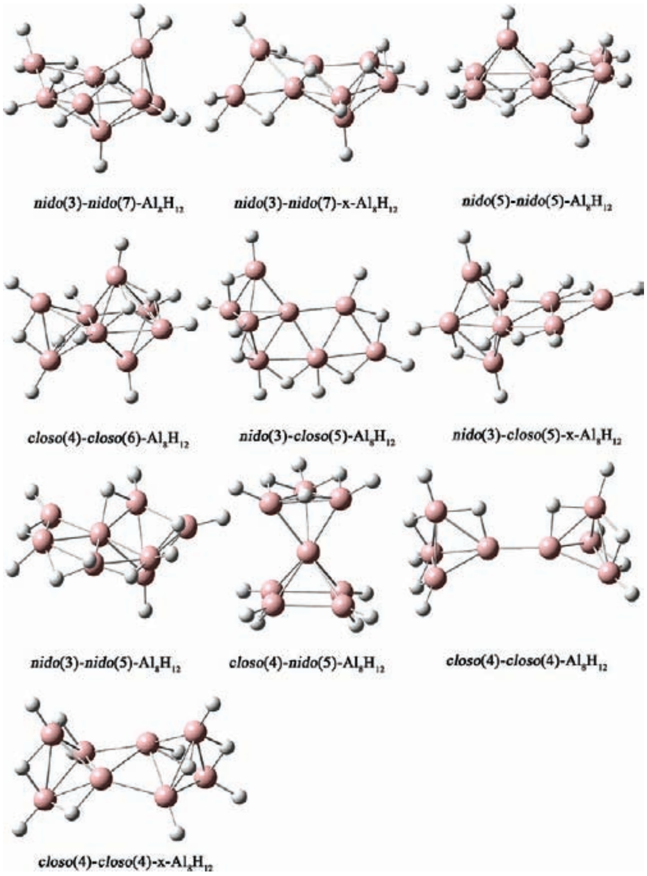
Grubisic et al.'s work has marked the opening of "a new chapter in aluminum hydrides". In the same year, in a flow reactor experiment together with theoretical investigations on the formation and etching of a series of $Al_nH_m^-$ clusters, Roach et al found that the $T_d$-like $Al_4H_7^-$ is very stable and could act as a resilient building block for aluminum cluster materials.[11]

Very recently, by performing the first comparative study on $X_nH_n^{2-}$ ($5 \leq n \leq 12$), $X_nH_{n+2}$ ($4 \leq n \leq 12$) (X = B,Al),[12] Fu et al found that both $Al_nH_n^{2-}$ and $Al_nH_{n+2}$ generally possess similar topologies to the corresponding boranes. Thus, the dianionic and neutral alanes with ($n + 1$) skeletal electron pairs could actually be viewed as the borane analogues.[12] Another important finding in Fu et al's work is that, since both $Al_nH_{n+2}$ and $B_nH_{n+2}$ adopt the *closo*−*nido* ground structures following the even−odd alternation in the number of Al atoms and both show distinct violation from the Wade−Mingos rule for the odd-numbered Al atoms, the analogy between alanes and boranes must be judged by the direct comparison between the corresponding structures rather than simply based on the ability of being explained by the Wade−Mingos rule.

Now that the borane analogy of the alanes $Al_nH_{n+2}$ with ($n + 1$) skeletal electron pairs has been proved, it is the right time to inspect the analogy of the $Al_nH_{n+4}$ with $n + 2$ skeletal electron pairs. Somewhat awkwardly, there exists a contrasting situation between boranes and alanes. On one hand, $B_nH_{n+4}$ has many synthetic examples,[1] whereas $B_nH_{n+2}$ still lacks unambiguous characterization, except $n = 2$. On the other hand, $Al_nH_{n+4}$ is almost unknown, except $n = 2$, whereas $Al_nH_{n+2}$ ($n = 2$, 4−8) has been recently identified in laboratory. Clearly, with two additional hydrogen atoms, $Al_nH_{n+4}$ should possess increased structural complexity than $Al_nH_{n+2}$. According to the Wade−Mingos rule, $Al_nH_{n+4}$ should each bear a *nido*-single cluster, as a result of removing a capping from the *closo*-$Al_nH_{n+2}$. Yet, is it the case? We are aware that for the well-known $B_nH_{n+4}$, Kiani and Hofmann[13] have found that the applicability of the Wade−Mingos rule fails for $n \geq 12$, for which the *nido*−*nido* fusion cluster becomes the ground-state structure. Since the Al−Al bond is much longer than B−B,[14] the *nido*-$Al_nH_{n+4}$ should afford a much larger space than the *nido*-$B_nH_{n+4}$. So, the repulsion between the bridged H atoms at the mouth of the former should be much less than that of the latter. This might significantly influence the relative competition between the *nido*-single cluster and the fusion cluster. Thus, whether or not the borane analogy in $Al_nH_{n+2}$ can be transplanted to $Al_nH_{n+4}$ is still a puzzle.

To stimulate future laboratory study, we report in this paper on the detailed structures and energetics of a wide range of $Al_nH_{n+4}$ series, with $n = 5$−19 at the B3PW91/TZVP level. To ensure the direct comparison, we also perform calculations on $B_nH_{n+4}$ ($n = 5$−19) at the same level. Besides the structural forms reported by Kiani and Hofmann,[13] we consider new fusion clusters that involve the *closo* subunit(s). We are aware that two small alanes, i.e., $Al_5H_9$ and $Al_6H_{10}$, were studied by Mckee in 1991 at the HF/3-21G (for geometrical optimization) and MP4SDTQ/6-31G(d) (for single-point energy) levels. We want to address the following issues: (1) Does $Al_nH_{n+4}$ adopt a *nido*-single cluster for each $n$? (2) If not, which $n$ is the turning point of $Al_nH_{n+4}$ from a single to a fusion cluster? and (3) Does $Al_nH_{n+4}$ have any new structural forms with high stability, compared to $B_nH_{n+4}$? Surely, besides the fundamental importance of exploring the analogy between $Al_nH_{n+4}$ and $B_nH_{n+4}$, the present systematic work should contribute to the design of potential hydrogen storage and energetic materials.[15]

**Scheme 1.** Designed Initial Fusion-Mode Structures of $Al_8H_{12}$ without Hydrogen Bridge Positions Changing



*nido*(3)-*nido*(7)-$Al_8H_{12}$

*nido*(3)-*nido*(7)-x-$Al_8H_{12}$

*nido*(5)-*nido*(5)-$Al_8H_{12}$

*closo*(4)-*closo*(6)-$Al_8H_{12}$

*nido*(3)-*closo*(5)-$Al_8H_{12}$

*nido*(3)-*closo*(5)-x-$Al_8H_{12}$

*nido*(3)-*nido*(5)-$Al_8H_{12}$

*closo*(4)-*nido*(5)-$Al_8H_{12}$

*closo*(4)-*closo*(4)-$Al_8H_{12}$

*closo*(4)-*closo*(4)-x-$Al_8H_{12}$

## 2. Results and Discussions

We obtain the most stable structures of each $Al_nH_{n+4}$ ($n = 5$−19) after having considered a large number (several thousands) of diverse initial configurations without any symmetry restriction. The structural optimization and frequency confirmation are performed at the B3PW91/TZVP level. All calculations are accomplished with the Gaussian-03 and Gaussian-09 program packages.[16] We consider single, *nido*−*nido*, *closo*−*nido*, and *closo*−*closo* forms with different bridging H positions for each $Al_nH_{n+4}$, which are exemplified for fusion-$Al_8H_{12}$ in Scheme 1. A total of 173 isomeric forms are obtained, which can be found in the Supporting Information. For simplicity and ease of comparison, only the low-lying single- and fusion-cluster structures of $X_nH_{n+4}$ (X = Al, B) are shown in Figures 1 and 2.

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[14] The B−B single bond distance (ca., 1.8 Å) is much shorter than the Al−Al bond distance (ca., 2.6 Å).

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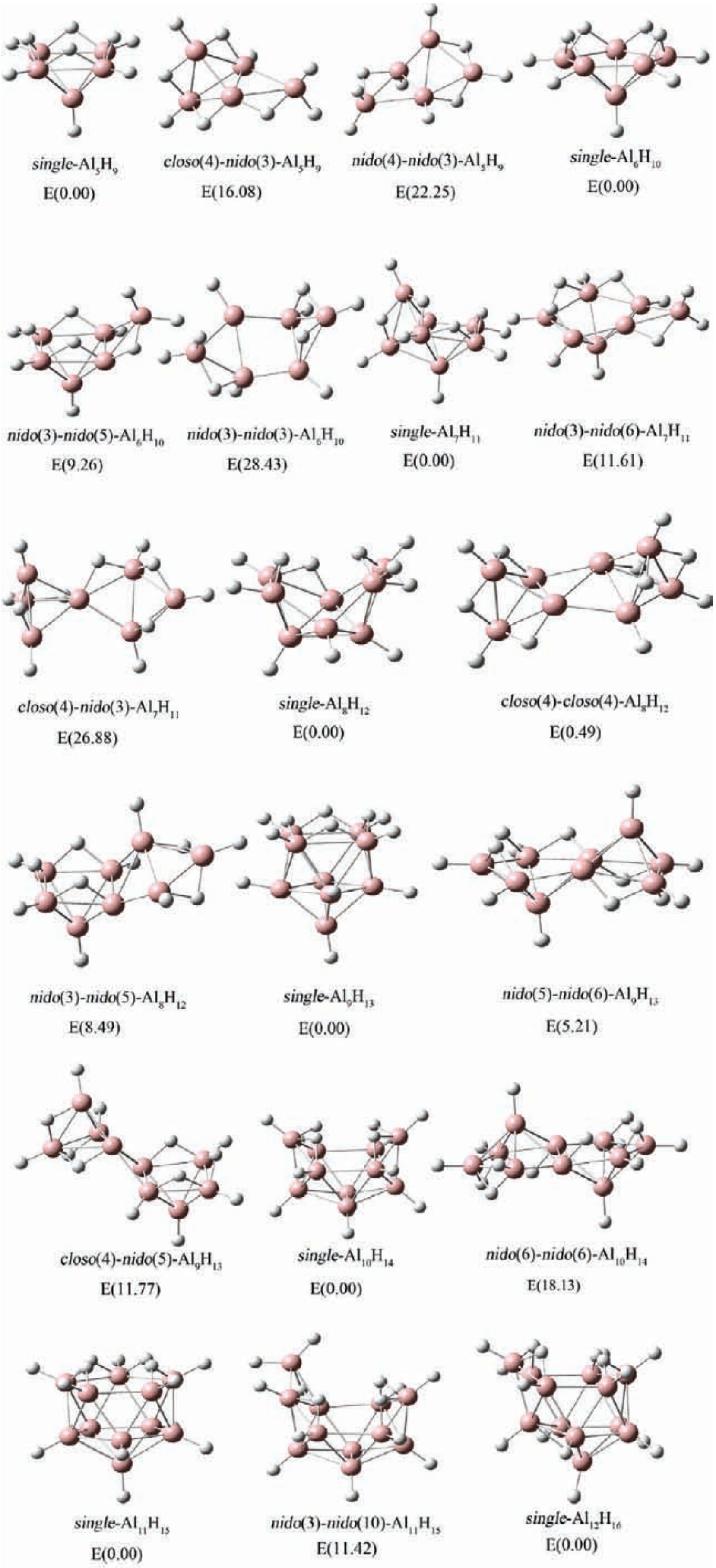


*single*-$Al_5H_9$ E(0.00)

*closo*(4)-*nido*(3)-$Al_5H_9$ E(16.08)

*nido*(4)-*nido*(3)-$Al_5H_9$ E(22.25)

*single*-$Al_6H_{10}$ E(0.00)

*nido*(3)-*nido*(5)-$Al_6H_{10}$ E(9.26)

*nido*(3)-*nido*(3)-$Al_6H_{10}$ E(28.43)

*single*-$Al_7H_{11}$ E(0.00)

*nido*(3)-*nido*(6)-$Al_7H_{11}$ E(11.61)

*closo*(4)-*nido*(3)-$Al_7H_{11}$ E(26.88)

*single*-$Al_8H_{12}$ E(0.00)

*closo*(4)-*closo*(4)-$Al_8H_{12}$ E(0.49)

*nido*(3)-*nido*(5)-$Al_8H_{12}$ E(8.49)

*single*-$Al_9H_{13}$ E(0.00)

*nido*(5)-*nido*(6)-$Al_9H_{13}$ E(5.21)

*closo*(4)-*nido*(5)-$Al_9H_{13}$ E(11.77)

*single*-$Al_{10}H_{14}$ E(0.00)

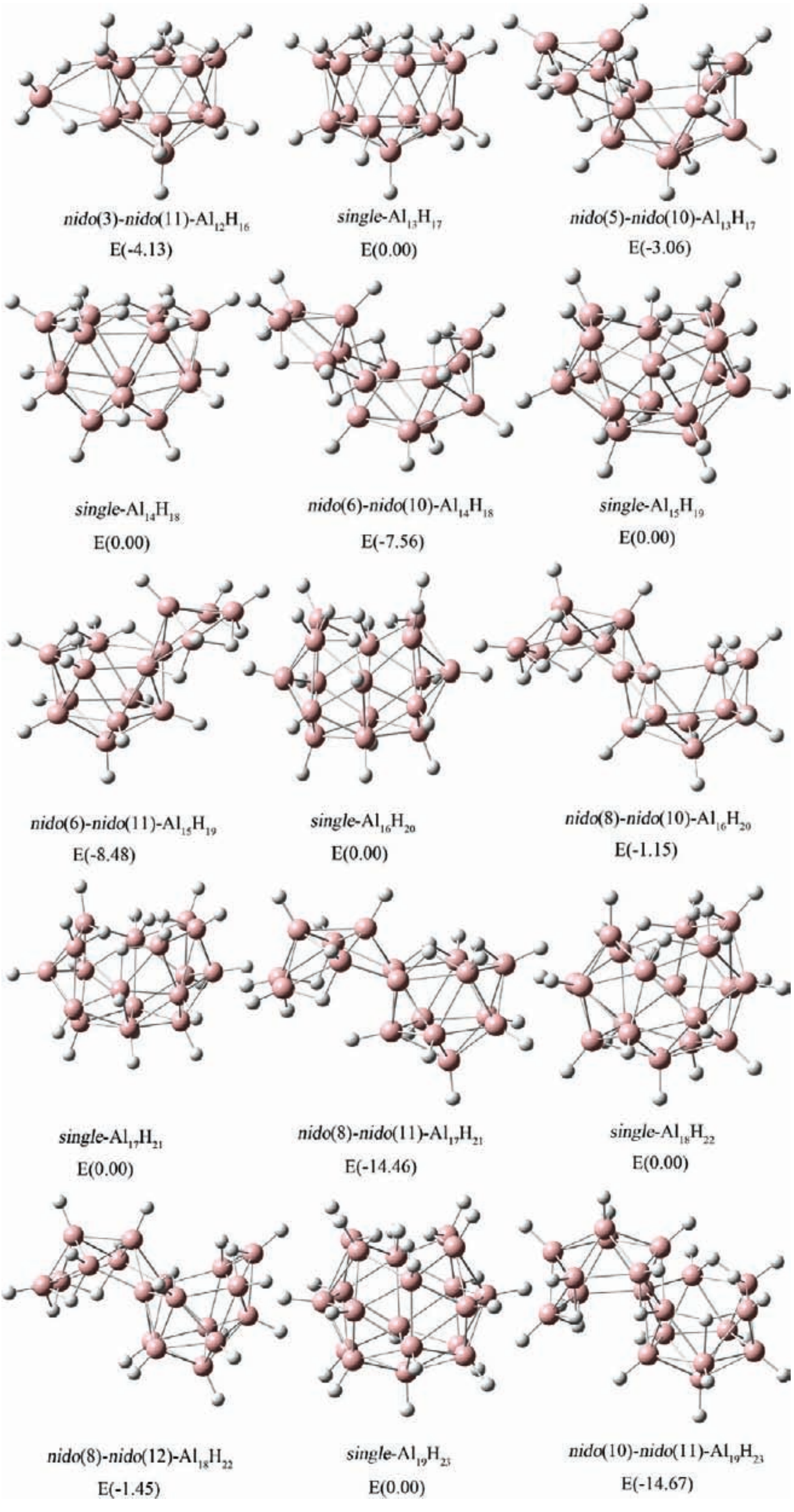
*nido*(6)-*nido*(6)-$Al_{10}H_{14}$ E(18.13)

*single*-$Al_{11}H_{15}$ E(0.00)

*nido*(3)-*nido*(10)-$Al_{11}H_{15}$ E(11.42)

*single*-$Al_{12}H_{16}$ E(0.00)

**Figure 1.** Continued



*nido*(3)-*nido*(11)-$Al_{12}H_{16}$ E(-4.13)

*single*-$Al_{13}H_{17}$ E(0.00)

*nido*(5)-*nido*(10)-$Al_{13}H_{17}$ E(-3.06)

*single*-$Al_{14}H_{18}$ E(0.00)

*nido*(6)-*nido*(10)-$Al_{14}H_{18}$ E(-7.56)

*single*-$Al_{15}H_{19}$ E(0.00)

*nido*(6)-*nido*(11)-$Al_{15}H_{19}$ E(-8.48)

*single*-$Al_{16}H_{20}$ E(0.00)

*nido*(8)-*nido*(10)-$Al_{16}H_{20}$ E(-1.15)

*single*-$Al_{17}H_{21}$ E(0.00)

*nido*(8)-*nido*(11)-$Al_{17}H_{21}$ E(-14.46)

*single*-$Al_{18}H_{22}$ E(0.00)

*nido*(8)-*nido*(12)-$Al_{18}H_{22}$ E(-1.45)

*single*-$Al_{19}H_{23}$ E(0.00)

*nido*(10)-*nido*(11)-$Al_{19}H_{23}$ E(-14.67)

**Figure 1.** Obtained single cluster and fusion-mode structures of $Al_nH_{n+4}$ ($n$ = 5−19) at the B3PW91/TZVP level.

We would first note that among $Al_nH_{n+4}$ the energies of *closo*-fusion cluster are lower than the edge-sharing *nido*−*nido* fusion clusters for $n = 5$ and 8. But when $n = 7$ and 9, the *closo*-fusion isomers are less competitive than the *nido*−*nido* fusion ones. For larger $Al_nH_{n+4}$ ($n = 10−19$), the *closo*-fusion clusters could not keep their initial geometries and would collapse to the low-lying *nido*−*nido* fusion isomers upon optimization.

**2.1. Structural and Energetic Characteristics.** As shown in Figure 1, $Al_nH_{n+4}$ each have a *nido*-single cluster ground structure for $n < 12$. According to the Wade−Mingos rule, species with $n$ skeletal atoms will adopt *nido* structures

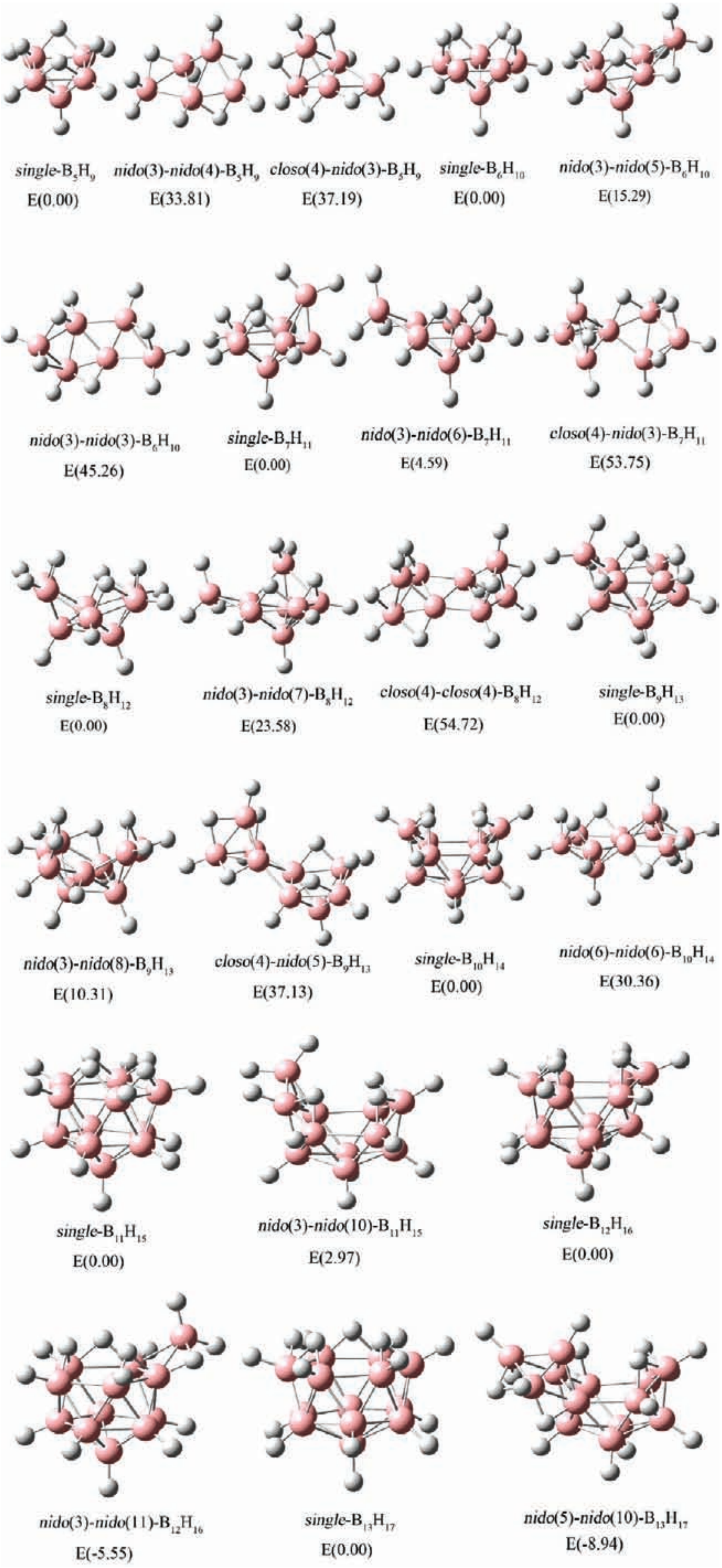
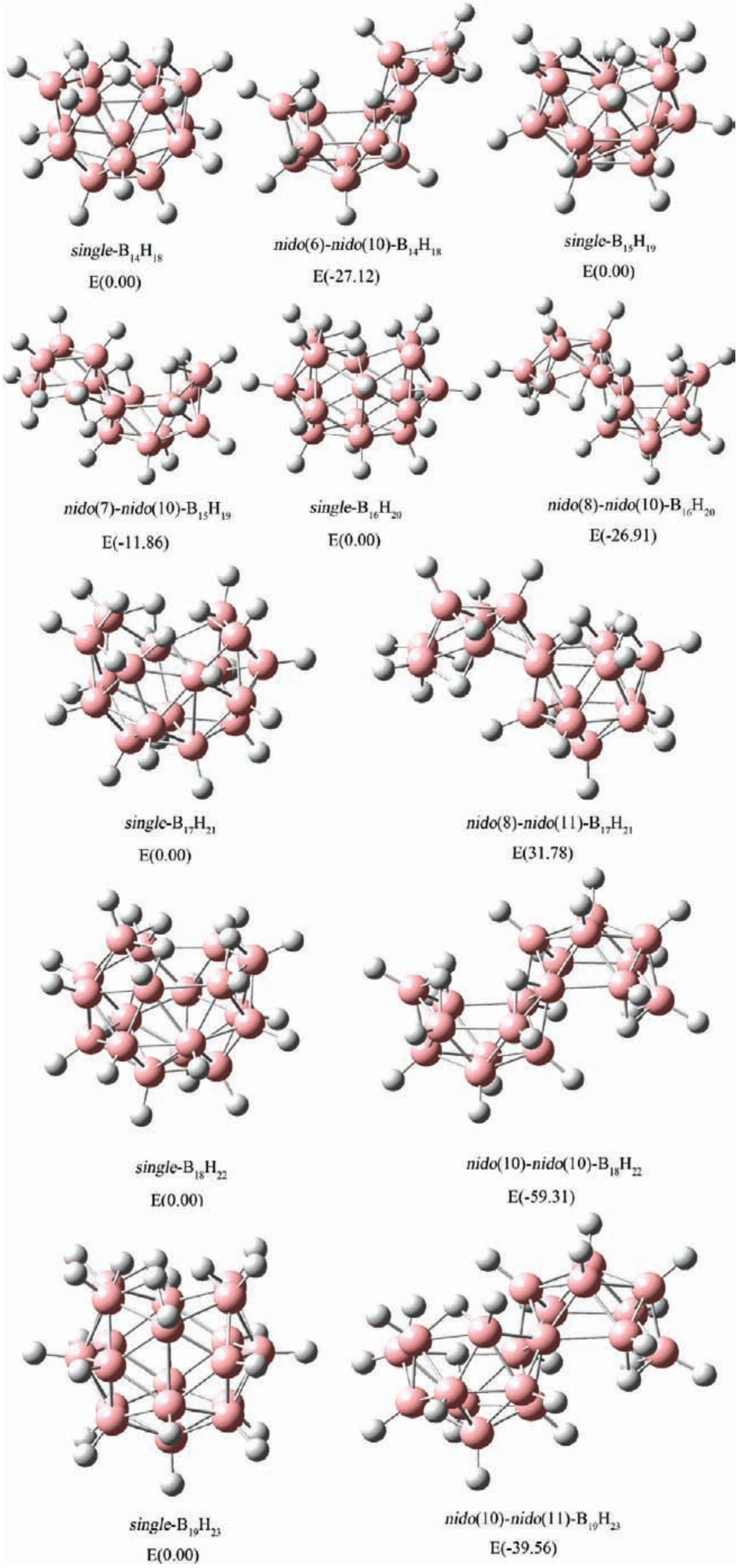


**Figure 2.** Continued



*single*-$B_{14}H_{18}$ E(0.00)

*nido*(6)-*nido*(10)-$B_{14}H_{18}$ E(-27.12)

*single*-$B_{15}H_{19}$ E(0.00)

*nido*(7)-*nido*(10)-$B_{15}H_{19}$ E(-11.86)

*single*-$B_{16}H_{20}$ E(0.00)

*nido*(8)-*nido*(10)-$B_{16}H_{20}$ E(-26.91)

*single*-$B_{17}H_{21}$ E(0.00)

*nido*(8)-*nido*(11)-$B_{17}H_{21}$ E(31.78)

*single*-$B_{18}H_{22}$ E(0.00)

*nido*(10)-*nido*(10)-$B_{18}H_{22}$ E(-59.31)

*single*-$B_{19}H_{23}$ E(0.00)

*nido*(10)-*nido*(11)-$B_{19}H_{23}$ E(-39.56)

**Figure 2.** Single-cluster and fusion-mode structures of $B_nH_{n+4}$ ($n$ = 5−19) at the B3PW91/TZVP level are shown for comparison.

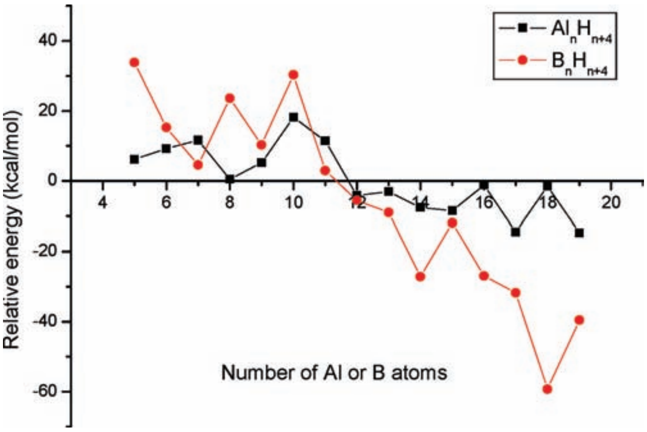


**Figure 3.** Relative energies (kcal/mol) of the most stable combined polyhedra relative to isomeric single cluster polyhedra at the B3PW91/TZVP level for $Al_nH_{n+4}$ and $B_nH_{n+4}$ ($n$ = 5−19).

**Table 1.** Relative Energies (in kcal/mol) of the Listed Three Low-Lying Isomers of Each $Al_nH_{n+4}$ ($n$ = 5−9) in Figure 2 at the B3PW91/TZVP, M05-2X/TZVP, M06/TZVP and G3B3//B3PW91/TZVP Levels

| isomer | B3PW91/TZVP | M05-2X/TZVP | M06/TZVP | G3B3// B3PW91/TZVP |
|---|---|---|---|---|
| single-$Al_5H_9$ | 0.00 | 0.00 | 0.00 | 0.00 |
| *closo*(4)−*nido*(3)-$Al_5H_9$ | 16.08 | 15.62 | 14.60 | 16.55 |
| *nido*(3)−*nido*(4)-$Al_5H_9$ | 22.25 | 21.84 | 20.36 | 23.03 |
| single-$Al_6H_{10}$ | 0.00 | 0.00 | 0.00 | 0.00 |
| *nido*(3)−*nido*(5)-$Al_6H_{10}$ | 9.26 | 9.53 | 8.46 | 8.35 |
| *nido*(3)−*nido*(3)-$Al_6H_{10}$ | 28.43 | 27.50 | 27.53 | 28.58 |
| single-$Al_7H_{11}$ | 0.00 | 0.00 | 0.00 | 0.00 |
| *nido*(3)−*nido*(6)-$Al_7H_{11}$ | 11.61 | 10.95 | 11.72 | 12.67 |
| *closo*(4)−*nido*(3)-$Al_7H_{11}$ | 26.88 | 27.28 | 27.70 | 29.03 |
| single-$Al_8H_{12}$ | 0.00 | 0.00 | 0.00 | 0.00 |
| *closo*(4)−*closo*(4)-$Al_8H_{12}$ | 0.49 | 0.22 | 0.65 | 1.44 |
| *nido*(3)−*nido*(5)-$Al_8H_{12}$ | 8.49 | 8.93 | 9.05 | 9.85 |
| single-$Al_9H_{13}$ | 0.00 | 0.00 | 0.00 | 0.00 |
| *nido*(5)−*nido*(6)-$Al_9H_{13}$ | 5.21 | 6.12 | 6.70 | 8.23 |
| *closo*(4)−*nido*(5)-$Al_9H_{13}$ | 11.77 | 12.68 | 13.05 | 15.65 |

if held together by ($n$ + 2) pairs of skeletal bonding electrons.[2a] Our work shows that $Al_nH_{n+4}$ with $n$ < 12 accord to the Wade−Mingos ($n$ + 2) rule, whereas for $n \geq 12$, the fusion cluster becomes energetically more competitive than the single cluster, i.e., $Al_nH_{n+4}$ each adopt a fusion cluster ground structure. Thus, the alanes $Al_nH_{n+4}$ with $n \geq 12$ clearly violate the Wade−Mingos rule.

To check the borane analogy, it is very desirable to compare the properties of $B_nH_{n+4}$ ($n$ = 5−19). Kiani and Hofmann have extensively investigated the structures and energetics of $B_nH_{n+4}$ ($n$ = 5−19) at the B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) levels.[13] For a parallel comparison, we repeat their calculations at the B3PW91/TZVP level. The relevant species are depicted in Figure 2. In addition, we calculate the previously unconsidered *closo*-fusion clusters of $B_nH_{n+4}$ due to their importance in $Al_nH_{n+4}$ ($n$ = 5, and 7−9). The results indicate that the *closo*-fusion clusters of $B_nH_{n+4}$ are all much less stable than the *nido*−*nido* fusion ones.[17] So we reach the same conclusion as Kiani and Hofmann, i.e., $B_nH_{n+4}$ adopt the Wade−Mingos *nido*-single cluster for $n$ < 12, and for $n \geq 12$, the *nido*−*nido* fusion cluster becomes the ground structure.

Clearly, in the wide range of $n$ = 5−19, the ground structural nature of the alanes $Al_nH_{n+4}$ well mimics the corresponding boranes $B_nH_{n+4}$. Both have the turning

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(17) The *closo*-fusion clusters of $B_nH_{n+4}$ ($n$ = 5 and 7−9) are 3.3, 49.16, 31.14, and 26.82kcal/mol less stable than the *nido*−*nido* fusion ones, respectively.

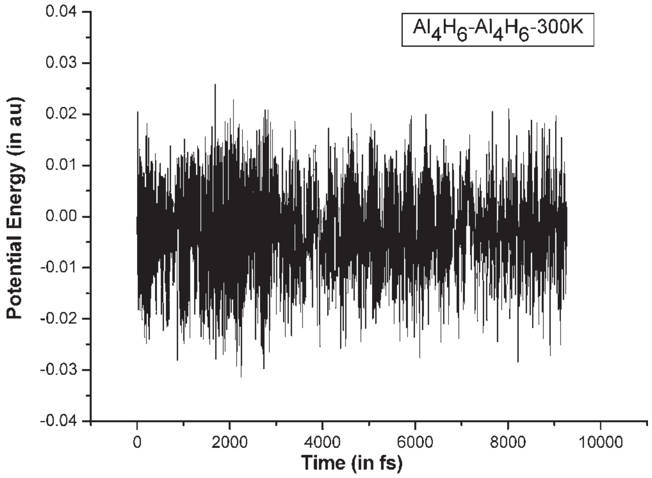

**Figure 4.** BOMD simulation of *closo*(4)−*closo*(4) $Al_8H_{12}$ at 300 K at the B3LYP/6-31G(d) level. Relative potential energy ($\Delta E$) (in au) vs time (in fs).

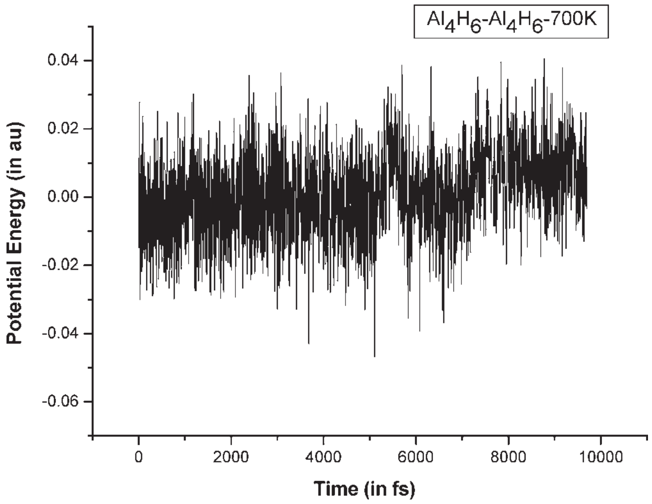

**Figure 5.** BOMD simulation of *closo*(4)−*closo*(4) $Al_8H_{12}$ at 700 K at the B3LYP/6-31G(d) level. Relative potential energy ($\Delta E$) (in au) vs time (in fs).

point at $n$ = 12 from single to fusion clusters. So the neutral alanes $Al_nH_{n+4}$ ($n$ = 5−19) could be viewed as the analogues of boranes. Figure 3 draws the curves that depicts the relative energy differences between the most stable fusion cluster and the most stable single cluster of $X_nH_{n+4}$ (X = Al, B; $n$ = 5−19). We can find that the curve of $Al_nH_{n+4}$ is much smoother than that of $B_nH_{n+4}$. This indicates that after $n$ = 12, $Al_nH_{n+4}$ violates the Wade−Mingos rule to a much less extent than $B_nH_{n+4}$. Especially, for $n$ = 16 and 18, the Wade−Mingos *nido*-single cluster lies only 1.15 and 1.45 kcal/mol above the fusion cluster. This is quite interesting since the Wade−Mingos rule was initially postulated for boranes. Such energetic discrepancies between alanes and boranes can be interpreted that the Al−Al bond is much longer than B−B, and so the bridging hydrogen (H) atoms in the alanes should pose much less repulsion to the open face of skeleton than in the boranes.

Table 1 lists the calculated energetics for the former three low-lying structures of each $Al_nH_{n+4}$ ($n$ = 5−9) using the two modern functionals M05-2X[18a,b] and M06[18b,c] together with the TZVP basis set. Also, the more costly and composite G3B3[19] single-point energy calculations using the B3PW91/TZVP optimized geometries are carried out. We can see that the B3PW91/TZVP relative energies agree excellently with the M05-2X and M06 results. Also, all the three density functional theory (DFT) methods predict comparable relative energies to the very costly G3B3 calculations. Thus, it is suitable to apply the B3PW91/TZVP method for predicting the properties of larger alanes.

**2.2. *Closo*(4)-*Closo*(4): A New Stable Structural Form of Octaalane.** The above calculations show that smaller $Al_nH_{n+4}$ ($n$ = 5 and 7−9) have a new kind of fusion cluster containing a tetrahedral-like *closo*-subunit $Al_4H_6$. In particular, such a *closo*-fusion isomer, which is denoted as "*closo*(4)−*closo*(4)", lies energetically very close to the single cluster at only 0.49 kcal/mol (B3PW91/TZVP). The direct trajectory calculations of Born−Oppenheimer molecular dynamics (BOMD) simulation[20] show that the

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*closo*(4)−*closo*(4) $Al_8H_{12}$ is intrinsically stable and can survive for at least 9.2 ps at 300 K (Figure 4) and 7 ps at 700 K (Figure 5), sufficiently allowing for future spectroscopic detection. The unique stability of such a *closo*(4)−*closo*(4) structure could reasonably be ascribed to the high stability of the subunit $T_d$-$Al_4H_6$, which has been very recently identified in the photoelectron spectroscopic study.[15] It should be noted that for $B_8H_{12}$, the *closo*(4)−*closo*(4) fusion isomer lies at 54.72 kcal/mol above the *nido*-single cluster ground structure at the B3PW91/TZVP level. The above sharp discrepancies between octaalane and octaborane should be ascribed to the much larger strain energy within the $B_3$-ring (33.77 kcal/mol) than that within the $Al_3$-ring (9.66 kcal/mol) at the B3PW91/TZVP level.[21a]

**2.3. Implications.** The present systematic work on $X_nH_{n+4}$ (X = B,Al; $n$ = 5−19) discloses two findings: (1) the $(n + 2)$ alanes can be viewed as the borane analogues, and (2) the octaalane has a uniquely stable fusion isomer with two $T_d$-like subunits $Al_4H_6$. When $n$ gets larger ($n \geq 12$), the transition from the single to the fusion cluster is inevitable. Interestingly, the violation from the Wade−Mingos rule is much less severe for the $(n + 2)$ alanes than for the boranes.

The present and recent Fu et al's studies consistently show that both the $(n + 1)$ and $(n + 2)$ alanes can be considered as the borane analogues. While the aluminum hydrides have long been conceived as the hydrogen storage energetic materials, the synthetic examples are much fewer compared to boranes. The recent gas-phase characterization of $Al_2H_6$, $Al_2H_4$, $Al_2H_2$, $Al_4H_4$, $Al_nH_{n+2}$ ($n$=4−8), and $Al_4H_7^-$ have provided us much hope to see the identification of more and more alanes in the near future. We optimistically hope that the first $(n + 2)$ alane could be $Al_8H_{12}$ via the direct fusion of $T_d$-$Al_4H_6$ (already identified in laboratory), i.e., $Al_4H_6 + Al_4H_6 \rightarrow$ fusion cluster $Al_8H_{12} \rightarrow$ single cluster $Al_8H_{12}$. In such a fusion process, the non-Wade−Mingos *closo*(4)−*closo*(4) $Al_8H_{12}$ should be first formed with the dimerization energy of −39.65 kcal/mol, which is comparable to −35.27 kcal/mol for the known dialane, i.e., $2AlH_3 \rightarrow Al_2H_6$, at the B3PW91/TZVP level. Under suitable conditions (low temperature and sufficient pressure), the formed *closo*(4)−*closo*(4) $Al_8H_{12}$ would be effectively stabilized. Clearly, due to the electron-deficient nature of alanes, the dimerization of the two $T_d$-$Al_4H_6$ is expected to take place easily under low temperature. Yet, the conversion of the fusion form to the single form of $Al_8H_{12}$ should overcome a high barrier. Thus only when the temperature is high enough, the Wade−Mingos single cluster isomer could be available. Moreover, with the very close entropy values, i.e., 126.773 and 125.982 cal/(mol·k) for both the single and the fusion cluster isomers of $Al_8H_{12}$, respectively, the relative stability between the single cluster isomer and fusion cluster isomer is little influenced by the entropy effect. Future experiments on the fusion of two $T_d$-$Al_4H_6$ are strongly recommended.

Very recently, an extensive theoretical study has revealed that the dominant structures of pure $Al_n$ clusters and nanoparticles ($2 \leq n \leq 65$) depend on both temperature and particle size and that one must consider the statistical mechanics as well as electronic structure in determining the dominant structures, stabilities, and properties of nanoparticles.[22] We are aware that up to now, the aluminum hydrides have been generated via the reactions of laser-ablated Al atoms with $H_2$ molecules during codeposition at very low temperatures (< 10 K).[6,8,10,15] Thus, the conclusions of alanes deduced from the present calculations should be reasonable. Surely, when we try to understand the burning properties of alanes in high temperatures, it is desirable to apply the statistical mechanics-based strategies, which will form our future task.

## 3. Conclusions

The direct comparison between the $(n + 2)$ alanes and the boranes ($n$ = 5−19) leads to the following conclusions:

(1) When $n$ < 12, $Al_nH_{n+4}$ each have a *nido*-single cluster ground structure as $B_nH_{n+4}$. Whereas $n \geq 12$, the fusion cluster becomes energetically more stable than the single cluster also as $B_nH_{n+4}$. Therefore, in view of the ground structures, the hitherto unknown $Al_nH_{n+4}$ ($n$ = 5−19) could be considered as the borane analogues.

(2) A novel fusion isomer via the dimerization of two $T_d$-$Al_4H_6$ lies only 0.49 kcal/mol above the single cluster $Al_8H_{12}$. The Born−Oppenheimer molecular dynamics (BOMD) simulation indicates that this structure possesses high kinetic stability, which could be ascribed to the stable subunit $T_d$-$Al_4H_6$ that has been very recently characterized in a gas phase.

(3) We propose that the direct dimerization of $T_d$-$Al_4H_6$ could effectively form the unprecedented non-Wade−Mingos octaalane *closo*(4)−*closo*(4) $Al_8H_{12}$, which might be the first example of the larger $Al_nH_{n+4}$ alanes.

The results presented in this paper are expected to enrich the alane chemistry. Future laboratory studies are strongly desired.

**Acknowledgment.** This work is supported by the National Natural Science Foundation of China (no. 20103003, 20573046, and 20773054), the Doctor Foundation by the Ministry of Education (20070183028), the Excellent Young Teacher Foundation of Ministry of Education of China, the Excellent Young People Foundation of Jilin Province (20050103), and the Program for New Century Excellent Talents in University (NCET). The reviewers' invaluable comments and suggestions for improving the manuscript are greatly acknowledged.

**Supporting Information Available:** A total of 173 isomeric forms are obtained. This material is available free of charge via the Internet at http://pubs.acs.org.

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