J. Am. Chem. Soc. **1998,** *120,* 12133−12134

Understanding Nonlinearity in Multiply-Bonded Digallium Molecules

Ian Bytheway and Zhenyang Lin*

Department of Chemistry
Hong Kong University of Science and Technology
Clear Water Bay, Kowloon, Hong Kong

Received May 28, 1998
Revised Manuscript Received September 21, 1998

The synthesis[1] of $Na_2[Mes^*_2C_6H_3\text{-GaGa-}C_6H_3\text{-}Mes^*_2]$ (Mes* = 2,4,6-*i*-$Pr_3C_6H_2$; also abbreviated to Trip[2]) has resulted in much discussion[3] about the nature of the Ga−Ga interaction in this molecule, in particular whether the digallium bond may be properly designated a triple bond. A natural orbital analysis of $[H\text{-GaGa-}H]^{2-}$ shows that the three occupied orbitals describing the Ga−Ga interaction comprise σ and π bonding orbitals and one orbital that is strongly localized on, but not restricted to, each Ga.[4] Analysis of these orbitals obtained from density functional calculations for more realistic digallium molecules[5] shows similar features, as do extensive calculations[6] for a variety of digallium species. Although the interpretation of these orbitals may differ, the body of calculations for $[R\text{-GaGa-}R]^{2-}$ suggests that the Ga−Ga interaction may be understood in terms of two bonding (σ and π) orbitals and one orbital that is variously ascribed as either non- or moderately π bonding.

This work is concerned with understanding why these $[R\text{-GaGa-}R]^{2-}$ species adopt a significantly bent geometry with a trans arrangement of R groups. In the experimental geometry[1] the two Ga−Ga−C bond angles are 128.5(4) and 133.3(4)°, and the theoretical predictions, regardless of the levels of theory used, reproduce this *trans*-bent geometry with Ga−Ga−C angles in the range of 120−130°, depending upon the substituent R (R = H, Me, Ph, and 2,5-$C_6H_3Ph_2$). Recent calculations[7] for [R-Si≡Si−R] molecules suggest that the *trans*-bent structure is favored over other structural isomers when R is sterically significant.

The preference for *trans*-bent geometries in these $[R_2Ga_2]^{2-}$ molecules has been explained in terms of the coupling of two RGa^- fragments[6−8] each in a $^2\Pi$ ground-state rather than the higher energy $^4\Sigma$ state. This localized atomic orbital explanation has also been used to account for bent cumulenones[8] and was originally suggested in the context of main group chemistry to explain the observed bent geometries of group 14 metallenes.[9] These explanations do not, however, provide a rationale for the energetics of bending, that is, what interactions keep the molecule oriented in a geometry akin to the coupling of its two fragments, preventing the reorganization of the molecule to become linear? We propose an alternative explanation based on molecular orbital (MO) arguments, which can explain the observed features of the Ga−Ga bond in these molecules and, importantly, provide a general picture for multiple bonding between heavier main group atoms.

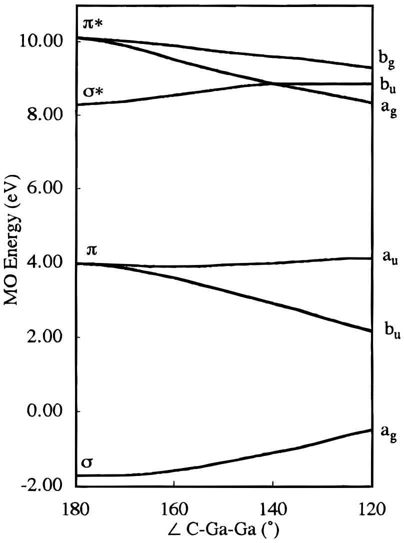

Figure 1. A Walsh diagram for $[Ga_2(CH_3)_2]^{2-}$ calculated in 10° increments of ∠C−Ga−Ga with reoptimization of the other structural parameters.

Our calculations[10] for $[Ga_2(CH_3)_2]^{2-}$ yielded a *trans*-bent optimized geometry with bond lengths and angles in agreement with those obtained previously.[4−6] The calculated Ga−Ga bond length (2.487 Å) is longer than observed (2.319 Å). It has been suggested[5] that the shortening is due to Na^+-arene interaction in the crystal structure. The central argument over the correct designation of the bond order for the Ga−Ga bond in molecules of the general type $[Ga_2R_2]^{2-}$ stems from the roles played by the σ and two π molecular orbitals describing the Ga−Ga interaction.

A Walsh diagram for the molecular orbitals involved in digallium bonding in $[Ga_2(CH_3)_2]^{2-}$ is instructive (Figure 1). When linear, the molecular orbitals are acetylene-like, with one σ and two π orbitals involved in the formation of a Ga≡Ga triple bond. On bending, the σ bonding MO increases in energy which is expected as the orbital overlap decreases. The energy of the b_u MO (derived from the in-plane π bonding MO), however, decreases significantly compared to the energy of the σ MO which increases and drives the bending of the R−Ga−Ga bond angle.

This phenomenon is perhaps unexpected as the $\pi-\pi$ overlap of the b_u orbital also decreases significantly on bending of the C−Ga−Ga bond angle. Examination of the behavior of the corresponding antibonding orbitals in Figure 1 indicates that this decrease in energy is a consequence of the mixing of the pure in-plane π orbital with the σ^* LUMO, as shown in Figure 2. If this MO argument is valid, the decrease in energy that accompanies less π orbital overlap requires explanation.

Consideration of the orbital interactions and relative energies of both the bonding and antibonding orbitals provides such an explanation. A schematic orbital interaction diagram is given in Figure 3 for both linear $[R-Ga\equiv Ga-R]^{2-}$ and R−C≡C−R, showing the relative energies of the highest occupied and lowest unoccupied molecular orbitals. The LUMO is σ^* for a linear $[R-Ga\equiv Ga-R]^{2-}$ while for R−C≡C−R it is π^*. The HOMO−LUMO gap is large for R−C≡C−R, while for $[R-Ga\equiv Ga-R]^{2-}$ this gap is smaller, which is a consequence of the larger energies separating the s and p orbitals in heavier main group elements. It is energetically possible, then, for mixing of the HOMO and LUMO orbitals to occur in linear $[R-Ga\equiv Ga-R]^{2-}$,

---

[1] Su. J.; Li, X.-W.; Crittendon, R. C.; Robinson, G. H. *J. Am. Chem. Soc.* **1997**, *119*, 5471.

[2] Haubrich, S. T.; Power, P. P. *J. Am. Chem. Soc.* **1998**, *120*, 2202.

[3] (a) Dagani, R. *Chem. Eng. News* **1997**, *75*, 5 (24), 9. (b) Dagani, R. *Chem. Eng. News* **1998**, *76* (11), 31.

[4] Klinkhammer, K. W. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2320.

[5] Cotton, F. A.; Cowley, A. H.; Feng, X. *J. Am. Chem. Soc.* **1998**, *120*, 1795.

[6] Xie, Y.; Grev, R. S.; Gu, J.; Schaefer, H. F.; Schleyer, P. v. R.; Su, J.; Li. X.-W.; Robinson, G. H. *J. Am. Chem. Soc.* **1998**, *120*, 3773.

[7] Kobayashi, K.; Nagase, S. *Organometallics* **1997**, *16*, 2489.

[8] Trinquier, G.; Malrieu, J.-P. *J. Am. Chem. Soc.* **1987**, *109*, 5303.

[9] Goldberg, D. E.; Hitchcock, P. B.; Lappert, M. F.; Thomas, K. M.; Thorne, A. J.; Fjeldberg, T.; Haaland, A.; Schilling, B. E. R. *J. Chem. Soc., Dalton Trans.* **1986**, 2387.

[10] Calculations were performed at the HF/6-311G* level of theory using the Gaussian 94 program (ref 11). Optimized Ga−Ga distances, C−Ga−Ga bond lengths, and Δ*E* (linear-bent) are: 248.7 pm, 129.7°, 19.1 kcal·mol.

10.1021/ja981851y CCC: $15.00

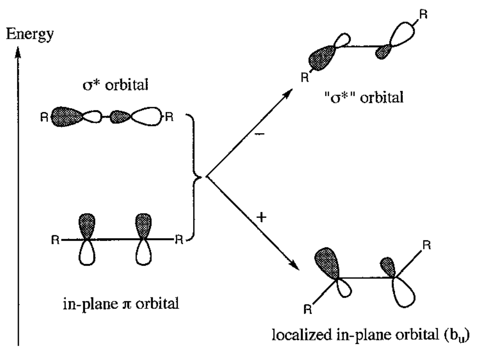

Figure 2. HOMO−LUMO orbital mixing in $[R-Ga\equiv Ga-R]^{2-}$ molecules resulting from a second-order Jahn Teller distortion.

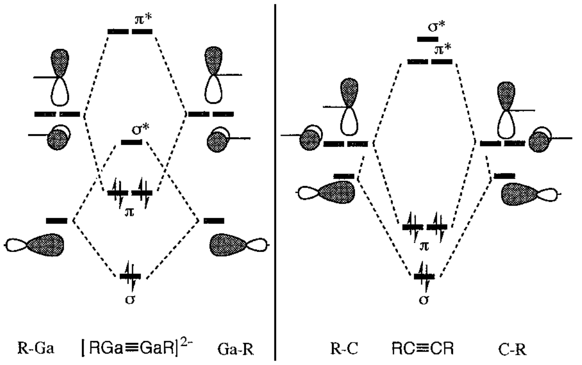

Figure 3. Schematic molecular orbital diagrams for linear $[R-Ga\equiv Ga-R]^{2-}$ and $R-C\equiv C-R$ showing the relative energies of HOMO and LUMO orbitals.

and the molecule undergoes a second-order Jahn−Teller distortion.[12] Thus the small HOMO−LUMO gap in linear $[R-Ga\equiv Ga-R]^{2-}$ can be used to account for the *trans*-bent distortion observed for $[R-GaGa-R]^{2-}$ molecules. Whereas the pyramidalization of ethylene[13] has also been explained in terms of a second-order Jahn−Teller distortion, it is indeed an interesting finding that the loss of $\pi-\pi$ overlap in these digallium molecules is compensated by mixing with a σ^* molecular orbital with substantial s character.

The orbital mixing and the behavior of the Walsh diagram are very similar to those discussed previously for the ethylene analogue Sn_2R_4.[9,12,14] The ethylene analogue does not, however, have a second π molecular orbital which remains energetically unchanged upon *trans*-bending.

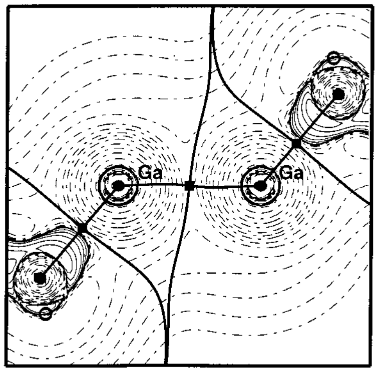

Figure 4. A plot of $\nabla^2\rho$ for $[Ga_2(CH_3)_2]^{2-}$ projected onto the C−Ga−Ga−C plane. Bond critical points, bond paths, and interatomic surfaces are also shown.

It is also of interest to understand the bonding in these molecules in terms of the total charge density (ρ).[15] The bond critical point[16] defining the Ga−Ga bond for the optimized *trans*-bent geometry shows significant ellipticity ($\epsilon = 0.3$) and a lower value of ρ (0.046 eÅ^{-3}) than for the linear (triply bonded) molecule ($\epsilon = 0.0$; $r = 0.076$ e Å^{-3}). The bond path connecting the two gallium nuclei in the *trans*-bent geometry is nonlinear (Figure 4) which is also indicative of bond distortion away from a conventional triple bond. Integrated atomic charges[17] are also helpful. For the *trans*-bent case the charge on Ga is −0.31 whereas in the linear molecule the charge is −0.39 which reflects a decrease in bond order and a transfer of charge from the Ga atom to the methyl groups, which is expected given the difference in electronegativity between these atoms. Figure 4 is a plot of the Laplacian of the charge density ($\nabla^2\rho$) showing charge density accumulated on the C atom, consistent with the notion that the extra electrons required to make this digallium molecule isoelectronic with the analogous acetylene molecule are not only used in Ga−Ga bonding.

The motivation for bent geometries in molecules of the general type $[Ga_2R_2]^{2-}$ can be understood in terms of a mixing of the in-plane π-HOMO and the σ^*-LUMO which results in decreased π-orbital overlap but overall stabilization of the molecule. This second-order Jahn Teller distortion accounts for the bending of the molecule. The Ga−Ga bonding in *trans*-bent $[Ga_2R_2]^{2-}$ molecules is thus better described as having a distorted σ bond, a significantly weakened π bond which is localized strongly on the Ga atoms, and a pure π-bond perpendicular to the Ga_2C_2 plane.

Acknowledgment. This work was supported by the Research Grants Council of Hong Kong and the Hong Kong University of Science and Technology.

JA981851Y

---

[11] *Gaussian 94*, Revision D.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. L.; 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, Inc.: Pittsburgh, PA, 1995.

[12] Albright, T. A.; Burdett, J. K.; Whangbo, M.-H. *Orbital Interactions in Chemistry*; Wiley: New York, 1985; p 166.

[13] Volland, W. V.; Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* **1979**, *101*, 533.

[14] Jacobsen, H.; Ziegler, T. *J. Am. Chem. Soc.* **1994**, *116*, 3667.

[15] Bader, R. F. W. *Atoms in Molecules: A Quantum Theory;* Oxford University Press: Oxford, 1990.

[16] Program MORPHY. Popelier, P. L. A. *Comput. Phys. Commun.* **1996**, *93*, 212.

[17] Program PROAIM. Biegler-König, F.; Bader, R. F. W. Tang, T.-H. *J. Comput. Chem.* **1982**, *13*, 317. Modified by T. A. Keith and J. R. Cheeseman. Charges for the Ga atom in $[Ga_2(CH_3)_2]^{2-}$ were obtained by subtraction after calculating integrated charges for the CH_3 group.