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Theoretical Study of the Interaction of Gallium Atoms with Methane, Ethylene, 1,3-Butadiene, and Benzene

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Abstract: A series of gallium-containing species ($HGaCH_3$, $Ga(C_2H_4)_n$ ($n = 1, 2$), GaC_4H_6, GaC_4H_8, and GaC_6H_6) were studied by ab initio methods. All geometries were located at the (U)MP2/3-21G(2d) level of theory (except GaC_6H_6), and single-point calculations were carried out at the PMP4 level of electron correlation in a basis set which included d-functions on carbon. A gallium atom plus ethylene is predicted to form a π-complex with a binding energy of 10.9 kcal/mol. A second ethylene can bind to the GaC_2H_4 complex in a π-fashion with a binding energy of at least 2-3 kcal/mol. A complex is predicted between gallium and benzene with a binding energy of 7.0 kcal/mol. In comparison to the aluminum–benzene complex, binding is predicted to occur with a much smaller degree of spin transfer, which is in agreement with experiment. Isotropic hyperfine coupling constants are evaluated at the UMP2 level and are in reasonable agreement with experiment.

Introduction

Gallium atoms,[1-4] like aluminum atoms,[5-24] are known to interact with hydrocarbons such as methane, ethylene, and benzene. In many cases the reactivity of gallium atoms toward hydrocarbons is very similar to that of aluminum atoms, though exceptions are known. Thus, while the mode of interaction of gallium atoms with methane[1] and ethylene[2,3] is similar to that of aluminum atoms,[5,11,12] ESR experiments indicate that the interaction with benzene is qualitatively different.[4,21,22] Very recent experimental and theoretical work suggests that gallium and aluminum behave similarly in the compounds GaC_5H_5 and AlC_5Me_5, respectively.[25,26]

Neither gallium[1] nor aluminum[5] atoms in the ground state (^2P) react with methane. However, atoms in the ^2S excited state will react, mostly probably to form the insertion products $HGaCH_3$ and $HAlCH_3$, respectively. The reactions of gallium[2,3] and aluminum[11,12] atoms with ethylene have also been studied by ESR spectroscopy. The dominant species formed in an argon matrix at 4 K or an adamantane matrix at 77 K is a π-complex where the unpaired electron is in an orbital on the metal parallel to the π bond.[3] From an analysis of the ESR spectrum of the GaC_2H_4 complex and by using the most reasonable signs of the elements of the hyperfine tensor, a value of 20 MHz is obtained for the isotropic hyperfine coupling constant (iso hfcc).[3] Further analysis leads to a predicted spin density in the 4s orbital (ρ_{4s}) of 0.0016 e^- and in the 4p orbital (ρ_{4p}) of 0.56 e^-.[3] The binding energy of gallium to ethylene is estimated to be about 10 kcal/mol,[2] which can be compared to about 18 kcal/mol[20] for the aluminum–ethylene complex. If the z-axis is directed along the symmetry axis and the y-axis is parallel to the C=C π bond, the ground electronic state is $^2B_2$.

A second species, tentatively assigned to gallacyclopentane ($\overline{GaCH_2CH_2CH_2CH_2}$), was also observed in the Ga/ethylene/adamantane matrix at 77 K.[3] The iso hfcc was 1650 MHz and the estimated spin density in the 4s orbital on gallium was ρ_{4s} = 0.13 e^-.[3] This value is very similar to the value observed[11b] for the congener $\overline{AlCH_2CH_2CH_2CH_2}$ (ρ_{3s} = 0.18 e^-).

ESR studies have also been carried out by Howard et al.[4,22] on the interaction of gallium and aluminum atoms with benzene in an adamantane matrix at 77 K. Their results suggested that the mode of interaction of gallium with benzene differed from that observed for aluminum with benzene under identical reaction conditions. In the case of aluminum, it was tentatively concluded that the metal added to the 1,4-positions of benzene and an analysis of the ESR spectrum revealed that aluminum had donated approximately 0.7 unpaired electrons to benzene. On the other hand, gallium was found to interact with benzene with a transfer of only 0.2 unpaired electrons. Two theoretical papers on aluminum–benzene binding have appeared[23,24] supporting the 1,4-addition complex as the most stable bonding for the Al–benzene complex. The spin density on aluminum was calculated to be 0.04[23] or 0.18[24] e^-, which indicates a substantial transfer of spin density. No theoretical calculations have been reported for any complexes of gallium with methane, ethylene, or benzene.

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Table I. Total Energies (hartrees), Zero-Point Energies (kcal/mol), and Spin-Squared Values at UMP2/3-21G(2d) Optimized Geometries[a]

			3-21G(2d)		3-21G(2d,C*)		
	sym	state	UMP2 (FULL)	ZPE[b]	PMP2 (FC)	PMP4 (FC)	$\langle S^2 \rangle$
Ga	K	^2P	–1 914.036 77		–1 914.028 77	–1 914.043 66	0.76
CH_4	T_d	$^1A_1$	–40.077 10	29.13 (0)	–40.143 33	–40.165 61	
C_2H_4	D_{2h}	^1A_g	–77.784 52	32.70 (0)	–77.916 73	–77.951 68	
C_4H_6	C_{2h}	^1A_g	–154.419 10	54.02 (0)	–154.690 12	–154.753 09	
1 $HGaCH_3$	C_s	$^2A'$	–1 954.107 90	26.02 (0)	–1 954.163 27	–1 954.196 10	0.76
2 GaC_2H_4	C_{2v}	$^2B_1$	–1 991.829 88	33.14 (0)	–1 991.954 58	–1 992.003 53	0.76
3 GaC_2H_4	C_{2v}	$^2B_2$	–1 991.841 07	33.70 (0)	–1 991.966 97	–1 992.014 30	0.76
4 GaC_4H_8	C_{2v}	$^2B_2$	–2 069.637 51	71.05 (1)	–2 069.895 08	–2 069.976 15	0.76
5 GaC_4H_8	C_s	$^2A''$	–2 069.634 93	68.47 (1)	–2 069.893 48	–2 069.974 29	0.77
6 GaC_4H_8	C_2	^2A	–2 069.688 16	70.29 (0)	–2 069.950 64	–2 070.023 53	0.76
7 GaC_4H_6	C_s	$^2A'$	–2 068.503 35	55.97 (0)	–2 068.770 44	–2 068.837 54	0.81

[a] Post-SCF calculations employ the frozen-coroe (FC) approximation unless otherwise indicated (i.e. FULL). Spin projection (PMP2, PMP4) is by the Schlegel method.[30] [b] Zero-point energy (kcal/mol) with the number of imaginary frequencies in parentheses.

Table II. Relative Energies (kcal/mol) of Various Gallium-Containing Species

	UMP2 (FULL)/3-21G(2d)	PMP2 (FC)/3-21G(2d,C*)	PMP4 (FC)/3-21G(2d,C*)	PMP4 (FC)/3-21G(2d,C*)+ZPC
Ga + CH_4	0.0	0.0	0.0	0.0
1 $HGaCH_3$	3.7	5.5	8.3	5.3
Ga + C_2H_4	0.0	0.0	0.0	0.0
2 GaC_2H_4 ($^2B_1$)	-5.4	-5.7	-5.1	–4.7
3 GaC_2H_4 ($^2B_2$)	-12.4	-13.5	-11.9	-10.9
Ga + $2C_2H_4$	12.4	13.5	11.9	10.9
C_2H_4 + **3**	0.0	0.0	0.0	0.0
4 GaC_4H_8	-7.5	-7.1	–6.4	-2.0
5 GaC_4H_8	-5.9	–6.1	-5.2	-3.0
6 GaC_4H_8	-39.3	–42.0	-36.1	-32.4
Ga + C_4H_6	0.0	0.0	0.0	0.0
7 GaC_4H_6[a]	-29.8	-32.3	-25.6	-23.6

[a] At the UHF/3-21G(2d)//3-21G(2d) level, the C_2 symmetry species is 7.1 kcal/mol more stable than the C_{2v} symmetry species (planar).

Table III. Isotropic Hyperfine Coupling Constants (MHz) for Several Gallium-Containing Species Calculated with the 3-21G(2d,C*) Basis Set

	UHF Density			UMP2 Density			Experimental Results	
species	charge on Ga	$a_{\mathrm{iso\ hfcc}}$	ρ_{4s}/ρ_{4p}	charge on Ga	$a_{\mathrm{iso\ hfcc}}$	ρ_{4s}/ρ_{4p}	$a_{\mathrm{iso\ hfcc}}$	ρ_{4s}/ρ_{4p}
1 $HGaCH_3$	0.27	1034	0.24/0.51	0.19	989	0.23/0.54		
2 GaC_2H_4	–0.09	–229	–0.02/1.00	–0.10	–129	–0.01/0.99		
3 GaC_2H_4	0.05	38	0.01/0.59	0.03	–44	–0.01/0.60	20[a]	–0.002/0.56
4 GaC_4H_8	–0.09	88	0.04/0.71	0.20	643	0.17/0.45		
5 GaC_4H_8	0.01	92	0.03/0.56	–0.08	–63	0.35/0.67		
6 GaC_4H_8	0.43	910	0.25/0.44	0.33	908	0.25/0.50	1650[b]	0.13
7 GaC_4H_6	0.29	306	0.11/0.29	0.20	644	0.18/0.45		
8 GaC_6H_6	–0.07	–237	–0.02/0.99	–0.08	–110	–0.01/0.97	–99.3[c]	–0.01/0.80
9 GaC_6H_6	0.34	–362	–0.03/0.09	0.23	–124	0.01/0.18		

[a] Reference 3. [b] Reference 3. [c] Reference 4.

Methods

All calculations have been made using the GAUSSIAN 90[27a] or GAUSSIAN 92 program system.[27b] Geometries have been optimized with the 3-21G(2d) basis set (the 3-21G* basis set[28] supplemented by a second set of cartesian d-functions on gallium (exponent = 0.207) as recommended by Huzinaga[29]) and including electron correlation at the (U)MP2 level except for C_6H_6 and GaC_6H_6 species, which were only optimized at the (U)HF/3-21G(2d) level. Single-point calculations were made at the PMP4 level of electron correlation (frozen-core approximation) with the 3-21G(2d) basis set supplemented with a set of d-functions (exponent = 0.8) on carbon (denoted 3-21G(2d,C*)). The effect of spin contamination has been projected out of the MP energies (PMP) by the spin–projection method developed by Schlegel and coworkers.[30] Geometry optimizations at correlated levels of theory included core orbitals (FULL option), while (P)MP4 calculations employed the frozen-core approximation.

Absolute energies (hartrees) are given in Table I and relative energies (kcal/mol) are given in Table II for species **1**–**7**, while selected geometric parameters are given in Figure 1 for species **1**–**10**. Vibrational frequencies have been calculated at the (U)MP2/3-21G(2d) level to characterize the nature of the stationary points and to the make zero-point corrections (0.95 scaling factor[31]). This level of theory has been shown to give reasonable results in several studies of gallium-containing species.[32-34]

Isotropic hyperfine coupling constants have been calculated for gallium using eq 1, where g and g_{Ga} are the electronic and nuclear g factors, β

$$a_{Ga} = (8\pi/3)gg_{Ga}\beta\beta_{Ga}\rho(Ga) \qquad (1)$$

and β_{Ga} are the Bohr and nuclear magnetons, and $\rho(Ga)$ is the Fermi

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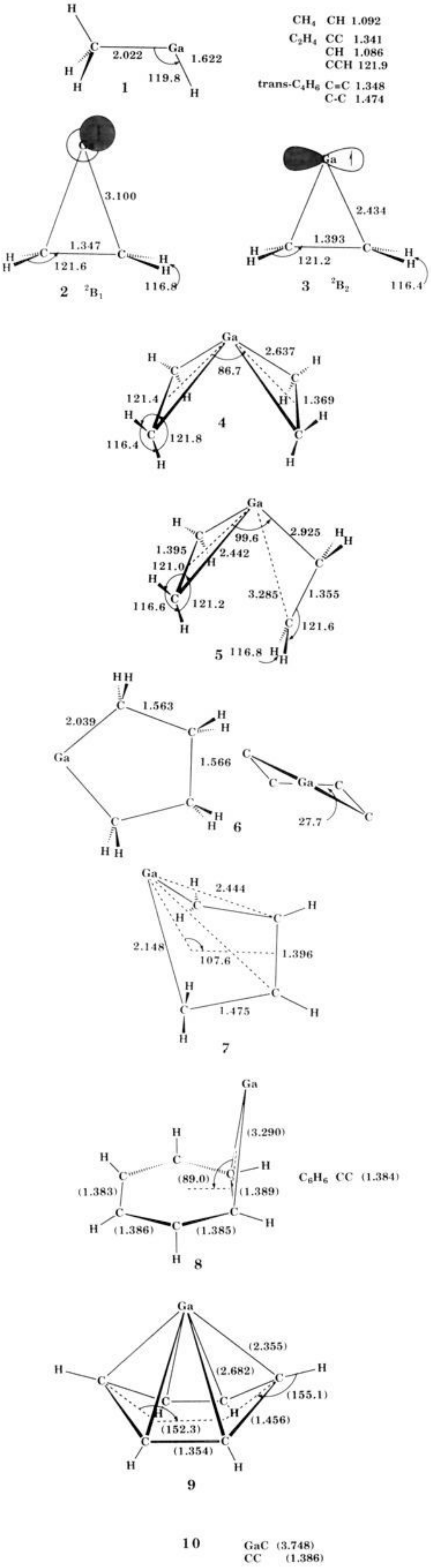

Figure 1. Selected geometric parameters (in angstroms and degrees) are given at the (U)MP2/3-21G(2d) level for all species except C_6H_6 and GaC_6H_6 species. The geometric parameters calculated at the (U)HF/3-21G(2d) level are given in parentheses.

contact integral.[35] To obtain the iso hfcc for gallium in MHz, the Fermi contact integral can be multiplied by the constant 1076.2. Cramer has shown[36] that the calculated iso hfcc's of aluminum-containing compounds are in reasonable agreement with experiment provided a flexible basis set is used and the Fermi contact integral is evaluated with the UMP2 density matrix.

Results and Discussion

$HGaCH_3$. While ground state (^2P) aluminum or gallium atoms do not react with CH_4, if the atoms are photoexcited into their ^2S excited state (~350 nm), insertion into the C–H bond occurs in a reaction that is reversible when photoexcited at >450 nm.[1,5] The inertness of ground state Al or Ga atoms with CH_4 is due to an avoided crossing on the ground state surface. The reaction is 10–11 kcal/mol exothermic for aluminum atoms (based on experimental bond-energy arguments[5]) and is predicted to be 5.3 kcal/mol endothermic for gallium (Table II).

The preferred conformation of $HGaCH_3$ is staggered, which is 0.2 kcal/mol more stable than the eclipsed orientation. The Ga–C bond length is calculated to be 2.022 Å and the H–Ga–C bond angle is 119.8° (**1**, Figure 1), which can be compared to analogous values in $HGaC_2H_5$ of Ga–C = 2.021 Å and H–Ga–C = 119.2° calculated[37] at the MP2/HUZSP* level (Huzinaga basis set).

A comparison of calculated frequencies is made in Table IV with the full experimental IR assignment of $HGaCH_3$ and the isotopomers $DGaCD_3$ and $HGa^{13}CH_3$.[1] The good agreement leaves little doubt as to the indentity of the species in the matrix. The calculated frequencies (unscaled) are on average 6.6% higher than the experimental frequency, which is typical for frequencies calculated with electron correlation.[30] The most intense band in the calculated spectrum is the Ga–H stretch (1817 cm^{-1}), which corresponds to the most intense band in the experimental spectrum[1] at 1719 cm^{-1} (Table IV).

While the iso hfcc for gallium in **1** has not been reported, the theoretical value is 989 MHz (Table III). The spin density on gallium in the 4p orbital is about twice as great as in the 4s orbital, which suggests that the unpaired electron resides mainly on gallium in an sp^2 hybridized orbital in the molecular plane (state symmetry is $^2A'$).

$Ga(C_2H_4)_n$, $n = 1, 2$. The complex formed between a gallium atom and one ethylene has been studied by ESR in a low-temperature matrix.[2,3] The spectrum indicates significant spin density in a gallium p orbital parallel to the π bond of ethylene. The binding energy has been estimated at 10 kcal/mol[2], which is less than the 18 kcal/mol[20] binding energy estimated for the aluminum–ethylene complex. Two electronic states were considered which differ in the orientation of the unpaired electron. In the $^2B_1$ state (**2**), the unpaired electron is in an orbital perpendicular to the π bond (Figure 1), while in the $^2B_2$ state (**3**), the unpaired electron is in an orbital parallel to the π bond. The $^2B_2$ state interacts more strongly with ethylene, due to the donation of electrons into the π^* orbital of ethylene. The effect of this donation can be seen in the length of the C–C bond in **3**, which has increased by 0.052 Å relative to ethylene (from 1.341 to 1.393 Å). On the other hand, the C=CH_2 groups remain nearly planar (sum of angles around C is 358.8°). The binding energy of the $^2B_2$ state is predicted to be 10.9 kcal/mol (Table II), compared to only 4.7 kcal/mol for the $^2B_1$ state (**2**).

The vibrational frequencies for the $^2B_2$ GaC_2H_4 complex (**3**) have been calculated at the UMP2/3-21G(2d) level (Table V). A comparison is made with the vibrational frequencies of ethylene calculated at the same level. All frequencies are predicted to decrease upon complexation with gallium except the b_2 wag of CH_2 at 1130 cm^{-1}, which is predicted to increase by 149 cm^{-1} with respect to the analogous mode in ethylene (Table V). This

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Table IV. Comparison of Vibrational Frequencies (cm^{-1}) of **1** $HGaCH_3$ Calculated at the UMP2 (FULL)/3-21G(2d) Level and by Experiment

	$HGaCH_3$			$DGaCD_3$			$HGa^{13}CH_3$			
	calcd[a]	exptl[b]	%Δ	calcd	exptl[b]	%Δ	calcd	exptl[b]	%Δ	assignment
a′	3187 (5)	2970	7	2357	2222	6	3176	2961	7	stre (C–H)
a″	3137 (13)	2970	6	2318	2222	4	3126	2961	6	stre (C–H)
a′	3061 (3)	2914	5	2192	2137	2	3058	2908	5	stre (C–H)
a′	1817 (230)	1719	6	1295	1244	4	1817	1719	6	stre (Ga–H)
a″	1561 (5)	1432	9	1132	1026	10	1558	1428	9	def (CH_3)
a′	1548 (2)	1432	8	1121	1026	9	1545	1428	8	def (CH_3)
a′	1308 (1)	1161	13	1012	899	12	1299	1154	12	def (CH_3)
a′	826 (79)	754	10	628	579	8	820	750	9	rock (CH_3)
a″	640 (0)	642	0	478			637	642	−1	rock (CH_3)
a′	549 (19)	528	4	504	484	4	535	514	4	stre (Ga–C)
a′	484 (30)			345			483			bend (Ga–H)
a″	86 (0)			62			86			tors

[a] Calculated intensity in km/mol is given in parentheses. [b] Reference 1.

Table V. Calculated Vibrational Frequencies for **3** GaC_2H_4 ($^2B_2$) at the UMP2 (FULL)/3-21G(2d) Level

sym	freq (int)[a]	assignment	C_2H_4	Δ
b_1	3278 (1)	stre (CH)	3280	−2
a_2	3249 (0)	stre (CH)	3250	−1
a_1	3182 (4)	stre (CH)	3194	−12
b_2	3171 (0)	stre (CH)	3175	−4
a_1	1606 (0)	stre (CC)	1694	−88
b_2	1548 (6)	sciss (CH_2)	1572	−24
a_1	1312 (3)	sciss (CH_2)	1434	−122
a_2	1278 (0)	rock (CH_2)	1304	−26
b_2	1130 (5)	wag (CH_2)	981	149
a_1	914 (56)	wag (CH_2)	1006	−92
a_2	894 (0)	twist (CH_2)	1092	−198
b_1	867 (1)	rock (CH_2)	893	−26
b_1	483 (1)	twist (CH_2)		
b_2	420 (5)	stre (GaC)		
a_1	235 (8)	stre (GaC)		

[a] Calculated intensity in km/mol is given in parentheses.

increase is probably due to the mixing with the Ga–C asymmetric stretch (420 cm^{-1}) which has the same symmetry. The asymmetric (b_2) and symmetric (a_1) Ga–C stretches are predicted at 420 and 235 cm^{-1}, respectively, which can be compared to the analogous Al–C stretches (394 and 365 cm^{-1}) in the $^2B_2$ state of AlC_2H_4 calculated at a similar level of theory.[7] However, experiment (226 and 352 cm^{-1})[13] and higher level theory (CISD, 232 and 387 cm^{-1})[16] reverse the ordering of the two bands, which suggests that even higher level theory may be required for an accurate prediction of these frequencies in GaC_2H_4. The most intense band is predicted to be the a_1 wag of CH_2 at 914 cm^{-1} (Table V).

The iso hfcc's for the $^2B_1$ (**2**) and $^2B_2$ (**3**) states of GaC_2H_4 are reported in Table III. The gallium atom in **2** has a negative Mulliken population, indicating a transfer of electrons from the π bond of ethylene. The unpaired electron in a p orbital on gallium (**2**) remains nearly unperturbed (UMP2/3-21G(2d,C*), ρ_{4p} = 0.99 e^-) because the orbital does not have the correct symmetry to mix with the π^* orbital of ethylene. The gallium atom in the $^2B_2$ state of GaC_2H_4 (**3**) can interact with the π^* orbital of ethylene as demonstrated by the smaller spin densities in the 4p orbital (UMP2/3-21G(2d,C*), ρ_{4p} = 0.60 e^-). The iso hfcc changes sign when electron correlation is included (Table III, UHF, 38; UMP2, −44 MHz), bracketing the experimental value[3] of 20 MHz. The spin density in the 4p orbital of gallium determined from the experimental spectrum[3] (ρ_{4p} = 0.56 e^-) is in excellent agreement with the calculated value (Table III, ρ_{4p} = 0.60 e^-).

In addition to GaC_2H_4, the reaction of gallium atoms with ethylene at 77 K in an adamantane matrix produced another species with an iso hfcc of 1650 MHz which was tentatively identified as gallacyclopentane ($\overline{GaCH_2CH_2CH_2CH_2}$).[3] Although no evidence for the most likely precursor, $Ga(C_2H_4)_2$, was found, theoretical calculations were carried out. Two geometries were considered: one in which both ethylenes interact with the gallium atom in a π-fashion (**4**) and one in which one ethylene interacts in a π-fashion and one in a σ-fashion (**5**). The binding energy of the second ethylene in **4** is predicted to be only 2.0 kcal/mol, while the C–C bonds are 0.028 Å longer than in ethylene and the sum of angles around carbon is 359.6°. The unpaired electron is predominantly in a 4p orbital on gallium which is parallel to both C–C π bonds. The simultaneous donation of charge to both π^* orbitals of ethylene (and the back-donation from the π orbital into the empty p orbital on gallium) is the reason for the small angle between the two GaCC planes (86.7°). At the correlated level, gallium in $Ga(C_2H_4)_2$ **4** has a greater positive charge (0.20 e^-) and a smaller spin density (ρ_{4p} = 0.45 e^-) compared to those of GaC_2H_4 **3** (0.03 e^-, ρ_{4p} = 0.60 e^-), both indications of more extensive charge transfer. One small imaginary frequency was calculated for **4** (b_1, 43*i* cm^{-1}) for the displacement of the gallium atom toward one of the ethylene units.

The starting geometry for **5** contained a π-interaction for gallium with one C_2H_4 unit and a σ-interaction with the second C_2H_4 unit. After optimization, the resulting geometry is best described as a bis π-complex with one symmetric π-interaction (Figure 1, Ga–C 2.442 Å) and one asymmetric π-interaction (Ga–C = 2.925 and 3.285 Å). Also, the sum of angles around each CH_2 group in the asymmetrically bonded ethylene deviates less than 0.1° from 360°, which indicates little change in hybridization. The energy of **5** is 1.2 kcal/mol higher than that of **4** at the PMP4/3-21G(2d,C*) level. However, the zero-point correction for **5** is less than that for **4**, and when included, **5** becomes 1.0 kcal/mol more stable than **4** (Table II). The large difference between the two C=C bond lengths (1.395 and 1.355 Å) indicates a much stronger interaction with one C_2H_4 unit than with the other. Since gallacyclopentane (**6**) is observed[3] in an adamantane matrix at 77 K while the bis π-complex (**4** or **5**) is not, the barrier for **4** → **6** or **5** → **6** must be small.

The C_2 ground state geometry of gallacyclopentane (**6**) is predicted to be to be 7.1 kcal/mol lower in energy than a planar C_{2v} geometry at the UHF/3-21G(2d) level. At the UMP2/3-21G(2d) level, the C_2-symmetry structure is predicted to have normal Ga–C single bonds (2.039 Å) only slightly longer than the Ga–C bond length in $HGaCH_3$ (**1**, 2.022 Å). The predicted iso hfcc for **6** (908 MHz) is considerably smaller than the iso hfcc of a species identified as gallacyclopentane in a low-temperature matrix (1650 MHz).[3] At this time, it is unclear whether deficiencies in the basis set or insufficient electron correlation is the source of difference between theory and experiment. However, the iso hfcc and spin density of **6** do not seem to be sensitive to the inclusion of electron correlation at the UMP2 level of theory (Table III).

The vibrational frequencies of **6** calculated at the UMP2/3-21G(2d) level are reported in Table VI. The CH_2 stretches are predicted to occur at 3058–3152 cm^{-1}. The most intense band,

Table VI. Calculated Vibrational Frequencies (cm^{-1}) for **6** GaC_4H_8 at the UMP2 (FULL)/3-21G(2d) Level

a symmetry		b symmetry	
freq (int)[a]	assignment	freq (int)[a]	assignment
3151 (0)	stre (CH_2)	3152 (26)	stre (CH_2)
3103 (22)	stre (CH_2)	3114 (37)	stre (CH_2)
3065 (0)	stre (CH_2)	3066 (18)	stre (CH_2)
3062 (33)	stre (CH_2)	3058 (20)	stre (CH_2)
1580 (1)	def (CH_2)	1581 (5)	def (CH_2)
1533 (0)	def (CH_2)	1532 (7)	def (CH_2)
1402 (2)	def (CH_2)	1398 (2)	def (CH_2)
1304 (4)	def (CH_2)	1325 (4)	def (CH_2)
1259 (5)	def (CH_2)	1156 (1)	def (CH_2)
1110 (8)	def (CH_2)	1061 (1)	def (CH_2)
1000 (19)	ring	958 (2)	def (CH_2)
932 (3)	def (CH_2)	858 (1)	ring
824 (0)	ring	709 (6)	ring
642 (4)	ring	540 (15)	def (CH_2)
521 (1)	def (CH_2)	451 (5)	ring
317 (10)	ring	136 (0)	ring/stre (Ga)
264 (1)	ring		

[a] Calculated intensity in km/mol is given in parentheses.

Table VII. Calculated Vibrational Frequencies (cm^{-1}) for **7** GaC_4H_6 at the UMP2 (FULL)/3-21G(2d) Level

a′ symmetry		a″ symmetry	
freq (int)[a]	assignment	freq (int)[a]	assignment
3233 (2)	stre (CH_2)	3232 (3)	stre (CH_2)
3201 (7)	stre (CH)	3181 (0)	stre (CH)
3121 (2)	stre (CH_2)	3139 (31)	stre (CH_2)
1561 (10)	def (CH_2)	1624 (468)	def (CH_2)
1503 (22)	stre (CC)	1480 (148)	def (CH_2)
1259 (12)	bend (CH)	1436 (132)	bend (CH)
1090 (1)	def (CH_2)	1208 (4)	stre (CC)
996 (12)	def (CH_2)	1055 (1)	def (CH_2)
953 (12)	stre (CC)	954 (14)	oop (CH)
819 (16)	def (CH_2)	768 (9)	def (CH_2)
765 (53)	oop (CH)	689 (0)	ring
430 (2)	ring	508 (35)	ring
261 (1)	stre (GaC)	466 (24)	ring
215 (5)	ring		

[a] Calculated intensity in km/mol is given in parentheses.

which is not a CH_2 stretch, is the ring stretch at 1000 cm^{-1} of the carbon atoms opposite the gallium atom.

GaC_4H_6. The reaction of 1,3-butadiene with aluminum atoms at 77 K in an adamantane matrix results in the formation of aluminum-substituted allyl and aluminum cyclopentene, AlC_4H_6.[19] Since it is likely that gallium atoms will afford the same product, the gallium-substituted cyclopentane (**7**) was calculated to aid in its identification. The gallium complex **7** adopts an envelope conformation and is 23.6 kcal/mol more stable than gallium plus *trans*-1,3-butadiene (Table II). The aluminum-containing cyclopentene adopts the same conformation and is calculated to be 30.2 kcal/mol more stable than aluminum plus *trans*-1,3-butadiene at the PMP4/6-31G*//UMP2/3-21G*+ZPC level of theory.[23] The C—C and C═C bonds in gallacyclopentene (**7**) only differ by 0.079 Å (1.475 and 1.396 Å), which is much less than in aluminum-substituted cyclopentene (0.114 Å).[23] This suggests weaker σ-interactions in gallacyclopentene (**7**). The Ga—C σ-interactions are 2.148 and 2.444 Å, which can be compared to a Ga—C σ-bond of 2.022 Å in $HGaCH_3$ (**1**) and a Ga—C π-interaction in GaC_2H_4 (**3**) of 2.434 Å. The predicted iso hfcc at the UMP2/3-21G(2d,C*) level is 644 MHz with corresponding gallium spin densities in the 4s and 4p orbitals of 0.18 and 0.45 e$^-$, respectively. The striking similarity of the iso hfcc's and spin densities on gallium between **7** and $Ga(C_2H_4)_2$ (**4**) suggests that the interaction might also be viewed as a gallium atom interacting in a π-fashion with both π bonds of *cis*-1,3-butadiene. However, the sum of angles around the CH_2 groups in **7** (346.4°) indicates a substantial degree of rehybridization.

The vibrational frequencies of **7** are reported in Table VII in anticipation that the values will aid in the experimental identification of this species in a low-temperature matrix. The three C–C stretches are predicted (unscaled) at 1503, 1208, and 953 cm^{-1} (Table VII), while in *trans*-1,3-butadiene, the three C–C stretches (unscaled) are 1694, 1653, and 1257 cm^{-1} at the same level of theory. Interestingly, the lowest C–C stretch in *trans*-1,3-butadiene (953 cm^{-1}) becomes the highest C–C stretch in gallacyclopentane (1694 cm^{-1}). A very characteristic region in the spectrum of **7** should be 1436–1624 cm^{-1} (unscaled), where three intense bands are predicted (Table VII).

GaC_6C_6. A number of metal atoms and ions are known to interact with benzene. These species can be broadly divided into two groups. Metal cations which interact primarily by accepting electron density include transition metal cations (Ag^+, Cu^+, etc.),[38,39] main group cations (Ga^+),[40] and active metal cations (Mg^+).[41] Metal atoms which interact primarily by donating electron density include group 1 and 3 metals (Li, Na, Al, and Ga)[4,21,22,42] and noble gases (Ne–Xe).[43,44] Acceptor cations that have empty np_x and np_y orbitals are usually situated on the 6-fold axis since the acceptor orbitals match the symmetry of the highest occupied donor orbital of benzene. Donor atoms that have a partially filled set of p-orbitals often bind more favorably off the 6-fold axis since there is no longer a symmetry match between the donor and acceptor orbitals.

The complexes formed between a noble gas and benzene (C_{6v} symmetry assumed) are very weak with a maximum binding energy (calculated) of about 1.7 kcal/mol for Xe.[43] When symmetry was reduced for the Ar–benzene complex,[44] the C_{6v} symmetry complex was still found to be more stable. In the complex Ag^+–benzene, the Ag^+ binds off-center (see experimental[45] and theoretical[39] results), which is probably due to the symmetry mismatch of the silver 6s orbital, which is doubly occupied, and the low-lying acceptor orbitals of benzene. In the case of lithium atoms,[42] experimental studies in a solid argon matrix indicate an off-center axial position for the metal, possibly due to a small Jahn–Teller effect.

The interaction of aluminum with benzene has been studied by ESR spectroscopy in an adamantane matrix at 77 K.[21,22] The binding energy in the gas phase has been determined to be 11.7 ± 1 kcal/mol from time-resolved resonance fluorescence spectroscopy.[20] The structure most consistent with experiment was judged to be the 1,4-addition of aluminum to benzene. An analysis of the ESR spectrum indicates considerable spin density has been transferred (~0.7 e$^-$) to the benzene such that the interaction may be considered that of an aluminum cation interacting with an benzene radical anion. Two theoretical papers have confirmed that 1,4-addition is the most favorable orientation.[23,24] Previous results by the present author[23] gave a binding energy of 7.4 kcal/mol at the [PMP4/6-31+G**] level, which can be compared to a binding energy of 3.5 kcal/mol calculated by Silva and Head.[24]

In the present work, three orientations of the gallium atom have been considered: an off-center position in C_s symmetry (**8**), a 1,4-addition position with C_{2v} symmetry (**9**), and an axial position in C_{6v} symmetry (**10**). Table VIII lists total energies (hartrees) and Table IX lists relative energies (kcal/mol) for species **8**–**10**. The symmetric C_{6v} structure (**10**) has a calculated $^2E_1$ electronic

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Table VIII. Total Energies (hartrees), Zero-Point Energies (kcal/mol), and Spin-Squared Values at UHF/3-21G(2d) Optimized Geometries

			3-21G(2d)		3-21G(2d,C*)		
	sym	state	UHF	ZPE[a]	PMP2	PMP4	$\langle S^2 \rangle$
C_6H_6	D_{6h}	$^1A_{1g}$	−229.419 44	68.28 (0)	−230.366 38	−230.439 42	
8 GaC_6H_6	C_s	$^2A'$	−2 143.404 46	68.46 (0)	−2 144.407 85	−2 144.494 60	0.76
9 GaC_6H_6	C_{2v}	$^2A_1$	−2 143.378 75	68.50 (2)	−2 144.408 74	−2 144.493 87	0.79
10 GaC_6H_6	C_{6v}	$^2E_1$	−2 143.403 77[b]		−2 144.405 38		0.76

[a] Zero-point energy (kcal/mol) with number of imaginary frequencies in parentheses. [b] The structure **10** is not a stationary point in C_{6v} symmetry; therefore, vibrational frequencies were not calculated.

Table IX. Relative Energies (kcal/mol) for Species on the GaC_6H_6 Potential Energy Surface

	HF/3-21G(2d)	PMP2/3-21G(2d,C*)	PMP4/3-21G(2d,C*)	PMP4/3-21G(2d,C*)+ZPC
Ga + C_6H_6	0.0	0.0	0.0	0.0
8 GaC_6H_6	−3.6	−8.0	−7.2	−7.0
9 GaC_6H_6	12.5	−8.5	−6.8	−9.3
10 GaC_6H_6	−3.2	−6.4		

state and therefore should distort to a lower energy structure with reduced symmetry. The off-center structure (**8**) has C_s symmetry and is 0.4 kcal/mol lower in energy than **10** at the level of theory used for geometry optimization (UHF/3-21G(2d)). At the PMP2/3-21G(2d,C*) level, the difference between **8** and **10** has increased to 1.6 kcal/mol. At the Hartree–Fock level, the 1,4-addition structure is much higher in energy than Ga plus benzene. However, electron correlation stabilizes this mode of interaction considerably and at the PMP2/3-21G(2d,C*) level, **9** is the most stable structure. Further electron correlation at the PMP4 level reverses the stability of **8** and **9** (**8** is 0.4 kcal/mol more stable than **9**), while zero-point correction reverses the stabilities again (**9** is 2.3 kcal/mol more stable than **8**). It is not possible, on energetic grounds, to predict which structure, **8** or **9**, should be the species observed in the adamantane matrix at 77 K. However, the experimental ESR results indicate unambiguously[4] that the observed structure is **8**. The aluminum–benzene complex is very similar to **9**, based on a combination of experimental[21,22] and theoretical results.[23,24] The ESR spectrum and theoretical calculations indicate that considerable spin density has been transferred to the benzene ring, which, due to the loss of aromatic stabilization, adopts a boat conformation. In contrast, the ESR spectrum for the gallium–benzene complex suggests a completely different mode of interaction.[4] The experimental spin density in the 4s orbital on gallium is 0.8 e^-, which compares much better with the calculated value of 0.97 e^- for **8** rather than 0.18 e^- for **9** (Table III, UMP2/3-21G(2d,C*)). The interaction in **8** is dominated by dispersion forces which are greater for the Ga–benzene complex compared to the Al–benzene complex due to the greater polarizability of gallium. The charge-transfer/electrostatic interaction, which dominates the Al–benzene interaction is less significant for the gallium–benzene complex (**9**) because the IP's for gallium and aluminum are about the same (IP_{Al} = 137.9, IP_{Ga} = 138.3 kcal/mol[46]), while the electrostatic attraction is less because the gallium is further from the benzene. The experimental iso hfcc for the Ga–benzene complex is −99.3 MHz (assuming the most probable signs of the diagonal elements of the hyperfine tensor, a_{xx}, a_{yy}, and a_{zz}), which compares well with the calculated iso hfcc's for both **8** and **9** (−110 and −124 MHz, respectively).

Conclusion

Ab initio methods are able to correctly describe the interaction between gallium atoms and several hydrocarbons and give properties (binding energies, frequencies, and iso hfcc's) in reasonable agreement with experiment. The insertion of gallium into a C–H bond of methane produces a compound which is endothermic by 5.3 kcal/mol. A π-complex is predicted between gallium and ethylene, which is exothermic by 10.9 kcal/mol. A second ethylene can add to the π-complex to form a new bis π-complex compound 3.2 kcal/mol more stable. The di-σ cyclic complexes, GaC_4H_8 and GaC_4H_6, are predicted to be 44.0 and 23.6 kcal/mol more stable than a gallium atom and two ethylenes or a gallium atom and *trans*-1,3-butadiene, respectively. Finally, two modes of interaction are predicted to be of similar strength in the interaction of gallium and benzene; one is dominated by dispersion forces and the other by electrostatics. Experimental ESR results are in agreement with the dispersion interaction.

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