of previous experimental and theoretical works reported in the literature for other molecular hydrogen complexes. The comparison is satisfactory. Theoretically calculated binding energies[15] of the molecular hydrogen ligand in several complexes range from 10 to 21 kcal/mol. Experimental data[23] give values between 7 and 10 kcal/mol, probably being underestimated by the interference of agostic effects in the ML_5 fragment. In any case, all these values are of the same order as those presented in this paper, which are 12.0 and 11.0 kcal/mol for the stable compounds **2** and **3**-par, respectively.

Conclusions

The present ab initio study on $[Fe(PH_3)_4H(H_2)]^+$ systems has shown the peculiar effects of the hydride ligand on the bonding between the hydrogen molecule and the metal. The presence of a hydride trans to the hydrogen molecule increases the strength of the bonding of hydrogen to metal relative to the same position being occupied by a phosphine. If the hydride ligand is placed in the cis position, there is an important distortion in the ML_4H fragment, although this distortion is independent of the orientation of the hydrogen molecule. However, the bonding of the hydrogen molecule to the metal depends strongly on this orientation. Actually, the bonding between the hydrogen molecule and the metal is unaffected by ligands oriented perpendicularly to the plane defined by the atoms of the metal and the hydrogen molecule. When suitably oriented, the hydride ligand in the cis position exhibits a strong attractive interaction, the hydrogen molecule being polarized in a process which can be considered to have essentially an electrostatic origin.

The optimized geometries present small distortions relative to a regular octahedron, but the coordination of the hydrogen molecule is very sensitive to such distortions. Bending of phosphines away from the hydrogen molecule increases the strength of its coordination and magnifies the different effects caused by the presence in a trans position of the hydride and phosphine ligands. This fact makes the optimization of the relative position of spectator ligands especially important in these cases.

The quantitative value of the results obtained is indeed relative owing to simplifications, namely, (a) the modeling of the systems, (b) the lack of correlation energy, and (c) the possible decompensations in the employed basis set. However, our results agree qualitatively with available experimental data, so we think that they are quite useful as a tool in interpreting qualitatively these types of complexes.

Understanding the peculiarities of the hydride ligand in molecular hydrogen complexes is a first step in the comprehension of the chemical interaction between these two ligands, i.e., the interchange reaction between hydrogen atoms. Really, the interaction between the hydride and the hydrogen molecule observed for the *cis*-$[Fe(PH_3)_4H(H_2)]^+$ complex is directly related to these processes. The interchange reaction, which has an obvious chemical interest, is presently the subject of theoretical research in our group.

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Properties of Small Group IIIA Hydrides Including the Cyclic and Pentacoordinate Structures of Trialane (Al_3H_9) and Trigallane (Ga_3H_9): Can Dialane Be Isolated?

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Abstract: The structure of small group IIIA hydrides up to the trimers are studied using the self-consistent field (SCF), single and double excitation configuration interaction (CISD), and single and double excitation coupled cluster (CCSD) methods in conjunction with a double-zeta plus polarization basis set (DZP). The dimerization energy for the unknown dialane is found to be significantly greater than that for the recently synthesized digallane. Unlike the analogous boron compound, cyclic trialane(9) and trigallane(9) incorporate planar six-membered rings according to the DZP SCF predictions. Acyclic trimer structures with pentacoordinated heavy atoms are also considered. The pentacoordinate trialane(9) is nearly isoenergetic with the cyclic structure, and the pentacoordinate triborane(9) is only slightly higher in energy than the cyclic triborane. This new pentacoordinated triborane may be involved in the pyrolysis of diborane and may be the key to the resolution of a dispute concerning the kinetics of this process.

1. Introduction

With the recent successful synthesis of digallane,[1] having a diborane-like structure, the absence of dialane poses a challenge to both experimentalists and theorists.[2,3] Two hypotheses can be made. First, dialane may be sufficiently stable to exist,[3] but no suitable synthetic route has yet been discovered. Certainly the key to the synthesis of digallane, and also galloborane,[4] was Downs' use of the monochlorogallane dimer as a precursor. The stability of dialane, as compared to diborane and digallane, has been studied by Lammertsma and Leszczynski[3] who reported the dimerization energies for borane, alane, and gallane obtained from molecular electronic structure theory with inclusion of electron correlation effects by Møller–Plesset perturbation theory. They concluded that dialane should be experimentally observable since its binding

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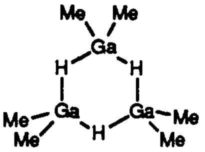
Table I. Total Energies (in au) of Borane, Alane, and Gallane and Their Dimers Obtained Using the DZP Basis Set

method	BH_3	B_2H_6	AlH_3	Al_2H_6	GaH_3	Ga_2H_6
SCF[a]	−26.392 18	−52.816 86	−243.623 12	−487.291 64	−1924.818 06	−3849.662 15
CISD[b]	−26.502 43	−53.050 84	−243.718 80	−487.484 49	−1924.913 96	−3849.855 81
Davidson[b]	−26.507 74	−53.071 72	−243.723 63	−487.501 74	−1924.919 24	−3849.874 51
CCSD[b]	−26.505 60	−53.069 33	−243.721 77	−487.500 27	−1924.917 13	−3849.872 84

[a] At SCF optimized geometries. [b] At CISD optimized geometries.

energy is higher than that for digallane and is just slightly lower than that for diborane. However, the basis sets and theoretical methods employed for the three systems were not directly comparable. In addition, they did not consider the possibility that the association of alane units to give polymers larger than the dimer (and ultimately the known infinite solid structure) may be energetically more favorable than for borane and gallane. One piece of experimental evidence for this possibility is that while dimethylgallane prefers a dimer to the trimer (I), the opposite is true for dimethylalane.[5] Thus, the present investigation is designed to determine the energetics for formation of dimers and trimers of borane, alane, and gallane to test the above hypotheses.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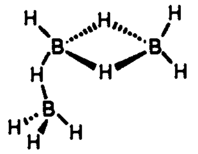
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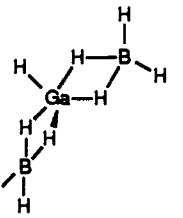
III

No trimers of borane, alane, or gallane have been characterized. Triborane(9) (B_3H_9) has been assumed to be an intermediate in the pyrolysis of diborane to give higher boranes such as tetraborane(10), pentaborane(9), and pentaborane(11).[6] It has also been reported that triborane was observed by mass spectrometry during the association process of borane and diborane,[7] but its structure is not known. Fehlner[8] suggested a structure with a single bridge formed from a terminal H of B_2H_6 to BH_3 (II). This structure can rearrange, explaining H–D exchange data in the pyrolysis reaction. However, a recent ab initio study[9] on the early stage of the pyrolysis of diborane focused only on the cyclic structure (I) of B_3H_9. A number of ab initio studies[10–14] on this compound concluded that it has C_{3v} symmetry with the bridging hydrogens about 0.46 Å above the plane of the boron atoms.[14]

There are, however, a few substituted trimers experimentally known. Dimethylalane[15] and dimethylgallane trimers[5] are thought to have the cyclic structure (I). Interestingly, mixed trimers, methylaluminum bis(tetrahydroborate)[16,17] and hydridogallium bis(tetrahydroborate) (III),[18,19] have structures with penta-coordinated metals, although the cyclic structure is topologically favored for B_3H_9.[20] No theoretical studies have been carried out to date for this type of structure.

Therefore, this study is designed to investigate (1) the dimerization of borane, alane, and gallane at high, uniform theoretical levels and (2) the structures and energetics of trimers of borane, alane, and gallane; in this regard, structures I, II, and III will be considered.

2. Theoretical Methods

In order to obtain comparable results for compounds containing all three group IIIA elements, comparable basis sets must be selected for all atoms. As a compromise between economy and accuracy, double-zeta plus polarization (DZP) basis sets were selected. This is probably as large a basis as can be readily used for high-level studies of the largest molecule, trigallane. In addition, this basis set makes possible geometry optimizations of the dimers using method including electron correlation.

Thus, the Huzinaga[21]–Dunning[22] standard double-zeta basis sets for boron (9s5p/4s2p), aluminum (11s7p/6s4p), and hydrogen (4s/2s) were used with the addition of polarization functions [$\alpha_d(B) = 0.70$; $\alpha_d(Al) = 0.40$; $\alpha_p(H) = 0.75$]. For gallium, we first studied the 10s8p2d (TZP) contraction of Dunning's 14s11p5d primitive basis[23] used by Liang et al.[2] for digallane (a set of d polarization functions, $\alpha_d = 0.16$, was added). It is found that adding 2s1p diffuse functions[24] to that basis set introduces essentially no change on the geometry of digallane. Decontracting the d functions to 3d also has negligible effect. We then further contracted Liang et al.'s basis set to 7s5p2d (designated as DZP) and found that it gives nearly comparable results to the TZP contraction: the DZP predicted bond lengths are shorter by less than 0.03 Å and bond angles larger by <0.1°. Adding one set of f-like functions ($\alpha_f = 0.33$) to this DZP basis set reduces the bridging Ga–H distances by 0.007 Å and bond angles by 0.7°. Therefore, this DZP basis set represents a reasonable compromise between economy and accuracy for this study. Cartesian sets of six d-like functions are used for aluminum and boron while pure 5d functions are used for gallium. In cases where the fully polarized DZP basis set is too large, the polarization functions on hydrogens are removed, yielding DZP basis sets.

For the monomers and dimers, optimum geometries were obtained using the self-consistent field (SCF) molecular orbital method and the configuration interaction method including all single and double excitations (CISD).[25–27] Energy evaluations for the optimized geometries were also performed using the coupled cluster method[28,29] including all single and double excitations (CCSD) [the MP2, MP3, MP4(SDQ) energies were also extracted from the CCSD iterations]. For the trimers, geometry optimizations were done at the SCF level of theory and energy evaluations at the CISD level. Harmonic vibrational frequencies for the monomers, dimers, and trimers were determined at the SCF level using analytical second-derivative methods.[30,31] In all of the correlated wave functions, the core electrons are not explicitly included; i.e., the core-like

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Table II. DZP Predicted Geometries for Diborane, Dialane, and Digallane (D_{2h} Symmetry Assumed)

	diborane (B_2H_6)		dialane (Al_2H_6)		digallane (Ga_2H_6)	
parameter	SCF	CI	SCF	CI	SCF	CI
M···M, Å	1.797	1.786	2.616	2.593	2.654	2.646
M—H_t, Å	1.188	1.188	1.566	1.561	1.560	1.563
M—H_b, Å	1.331	1.323	1.732	1.718	1.774	1.768
MH_bM, deg	84.9	84.9	98.1	98.0	96.8	96.9
H_tMH_t, deg	122.5	122.9	127.1	127.4	129.1	129.9

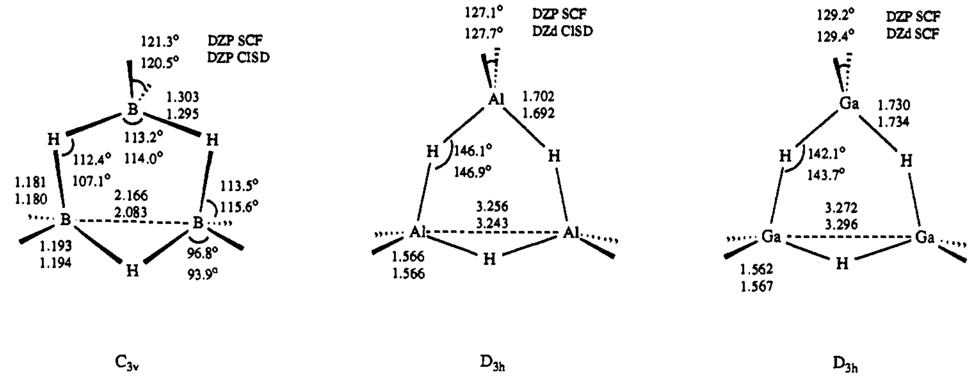

Figure 1. The theoretical structures of cyclic triborane, trialane, and trigallane. Bond lengths are in Å. The six terminal hydrogen atoms are not explicitly shown.

molecular orbitals are held doubly occupied in all configurations.

Unlike SCF and CCSD, the CISD method is not size consistent. To overcome this problem in evaluating dimerization and trimerization energies, the CISD method was applied to the clusters $(MH_3)_2$ and $(MH_3)_3$, with the atoms M (=B, Al, and Ga) separated by 500 bohrs and the monomer units having geometries determined for the isolated monomer.

3. Results

3.1. Structure of Monomers. All monomer structures are optimized using D_{3h} symmetry and the total energies are reported in Table I. The SCF and CISD predicted bond lengths are the following: borane, 1.193 and 1.194; alane, 1.573 and 1.568; gallane, 1.573 and 1.578 Å. It is interesting to note that electron correlation has opposite effects on the geometries of alane and gallane and has little effect on that of borane. All SCF harmonic vibrational frequencies of borane, alane, and gallane are real. Considering the fact that higher group IVA elements, silicon and germanium, show pyramidalization in their ethylene-analogous compounds and that electron correlation is important in the studies of their pyramiderization,[32] the DZP CISD frequencies were also determined for gallane, and they are likewise all real (2009 a_1', 1992 e′, 770 e′, 728 cm^{-1} a_2''). This and additional DZP CISD searching of its potential energy surface shows that gallane is indeed planar.

3.2. Dimers. The SCF and CISD predicted structures of the dimers (in D_{2h} symmetry) are given in Table II (total energies are reported in Table I). Apparently, electron correlation has only modest effects on the geometries of the dimers. However, relatively large changes are observed for the M···M and M—H_b distances, which CISD reduces by 0.006–0.02 Å.

Binding energies of the three dimers are shown in Table III. All energies, except the SCF energies, were evaluated at the optimum geometries obtained using the DZP CISD method. As one may expect, using the DZP SCF predicted geometries (which are very similar to the DZP CISD structures) has little effect on the binding energies. For instance, the CISD and CCSD predicted dimerization energies for digallane were not changed significantly when the DZP SCF geometries were used. The TZP basis set for digallane used by Liang et al.[2] is also employed to investigate the basis set effect. The dimerization energies for digallane predicted using this basis set with the SCF, CISD, and CISD plus Davidson's correction[33] methods are 15.9, 23.2, and 24.4 kcal mol^{-1}, respectively, and they differ by less than 0.4 kcal mol^{-1} from the DZP SCF results. The zero-point energies were evaluated using the DZP SCF harmonic vibrational frequencies (Table III).

Table III. Dimerization Energies (in kcal mol^{-1}) of Diborane, Dialane, and Digallane Determined at the DZP CISD Equilibrium Geometries Using the DZP Basis Set

method	B_2H_6	Al_2H_6	Ga_2H_6
SCF[a]	20.4	28.5	16.3
CISD	34.9	34.9	23.4
Davidson	37.0	35.8	24.5
MP2	39.3	35.6	24.8
MP3	38.1	36.2	25.1
MP4(SDQ)	37.0	35.9	24.6
CCSD	36.5	35.6	24.2
CCSD + ΔZPE[b]	29.6	30.9	20.6
MP4 + ΔZPE[c]	37.0	31.5	23.4
experiment[34]	36.5 ± 2.5		

[a] At SCF geometry. [b] Zero-point energies (ZPE) determined from the DZP SCF vibrational frequencies. [c] From Lammertsma, K.; Leszczynski, J. *J. Phys. Chem.* **1990**, *94*, 2806. Note that different theoretical methods were employed there for the three molecules.

The DZP CCSD binding energy for diborane (36.5 kcal mol^{-1}) falls in the range of a recent experimental estimate (34–39 kcal mol^{-1}),[34] but the zero-point energy correction brings the dissociation energy down to 29.6 kcal mol^{-1}. The CCSD method may have underestimated the binding energies slightly due to the neglect of connected triple and higher excitations. The (unscaled) DZP SCF evaluated zero-point energy correction should be too high by about 10%.

It is clear from Table III that the binding energy of dialane is comparable to that of diborane and is significantly greater than that of digallane, in agreement with Lammertsma and Leszczynski's results.[3] This suggests that dialane might exist and it gives no reason for the absence of dialane.

3.3. Structures of Cyclic Trimers. The structure of cyclic triborane(9) was optimized within C_{3v} symmetry using the CISD as well as the SCF method (Figure 1), since electron correlation has been shown to have a large effect on its geometry.[14] Our DZP CISD predicted geometry is very close to that obtained from the MP2 method with a similar basis set.[14] The three bridge hydrogens are about 0.41 Å above the plane of the boron atoms in

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Table IV. Harmonic Vibrational Frequencies (in cm^{-1}) and IR Intensities (in km mol^{-1}) for Cyclic Triborane, Trialane, and Trigallane Obtained from the DZP SCF (for B_3H_9 and Al_3H_9) and DZd SCF (for Ga_3H_9) Methods

B_3H_9 (C_{3v})			Al_3H_9 (D_{3h})			Ga_3H_9 (D_{3h})		
freq	int	sym	freq	int	sym	freq	int	sym
2839	275	a_1	2094	285	e'	2068	1	e'
2823	11	e	2066	648	a_2''	2064	626	a_2''
2703	19	a_1	2061	–0–	a_1'	2063	–0–	a_1'
2690	103	e	2060	–0–	e''	2057	–0–	e''
2294	–0–	a_2	1980	1578	e'	1853	2140	e'
2251	749	e	1853	–0–	a_2'	1702	–0–	a_2'
1820	22	e	1128	–0–	a_1'	1032	–0–	a_1'
1776	5	a_1	962	570	a_2''	872	405	e'
1233	1	a_1	952	800	e'	842	339	a_2''
1208	97	e	872	–0–	e''	813	–0–	e''
1149	98	e	813	–0–	a_1'	770	–0–	a_1'
1077	2	a_1	771	806	e'	725	7	e'
988	–0–	a_2	614	156	e'	619	231	e'
962	55	e	544	–0–	a_2'	423	–0–	a_2'
868	5	e	489	–0–	a_1''	500	–0–	a_1''
848	–0–	a_2	488	–0–	e''	473	–0–	e''
570	1	e	301	–0–	a_1'	180	–0–	a_1'
520	<1	a_1	245	3	e'	152	1	e'
374	14	a_1	116	10	a_2''	90	2	a_2''
224	2	e'	72	–0–	e''	53	–0–	e''

the DZP CISD optimized geometry. Electron correlation included via the CISD method reduces the SCF predicted B···B distances (by 0.083 Å) and the B–H_t–B angles (by 5.3°) considerably, but this effect is not as large as with the MP2 method.[14] When our DZP SCF geometry for triborane(9) is compared to the 3-21G SCF results,[13] it is found that polarization functions also reduce the B···B distances and the B–H_t–B angles significantly. Harmonic vibrational frequencies (Table IV) confirm that the C_{3v} structure is a minimum on the B_3H_9 potential energy hypersurface. The constrained planar structure has three imaginary vibrational frequencies as found by Mckee and Lipscomb at the lower 3-21G SCF level of theory.[13] This structure, not surprisingly, is not the transition state for the "flip" between the two nonplanar structures. The transition presumably "flips" the bridge hydrogen atoms in sequence rather than simultaneously in a manner analogous to the "flip" of chair cyclohexane.

Al_3H_9 and Ga_3H_9 have not been the subject of any previous theoretical study. The structure of cyclic trialane is found to be planar (in the central Al_3H_3 subunit) since the DZP SCF vibrational frequencies for the planar structure with D_{3h} symmetry are all real (Table IV), and optimizations from C_{3v} geometries using the DZP SCF and the DZD CISD methods lead to the D_{3h} planar structure. Cyclic trigallane is also predicted to be planar with D_{3h} symmetry, but C_{3v} structures were not considered. These theoretical structures are shown in Figure 1. A possible reason for the planarity of trialane and trigallane is that the M···M bonding, which is responsible for the nonplanarity of triborane,[14] may not be as important for aluminum and gallium as for boron. The other main difference between the triborane structure and the structures of trialane and trigallane is the angle to the bridge hydrogen atoms. This angle is much larger in trialane (146°) and trigallane (142°) than in the C_{3v} symmetry triborane (112°) or the D_{3h} symmetry triborane (119°) according to DZP SCF predictions. This may be attributable to two factors. (1) Aluminum and gallium, like other heavy main group elements such as phosphorus and arsenic, tend to form bonds with small bond angles, thereby forcing the MH_bM angles to be large. (2) Since the atomic charges on the bridge hydrogens derived from Mulliken population analysis[35] are negative for trialane (–0.49 e) and trigallane (–0.24 e) but positive for triborane (0.05 e), bonds to the bridge hydrogens need to form larger angles in trialane and trigallane than in triborane to minimize electrostatic repulsion (the atomic charges on the heavy atoms in these molecules are –0.11 e for boron, +0.96 for aluminum, and +0.30 for gallium, and these data correlate with the electronegativities of these atoms[36]). The lack of monotonic trends from B to Al to Ga contributes to our fascination with the group IIIA elements.

The Al–H_t terminal hydrogen stretching vibrational frequencies in the D_{3h} symmetry Al_3H_9 (2060–2094 cm^{-1}, DZP SCF) are very similar to those in Al_2H_6 (2051–2062 cm^{-1}, TZP SCF).[2] But the Al–H_b bridging stretching vibrational frequencies of Al_3H_9 (1980 e′, 1853 a_2') are somewhat different from those of Al_2H_6. In particular, the e′ symmetry Al–H_b bridging vibration of Al_3H_9 has a frequency of 1980 cm^{-1}, higher than the bridging stretches in Al_2H_6 (1350–1652 cm^{-1}).[2] This 1980-cm^{-1} vibration is the strongest band in the DZP SCF predicted IR spectrum of cyclic Al_3H_9 (Table IV). The difference in Al–H_b bridging stretching frquencies between the two molecules is consistent with the shorter Al–H_b distance in Al_3H_9 (1.702 Å) than in Al_2H_6 (1.732 Å). The asymmetric torsional e″ vibration of the six-membered ring possesses the lowest frequency (72 cm^{-1}), while the symmetric a_2'' torsion is the next lowest. Similar observations may be made regarding the DZd SCF predicted vibrational frequencies of cyclic Ga_3H_9.

3.4. Structures of Pentacoordinated Trimers. Figure 2 shows the DZP SCF predicted stationary point geometries for pentacoordinated triborane, trialane, and trigallane with C_2 symmetry (hereafter referred to as p-triborane, p-trialane, and p-trigallane, respectively). As may be seen, these structures are all quite different. The DZP SCF predicted stationary point for p-triborane is actually a transition state with the vibrational frequency for the asymmetric combination of the B_1–H_5 and B_1–H_6 stretches being imaginary (Table V). The B_1–H_5 and B_1–H_6 distances (1.596 Å) in p-triborane obtained from this method are much longer than the other B–H_t distances (1.248–1.354 Å, which are close to the ones in diborane, 1.331 Å, DZP SCF). The DZP CISD method reduces the B_1–H_5 and B_1–H_6 distances significantly (by 0.093 Å), while it lengthens the other B_1–H_b distances (by 0.037 Å). When the asymmetric combination of the B_1–H_5 and B_1–H_6 stretches is displaced by 0.005 Å from the DZP CISD optimum geometry while all other internal coordinates are kept unchanged, the DZP CISD evaluated energy is slightly higher than that for the optimum geometry. This suggests that the DZP CISD predicted structure for p-triborane (with C_2 symmetry) shown in Figure 2 might be an energy minimum.

Interestingly, the pentacoordinated trialane structure (Figure 2) is an energy minimum on the DZP SCF energy hypersurface, as all of its harmonic vibrational frequencies are real (Table V). Unlike the p-triborane molecule, the DZP SCF predicted Al–H_b distances in p-trialane (1.680–1.817 Å) are not very different; and the longest of them is only 0.086 Å longer than that in dialane. The vibrational frequencies for Al–H_b stretches fall in the range

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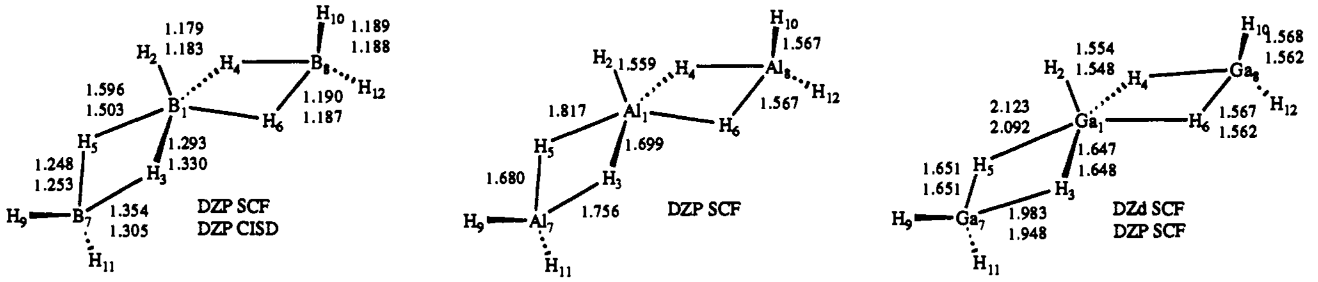

Angles	SCF	CISD
$<H_2B_1H_3$	119.0°	114.9°
$<H_2B_1H_5$	98.5°	100.3°
$<H_3B_1H_5$	86.9°	87.9°
$<H_1B_3H_7$	90.8°	88.2°
$<H_3B_7H_5$	100.3°	100.7°
$<B_1H_5B_7$	82.0°	82.9°
$<H_9B_7H_{11}$	122.8°	123.9°
$<B_1H_3B_7H_5$	-1.2°	-4.6°

Angles	DZP
$<H_2Al_1H_3$	122.1°
$<H_2Al_1H_5$	101.7°
$<H_3Al_1H_5$	79.9°
$<H_1Al_3H_7$	99.8°
$<H_3Al_7H_5$	82.2°
$<Al_1H_5Al_7$	98.1°
$<H_9Al_7H_{11}$	127.5°
$<Al_1H_3Al_7H_5$	0.9°

Angles	DZd	DZP
$<H_2Ga_1H_3$	123.7°	126.3°
$<H_2Ga_1H_5$	98.9°	99.1°
$<H_3Ga_1H_5$	79.6°	79.9°
$<H_1Ga_3H_7$	101.0°	100.7°
$<H_3Ga_7H_5$	83.9°	84.3°
$<Ga_1H_5Ga_7$	95.4°	95.0°
$<H_9Ga_7H_{11}$	127.4°	127.5°
$<Ga_1H_3Ga_7H_5$	-0.1°	0.1°

Figure 2. The theoretical structures of pentacoordinated triborane, trialane, and trigallane. Bond lengths are in Å and angles in degrees.

Table V. Harmonic Vibrational Frequencies (in cm^{-1}) and IR Intensities (in km mol^{-1}) for Pentacoordinated Triborane, Trialane, and Trigallane with C_2 Symmetry Obtained from the DZP SCF (for B_3H_9 and Al_3H_9) and DZd SCF (for Ga_3H_9) Methods

B_3H_9			Al_3H_9			Ga_3H_9		
freq	int	sym	freq	int	sym	freq	int	sym
2835	117	a	2082	149	a	2108	115	a
2794	163	a	2058	272	a	2058	72	a
2791	62	b	2057	157	b	2057	101	b
2696	39	a	2052	43	a	2054	262	a
2690	160	b	2050	37	b	2052	136	b
2400	144	b	1756	350	a	1763	375	a
2397	46	a	1713	203	b	1729	388	b
2160	150	b	1660	121	a	1708	1	a
2110	31	a	1574	1623	b	1702	828	b
1968	655	b	1560	149	b	1170	115	b
1876	48	a	1383	24	a	1078	<1	a
1420	15	a	1225	1469	b	894	51	a
1271	246	b	1220	12	a	850	263	b
1234	15	a	1000	444	a	816	311	b
1224	34	b	954	377	b	815	230	a
1199	252	b	814	76	b	779	19	a
1189	2	a	804	169	a	763	153	a
1131	413	b	784	827	b	761	81	b
1041	6	a	758	1	a	672	1859	b
1035	3	b	665	360	b	608	31	b
974	16	b	574	195	b	531	10	a
895	<1	a	546	11	a	488	329	b
893	44	b	510	8	b	390	361	b
763	<1	a	421	5	a	380	<1	a
508	2	a	402	5	b	240	2	b
478	111	b	310	3	a	231	<1	a
384	23	b	277	22	b	171	44	b
334	<1	a	204	2	b	116	<1	a
178	8	a	200	1	a	42	<1	a
478i	679	b	78	2	a	109i	93	b

of 1756–1220 cm^{-1}, and the lowest frequency vibration corresponds to the ring deformation. Therefore, p-trialane may be considered as a compound with five genuine bonds.

Perhaps it is surprising to find out that pentacoordinated trigallane consists of three loosely linked GaH_3 units (Figure 2), as the Ga–H_b distances (1.948 and 2.092 Å) linking the three GaH_3 units are much longer than the Ga–H_b distances in digallane (1.774 Å) or cyclic trigallane (1.730 Å), according to the DZP SCF predictions. The DZd SCF structure has one imaginary frequency, similar to p-triborane (Table V). Thus, we again see discontinuities in the B–Al–Ga progression.

It may be of interests to note that the central boron atom in p-triborane bears a fraction of a positive charge (0.18 e) while the other boron atoms have negative charges (−0.18 e). The atomic charge on the central aluminum is +1.03 e and that on the central gallium is +0.34 e. This seems to suggest that an electropositive atom at the center of a pentacoordinated structure is topologically favored. If it is indeed the case, the finding that this pentacoordinated structure for M_3H_9 is better for M being aluminum than for M being boron and gallium may be explained, since aluminum is thought to be the most electropositive atom among the three.[35]

3.5. Energetics of Trimers. Table VI reports the total and relative energies of the trimers. At all levels of theory considered, the cyclic isomers of B_3H_9, Al_3H_9, and Ga_3H_9 are more stable than the pentacoordinated structures, but the energy differences are surprisingly small, particularly for triborane and trialane. The implications of the existence of this low-lying structure of triborane with C_2 symmetry will be discussed in the next section. Note that the two trialane structures are essentially isoenergetic, and it is not implausible that the C_2 structure may be even lower in energy than the cyclic one at higher levels of theory, since electron correlation reduces the energy difference significantly in favor of the C_2 structure.

The binding energies of the cyclic trimers are given in Table VII. When these are compared to those of the dimers in Table III, it is obvious that going from dimer to cyclic trimer the binding energy per unit MH_3 decreases for boron (from 17.5 to 12.6 kcal mol^{-1}) but increases for aluminum (from 17.5 to 18.7 kcal mol^{-1})

Table VI. Total Energies (in au) of Triborane, Trialane, and Trigallane Obtained Using the DZP Basis Set[a]

	B_3H_9		Al_3H_9		Ga_3H_9	
method	C_{3v}	C_2	D_{3h}	C_2	D_{3h}	C_2
SCF	-79.195 29	-79.188 95 (4.0)	-730.944 36	-730.935 70 (5.4)	-5774.500 58	-5774.482 63 (11.3)
CISD	-79.541 13[b]	-79.535 40 (3.6)[b]	-731.222 02	-731.217 83 (2.6)	-5774.780 05	
Davidson	-79.582 83[b]	-79.577 25 (3.5)[b]	-731.254 49	-731.251 35 (2.0)	-5774.814 98	
CCSD	-79.585 35[b]	-79.579 81 (3.5)[b]	-731.257 34			

[a] Relative energies (in kcal mol^{-1}) of the pentacoordinated structures (with C_2 symmetry) with respect to the cyclic structures are given in parentheses. DZP SCF predicted geometries are used except as noted. [b] At CISD optimized geometries.

Table VII. Binding Energies (for $X_3H_9 \rightarrow 3XH_3$, in kcal mol^{-1}) of Cyclic Triborane, Trialane, and Trigallane Obtained Using the DZP Basis Set

method	B_3H_9	Al_3H_9	Ga_3H_9
SCF	11.8	47.1	29.1
CISD	37.9	56.2	40.1
Davidson	43.0	57.8	42.1
MP2	48.9	57.8	
MP3	46.1	58.6	
MP4 (SDQ)	44.1	58.2	
CCSD	43.0	57.8	

[a] The DZP CISD geometry is used for triborane and the DZP SCF geometries for trialane and trigallane.

and for gallium (from 11.7 to 13.4 kcal mol^{-1}) according to DZP CISD predictions. Thus, the energy change for the following hypothetical reaction,

$$3B_2H_6 \rightleftharpoons 2B_3H_9$$

is positive for boron (28.9 kcal mol) but negative for aluminum (−7.7 kcal mol^{-1}) and gallium (−10.0 kcal mol^{-1}, DZP CISD), suggesting that alane and gallane prefer trimer to dimer while borane prefers dimer to trimer. However, it should be noted that these results suggest that gallane may have a stronger tendency to form the trimer (over the dimer) than alane, in apparent disagreement with the observation that dimethylgallane prefers a dimer while dimethylalane favors the trimer structure.[5]

4. Discussion

In this section, we shall discuss two problems on the basis of the results presented above. One is the role of triborane(9) in the pyrolysis of diborane, and the other is the possibility of isolating dialane in light of the tendency of alane and gallane to polymerize.

4.1. Triborane(9) in the Pyrolysis of Diborane. It seems to be established that the pyrolysis of diborane to give higher boranes starts with the following steps:[6-8]

$$B_2H_6 \rightleftharpoons 2BH_3$$

$$BH_3 + B_2H_6 \rightleftharpoons B_3H_9$$

$$B_3H_9 \rightleftharpoons B_3H_7 + H_2$$

A recent extensive theoretical study[9] of this process shows that the second step may be the rate-determining step, while the third step proceeds without a barrier, in contradiction with experimental kinetic conclusions that the third step is rate determining. Fehlner, in a communication to the authors of ref 9, pointed out that the measured rate might have corresponded to formation of a weak adduct of B_2H_6 and BH_3 which may or may not rearrange to the ground state of B_3H_9. We tried to locate a minimum resembling structure II as Fehlner suggested elsewhere,[8] but without success. The DZP SCF, DZD CISD, and DZP CISD geometry optimizations of II constrained to C_s symmetry lead to separated B_2H_6 and BH_3.

However, if the pentacoordinated triborane shown in Figure 2 is indeed an energy minimum as preliminary DZP CISD results suggest, it could be the adduct that Fehlner thought was observed. If this is the case, the association of diborane with borane might proceed in two steps:

$$BH_3 + B_2H_6 \rightleftharpoons \text{p-}B_3H_9$$

$$\text{p-}B_3H_9 \rightleftharpoons \text{cyclic } B_3H_9$$

The first step should be very fast since its transition state (not located yet) should be low-lying, as the energy difference between the reactant and product is very small (about 3–4 kcal mol^{-1}, DZP CISD). The second step could be slow as large structural changes are involved. This mechanism seems to fit the experimental kinetics results[6-8] and the recent theoretical results:[9] The formation of (pentacoordinated) triborane(9) is fast and so is the release of H_2 molecule from triborane(9). The "slow" step is the rearrangement of p-triborane to cyclic triborane, which previous experimental and theoretical studies have not considered. (Another possibility is that p-B_3H_9 releases a hydrogen molecule directly without going through the cyclic structure, but it is not clear whether this reaction has a high energy barrier.) Of course, more research is necessary to test this hypothesis.

4.2. Polymerization of Alane and Gallane. Although the results in the last section suggest that gallane has a stronger tendency to form the trimer over the dimer than alane, it does not necessarily mean that it is easier for digallane to polymerize. One very important factor for the stability of polymers of alane and gallane higher than the dimer is not included in the study of cyclic trimers. That is the stability of aluminum and gallium compounds in which the central atom has more than four ligands. The above results on the pentacoordinated trimers indicate that aluminum has a stronger tendency to form pentacoordinated structures than does gallium. There is experimental evidence that alane may prefer hexacoordinated structures. For instance, hydridoaluminum bis(tetrahydroborate), $AlH(BH_4)_2$, appears to dimerize, giving a structure with hexacoordinated aluminum atoms,[37] while the analogous compound hydridogallium bis(tetrahydroborate), $GaH(BH_4)_2$, exists as a monomer.[18,19] It is also interesting to note that the reaction of $LiBH_4$ with gallium(III) chloride affords the pentacoordinated $GaH(BH_4)_2$, instead of the hexacoordinated $Ga(BH_4)_3$ as is expected from the analogous reaction for aluminum.[38,39] In fact, it is well-known that aluminum is six-coordinate in the infinite structure for alane,[40] while the structure for infinite gallane has not been elucidated.[37] Therefore, it seems that aluminum tends more to form "hyper"-valent structures than does gallium, and this may explain in part the difficulty in isolating dialane.

5. Concluding Remarks

It is predicted that the binding energy for dialane (35.6 kcal mol^{-1}) is just slightly smaller than that for diborane (36.5 kcal mol^{-1}) but is significantly larger than that for the recent-made digallane (24.2 kcal mol^{-1}, DZP CCSD).[1] Thus, the binding energies of dimers of group IIIA hydrides cannot explain the absence of the successful isolation of dialane. The lack of monotonic trends from B to Al to Ga compounds is interesting, though not unexpected. Boron is basically a nonmetal, while aluminum is well-known to be amphoteric and Ga may be treated as a semimetal.

Our predicted molecular structure for the unknown dialane molecule is in qualitative agreement with that determined by electron diffraction[41] for the tetramethyl-substituted $(CH_3)_2Al(\mu\text{-}H_2)Al(CH_3)_2$ molecule. Specifically the Al···Al distance predicted for parent dialane (2.593 Å, DZP CISD) is reasonably close to that observed (2.617 Å) by Almenningen[41] for the known substituted compound. Similarly the bridging Al–H distances are 1.718 Å (parent, DZP CISD) and 1.676 Å (the tetramethyl-substituted compound).

The theoretical structures for the trimers show several very interesting features. First, unlike triborane(9), cyclic trialane(9) and trigallane(9) are planar with D_{3h} symmetry. The bond angles about the bridge hydrogens in the cyclic structures are much larger in Al_3H_9 and Ga_3H_9 than in B_3H_9. Secondly, the acyclic pentacoordinated isomers of the trimers are very different. (a) B_3H_9 may be an energy minimum with two B–H bonds (1.330 Å) similar to the bridge B–H$_b$ bonds in diborane and two long B–H bonds (1.503 Å) to the central boron atom (DZP CISD). (b) Pentacoordinated Al_3H_9 is shown to be an energy minimum at the DZP SCF potential hypersurface and none of its bridge Al–H bonds (ranging from 1.680 to 1.817) is significantly different from those in dialane (1.732 Å, DZP SCF). (c) Pentacoordinated Ga_3H_9 is a transition state with three GaH_3 units weakly linked

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as DZP SCF results indicate. In agreement with some experimental evidence,[19] the present theoretical study suggests that aluminum has a stronger tendency to form "hyper"-valent structures than does gallium, and this may explain the difficulty in isolating dialane in spite its relatively high dimerization energy.

The energy differences between the cyclic and pentacoordinated trimers are surprisingly small. The DZP CISD predictions indicate that these two structures for trialane(9) may be nearly isoenergetic. The pentacoordinated triborane(9) is predicted to be only 3–4 kcal mol^{-1} (DZP CCSD) higher in energy than its well-known cyclic isomer. This new structure for triborane(9) may be involved in the early pyrolysis of diborane and could explain the dispute on the kinetics of this process.[8,9]

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Butadiene. 2. Examination of the Energetic Preference for Coplanarity of Double Bonds. Comparison of Butadiene, Acrolein, and Vinylamine

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Abstract: Experimental and theoretical studies show a 4–5 kcal/mol barrier to rotation for butadiene. What causes this barrier and what other features of butadiene change upon rotation? We have examined this question in terms of Hückel theory and Simpson's resonance force model. The latter predicts an important component from electron correlation which was not found. Hückel theory predicts significant double bond character for the central bond of planar butadiene. Butadiene and the related compounds acrolein and vinylamine were compared to the unconjugated model compounds, butane and the three butenes. Geometries, force constants, and integrated charge distributions of the conjugated compounds were found to be similar to their unconjugated 90° structures and to the model compounds. Integration of the charge density at the center of the single bond for the two π-MO's of butadiene relative to its 90° isomer did reveal significant extra π-electron density. However, the σ electrons were polarized in the opposite direction so as to minimize electron repulsion. The σ–π interaction explains why only small changes in bond lengths or force constants are seen. The electrostatic potential maps for the three compounds also were studied and were converted to their equivalent point charge models. Electrostatic potential differences among butadiene, acrolein, and vinylamine were found to be consistent with their reactivity differences.

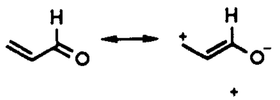
1. Introduction

Butadiene has been of special interest to chemists for years. Despite the many studies, there remains the question of the origin of the preference for a planar conformation. This energetic preference is found from both thermochemical measurements and ab initio theory to be 3-5 kcal/mol.[1-3] Is this preference due to electron conjugation or to some other interactions such as a resonance force?[4] Simple Hückel theory successfully accounts for the energy preference and also predicts significant interaction across the C_2–C_3 bond of conjugated butadienes.[5] This results in double bond character imparted to the single bond and single bond character to the double bonds. We sought some evidence for this interaction. We have examined geometries looking at bond lengths as the torsional angle was changed. We have compared the butadiene rotamers to butane, the three butenes, acrolein, and vinylamine looking specifically for anomalous bond lengths. Acrolein was included as a case that may be expected to have more interaction across the 2,3 bond due to the contribution of the zwitterionic resonance structure caused by the polarization of the carbon oxygen bond. Vinylamine presumably would have a complementary zwitterionic resonance structure to that of acrolein, and also was examined. Ab initio calculations yielded force constants for the C—C and C=C bonds of the butadienes and butenes, acroleins, and vinylamines which were compared. The electron populations of the above compounds also were examined. The σ and π charge densities for planes perpendicular to the bond

Table I. Calculated Energies for Butadiene at Fixed Torsional Angles[a-c]

τ, deg	MP2/ 6-31G*	E_{rel}	MP3/ 6-311++G**	E_{rel}	ZPE	ΔH
0	−155.435 99	3.59	−155.561 27	3.59	51.53	3.42
37.73	−155.437 44	2.68	−155.563 17	2.40	51.66	2.36
45	−155.437 30	2.77	−155.563 12	2.43		
90.0	−155.432 66	5.68	−155.559 14	4.93		
101.64	−155.432 15	6.00	−155.558 76	5.16	51.31	4.78
135	−155.436 45	3.30	−155.562 61	2.75		
180	−155.441 71	0.00	−155.566 99	0.00	51.69	0.00

[a] The total energies are given in hartrees, and the relative energies and zero-point energies are given in kcal/mol. The MP3 energies were calculated at the MP2 geometries. [b] The gauche form had τ = 37.73° and the transition state had τ = 101.64°. [c] The MP2/6-31G* energies are slightly different than those reported in ref 2. They were obtained assuming the vinyl groups maintained planarity, whereas in the present calculations, this assumption was not made.



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