1646 *Organometallics* **2001,** *20,* 1646−1651

Ga−Ga Multiple Bond in $Na_2[Ar^*GaGaAr^*]$ ($Ar^* = C_6H_3\text{-}2,6\text{-}(C_6H_2\text{-}2,4,6\text{-}i\text{-}Pr_3)_2$)

Nozomi Takagi, Michael W. Schmidt, and Shigeru Nagase*

Department of Chemistry, Graduate School of Science, Tokyo Metropolitan University, Hachioji, Tokyo 192-0397, Japan

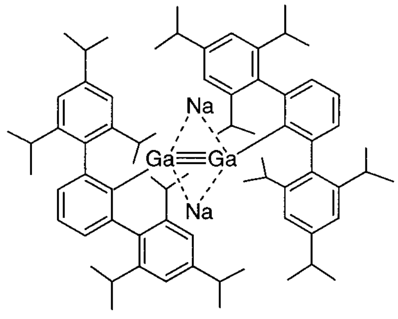
Received November 20, 2000

Theoretical calculations are carried out to investigate the Ga−Ga bond in the title compound, whose description as the first example of a triple bond between group 13 elements has sparked considerable interest. The short Ga−Ga bond length is found to be the result of several factors, including Na−terphenyl and terphenyl−terphenyl ionic interactions, direct Ga−Na−Ga bridge bonding, and adjustments in the C−Ga−Ga angles due to the steric requirements of the *i*-Pr groups on the bulky *m*-terphenyl ligands.

Introduction

In 1997, Robinson and co-workers reported the synthesis of a novel compound, $Na_2[Ar^*GaGaAr^*]$ ($Ar^* =$ 2,6-bis(2,4,6-triisopropylphenyl)phenyl), as the first example containing a triple bond between main group 13 elements.[1,2] The X-ray crystal structure reveals that the two Na atoms reside on either side of the Ga−Ga bond, forming a nearly planar Ga_2Na_2 ring; the core of the molecule is not linear, but rather the two Ga−Ga−C fragments are each bent 128.5° and 133.5° (an average = 131.0°). The most noticeable structural point is that the Ga−Ga bond length is 2.319 Å; this is the shortest on record, according to review articles comparing the bond length with those of other interesting gallium compounds, including an aromatic Ga_3^{2-} ring.[3,4]Since triple bonding between heavier main group elements has long attracted widespread interest, the successful synthesis of $Na_2[Ar^*GaGaAr^*]$ is a remarkable advance in this field. However, the formal assignment of a Ga−Ga triple bond has been questioned.[5,6] For example, Power and co-workers have suggested that the Ga−Ga bond order may be 2 rather than 3.[7] Very recently, an experiment using the larger K rather than Na as the reducing agent produced $K_2[Ar^*Ga_4Ar^*]$ (not $K_2[Ar^*Ga_2Ar^*]$), with a nearly square arrangement of Ga atoms and no possible triple bonding.[8] This demonstrates that the alkali is not simply a reducing agent but is an integral part of the structure. There are several recent reviews containing information on multiple bonding involving group 13 elements.[2−4,9,10]

Chart 1



A number of theoretical calculations have been performed for simple model systems, $Na_2[RGaGaR]$ and $[RGaGaR]^{2-}$ (R = H, Me, and Ph).[5,11−17] These establish that the HOMO is a π bond bridged at the top and bottom by Na atoms for $Na_2[RGaGaR]$, or a true π bond for $[RGaGaR]^{2-}$. The HOMO-1 is more controversial. This orbital's shape[5,11,14] is that of an antisymmetric combination of lone pairs on each Ga, with some in-plane π bonding to the other Ga atom. This shape has been considered by some authors[11,12,13,15] as a slipped π bond, who accordingly count the pair of electrons as involved in Ga−Ga bonding. The maximum in this orbital's density occurs at about a 95° Ga−Ga−lone pair angle, so its position outside 90° has led others to prefer to consider it as nonbonding.[5,14] Thus, the Ga−Ga bonding has been described as a triple bond consisting of "a distorted σ bond, a significantly weakened π

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* Corresponding author. E-mail: nagase@SNL70.chem.metro-u.ac.jp. Fax: +81-426-77-2525.

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10.1021/om0009841 CCC: $20.00
Publication on Web 03/22/2001

bond which is localized strongly on the Ga atoms, and a pure π bond”[13] (or, equivalently, “two weak dative bonds and one π bond”)[2] or as a double bond, denying any bonding from the slipped π, which “is indistinguishable from a lone pair orbital”.[14] Force constant calculations of Na_2[HGaGaH] and $[HGaGaH]^{2-}$ have suggested the softness of the Ga−Ga bonding.[16,17]

The Ga−Ga bond lengths calculated for the simplified model systems are considerably longer than the experimental value. Cotton and co-workers[5] have carried out a calculation on a more realistic model system for Na_2[Ar*GaGaAr*] by replacing the *i*-Pr groups on the Ar* ligand by H atoms (this *m*-terphenyl ligand lacking *i*-Pr groups is denoted hereafter as Arx*). On the basis of density functional calculations at the B3PW91 level, they suggested that an interaction between the Na cations and terphenyl ligands shortens the Ga−Ga bond length.[5] Very recently, Xie, Schaefer, and Robinson have recalculated the same model system of C_{2h} symmetry, Na_2[Arx*GaGaArx*], with density functional theory at the B3LYP level using a high-quality basis set.[18] They have found that the Ga−Ga bond length is 2.404 Å, which is 0.085 Å longer than the experimental value. In addition, the Ga−Ga−C angle was calculated to be 120.6°; this degree of trans-bending is about 10° larger than that in the synthesized compound. It was suggested that these discrepancies are due to the crystal structure.[18]

In this study, we demonstrate that the *i*-Pr groups present in Robinson’s compound[1] play an important role in shortening the Ga−Ga bond length, using density functional theory calculations. We confirm the presence of an attractive interaction between Na cations and terphenyl ligands using electron density analysis. We also consider an electropositive substituent, SiH_3, instead of the experimental organic ligand. Finally, we present a natural orbital analysis to further understanding of the bonding in a Na_2[MeGaGaMe] model.

Computational Methods

Geometries were optimized with nonlocal hybrid density functional theory (DFT)[19] at the B3LYP and B3PW91 levels using the Gaussian 98 program.[20] In these, Becke’s exchange functional (B3)[21] was used in conjunction with either the Lee−Yang−Parr (LYP)[22] or the Perdew−Wang (PW91)[23] correlation functional. Two kinds of basis sets were employed. The first one referred to as basis-A is a set of 6-311G(d) for Ga and Na and 3-21G for C and H, and the second one referred to as basis-B is a larger set of 6-311+G(2df) for Ga, 6-311G(d) for Na, and 6-31G(d) for C, Si, and H; these are all incorporated in the Gaussian 98 program. In quality, basis-B is very similar to that employed by Schaefer and co-workers.[18] Geometry optimization was also carried out with second-order Møller−Plesset (MP2) perturbation[24] and multiconfigurational self-consistent-field (MCSCF)[25] methods. Bonding analysis was performed with natural populations,[26] atoms in molecules (AIM) theory,[27] and MCSCF natural orbitals.[25] MCSCF and MP2 calculations were carried out using the GAMESS program.[28]

Table 1. Bond Lengths (Å), Bond Angles (deg), and Natural Charges (*Q*) Calculated Using Basis-B at the B3LYP Level for Na_2[RGaGaR], $[RGaGaR]^{2-}$, and RGaGaR; All Systems Optimized with C_{2h} Symmetry

	R				
	H	Me	SiH_3	Ph	Arx*
Na_2[RGaGaR]					
Ga−Ga	2.427	2.485	2.406	2.507	2.402
Ga−Na	2.959	2.974	2.954	2.985	3.082
Ga−R	1.624	2.055	2.492	2.049	2.121
Ga−Ga−R	123.7	127.2	126.7	124.7	121.5
Q on Na	0.759	0.699	0.813	0.729	0.850
Q on Ga	−0.456	−0.161	−0.546	−0.155	−0.271
$[RGaGaR]^{2-}$					
Ga−Ga	2.464	2.531	2.435	2.496	2.535
Ga−R	1.648	2.066	2.550	2.078	2.110
Ga−Ga−R	124.0	125.7	127.0	124.3	117.8
Q on Ga	−0.606	−0.385	−0.527	−0.340	−0.291
RGaGaR					
Ga−Ga	2.608	2.662	2.575	2.724	2.716
Ga−R	1.628	2.027	2.513	2.024	2.060
Ga−Ga−R	120.8	123.7	123.3	121.2	115.9
Q on Ga	0.399	0.573	0.277	0.619	0.603

Results and Discussion

Model Systems. The optimized geometrical parameters and natural charges calculated using the large basis-B at the B3LYP level for several model compounds, Na_2[RGaGaR] (R = H, Me, SiH_3, Ph, and Arx*), are given in Table 1. A trans-bent structure with C_{2h} symmetry is the probable energy minimum for R = Arx*, as optimization of C_i, C_s, or C_2 trial structures regains C_{2h} symmetry. For comparison, the others are all optimized assuming C_{2h} symmetry. The Ga atom belongs to group 13 and has only three valence electrons. Since one of the valence electrons is tied up in bonding to R, Ga does not have the necessary number of electrons to make a triple bond. The final two electrons needed are donated from Na to Ga. This is supported by two factors. One is that the charge on each Na is about +0.7 to +0.8. The other is that the Ga−Ga π orbital is the LUMO for RGaGaR and becomes occupied after the Na atoms are coordinated.

As Table 1 shows, the Ga−Ga bond length in Na_2[RGaGaR] increases as R changes from H (2.427 Å) to Me (2.485 Å) and Ph (2.507 Å). Theoretical studies of substituent effects on heavier triple bonding have

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previously shown that electropositive silyl substituents help to shorten heavier triple bond lengths.[29] Accordingly, the SiH_3 group generates a shorter Ga−Ga bond length (2.406 Å). On the other hand, although the Arx* group is less electropositive, this substituent leads to a still shorter Ga−Ga bond length (2.402 Å). This length is about 0.1 Å shorter than the value of 2.507 Å for R = Ph. Cotton and co-workers[5] have suggested that the short Ga−Ga bond length is due to an interaction between Na cations and two terminal phenyl groups on each Arx*.

We also calculated the dianion $[RGaGaR]^{2-}$ system, in which the Na atoms are absent, and these results are shown in Table 1. In this dianion system, six electrons exist on the Ga atoms, which can participate in a Ga−Ga triple bond. The Ga−Ga bond lengths are 0.04 Å longer for R = H and Me and 0.01 Å shorter for R = Ph than those in $Na_2[RGaGaR]$, while the SiH_3 group gives the shortest Ga−Ga bond length. It is noticeable that the Ga−Ga bond length for R = Arx* is elongated to 2.535 Å by 0.133 Å in $[RGaGaR]^{2-}$ and becomes rather longer than that for R = Ph. This result is quite different from the $Na_2[RGaGaR]$ case and confirms Cotton's viewpoint,[5] stressed by Power,[9,10] that part of the reason for the short Ga−Ga bond length is an attractive sodium−terphenyl interaction. We also calculated the neutral RGaGaR system, in which the number of valence electrons, 4, is not sufficient to make a triple bond. As shown in Table 1, the Ga−Ga lengths in RGaGaR are all longer than those in $Na_2[RGaGaR]$ or $[RGaGaR]^{2-}$. Once again, the shortest Ga−Ga bond length in RGaGaR occurs for R = SiH_3. The Ga−Ga bond length for R = Arx* differs little from that for R = Ph.

As is apparent from the results as stated above, a Ga−Ga bond length approaching 2.4 Å for organic ligands is observed only in the presence of Na atoms that can interact with the terphenyl groups. This type of interaction was confirmed by an electron density analysis based on AIM theory.[27] The results of these AIM calculations on $Na_2[Arx^*GaGaArx^*]$, using the HF/3-21G method, are shown in Figure 1. It is interesting that bond critical points and bond paths (i.e., bonding interactions[27b]) can be found between each Na and terphenyl group as well as between two terphenyl groups. The values of electron density (ρ_b) and its Laplacian ($\nabla^2\rho_b$) at bond critical points are 0.006 and 0.052 au for the C−Na bond path and 0.003 and 0.010 au for the C−C bond path, respectively. The positive values of $\nabla^2\rho_b$ suggest that both interactions have ionic character. Although the ρ_b and $\nabla^2\rho_b$ values are small, both types of interaction contribute to shortening the Ga−Ga bond length.

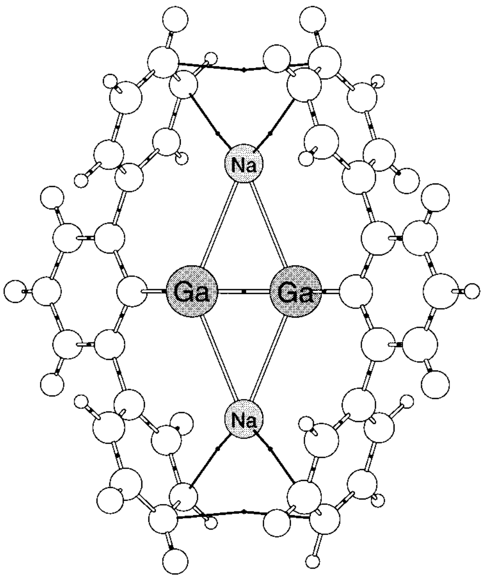

Figure 1. Bond critical points (dots) and bond paths (lines) obtained by AIM calculations for $Na_2[Arx^*GaGaArx^*]$. The Na−C bond path connects to the carbon closest to sodium.

Table 2. Ga−Ga Bond Lengths of $Na_2[RGaGaR]$ at Idealized and Minimum Energy Structures, and Comparison of Computational Methods with Basis-B

	R					
	H		Me		SiH_3	
	C_{2h}[a]	C_s[b]	C_{2h}[a]	C_s[b]	C_{2h}[a]	C_1[b]
B3LYP	2.427	2.442	2.485	2.437	2.406	2.393
MP2	2.408	2.412	2.450	2.406	2.382	2.368
B3PW91	2.385	2.403	2.434	2.394	2.366	2.362[c]

[a] Values at idealized C_{2h} structures. [b] Values at minimum energy structures identified by vibrational frequency analysis. [c] C_s symmetry.

It is known that C_{2h} structures for small models such as R = H and Me are not minima.[12] These two models distort to C_s structures, with the Na atoms making an angle of about 120° with the center of the Ga−Ga bond, instead of being about 180° apart as in the synthesized compound. The results of searches for the lower symmetry minima are given in Table 2, which also compares computational procedures. Note that the minima[30] have shorter Ga−Ga bond lengths than the idealized C_{2h} structures, by as much as 0.04 Å for R = Me, but about 0.01 Å for R = H or SiH_3. Second, note that the B3LYP lengths are consistently about 0.03 Å longer than MP2 values, which in turn are about 0.01 Å longer than B3PW91.

Real System. The Ga−Ga bond length of 2.402 Å calculated using the large basis-B at the B3LYP level for the model $Na_2[Arx^*GaGaArx^*]$ system is very close to the value of 2.404 Å calculated very recently by Schaefer and co-workers.[18] These values are 0.083 and 0.085 Å longer than the experimental value of 2.319 Å.[1] This discrepancy was little changed by employing still larger basis sets (i.e., 6-311+G(3df) on Ga and 6-311G(2d) on Na). We now seek to uncover the reason for the 0.08 Å discrepancy between calculations and experiment.

Each ligand ($Ar^* = C_6H_3$-2,6-(C_6H_2-2,4,6-*i*-$Pr_3)_2$) in the synthesized compound contains six *i*-Pr groups. The presence of these *i*-Pr groups is of crucial importance in synthesizing the compound, as the same type of

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[30] An additional minimum exists, with both Na atoms on the same side of the RGaGaR plane, rather than opposite sides. For each ligand, this alternative dibridged minimum is of lower energy than the local minima reported in Table 2, by 0.6, 2.0, and 0.5 kcal/mol for H, Me, and SiH_3, respectively. The MP2 Ga−Ga bond lengths for the same three ligands are 2.395, 2.403, and 2.363 Å, which are very similar to those for the relative minima given in Table 2.

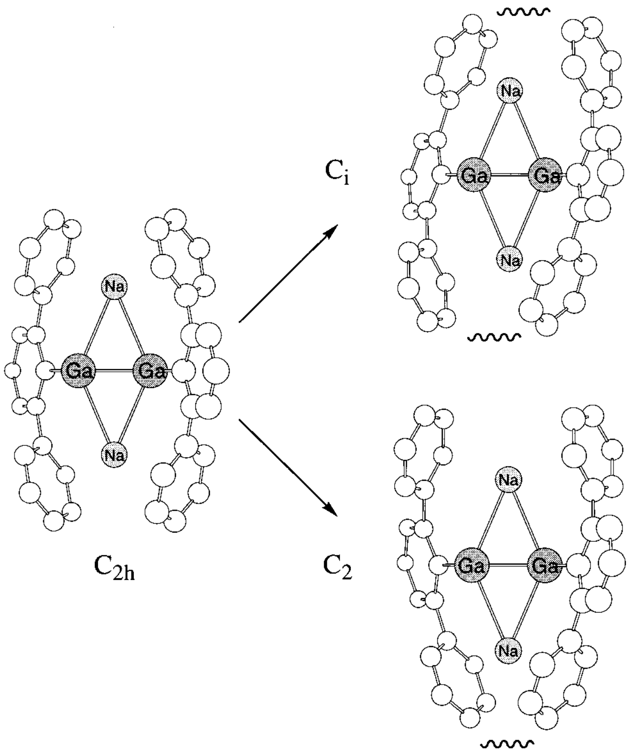

Figure 2. Two possible distortions to decrease steric repulsion. For simplicity, all *i*-Pr groups and H atoms are omitted.

synthetic procedure using Me groups instead of *i*-Pr, i.e., the 2,6-bis(2,4,6-trimethylphenyl)phenyl ligand, leads to a Na-coordinated Ga_3^{2-} aromatic ring, not the Ga−Ga triply bonded compound.[2] Accordingly, we report calculations on Robinson's synthesized compound, Na_2[Ar*GaGaAr*]. Because of the size of the compound (the number of contracted basis functions becomes 1376 for basis-B), we performed a full B3LYP geometry optimization using basis-A.

As shown in Figure 2, when *i*-Pr groups are introduced, the molecule can distort from C_{2h} to C_2 or C_i to decrease steric effects. Distortion to C_i does not lower the energy. Upon lowering the symmetry to C_2, the steric repulsion between one pair of terphenyl groups decreases, but that of the other pair increases, since these terphenyl groups grow close. This contact is diminished by means of increasing the Ga−Ga−C angle. Thus, distortion from C_{2h} to C_2 leads to an energy lowering and an increased Ga−Ga−C angle (i.e., a decrease in the trans-bending).

Figure 3 shows the resultant optimized geometry for the real Na_2[Ar*GaGaAr*] system. In Table 3, the key geometrical parameters are compared with those for the model Na_2[Arx*GaGaArx*] system. It is noteworthy that the Ga−Ga−C angle of 132.0° calculated for the real system is much closer to the experimental average value of 131.0°[1] than the value of 119.0° calculated for the model system. Furthermore, inclusion of the *i*-Pr groups leads to a 0.042 Å shortening of the Ga−Ga bond length, which is about one-half the discrepancy that was already pointed out. These results suggest that it is important to perform calculations with the actual ligands. However, Table 3 shows that the use of basis-A rather than basis-B underestimates the Ga−Ga bond length by about 0.03 Å. This underestimation is enhanced as basis sets become smaller, and care must be taken not to use basis sets so small they produce spurious agreement with experiment.

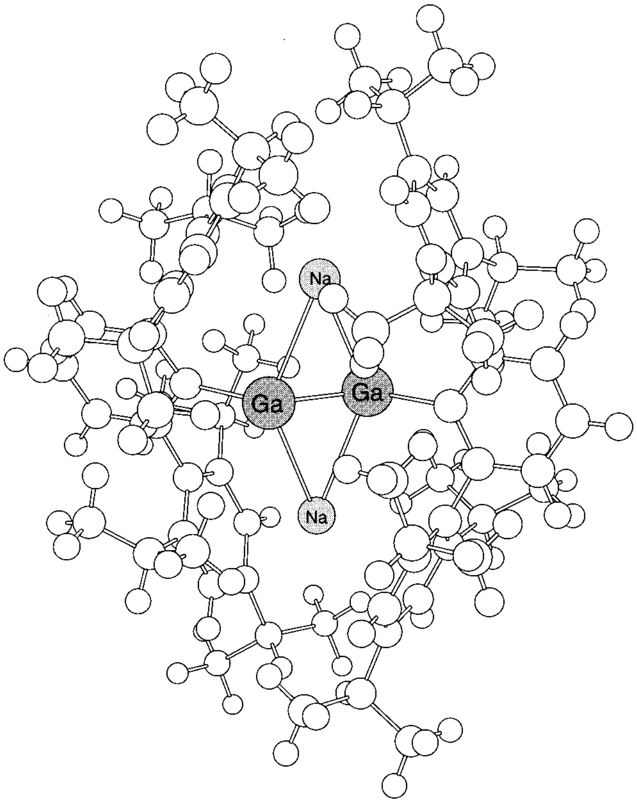

Figure 3. Optimized geometry of Na_2[Ar*GaGaAr*] calculated using basis-A at the B3LYP level.

Table 3. Geometrical Parameters Optimized Using Basis-A and Basis-B at the B3LYP Level for Na_2[RGaGaR] (R = Arx* and Ar*)

	R					
	Arx* C_{2h}		Arx*[a] C_{2h}		Ar* C_2	
	basis-A	basis-B	basis-A	basis-B	basis-A	basis-B
Ga−Ga	2.375	2.402	2.329	2.363	2.333	2.367[b]
Ga−Na	3.092	3.082	3.083	3.073	3.075	
Ga−C	2.105	2.121	2.069	2.093	2.076	
Ga−Ga−C	119.0	121.5	131.0	131.0	132.0	

[a] The Ga−Ga−C angle is fixed at 131.0°. [b] Predicted value, 2.367 = (2.363 − 2.329) + 2.333.

In Table 3, the fully optimized geometrical parameters of Na_2[Arx*GaGaArx*] are compared with those optimized by fixing the Ga−Ga−C angle at the experimental average value of 131.0°. It is notable that a Ga−Ga bond shortening of 0.04 Å is obtainable by fixing the angle at 131.0°, as found for inclusion of *i*-Pr groups; the basis-A results for Na_2[Arx*GaGaArx*] and Na_2[Ar*GaGaAr*] are almost identical, about 2.33 Å. From the data in Table 3, it is possible to estimate that the Ga−Ga bond length for the real system is around 2.367 Å at the B3LYP/basis-B level, if the same basis correction found for Na_2[Arx*GaGaArx*] is applied to Na_2[Ar*GaGaAr*].

The average distance between Na and the terphenyl carbons is 2.930 Å in Na_2[Arx*GaGaArx*] and 3.133 Å in Na_2[Ar*GaGaAr*]. Because the interactions between Na and terphenyl carbons have ionic character, the

Table 4. Geometrical Parameters Optimized Using Basis-B at the B3PW91 Level for $Na_2[RGaGaR]$ (R = Arx* and Ar*)

	R		
	Arx* C_{2h}	Arx*[a] C_{2h}	Ar* C_2
Ga−Ga	2.365	2.331	2.335[b]
Ga−Na	3.076	3.070	
Ga−C	2.092	2.067	
Ga−Ga−C	122.8	131.0	

[a] The Ga−Ga−C angle is fixed at 131.0°. [b] Predicted value, 2.335 = (2.333 − 2.329) + 2.331.

strengths should depend on the distances between them. Since the average distance increases in the real system, the interactions are weaker than in the model system. However, the closest Na−C contact in Na_2[Ar*GaGaAr*] is 2.810 Å, shorter than the closest contact of 2.895 Å in Na_2[Arx*GaGaArx*].

Finally, we show the results of calculations with the B3PW91 functional using basis-B, which Cotton and coworkers employed without polarization functions.[5] As Table 4 shows, this functional yields Ga−Ga bond lengths that are shorter than the B3LYP results, by about the same amount as found for the small models in Table 2. So, the Ga−Ga length in the real system is estimated to be 2.335 Å at the B3PW91/basis-B level, very close to the experimental value of 2.319 Å[1] (for a very recent experimental value of 2.324 Å, see ref 8).

Natural Orbital Analysis of the Ga−Ga bonding. A wide variety of methods have already been used to understand the nature of the Ga−Ga bonding in Na_2[RGaGaR]. These include plots of Hartree−Fock (HF) orbitals,[11] B3PW91 orbitals,[5] localized orbitals and two types of bond orders,[12] Walsh diagrams and the Laplacian of electron density,[13] generalized valence bond (GVB) and HF orbitals,[14] the electron localization function,[15] and B3LYP orbitals.[18] Two of these studies have been done with Na present for R = Ph[5] and Arx*,[18] while one of these was done with Li for R = Me.[14] Nearly all other studies were conducted on $[RGaGaR]^{2-}$ (R = H[11,12,15] and Me[12,13]), which surely exaggerate the spatial extent of orbitals due to the large charge.

Our contribution to understanding the electronic structure is to present the natural orbitals of an MCSCF wave function. We focus on the Na_2[MeGaGaMe] system. The geometry was taken to be the idealized C_{2h} structure rather than its actual C_s minimum, since this is closer to the structure of Na_2[Ar*GaGaAr*]. Results for both Na_2[MeGaGaMe] and $[MeGaGaMe]^{2-}$ are presented using the B3LYP geometries given in Table 1, since these have more realistic bond lengths. The MCSCF active space consists of the six electrons presumed to be involved in the Ga−Ga bonding, in eight orbitals arising from three orbitals on each Ga and one valence 3s orbital on each Na. This gives a total of 318 configurations for MCSCF calculations. The resultant natural orbitals are shown in Figure 4. The first three orbitals, with occupation numbers near 2, are similar to the occupied HF or DFT orbitals, while the other five valence orbitals recover near-degeneracy correlation.

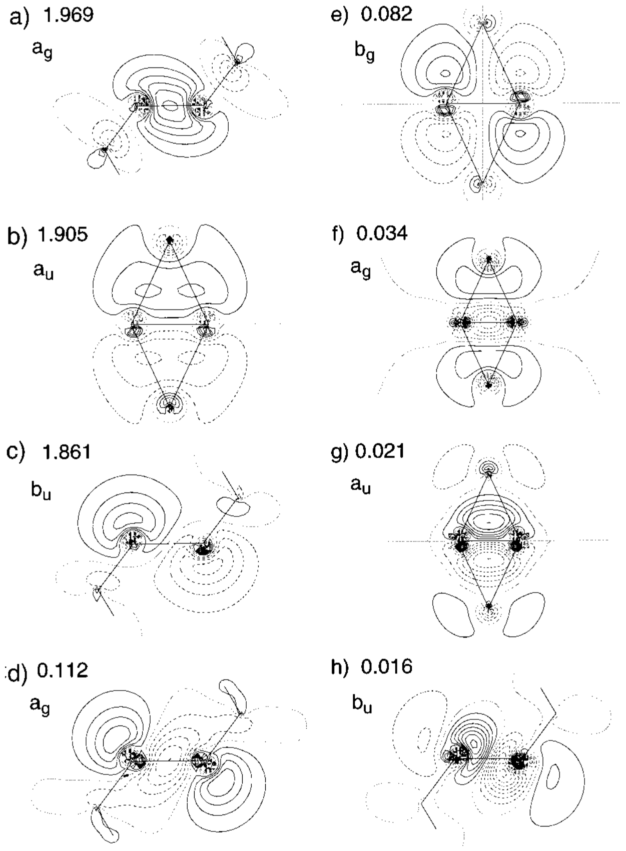

Figure 4. MCSCF natural orbitals and electron occupation numbers for Na_2[MeGaGaMe] using basis-B at the B3LYP optimized geometry. The contour increment is 0.025 $bohr^{-3/2}$. Orbitals **a**, **c**, **d**, and **h** are shown in the CGaGaC mirror plane, while the others are drawn in the Na_2Ga_2 plane.

Orbital **a** represents the Ga−Ga σ bond. Orbital **b** shows what the π orbital looks like when Na atoms are present. The presence of Na causes the maximum electron density to be situated along the Ga−Na bonds, not directly above and below the Ga atoms, as would be the case in a pure π bond. Clearly, Na is participating directly in forming bridging bonds, not acting simply as an electron donor. Orbital **c** closely resembles previous images of the "slipped π". The maximum electron density lies outside 90°, which has led to its description as a lone pair, but some partial π bonding exists (at amplitude values smaller than the smallest contour drawn, the two positive and two negative regions are connected). Note that the "slippage" of the π bond, whose node would lie on the Ga−Ga bond in a linear geometry, causes this node to curve between the Ga atoms and thus introduces some antibonding in the center of this orbital. This degree of antibonding has been noted before.[14]

Orbital **d**, which is the symmetric combination of the two Ga lone pairs, is the principal correlating orbital for orbital **c**. Symmetry requires orbital **d** to possess bonding character between the Ga atoms. Its occupation number of 0.112 is significant, in view of the usual recommendation[31] that MCSCF computations are required for any system exhibiting HF instabilities (which for the case of two electrons in two orbitals occurs when a correlating orbital's occupation exceeds 0.106). Another measure of the significant multiconfigurational character is that the leading configuration has a mixing coefficient of 0.934 and thus a weight of 87.3% in the

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(31) Bofill, J. M.; Pulay, P. *J. Chem. Phys.* **1989**, *90*, 3637−3646.

MCSCF wave function. Orbitals **f** and **g** are weakly occupied correlating orbitals rising from the inclusion of the Na 3s orbitals in the active space and are considerably nonspherical around Na. The Ga−Ga σ^* antibonding orbital is the least occupied orbital **h**.

The unusual circumstance of the correlating orbital **d** being of bonding character means that the significant double excitation from **c** to **d** acts to shorten the Ga−Ga bond length. For the C_{2h} structure of Na_2[MeGaGaMe], the Ga−Ga bond lengths optimized using basis-B are 2.533 (HF), 2.514 (MCSCF), 2.485 (B3LYP), and 2.450 (MP2) Å. The occupation of orbital **d** clearly causes a decrease in the Ga−Ga bond length, although inclusion of additional dynamical correlation effects through DFT or MP2 calculations is needed to produce bond lengths in approximate agreement with experiment. One conclusion that might be drawn from the MCSCF Ga−Ga distance being shorter is that orbital **c**'s central node makes it slightly antibonding, despite the small π interaction each of its lone pairs possesses.

Results for $[MeGaGaMe]^{2-}$ are similar to those for Na_2[MeGaGaMe]. At the B3LYP geometry, the leading configuration carries 90.1% weight in a six-electron, six-orbital MCSCF wave function, with natural orbital occupancies 1.984 (a_g, Ga−Ga σ), 1.984 (a_u, Ga−Ga π), 1.832 (b_u, "slipped π"), 0.157 (a_g, symmetric lone pair combination, denoted n_s), 0.029 (b_g, Ga−Ga π^*), and 0.014 (b_u, Ga−Ga σ^*). In the absence of Na, the π (a_u) orbital occupancy is much closer to 2, but this is due primarily to the Na case's wave function having two additional weakly occupied orbitals correlating the π. The influence of the correlating n_s orbital on the Ga−Ga bond length is more pronounced in $[MeGaGaMe]^{2-}$: 2.746 (HF), 2.647 (MCSCF), and 2.531 (B3LYP) Å.[32]

Conclusion

The present calculations, which are the first reported for Robinson's fascinating Na_2[Ar*GaGaAr*] compound, show that the *i*-Pr group crowding is relaxed by increasing the Ga−Ga−C angle, as well as by relaxation to C_2 symmetry. The increased Ga−Ga−C angle leads to a Ga−Ga bond shortening of about 0.04 Å. The best estimate for the Ga−Ga bond length at the B3LYP level using the large basis-B is about 2.37 Å, which is about 0.05 Å longer than experiment. Thus, inclusion of the *i*-Pr groups removes about one-half the discrepancy between calculation and experiment. The remaining discrepancy might be attributed to crystal forces, since the Ga−Ga bond is soft, or as indicated by computations with the B3PW91 functional and the closer agreement between B3PW91 and MP2 for small models, may be an error in the B3LYP functional's description of Ga bonding.

The results presented here indicate it may not be reasonable to discuss whether the experimental compound contains a Ga−Ga triple bond. The Na atom's contribution to the short Ga−Ga bond length is considerable, both in its direct participation in the π bond, which means the heart of the molecule is a Ga_2Na_2 cluster rather than a simple Ga−Ga bond, and through its ionic interactions with the terphenyl groups. For this reason, we draw no distinct conclusion about a Ga−Ga triple bond in the Ga_2Na_2 core. Evidence was presented that shows the "slipped π" orbital may actually be slightly antibonding, as its small depopulation in MCSCF wave functions causes a shortening of the Ga−Ga bond length, confirming the growing view[13,18] that its contribution to bonding is weak.

Finally, a result with possible synthetic implications is that silyl substituents on Ga may lead to still shorter Ga−Ga bond lengths.[33,34]

Acknowledgment. This work was supported in part by a Grant-in-Aid from the Ministry of Education, Science, Sports, and Culture of Japan.

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[32] Models lacking Na are unrealistic in another way, as the double occupation of a n_s orbital instead of the Ga−Ga π (a_u) produces a lower HF energy when large basis sets are used (by 0.0031 au using basis-B at the B3LYP geometry). Geometry optimization of this lower energy configuration leads to Ga−Ga = 2.798 Å.

[33] An attempt to synthesize the lithium analogue, Li_2[Ar*GaGaAr*], has been unsuccessful.[8] However, it is interesting that the Ga−Ga bond lengths of 2.335 (B3LYP) and 2.313 (B3PW1) Å calculated using basis-B for the Li_2[Arx*GaGaArx*] model are 0.067 and 0.052 Å shorter than those of 2.402 (B3LYP) and 2.365 (B3PW1) Å for the Na_2[Arx*GaGaArx*] model, respectively. These suggest that Li_2[Ar*GaGaAr*] would have a significantly shorter Ga−Ga bond length than Na_2[Ar*GaGaAr*].

[34] Note added in proof. For a short Ga−Ga length of 2.35 Å found very recently in a $[Ga_{84}(N(SiMe_3)_2)_{20}]^{4-}$ cluster, see: Schnepf, A.; Schnöckel, H. *Angew. Chem., Int. Ed.* **2001**, *40*, 712−715.