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The Nature of the Gallium−Gallium Triple Bond

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Abstract: To simulate and help interpret the nature of the newly synthesized $Ga_2R_2Na_2$ molecule with bulky groups, ab initio and density functional quantum mechanical methods were applied to study the structures and bonding of the model $[HGaGaH]^{2-}$, $[H_2GaGaH_2]^{2-}$, and $[H_3CGaGaCH_3]^{2-}$ dianions, as well as the neutral $Na_2[H_2GaGaH_2]$, $Na_2[H_3CGaGaCH_3]$, Ga_2H_2, and Ga_2H_4 species. Basis sets of triple-ζ 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 $Na_2[Mes^*{}_2C_6H_3-Ga\equiv Ga-C_6H_3Mes^*{}_2]$ ($Mes^* = 2,4,6\text{-}i\text{-}Pr_3C_6H_2$) (**1**) was synthesized and characterized as the first triple bond between main group 13 metals.[1] However, the formal assignment of a $-Ga\equiv Ga-$ triple bond has been questioned, since the bond length is only marginally shorter than that of some known Ga−Ga single bonds.[2]

Indirect support for a triple bond comes from previous theoretical studies on similar systems, such as $HSi\equiv SiH$,[3] $HGe\equiv GeH$,[4] and $RSi\equiv SiR$ (R = bulky aryl substituent).[5] However, $[R-Ga\equiv Ga-R]^{2-}$ 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 $[H-Ga\equiv Ga-H]^{2-}$ and $[H_3C-Ga\equiv Ga-CH_3]^{2-}$, as well as the related neutral molecules $Na_2[HGa\equiv GaH]$ and $Na_2[H_3CGa\equiv GaCH_3]$, to better understand the bonding between Ga atoms. We also compare results using the same methods on neutral HGaGaH and H_2GaGaH_2, as well as the $H_3GaGaH_3{}^{2-}$ and $H_2GaGaH_2{}^{2-}$ 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[6] and the Lee−Yang−Parr nonlocal correlation functional.[7] 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 $[H-Ga\equiv Ga-H]^{2-}$.

The basis sets were of triple-ζ (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.[8] For C, the TZ part is from Dunning's (10s6p/5s3p).[9] 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 $\alpha_s(Ga) = 0.01838$, $\alpha_p(Ga) = 0.01472$, and $\alpha_s(C) = \alpha_p(C) = 0.04380$.[10] The exponents of the polarization functions were $\alpha_d(Ga) = 0.216, 0.068$, $\alpha_d(C) = 1.50, 0.375$. For H, Huzinaga's 5s primitive set[11] was contracted to 3s, and then augmented with one s diffuse function $\alpha_s(H) = 0.03016$ and two sets of p-polarization functions $\alpha_p(H) = 1.50, 0.375$. 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.[12−14] Harmonic vibrational frequencies were determined via analytic second derivative methods.[15,16] Computations were carried out with the Gaussian 94[17] and PSI 2.0.8 programs.[18]

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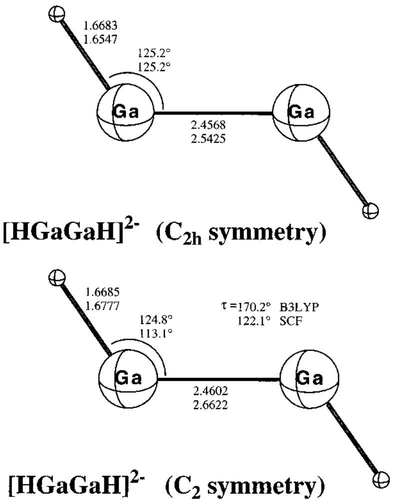


$[HGaGaH]^{2-}$ (C_{2h} symmetry)

$[HGaGaH]^{2-}$ (C_2 symmetry)

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

Table 1. The Relative Energies (kcal/mol, in Parentheses) of $[HGaGaH]^{2-}$, $[H_3CGaGaCH_3]^{2-}$, and H_2GaGaH_2 and the Numbers of Imaginary Vibrational Frequencies (NIMG)[a]

structure	SCF energy	SCF NIMG	B3LYP energy	B3LYP NIMG	Ga−Ga, Å
trans $[HGaGaH]^{2-}$ (C_{2h})	10.7	1	9.9	1	2.457
trans $[HGaGaH]^{2-}$ (C_2)	8.6	0	9.9	0	2.460
dibridge $[HGaGaH]^{2-}$ (D_{2h})	0.0	1	1.6	1	2.855
dibridge $[HGaGaH]^{2-}$ (C_{2v})	0.0	0	0.0	0	2.625
$[H_3CGaGaCH_3]^{2-}$ (C_{2h}, 1)	5.6	2	6.0	1	2.522
$[H_3CGaGaCH_3]^{2-}$ (C_{2h}, 2)	1.0	1	6.0	2	2.519
$[H_3CGaGaCH_3]^{2-}$ (C_2)	0.7	0	4.4	0	2.572
$[H_3CGaGaCH_3]^{2-}$ (C_i)	0.0	0	0.0	0	2.538
$[H_3CGaGaCH_3]Na_2$ (C_{2h})		1		1	2.508
HGaGaH ($C_{\infty h}$)		2		2	2.251
trans HGaGaH (C_{2h})		0		0	2.636
$[H_2GaGaH_2]^{2-}$ (D_{2h})		1		1	2.406
H_2GaGaH_2 (D_{2h})	1.8	1	2.9	1	2.522
H_2GaGaH_2 (D_{2d})	0.0	0	0.0	0	2.474
$[H_3GaGaH_3]^{2-}$ (D_{3d})		0		0	2.592

[a] The total energies in hartrees are available in the Supporting Information.

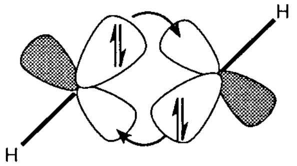
Results and Discussion

To mimic the newly synthesized $Na_2[Mes^*{}_2C_6H_3-Ga\equiv Ga-C_6H_3Mes^*{}_2]$ molecule (**1**) suggested to have a formal $-Ga\equiv Ga-$ triple bond,[1] we studied simple model dianions: $[H-Ga\equiv Ga-H]^{2-}$, $[H_2Ga=GaH_2]^{2-}$, $[H_3Ga-GaH_3]^{2-}$, and $[H_3C-Ga\equiv Ga-CH_3]^{2-}$, as well as their related neutral molecules—$Na_2[H-Ga\equiv Ga-H]$, $Na_2[H_3C-Ga\equiv Ga-CH_3]$, $HGa=GaH$, and $H_2Ga-GaH_2$.

$[H-Ga\equiv Ga-H]^{2-}$ and $Na_2[H-Ga\equiv Ga-H]$. Like the geometry of the experimentally observed **1**, the $[H-Ga\equiv Ga-H]^{2-}$ 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 H−Ga−Ga−H torsion angle is 122° at the SCF level but 170° 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 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 Ge_2H_2 system,[4] the trans-bent structure is not a global minimum on the $[H-Ga\equiv Ga-H]^{2-}$ 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 $[H_2Ga=GaH_2]^{2-}$, and the *neutral* trans HGaGaH, which should have Ga=Ga double bonds, as well as $[H_3Ga-GaH_3]^{2-}$ and the H_2GaGaH_2 molecules, which should have Ga−Ga single bonds. Our results agree well with previous theoretical studies on some of these species.[19−21] The linear H−Ga=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 ∼ 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 H_2Al_2 [22,23] and the H_2Ge_2 molecules.[4] The electronic structure of the long Ga=Ga double bond in the neutral trans-bent HGaGaH molecule was described by Treboux et al.[19] 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 $\sigma-\pi$ Ga=Ga double bond in the linear H−Ga=Ga−H structure (2.251 Å) but also, surprisingly, is even *longer* than the Ga−Ga *single* bond in $H_2Ga-GaH_2$ (2.522 Å in D_{2h} symmetry, Figure 4). (Although D_{2h} $H_2Ga-GaH_2$ 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 HGaGaH structure is composed of two pairs of

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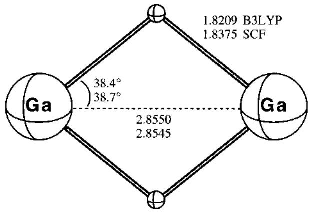
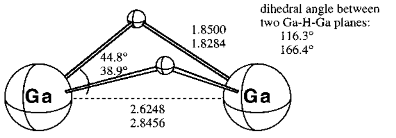
Table 2. The Harmonic Vibrational Frequencies (cm^{-1}) and the Infrared Intensities (km/mol, in Parentheses) of $[HGaGaH]^{2-}$ (C_{2h} and C_2)

	$[HGaGaH]^{2-}$ (C_{2h})				$[HGaGaH]^{2-}$ (C_2)		
	sym	SCF	B3LYP	B3LYP/ 6-311+G**	sym	SCF	B3LYP
Ga−H stretch	b_u	1624(754)	1487(787)	1529	b	1526(7326)	1505(734)
Ga−H stretch	a_g	1613(0)	1469(0)	1518	a	1527(796)	1485(164)
Ga−Ga stretch	a_g	488(0)	491(0)	498	a	446(2)	494(0.5)
Ga−Ga−H bend	b_u	111(179)	240(59)	221	b	207(765)	252(38)
Ga−Ga−H bend	a_g	157(0)	195(0)	189	a	228(15)	199(96)
torsion	a_u	519*i*	81*i*	206	a	140(8)	91(2064)

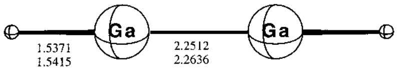


$[HGaGaH]^{2-}$ (D_{2h} symmetry, TS)

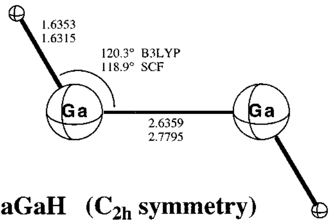


$[HGaGaH]^{2-}$ (C_{2v} symmetry)

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



HGaGaH ($D_{\infty h}$ symmetry, TS)

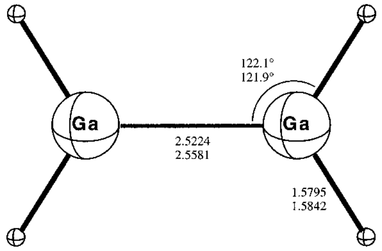


HGaGaH (C_{2h} symmetry)

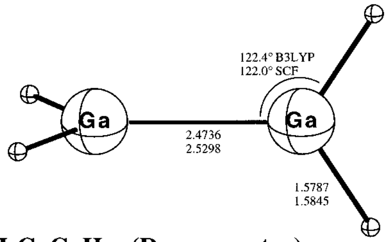
Figure 3. The optimized geometries of neutral HGaGaH ($D_{\infty h}$ symmetry, transition state) and HGaGaH (C_{2h} symmetry) at the TZ+2P+diff B3LYP and SCF levels of theory.

electrons which form weak dative bonds. Hence, it should be considered formally as a *double* bond. Indeed, Lappert's 1976 description[24] 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,[25] even though the distance is very close to that of a single Sn−Sn bond (2.770 Å).[26] Such bent and weak bonds also have been reported and analyzed for related systems, such as H_2Si_2, by Grev and Schaefer.[3]

In the trans-bent dianion $[H−Ga≡Ga−H]^{2-}$, the additional pair of electrons forms a π-bond between the two Ga atoms perpendicular to the C_s plane. This additional π-bonding reduces the Ga−Ga distance from 2.640 Å in the bent neutral 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 π bond, as a *triple* bond. The preference of two dative bonds and a π bond can be explained as that each GaH fragment has $^2\Pi$ ground state corresponding to $n_\sigma^2\ p_{\pi x}$ 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.)[3,19] Our localized molecular orbital analysis confirms the above description. The contour maps based on the CCSD geometry (C_{2h}) 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 π-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 π bonding are weak. Hence, the GaGa bond in $[H−Ga≡Ga−H]^{2-}$ has an exceptionally long distance (2.460 Å), only 0.06 Å shorter than a regular σ Ga−Ga single bond (2.522 Å in the D_{2h} $H_2Ga−GaH_2$ structure, Figure 4).



H_2GaGaH_2 (D_{2h} symmetry, TS)



H_2GaGaH_2 (D_{2d} symmetry)

Figure 4. The optimized geometries of H_2GaGaH_2 (D_{2h} symmetry, transition state) and H_2GaGaH_2 (D_{2d} symmetry) at the TZ+2P+diff B3LYP and SCF levels of theory.

We computed a model molecule $Na_2[HGaGaH]$ to study the effect of the alkali atoms in the experimental system $Na_2[Mes^*{}_2C_6H_3−Ga≡Ga−C_6H_3Mes^*{}_2]$ (**1**). A stationary point was optimized in C_{2h} symmetry (Figure 6). The Ga−Ga bond distance (2.441 Å) is about 0.02 Å shorter than that in the $[H−Ga≡Ga−H]^{2-}$ dianion with the B3LYP method, but the

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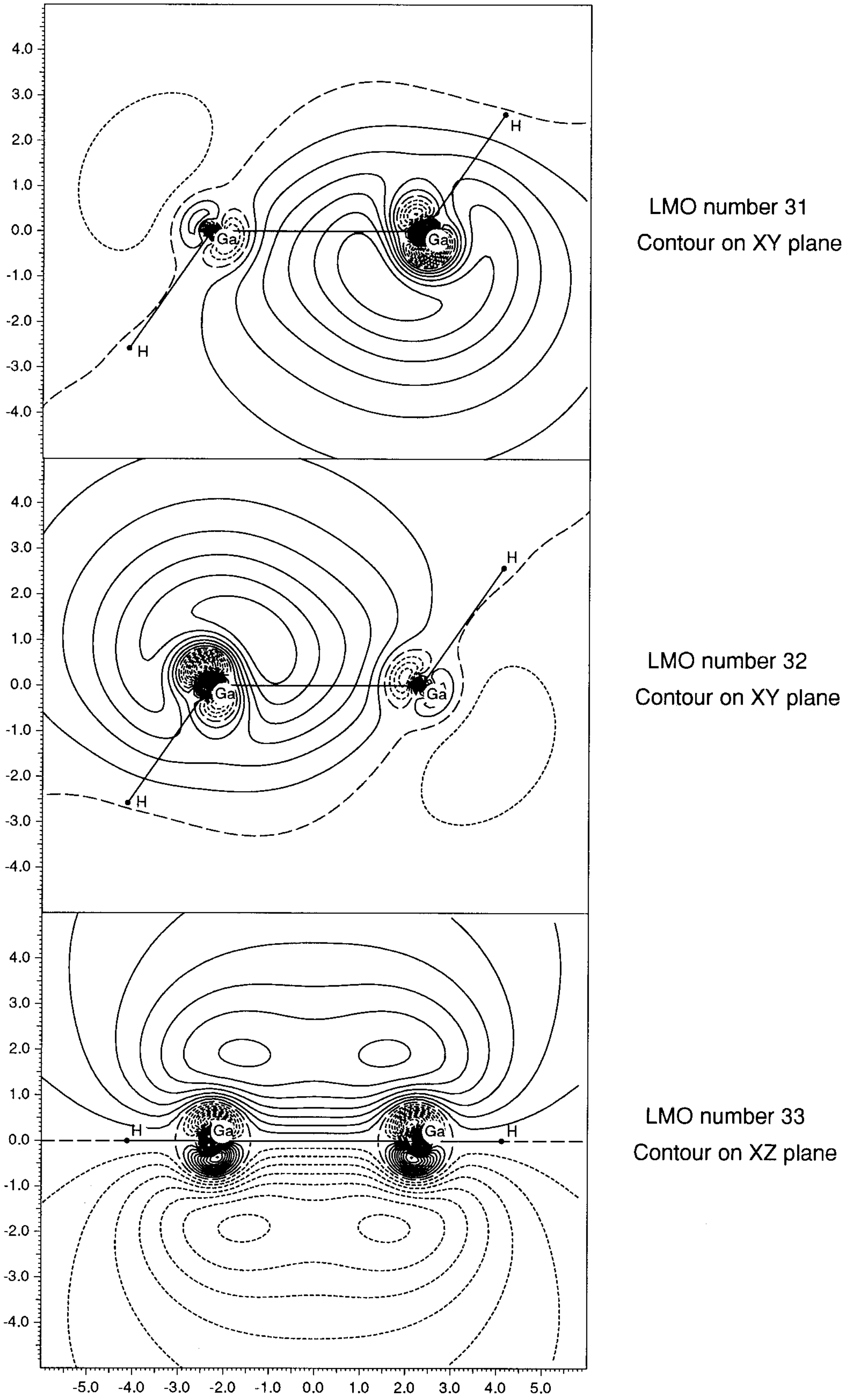
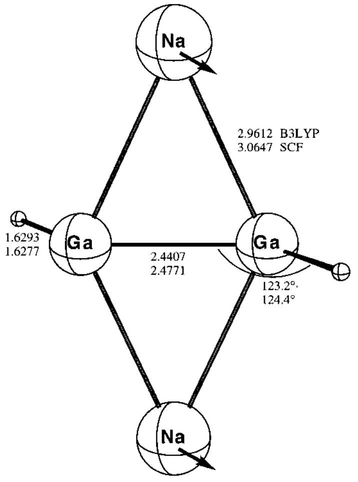


Figure 5. The contour maps of the three bonding orbitals of $[HGaGaH]^{2-}$ (C_{2h} symmetry). Those at the top and the middle are the dative bond orbitals (XY plane), and the one at the bottom is the π bond orbital (XZ plane).

bond character should be the same in both. The single imaginary vibrational frequency (30*i* cm^{-1} at B3LYP, or 29*i* 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

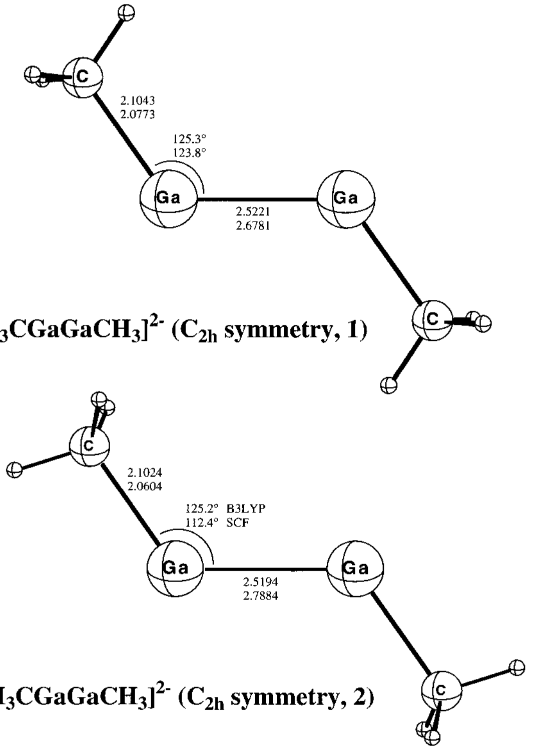
Table 3. The Harmonic Vibrational Frequencies (cm^{-1}) and the Infrared Intensities (km/mol, in parentheses) of $[H_3CGaGaCH_3]^{2-}$ (C_2 and C_i) at the TZ+2P+Diff B3LYP Level of Theory

$[H_3CGaGaCH_3]^{2-}$ (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), 62*i*
$[H_3CGaGaCH_3]^{2-}$ (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), 63*i*, 83*i*
$[H_3CGaGaCH_3]^{2-}$ (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)
$[H_3CGaGaCH_3]^{2-}$ (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)



$H_2Ga_2Na_2$ (C_{2h} symmetry)

Figure 6. The optimized geometry of $Na_2[HGaGaH]^{2-}$ 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.

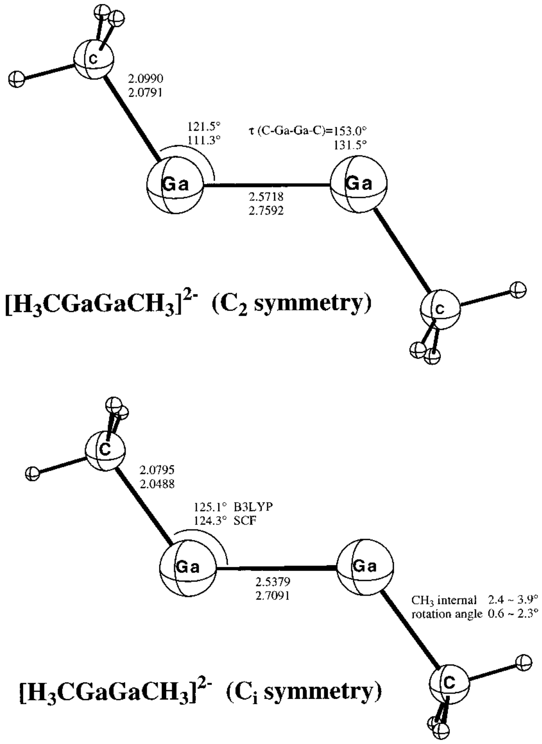


$[H_3CGaGaCH_3]^{2-}$ (C_{2h} symmetry, 1)

$[H_3CGaGaCH_3]^{2-}$ (C_{2h} symmetry, 2)

Figure 7. Two optimized geometries of $[H_3CGaGaCH_3]^{2-}$ 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.)



$[H_3CGaGaCH_3]^{2-}$ (C_2 symmetry)

$[H_3CGaGaCH_3]^{2-}$ (C_i symmetry)

Figure 8. The optimized geometries of $[H_3CGaGaCH_3]^{2-}$ with C_i and C_2 symmetry at the TZ+2P+diff B3LYP and SCF levels of theory.

$[H_3C{-}Ga{\equiv}Ga{-}CH_3]^{2-}$ and $Na_2[H_3C{-}Ga{\equiv}Ga{-}CH_3]$. There are two stationary C_{2h} structures (**2** and **3**) for the larger model dianion $[H_3C{-}Ga{\equiv}Ga{-}CH_3]^{2-}$, 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 (63*i* 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 (63*i* and 83*i* 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 π-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° 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 $[H_3C{-}Ga{\equiv}Ga{-}CH_3]^{2-}$ is similar to that in $[H{-}Ga{\equiv}Ga{-}H]^{2-}$, but the Ga−Ga bond length in $[H_3C{-}Ga{\equiv}Ga{-}CH_3]^{2-}$ is about 0.1 Å longer at both the B3LYP and SCF levels of theory (Figures 1). The same trend has been reported for HSi−SiH,[5] where methyl substitution increases the Si−Si bond length (from 2.111 to

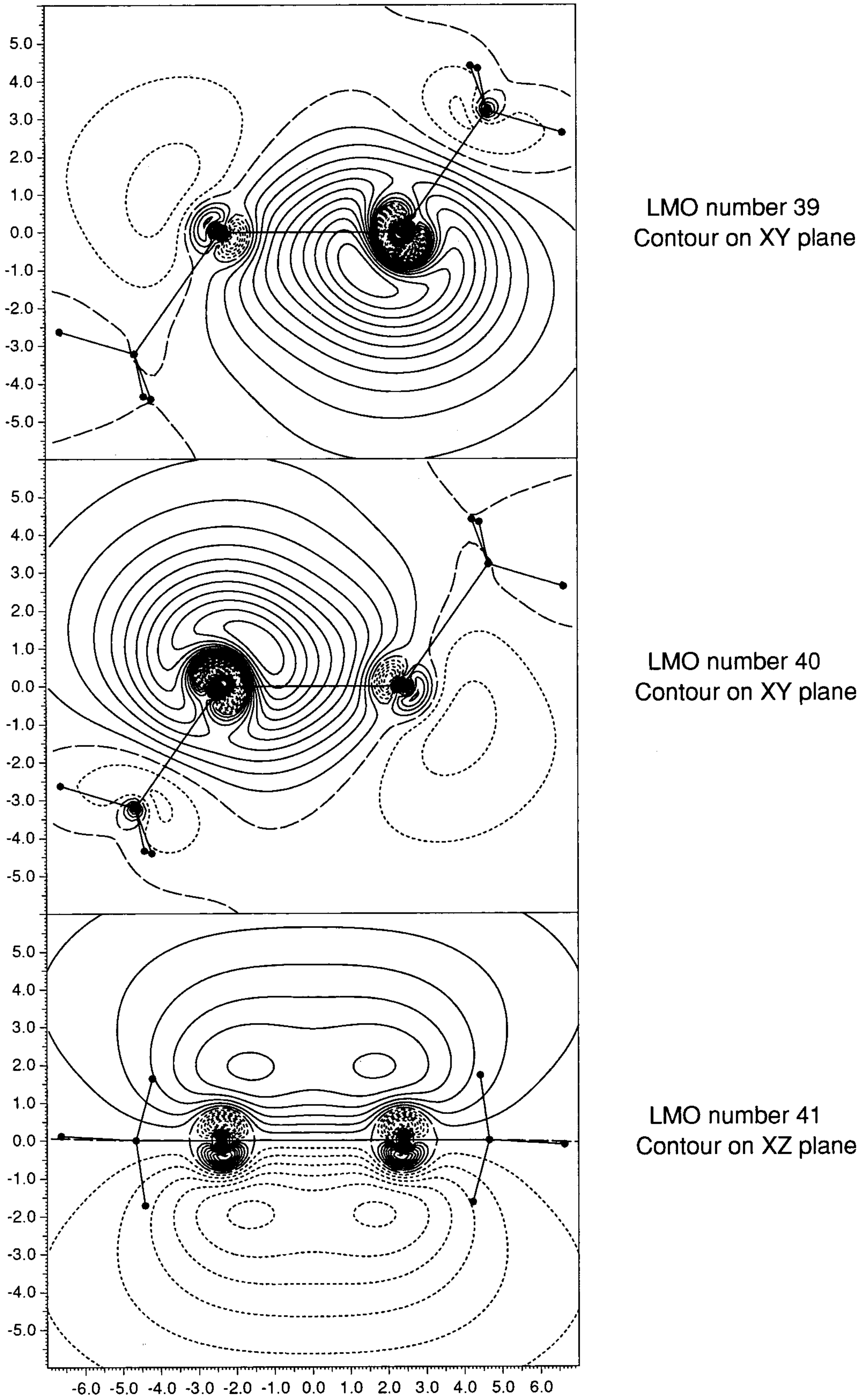


Figure 9. The contour maps of the three bonding orbitals of $[H_3CGaGaCH_3]^{2-}$ (C_i symmetry). Those at the top and the middle are the dative bond orbitals (XY plane), and the contour map at the bottom is the π bond orbital (XZ plane).

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 HSiSiH to 2.094 Å for $F_3Si{-}SiSi{-}SiF_3$ or to 2.095 Å for $Me_3Si{-}SiSi{-}SiMe_3$). As with −Si≡Si−, the $[-Ga{\equiv}Ga-]^{2-}$ length may also be decreased by large susbtituents. The contour maps of the three bonding LMOs of $[H_3C{-}Ga{\equiv}Ga{-}CH_3]^{2-}$ are shown in Figure 9. The dative bond orbitals and the π-bond orbital have almost the same shape as in $[H{-}Ga{\equiv}Ga{-}H]^{2-}$.

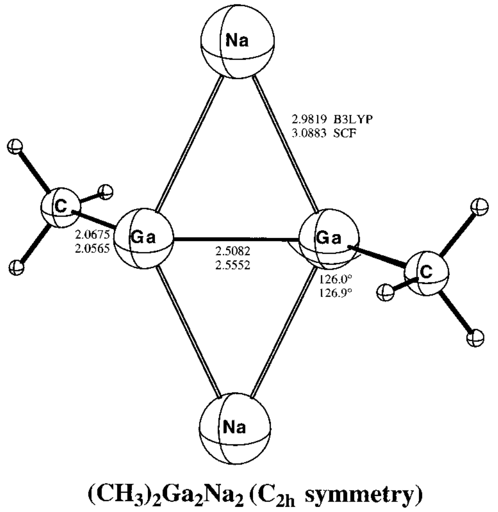


Figure 10. The optimized geometry of $Na_2[H_3CGaGaCH_3]^{2-}$ with C_{2h} symmetry at the TZ+2P+diff B3LYP and SCF levels of theory.

As discussed above for $[H{-}Ga{\equiv}Ga{-}H]^{2-}$, there should be a Ga≡Ga triple bond in this molecule as well.

The energy of the C_2 structure of $[H_3C{-}Ga{\equiv}Ga{-}CH_3]^{2-}$ (Figure 8), which is similar to $[HGa{\equiv}GaH]^{2-}$, is about 4.4 kcal/mol higher than the C_i 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_{2h} 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 $[H{-}Ga{\equiv}Ga{-}H]^{2-}$ (but increases from 122.1° to 131.5° at the SCF level). Qualitatively, the Ga≡Ga bond character in $[H_3C{-}Ga{\equiv}Ga{-}CH_3]^{2-}$ is similar to that in $[H{-}Ga{\equiv}Ga{-}H]^{2-}$.

Like $[H_3C{-}Ga{\equiv}Ga{-}CH_3]^{2-}$, two stationary points for the neutral $Na_2[H_3C{-}Ga{\equiv}Ga{-}CH_3]$ in C_{2h} symmetry were optimized. The CH_3 orientations differ, but their energies are nearly the same (within 0.4 kcal/mol). The Ga−Ga bond length of the $[H_3C{-}Ga{\equiv}Ga{-}CH_3]^{2-}$ form with the lower energy is about 0.02 Å (B3LYP) shorter than that of the C_{2h} structure. Neither are minima. One has a single imaginary vibrational frequency ($15i$ cm^{-1}, B_u), but the second has three (A_u, B_g, B_u). The B_u mode leads to a minimum with C_s symmetry (like $Na_2[H{-}Ga{\equiv}Ga{-}H]$), which has an energy 0.22 kcal/mol lower than the first C_{2h} structure. In comparison with $Na_2[H{-}Ga{\equiv}Ga{-}H]$, the magnitude of the B_u imaginary vibrational frequency and the energy difference between the C_s and C_{2h} structures become smaller, indicating that the potential curve is much flatter for $Na_2[H_3C{-}Ga{\equiv}Ga{-}CH_3]$. We expect that the C_{2h} 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)[27] and NLMO/NPA[28] results in Table 4 (obtained as implemented in Gaussian94[17]) 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 $[H_2Ga{=}GaH_2]^{2-}$ (D_{2h} and C_{2h}) is much longer, 2.40 Å. Constrained linear $[H{-}Ga{\equiv}Ga{-}H]^{2-}$ unambiguously has a *triple bond,* but the GaGa distance 2.2 Å is comparable to that of the *double bond* in linear HGa═GaH.

Table 4. Wiberg Bond Index (WBI) and Natural Localized Molecular Orbital Natural Population Analysis (NLMO/NPA) Bond Orders Compared with Bond Lengths (Å) of $[HGaGaH]^{2-}$, $[H_3CGaGaCH_3]^{2-}$, and H_2GaGaH_2 in Various Geometries

	bond order		Ga−Ga
molecule	WBI	NIMG/NPA	bond length, Å
single			
$[H_3Ga{-}GaH_3]^{2-}$ (D_{3d})	0.95	1.02	2.592
$H_2Ga{-}GaH_2$ (D_{2h})	0.85	0.93	2.522
$H_2Ga{-}GaH_2$ (D_{2d})	0.89	1.05	2.474
double			
$[H_2Ga{=}GaH_2]^{2-}$ (D_{2h})	1.94	2.21	2.406
$[H_2Ga{=}GaH_2]^{2-}$ (C_{2h})	1.88	1.94	2.407
$HGa{=}GaH$ ($D_{\infty h}$)	1.86	1.95	2.251
triple			
$[HGa{\equiv}GaH]^{2-}$ ($D_{\infty h}$)	2.95	3.02	2.214
$[HGa{\equiv}GaH]^{2-}$ (C_{2h})	2.36	3.02	2.457

Bending lengthens the GaGa separations in $[RGaGaR]^{2-}$ derivatives considerably, but in $[H_2Ga{=}GaH_2]^{2-}$ 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 $[H{-}Ga{\equiv}Ga{-}H]^{2-}$, $[H_3C{-}Ga{\equiv}Ga{-}CH_3]^{2-}$, $Na_2[H{-}Ga{\equiv}Ga{-}H]$, and $Na_2[H_3C{-}Ga{\equiv}Ga{-}CH_3]$ 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,[29] cyclohexyne, cyclopentyne, and cyclobutyne. It may also be noted that $HBBH^{2-}$ and HCCH, when bent to 120°, show very little change in the Wiberg bond index (e.g. 2.992 for $HBBH^{2-}$ and 2.977 for HCCH). On bending $HGaGaH^{2-}$, there is much more mixing of the Ga σ orbitals into the in-plane "π" bond hydridization than in the first row cases. This is the main difference with respect to $HBBH^{2-}$ in the bonding

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[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**, 2761.

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 $HGaGaH^{2-}$, linear or bent, are quite weak energetically.

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Supporting Information Available: Table of total energies of $[HGaGaH]^{2-}$, $[H_3CGaGaCH_3]^{2-}$, and H_2GaGaH_2 (1 page, print/PDF). See any current masthead page for ordering information and Web access instructions.

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