

# Gallanes, Gallenes, Cyclogallenes, and Gallynes: Organometallic Chemistry about the Gallium–Gallium Bond

GREGORY H. ROBINSON

Department of Chemistry, The University of Georgia,  
Athens, Georgia 30602-2556

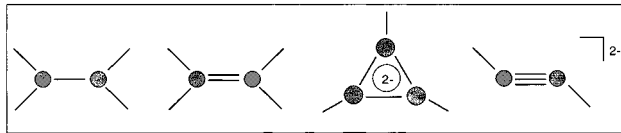
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*“The most striking characteristic of the bond that holds atoms together in a metallic aggregate is the mobility of the bonding electrons...”* (Linus Pauling, *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 10).

So begins a brief passage from perhaps the most significant chemistry text of this century, written by the discipline’s most influential and celebrated practitioner. As evidenced by the striking range and diversity of organometallic compounds containing metal–metal bonds which have been brought to the fore, the stark insight of Pauling is all the more poignant with the passing of nearly four decades.

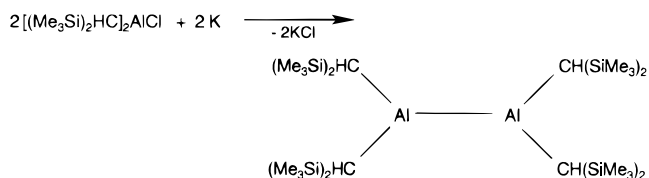
The organometallic chemistry of the main group metal–metal bond, particularly that of group 13 (III), has not developed in parallel with that of the transition metals. From boron to thallium, group 13 embodies a remarkably diverse collection of elements. Despite a vigorous research thrust which has largely been driven by a seemingly insatiable quest for group 13-based single-source molecular precursors, fundamental issues of structure and bonding remain. Moreover, a credible argument may be advanced that the organometallic chemistry of the 13th main group is enjoying unprecedented activity. The discovery of main group 13 compounds possessing homonuclear metal–metal bonds is particularly noteworthy in this regard. In a surprisingly brief period of time, organometallic compounds containing gallium–gallium bonds have blossomed at once into an engaging and intriguing,

if still emerging, area of chemistry. This Account seeks to draw a sharper focus, and a measure of perspective, to this rapidly expanding body of work. *Gallanes, gallenes, cyclogallenes*, and *gallynes*<sup>1</sup> (below), organogallium analogues of the ubiquitous fundamental fragments of organic chemistry, are noteworthy additions to the diverse tapestry of inorganic chemistry.



## Gallanes

Even as this Account is concerned with the organometallic chemistry of the gallium–gallium bond, it is apropos to acknowledge the first organometallic compound containing an aluminum–aluminum bond—the first *alane*. Although initial reports of organometallic compounds containing Al–Al bonds were first suggested more than three decades ago,<sup>2</sup> considerable ambiguity was associated with these early efforts as characterization, lacking compelling spectroscopic or structural data, was based upon molecular weight and stoichiometric arguments. The first organometallic compound unambiguously shown to contain an Al–Al bond was reported by Uhl in 1988 with tetrakis[bis(trimethylsilyl)methyl]dialane, [(Me<sub>3</sub>Si)<sub>2</sub>HC]<sub>2</sub>Al–Al[CH(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>, isolated as a crystalline solid from the potassium reduction of bis[(trimethylsilyl)methyl]aluminum chloride.<sup>3</sup> The aluminum atoms were shown to reside in

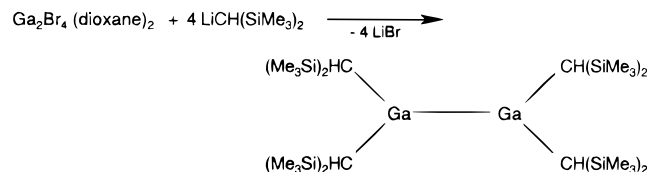


almost idealized trigonal planar environments about a nearly planar C<sub>2</sub>Al–AlC<sub>2</sub> central core. Most importantly, the Al–Al bond distance in [(Me<sub>3</sub>Si)<sub>2</sub>HC]<sub>2</sub>Al–Al[CH(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> was determined to be 2.660(1) Å. The authors noted that the unexpected planarity of the C<sub>2</sub>Al–AlC<sub>2</sub> core could not be satisfactorily addressed on steric arguments; rather, an “electronic system delocalized over the Al–Al bond” was suggested.<sup>4</sup> The authors cited two stabilizing factors associated with the bis(trimethylsilyl)methyl ligand, as it offered (1) considerable steric shielding, thereby discouraging disproportionation, and (2) favorable electronic capabilities. The synthesis and molecular structure determination of [(Me<sub>3</sub>Si)<sub>2</sub>HC]<sub>2</sub>Al–Al[CH(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> was a singularly unique accomplishment, effectively launching an entirely new area of research: the organometallic chemistry of the group 13 metal–metal bond.

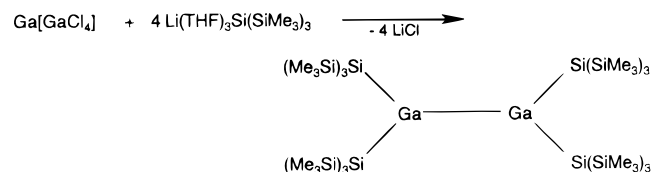
The first *gallane* determined to contain a gallium–gallium bond was reported only a decade ago by Uhl with tetrakis[bis(trimethylsilyl)methyl]digallane, [(Me<sub>3</sub>Si)<sub>2</sub>HC]<sub>2</sub>Ga–Ga[CH(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>.<sup>5</sup> The preparation of [(Me<sub>3</sub>Si)<sub>2</sub>HC]<sub>2</sub>Ga–

Gregory H. Robinson was born 2 May 1958 in Anniston, Alabama. He received his B.S. degree in chemistry from Jacksonville State University in 1980. During his undergraduate years, he was also a member of the football team, garnering All-Conference and All-American honors. Attending graduate school at The University of Alabama, working under the direction of Professor Jerry L. Atwood, he obtained his Ph.D. degree in 1984. Beginning his academic career in 1985 at Clemson University, he was promoted to full professor in 1995. He was awarded an Alexander von Humboldt Research Fellowship in 1994, conducting research at the Technische Universität Berlin in the laboratory of Prof. Dr. Herbert Schumann. In 1995 he joined the faculty at The University of Georgia. His honors include the 1998 Chemist of the Year for Research by the Northeast Georgia Section of the American Chemical Society (ACS), the 1998 Southern Chemist Award from the Memphis Section of the ACS, and the 1999 Henry H. Hill Award from the National Organization of Black Chemists and Chemical Engineers (NOBCChE) and the Northeast Section of the ACS. His research interests are in the organometallic chemistry of the main group elements.

$\text{Ga}[\text{CH}(\text{SiMe}_3)_2]_2$  proceeded in an elegantly straightforward manner with gallium(II) bromide bis(1,4-dioxane),  $\text{Ga}_2\text{Br}_4(\text{dioxane})_2$ , and  $\text{LiCH}(\text{SiMe}_3)_2$ . Particularly significant is the fact that 1,4-dioxane stabilizes the Ga(II) oxidation state and, by consequence, the Ga–Ga bond in  $\text{Ga}_2\text{Br}_4(\text{dioxane})_2$  at a distance of 2.395(6) Å.<sup>6</sup> The Ga–Ga distance of 2.541(1) Å in  $[(\text{Me}_3\text{Si})_2\text{HC}]_2\text{Ga}-\text{Ga}[\text{CH}(\text{SiMe}_3)_2]_2$  represents an elongation of 0.146 Å from that observed for the gallium(II) halide. Similar to the corresponding alane, the gallane resides about a nearly planar  $\text{C}_2\text{Ga}-\text{GaC}_2$  core.



A related dimeric gallane containing Ga–Si bonds has been prepared by reaction of the mixed-valent gallium(I,III) chloride,  $\text{Ga}[\text{GaCl}_4]$ , with  $\text{Li}(\text{THF})\text{Si}(\text{SiMe}_3)_3$ , yielding  $[(\text{Me}_3\text{Si})_3\text{Si}]_2\text{Ga}-\text{Ga}[\text{Si}(\text{SiMe}_3)_3]_2$ .<sup>7</sup> The Ga–Ga bond distance in this compound is rather long, at 2.599(4) Å. Perhaps most interesting, however, is the fact that, unlike the other dimeric gallanes, the  $\text{Si}_2\text{Ga}-\text{GaSi}_2$  core trigonal planes of  $[(\text{Me}_3\text{Si})_3\text{Si}]_2\text{Ga}-\text{Ga}[\text{Si}(\text{SiMe}_3)_3]_2$  are approaching orthogonality at angles of 80°.

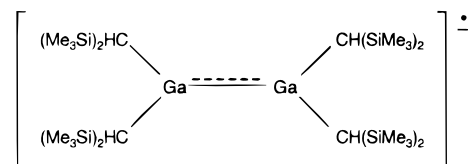


## Gallenes

As molecular targets, gallenes—gallanes possessing a measure of  $\pi$ -bonding—are synthetically challenging and intellectually intriguing. The literature reveals only two examples which offer a direct *gallane:gallene* structural comparison. The  $[(i\text{-Pr}_3\text{C}_6\text{H}_2)]_2\text{Ga}-\text{Ga}[(i\text{-Pr}_3\text{C}_6\text{H}_2)]_2$  gallane was reported with a Ga–Ga bond distance of 2.515(3) Å and a  $\text{C}_2\text{Ga}-\text{GaC}_2$  core torsion angle of 43.8° (while the Ga–C bond distance was shown to be 2.008(7) Å). Lithium metal reduction of this gallane afforded the radical anionic gallene  $[(i\text{-Pr}_3\text{C}_6\text{H}_2)]_2\text{Ga}-\text{Ga}[(i\text{-Pr}_3\text{C}_6\text{H}_2)]_2\cdot^-$  as black (red/brown colored in transmitted light) crystals.<sup>8</sup> Two important structural changes were observed in the radical anion: (1) a decrease in the Ga–Ga bond distance of 0.172 Å from 2.515(3) to 2.343(2) Å and (2) a decrease in the  $\text{C}_2\text{Ga}-\text{GaC}_2$  torsion angle by almost 30° to 15.5° (the Ga–C bond distance was a bit longer, at 2.038(2) Å). These two facts, the authors argued, “are consistent with the formation of a *one-electron*  $\pi$ -bond between the two galliums”.

A second radical anionic *gallene*, appropriately derived from the first gallane,  $[(\text{Me}_3\text{Si})_2\text{HC}]_2\text{Ga}-\text{Ga}[\text{CH}(\text{SiMe}_3)_2]_2$ , has also been reported. The ethyllithium reduction of this gallane yields dark red/black crystals of the corresponding radical anion  $[(\text{Me}_3\text{Si})_2\text{HC}]_2\text{Ga}-\text{Ga}[\text{CH}(\text{SiMe}_3)_2]_2\cdot^-$ .<sup>9</sup> The Ga–Ga bond distance in this radical anion was shown to

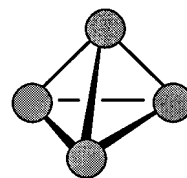
decrease an impressive 0.240 Å from 2.541(1) (in the neutral gallane) to 2.301(1) Å. Detailed EPR spectroscopy revealed temperature-dependent  $^{69}\text{Ga}$ ,  $^{71}\text{Ga}$ , and  $^{29}\text{Si}$  hyperfine splitting with extreme line broadening. The  $\text{C}_2\text{Ga}-\text{GaC}_2$  core in the radical anion remained planar (as it was shown to be in the neutral gallane).



Two points are worthy of note relative to gallenes: (1) gallenes have only been approached by the alkali metal reduction of the corresponding discrete gallanes; and (2) only “one electron  $\pi$ -bond” gallenes have thus far been reported.

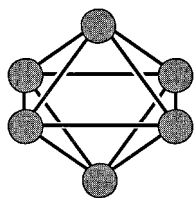
## Gallane Clusters

Utilizing a procedure similar to that employed for  $[(\text{Me}_3\text{Si})_2\text{HC}]_2\text{Ga}-\text{Ga}[\text{CH}(\text{SiMe}_3)_2]_2$ , while using the more sterically demanding lithium alkyl  $\text{LiC}(\text{SiMe}_3)_3$  with  $\text{Ga}_2\text{Br}_4(\text{dioxane})_2$ , Uhl et al. prepared a most unexpected organometallic compound containing a  $\text{Ga}_4$  tetrahedral core.<sup>10</sup> Isolated as red crystals from an admittedly dynamic system,  $[\text{Ga}\{\text{C}(\text{SiMe}_3)_3\}]_4$  is remarkable. The workers reported that the reactant molar ratio of 1:3 ( $\text{Ga}_2\text{Br}_4(\text{dioxane})_2:\text{LiC}(\text{SiMe}_3)_3$ ) gave the best product yields but noted that the same  $\text{Ga}_4$  compound was obtained by changing the ratio in the range from 1:2 to 1:4 (cautioning that the pure product was only obtained after repeated recrystallizations from *n*-pentane or toluene). It is interesting that mass spectroscopy and molar mass determinations suggested different reaction products. The mass spectrum was supportive only of the monomer (with the isotope pattern consistent with the calculated distribution of masses while heavier fragments were not observed). Cryoscopic molar mass determination in benzene (in the concentration range of 0.023 mol/L) however, indicated a trimer. Increasing the dilution (to 0.0014 mol/L) suggested the monomer exclusively. An almost idealized  $\text{Ga}_4$  tetrahedral core (below) was indicated by the crystal structure determination with Ga–Ga bond distances shown in the range 2.678(4)–2.702(4) Å (with a mean value of 2.688 Å).



Another interesting gallane cluster was recently reported by Linti et al.,<sup>11</sup> involving a “silicon-capped”  $\text{Ga}_4\text{-Si}$  trigonal bipyramidal anion (the counteranion is  $[\text{Li}(\text{THF})_4]^+$ ). This molecule, prepared by reaction of “ $\text{Ga}_2\text{I}_3$ ” with  $[(\text{THF})_3\text{LiSi}(\text{SiMe}_3)_3]$ , yielded Ga–Ga bond distances of 2.440(1) and 2.790(1) Å.

The pentamethylcyclopentadienyl ligand has been utilized, principally by Schnöckel, in the realm of gallium(I) cluster chemistry. Pentamethylcyclopentadienylgallium(I), GaCp\*, was prepared by reaction of a metastable solution of GaCl with either LiCp\* or MgCp\*<sub>2</sub> in toluene/Et<sub>2</sub>O at –30 °C (in both cases, metallic gallium is formed as a byproduct).<sup>12</sup> While characterization consisted of mass spectroscopy and multinuclear NMR (<sup>1</sup>H, <sup>13</sup>C, and <sup>71</sup>Ga), *ab initio* studies<sup>13</sup> (of [GaCp]) were supportive of an η<sup>5</sup> bonding mode for the Cp\* moiety. The calculated [GaCp] structure revealed the distance of the metal atom to the center of the ring as being 2.096 Å. A Mulliken population analysis confirmed strong π(Cp)–π(Ga) interactions. The η<sup>5</sup> bonding mode (in the gas phase) for the Cp\* ligand in GaCp\* was confirmed by gas-phase electron diffraction.<sup>14</sup> A pentagonal pyramidal structure of C<sub>5v</sub> symmetry was revealed, with a Ga–C bond distance of 2.405 Å. Through a rather rigorous procedure involving cooling a molten sample of the pure material in a “preconditioned” Pyrex glass capillary at +4 °C, a single crystal of pentamethylcyclopentadienylgallium(I) was ultimately grown and examined by single-crystal X-ray diffraction, revealing a hexameric [GaCp\*]<sub>6</sub> moiety (Ga<sub>6</sub> core below) at 200 K.<sup>15</sup> The workers cautioned that the



Ga<sub>6</sub> unit “is not strictly octahedral but compressed along a C<sub>3</sub> axis to give two distinct Ga<sub>3</sub> units”, with a Ga···Ga separation between the units of 4.173(3) and 4.073(2) Å. The workers further noted that the orientation of the Cp\* ligands relative to the Ga<sub>6</sub> metallic core is consistent with second-order Jahn–Teller effect.<sup>16</sup> The phenomena of second-order Jahn–Teller effect will prove important in other organometallic compounds containing Ga–Ga bonds later in this Account (*vide infra*).

## Cyclogallenes and Metalloaromaticity

Even as the majority of gallanes and gallenes assumed simple dimeric frameworks, the notable exceptions of tetrahedral and octahedral metallic cores piqued our interest. Specifically, this laboratory was intrigued with the possibility of synthesizing organometallic compounds residing about unprecedented metallic skeletons of gallium. To this end, it seemed reasonable that the organic ligand may well prove critical. We sought, perhaps somewhat fortuitously, to examine the organogallium chemistry of the *m*-terphenyl ligands. The 2,6-dimesitylphenyl ligand, chosen to initiate these studies, may be approached by a convenient one-pot synthesis beginning with 2,6-dibromoaniline, as reported by Hart *et al.*<sup>17</sup>

The initial task was to gain an appreciation of the affinity of gallium for these sterically demanding ligands.

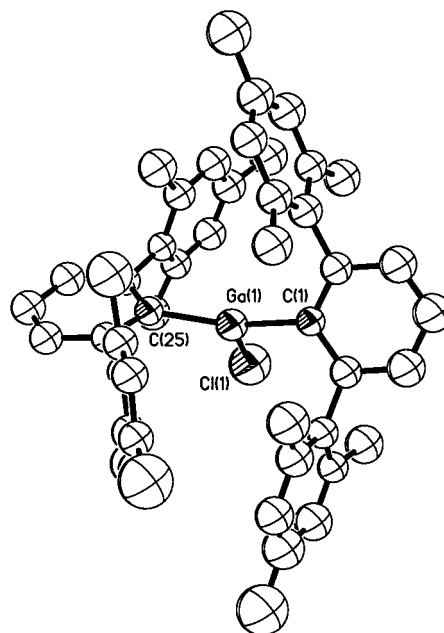
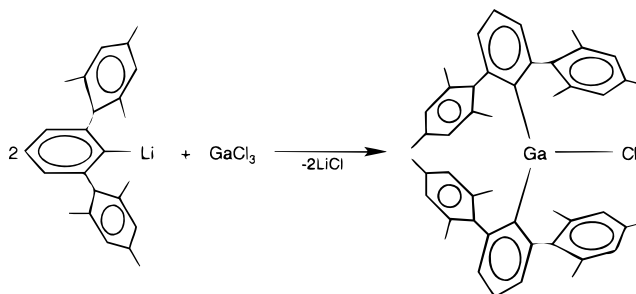


FIGURE 1. Crystal structure of (Mes<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>GaCl.

Bis(2,6-dimesitylphenyl)gallium chloride, (Mes<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>GaCl, was isolated from reaction of the lithium aryl with gallium chloride.<sup>18</sup> The fact that the gallium atom in



(Mes<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>GaCl accommodated two 2,6-dimesitylphenyl moieties is noteworthy. An X-ray crystal examination of bis(2,6-dimesitylphenyl)gallium chloride revealed (Figure 1) a number of interesting points. The Ga–C bond distances of 1.956(16) and 2.001(16) Å are generally unremarkable, even as the Ga–Cl bond distance (2.177–(5) Å) is comparable to other arylgallium chlorides. The coordination about the gallium center is most significant. The substantial steric interaction of the two ligands is most manifest in the C–Ga–C bond angle of 153.5(5)°. This value far exceeds the 120° generally expected for trigonal planar coordination, even as the C–Ga–Cl bond angles, 103.2(4)° and 103.4(5)°, are considerably less than 120°. The designation of the metal environment in (Mes<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>GaCl as T-shaped, rather than trigonal planar, was the first such coordination reported for a gallium center. In notable contrast, the coordination about the metal center in (Ph<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>GaI is trigonal planar, albeit a bit distorted, with a C–Ga–C bond angle of 134.3(3)°.<sup>19</sup>

Alkali metal reduction of (Mes<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>GaCl, as a means to approach the corresponding gallane, repeatedly proved unsuccessful in this laboratory. It is reasonable that the sheer steric demands of the 2,6-dimesitylphenyl ligand

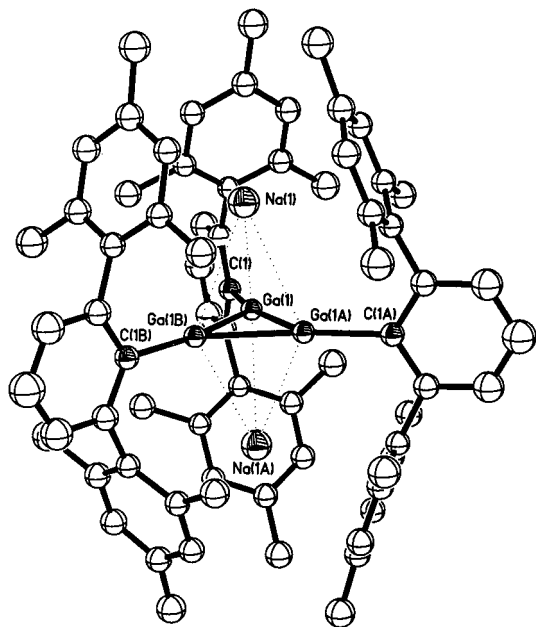


FIGURE 2. Crystal structure of  $\text{Na}_2[(\text{Mes}_2\text{C}_6\text{H}_3)\text{Ga}]_3$ .

effectively prevented sufficient approach of the two metal centers to afford adequate gallium–gallium interaction. Steadfast that there may well be some interesting gallane/gallene chemistry with this ligand, we prepared the corresponding arylgallium dichloride, which has subsequently been shown to be a  $\mu^2$ -chloride-bridged dimer,<sup>20</sup> *in situ* and allowed it to undergo alkali metal reduction. The resulting dark red-black hexagonal crystals from the deep red solution were shown to be  $\text{Na}_2[(\text{Mes}_2\text{C}_6\text{H}_3)\text{Ga}]_3$  (Figure 2).<sup>21</sup> Most striking is the fact that this highly symmetrical compound resided about an unprecedented, and inherently planar,  $\text{Ga}_3$  ring with Ga–Ga–Ga bond angles of  $60.0(1)^\circ$ . The metallic core of  $\text{Na}_2[(\text{Mes}_2\text{C}_6\text{H}_3)\text{Ga}]_3$  is completed by two sodium atoms perfectly centered about the centroid of the  $\text{Ga}_3$  ring ( $\text{Ga}\cdots\text{Na}$ ,  $3.220(2)$  Å). The independent Ga–Ga bond distance of  $2.441(1)$  Å in  $\text{Na}_2[(\text{Mes}_2\text{C}_6\text{H}_3)\text{Ga}]_3$  is significant, as it is among the shortest Ga–Ga distances on record (e.g., this distance is only  $0.098$  and  $0.14$  Å longer than that reported for  $[(i\text{-Pr}_3\text{C}_6\text{H}_2)_2\text{Ga}]\text{Ga}[(i\text{-Pr}_3\text{C}_6\text{H}_2)_2]_2^-$  and  $[(\text{Me}_3\text{Si})_2\text{HC}]_2\text{Ga}]\text{Ga}[\text{CH}(\text{SiMe}_3)_2]_2^-$ , respectively). The phrase *cyclogallene* was coined to distinguish this class of cyclic gallium ring compounds.<sup>22</sup> This laboratory subsequently reported the corresponding potassium-based cyclogallene,  $\text{K}_2[(\text{Mes}_2\text{C}_6\text{H}_3)\text{Ga}]_3$ ,<sup>23</sup> with Ga–Ga bond distances of  $2.4260(5)$ ,  $2.4317(5)$ , and  $2.4187(5)$  Å, along with a mean Ga–Ga–Ga bond angle of  $60.0^\circ$ .

The concept of aromaticity has almost exclusively fallen within the realm of organic chemistry, benzene being the quintessential example. From an inorganic perspective, the concept of aromaticity has been the unique, if largely historical, domain of borazine<sup>24</sup>—the boron–nitrogen six-membered ring compound often referred to as “inorganic benzene” (above). Even though benzene and borazine share similar physical properties, the chemical behavior of these two compounds is quite different, as benzene

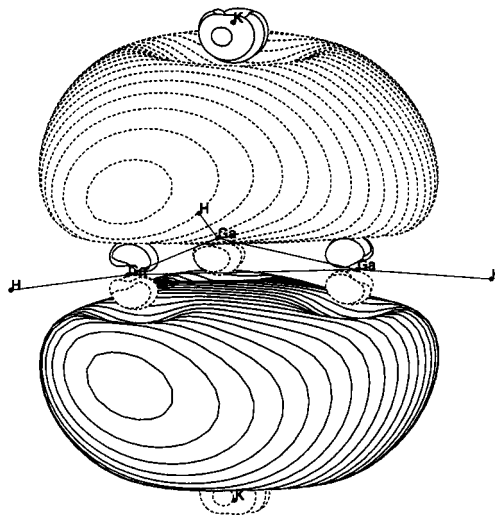
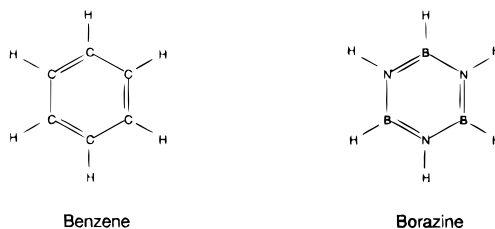


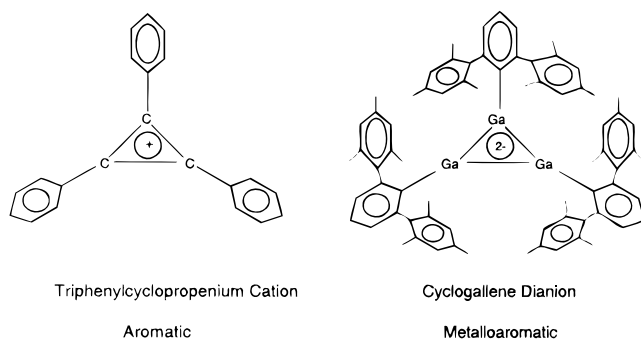
FIGURE 3.  $\pi$ -Electron cloud of  $\text{K}_2[\text{GaH}]_3$ .

readily undergoes electrophilic aromatic substitution reactions, while in similar systems borazine exclusively yields addition products. Such profound differences in chemical behavior may largely be traced to the polar B–N bonds about the borazine ring,<sup>25</sup> in notable contrast to the nonpolar C–C bonds of benzene.



Relative to the electronic characteristics of cyclogallenes, the gallium atoms are three-coordinate, each bonding to one *m*-terphenyl ligand and to the two remaining gallium atoms. The hybridization of the three gallium atoms may be considered as  $sp^2$ , leaving one empty unhybridized p-orbital on each gallium atom. This arrangement allows the two alkali metals each to donate one electron to the unoccupied p-orbitals of the three gallium atoms, thus providing the required  $2\pi$ -electrons for aromaticity and populating the  $\pi$ -electron cloud, as evidenced by the potassium-based model cyclogallene  $\text{K}_2[\text{GaH}]_3$  (Figure 3). Moreover, the dianionic cyclogallenes bear a striking electronic resemblance to the well-known  $2\pi$ -electron triphenylcyclopropenium cation, the smallest aromatic ring system, reported by Breslow<sup>26</sup> more than 40 years ago (Chart 1). Even as this new class of organometallic compounds was shown to possess planar rings, coupled with the fact that they hold a striking resemblance to the aromatic triphenylcyclopropenium cation, their magnetic behavior—specifically, the existence of a ring current—had to be addressed. Due to the highly quadrupolar nature of the Ga nucleus, our considerable experimental efforts at obtaining unambiguous evidence of a ring current repeatedly proved inconclusive. This point was examined in an article from this laboratory entitled,

Chart 1



“Are Cyclogallenes  $[M_2(GaH)_3]$  Aromatic?”<sup>27</sup> In an effort to assess the aromatic character of the cyclic cyclogallene  $\pi$ -systems, the absolute magnetic shieldings, “nucleus-independent chemical shifts” (NICSs), at selected points in space were computed as a function of the electron density, as previously described by Schleyer et al.<sup>28</sup> While NICSs are a purely calculational quantity (and are not a chemically observable entity), they have been shown to correlate exceedingly well to observable measures of aromaticity, such as bond length equalization, aromatic stabilization energies (ASEs), and magnetic susceptibility exaltations ( $\Delta$ ). Consistent with convention, NICS values are taken as negative. The NICS value for benzene is  $-11.5$ . Relative to a ring current, an appreciable ring current in the cyclogallene moiety should lead to a reduced magnetic field strength and to an upfield shift for atoms positioned along the center axis of the three-membered ring (as for M). This is, indeed, the case: the M’s are shifted upfield by 6, 57, and 108 ppm for M = Li, Na, and K, respectively. As a second measure, the computed NICS values for the cyclogallene model molecules were shown to be  $-13$ ,  $-15$ , and  $-15$  ppm for Li, Na, and K, respectively. A metallic ring system demonstrating traditional organic aromatic behavior is a sufficiently novel phenomena such that the term *metalloaromaticity* was employed. Metalloaromaticity is utilized in this context to describe a compound containing a metal ring system exhibiting traditional (organic) aromatic behavior.<sup>29</sup> This laboratory has further suggested that heteroatomic cyclogallene systems (three-membered rings containing a combination of carbon, silicon, and gallium atoms) should also be synthetically accessible.<sup>30</sup> The advent of cyclogallenes presents a credible challenge to borazine as the most important inorganic “aromatic” species.

## Gallynes

The 2,6-dimesitylphenyl ligand proved critical in the stabilization of the  $2\pi$ -electron metalloaromatic cyclogallene  $Ga_3^{2-}$  systems. In an effort to further assess the ramifications of additional ligand steric loading coupled with potentially different electronic capabilities relative to the Ga–Ga bond as a function of *m*-terphenyl ligands, this laboratory endeavored to examine the organogallium chemistry of the even more sterically demanding 2,6-bis-(2,4,6-triisopropylphenyl)phenyl ligand,  $(i\text{-Pr}_3C_6H_2)_2C_6H_3$ .

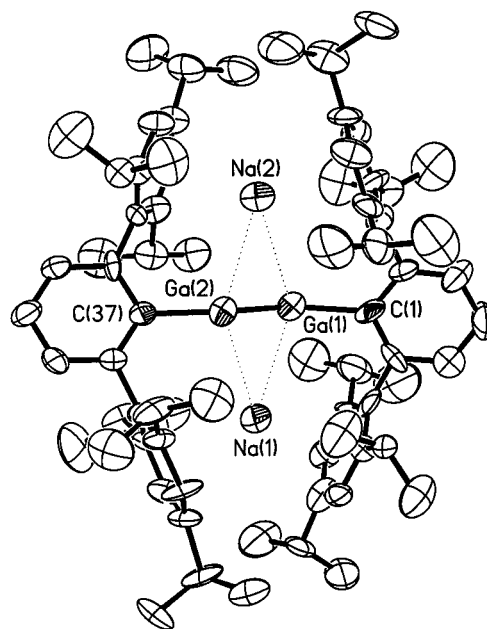


FIGURE 4. Crystal structure of  $Na_2\{[(i\text{-Pr}_3C_6H_2)_2C_6H_3]Ga\equiv Ga\{C_6H_3(i\text{-Pr}_3C_6H_2)_2\}\}$ .

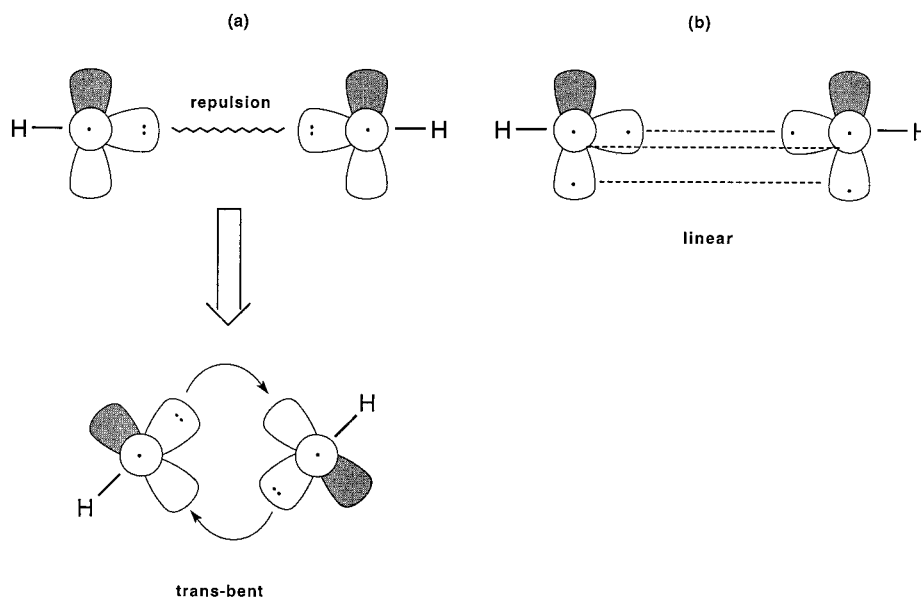
Reaction of the lithium aryl derivative with  $GaCl_3$  affords the gallium dichloride crystalline dimer  $[(i\text{-Pr}_3C_6H_2)_2C_6H_3-GaCl_2]_2$ .<sup>31</sup> The Ga–C bond is determined to be  $1.949(8)$  Å, even as the structural metrics of this dimer are generally unremarkable.

Sodium metal reduction of  $[(i\text{-Pr}_3C_6H_2)_2C_6H_3GaCl_2]_2$  in ether produced a multitude of deep red (almost black) crystals which were shown to be  $Na_2\{[(i\text{-Pr}_3C_6H_2)_2C_6H_3-Ga\equiv Ga\{C_6H_3(i\text{-Pr}_3C_6H_2)_2\}\}]$ . As shown in Figure 4, the molecular structure of this compound consisted of two *m*-terphenyl ligands bridged by two gallium atoms and a pair of sodium atoms.

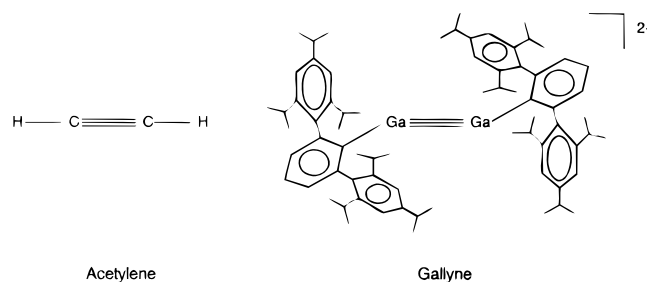
Even as the Ga–Ga bond distance was shown to be very short at  $2.319(3)$  Å and the Ga–Ga–C linkages were shown to be markedly nonlinear with bond angles of  $128.5(4)^\circ$  and  $133.5(4)^\circ$ , this compound was described by this laboratory as the first example of a gallium–gallium triple bond—the first *gallyne*.<sup>32</sup>

The perfectly linear H–C–C–H acetylene molecular structure, complete with  $sp$ -hybridized carbon atoms and tubular-shaped  $\pi$ -electron density, is elegant in its simplicity. A digallium molecule, at once possessing a short Ga–Ga bond while residing about a nonlinear trans-bent C–Ga–Ga–C fragment, yet purporting to contain a gallium–gallium triple bond, is perhaps sufficient to initially give pause. Indeed, the proposal of a Ga–Ga triple bond in  $Na_2\{[(i\text{-Pr}_3C_6H_2)_2C_6H_3]Ga\equiv Ga\{C_6H_3(i\text{-Pr}_3C_6H_2)_2\}\}$  sparked a rather spirited debate.<sup>33</sup> Furthermore, a report by Cotton, Cowley, and Feng<sup>34</sup> strongly asserted that the gallyne actually contained a Ga–Ga double bond and that the short metal–metal bond was due in large measure to  $Na^+-\pi$ -aryl ligand interactions. This report notwithstanding, a cursory examination of the theoretical and experimental literature reveals a preponderance of studies in support of both the trans-bent molecular geometry and

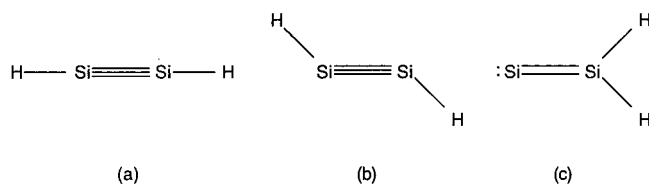
Scheme 1



the metal–metal triple bonding proposed in the gallyne—a digallium analogue of acetylene (below).



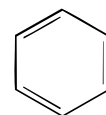
In support of the gallyne, we first turn to the chemistry of silicon. The synthesis<sup>35</sup> and molecular structure<sup>36</sup> of  $\text{Mes}_2\text{Si}=\text{SiMes}_2$  (Mes =  $\text{Me}_3\text{C}_6\text{H}_2$ ) by West as the first compound containing a Si=Si double bond, a *disilene*, was a singular achievement. To date, a silicon derivative of acetylene, a *disilyne*—a compound containing a silicon–silicon triple bond—has not been reported.<sup>37</sup> Nonetheless, recently Kobayashi and Nagase,<sup>38</sup> among a host of other workers,<sup>39</sup> having performed calculations on the elusive  $-\text{Si}\equiv\text{Si}-$  fragment, have repeatedly and unambiguously reached the same conclusion: *Unlike carbon, the linear geometry (a) is not a minimum on the potential energy surface of  $\text{HSiSiH}$ , but rather a nonlinear trans-bent geometry (b) is favored.* Specifically, depending on the level of the-



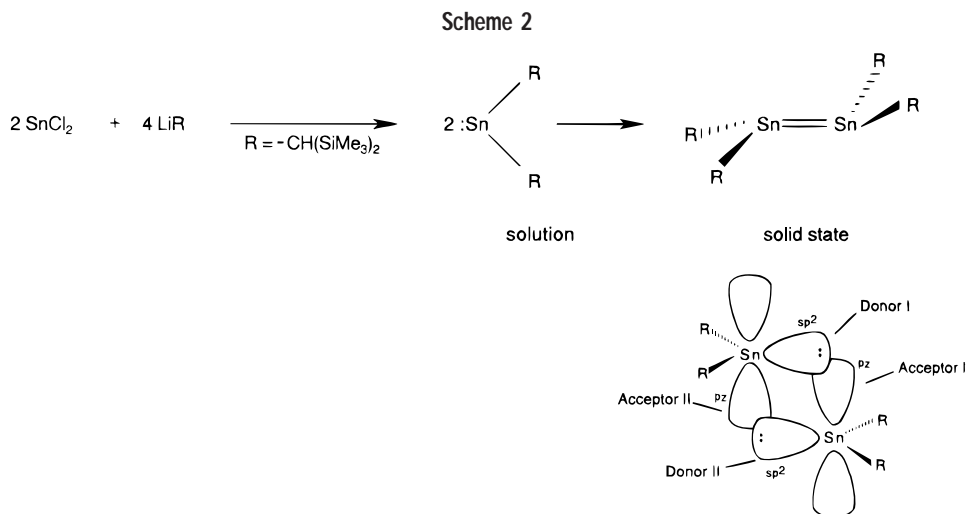
ory, isomer b was shown by Kobayashi and Nagase to be 20.3 (3-21G\*) and 22.1 (6-31G\*) kcal/mol more stable than the linear structure, a. The well-documented isomerization of b to a 1,2-H-shifted isomer,  $:\text{Si}=\text{SiR}_2$  (c), can be greatly

inhibited by the utilization of sterically demanding ligands. Indeed, Kobayashi and Nagase suggested that the utilization of  $-\text{Si}(t\text{-Bu})_3$  and  $-\text{Si}(2,6\text{-Et}_2\text{C}_6\text{H}_3)_3$  groups (used instead of H) make isomer b 9.7 and 12.0 kcal/mol, respectively, more stable than c. Moreover, depending on the ligand system employed, the R–Si–Si bond angle was calculated to range from  $124.9^\circ$  (H) to  $141.0^\circ$  ( $\text{Si}(2,6\text{-Et}_2\text{C}_6\text{H}_3)_3$ ) at the 3-21G\* level of theory—easily spanning the R–Ga–Ga gallyne bond angles of  $128.5(4)^\circ$  and  $133.5(4)^\circ$ . By way of explanation, as Kobayashi and Nagase pointed out, it is informative to view  $\text{H}-\text{Si}\equiv\text{Si}-\text{H}$  as consisting of two SiH units. Principally, two interaction modes are possible (Scheme 1). In direct contrast to the case for acetylene with CH units, the doublet ground state ( $^2\Pi$ ) was shown to be 42.6 kcal/mol (3-21G\*) more stable than the corresponding quartet state ( $^4\Sigma$ ) (with CH units, the quartet state has been shown to be only 17.9 kcal/mol (3-21G\*) less stable than the doublet state). This behavior originates from the well-recognized tendency of silicon to favor the  $3s^2 3p^1 3p^1$  valence configuration, often foregoing “carbon-like” hybridization. Kobayashi and Nagase further argued that, with mode a, “the central Si–Si bond is not only elongated to avoid the repulsions, but its structure is ‘trans-bent’ to gain stabilization due to electron transfer, donor–acceptor bonds (denoted by arrows).” Thus, there is ample existing data suggesting that, even for silicon, the element most “carbon-like”, the nonlinear trans-bent geometry is favored over the linear orientation for the model R–Si≡Si–R (R = H, alkyl, or aryl) molecules.

At this point, it is appropriate to examine *o*-benzyne, 1,2-didehydrobenzene (below), postulated by Wittig et

*o*-Benzyne

al.<sup>40</sup> as an unstable intermediate almost 60 years ago,



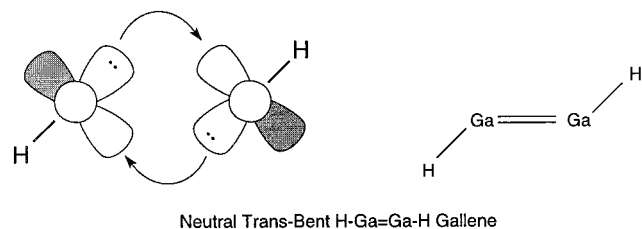
wherein a “bent  $\text{C}\equiv\text{C}$  triple bond” is suggested. In addition to theoretical studies on this moiety,<sup>41</sup> this reactive species has been postulated to participate in a host of organic transformations.<sup>42</sup> It is particularly significant that experimental evidence of *o*-benzyne has been obtained. Radziszewski et al.<sup>43</sup> measured a  $\text{C}\equiv\text{C}$  stretching vibration of  $1846 \text{ cm}^{-1}$  in a neon matrix. Not only does this value compare well with values obtained from a laser photo-detachment study ( $1860 \pm 15 \text{ cm}^{-1}$ ), but it is also considerably closer to the stretching vibration of acetylene ( $1974 \text{ cm}^{-1}$ ) than to the  $\text{C}=\text{C}$  stretch of ethylene ( $1623 \text{ cm}^{-1}$ ).<sup>44</sup> Consequently, there is credible data suggesting that *nonlinear*  $\text{C}\equiv\text{C}$  triple bonds exist.

We now turn to the organometallic chemistry of tin, examining the 1976 report by Lappert et al. of the first  $\text{Sn}=\text{Sn}$  double-bonded compound, the first *distannene*,  $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Sn}=\text{Sn}[\text{CH}(\text{SiMe}_3)_2]_2$ .<sup>45</sup> In the solid state (Scheme 2), this compound is diamagnetic, resulting from the aggregation of “two singlet bent  $\{[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Sn}\}$  monomers, whereby the approximately  $\text{sp}_y\text{p}_y$  lone-pair hybrid filled orbital on the tin atom of one of the partners overlaps with the vacant  $p_z$  orbital of the other”. The  $\text{Sn}-\text{Sn}$  bond distance was shown to be  $2.764(2) \text{ \AA}$ , while the coordination about the tin atoms was decidedly nonplanar, with a mean  $\text{Sn}-\text{Sn}-\text{C}$  bond angle of  $115^\circ$ . Even as the  $\text{Sn}-\text{Sn}$  single bond distance in  $\text{Ph}_3\text{Sn}-\text{SnPh}_3$  was shown to be only  $0.006 \text{ \AA}$  longer, at a distance of  $2.770(4) \text{ \AA}$ ,<sup>46</sup> the bonding in  $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Sn}=\text{Sn}[\text{CH}(\text{SiMe}_3)_2]_2$  was described by Lappert as “a ‘bent’ and weak  $\text{SnSn}$  double bond”.

Despite the facts that the  $\text{Sn}-\text{Sn}$  double bond distance is virtually identical to the  $\text{Sn}-\text{Sn}$  single bond distance and the coordination about the tin atoms is decidedly nonplanar, the description of the bonding in  $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Sn}=\text{Sn}[\text{CH}(\text{SiMe}_3)_2]_2$  as a  $\text{Sn}=\text{Sn}$  double bond has largely been accepted by the chemistry community.<sup>47</sup> Indeed, in a review concerning multiple bonding involving main group metals, Power and Brothers,<sup>48</sup> describing  $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Sn}=\text{Sn}[\text{CH}(\text{SiMe}_3)_2]_2$  as “a tin analogue of a substituted ethene”, prophetically opined: “The discovery of such compounds has shown that the classical  $\sigma/\pi$ -model of the double bond in carbon, nitrogen, or oxygen compounds

does not necessarily apply to the heavier elements.”

It is appropriate at this point to progress to the chemistry of gallium considering the neutral model gallene molecule,  $\text{H}-\text{Ga}=\text{Ga}-\text{H}$ , containing a  $\text{Ga}=\text{Ga}$  double bond. Treboux and Barthelat<sup>49</sup> described the bonding in the neutral trans-bent model  $\text{H}-\text{Ga}=\text{Ga}-\text{H}$  molecule as being composed of two dative (donor–acceptor) bonds, as each  $\text{HGa}$  moiety donates a pair of electrons from the occupied  $\text{sp}$  hybrid orbital to an empty  $p$  orbital of another  $\text{HGa}$  moiety (below). The bonding proposed for the model



gallene bears a striking similarity to both the theoretical disilyne and the experimental *distannene*.

Support specific for the triple bond formulation for the gallyne has also begun to appear in the literature. Shortly after the publication of the gallyne, a brief article by Klinkhammer<sup>50</sup> was published, in which the  $[\text{H}-\text{Ga}\equiv\text{Ga}-\text{H}]^{2-}$  dianion was examined using natural bond orbital (NBO) analysis. In addition, this article also brought forth a measure of historical perspective to the interpretation of the  $\text{Ga}-\text{Ga}$  bonding. This article began with the premise that theoretical calculations and *ab initio* analysis “show that the elements from the second row of the periodic table have an exceptional position” and that the “normal criteria that is ascribed to ascertain multiple bonding in these elements are not imperative for multiple bonds between heavy main group elements.”<sup>51</sup> It was concluded that the bonding in the gallyne may best be compared to that of the *distannene*: “In the present gallyne, the [two] donor–acceptor bonds [evident in the *stannene*] are augmented by an additional  $\pi$  bond to yield a  $\text{Ga}-\text{Ga}$  triple bond.”

In a rather erudite examination, Bytheway and Lin,<sup>52</sup> while principally seeking to address the trans-bent geom-

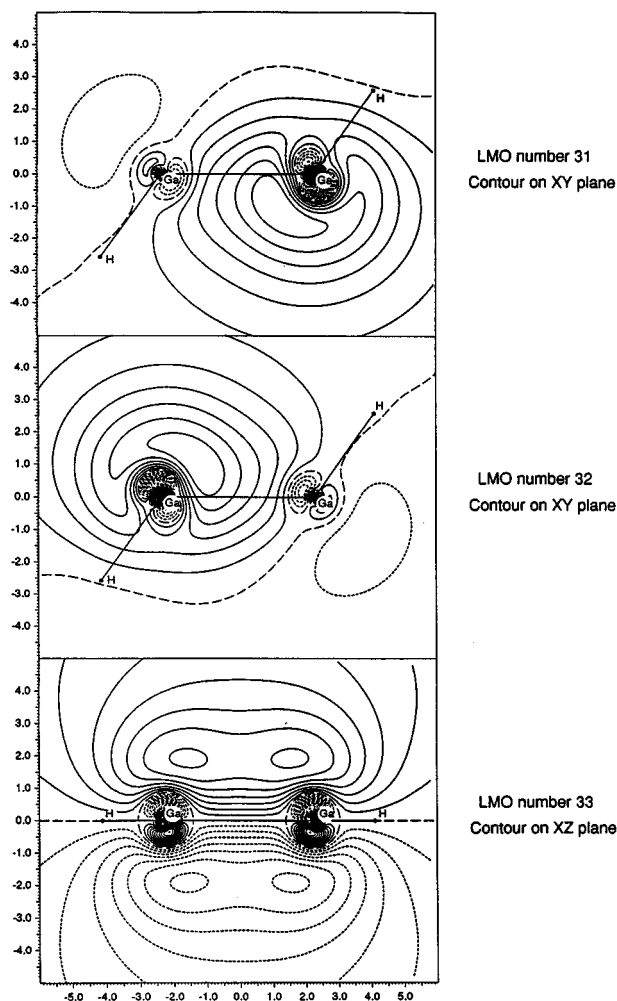


FIGURE 5. Contour maps of gallyne.

etry as a function of second-order Jahn–Teller distortion, noted that the bonding in the gallyne “is better described as having a distorted  $\sigma$  bond, a significantly weakened  $\pi$  bond which is localized strongly on the Ga atoms, and a pure  $\pi$  bond perpendicular to the  $\text{Ga}_2\text{C}_2$  plane”—essentially, a Ga–Ga triple bond. These workers further suggested that the trans-bent geometry “can be best understood in terms of a mixing of the in plane  $\pi$ -HOMO and the  $\sigma^*$ -LUMO which results in a decreased  $\pi$ -orbital overlap but overall stabilization of the molecule”.

It appears, therefore, that the critical point in the gallyne bonding is the donor–acceptor bonds. After the publication of the gallyne, this laboratory published a detailed theoretical examination, entitled “The Nature of the Gallium–Gallium Triple Bond”,<sup>53</sup> wherein this point was specifically addressed. We reached the conclusion, based upon detailed *ab initio* and density functional quantum mechanical methods, that the bonding in the gallyne consists of a “weak bent double bond plus a  $\pi$  bond”, thus affording a Ga–Ga “triple bond”. The preference for two dative (donor–acceptor) bonds is reasonable in that each GaH fragment has a  $^2\Pi$  ground state. The coupling of two such GaH fragments would favor a trans-bent molecular geometry. This description was supported by localized molecular orbital analysis. The contour maps (Figure 5),

**Table 1. Wiberg Bond Index (WBI) and Natural Localized Molecular Orbital Natural Population Analysis (NLMO/NPA) Bond Orders Compared with Bond Distances (Å) of Gallanes, Gallenes, and Gallynes in Various Geometries (Reprinted with Permission from Ref 53)**

molecule	bond order		bond distance Ga–Ga
	WBI	NIMG/NPA	
Single			
$[\text{H}_3\text{Ga}–\text{GaH}_3]^{2-}$ ( $D_{3d}$ )	0.95	1.02	2.592
$\text{H}_2\text{Ga}–\text{GaH}_2$ ( $D_{2h}$ )	0.85	0.93	2.522
$\text{H}_2\text{Ga}–\text{GaH}_2$ ( $D_{2d}$ )	0.89	1.05	2.474
Double			
$[\text{H}_2\text{Ga}=\text{GaH}_2]^{2-}$ ( $D_{2h}$ )	1.94	2.21	2.406
$[\text{H}_2\text{Ga}=\text{GaH}_2]^{2-}$ ( $C_{2h}$ )	1.88	1.94	2.407
$\text{HGa}=\text{GaH}$ ( $D_{\infty h}$ )	1.86	1.95	2.251
Triple			
$[\text{HGa}\equiv\text{GaH}]^{2-}$ ( $D_{\infty h}$ )	2.95	3.02	2.214
$[\text{HGa}\equiv\text{GaH}]^{2-}$ ( $C_{2h}$ )	2.36	3.02	2.457

based upon the CCSD geometry ( $C_{2h}$ ), clearly show that there are three occupied localized molecular orbitals connecting the two gallium atoms. The top and middle are “obviously dative [donor] orbitals (not lone pairs)”. The bottom contour can be regarded as a  $\pi$ -bonding orbital. Thus, these results support the position that there are three occupied bonding orbitals connecting the two gallium atoms in the gallyne, supporting the position that a  $–\text{Ga}\equiv\text{Ga}–$  triple bond is involved. However, it should be noted that each dative (donor–acceptor) bond is much weaker than a regular covalent bond. As a consequence, the Ga–Ga distance (2.636 Å at the B3LYP level of theory) is calculated to be much longer than a “traditional”  $\sigma$ – $\pi$  Ga=Ga double bond in the linear H–Ga=Ga–H structure (2.251 Å) (which has been shown to be a transition state). Thus, it should be evident that the electron pairs on each gallium atom demonstrate a measure of mobility, “donor–mobility”, reminiscent of the words of Pauling which appropriately marked the beginning of this Account.

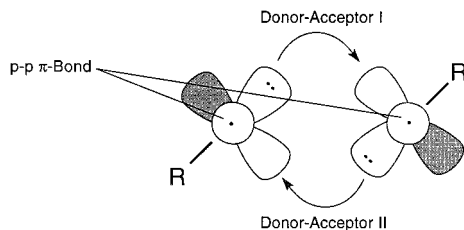
We finally come to bond orders. We cautioned in the same work<sup>53</sup> that the concept of bond orders depends on the definition, but that trends should emerge if the same method is applied to a related set of molecules. As shown in Table 1, bending lengthens the Ga–Ga bond in  $[\text{HGaGaH}]^{2-}$  derivatives. This observation is consistent with the bonding description of two (weak) dative bonds and one  $\pi$ -bond. Note that bond order values on both the Wiberg bond index<sup>54</sup> and the natural localized molecular orbital natural population analysis (NLMO/NPA)<sup>55</sup> are consistent with a Ga≡Ga triple bond.

## Concluding Remarks

The first compound containing a Ga–Ga bond was reported a mere decade ago. In the intervening years, a number of interesting Ga–Ga compounds have been prepared by a host of workers. The utilization of *m*-terphenyl ligands by this laboratory has contributed to this effort. The cyclogallenes prepared by this laboratory are the first examples of metalloaromaticity. Relative to the gallyne, it is our position, as supported by a preponderance of existing data and literature precedent, that it is reasonable to regard the bonding in  $\text{Na}_2\{[(i\text{-Pr}_3\text{C}_6\text{H}_2)_2\text{C}_6\text{H}_3]–$



$\text{Ga}\equiv\text{Ga}\{\text{C}_6\text{H}_3(i\text{-Pr}_3\text{C}_6\text{H}_2)_2\}$  as consisting of two weak donor–acceptor bonds and one  $\pi$ -bond (below)—a  $\text{Ga}\equiv\text{Ga}$  triple bond. The nature of a chemical bond is primarily determined by the electronic structure, not by the molecular geometry.



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