

Large gallanes and the PSEPT theory: a theoretical study of $\text{Ga}_n\text{H}_{n+2}$ clusters ($n=7-9$)

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Abstract Do alanes $\text{Al}_n\text{H}_{n+2}$ and gallanes $\text{Ga}_n\text{H}_{n+2}$ satisfy the polyhedral skeletal electron pair theory (PSEPT)? Taking into account previous work on this question, this paper provides a convincing answer and proposes the reformulation of the $(n+1)$ electron pairs rule of Wade and Mingos (W–M) for such systems. Following recent studies of tetra-, penta-, hexa-, hepta-, octa-, and nonaalanes as well as valence-isoelectronic/related gallanes, in this paper we present an analysis of the hydrides of aluminum and gallium A_nH_{n+2} ($\text{A} = \text{Al}, \text{Ga}$ and $n=7-9$). The aim is still to examine the applicability of PSEPT, especially the W–M rule, to these clusters. Exploration of the total potential energy surfaces (PESs) of hepta-, octa-, and nonagallanes shows that the absolute minima have a *nido*-like polyhedron arrangement. Unlike the smaller $\text{Ga}_n\text{H}_{n+2}$ ($n=4, 5, 6$), it seems that the size of the cluster largely dictates its preferred geometry. Although none of them have closed (totally triangular) cages, these clusters exhibit significant compactness, comparable to borane double anions, $\text{B}_n\text{H}_n^{2-}$, which are the archetypes for the PSEPT theory.

Keywords Polyhedral skeletal electron pair theory · PSEPT · Alane · Gallane · Clusters · Polyhedron

Introduction

Neutral hydrides of group 13 elements have interested and motivated inorganic chemists ever since the first report of the unusual structure of diborane (B_2H_6) from Schlesinger and Burg [1]. After boranes, alanes with the empirical formulae Al_nH_m ($m = n$ and $m = n+2$) are the next most popular set of neutral group 13 hydrides to study [2–10]; the first such cluster was characterized by Bowen and coworkers [7] using infrared spectroscopy with a pulsed arc cluster ionization source (PACIS) [11]. Their study prompted an active field of research into species that are designed to store as much hydrogen as possible [12–20]. Those authors also investigated, via theoretical calculations, the relationship between these alanes ($\text{Al}_n\text{H}_{n+2}$, $n=5, \dots, 8$) and the corresponding boranes. According to Bowen's group, the structure of the alane cluster can be deduced from that of its corresponding borane, which can be understood by considering the polyhedron skeletal electron pair theory (PSEPT) and the Wade–Mingos (W–M) rule [21–24]. This latter rule is based on the geometries of the boranes $\text{B}_n\text{H}_n^{2-}$, in which the heavy (i.e., non-hydrogen) atom cage is held together by $n+1$ electron pairs. Thus, $\text{Al}_n\text{H}_{n+2}$ is considered $\text{Al}_n\text{H}_n^{2-} + 2\text{H}^+$, where the two additional hydrogens (as protons) occupy bridging positions between the heavy atoms. We call this the “modified W–M rule,” and it leads to new perspectives on aluminum hydrides.

These experimental and theoretical results have encouraged us [25], and other groups [26, 27], to examine this analogy by considering other clusters and investigating the applicability of the W–M rules to such structures [21–24]. Martinez et al. [26]

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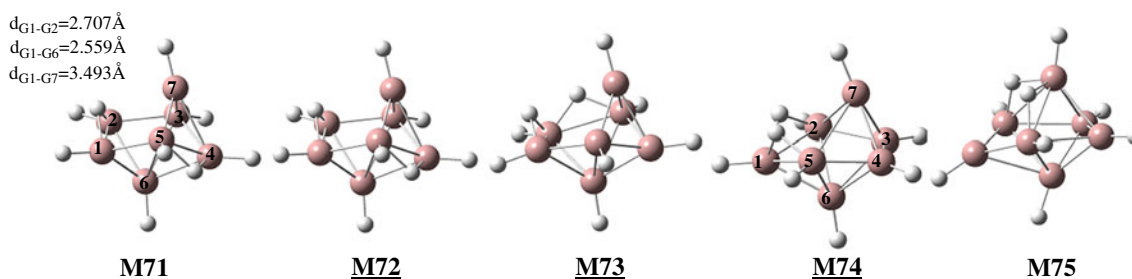


Fig. 1 Low-lying isomers on the total PES of Ga_7H_9

indicated that the high chemical stability of $\text{Al}_n\text{H}_{n+2}$ clusters derives from their large HOMO–LUMO energy gaps. They also reported that only Al_4H_6 , Al_5H_7 , Al_6H_8 , Al_7H_9 , and $\text{Al}_{10}\text{H}_{12}$ comply with the W–M rules; Al_8H_{10} , Al_9H_{11} , and $\text{Al}_{11}\text{H}_{13}$ do not. In turn, Fu et al. [27] explained that alanes containing $(n + 1)$ electron pairs can be considered to be analogous to their corresponding boranes, although a direct comparison between the corresponding structures must take into account additional isomers that do not fulfill the rule. The two additional hydrogen ions (protons) can be expected to disrupt the regularity of the polyhedral *closo*- structures, even though they do not contribute skeletal electrons. This may be understood by considering one the simplest of the group 13 hydrides. Recall that the double hydrogen-bridged B_2H_6 can be thought of as a diprotonated boron–boron double bond analogous to ethylene [28–30]. Accordingly, B_4H_{10} is a conjugated species, bis(diborane) $(\text{B}_2\text{H}_5)_2$, analogous to 1,3-butadiene, but the former has a lower conjugation energy than the latter because the π orbitals are more stabilized and therefore more localized than in the latter. By contrast, the CH–CH_2 bonds in the isomeric bicyclobutane are bent and would be stabilized by protonation in the isoelectronic boron species isomer. Accordingly, calculations indicate that B_4H_{10} should preferentially adopt an *arachno* butterfly geometry [31–32; Yaniger SI, Simons J, Liebman JF, unpublished

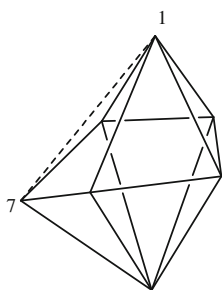
studies], and experimental results have indeed found that this is the only geometry adopted by B_4H_{10} [33, 34]. Alternatively, consider BH_3 and its hypothetical protonation to form BH_4^+ . This ion is expected [35] to have a square planar geometry; it is distorted from a tetrahedral geometry because there are too few electrons to fill the triply degenerate HOMO of a species with two more electrons, such as BH_4^- . The HOMO is then doubly degenerate. Many of the orbitals in each anion $\text{A}_n\text{H}_n^{2-}$ are expected to be doubly degenerate. Protonation removes these degeneracies and the molecule distorts. Recall that the HOMO for D_{6h} benzene is doubly degenerate, and the HOMO for T_d methane is triply degenerate. In general, protonation reduces geometric symmetry and decreases orbital degeneracy. However, this alone does not tell us what the structure for an arbitrary hydride A_nH_{n+2} will be; many distorted minima are plausible, so many isomers with comparable energies would be expected, and are found.

We have extended these theoretical studies to the gallium hydride compounds $\text{Ga}_n\text{H}_{n+2}$ ($n=4–6$) [21], which had not previously been studied theoretically or experimentally. We focused on their geometric and electronic properties. As with the other hydrides, we sought a structural relationship with their congeners (alanes and boranes). In that work, we showed that, except for Al_4H_6 , these clusters do not adopt

Table 1 Relative energies^a [kcal mol^{-1} , at the L1=B3PW91/6-311G(d,p), L2=B3LYP/6-311+G(d,p), and L3=B3LYP/6-311+G(3df,2p) levels of theory] of the five low-lying isomers on the total PES of Ga_7H_9 , average Ga–Ga distances $d_{\text{Ga–Ga}}$ (Å), and weighted average distances (WD)

Isomer	L1	L2	L3	Min–max Ga–Ga distance	Average distance $d_{\text{Ga–Ga}}$ (using L3)	Weighted average distance WD (using L3)
M71	2.47	0.00	0.00	2.473–4.339	3.201	1.231
M72	0.77	0.37	0.44	2.426–4.448	3.182	1.224
M73	-	0.41	0.28	2.434–4.242	3.215	1.237
M74	0.00	1.64	1.28	2.562–4.182	3.139	1.207
M75	7.75	7.99	8.07	2.486–4.564	3.184	1.224

^a Calculated relative to the Ga_7H_9 isomer **M71** [$E = -13479.52528$ and -13479.53733 at B3LYP/6-311+G(d,p) and B3LYP/6-311+G(3df,2p), respectively] or **M74** [$E = -13479.31676$ au at B3PW91/6-311G(d,p)]

Scheme 1 Distorted PBBP

the *closo* structures predicted by the W–M rule based on their $(n+1)$ electron pairs. Indeed, the tetragallane Ga_4H_6 has a completely open structure that consists of a linear linking chain doubly and triply bridged gallium atoms. In a similar way, Ga_5H_7 has an open structure that consists of two cycles (Ga_3 and Ga_4), while the arrangement of the heavy atoms in Ga_6H_8 is best presented as a *nido* structure derived from a pentagonal-based bipyramid (PBBP) polyhedron. This can be achieved after removing one atom from the pentagonal-based bipyramidal Ga_7 framework. We also reported that the compactness of the clusters and the agreement with the W–M rule depended on the additional hydrogen atoms in the bridging positions.

The study described in this paper is a continuation of the theoretical analysis of other aluminum and gallium hydrides with the formula A_nH_{n+2} ($\text{A} = \text{Al}$ and Ga , $n=7-9$), where we continue to use the same density functional theory (DFT), and follow the same calculation procedure as we did in [21]. We note that B, Al, and Ga are three quite “simple” main group elements, each with three valence electrons. They are thus valence isoelectronic, and are thus expected to have many similarities. There are indeed many similarities between them, but there are also a lot of differences.

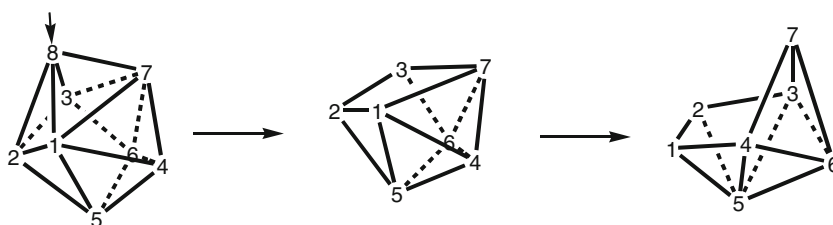
Two of these elements are metallic (Al, Ga) and one is not (B); two are high melting point solids (B, Al) while one is almost a liquid (Ga) at room temperature. In terms of their chemistry, two elements have been actively explored (B, Al), while one is much less understood and studied (Ga). A simple generality is that boron forms covalent compounds in which it is trivalent and presents coordination numbers of 3 and 4, while aluminum compounds are much more ionic

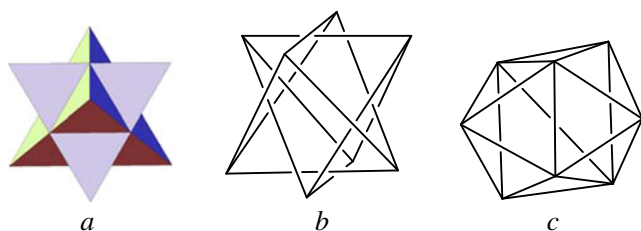
and exhibit coordination numbers of 4 and 6. Aluminum is most often trivalent, while gallium is often univalent. The question is then: can we really assume that gallanes are like boranes and alanes? The current study provides information on these novel binary species.

This study thus affirms that models—however primitive, simple, and “old”—can be interesting, instructive, and informative. The number of group 13 hydrides that are interesting far exceeds the time, resources, personnel, and effort that can be directed into measuring, computing, and carefully investigating them. These simple models can continue to provide guidance for more detailed studies, as they generally correspond better to intuition than sophisticated calculations and experiments. There are two expressions that we have used previously which seem particularly appropriate in the current context: ‘things are intuitive only when you have intuition’ [36] and ‘there is more than you think and less than you need’ [37]. So, let us now explore alanes and gallanes.

Computational details

We started from all possible structures by imposing some geometrical restrictions in order to maintain the molecular symmetry. After that, the symmetry group was reduced stepwise by relaxing some geometrical parameters until we finally treated the molecules with C_1 symmetry. Calculations were performed using density functional theory (DFT) with the B3LYP [38–40] and B3PW91 [41–45] functionals and the 6-311+G(d,p) and 6-311+G(3df,2p) basis sets for the first and the 6-311G(d,p) basis set for the second functional, respectively. Each structure was further characterized by performing a vibrational calculation that diagonalized the second derivative matrix of the energy. All presented structures are minima (all frequencies are positive) as opposed to transition states with one imaginary frequency or saddle points with more than one imaginary frequency. To perform these calculations, the GAUSSIAN09 software package [46] was used. To compare the compactness between structures of the same cluster, we determined the average distance d_{A-A} by dividing the sum of all A–A distances ($\text{A} = \text{heavy atom}$, i.e., non-hydrogen) between all possible pairs of heavy atoms by the n heavy atoms available. In order to compare the compactnesses of the

Scheme 2 Removing a heavy atom from Ga_8 leads to an open Ga_7 framework



Scheme 3 An icosahedron, which can be described as two interpenetrating tetrahedra (**a** and **b**) or as a distorted square antiprism (**c**)

alanes and gallanes, we determined the weighted compactness (WC), which corresponds to the weighted average distance (WD) evaluated as the ratio of d_{A-A} to twice the atomic radius of the species of heavy atom that forms the cages (WD = $d_{A-A}/2\rho$, where ρ is the atomic radius [47]).

Results and discussion

Heptagallane (9)

Ga₇H₉ has eight electron pairs (i.e., $n+1$ with $n=7$) involved in the skeletal bonding. As predicted by the W–M rule [21–24], the isoelectronic borane B₇H₇²⁻ adopts a pentagonal-based bipyramidal (PBBP) heavy atom framework. The modified W–M rule indicates that Al₇H₉ has a PBBP geometry with two bridged bonds involving two hydrogen atoms and seven other terminal hydrogens on the seven vertices. Martinez et al. [26] reported the same structure with two facial hydrogen atoms, thus fulfilling the W–M ($n+1$) rule [21–24], whereas Fu et al. [27] reported a *nido* structure, which clearly violates this rule.

Our treatment, based on full exploration of the potential energy surface (PES), shows that the heptagallane can adopt many structures—many energy minima. We will only present the five lowest-energy ones here. Indeed, the PES is very flat in its lowest region, so it is difficult

to distinguish between the four low-lying minima (isomers **M71**–**M74**; Fig. 1 and Table 1). **M71**, **M72**, and **M73** exhibit roughly the same heavy atom arrangement (their Ga–Ga distances range between ~2.43 and 4.45 Å), and if we attempt to rank them in terms of energy, we find that the ranking depends on the computational level (Table 1). **M74**, which has C_s symmetry, is slightly different from the three other isomers, exhibits the lowest energy on the total PES at the B3PW91/6-311G(d,p) level, and is the most compact. Its structure is somewhat similar to a slightly distorted pentagonal bipyramid (PBP), and close to what the PSEPT rule predicts. Nevertheless, one of the gallium atoms in the Ga₅ base is positioned outside of the pentagonal basal plane. This makes the bond length between this atom and the summit longer (3.7 Å) (Scheme 1) than the average $d_{\text{Ga-Ga}}$, which is about 3.14 Å. The additional hydrogen atoms form two bridged bonds on two adjacent edges of the same side of the base. This probably affects the Ga₁–Ga₇ bond length. Note that this structure was characterized as an absolute minimum in the case of Al₇H₉ by Fu et al. [27] at the B3PW91/TZVP level, and was considered a *nido* polyhedron. However, vibrational calculations indicate that **M74** is a transition state at both B3LYP levels, with the normal mode corresponding to the imaginary frequency reflecting the directions of two equivalent **M73** minima. This assignment was checked by performing an intrinsic reaction coordinate (IRC) calculation.

Note that **M71**–**M74** can be derived from the absolute minimum of octagallane, Ga₈H₁₀, by removing a heavy atom, as shown in Scheme 2. The slight rearrangement of the Ga atoms caused by the presence of a bridging hydrogen atom allows the metallic skeleton to adopt an open cage.

The polyhedral structures of these isomers have more than one open side (i.e., two or more nontriangular faces). Hence they have *arachno*-like structures, although they have only $n+1$ ($n=7$) electron pairs: again the PSEPT rules are violated. All of these structures are characterized by the locations of two bridged bonds; one is at the same position in all of them, but the position of the second one varies.

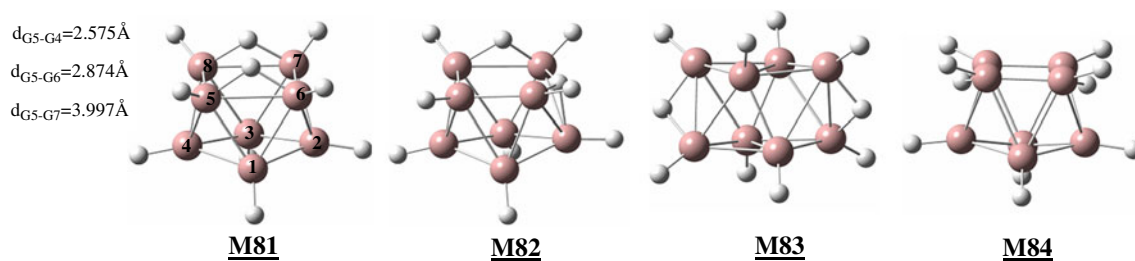


Fig. 2 Lowest-lying isomers of Ga₈H₁₀ on the total PES

Table 2 Relative energies^a [kcal mol⁻¹, at the L1=B3PW91/6-311G(d,p), L2=B3LYP/6-311+G(d,p), and L3=B3LYP/6-311+G(3df,2p) levels of theory] of the four low-lying isomers on the total PES of Ga₈H₁₀, average Ga–Ga distances $d_{\text{Ga-Ga}}$ (Å), and weighted average distances (WD)

Isomers	L1	L2	L3	Min–max Ga–Ga distance	Average distance $d_{\text{Ga-Ga}}$	Weighted average distance WD
M81	0.00	0.00	0.00	2.539–4.258	3.257	1.253
M82	3.90	2.50	2.73	2.437–4.303	3.297	1.268
M83	6.42	9.57	9.54	2.539–4.711	3.233	1.243
M84	12.89	10.61	10.86	2.404–4.270	3.340	1.285

^a Calculated relative to the Ga₈H₁₀ isomer **M81** [$E = -15405.01952, -15404.78448, -15405.03398$ au at the B3LYP/6-311+G(d,p), B3PW91/6-311G(d,p), and B3LYP/6-311+G(3df,2p) levels of theory, respectively]

If we place the isomers in order of ascending energy, **M75** is fifth, about 8 kcal mol⁻¹ above **M71**. **M75** differs from **M74** in the positions of the bridging hydrogen atoms; they bridge two Ga–Ga pairs on the pentagonal base in the latter structure, whereas they bridge Ga(base)–Ga(summit) pairs in the former.

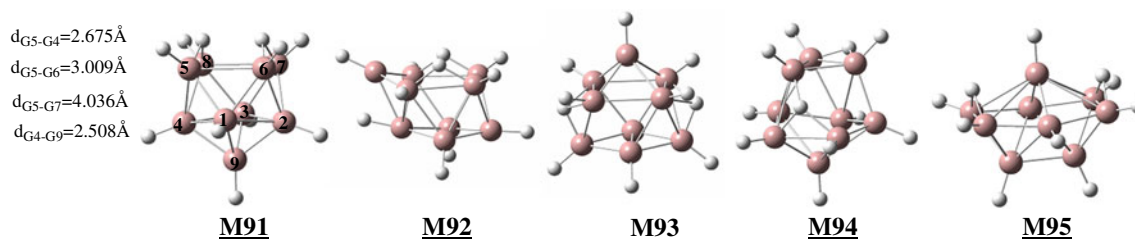
By comparing heptaalane(9) and heptagallane(9) to heptaborane(9), we can see that the Al and Ga species do not fulfill the rule. Nevertheless, Ga₇H₉ appears to be more compact than smaller gallanes (Ga_{*n*}H_{*n*+2}, $n=4-6$) [21], since its WD is 1.231 Å, which is close to the values of its boron and aluminum homologs: 1.176 Å and 1.263 Å for B₇H₇²⁻ and Al₇H₉, respectively. We therefore suggest that oversized gallanes will be rather compact, due to the nature of the Ga atom, which does not favor small, strained clusters.

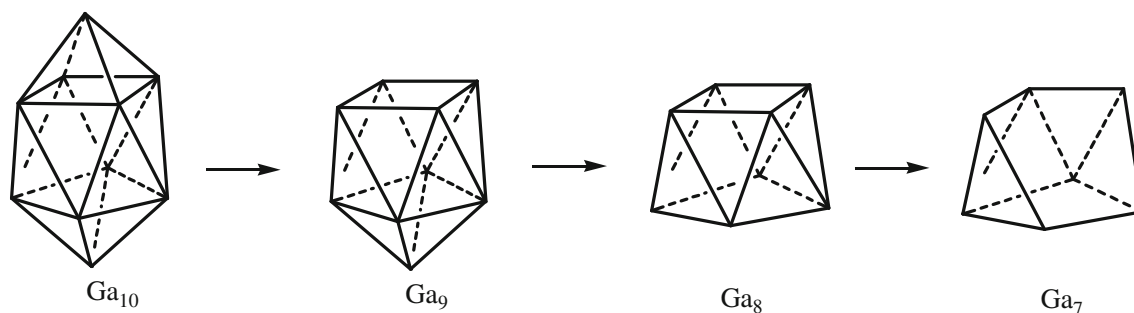
Octagallane (10)

In accordance with the modified W–M rule [8], the octagallane Ga₈H₁₀ should adopt a closed structure with the same arrangement as B₈H₈²⁻ [48, 49]—called a dodecahedron or bisdisphenoid (eight vertices, twelve edges, and twelve triangular facets)—with eight terminal hydrogen atoms and two others, ensuring two Ga–Ga bridged bonds. It can also be described as two interpenetrating tetrahedra, or it can be

derived from a square antiprism in which the square bases become folded lozenges (Scheme 3). An earlier example of octagallane, the $\sigma(\text{C-Ga})$ -bonded fluorenylgallium cluster Ga₈(C₁₃H₉)₈²⁻, was chronicled by Schnepf et al. in 2000 [50] and by King in 2001 [51] as having an antiprism-like structure, whereas the earliest square antiprism geometry was reported for a transition metal cluster, Co₈C(CO)₁₈²⁻, in 1978 by Albano et al. [52]; this also has 18 skeletal electrons ($n+1$ pair with $n=8$).

Full geometry optimization starting from all possible configurations leads to the four lowest-energy structures presented in Fig. 2. Three of them—**M81**, **M82**, and **M84**—have the same heavy atom skeleton with Ga–Ga distances ranging between 2.40 and 4.30 Å, but differing in the positions of the bridging hydrogens. **M81** is the absolute minimum at all levels of theory. Unlike for Ga₇H₉, the bridged positions lead to a spread of energies among these isomers (Table 2). The difference between **M81** and **M84** depends on the orientations of the bridging hydrogen atoms. In the former, they are on the same side as the terminal hydrogens, but in the latter they are on the opposite side. **M82** and **M84** have higher energies than **M81**, by 2.5 and 9.5 kcal mol⁻¹, respectively. Like the octaalane Al₈H₁₀, those three minima are characterized by an open square face that causes them to lose their compactness. For example, for the absolute minimum (**M81**),

**Fig. 3** Lowest-lying isomers of Ga₉H₁₁ on the total PES



Scheme 4 Stepwise removal of Ga, and most stable structures on the total PES

the average Ga–Ga distance on the side formed by the four metallic atoms $\text{Ga}_5\text{--Ga}_6\text{--Ga}_7\text{--Ga}_8$ is 3.22 Å, whereas that on the $\text{Ga}_1\text{--Ga}_2\text{--Ga}_3\text{--Ga}_4$ side is 2.88 Å. The isomer **M83**, which can be considered the most compact of them ($d_{\text{Ga--Ga}}=3.23$ Å), is the third most energetic. It exhibits an antiprismatic structure where the bridged Ga–Ga bonds are counterposed. Its polyhedral arrangement is analogous to that of the isomer **M2** found for Al_8H_{10} and proposed by Bowen and coworkers [8] and Fu et al. [27] to be the absolute minimum (see the “Electronic supplementary material,” ESM).

Unlike $\text{Ga}_n\text{H}_{n+2}$ ($n=4\text{--}6$), from a heavy atom compactness point of view, we can advance that a closed structure is preferred by large gallanes ($n=8$). Here, we can say that the W–M rule is fulfilled by $n+1$ electron fulfilling pairs. So the modified W–M rule should take into account the bridged hydrogen atoms.

Nonagallane (11)

The case of nonagallane, Ga_9H_{11} , is a little bit different from all the other gallanes and alanes we presented above and have reported previously [25–27]. Again, we will only present the lowest-energy structures on the total PES (Fig. 3).

The absolute minimum agrees structurally with the nonagallane previously reported by Fu et al. [27], which has been described as a *nido* polyhedron. Just as for its aluminum congener, the heavy atom cage of the absolute minimum **M91** can be seen as the result of removing a Ga from a *closo* Ga_{10} framework (Scheme 4). It exhibits a *nido* structure even though it has only 10 (9+1) electron pairs. The PSEP theory expects a *closo* arrangement for this number of electrons. Table 3 shows that the energy spread between the lowest-energy isomer **M91** and the fifth highest one **M95** does not exceed 10 kcal mol^{−1} at the highest level of theory [B3LYP/6-311+G(3df,2p)]. Slight energetic activation could allow the nonagallane to change its geometric structure via fluxional behavior of hydrogen or gallium atoms, especially between the three low-lying isomers **M91**, **M92**, and **M93**. These three isomers exhibit geometries similar to a bicapped trigonal prism, but with a third capping GaH entity that changes the position in these three isomers. **M93** seems to fulfill the W–M rule with a *closo* arrangement. This is supported by its compactness (lowest $d_{\text{Ga--Ga}}$) and by the forms of its triangular facets. Indeed, **M93** exhibits two triply bridged hydrogen structures where the bridging atom is bound to three heavy atoms, forming a triangular facet. This fascinating type of bonding was

Table 3 Relative energies^a [kcal mol^{−1}, at the L1=B3PW91/6-311G(d,p), L2=B3LYP/6-311+G(d,p), and L3=B3LYP/6-311+G(3df,2p) levels of theory] of the five low-lying isomers on the total PES of Ga_9H_{11} , average Ga–Ga distances $d_{\text{Ga--Ga}}$ (Å), and weighted average distances (WD)

Isomers	L1	L2	L3	Min–max Ga–Ga distance	Average distance $d_{\text{Ga--Ga}}$	Weighted average distance WD
M91	0.00	0.00	0.00	2.508–4.393	3.363	1.294
M92	6.01	9.5	6.62	2.535–5.536	3.501	1.347
M93	7.15	5.63	7.05	2.553–4.461	3.338	1.284
M94	8.87	10.51	9.25	2.455–5.112	3.417	1.314
M95	9.98	8.31	10.03	2.549–5.577	3.429	1.319

^a Calculated relative to the Ga_9H_{11} isomer **M91** [$E = -17330.50500$, -17330.24513 , and -17330.52185 au at B3LYP/6-311+G(d,p), B3PW91/6-311G(d,p), and B3LYP/6-311+G(3df,2p), respectively]

Table 4 Weighted average distances^a for the absolute minima of boranes, alanes, and gallanes

<i>n</i>	B _{<i>n</i>} H _{<i>n</i>} ²⁻	Al _{<i>n</i>} H _{<i>n+2</i>}	Ga _{<i>n</i>} H _{<i>n+2</i>}
4	1.014	1.054	1.573
5	1.069	1.144	1.271
6	1.106	1.167	1.143
7	1.176	1.263	1.231
8	1.252	1.324	1.253
9	1.308	1.366	1.294

^aGeometric data for systems that are not discussed here are reported in the ESM

reported by Moc [53] for Al₆ cluster hydrogenation, and by us for the Al₅H₇ structure [21]. Two other isomers, **M94** and **M95**, are close to each other energetically (localized about 9 kcal mol⁻¹ above the absolute minimum) and in terms of compactness (*d*_{Ga–Ga}=3.42 and 3.43 Å, respectively).

WD analysis (Table 4 and Fig. 4) shows that when the cluster size increases (*n*>5), the compactness of the hydride decreases, but gallanes become more compact than alanes and closer to boranes, even though the energetically favored structures are not closed. This supports the above conclusion that the W–M rule should be reinvestigated to account for cluster size and additional hydrogen atoms.

Conclusions

Like their aluminum homologs, hepta-, octa-, and non-gallanes exhibit a variety of compact structures but do not fulfill the *n*+1 electron pairs rule of Wade–Mingos (PSEPT theory). They are arranged in *nido*-like polyhedra with two Ga–Ga bonds bridged by two hydrogen atoms. This is not seen for small gallanes, especially tetra- and pentagallane, which are totally open. Even though the larger gallanes are not *closo* polyhedra, they become as compact as their homologous borane dianions once the heavy atom framework increases. We thus suggest that the applicability of PSEPT theory to such clusters should be reinvestigated, and the link between compactness and the descriptors *closo* and *nido* should be redefined.

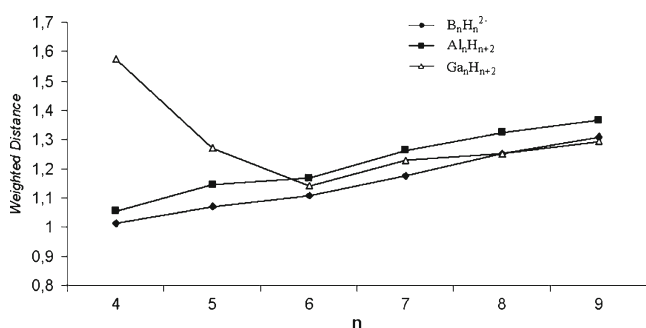


Fig. 4 Evolution of the compactness (WD) of borane dianions and related alanes and gallanes

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