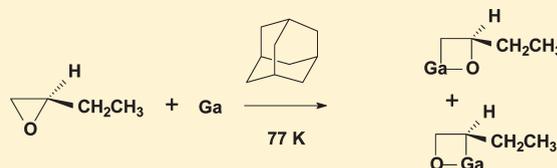


# Formation of Gallaoxetanes: C–O Activation of 1,2-Epoxybutane by Ground-State Ga Atoms

Helen A. Joly,\* Luc Beaudet, Michelle Levesque,<sup>†</sup> and Maxine Myre

Department of Chemistry and Biochemistry, Laurentian University, Sudbury, Ontario, Canada P3E 2C6

**ABSTRACT:** <sup>69/71</sup>Ga atoms were reacted with 1,2-epoxybutane and its isotopomers, 1,2-epoxybutane-1,1-*d*<sub>2</sub> (CH<sub>3</sub>CH<sub>2</sub>CHOCD<sub>2</sub>) and 1,2-epoxybutane-2-*d*<sub>1</sub> (CH<sub>3</sub>CH<sub>2</sub>CDOCH<sub>2</sub>), under matrix-isolation conditions. The novel gallaoxetanes CH<sub>3</sub>CH<sub>2</sub>CHCH<sub>2</sub>GaO and CH<sub>3</sub>CH<sub>2</sub>CHCH<sub>2</sub>OGa, resulting from the insertion of the metal atom in the C<sub>1</sub>–O and C<sub>2</sub>–O bonds, respectively, of the 1,2-epoxybutane, were detected by EPR spectroscopy. The Ga and H hyperfine interaction (hfi) values of the gallaoxetanes, calculated using a DFT method, were used to help assign the EPR spectra. A third Ga-centered species, detected at 190 K, underwent spectral changes similar to those of the C<sub>2</sub>–O insertion product upon isotopic substitution of the 1,2-epoxybutane. Although the Ga hfi for this species was 36% smaller than that of the C<sub>2</sub>–O insertion product, the values for the H hfi were similar, suggesting that the carrier of the spectrum was the C<sub>2</sub>–O insertion product where Ga was perturbed by the matrix constraints. The alkyl radical CH<sub>3</sub>CH<sub>2</sub>(•CH)CH<sub>2</sub>OGa, resulting from ring-opening at the C<sub>2</sub>–O bond of 1,2-epoxybutane, was observed at temperatures below 150 K. This radical has been implicated in the formation of the C<sub>2</sub>–O insertion product. The unusually small value found for two of the β-hydrogens of the alkyl radical is discussed.



## INTRODUCTION

Group 13 metal atoms (M) have been shown to react with substrates, under matrix-isolation conditions, to form divalent compounds. For example, Al atoms react spontaneously with H<sub>2</sub>O to produce the O–H insertion product HAlOH.<sup>1</sup> Ga,<sup>2,3</sup> In,<sup>2</sup> and Tl,<sup>2</sup> on the other hand, first form a photolabile complex, M••OH<sub>2</sub>, which tautomerizes to HMOH upon UV irradiation.<sup>1,2</sup> Whereas HAlOH has been characterized by both EPR (electron paramagnetic resonance)<sup>4–7</sup> (in inert gas matrixes at 4 K and in adamantane at 77 K) and IR<sup>1,2</sup> (in inert gas matrixes at 4 K) spectroscopies, characterization of HGaOH, HInOH, and HTlOH<sup>1,2</sup> has been limited to IR spectroscopy. Similarly, the EPR spectra of the products formed in the Al–H<sub>2</sub>S and Al–H<sub>2</sub>Se reactions, carried out in an adamantane matrix at 77 K, were consistent with the spontaneous formation of HAlSH and HAlSeH, respectively.<sup>7</sup> In the same study, no definitive evidence was found for the Ga–H<sub>2</sub>S and Ga–H<sub>2</sub>Se insertion products. These results are consistent with the fact that divalent Ga compounds are often observed only after UV irradiation of the deposit. The wavelength of UV radiation required to bring about the rearrangement of the Ga–substrate complex depends on the extent of interaction between the Ga and the substrate.<sup>8</sup>

Al and Ga were reported to react with group 6 hydrides, namely, CH<sub>4</sub> and SiH<sub>4</sub>. Using IR and EPR spectroscopies, Parnis et al.<sup>9–11</sup> showed that photoexcitation of Al in a methane matrix at 12 K leads to the formation of the insertion product, CH<sub>3</sub>AlH. In subsequent studies, IR evidence was provided to show that CH<sub>3</sub>GaH forms upon irradiation of matrixes prepared by co-condensing Ga with methane-doped argon,<sup>12–15</sup> krypton,<sup>13</sup> and pure methane.<sup>13</sup> EPR evidence for the Ga-insertion product and its isotopomer, CD<sub>3</sub>GaD, prepared by irradiating Ga in a methane-doped neon matrix at 4 K, was reported<sup>16</sup> by Knight et al.

Methane-doped argon matrixes co-condensed with In also yield a divalent insertion compound, HInOH, upon photoexcitation of the atoms.<sup>15</sup> The deposition of Al and Ga in a silane-doped argon matrix at 12 K initially results in a loosely bonded M••SiH<sub>4</sub> complex that tautomerizes to the divalent insertion product HMSiH<sub>3</sub> upon photolysis.<sup>17</sup>

The IR spectra of the products formed upon reacting Al, Ga, and In with ammonia<sup>18,19</sup> and phosphine<sup>20</sup> are consistent with the formation of M••XH<sub>3</sub> complexes, where X = N or P. Photoactivation of the complexes causes the metal atom to insert into the X–H bond to form the divalent compound HMXH<sub>2</sub>. EPR spectroscopy was used to characterize the HAlNH<sub>2</sub> product isolated in an argon matrix at 4 K<sup>21,22</sup> and a hydrocarbon matrix at 77 K.<sup>23</sup> It is interesting to note that HAlNH<sub>2</sub> formed spontaneously in the hydrocarbon matrix.

The reaction of Al with HCl<sup>24</sup> and cyclopropyl bromide<sup>25</sup> in an adamantane matrix at 77 K proceeds in the absence of photoirradiation to give the divalent H–Cl and C–Br insertion products, as characterized by EPR spectroscopy.

There have been reports of Al–C–O insertion reactions of ethers.<sup>26–28</sup> EPR studies of the products generated in the reaction of Al with dimethyl ether,<sup>27,28</sup> diethyl ether,<sup>26,27</sup> tetrahydrofuran,<sup>27</sup> and trimethylene oxide<sup>28</sup> under matrix-isolation conditions indicated that RAlOR' (where R and R' correspond to the appropriate alkyl groups for the ether in question) was one of the major spontaneously formed products. In a more recent study,<sup>29</sup> the reaction of Al and 1,2-epoxybutane resulted in the formation of the two novel four-membered aluminaoxetanes, CH<sub>3</sub>CH<sub>2</sub>CHCH<sub>2</sub>AlO

Received: July 14, 2011

Revised: September 6, 2011

Published: September 07, 2011

**Table 1.** Comparison of the Experimental Ga and H hfi Values (MHz) for GaH<sub>2</sub> and HGaCH<sub>3</sub> with Those Calculated Using the B3LYP Functional and a Series of Different Basis Sets<sup>a</sup>

	method					expt <sup>b</sup>
	B3LYP/6-31G(d,p)	B3LYP/6-311+G(d,p)	B3LYP/6-311+G(df,p)	B3LYP/6-311+G(2df,p)	B3LYP/6-311+G(3df,p)	
GaH <sub>2</sub> : Geometry Optimized with B3LYP/6-31G(d,p)						
Ga	2231 (7%)	1800 (14%)	1793 (14%)	1797 (14%)	1794 (14%)	2084
H	194 (8%)	200 (12%)	200 (12%)	200 (12%)	200 (12%)	179
HGaCH <sub>3</sub> : Geometry Optimized with B3LYP/6-31G(d,p)						
Ga	2047 (2%)	1652 (17%)	1643 (18%)	1643 (18%)	1632 (18%)	1999
H	199 (2%)	212 (4%)	212 (4%)	212 (4%)	212 (4%)	203

<sup>a</sup> Values in parentheses are the differences between the experimental and calculated hfi values. <sup>b</sup> Experimental values taken from ref 16.

and CH<sub>3</sub>CH<sub>2</sub>CHCH<sub>2</sub>OAl, from insertion of Al into the C<sub>1</sub>–O and C<sub>2</sub>–O bonds, respectively.

In the present study, we have reacted Ga atoms and 1,2-epoxybutane in an adamantane matrix at 77 K. Two new gallaoxetanes, resulting from the insertion of Ga atoms into the C<sub>1</sub>–O and C<sub>2</sub>–O bonds of 1,2-epoxybutane, formed spontaneously. From an EPR spectroscopic analysis, the Ga hyperfine interaction (hfi) of the C<sub>1</sub>–O gallaoxetane was found to be greater than that of the C<sub>2</sub>–O gallaoxetane. Support for the spectral assignments was obtained from isotopomeric gallaoxetanes formed in the Ga reactions of 1,2-epoxybutane-1,1-*d*<sub>2</sub> and 1,2-epoxybutane-2-*d*<sub>1</sub> and the relative Ga and H hyperfine interactions of the gallaoxetanes calculated using a DFT method. To our knowledge, this is the first report detailing the formation and EPR characterization of gallaoxetanes.

## EXPERIMENTAL SECTION

**Materials.** Adamantane and 1,2-epoxybutane were purchased from Aldrich Chemical Co. These compounds were subjected to several freeze–thaw cycles on a vacuum line prior to use in the metal-atom reaction. The method used to prepare 1,2-epoxybutane-1,1-*d*<sub>2</sub> and 1,2-epoxybutane-2-*d*<sub>1</sub> is described in ref 29.

**Preparation and Characterization of the Paramagnetic Products.** Ga atoms, 1,2-epoxybutane or one of its isotopomers, and adamantane were co-condensed in a metal-atom reactor known as a rotating cryostat. The details of the operation of the rotating cryostat are described elsewhere.<sup>30</sup> Briefly, the apparatus consists of a rotating liquid-nitrogen-filled drum (77 K) situated in the center of a stainless steel reaction vessel maintained at <10<sup>−6</sup> Torr. The atoms, generated by resistively heating pieces of Ga (20 mg, Fisher) placed in a tungsten basket (no. 12070, Ernest F. Fullam, Schenectady, NY) suspended between the electrodes of a furnace, were introduced along with 1,2-epoxybutane and adamantane through portholes in the reaction vessel. After a deposition time of approximately 10 min, the reaction mixture was scraped off the drum into a suprasil quartz tube at 77 K and <10<sup>−6</sup> Torr. The tube was sealed, and the sample was subjected to EPR analysis (77 K) on a Varian E109 spectrometer equipped with a Varian gaussmeter and a Systron-Donner 6016 frequency counter. The samples were subsequently annealed (from 77 to 298 at 10 K intervals) with the aid of a Lakeshore 330 temperature controller. EPR spectra were recorded, and the effect of temperature on the spectral lines was analyzed.

**Data Analysis and Computer Simulation.** The nuclear hfi and g values for the Ga-centered radicals formed in the reaction

of Ga atoms and 1,2-epoxybutane were determined from the exact solution of the spin Hamiltonian using the computer program ESRSQ.<sup>31</sup> The computer program ISOPLOT<sup>31</sup> was used to generate the EPR simulations presented in this article.

**Computational Methods: Calculation of Geometry and Nuclear Hyperfine Interaction (hfi) Values.** The Gaussian 09<sup>32</sup> suite of programs was used to calculate the Ga and H hfi values for GaH<sub>2</sub>, HGaCH<sub>3</sub>, and the Ga-atom insertion products of 1,2-epoxybutane. Full geometry optimization of the Ga-centered radicals was carried out using the B3LYP functional,<sup>33</sup> which combines Becke's three-parameter exchange functional<sup>34</sup> with Lee, Yang, and Parr's correlation functional, including both local and nonlocal terms.<sup>35</sup> The split-valence 6-31G(d,p) basis set was used in the geometry optimization of the Ga-centered radicals. The radicals were characterized using frequency analysis. The Ga and H nuclear hfi values were determined from single point calculations using the functional and basis sets indicated in Tables 1–4.

## RESULTS

**Ga/1,2-Epoxybutane/Adamantane.** Ga atoms were co-condensed with 1,2-epoxybutane in an adamantane matrix at 77 K in a metal-atom reactor maintained at <10<sup>−6</sup> Torr. The EPR spectrum of the resulting olive green deposit was recorded at 77 K. The 12 visible transition lines were organized in four groups of three, labeled A, A', B, and B' (Figure 1). Annealing the sample in the cavity of the spectrometer to 210 K resulted in better spectral resolution. In addition, eight new transition lines, labeled C and C', were detected (Figure 2). The transition lines for A/A', B/B', and C/C' show superhyperfine interactions. Representative transition lines for A', B', and C/C' are presented in Figure 3.

Naturally occurring Ga is a mixture of two EPR-active isotopes, <sup>69</sup>Ga (*I* = 3/2) and <sup>71</sup>Ga (*I* = 3/2) with natural abundances of 60.4% and 39.6%, respectively.<sup>36</sup> The ratios of the intensities of the A<sub>3/2</sub>/A<sub>3/2</sub>', A<sub>1/2</sub>/A<sub>1/2</sub>', and A<sub>−3/2</sub>/A<sub>−3/2</sub>' transition lines are roughly equal to the ratio of the natural abundances of <sup>69</sup>Ga/<sup>71</sup>Ga. The same is true for the B/B' and C/C' transitions. This suggests that the <sup>69</sup>Ga- and <sup>71</sup>Ga-containing isotopomers of three different mononuclear Ga species were formed in the reaction. Ga-centered radicals are expected to have four EPR transition lines, namely, *M<sub>I=+3/2</sub>*, *M<sub>I=+1/2</sub>*, *M<sub>I=−1/2</sub>*, and *M<sub>I=−3/2</sub>*. Only three of the transition lines are visible for A, A', B, and B' because the *M<sub>I=−1/2</sub>* region happens to coincide with features belonging to radical D.

**Table 2. Comparison of the Experimental Ga and H hfi Values (MHz) for GaH<sub>2</sub> and HGaCH<sub>3</sub> with Values Calculated Using a Number of Different Density Functionals and the 6-31G(d,p) Basis Set<sup>a</sup>**

	method						expt <sup>b</sup>
	B3LYP/6-31G(d,p)	MPW1PW91/6-31G(d,p)	BP86/6-31G(d,p)	BPW91/6-31G(d,p)	BHandHLYP/6-31G(d,p)	PBE0/6-31G(d,p)	
GaH <sub>2</sub> : Geometry Optimized with B3LYP/6-31G(d,p)							
Ga	2231 (7%)	2247 (8%)	2124 (2%)	2125 (2%)	2332 (7%)	2220 (7%)	2084
H	194 (8%)	164 (18%)	171 (4%)	169 (6%)	192 (7%)	163 (9%)	179
HGaCH <sub>3</sub> : Geometry Optimized with B3LYP/6-31G(d,p)							
Ga	2047 (2%)	2092 (5%)	1955 (2%)	1962 (2%)	2156 (8%)	2074 (4%)	1999
H	199 (2%)	173 (15%)	178 (12%)	176 (12%)	199 (2%)	173 (15%)	203

<sup>a</sup> Values in parentheses are the differences between the experimental and calculated hfi values. <sup>b</sup> Experimental values taken from ref 16.

**Table 3. Comparison of the Experimental Ga and H hfi Values (MHz) for GaH<sub>2</sub> and HGaCH<sub>3</sub> with Values Calculated Using a Number of Different Density Functionals and the 6-311+G(2df,p) or TZVP Basis Set<sup>a</sup>**

	method						expt <sup>b</sup>
	B3LYP/ 6-311+G(2df,p)	MPW1PW91/ 6-311+G(2df,p)	BP86/ 6-311+G(2df,p)	BPW91/ 6-311+G(2df,p)	BHandHLYP/ 6-311+G(2df,p)	PBE0/ TZVP	
GaH <sub>2</sub> : Geometry Optimized with B3LYP/6-31G(d,p)							
Ga	1797 (14%)	1806 (13%)	1709 (18%)	1709 (18%)	1876 (10%)	1733 (17%)	2084
H	200 (12%)	169 (6%)	178 (0.6%)	174 (3%)	197 (10%)	164 (8%)	179
HGaCH <sub>3</sub> : Geometry Optimized with B3LYP/6-31G(d,p)							
Ga	1643 (18%)	1674 (16%)	1567 (22%)	1571 (21%)	1726 (14%)	1621 (19%)	1999
H	212 (4%)	183 (10%)	190 (6%)	188 (7%)	209 (3%)	180 (11%)	203

<sup>a</sup> Values in parentheses are the differences between the experimental and calculated hfi values. <sup>b</sup> Experimental values taken from ref 16.

Spectrum A is best described as a quartet of doublets of triplets centered at  $g = 1.991 \pm 0.003$ , indicating that the unpaired electron interacts with Ga, and two different types of H nuclei. The high- and low-field features were simulated by assuming  $a_{\text{Ga}} = 2255 \pm 12$  MHz,  $a_{\text{H}}(1) = 64$  MHz, and  $a_{\text{H}}(2) = 17$  MHz. Spectrum A' has identical magnetic parameters with the exception that  $g = 1.9917 \pm 0.0002$  and  $a_{\text{Ga}} = 1782 \pm 1$  MHz (Figure 3b). The ratio of the Ga hfi values, A/A', equals 1.27; as expected, this is close to the ratio of the magnetic moments ( $\mu$ ) of <sup>71</sup>Ga and <sup>69</sup>Ga, that is,  $\mu_{^{71}\text{Ga}}/\mu_{^{69}\text{Ga}}$ .<sup>36</sup>

Spectra B and B', two quartets of doublets of doublets of triplets, are centered at  $g = 1.991$  and  $1.992$ , respectively. The unpaired electron interacts with Ga and three different types of H nuclei. Simulation of the high- and low-field transitions gave  $a_{\text{Ga}} = 1623$  MHz,  $a_{\text{H}}(1) = 81$  MHz,  $a_{\text{H}}(1) = 33$  MHz, and  $a_{\text{H}}(2) = 29$  MHz for B and  $a_{\text{Ga}} = 1282$  MHz,  $a_{\text{H}}(1) = 81$  MHz,  $a_{\text{H}}(1) = 33$  MHz, and  $a_{\text{H}}(2) = 29$  MHz for B'. The ratio of the Ga hfi values is B/B' = 1.27. The simulation of the  $M_{I=1/2}$  transition of B' is shown in Figure 3d.

Spectra C and C' can also be described as quartets of doublets of doublets of triplets. The magnetic parameters were found to be  $g = 2.005 \pm 0.002$ ,  $a_{\text{Ga}} = 1033 \pm 9$  MHz,  $a_{\text{H}}(1) = 84$  MHz,  $a_{\text{H}}(1) = 55$  MHz, and  $a_{\text{H}}(2) = 40$  MHz for C and  $g = 2.001 \pm 0.002$ ,  $a_{\text{Ga}} = 818 \pm 8$  MHz,  $a_{\text{H}}(1) = 84$  MHz,  $a_{\text{H}}(1) = 55$  MHz, and  $a_{\text{H}}(2) = 40$  MHz for C' (Figure 3e,f). The ratio of the Ga hfi values in this case is C/C' = 1.26.

**Ga/1,2-Epoxybutane-1,1-d<sub>2</sub>/Adamantane.** When the experiment was repeated with 1,2-epoxybutane-1,1-d<sub>2</sub>, the values of  $a_{\text{Ga}}$  and  $g$  for A, A', B, B', C, and C' did not change significantly.

However, the superhyperfine interaction of the Ga transition lines corresponding to A and A' changed from a doublet of triplets (Figure 4a) to a doublet of unresolved quintets (Figure 4b), indicating that the unpaired electron interacts with a H nucleus and the two D nuclei. The doublet splitting remained unchanged, namely, 64 MHz, and the quintet splitting [ $a_{\text{D}}(2)$ ] was estimated as  $a_{\text{H}}(2)/6.5$ , that is, 17/6.5 or 2.6 MHz. The following magnetic parameters were used to simulate the spectra:  $g = 1.995$ ,  $a_{\text{Ga}} = 2272$  MHz,  $a_{\text{H}}(1) = 64$  MHz, and  $a_{\text{D}}(2) = 2.5$  MHz for A and  $g = 1.994 \pm 0.002$ ,  $a_{\text{Ga}} = 1798$  MHz,  $a_{\text{H}}(1) = 64$  MHz, and  $a_{\text{D}}(2) = 2.5$  MHz for A'.

For B and B' (Figure 5), the superhyperfine spectral pattern of the Ga transition lines was also affected by the isotopic substitution. The presence of the two D nuclei caused a narrowing of the spectral lines (Figure 5b). B and B' are thought to be two quartets of doublets of doublets of quintets. The magnetic parameters used to simulate B were  $g = 1.994$ ,  $a_{\text{Ga}} = 1623$  MHz,  $a_{\text{H}}(1) = 33$  MHz,  $a_{\text{H}}(1) = 81$  MHz, and  $a_{\text{D}}(2) = 4.5$  MHz. The same parameters were used for B', with the exception of  $a_{\text{Ga}} = 1282$  MHz.

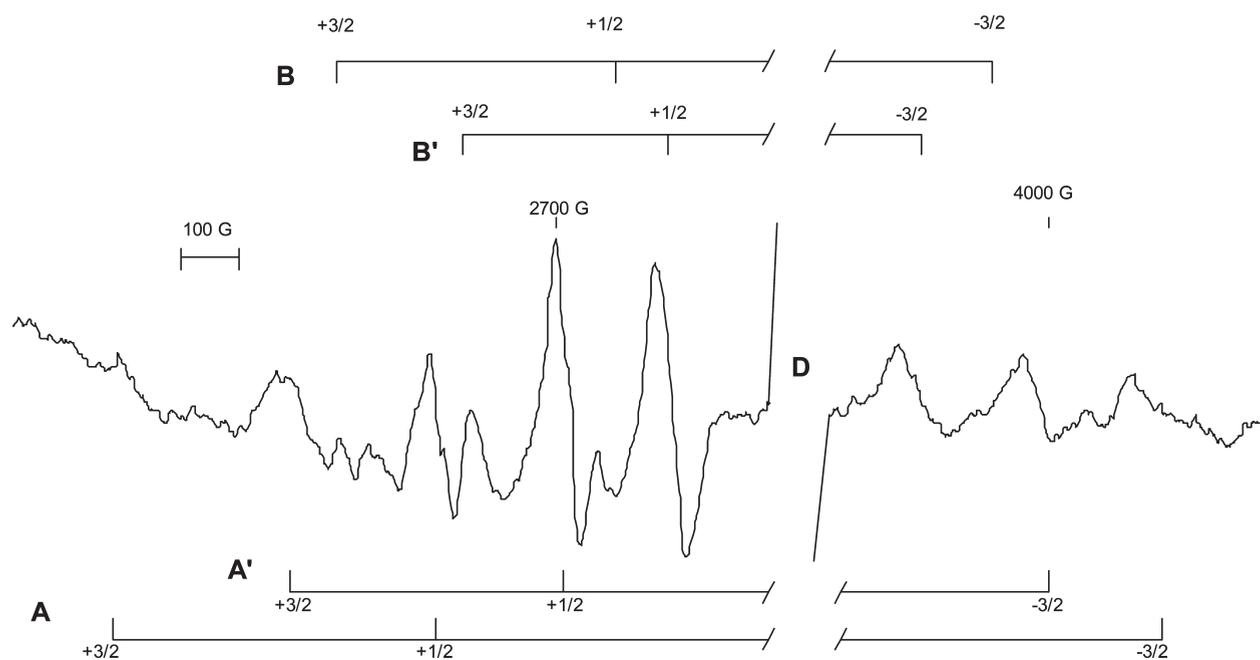
Similarly, the C and C' superhyperfine spectral pattern was altered upon substituting the C<sub>1</sub> hydrogens by deuterium. The doublet of doublets of triplets (Figure 6a) collapsed into a doublet of doublets of unresolved quintets (Figure 6b). The following magnetic parameters were used to simulate spectra C and C':  $g = 2.000$ ,  $a_{\text{H}}(1) = 55$  MHz,  $a_{\text{H}}(1) = 84$  MHz,  $a_{\text{D}}(2) = 6.2$  MHz, and  $a_{\text{Ga}} = 1040 \pm 1$  MHz (for C) or  $a_{\text{Ga}} = 818$  MHz (for C').

**Ga/1,2-Epoxybutane-2-d<sub>1</sub>/Adamantane.** Mononuclear Ga species with  $a_{\text{Ga}}$  and  $g$  values similar, within experimental error,

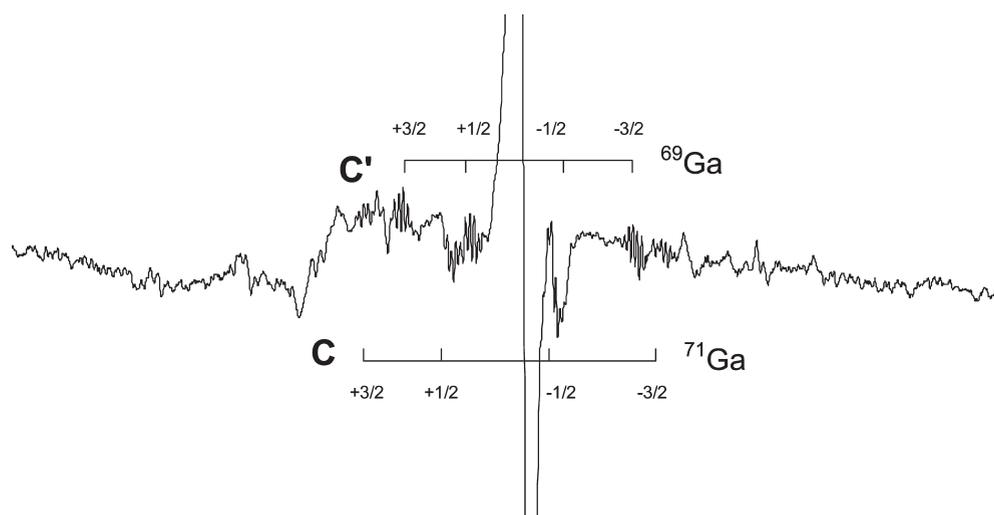
**Table 4.** Calculated Ga and H hf Values and Potential Energies ( $E$ ) for the Lowest-Energy Conformations of the Ga–C<sub>1</sub>–O, Ga–C<sub>2</sub>–O, and Ga–C<sub>1</sub>–C<sub>2</sub> 1,2-Epoxybutane Insertion Products

nuclear hf <sup>d</sup> (MHz)	method						
	MPW1PW91 <sup>a</sup>	BP86 <sup>a</sup>	BPW91 <sup>a</sup>	B3LYP <sup>a</sup>	B3LYP <sup>b</sup>	BHandHLYP <sup>a</sup>	PBE0 <sup>c</sup>
Ga–C <sub>1</sub> –O: Geometry Optimized with B3LYP/6-31G(d,p)							
$a_{\text{Ga}}$	1427	1429	1434	1386	1696	1311	1426
$a_{\text{H}(1)}$	–20	–16	–17	–18	–21	–24	–21
$a_{\text{H}(2)}$	–22	–18	–19	–20	–23	–26	–23
$a_{\text{H}(3)}$	51	58	57	56	56	50	52
$a_{\text{H}(4)}$	–0.93	–0.79	–0.84	–0.82	–0.8	–0.93	–0.89
$a_{\text{H}(5)}$	0.23	0.71	0.63	0.38	0.38	–0.09	0.30
$E$ (hartree)	–2157.4255	–2157.5935	–2157.4842	–2157.3836	–2155.3834	–2157.1549	–2156.8424
Ga–C <sub>2</sub> –O: Geometry Optimized with B3LYP/6-31G(d,p)							
$a_{\text{Ga}}$	976	1056	1057	972	1195	811	982
$a_{\text{H}(1)}$	10	9	9	10	10	12	10
$a_{\text{H}(2)}$	42	46	46	46	45	43	44
$a_{\text{H}(3)}$	–21	–14	–16	–18	–22	–26	–22
$a_{\text{H}(4)}$	69	71	71	74	74	74	69
$a_{\text{H}(5)}$	10	10	10	10	10	10	10
$E$ (hartree)	–2157.4215	–2157.5904	–2157.4813	–2157.3805	–2155.3811	–2157.1510	–2156.8382
Ga–C <sub>1</sub> –C <sub>2</sub> : Geometry Optimized with B3LYP/6-31G(d,p)							
$a_{\text{Ga}}$	379	410	398	392	466	359	374
$a_{\text{H}(1)}$	27	34	33	31	32	23	28
$a_{\text{H}(2)}$	–12	–10	–11	–12	–13	–14	–12
$a_{\text{H}(3)}$	27	34	33	31	32	23	28
$a_{\text{H}(4)}$	4.7	5	5	4.9	4.7	4.7	4.8
$a_{\text{H}(5)}$	2.9	2.8	2.8	2.9	3.1	3.2	2.9
$E$ (hartree)	–2157.3739	–2157.5461	–2157.4367	–2157.3340	–2155.3334	–2157.1004	–2156.7905

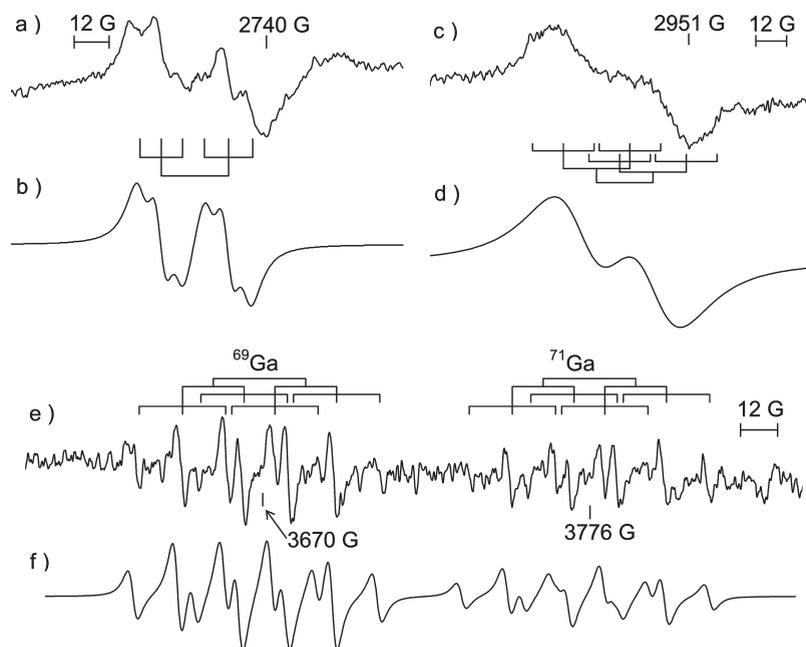
<sup>a</sup> 6-311+G(2df,p). <sup>b</sup> 6-31G(d,p). <sup>c</sup> TZVP. <sup>d</sup> Numbers in parentheses represent H-atom positions as per Chart 1.



**Figure 1.** EPR spectrum recorded at 77 K [ $\nu = 9138$  MHz, microwave power (mp) = 2 mW] of the paramagnetic products (A/A' and B/B') formed in the reaction of Ga atoms with 1,2-epoxybutane in adamantane at 77 K. D is the central feature and is off scale at the gain required to observe A (A') and B (B').



**Figure 2.** EPR spectrum recorded at 190 K ( $\nu = 9114$  MHz,  $mp = 2$  mW) of the paramagnetic products formed in the reaction of Ga atoms with 1,2-epoxybutane in adamantane at 77 K. In addition to the transitions for A, A', B, and B', eight new transitions labeled C and C' developed upon annealing the sample. The center of the spectrum is 3050 G, and the sweep width is 4000 G. The central feature is off scale at the gain required to observe C and C'.

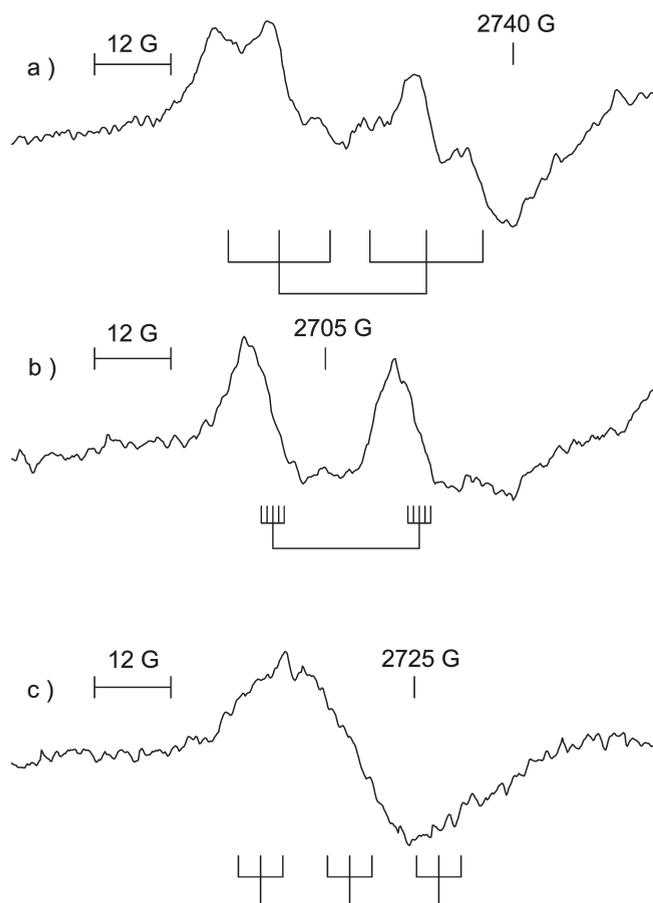


**Figure 3.** Representative transition lines ( $mp = 2$  mW) of species A', B', C, and C' formed in the Ga–1,2-epoxybutane reaction. (a)  $M_{I=1/2}$  line of species A' ( $\nu = 9113$  MHz,  $T = 140$  K); (b) simulation of the spectral line assuming the interaction of the unpaired electron of species A' with three H nuclei, one with  $a_H = 64$  MHz and two with  $a_H = 17$  MHz; (c)  $M_{I=1/2}$  line of species B' ( $\nu = 9113$  MHz,  $T = 140$  K); (d) simulation of the spectral line assuming the interaction of the unpaired electron of species B' with four H nuclei, one with  $a_H = 81$  MHz, one with  $a_H = 33$  MHz, and two with  $a_H = 29$  MHz; (e)  $M_{I=-3/2}$  line of species C and C' ( $\nu = 9116$  MHz,  $T = 190$  K); (f) simulation of the spectral lines of C and C' assuming the interaction of the unpaired electron with four H nuclei, one with  $a_H = 84$  MHz, one with  $a_H = 55$  MHz, and two with  $a_H = 40$  MHz.

to those of species A/A', B/B', and C/C', reported above, were observed in the Ga-atom–1,2-epoxybutane-2- $d_1$  reaction. However, the superhyperfine spectral pattern for Ga transitions of A/A', B/B', and C/C' was modified as a consequence of deuterium substitution at C<sub>2</sub>. The transition line for A' (Figure 4c) was simulated assuming that the unpaired electron interacts with two H nuclei and one D nucleus with  $g = 1.9930 \pm 0.0003$ ,  $a_{Ga} = 1786$  (A'),  $a_H(2) = 16.7$  MHz, and  $a_D(1) = 9.8$  MHz. The transitions for species B' (Figure 5c) were simulated using the magnetic

parameters  $g = 1.993$ ,  $a_{Ga} = 1277$  MHz,  $a_H(1) = 81$  MHz,  $a_H(2) = 29$  MHz, and  $a_D(1) = 5.1$  MHz. The transitions for species C/C', sextets of doublets of triplets of triplets (Figure 6c), were simulated using the magnetic parameters  $g = 2.002$ ,  $a_{Ga} = 1044$  MHz (C),  $a_{Ga} = 820$  MHz (C'),  $a_H(1) = 84$  MHz,  $a_H(2) = 40$  MHz, and  $a_D(1) = 3.0$  MHz.

**Central Feature.** The EPR spectrum of the Ga–1,2-epoxybutane reaction mixture recorded at 160 K is dominated by four strong features centered at  $g = 2.001$  and separated by  $\sim 59$  MHz

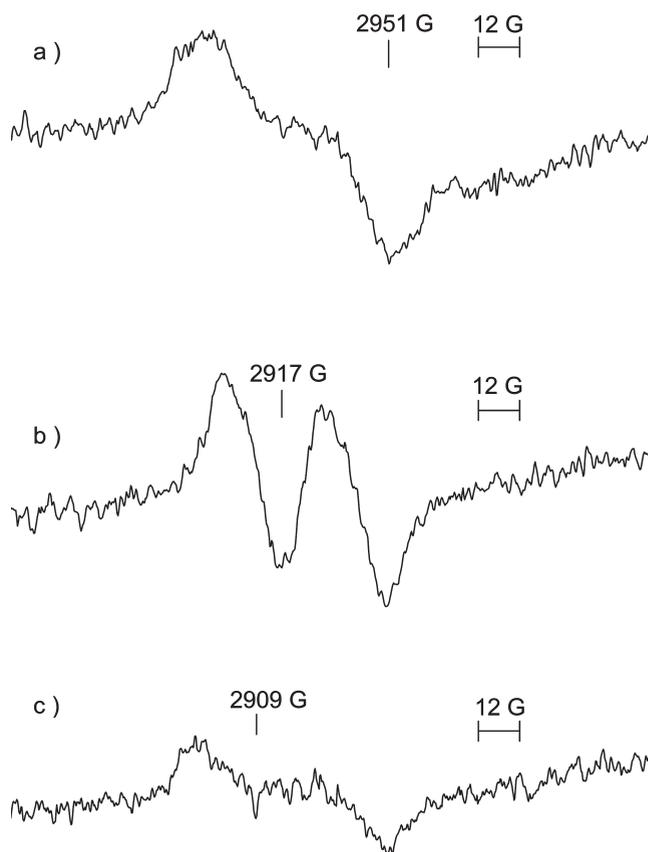


**Figure 4.** Comparison of the Ga  $M_{I=1/2}$  transition line of species A' formed in (a) the Ga-1,2-epoxybutane reaction ( $\nu = 9113$  MHz, mp = 2 mW,  $T = 140$  K), (b) the Ga-1,2-epoxybutane-1,1- $d_2$  reaction ( $\nu = 9115$  MHz, mp = 2 mW,  $T = 140$  K), and (c) the Ga-1,2-epoxybutane-2- $d_1$  reaction ( $\nu = 9116$  MHz, mp = 2 mW,  $T = 140$  K).

(Figure 7a). The spectrum was simulated (Figure 7b) assuming one H atom with  $a_H = 56.5$  MHz, two H atoms with  $a_H = 61.9$  MHz, and two H atoms with  $a_H = 17.9$  MHz. Isotopic substitution at  $C_1$  and  $C_2$  of 1,2-epoxybutane caused the EPR spectrum of the central radical to change, suggesting that the unpaired electron in the two isotomeric radicals interacts with the  $C_1$  and  $C_2$  hydrogen nuclei. A triplet pattern results when  $C_2$  is deuterated (Figure 7c). Simulation of the spectrum was accomplished assuming one D atom with  $a_D = 8.69$  MHz, two H atoms with  $a_H = 61.9$  MHz, and two H atoms with  $a_H = 17.9$  MHz (Figure 7d). Deuteration at  $C_1$  (Figure 7e) results in a spectrum that can be simulated assuming one H atom with  $a_H = 56.5$  MHz, two H atoms with  $a_H = 61.9$  MHz, and two D atoms with  $a_D = 2.75$  MHz (Figure 7f).

## COMPUTATIONAL RESULTS

Full geometry optimization of GaH<sub>2</sub> and HGaCH<sub>3</sub> was carried out using the 6-31G(d,p) basis set and the B3LYP functional,<sup>33</sup> which combines Becke's three-parameter exchange functional<sup>34</sup> with Lee, Yang, and Parr's correlation functional, including both local and nonlocal terms.<sup>35</sup> The values for the Ga and H hyperfine interactions determined from single-point calculations using the B3LYP functional and a number of different basis sets, namely, 6-31G(d,p), 6-311+G(d,p), 6-311+G(df,p), 6-311+G(2df,p),

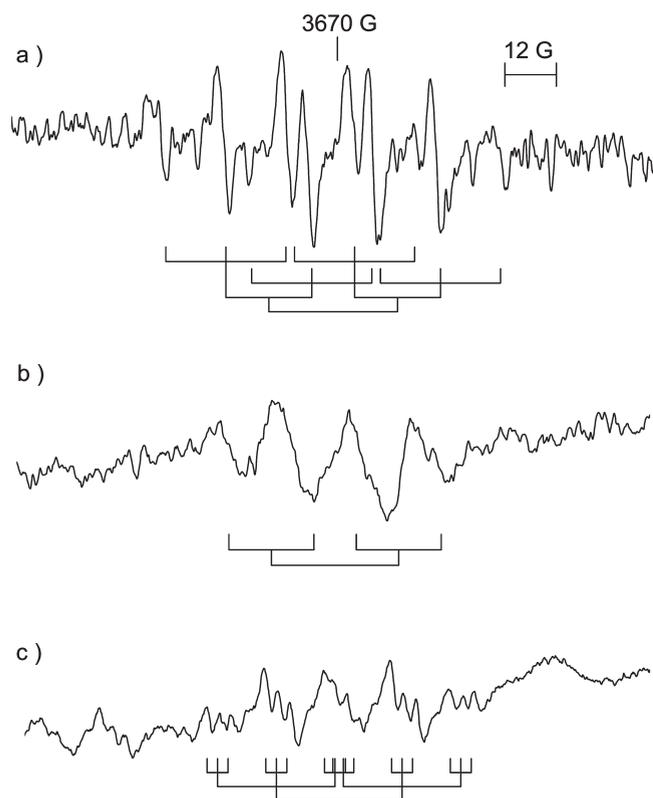


**Figure 5.** Comparison of the Ga  $M_{I=1/2}$  transition line of species B' formed in (a) the Ga-1,2-epoxybutane reaction ( $\nu = 9113$  MHz, mp = 2 mW,  $T = 140$  K), (b) the Ga-1,2-epoxybutane-1,1- $d_2$  reaction ( $\nu = 9115$  MHz, mp = 2 mW,  $T = 140$  K), and (c) the Ga-1,2-epoxybutane-2- $d_1$  reaction ( $\nu = 9116$  MHz, mp = 2 mW,  $T = 140$  K).

and 6-311+G(3df,p), are reported in Table 1. The best agreement with the experimental values (differences of  $\sim 7\%$  for GaH<sub>2</sub> and 2% for HGaCH<sub>3</sub>) was given by the B3LYP/6-31G(d,p) calculation. The hfi values calculated using the 6-311+G(d,p), 6-311+G(df,p), 6-311+G(2df,p), and 6-311+G(3df,p) basis sets did not change significantly; specifically, the differences for the Ga hfi were 14% for GaH<sub>2</sub> and 18% for HGaCH<sub>3</sub>, whereas those for the H hfi were 12% for GaH<sub>2</sub> and 4% for HGaCH<sub>3</sub>.

The Ga and H hfi values were calculated using a number of different functionals (i.e., B3LYP,<sup>33,34,35</sup> MPW1PW91,<sup>37</sup> BP86,<sup>38,39</sup> BPW91,<sup>38,40</sup> BHandHLYP,<sup>35,38,39,41</sup> and PBE0<sup>42</sup>) with the 6-31G(d,p), 6-311+G(2df,p), or TZVP basis sets, Tables 2 and 3. In the case of GaH<sub>2</sub>, the Ga and H hfi values calculated using the functionals listed above and the 6-31G(d,p) basis set vary from the experimental values by 2–8% and 4–18%, respectively; the best agreement was obtained with the BP86 functional. For HGaCH<sub>3</sub>, the Ga and H hfi values calculated using the 6-31G(d,p) basis set differ by 2–8% and 2–15%, respectively, depending on the functional. The values calculated with the B3LYP functional are in closest agreement with the experimental values.

Calculation of the Ga and H hfi values for GaH<sub>2</sub> using the 6-311+G(2df,p) basis set resulted in values that varied by 10–18% and 0.6–12%, respectively (Table 3). The BHandHLYP functional gave the Ga hfi that best agreed with the experimental value, whereas the BP86 functional was best for the H hfi. In the case of HGaCH<sub>3</sub>, values for the Ga hfi, calculated using the



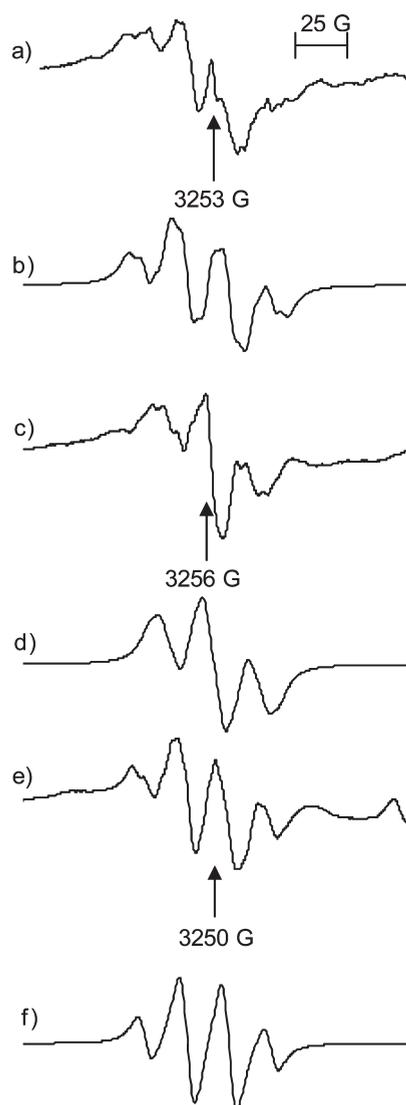
**Figure 6.** Comparison of the Ga  $M_I = -3/2$  transition line of species  $C'$  formed in (a) the Ga-1,2-epoxybutane reaction ( $\nu = 9116$  MHz,  $mp = 2$  mW,  $T = 190$  K), (b) the Ga-1,2-epoxybutane-1,1- $d_2$  reaction ( $\nu = 9114$  MHz,  $mp = 2$  mW,  $T = 160$  K), and (c) the Ga-1,2-epoxybutane-2- $d_1$  reaction ( $\nu = 9116$  MHz,  $mp = 2$  mW,  $T = 170$  K).

6-311+G(2df,p) basis set, deviated from the experimental value by 14–22%; the calculated values for the H hfi varied by 3–11%. The best agreement between the experimental and the calculated hfi, for both Ga and H, was obtained with the BHandHLYP functional.

The geometries of a number of conformers of the Ga- $C_1$ -O, Ga- $C_2$ -O, and the Ga- $C_1$ - $C_2$  1,2-epoxybutane insertion products were optimized using the B3LYP functional and the split-valence 6-31G(d,p) basis set. The optimized geometries of the lowest-energy conformations of the Ga- $C_1$ -O, Ga- $C_2$ -O, and Ga- $C_1$ - $C_2$  1,2-epoxybutane insertion products are shown in Chart 1. The calculated potential energies suggest that the  $C_1$ -O insertion product is more stable than the  $C_2$ -O insertion product by about 2 kcal and more stable than the  $C_1$ - $C_2$  insertion product by 29 kcal (Table 4). The Ga and H hfi values calculated for the lowest-energy conformations of the Ga-epoxybutane insertion products are presented in Table 4. The variation in the Ga hfi calculated using a number of different functionals is about 8% for both the  $C_1$ -O and  $C_1$ - $C_2$  insertion products and 12% for the  $C_2$ -O insertion product. In general, the order found was  $a_{Ga}(C_1-O) > a_{Ga}(C_2-O) > a_{Ga}(C_1-C_2)$ , with a 30% decrease in the Ga hfi of  $C_2$ -O insertion product compared to that of  $C_1$ -O insertion product and a 59% decrease in the  $C_1$ - $C_2$  insertion product Ga hfi with respect to that of  $C_2$ -O insertion product.

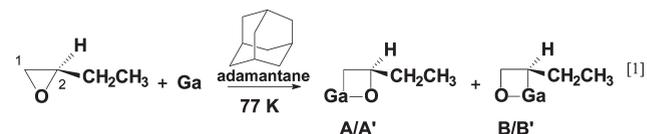
## DISCUSSION

Three  $^{69/71}\text{Ga}$ -centered radicals, A/A', B/B', and C/C', were detected in the EPR analysis of the paramagnetic products formed



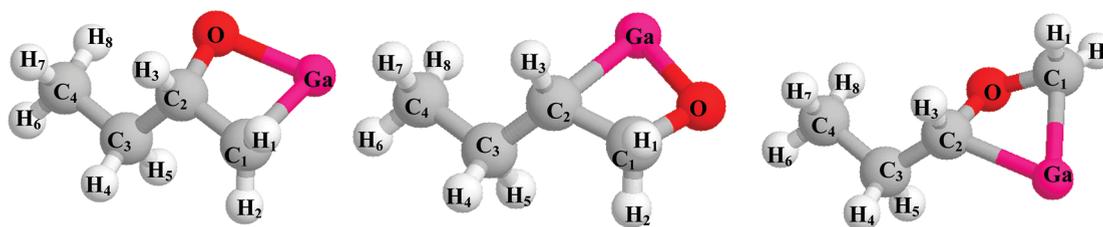
**Figure 7.** Central features ( $g = 2.001$ ) of the low-temperature EPR spectra for the Ga-1,2-epoxybutane reaction mixture, as well as the corresponding simulations: (a) 1,2-epoxybutane ( $\nu = 9116$  MHz, 160 K,  $mp = 2$  mW); (b) simulation assuming one H with  $a_H = 56.5$  MHz, two H with  $a_H = 61.9$  MHz, and two H with  $a_H = 17.9$  MHz; (c) 1,2-epoxybutane-2- $d_1$  ( $\nu = 9113$  MHz, 160 K,  $mp = 2$  mW); (d) simulation assuming one D with  $a_D = 8.69$  MHz, two H with  $a_H = 61.9$  MHz, and two H with  $a_H = 17.9$  MHz; (e) 1,2-epoxybutane-1,1- $d_2$  ( $\nu = 9114$  MHz, 160 K,  $mp = 2$  mW); (f) simulation assuming one H with  $a_H = 56.5$  MHz, two H with  $a_H = 61.9$  MHz, and two D with  $a_D = 2.75$  MHz.

in the  $^{69/71}\text{Ga}$ -atom-1,2-epoxybutane reaction in adamantane at 77 K (eq 1). The magnetic parameters extracted from the EPR spectra are summarized in Table 5.



Repetition of the  $^{69/71}\text{Ga}$ -atom reactions with the deuterated substrates 1,2-epoxybutane-1,1- $d_2$  and 1,2-epoxybutane-2- $d_1$  resulted in products with  $a_{Ga}$  values similar to those of A/A', B/B', and C/C' but with different spectral patterns. This information

Chart 1



C <sub>1</sub> -O Insertion Product		C <sub>2</sub> -O Insertion Product		C <sub>1</sub> -C <sub>2</sub> Insertion Product	
C <sub>1</sub> -Ga	2.104 Å	C <sub>2</sub> -Ga	2.170 Å	C <sub>1</sub> -Ga	2.120 Å
Ga-O	1.872 Å	Ga-O	1.876 Å	C <sub>2</sub> -Ga	2.138 Å
C <sub>2</sub> -O	1.439 Å	C <sub>1</sub> -O	1.427 Å	C <sub>2</sub> -O	1.424 Å
C <sub>1</sub> -C <sub>2</sub>	1.544 Å	C <sub>1</sub> -C <sub>2</sub>	1.540 Å	C <sub>1</sub> -O	1.426 Å
C <sub>2</sub> -C <sub>3</sub>	1.531 Å	C <sub>2</sub> -C <sub>3</sub>	1.511 Å	C <sub>2</sub> -C <sub>3</sub>	1.509 Å
C <sub>3</sub> -C <sub>4</sub>	1.530 Å	C <sub>3</sub> -C <sub>4</sub>	1.532 Å	C <sub>3</sub> -C <sub>4</sub>	1.537 Å
<C <sub>2</sub> OGa	94.3 °	<C <sub>1</sub> OGa	95.6 °	<C <sub>2</sub> OC <sub>1</sub>	110.2 °
<C <sub>1</sub> GaO	74.3 °	<C <sub>2</sub> GaO	73.2 °	<C <sub>1</sub> GaC <sub>2</sub>	66.6 °
<GaC <sub>1</sub> C <sub>2</sub>	82.7 °	<GaC <sub>2</sub> C <sub>1</sub>	81.4 °	<GaC <sub>1</sub> O	83.9 °
<C <sub>1</sub> C <sub>2</sub> O	107.7 °	<C <sub>2</sub> C <sub>1</sub> O	109.5 °	<GaC <sub>2</sub> O	83.2 °
<C <sub>1</sub> C <sub>2</sub> C <sub>3</sub>	112.5 °	<C <sub>1</sub> C <sub>2</sub> C <sub>3</sub>	119.5 °	<GaC <sub>2</sub> C <sub>3</sub>	126.8 °
<C <sub>2</sub> C <sub>3</sub> C <sub>4</sub>	112.6 °	<C <sub>2</sub> C <sub>3</sub> C <sub>4</sub>	114.0 °	<C <sub>2</sub> C <sub>3</sub> C <sub>4</sub>	114.0 °
D(C <sub>2</sub> OGaC <sub>1</sub> )	6.8 °	D(C <sub>2</sub> GaOC <sub>1</sub> )	-3.6 °	D(C <sub>2</sub> OC <sub>1</sub> Ga)	-36.7 °

**Table 5. Summary of the EPR Parameters of the Mononuclear <sup>69</sup>Ga Products of the Reaction of Ga with 1,2-Epoxybutane and Its Isotopomers in Adamantane at 77 K<sup>a</sup>**

1,2-Epoxybutane					
	<i>a</i> <sub>Ga</sub> (MHz)	<i>a</i> <sub>H(1)</sub> (MHz)	<i>a</i> <sub>H(2)</sub> (MHz)	<i>a</i> <sub>H(1)<sup>b</sup></sub> (MHz)	
A'	1782	64	17	—	1.992
B'	1282	33	29	81	1.992
C'	818	55	40	84	2.001
1,2-Epoxybutane-1,1- <i>d</i> <sub>2</sub>					
	<i>a</i> <sub>Ga</sub> (MHz)	<i>a</i> <sub>H(1)</sub> (MHz)	<i>a</i> <sub>D(2)</sub> (MHz)	<i>a</i> <sub>H(1)</sub> (MHz)	<i>g</i> <sub>iso</sub>
A'	1798	64	2.5	—	1.994
B'	1282	33	4.5	81	1.994
C'	818	55	6.2	84	2.000
1,2-Epoxybutane-2- <i>d</i> <sub>1</sub>					
	<i>a</i> <sub>Ga</sub> (MHz)	<i>a</i> <sub>D(1)</sub> (MHz)	<i>a</i> <sub>H(2)</sub> (MHz)	<i>a</i> <sub>H(1)</sub> (MHz)	<i>g</i> <sub>iso</sub>
A'	1786	9.8	16.7	—	1.993
B'	1277	5.1	29	81	1.993
C'	820	3.0	40	84	2.002

<sup>a</sup> Numbers of nuclei indicated in parentheses. <sup>b</sup> This hfi corresponds to one of the hydrogen atoms attached to C<sub>3</sub>.

indicates that the unpaired electron residing on <sup>69/71</sup>Ga interacts with the hydrogen nuclei on both C<sub>1</sub> and C<sub>2</sub>. For A/A', deuteration at C<sub>1</sub> causes collapse of the triplet splitting, meaning that the hfi for H<sub>1</sub> and H<sub>2</sub> is 17 MHz, whereas labeling C<sub>2</sub> with deuterium causes the doublet splitting to collapse, suggesting that the hfi for H<sub>3</sub> is 64 MHz. Similarly, for B/B' and C/C', the spectral pattern changes upon use of the deuterated analogues of 1,2-epoxybutane, also indicating that these hydrogen nuclei interact with the unpaired electron on the Ga nucleus. Deuteration at C<sub>1</sub> results in a change in the triplet splitting, indicating that the hfi for H<sub>1</sub> and

H<sub>2</sub> is 29 MHz for B/B' and 40 MHz for C/C'. Similarly, deuteration at C<sub>2</sub> affects the doublet splitting, showing that the hfi for H<sub>3</sub> in B/B' and C/C' is 33 and 55 MHz, respectively. The large H hfi of 81 MHz observed for B/B' and 84 MHz observed for C/C' must be due to a hydrogen nucleus of the alkyl chain, that is, a hydrogen attached to C<sub>3</sub>. This is consistent with the fact that the value does not change upon deuteration at C<sub>1</sub> and C<sub>2</sub>.

In an earlier study,<sup>29</sup> Al atoms were found to react with 1,2-epoxybutane to give the C<sub>1</sub>-O and C<sub>2</sub>-O Al-atom insertion products. The EPR magnetic parameters for these divalent mononuclear Al species were determined to be *g* = 2.001, *a*<sub>Al</sub> = 855 MHz, *a*<sub>H(1)</sub> = 29 MHz, and *a*<sub>H(2)</sub> = 14 MHz for the C<sub>1</sub>-O insertion product and *g* = 2.000, *a*<sub>Al</sub> = 739 MHz, *a*<sub>H(1)</sub> = 15 MHz, *a*<sub>H(2)</sub> = 19 MHz, and *a*<sub>H(1)</sub> = 38 MHz for the C<sub>2</sub>-O insertion product. The Al hfi for the C<sub>1</sub>-O Al-atom species is the same as that observed for the Ga-atom species labeled A/A'. This would suggest that A/A' are the <sup>71</sup>Ga/<sup>69</sup>Ga isotopomers of the C<sub>1</sub>-O insertion product, CH<sub>3</sub>CH<sub>2</sub>CHCH<sub>2</sub>GaO. The species corresponding to B/B' and C/C' have H hfi values that follow the same trend as the Al-atom C<sub>2</sub>-O insertion product. The Ga hfi for B/B' differs from the Ga-atom C<sub>2</sub>-O insertion product by 28%, whereas that for C/C' differs by 54%. Either B/B' or C/C' could be the Ga-atom C<sub>2</sub>-O insertion product, as the information available is not sufficient to make a definitive assignment. Therefore, molecular orbital calculations were carried out to try to resolve the problem.

We first tested the ability of various density functional methods and basis sets to predict the nuclear hfi values of two divalent Ga compounds, namely, GaH<sub>2</sub> and HGaCH<sub>3</sub>. The deviation of the calculated Ga hfi from the experimental value ranges from 2% to 18% for GaH<sub>2</sub> and from 2% to 22% for HGaCH<sub>3</sub>, depending on the theoretical model used.

Next, the nuclear hfi values of the C<sub>1</sub>-O and C<sub>2</sub>-O Ga-atom insertion products were calculated. In comparing the <sup>69</sup>Ga hfi values of A', B', and C' to those calculated for the insertion

**Table 6.** Comparison of the Nuclear hfi Values (MHz),  $a_M$  and  $a_H$ , and the Corresponding Unpaired Spin Densities ( $\rho_{ns}$ ) for a Number of Related Group 13 Radicals

radical	$a_M$	$a_H$	$M\rho_{ns}^a$	$M\rho_{ns} + \Sigma H\rho_{1s}^b$	conditions
AlH <sub>2</sub>	834 (Al)	128 (2H)	0.21	0.39	neon at 4 K <sup>c</sup>
GaH <sub>2</sub>	2085 ( <sup>69</sup> Ga)	179 (2H)	0.17	0.42	neon at 4 K <sup>c</sup>
AlCH <sub>3</sub>	772 (Al)	152 (1H)	0.20	0.31	neon at 4 K <sup>c</sup>
HGaCH <sub>3</sub>	1999 ( <sup>69</sup> Ga)	203 (1H)	0.16	0.30	neon at 4 K <sup>c</sup>
CH <sub>3</sub> CH <sub>2</sub> $\overline{\text{CHCH}_2\text{AlO}}$	855 (Al)	28.8 (1H), 13.6 (2H)	0.22	0.26	adamantane at 77 K <sup>d</sup>
CH <sub>3</sub> CH <sub>2</sub> $\overline{\text{CHCH}_2\text{OAl}}$	739 (Al)	37.8 (1H), 18.5 (2H), 15.1 (1H)	0.19	0.25	adamantane at 77 K <sup>d</sup>
CH <sub>3</sub> CH <sub>2</sub> $\overline{\text{CHCH}_2\text{GaO}}$	1782 ( <sup>69</sup> Ga)	64 (1H), 17 (2H)	0.15	0.22	adamantane at 77 K <sup>e</sup>
CH <sub>3</sub> CH <sub>2</sub> $\overline{\text{CHCH}_2\text{OGa}}$ (I)	1282 ( <sup>69</sup> Ga)	81 (1H), 29 (2H), 33 (1H)	0.10	0.22	adamantane at 77 K <sup>e</sup>
CH <sub>3</sub> CH <sub>2</sub> $\overline{\text{CHCH}_2\text{OGa}}$ (II)	818 ( <sup>69</sup> Ga)	84 (1H), 40 (2H), 55 (1H)	0.07	0.22	adamantane at 77 K <sup>e</sup>

<sup>a</sup> Spin density obtained by dividing the hfi of Al or Ga by the electron atomic parameter, namely, 3911 MHz for the Al 3s orbital or 12210 MHz for the Ga 4s orbital.<sup>36</sup> <sup>b</sup> Sum of the unpaired s spin density due to the metal ( $M\rho_{ns}$ ) and the H nuclei ( $H\rho_{1s}$ ).  $H\rho_{1s} = \Sigma a_H/1420$  MHz.<sup>36</sup> <sup>c</sup> Taken from ref 16. <sup>d</sup> Taken from ref 29. <sup>e</sup> This work.

products; A' was found to correspond best to the C<sub>1</sub>–O insertion product. The average deviation from the experimental Ga hfi is within the range found for GaH<sub>2</sub> and HGaCH<sub>3</sub>, namely, 19%. In addition, the calculated H hfi values for H<sub>1</sub>, H<sub>2</sub>, H<sub>3</sub>, and H<sub>4</sub> of the C<sub>1</sub>–O insertion product correlate best with the experimental values obtained by spectral simulation of A'. This finding supports the analysis based on the Al–epoxybutane system presented above.

The <sup>69</sup>Ga hfi calculated for the C<sub>2</sub>–O insertion product matches that of B' best, with an average deviation, 21%, that is close to the error range determined for GaH<sub>2</sub> and HGaCH<sub>3</sub>. The calculated hfi for H<sub>4</sub> of the C<sub>2</sub>–O insertion product, 72 MHz, correlates best with the experimental value obtained by spectral simulation of B'. Although the difference between the <sup>69</sup>Ga hfi of C' and that calculated for the C<sub>2</sub>–O insertion product is about 23%, the calculated value is larger than the experimental value. As stated previously, the calculated Ga hfi is underestimated by all of the DFT methods with the exception of the calculation using the B3LYP method and the 6-31G(d,p) basis set. The calculated <sup>69</sup>Ga hfi values for the C<sub>1</sub>–O and C<sub>2</sub>–O insertion products differ on average by about 30%. This is consistent with the difference between the experimental Ga hfi values for A' and B' (i.e., 28%), whereas the difference in experimental Ga hfi values for A' and C' (i.e., 54%) is much larger. We are therefore confident that the Ga-atom C<sub>2</sub>–O insertion product, CH<sub>3</sub>CH<sub>2</sub>CHCH<sub>2</sub>OGa, is the carrier of spectrum B (B').

Because the unpaired electron in C/C' interacts with both the C<sub>1</sub> and C<sub>2</sub> hydrogens, the nuclear hfi for the Ga–C<sub>1</sub>–C<sub>2</sub> insertion product was calculated. The difference between the <sup>69</sup>Ga hfi for C' and that calculated for the C<sub>1</sub>–C<sub>2</sub> insertion product is 51%, which is greater than those observed for the C<sub>1</sub>–O insertion product and A' and for the C<sub>2</sub>–O insertion product and B'. In addition, the H hfi values calculated for the C<sub>1</sub>–C<sub>2</sub> insertion product are much smaller than those observed for C'.

As suggested previously, the fact that the magnitude of the hfi for the H atoms in C/C' changes in similar fashion to those of CH<sub>3</sub>CH<sub>2</sub>CHCH<sub>2</sub>OGa upon isotopic substitution indicates that the connectivity is the same in both B/B' and C/C'. Having said this, there must be some factor that perturbs the Ga causing a 36% decrease in the Ga hfi. In Al-atom systems involving reactants with lone pairs, there is evidence for the formation of complexed insertion products. For example, in the reaction of Al atoms with cyclopropylamine (CpNH<sub>2</sub>), the complexed insertion product CpNH(AlH):CpNH<sub>2</sub> was detected.<sup>43</sup> Complexation

causes the Al and H hfi values to decrease by 11–13% and 47–53%, respectively. The <sup>69</sup>Ga hfi of the complexed C<sub>2</sub>–O insertion product, CH<sub>3</sub>CH<sub>2</sub>CHCH<sub>2</sub>OGa:CH<sub>3</sub>CH<sub>2</sub>CHCH<sub>2</sub>O, calculated at the B3LYP level of theory with a 6-311(2df,p) basis set, was larger (1622 MHz) than the calculated hfi of the uncomplexed species (972 MHz), ruling this out as a possible explanation for the perturbation. Seeing that C appears at 190 K, small conformational changes in CH<sub>3</sub>CH<sub>2</sub>CHCH<sub>2</sub>OGa might be responsible for the observation of the new quartet with a smaller Ga hfi. Conformational changes have been shown to influence the magnitude of the Al hfi in Al-atom-centered radicals. For instance, the Al hfi values for *cis*- and *trans*-CH<sub>3</sub>OAlCH<sub>3</sub> vary by 14%.<sup>28</sup> Ring strain was also found to contribute to the magnitude of the Al hfi. More specifically, the Al hfi was found to increase from 739 or 855 to 953 MHz in going from a four- to a five-membered aluminaoxtane.<sup>28,29</sup> Preliminary DFT calculations involving slight changes in the C<sub>2</sub>–Ga–O bond angle of the C<sub>2</sub>–O insertion product yielded large decreases in the calculated hfi. The perturbation of the Ga in the C<sub>2</sub>–O insertion product imposed by the adamantane matrix is a possible explanation for the development of a new quartet (C/C') with a smaller Ga hfi value but similar H hfi values and response to isotopic labeling as that found for the C<sub>2</sub>–O insertion product.

The nuclear hfi values of the Ga-atom–C<sub>1</sub>–O and Ga-atom–C<sub>2</sub>–O insertion products can be compared to those obtained for the corresponding Al insertion products, as well as to the magnetic parameters for a number of Ga-containing radicals studied under matrix-isolation conditions (Table 6). The Al and Ga spin densities,  $\rho_{3s}$  and  $\rho_{4s}$ , respectively, can be estimated by dividing the isotropic hfi by the electron atomic parameter, namely, 3911 MHz for the Al 3s orbital or 12210 MHz for the Ga 4s orbital.<sup>36</sup> The  $\rho_{ns}$  values are greater for the Al-containing radicals, indicating that their semiooccupied molecular orbital (SOMO) has higher s character. This is reflected in the increase in the values of H hfi in going from the Al species to the Ga analogues. It is interesting that the sum of the  $H\rho_{1s}$  and the  $M\rho_{ns}$  values for the alumina and gallaoxtanes lie within a narrow range, namely, between 0.22 and 0.26. The values for unstrained group 13 radicals are higher; specifically, for GaH<sub>2</sub> and HGaCH<sub>3</sub>, the values are 0.42 and 0.45, respectively, and for AlH<sub>2</sub> and AlCH<sub>3</sub>, they are 0.31 and 0.30, respectively. This is consistent with the change in hybridization in going from a small cyclic system to one that is unstrained.

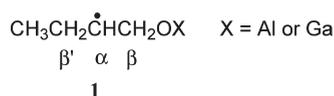
**Table 7. Comparison of the H hfi Values for  $\beta$ -Substituted Isopropyl Radicals**

radical	T (K)	$\alpha$ $a_{\text{H}}$ (MHz)	$\beta$ $a_{\text{H}}$ (MHz)	$\beta'$ $a_{\text{H}}$ (MHz)	solvent <sup>a</sup>
CH <sub>3</sub> CH <sub>2</sub> (•CH)CH <sub>3</sub>	183	61.4	76.2	69.0	cyclopropane
CH <sub>3</sub> OCH <sub>2</sub> (•CH)CH <sub>3</sub>	185	61.4	66.9	70.5	cyclopropane
CF <sub>3</sub> OCH <sub>2</sub> (•CH)CH <sub>3</sub>	173	63.6	46.4	71.6	freon
CH <sub>3</sub> SCH <sub>2</sub> (•CH)CH <sub>3</sub>	192	59.9	36.3	67.6	cyclopropane
CF <sub>3</sub> SCH <sub>2</sub> (•CH)CH <sub>3</sub>	171	60.0	33.2	68.1	freon
GaOCH <sub>2</sub> (•CH)CH <sub>2</sub> CH <sub>3</sub>	160	56.5	17.9	61.9	adamantane <sup>b</sup>

<sup>a</sup>Taken from ref 44. <sup>b</sup>This work.

The ratio of the intensities of the transition lines for the two gallaoxetanes is approximately equal, as was the case in the Al-1,2-epoxybutane experiment.<sup>29</sup> This suggests that the Ga atom interacts with the 1,2-epoxybutane in such a way as to allow for equal insertions into the C<sub>1</sub>-O and C<sub>2</sub>-O bonds. Acid-catalyzed ring-opening of asymmetric epoxides gives a mixture of ring-opened product due to the coordination of the O with the proton. In a similar fashion, Ga atoms could coordinate to the O of the 1,2-epoxybutane, facilitating the cleavage of either the C<sub>1</sub>-O or C<sub>2</sub>-O bond followed by oxidative addition to the metal center.

The central features produced when Ga atoms react with 1,2-epoxybutane and its isotopomers, 1,2-epoxybutane-2-*d*<sub>1</sub> and 1,2-epoxybutane-1,1-*d*<sub>2</sub>, are similar to those obtained at low temperatures in an earlier study involving the Al-1,2-epoxybutane reaction.<sup>29</sup> The good spectral resolution obtained in the present study allowed for simulation of the spectra and extraction of the H hfi values, specifically, one H atom with  $a_{\text{H}} = 56.5$  MHz, two H atoms with  $a_{\text{H}} = 61.9$  MHz, and two H atom with  $a_{\text{H}} = 17.9$  MHz. These H hfi values are consistent with an alkyl radical resulting from ring-opening of 1,2-epoxybutane at C<sub>2</sub>-O (1).



This radical would be the precursor for the formation of the C<sub>2</sub>-O gallaoxetane. Isotopic substitution at C<sub>1</sub> and C<sub>2</sub> indicates that the  $\alpha$ -H hfi is 56.5 MHz, the  $\beta$ -H hfi is 17.9 MHz, and the  $\beta'$ -H hfi is 61.9 MHz. Unlike the Al-1,2-epoxybutane study, there is no evidence for the formation of the *cis*-1-methallyl radical upon annealing the sample in the cavity of the EPR spectrometer.

These H hfi values can be compared to values reported for a number of related  $\beta$ -substituted isopropyl radicals (Table 7).<sup>44</sup> Whereas the  $\alpha$ -H and  $\beta'$ -H hfi values remain relatively constant for the different radicals, the  $\beta$ -H hfi values vary significantly. Chen and Kochi<sup>44</sup> attributed these large differences to the nature of the  $\beta$  substituents. Electronegative groups tend to cause a significant decrease in the magnitude of the  $\beta$ -H hfi. In addition, the authors suggest that  $\beta$  substituents imposing restricted rotation about the C <sub>$\alpha$</sub> -C <sub>$\beta$</sub>  bond that results in distortion at C <sub>$\beta$</sub>  cause the values of the  $\beta'$ -H hfi to decrease.

It is worth noting that there is no evidence that the Ga atoms react with the matrix material to form adamantyl radicals. The H hfi values found for 1-adamantyl [17.9 (6H), 12.6 (3H), and 8.7 (3H) MHz] and 2-adamantyl [57.5 (1H) MHz] radicals<sup>45</sup> prepared by co-condensing Na atoms with 1- or 2-bromoadamantane at 77 K

in an adamantane matrix are very different from those obtained in the present study.

## CONCLUSIONS

The products formed in the reaction of Ga atoms and 1,2-epoxybutane under matrix-isolation conditions were studied using EPR spectroscopy. A comparison of the nuclear hfi values extracted from the EPR spectra to those calculated using a DFT method, as well as the effect of isotopic substitution of the 1,2-epoxybutane on the spectra, were used to confirm the formation of the novel gallaoxetanes CH<sub>3</sub>CH<sub>2</sub>CHCH<sub>2</sub>GaO and CH<sub>3</sub>CH<sub>2</sub>CHCH<sub>2</sub>OGa. These products result from metal-atom insertion into the C<sub>1</sub>-O and C<sub>2</sub>-O bonds, respectively. A conformer of the C<sub>2</sub>-O-Ga insertion product characterized by a smaller Ga hfi was detected at 190 K. Conformational changes of the C<sub>2</sub>-O insertion product imposed by the matrix might be responsible for the decrease in the Ga hfi. The strong central features present at low temperatures have been assigned to the alkyl radical CH<sub>3</sub>CH<sub>2</sub>(•CH)CH<sub>2</sub>OGa. There is some thought that this radical is a precursor of the C<sub>2</sub>-O gallaoxetane.

## AUTHOR INFORMATION

### Corresponding Author

\*E-mail: HJoly@laurentian.ca. Tel.: (705)675-1151 ext. 2333. Fax: (705)675-4844.

### Present Addresses

<sup>†</sup>Golder Paste Technology Ltd., Sudbury, ON, Canada, P3C 4R9.

## ACKNOWLEDGMENT

We gratefully acknowledge the financial support provided by the Natural Science and Engineering Research Council and the Laurentian University Research Fund and Work Study Program. We thank Ms. Julie Proulx and Mr. Xiaobing Dai for their technical assistance and help in preparing the figures and Drs. S. Montaut and G. Arteca for helpful discussion.

## REFERENCES

- (1) Hauge, R. H.; Kauffman, J. W.; Margrave, J. L. *J. Am. Chem. Soc.* **1980**, *102*, 6005.
- (2) Douglas, M. A.; Hauge, R. H.; Margrave, J. L. *J. Chem. Soc., Faraday Trans. 1* **1983**, *79*, 1533.
- (3) Macrae, V. A.; Downs, A. J. *Phys. Chem. Chem. Phys.* **2004**, *6*, 4571.
- (4) Knight, L. B., Jr.; Gregory, B.; Cleveland, J.; Arrington, C. A. *Chem. Phys. Lett.* **1993**, *204*, 168.
- (5) Knight, L. B., Jr.; Martin, R. L.; Davidson, E. R. *J. Chem. Phys.* **1979**, *71*, 3991.
- (6) Knight, L. B., Jr.; Cobranchi, S. T.; Gregory, B. W.; Earl, E. *J. Chem. Phys.* **1987**, *86*, 3143.
- (7) Joly, H. A.; Howard, J. A.; Tomietto, M.; Tse, J. S. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 3145.
- (8) Downs, A. J.; Himmel, H.-J.; Manceron, L. *Polyhedron* **2002**, *21*, 473.
- (9) Parnis, J. M.; Ozin, G. A. *J. Am. Chem. Soc.* **1986**, *108*, 1699.
- (10) Parnis, J. M.; Ozin, G. A. *J. Phys. Chem.* **1989**, *93*, 1204.
- (11) Parnis, J. M.; Ozin, G. A. *J. Phys. Chem.* **1989**, *93*, 1220.
- (12) Lafleur, R. D.; Parnis, J. M. *J. Phys. Chem.* **1992**, *96*, 2429.
- (13) Xiao, Z. L.; Hauge, R. H.; Margrave, J. L. *Inorg. Chem.* **2001**, *32*, 642.
- (14) Himmel, H.-J.; Downs, A. J.; Greene, T. M.; Andrews, L. *Organometallics* **2000**, *19*, 1060.

- (15) Himmel, H.-J.; Downs, A. J.; Greene, T. M.; Andrews, L. *J. Chem. Soc., Chem. Commun.* **1999**, 2243.
- (16) Knight, L. B., Jr.; Banisaukas, J. J., III; Babb, R.; Davidson, E. R. *J. Chem. Phys.* **1996**, *105*, 6607.
- (17) Gaertner, B.; Himmel, H.-J.; Macrae, V. A.; Downs, A. J.; Greene, T. M. *Chemistry* **2004**, *10*, 3430.
- (18) Himmel, H.-J.; Downs, A. J.; Greene, T. M. *J. Chem. Soc., Chem. Commun.* **2000**, 871.
- (19) Himmel, H.-J.; Downs, A. J.; Greene, T. M. *J. Am. Chem. Soc.* **2000**, *122*, 9793.
- (20) Himmel, H.-J.; Downs, A. J.; Greene, T. M. *Inorg. Chem.* **2001**, *40*, 396.
- (21) Kasai, P. H.; Himmel, H.-J. *J. Phys. Chem. A* **2002**, *106*, 6765.
- (22) Fängström, T.; Lunell, S.; Kasai, P. H.; Eriksson, L. A. *J. Phys. Chem. A* **1998**, *102*, 1005.
- (23) Howard, J. A.; Joly, H. A.; Edwards, P. P.; Singer, R. J.; Logan, D. E. *J. Am. Chem. Soc.* **1992**, *114*, 474.
- (24) Köppe, R.; Kasai, P. H. *J. Am. Chem. Soc.* **1996**, *118*, 135.
- (25) Joly, H. A.; Levesque, M. Y.; Koudra, F.; Rank, J. P. *Chem. Phys. Lett.* **2006**, *420*, 140.
- (26) Howard, J. A.; Joly, H. A.; Mile, B. *J. Chem. Soc., Faraday Trans.* **1990**, *86*, 219.
- (27) Chenier, J. H. B.; Howard, J. A.; Joly, H. A.; LeDuc, M.; Mile, B. *J. Chem. Soc., Faraday Trans.* **1990**, *86*, 3321.
- (28) Kasai, P. H. *J. Phys. Chem. A* **2002**, *106*, 83.
- (29) Joly, H. A.; Beaudet, L.; Dai, X. *J. Phys. Chem. A* **2006**, *110*, 5656.
- (30) Buck, A. J.; Mile, B.; Howard, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 3381.
- (31) Preston, K. F.; Morton, J. R. ISOPLOT and EPRLSQ; National Research Council of Canada: Ottawa, ON, Canada.
- (32) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R. E.; Stratmann, O.; Yazyev, A. J.; Austin, R.; Cammi, C.; Pomelli, J. W.; Ochterski, R.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, revision A.1; Gaussian, Inc.: Wallingford, CT, 2009.
- (33) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623.
- (34) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.
- (35) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.
- (36) Weltner, W., Jr. *Magnetic Atoms and Molecules*; Dover: New York, 1989.
- (37) Adamo, C.; Barone, V. *J. Chem. Phys.* **1998**, *108*, 664.
- (38) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.
- (39) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822.
- (40) Perdew, J. P.; Burke, K.; Wang, Y. *Phys. Rev. B* **1996**, *54*, 16533.
- (41) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200.
- (42) Adamo, C.; Barone, V. *Chem. Phys. Lett.* **1998**, *298*, 113.
- (43) Joly, H. A.; Ashley, J.; Levesque, M. Y.; Rank, J. P. *J. Phys. Chem. A* **2006**, *110*, 911.
- (44) Chen, K. S.; Kochi, J. K. *J. Am. Chem. Soc.* **1974**, *96*, 1383.
- (45) Lloyd, R. V.; DiGregorio, S.; DiMauro, L.; Wood, D. E. *J. Phys. Chem.* **1980**, *84*, 2891.