

## The Nature of the Gallium–Gallium Triple Bond

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**Abstract:** To simulate and help interpret the nature of the newly synthesized Ga<sub>2</sub>R<sub>2</sub>Na<sub>2</sub> molecule with bulky groups, ab initio and density functional quantum mechanical methods were applied to study the structures and bonding of the model [HGaGaH]<sup>2-</sup>, [H<sub>2</sub>GaGaH<sub>2</sub>]<sup>2-</sup>, and [H<sub>3</sub>CGaGaCH<sub>3</sub>]<sup>2-</sup> dianions, as well as the neutral Na<sub>2</sub>[H<sub>2</sub>GaGaH<sub>2</sub>], Na<sub>2</sub>[H<sub>3</sub>CGaGaCH<sub>3</sub>], Ga<sub>2</sub>H<sub>2</sub>, and Ga<sub>2</sub>H<sub>4</sub> species. Basis sets of triple- $\zeta$  plus double polarization quality augmented with diffuse functions were employed. No general bond length–bond order relationship is found. Bending from linearity of the acetylene analogues increases the GaGa separation more than the bond order is decreased. The GaGa bonding in the experimental molecule is concluded to be between triple and double in character despite the relatively long bond length.

## Introduction

Recently a gallyne Na<sub>2</sub>[Mes\*<sub>2</sub>C<sub>6</sub>H<sub>3</sub>–Ga≡Ga–C<sub>6</sub>H<sub>3</sub>Mes\*<sub>2</sub>] (Mes\* = 2,4,6-*i*-Pr<sub>3</sub>C<sub>6</sub>H<sub>2</sub>) (**1**) was synthesized and characterized as the first triple bond between main group 13 metals.<sup>1</sup> However, the formal assignment of a –Ga≡Ga– triple bond has been questioned, since the bond length is only marginally shorter than that of some known Ga–Ga single bonds.<sup>2</sup>

Indirect support for a triple bond comes from previous theoretical studies on similar systems, such as HSi≡SiH,<sup>3</sup> HGe≡GeH,<sup>4</sup> and RSi≡SiR (R = bulky aryl substituent).<sup>5</sup> However, [R–Ga≡Ga–R]<sup>2-</sup> is the first known example among heavier main group metals that has been realized experimentally, and no prior theoretical study has been reported. Herein we report a theoretical analysis of the electronic structure of model dianions [H–Ga≡Ga–H]<sup>2-</sup> and [H<sub>3</sub>C–Ga≡Ga–CH<sub>3</sub>]<sup>2-</sup>, as well as the related neutral molecules Na<sub>2</sub>[HGa≡GaH] and Na<sub>2</sub>[H<sub>3</sub>CGa≡GaCH<sub>3</sub>], to better understand the bonding between Ga atoms. We also compare results using the same methods on neutral HGaGaH and H<sub>2</sub>GaGaH<sub>2</sub>, as well as the H<sub>3</sub>GaGaH<sub>3</sub><sup>2-</sup> and H<sub>2</sub>GaGaH<sub>2</sub><sup>2-</sup> dianions, which possess double or single Ga–Ga bonds.

## Methods

Geometries were fully optimized at the self-consistent field (SCF) and the density functional theory (DFT) levels of theory. In this paper, the DFT method we employed is B3LYP, Becke's three parameter

hybrid exchange functional<sup>6</sup> and the Lee–Yang–Parr nonlocal correlation functional.<sup>7</sup> B3LYP is a hybrid Hartree–Fock/density functional theory (HF/DFT) approach. The coupled-cluster with single and double excitation (CCSD) method was also used to investigate the effect of electron correlation on the geometry of [H–Ga≡Ga–H]<sup>2-</sup>.

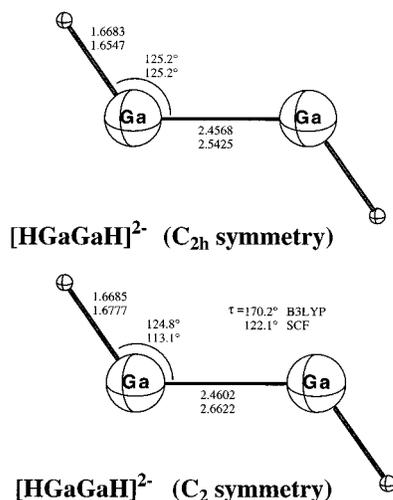
The basis sets were of triple- $\zeta$  (TZ) quality augmented with two sets of d-polarization functions (+2P) augmented with diffuse functions. For Ga, the TZ functions are from Dunning's 14s11p5d primitive basis set contracted to 10s8p2d.<sup>8</sup> For C, the TZ part is from Dunning's (10s6p/5s3p).<sup>9</sup> All these basis sets were augmented with one diffuse s and one set of p diffuse functions as well as two sets of d-polarization functions. The exponents of the diffuse functions were  $\alpha_s(\text{Ga}) = 0.01838$ ,  $\alpha_p(\text{Ga}) = 0.01472$ , and  $\alpha_s(\text{C}) = \alpha_p(\text{C}) = 0.04380$ .<sup>10</sup> The exponents of the polarization functions were  $\alpha_d(\text{Ga}) = 0.216$ , 0.068,  $\alpha_d(\text{C}) = 1.50$ , 0.375. For H, Huzinaga's 5s primitive set<sup>11</sup> was contracted to 3s, and then augmented with one s diffuse function  $\alpha_s(\text{H}) = 0.03016$  and two sets of p-polarization functions  $\alpha_p(\text{H}) = 1.50$ , 0.375. The technical description of this final basis set is Ga(15s12p7d/11s9p4d), C(11s7p2d/6s4p2d), and H(6s2p/4s2p).

Analytic gradient methods were used for geometry optimizations.<sup>12–14</sup> Harmonic vibrational frequencies were determined via analytic second derivative methods.<sup>15,16</sup> Computations were carried out with the Gaussian 94<sup>17</sup> and PSI 2.0.8 programs.<sup>18</sup>

(6) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.(7) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev.* **1988**, *37*, 785.(8) Dunning, T. H., Jr. *J. Chem. Phys.* **1977**, *66*, 1382.(9) Dunning, T. H., Jr. *J. Chem. Phys.* **1971**, *55*, 716.(10) Clark, T.; Schleyer, P. v. R. *J. Comput. Chem.* **1983**, *4*, 295.(11) Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293.(12) Pulay, P. *Phys. Rev.* **1969**, *17*, 197.(13) Scheiner, A. C.; Scuseria, G. E.; Rice, J. E.; Lee, T. L.; Schaefer, H. F. *J. Chem. Phys.* **1987**, *87*, 5361.(14) Johnson, B. G.; Frisch, M. J. *J. Chem. Phys.* **1994**, *100*, 7429.(15) Pople, J. A.; Raghavachari, K.; Schlegel, H. B.; Binkley, J. S. *Int. J. Quantum Chem. Symp.* **1979**, *13*, 225.(16) Johnson, B. G.; Frisch, M. J. *J. Chem. Phys. Lett.* **1993**, *216*, 133.

(17) Gaussian 94, Revision C.3, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. GAUSSIAN-94, Inc.: Pittsburgh, PA, 1995.

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**Figure 1.** The optimized geometries of  $[\text{HGaGaH}]^{2-}$  ( $C_{2h}$  symmetry, transition state) and  $[\text{HGaGaH}]^{2-}$  ( $C_2$  symmetry) at the TZ+2P+diff B3LYP and SCF levels of theory.

**Table 1.** The Relative Energies (kcal/mol, in Parentheses) of  $[\text{HGaGaH}]^{2-}$ ,  $[\text{H}_3\text{CGaGaCH}_3]^{2-}$ , and  $\text{H}_2\text{GaGaH}_2$  and the Numbers of Imaginary Vibrational Frequencies (NIMG)<sup>a</sup>

structure	SCF		B3LYP		Ga–Ga, Å
	energy	NIMG	energy	NIMG	
trans $[\text{HGaGaH}]^{2-}$ ( $C_{2h}$ )	10.7	1	9.9	1	2.457
trans $[\text{HGaGaH}]^{2-}$ ( $C_2$ )	8.6	0	9.9	0	2.460
dibridge $[\text{HGaGaH}]^{2-}$ ( $D_{2h}$ )	0.0	1	1.6	1	2.855
dibridge $[\text{HGaGaH}]^{2-}$ ( $C_{2v}$ )	0.0	0	0.0	0	2.625
$[\text{H}_3\text{CGaGaCH}_3]^{2-}$ ( $C_{2h}$ , 1)	5.6	2	6.0	1	2.522
$[\text{H}_3\text{CGaGaCH}_3]^{2-}$ ( $C_{2h}$ , 2)	1.0	1	6.0	2	2.519
$[\text{H}_3\text{CGaGaCH}_3]^{2-}$ ( $C_2$ )	0.7	0	4.4	0	2.572
$[\text{H}_3\text{CGaGaCH}_3]^{2-}$ ( $C_i$ )	0.0	0	0.0	0	2.538
$[\text{H}_3\text{CGaGaCH}_3]\text{Na}_2$ ( $C_{2h}$ )		1		1	2.508
$\text{HGaGaH}$ ( $C_{\infty h}$ )		2		2	2.251
trans $\text{HGaGaH}$ ( $C_{2h}$ )		0		0	2.636
$[\text{H}_2\text{GaGaH}_2]^{2-}$ ( $D_{2h}$ )		1		1	2.406
$\text{H}_2\text{GaGaH}_2$ ( $D_{2h}$ )	1.8	1	2.9	1	2.522
$\text{H}_2\text{GaGaH}_2$ ( $D_{2d}$ )	0.0	0	0.0	0	2.474
$[\text{H}_3\text{GaGaH}_3]^{2-}$ ( $D_{3d}$ )		0		0	2.592

<sup>a</sup> The total energies in hartrees are available in the Supporting Information.

## Results and Discussion

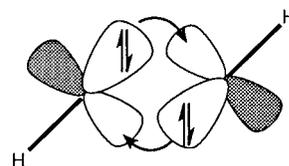
To mimic the newly synthesized  $\text{Na}_2[\text{Mes}^*_2\text{C}_6\text{H}_3\text{–Ga}\equiv\text{Ga–C}_6\text{H}_3\text{Mes}^*_2]$  molecule (**1**) suggested to have a formal  $\text{–Ga}\equiv\text{Ga–}$  triple bond,<sup>1</sup> we studied simple model dianions:  $[\text{H–Ga}\equiv\text{Ga–H}]^{2-}$ ,  $[\text{H}_2\text{Ga}=\text{GaH}_2]^{2-}$ ,  $[\text{H}_3\text{Ga–GaH}_3]^{2-}$ , and  $[\text{H}_3\text{C–Ga}\equiv\text{Ga–CH}_3]^{2-}$ , as well as their related neutral molecules— $\text{Na}_2[\text{H–Ga}\equiv\text{Ga–H}]$ ,  $\text{Na}_2[\text{H}_3\text{C–Ga}\equiv\text{Ga–CH}_3]$ ,  $\text{HGa}=\text{GaH}$ , and  $\text{H}_2\text{Ga–GaH}_2$ .

**$[\text{H–Ga}\equiv\text{Ga–H}]^{2-}$  and  $\text{Na}_2[\text{H–Ga}\equiv\text{Ga–H}]$ .** Like the geometry of the experimentally observed **1**, the  $[\text{H–Ga}\equiv\text{Ga–H}]^{2-}$  dianion model prefers a bent geometry. However, this may have  $C_{2h}$  or  $C_2$  symmetry depending on the level of theory (see Figure 1). The energies and the harmonic vibrational frequencies are shown in Tables 1 and 2, respectively. The difference between the  $C_{2h}$  and the  $C_2$  results is significant at

the SCF level of theory, but is quite small at B3LYP and vanishes at the CCSD level. The  $\text{H–Ga–Ga–H}$  torsion angle is  $122^\circ$  at the SCF level but  $170^\circ$  at B3LYP. The energy of the  $C_{2h}$  structure is 2.1 kcal/mol higher than the  $C_2$  form at SCF, but only 0.004 kcal/mol at B3LYP. The coupled-cluster single and double excitation (CCSD) method in conjunction with the same basis set gave a  $C_{2h}$  minimum, with the Ga–Ga bond distance 2.442 Å; the lowest vibrational frequency ( $157\text{ cm}^{-1}$ ) is real and corresponds to the torsion mode. The B3LYP result with the 6-311+G\*\* basis set is quite similar (Table 2).

Like the isoelectronic  $\text{Ge}_2\text{H}_2$  system,<sup>4</sup> the trans-bent structure is not a global minimum on the  $[\text{H–Ga}\equiv\text{Ga–H}]^{2-}$  potential hypersurface; two doubly bridged stationary points are lower in energy (Figure 2). The planar  $D_{2h}$  dibridged structure is a transition state, while a  $C_{2v}$  structure (butterfly shape) is the global minimum. These two doubly bridged structures differ in energy by only 1.6 kcal/mol (B3LYP). The minimum  $C_{2v}$  dibridged structure lies 8.6 (SCF) or 9.9 (B3LYP) kcal/mol below the energy of trans-bent structure with  $C_2$  symmetry (Table 1).

For comparison and in order to study the bonding character, we also investigated  $[\text{H}_2\text{Ga}=\text{GaH}_2]^{2-}$ , and the neutral trans  $\text{HGaGaH}$ , which should have  $\text{Ga}=\text{Ga}$  double bonds, as well as  $[\text{H}_3\text{Ga–GaH}_3]^{2-}$  and the  $\text{H}_2\text{GaGaH}_2$  molecules, which should have Ga–Ga single bonds. Our results agree well with previous theoretical studies on some of these species.<sup>19–21</sup> The linear  $\text{H–Ga}=\text{Ga–H}$  structure is a transition state, while the trans-bent structure ( $C_{2h}$  symmetry) is a minimum. The Ga–Ga distance in the trans structure is much longer ( $0.4 \sim 0.5$  Å) than that in the linear geometry (see Figure 3), although the linkages between Ga atoms in both linear and trans structures may be regarded formally as double bonds. The same phenomena have also been reported for the  $\text{H}_2\text{Al}_2$ <sup>22,23</sup> and the  $\text{H}_2\text{Ge}_2$  molecules.<sup>4</sup> The electronic structure of the long  $\text{Ga}=\text{Ga}$  double bond in the neutral trans-bent  $\text{HGaGaH}$  molecule was described by Treboux et al.<sup>19</sup> as being composed of two dative bonds:



Each Ga–H moiety donates a pair of electrons from the occupied  $sp$  hybrid orbital to an empty  $p$  orbital of another Ga–H moiety. However, each dative bond is much weaker than a regular covalent bond. Consequently, the Ga–Ga distance (2.636 Å at the B3LYP level of theory) not only is much longer (by about 0.4 Å) than a  $\sigma\text{–}\pi$   $\text{Ga}=\text{Ga}$  double bond in the linear  $\text{H–Ga}=\text{Ga–H}$  structure (2.251 Å) but also, surprisingly, is even longer than the Ga–Ga single bond in  $\text{H}_2\text{Ga–GaH}_2$  (2.522 Å in  $D_{2h}$  symmetry, Figure 4). (Although  $D_{2h}$   $\text{H}_2\text{Ga–GaH}_2$  is a transition state, it affords the best comparison. There is no hyperconjugation, which reduces the Ga–Ga bond distance in the  $D_{2d}$  minimum structure by about 0.05 Å.) Although exceptionally long, the Ga–Ga bond in the trans-bent  $\text{HGaGaH}$  structure is composed of two pairs of

(19) (a) Treboux, G.; Barthelat, J.-C. *J. Am. Chem. Soc.* **1993**, *115*, 4870. (b) Treboux, G.; Malrieu, J.-P. *J. Am. Chem. Soc.* **1987**, *109*, 5311.

(20) Palagyi, Z.; Schaefer, H. F.; Kapuy, E. *Chem. Phys. Lett.* **1993**, *203*, 195.

(21) Lammertsma, K.; Leszczynski, J. *J. Phys. Chem.* **1990**, *94*, 5543.

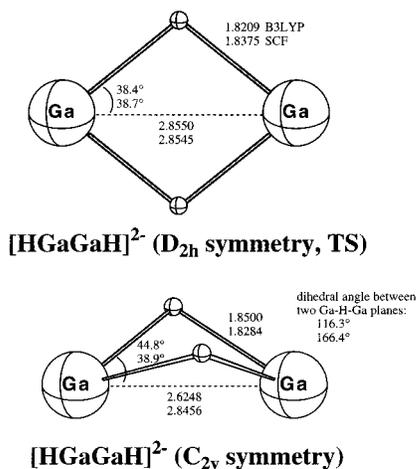
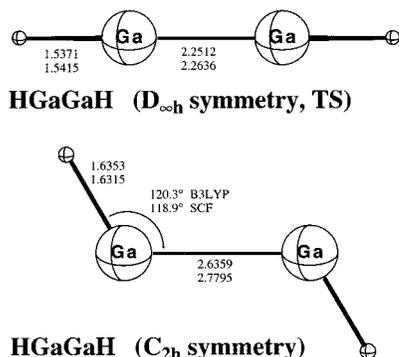
(22) Palagyi, Z.; Grev, R. S.; Schaefer, H. F. *J. Am. Chem. Soc.* **1993**, *115*, 1936.

(23) Lammertsma, K.; Güner, O. F.; Drewes, R. M.; Reed, A. E.; Schleyer, P. v. R. *Inorg. Chem.* **1989**, *28*, 313.

(18) PSI 2.0.8, Janssen, C. L.; Seidl, E. T.; Scuseria, G. E.; Hamilton, T. P.; Yamaguchi, Y.; Remington, R. B.; Xie, Y.; Vacek, G.; Sherrill, C. D.; Crawford, T. D.; Fermann, J. T.; Allen, W. D.; Brooks, B. R.; Fitzgerald, G. B.; Fox, D. J.; Gaw, J. F.; Handy, N. C.; Laidig, W. D.; Lee, T. J.; Pitzer, R. M.; Rice, J. E.; Saxe, P.; Scheiner, A. C.; Schaefer, H. F. PSITECH Inc.: Watkinsville, GA, 1994.

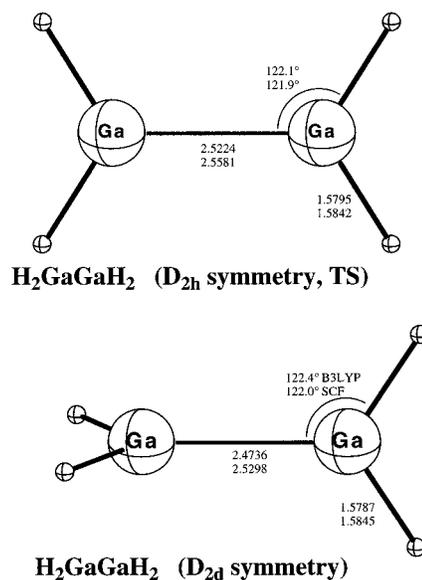
**Table 2.** The Harmonic Vibrational Frequencies (cm<sup>-1</sup>) and the Infrared Intensities (km/mol, in Parentheses) of [HGaGaH]<sup>2-</sup> (C<sub>2h</sub> and C<sub>2</sub>)

	[HGaGaH] <sup>2-</sup> (C <sub>2h</sub> )				[HGaGaH] <sup>2-</sup> (C <sub>2</sub> )		
	sym	SCF	B3LYP	B3LYP/ 6-311+G**	sym	SCF	B3LYP
Ga–H stretch	b <sub>u</sub>	1624(754)	1487(787)	1529	b	1526(7326)	1505(734)
Ga–H stretch	a <sub>g</sub>	1613(0)	1469(0)	1518	a	1527(796)	1485(164)
Ga–Ga stretch	a <sub>g</sub>	488(0)	491(0)	498	a	446(2)	494(0.5)
Ga–Ga–H bend	b <sub>u</sub>	111(179)	240(59)	221	b	207(765)	252(38)
Ga–Ga–H bend	a <sub>g</sub>	157(0)	195(0)	189	a	228(15)	199(96)
torsion	a <sub>u</sub>	519i	81i	206	a	140(8)	91(2064)

**Figure 2.** The optimized geometries of dibridged [HGaGaH]<sup>2-</sup> (D<sub>2h</sub> symmetry, transition state) and [HGaGaH]<sup>2-</sup> (C<sub>2v</sub> symmetry) at the TZ+2P+diff B3LYP and SCF levels of theory.**Figure 3.** The optimized geometries of neutral HGaGaH (D<sub>∞h</sub> symmetry, transition state) and HGaGaH (C<sub>2h</sub> symmetry) at the TZ+2P+diff B3LYP and SCF levels of theory.

electrons which form weak dative bonds. Hence, it should be considered formally as a *double* bond. Indeed, Lappert's 1976 description<sup>24</sup> of the 2.764 Å Sn–Sn bond, comprised of two dative bonding orbitals, as a bent and weak *double* bond has been widely accepted,<sup>25</sup> even though the distance is very close to that of a single Sn–Sn bond (2.770 Å).<sup>26</sup> Such bent and weak bonds also have been reported and analyzed for related systems, such as H<sub>2</sub>Si<sub>2</sub>, by Grev and Schaefer.<sup>3</sup>

In the trans-bent dianion [H–Ga≡Ga–H]<sup>2-</sup>, the additional pair of electrons forms a  $\pi$ -bond between the two Ga atoms perpendicular to the C<sub>s</sub> plane. This additional  $\pi$ -bonding reduces the Ga–Ga distance from 2.640 Å in the bent neutral

**Figure 4.** The optimized geometries of H<sub>2</sub>GaGaH<sub>2</sub> (D<sub>2h</sub> symmetry, transition state) and H<sub>2</sub>GaGaH<sub>2</sub> (D<sub>2d</sub> symmetry) at the TZ+2P+diff B3LYP and SCF levels of theory.

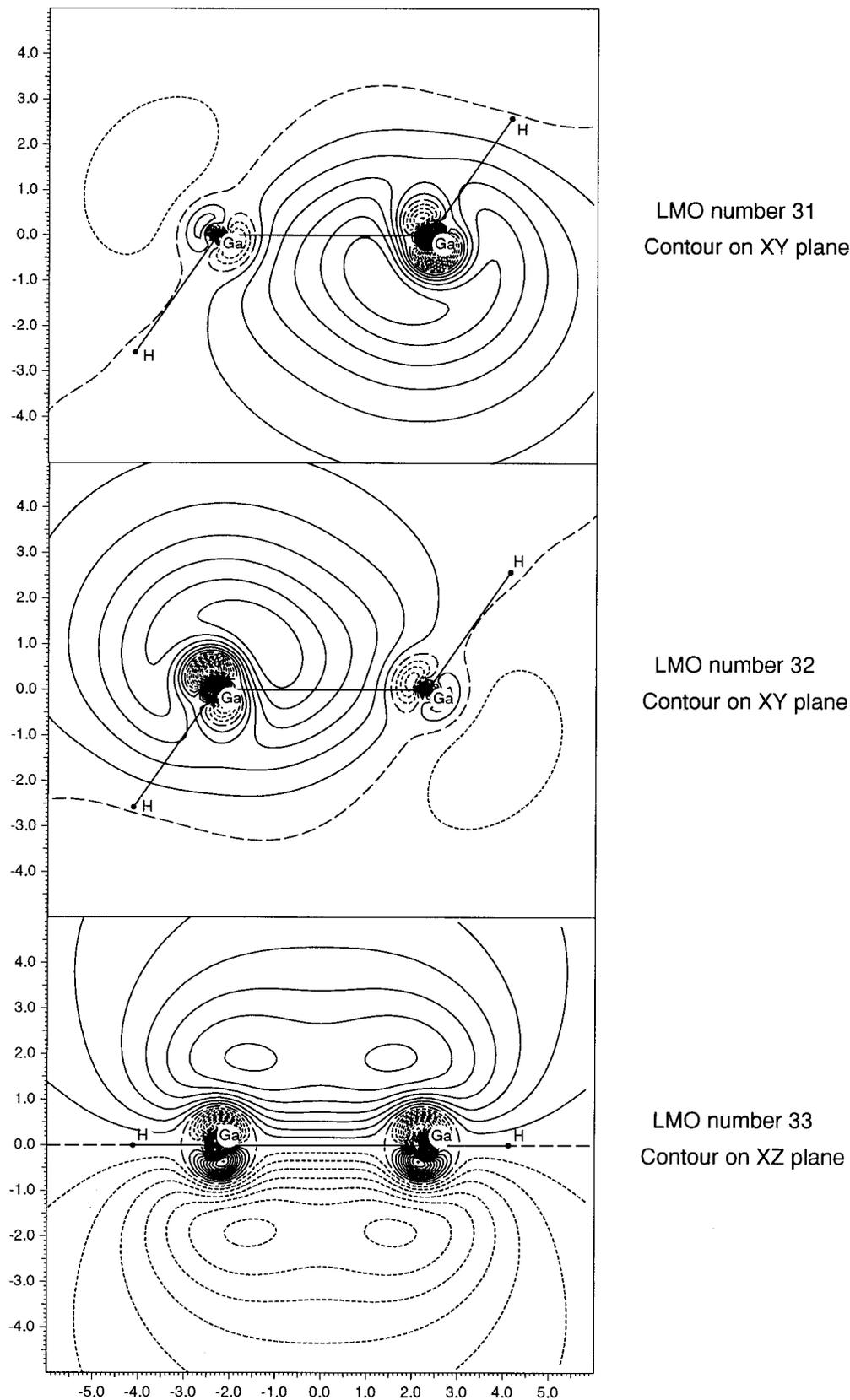
system (Figure 3) to 2.460 Å in the bent dianion (Figure 1). It is reasonable to describe this Ga–Ga bonding, which involves a weak bent double bond plus a  $\pi$  bond, as a *triple* bond. The preference of two dative bonds and a  $\pi$  bond can be explained as that each GaH fragment has <sup>2</sup>Π ground state corresponding to n<sub>σ</sub><sup>2</sup> p<sub>πx</sub> configuration. The coupling of the two fragments would favor a trans-bent structure. (For comparison, each CH fragment has a low-lying quartet state, and the coupling of two quartet CH fragments would favor  $\sigma + 2\pi$  bonds with the linear H–C≡C–H structure.)<sup>3,19</sup> Our localized molecular orbital analysis confirms the above description. The contour maps based on the CCSD geometry (C<sub>2h</sub>) in Figure 5 show that there are three occupied localized molecular orbitals connecting the Ga atoms. Two of them (at the top and the center of Figure 5) are obviously dative bonding orbitals (not lone pairs). The other one (at the bottom of Figure 5) can be regarded as a  $\pi$ -bonding orbital. These results show that three occupied bonding orbitals connect the two Ga atoms, supporting the conclusion that a Ga≡Ga triple bond is involved. However, both the dative and the  $\pi$  bonding are weak. Hence, the GaGa bond in [H–Ga≡Ga–H]<sup>2-</sup> has an exceptionally long distance (2.460 Å), only 0.06 Å shorter than a regular  $\sigma$  Ga–Ga single bond (2.522 Å in the D<sub>2h</sub> H<sub>2</sub>Ga–GaH<sub>2</sub> structure, Figure 4).

We computed a model molecule Na<sub>2</sub>[HGaGaH] to study the effect of the alkali atoms in the experimental system Na<sub>2</sub>[Mes\*<sub>2</sub>C<sub>6</sub>H<sub>3</sub>–Ga≡Ga–C<sub>6</sub>H<sub>3</sub>Mes\*<sub>2</sub>] (**1**). A stationary point was optimized in C<sub>2h</sub> symmetry (Figure 6). The Ga–Ga bond distance (2.441 Å) is about 0.02 Å shorter than that in the [H–Ga≡Ga–H]<sup>2-</sup> dianion with the B3LYP method, but the

(24) Goldberg, D. E.; Harris, D. H.; Lappert, M. F.; Thomas, K. M. J. *Chem. Soc., Chem. Commun.* **1976**, 261.

(25) Elschenbroich, Ch.; Salzer, A. *Organometallics*, 2nd ed.; VCH Publishers: New York, 1992; p 133.

(26) Preut, V. H.; Haupt, H.-J.; Huber, F. Z. *Anorg. Allg. Chem.* **1973**, 396, 81.



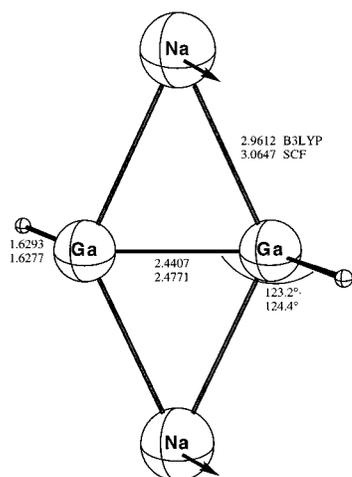
**Figure 5.** The contour maps of the three bonding orbitals of  $[\text{HGaGaH}]^{2-}$  ( $C_{2h}$  symmetry). Those at the top and the middle are the dative bond orbitals (XY plane), and the one at the bottom is the  $\pi$  bond orbital (XZ plane).

bond character should be the same in both. The single imaginary vibrational frequency ( $30i \text{ cm}^{-1}$  at B3LYP, or  $29i \text{ cm}^{-1}$  for SCF), a  $B_u$  normal mode, moves the two Na atoms the direction shown by the arrows in Figure 6, leading to a

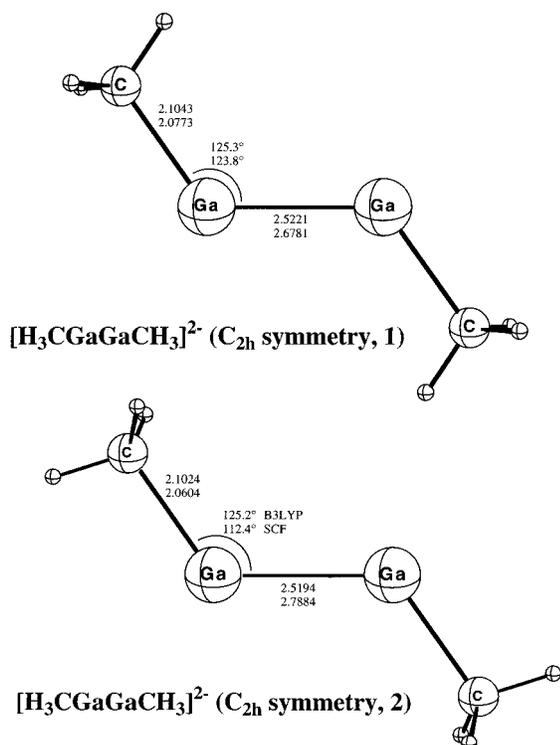
minimum with  $C_s$  symmetry. This  $C_s$  structure lies ca. 4.1 kcal/mol lower in energy at B3LYP. Since the potential curve for this  $B_u$  mode is very flat, the  $C_s$  structure is not chemically meaningful, and such a small imaginary frequency might not

**Table 3.** The Harmonic Vibrational Frequencies ( $\text{cm}^{-1}$ ) and the Infrared Intensities ( $\text{km/mol}$ , in parentheses) of  $[\text{H}_3\text{CGaGaCH}_3]^{2-}$  ( $C_2$  and  $C_i$ ) at the TZ+2P+Diff B3LYP Level of Theory

$[\text{H}_3\text{CGaGaCH}_3]^{2-}$ ( $C_{2h}$ symmetry, 1)	3090 (6633), 3077 (0), 3077 (248), 3044 (0), 2996 (0), 2995 (246), 1461 (0), 1460 (271), 1454 (68), 1453 (0), 1124 (0), 1124 (152), 647 (155), 621 (0), 569 (0), 565 (30), 423 (132), 422 (0), 161 (0), 125 (0), 63 (63), 58 (2), 5 (34), 62i
$[\text{H}_3\text{CGaGaCH}_3]^{2-}$ ( $C_{2h}$ symmetry, 2)	3086 (1347), 3064 (0), 3063 (80), 3061 (0), 2992 (0), 2992 (60), 1458 (0), 1455 (71), 1453 (1036), 1442 (0), 1117 (0), 1117 (79), 633 (0), 609 (46), 589 (553), 527 (0), 425 (124), 423 (0), 162 (0), 121 (0), 55 (144), 53 (5), 63i, 83i
$[\text{H}_3\text{CGaGaCH}_3]^{2-}$ ( $C_2$ symmetry)	3078 (10139), 3076 (<1), 3070 (11787), 3053 (2055), 2995 (2633), 2994 (8), 1459 (42), 1457 (179), 1455 (1600), 1451 (58), 1127 (1264), 1124 (29), 637 (116), 611 (276), 573 (2697), 562 (155), 433 (3958), 419 (137), 145 (6), 115 (5), 84 (<1), 75 (176), 46 (300), 38 (12)
$[\text{H}_3\text{CGaGaCH}_3]^{2-}$ ( $C_i$ symmetry)	3083 (303), 3083 (0), 3065 (0), 3064 (993), 2995 (104), 2995 (0), 1465 (0), 1462 (43), 1456 (0), 1455 (162), 1155 (404), 657 (0), 633 (360), 576 (0), 575 (182), 445 (246), 441 (0), 159 (0), 155 (0), 138 (0), 128 (0), 115 (17), 62 (7), 60 (45)

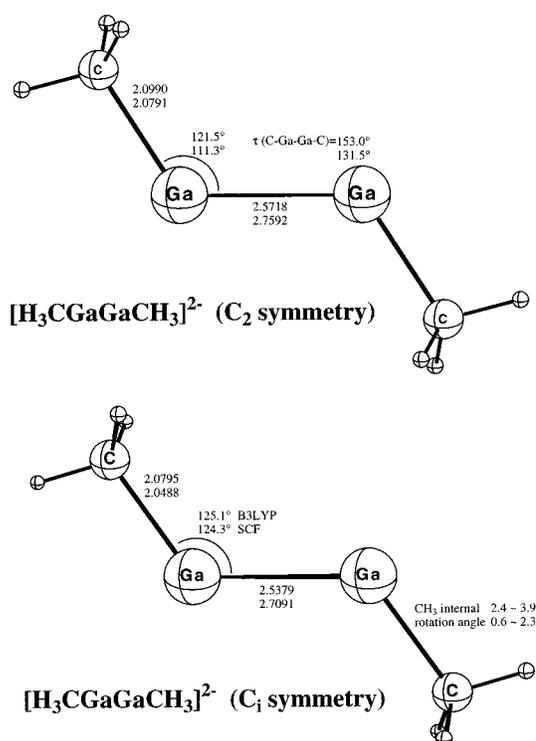
 **$\text{H}_2\text{Ga}_2\text{Na}_2$  ( $C_{2h}$  symmetry)**

**Figure 6.** The optimized geometry of  $\text{Na}_2[\text{HGaGaH}]^{2-}$  with  $C_{2h}$  symmetry at the TZ+2P+diff B3LYP and SCF levels of theory. The arrows on the Na atoms indicate the direction corresponding to the normal mode of the imaginary vibrational frequency.



**Figure 7.** Two optimized geometries of  $[\text{H}_3\text{CGaGaCH}_3]^{2-}$  with the constraint of  $C_{2h}$  symmetry (second saddle point or transition state) at the TZ+2P+diff B3LYP and SCF levels of theory.

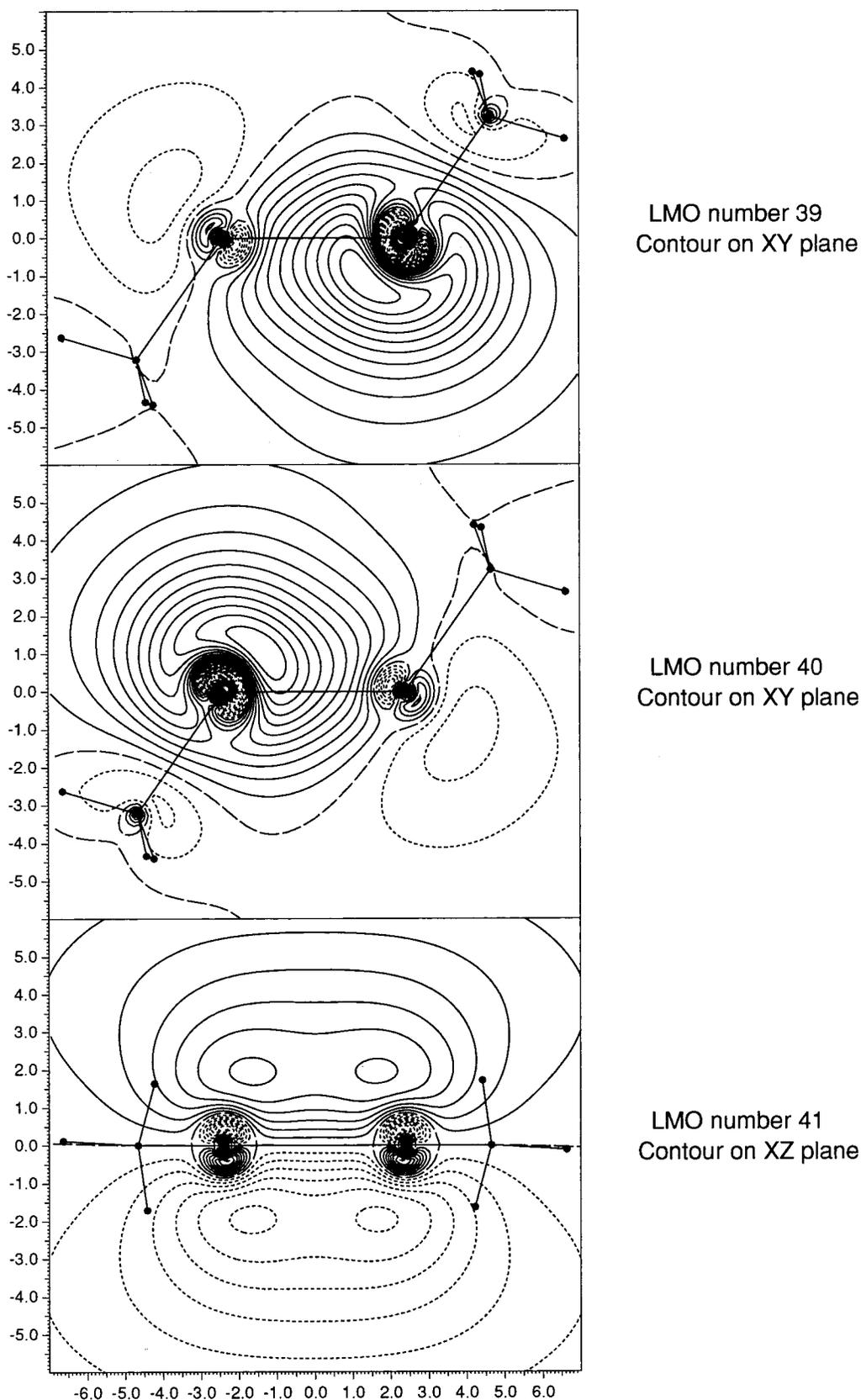
survive at higher theoretical levels. (Further discussion will be found below.)



**Figure 8.** The optimized geometries of  $[\text{H}_3\text{CGaGaCH}_3]^{2-}$  with  $C_i$  and  $C_2$  symmetry at the TZ+2P+diff B3LYP and SCF levels of theory.

**$[\text{H}_3\text{C}-\text{Ga}\equiv\text{Ga}-\text{CH}_3]^{2-}$  and  $\text{Na}_2[\text{H}_3\text{C}-\text{Ga}\equiv\text{Ga}-\text{CH}_3]$ .** There are two stationary  $C_{2h}$  structures (2 and 3) for the larger model dianion  $[\text{H}_3\text{C}-\text{Ga}\equiv\text{Ga}-\text{CH}_3]^{2-}$ , corresponding to the different internal-rotation positions of the methyl groups (Figure 7). The energy difference (0.07 kcal/mol) is very small at the B3LYP level, but is 4.6 kcal/mol at SCF. The higher energy form ( $C_{2h}$ , 1) has one imaginary vibrational frequency ( $63i \text{ cm}^{-1}$ ); this corresponds to a  $B_g$  mode, which leads to  $C_i$  symmetry (Table 3). The lower energy ( $C_{2h}$ , 2) form has, surprisingly, two imaginary vibrational frequencies ( $63i$  and  $83i \text{ cm}^{-1}$ , Table 3) corresponding to  $B_g$  and  $A_u$  modes. Optimization following these modes gave two minima with  $C_i$  and  $C_2$  symmetry, respectively (Figure 8). The p orbitals form better  $\pi$ -bonds in the planar skeleton; the Ga–Ga bond distance in the  $C_i$  structure (2.538 Å) is 0.034 Å shorter than that in  $C_2$  symmetry.

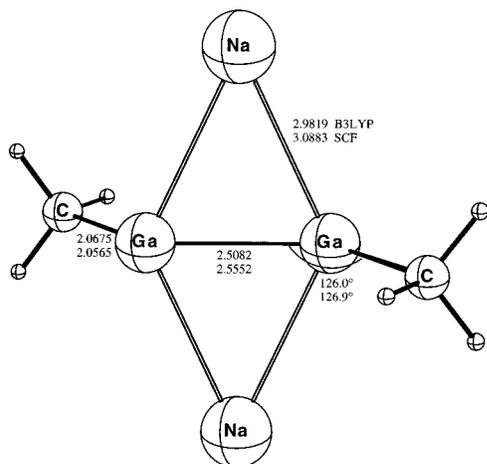
The methyl groups in the  $C_i$  structure are rotated around the Ga–C bonds by about  $3^\circ$  from the  $C_{2h}$  position. The  $C_i$  energy is lower than the  $C_{2h}$  energy by 6.0 kcal/mol at the B3LYP level. The Ga–Ga bonding character of  $[\text{H}_3\text{C}-\text{Ga}\equiv\text{Ga}-\text{CH}_3]^{2-}$  is similar to that in  $[\text{H}-\text{Ga}\equiv\text{Ga}-\text{H}]^{2-}$ , but the Ga–Ga bond length in  $[\text{H}_3\text{C}-\text{Ga}\equiv\text{Ga}-\text{CH}_3]^{2-}$  is about 0.1 Å longer at both the B3LYP and SCF levels of theory (Figures 1). The same trend has been reported for  $\text{HSi}-\text{SiH}$ ,<sup>5</sup> where methyl substitution increases the Si–Si bond length (from 2.111 to



**Figure 9.** The contour maps of the three bonding orbitals of  $[\text{H}_3\text{CGaGaCH}_3]^{2-}$  ( $C_i$  symmetry). Those at the top and the middle are the dative bond orbitals (XY plane), and the contour map at the bottom is the  $\pi$  bond orbital (XZ plane).

2.123 Å). However, as reported in the same paper, the larger substituents actually reduce the Si-Si bond length (from 2.111 Å for  $\text{HSiSiH}$  to 2.094 Å for  $\text{F}_3\text{Si-SiSi-SiF}_3$  or to 2.095 Å for  $\text{Me}_3\text{Si-SiSi-SiMe}_3$ ). As with  $-\text{Si}=\text{Si}-$ , the  $[-\text{Ga}=\text{Ga}-]^{2-}$

length may also be decreased by large substituents. The contour maps of the three bonding LMOs of  $[\text{H}_3\text{C-Ga}=\text{Ga-CH}_3]^{2-}$  are shown in Figure 9. The dative bond orbitals and the  $\pi$ -bond orbital have almost the same shape as in  $[\text{H-Ga}=\text{Ga-H}]^{2-}$ .

(CH<sub>3</sub>)<sub>2</sub>Ga<sub>2</sub>Na<sub>2</sub> (C<sub>2h</sub> symmetry)

**Figure 10.** The optimized geometry of Na<sub>2</sub>[H<sub>3</sub>CGaGaCH<sub>3</sub>]<sup>2-</sup> with C<sub>2h</sub> symmetry at the TZ+2P+diff B3LYP and SCF levels of theory.

As discussed above for [H–Ga≡Ga–H]<sup>2-</sup>, there should be a Ga≡Ga triple bond in this molecule as well.

The energy of the C<sub>2</sub> structure of [H<sub>3</sub>C–Ga≡Ga–CH<sub>3</sub>]<sup>2-</sup> (Figure 8), which is similar to [HGa≡GaH]<sup>2-</sup>, is about 4.4 kcal/mol higher than the C<sub>i</sub> minimum with the B3LYP method (but only 0.7 kcal/mol at SCF). It is 1.6 kcal/mol lower in energy than that of C<sub>2h</sub> structures. The B3LYP Ga–Ga bond length is 2.572 Å (2.759 Å with SCF). The torsion angle, 153.0° at B3LYP, decreases from 170.2° in [H–Ga≡Ga–H]<sup>2-</sup> (but increases from 122.1° to 131.5° at the SCF level). Qualitatively, the Ga≡Ga bond character in [H<sub>3</sub>C–Ga≡Ga–CH<sub>3</sub>]<sup>2-</sup> is similar to that in [H–Ga≡Ga–H]<sup>2-</sup>.

Like [H<sub>3</sub>C–Ga≡Ga–CH<sub>3</sub>]<sup>2-</sup>, two stationary points for the neutral Na<sub>2</sub>[H<sub>3</sub>C–Ga≡Ga–CH<sub>3</sub>] in C<sub>2h</sub> symmetry were optimized. The CH<sub>3</sub> orientations differ, but their energies are nearly the same (within 0.4 kcal/mol). The Ga–Ga bond length of the [H<sub>3</sub>C–Ga≡Ga–CH<sub>3</sub>]<sup>2-</sup> form with the lower energy is about 0.02 Å (B3LYP) shorter than that of the C<sub>2h</sub> structure. Neither are minima. One has a single imaginary vibrational frequency (15i cm<sup>-1</sup>, B<sub>u</sub>), but the second has three (A<sub>u</sub>, B<sub>g</sub>, B<sub>u</sub>). The B<sub>u</sub> mode leads to a minimum with C<sub>s</sub> symmetry (like Na<sub>2</sub>[H–Ga≡Ga–H]), which has an energy 0.22 kcal/mol lower than the first C<sub>2h</sub> structure. In comparison with Na<sub>2</sub>[H–Ga≡Ga–H], the magnitude of the B<sub>u</sub> imaginary vibrational frequency and the energy difference between the C<sub>s</sub> and C<sub>2h</sub> structures become smaller, indicating that the potential curve is much flatter for Na<sub>2</sub>[H<sub>3</sub>C–Ga≡Ga–CH<sub>3</sub>]. We expect that the C<sub>2h</sub> structure may become a genuine minimum if bulky groups replace the methyl substituents.

“Bond orders” depend on the definition, but should be consistent if the same method is applied to a related set of molecules. The Wiberg bond index (WBI)<sup>27</sup> and NLMO/NPA<sup>28</sup> results in Table 4 (obtained as implemented in Gaussian94<sup>17</sup>) are not only quite similar for most of the species, but also correspond closely to the expectation of single, double, and triple bonds for the model compounds in their idealized geometries. However, there is no general bond length–bond order relationship. The GaGa distances are considerably shorter in the neutral molecules than in the dianions.

The GaGa distance of 2.25 Å in linear neutral HGa≡GaH corresponds to a double bond, but the GaGa double bond in [H<sub>2</sub>Ga=GaH<sub>2</sub>]<sup>2-</sup> (D<sub>2h</sub> and C<sub>2h</sub>) is much longer, 2.40 Å.

**Table 4.** Wiberg Bond Index (WBI) and Natural Localized Molecular Orbital Natural Population Analysis (NLMO/NPA) Bond Orders Compared with Bond Lengths (Å) of [HGaGaH]<sup>2-</sup>, [H<sub>3</sub>CGaGaCH<sub>3</sub>]<sup>2-</sup>, and H<sub>2</sub>GaGaH<sub>2</sub> in Various Geometries

molecule	bond order		Ga–Ga bond length, Å
	WBI	NIMG/NPA	
single			
[H <sub>3</sub> Ga–GaH <sub>3</sub> ] <sup>2-</sup> (D <sub>3d</sub> )	0.95	1.02	2.592
H <sub>2</sub> Ga–GaH <sub>2</sub> (D <sub>2h</sub> )	0.85	0.93	2.522
H <sub>2</sub> Ga–GaH <sub>2</sub> (D <sub>2d</sub> )	0.89	1.05	2.474
double			
[H <sub>2</sub> Ga=GaH <sub>2</sub> ] <sup>2-</sup> (D <sub>2h</sub> )	1.94	2.21	2.406
[H <sub>2</sub> Ga=GaH <sub>2</sub> ] <sup>2-</sup> (C <sub>2h</sub> )	1.88	1.94	2.407
HGa=GaH (D <sub>∞h</sub> )	1.86	1.95	2.251
triple			
[HGa≡GaH] <sup>2-</sup> (D <sub>∞h</sub> )	2.95	3.02	2.214
[HGa≡GaH] <sup>2-</sup> (C <sub>2h</sub> )	2.36	3.02	2.457

Constrained linear [H–Ga≡Ga–H]<sup>2-</sup> unambiguously has a triple bond, but the GaGa distance 2.2 Å is comparable to that of the double bond in linear HGa=GaH.

Bending lengthens the GaGa separations in [RGaGaR]<sup>2-</sup> derivatives considerably, but in [H<sub>2</sub>Ga=GaH<sub>2</sub>]<sup>2-</sup> reduces the WBI (to about 2.4) and the NLMO/NPA bond order hardly at all (Table 4). This is consistent with our description of bonding comprised of a σ and two weak dative bonds. The electronic structure, rather than bond lengths, determines the nature of multiple bonds.

### Concluding Remarks

The bent structures of the model molecules [H–Ga≡Ga–H]<sup>2-</sup>, [H<sub>3</sub>C–Ga≡Ga–CH<sub>3</sub>]<sup>2-</sup>, Na<sub>2</sub>[H–Ga≡Ga–H], and Na<sub>2</sub>[H<sub>3</sub>C–Ga≡Ga–CH<sub>3</sub>] are confirmed to have essentially –Ga≡Ga– triple bonds, composed of two dative and a π bond. However, the dative bonds in these molecules are weak, and their bond orders may be decreased somewhat. Consequently, such triple bonds in bent systems are not as strong as those in linear molecules. Bond lengths are larger in dianions than corresponding neutral molecules. Accordingly, the Ga≡Ga distance in a bent dianion may be only slightly shorter than a Ga–Ga single bond in a neutral reference molecule.

The nature of a chemical bond is determined primarily by the electronic structure, not by the molecular geometry. A weak triple bond is different from a double bond, which in turn is different from a single bond, even though bond lengths may be similar. Triple bonds with an ideal acetylene-like linear geometry should be shorter than an ethylene-like double bond and much shorter than a single bond, not only because more electron pairs are involved in bonding, but also because of the smaller number of repulsive interactions involving the bonds to the substituents. “Bond orders” depend on their definition, but bond length comparisons are only valid if there is no significant variation in the bond strengths of the individual bonds. There are large differences even in the simple models.

Triple bonds do not require geometries to be linear. Well-known exceptions include bent acetylenes in small rings, e.g. benzyne,<sup>29</sup> cyclohexyne, cyclopentyne, and cyclobutyne. It may also be noted that HBBH<sup>2-</sup> and HCCH, when bent to 120°, show very little change in the Wiberg bond index (e.g. 2.992 for HBBH<sup>2-</sup> and 2.977 for HCCH). On bending HGaGaH<sup>2-</sup>, there is much more mixing of the Ga σ orbitals into the in-plane “π” bond hybridization than in the first row cases. This is the main difference with respect to HBBH<sup>2-</sup> in the bonding

(27) Wiberg, K. B. *Tetrahedron* **1968**, *24*, 1083.

(28) Reed, A. E.; Schleyer, P. v. R. *Inorg. Chem.* **1988**, *27*, 3969.

(29) Jiao, H.; Schleyer, P. v. R.; Beno, B. R.; Houk, K. N.; Warmuth, R. *Angew. Chem., Int. Ed. Engl.* **1997**, *27*, 61.

changes and arises from the well-known tendency of heavier main group elements to place electrons, which are only weakly involved in bonding, into s-rich orbitals. All the GaGa bonds in  $\text{HGaGaH}^{2-}$ , linear or bent, are quite weak energetically.

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**Supporting Information Available:** Table of total energies of  $[\text{HGaGaH}]^{2-}$ ,  $[\text{H}_3\text{CGaGaCH}_3]^{2-}$ , and  $\text{H}_2\text{GaGaH}_2$  (1 page, print/PDF). See any current masthead page for ordering information and Web access instructions.

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