

# On the organometallic chemistry of gallium and the dynamics of Ga–Ga bond formation

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Recent advances in the organometallic chemistry of gallium are presented with an historical perspective and a particular emphasis toward the dynamics of the Ga–Ga bond.

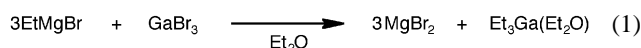
## Introduction

Due to the fortuitously combined efforts of Dmitri Mendeleev and Paul-Émile Lecoq de Boisbaudran, the main group metal gallium holds a paradoxically unique distinction of having many of its physical and chemical properties foretold *prior* to its actual discovery. While developing the theory of chemical periodicity in 1870, Mendeleev not only predicted the existence of a yet to be discovered element thought to reside between aluminium and indium, *eka-aluminium*, in his periodic arrangement of the elements, but he also boldly and accurately predicted a number of properties of this mystery element. Indeed, Mendeleev proposed a value of  $5.9 \text{ g cm}^{-3}$  for the density of eka-aluminium and predicted that this element would be discovered using spectroscopic analysis.<sup>1</sup> The fact that the actual events regarding the discovery of gallium and the subsequent development of organogallium chemistry would rival a compelling work of fiction only adds to the lore.

In the summer of 1875, following more than a decade of fundamental research upon which the science of spectroscopy would ultimately rest, Lecoq de Boisbaudran observed the first spectroscopic evidence of what he believed to be a new chemical element. While working in Paris in September 1875 Lecoq de Boisbaudran proudly obtained more than a gram of this mysterious element after having begun with several hundred kilograms of the appropriate zinc blende ore. Lecoq de Boisbaudran aptly named this new element *Gallia*, in honor of his beloved France (Latin, *Gallia*: France). Upon the determination of several chemical and physical properties of gallium, it became increasingly apparent that this low-melting metal was indeed the element which had been so confidently predicted by Mendeleev in 1870. The genius, if not the persistence, of

Mendeleev emerged once more when Lecoq de Boisbaudran initially reported the density of gallium as  $4.7 \text{ g cm}^{-3}$ . Mendeleev wrote to Lecoq de Boisbaudran suggesting that he re-examine the value of  $4.7 \text{ g cm}^{-3}$  as it was at odds with his predicted value of  $5.9 \text{ g cm}^{-3}$ .<sup>2</sup> The correct value for the density of gallium is  $5.904 \text{ g cm}^{-3}$ .

The historical development of the organometallic chemistry of gallium is no less dramatic than that just offered concerning its discovery. Triethylgallium,  $\text{Et}_3\text{Ga}$ , as described by Dennis and Patnode in 1932, was the first reported organometallic compound of gallium.<sup>3</sup> The saga of the synthesis of triethylgallium is of an unusually intriguing, if not tragic, nature. Clearly noted in the 1932 article, another graduate student, Mr. H. A. Lovenberg, had been pursuing the synthesis of the first organogallium compounds and had actually begun the preparation of triethylgallium several years prior to the Dennis and Patnode 1932 article. Shortly after the flask had been charged with the ethylmagnesium bromide/gallium bromide reaction mixture and the flask had been sealed and secured, Mr. Lovenberg met an untimely death. This same flask containing the  $\text{EtMgBr/GaBr}_3$  reaction mixture remained untouched, perhaps even lost, until Mr. Pathode happened upon it in January 1931 and continued the synthesis.<sup>3</sup> Triethylgallium monoetherate was isolated by Dennis and Pathode as a colorless, moderately viscous, pyrophoric liquid [eqn. (1)]:



Dennis and Patnode also reported that ether-free triethylgallium could be isolated by reaction of gallium metal with diethylmercury. In an ironic postscript, the contribution of Mr. Lovenberg did not result in his being granted posthumous co-authorship on the 1932 article.

Although the simple gallium alkyls share some similarities to aluminium alkyls (*i.e.*, colorless, air-sensitive liquids), there are notable differences. For example, simple aluminium alkyls, such as trimethylaluminium,<sup>4</sup> are dimeric, bridging through electron deficient three center–two electron,  $3c-2e$ , bonds, while the corresponding organogallium compounds are exclusively monomeric. In addition, the pyrophoric nature of aluminium alkyls is generally more substantial than that observed for gallium alkyls.

For decades following their discovery, organogallium compounds garnered limited attention and were largely considered little more than laboratory curiosities. Indeed, Pauling once opined that the chemistry of gallium [along with indium and thallium] was limited and of ‘little practical importance’.<sup>5</sup> Insofar as this may have been a perfectly accurate description of the chemistry of gallium of the day, the organometallic chemistry of gallium (and indium and thallium) has since been shown to be as rich as it is varied. This Feature Article will examine some of the more significant recent discoveries in organogallium chemistry with a particular emphasis on ster-

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Gregory H. Robinson (*b.* 1958) gained a B.S. degree in chemistry from Jacksonville State University (1980) and a Ph.D. degree at The University of Alabama (1984), working under the direction of Professor Jerry L. Atwood. Beginning his academic career at Clemson University (1985), he was promoted to full professor in 1995. Robinson 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 where he now holds the title of Distinguished Research Professor of Chemistry. His research interests are in the organometallic chemistry of the main group elements.

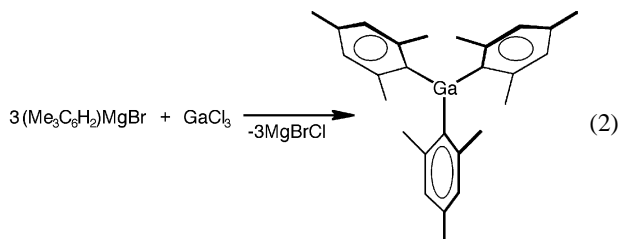
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ically demanding organogallium compounds and the nature of the gallium–gallium bond.

### Sterically demanding organogallium compounds

Generally, the phenyl substituent is not considered to be very bulky or sterically demanding. Nonetheless, the phenyl ligand is quite significant as it serves as the base unit from which very important sterically demanding ligands are derived. Much like trimethylaluminium, triphenylaluminium was shown to be dimeric,<sup>6</sup> bridging through a carbon atom of the phenyl ring. In contrast, triphenylgallium was demonstrated to be monomeric.<sup>7</sup> Interestingly, the phenyl rings of Ph<sub>3</sub>Ga were observed to only be slightly out of the plane of the GaC<sub>3</sub> core. The nearly coplanar nature of the phenyl rings with the gallium core in Ph<sub>3</sub>Ga allowed for secondary interactions of each gallium center with the *meta*-carbon atoms of other Ph<sub>3</sub>Ga moieties in the unit cell.

The fact that sixteen years passed between the structural characterization of triphenylgallium and its next logical aryl derivative of trimesitylgallium, (Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)<sub>3</sub>Ga, belies the latent development of this chemistry. Ironically, the preparation of (Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)<sub>3</sub>Ga in 1986 was analogous to that employed more than five decades earlier in the 1932 synthesis of triethylgallium, namely the reaction of the appropriate Grignard reagent with a gallium halide [eqn. (2)].<sup>8</sup>



Trimesitylgallium was isolated as colorless, air-sensitive crystals. It is an interesting coincidence that the synthesis and molecular structure of trimesitylaluminium<sup>9</sup> and trimesitylgallium<sup>8</sup> were published as consecutive articles in the same issue of the journal *Organometallics*. Although the molecular structure of (Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)<sub>3</sub>Ga revealed the gallium center to be in a virtually idealized trigonal planar environment, the aromatic rings of the mesityl ligands assumed a propeller-like arrangement about the gallium center at an angle of 55.9° between each ring and the metal coordination plane. This is most unlike the case for triphenylgallium wherein the aromatic rings were only slightly out of the metal center plane. As a consequence of the steric crowding about the metal center, trimesitylgallium was shown to be a very weak Lewis acid incapable of forming stable adducts with either Et<sub>2</sub>O or THF.

Significant developments in the organometallic chemistry of sterically demanding organogallium compounds were few for the next ten years at which point an even more sterically demanding ligand system was examined relative to gallium. The ligand system which was chosen by this laboratory was the substituted *m*-terphenyl ligands initially reported by Hart and coworkers.<sup>10</sup> In notable contrast to the syntheses of triethylgallium and trimesitylgallium, wherein Grignard reagents were utilized in the syntheses, we employed lithium derivatives of *m*-terphenyl ligands. Reaction of 2,6-dimesitylphenyllithium with gallium chloride affords bis(2,6-dimesitylphenyl)gallium chloride, [(Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]<sub>2</sub>GaCl (Fig. 1).<sup>11</sup> This organometallic compound was the first example of an *m*-terphenyl ligand being attached to a main group metal. Secondly, it is noteworthy that two such bulky ligands were accommodated by the gallium atom. This point is particularly manifested in the geometry about the metal center. Unlike triethylgallium and trimesitylgallium, in which the metal center is trigonal planar, the steric interaction between the two *m*-terphenyl ligands in

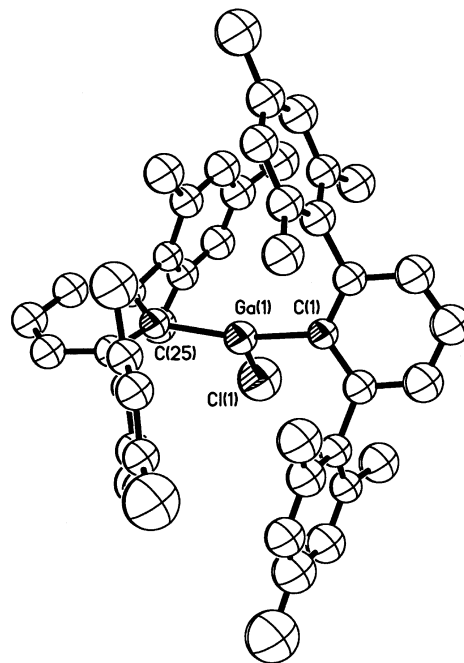


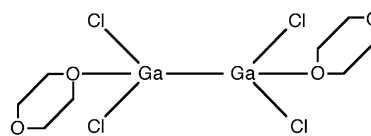
Fig. 1 Crystal structure of [(Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]<sub>2</sub>GaCl.

[(Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]<sub>2</sub>GaCl was such that the C–Ga–C bond angle was widened substantially beyond the 120° expected for trigonal planar to 154°. This is sufficient to warrant the description of this compound as T-shaped. Normally, the T-shaped orientation is reserved for the well known interhalogen compounds such as ClF<sub>3</sub> and BrF<sub>3</sub> wherein the central atom has two lone pairs of electrons to assist in stabilizing this rather obscure geometry. Thus, [(Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]<sub>2</sub>GaCl is the first unambiguous example of a Group 13 metal organometallic complex assuming a T-shaped geometry. The synthesis and molecular structure of the corresponding T-shaped bis(2,6-dimesitylphenyl)gallium bromide has also been recently reported.<sup>12</sup>

Perhaps the only tri(aryl)-based molecule possibly more sterically crowded than the T-shaped bis(2,6-dimesitylphenyl)gallium halides is (2,6-dimesitylphenyl)(dimesityl)gallium, (Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>Ga(C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>)<sub>2</sub>.<sup>12</sup> This compound, isolated from reaction of (Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>GaCl<sub>2</sub> with two equivalents of mesityllithium, arguably, represents the most sterically crowded gallium center ever observed. The aromatic rings about the GaC<sub>3</sub> core approach orthogonality at angles of 82.4, 82.4 and 86.3°.

### Gallium(II) halides: useful synthetic reagents

As recently as 1979 the notion of discrete ‘gallium(II) dihalides’ was a novel concept. A study by Beamish, Small, and Worrall offered an unambiguous perspective on the existence of gallium(II) halides with the synthesis and molecular structure of Ga<sub>2</sub>Cl<sub>4</sub>(dioxane)<sub>2</sub>,<sup>13</sup> isolated from recrystallization of Ga<sub>2</sub>Cl<sub>4</sub> from 1,4-dioxane at 0 °C. The gallium atoms are clearly four-coordinate, each bonding to two chlorine atoms, one dioxane adduct, and the other gallium atom with a Ga–Ga distance of 2.406(1) Å.



The bromide derivative, Ga<sub>2</sub>Br<sub>4</sub>(dioxane)<sub>2</sub>, has a similar structure along with a Ga–Ga bond distance of 2.395(6) Å.<sup>14</sup> Gallium(II) chloride bis(dioxane) will prove pivotal in the

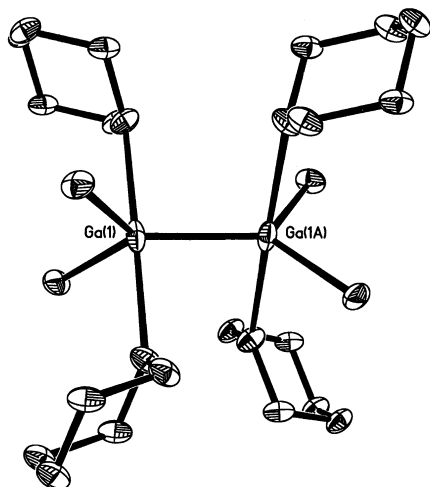


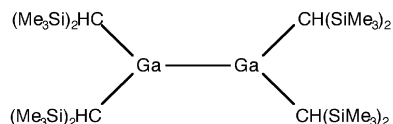
Fig. 2 Crystal structure of  $\text{Ga}_2\text{Cl}_4(\text{dioxane})_4$ .

development of the stabilization of the Ga–Ga bond in some organometallic gallanes (*vide infra*).

Recently we made a surprising discovery concerning 1,4-dioxane adducts of gallium(III) chloride. Upon slow room temperature (as opposed to 0 °C) recrystallization of  $\text{Ga}_2\text{Cl}_4$  from 1,4-dioxane we isolated a tetrameric dioxane adduct,  $\text{Ga}_2\text{Cl}_4(\text{dioxane})_4$ .<sup>15</sup> Both gallium atoms in  $\text{Ga}_2\text{Cl}_4(\text{dioxane})_4$  reside in almost idealized trigonal bipyramidal environments [O–Ga–O 179.10(10)°] about the two gallium atoms (Fig. 2).

The five-coordinate trigonal bipyramidal gallium atoms of  $\text{Ga}_2\text{Cl}_4(\text{dioxane})_4$  are easily compared with the four-coordinate tetrahedral gallium atoms of  $\text{Ga}_2\text{Cl}_4(\text{dioxane})_2$  which was prepared more than twenty years earlier. Surprisingly, the Ga–Ga bond distance of 2.3825(9) Å in  $\text{Ga}_2\text{Cl}_4(\text{dioxane})_4$  is shorter than the values reported for  $\text{Ga}_2\text{Cl}_4(\text{dioxane})_2$  [2.406(1) Å] and  $\text{Ga}_2\text{Br}_4(\text{dioxane})_2$  [2.395(6) Å]. The Ga–O bond distance in  $\text{Ga}_2\text{Cl}_4(\text{dioxane})_4$  (2.4087 Å), however, is notably longer than that reported for  $\text{Ga}_2\text{Cl}_4(\text{dioxane})_2$  [2.027(2) Å]. The Ga–Cl bonds are generally unremarkable. While very weak secondary  $\text{Cl}_{(\text{Ga})} \cdots \text{H}_{(\text{dioxane})}$  interactions were suggested in the original paper, this compound is perhaps best described as a monomeric unit. It is important to note that the tetra-dioxane adduct bears a striking resemblance to an indium compound containing an In–In bond and stabilized by four THF units,  $\text{In}_2\text{Cl}_4(\text{THF})_4$ , recently reported by Schmidbauer and coworkers.<sup>16</sup>  $\text{Ga}_2\text{Cl}_4(\text{dioxane})_4$  is a rare example of five-coordinate gallium atoms engaging in Ga–Ga bond formation.

Gallium(III) dichloride bis(dioxane),  $\text{Ga}_2\text{Cl}_4(\text{dioxane})_2$ ,<sup>13</sup> proved critical in the preparation of the first organometallic compound unambiguously shown to contain a Ga–Ga bond. Uhl *et al.* prepared  $[(\text{Me}_3\text{Si})_2\text{HC}]_2\text{Ga}–\text{Ga}[\text{CH}(\text{SiMe}_3)_2]_2$  (below) by reaction of  $\text{Ga}_2\text{Cl}_4(\text{dioxane})_2$  with  $\text{LiCH}(\text{SiMe}_3)_2$ .<sup>17</sup>



The Ga–Ga bond distance in  $[(\text{Me}_3\text{Si})_2\text{HC}]_2\text{Ga}–\text{Ga}[\text{CH}(\text{SiMe}_3)_2]_2$  was shown to be 2.541(1) Å.

In an effort to approach a measure of multiple bond character in the Ga–Ga bond, the same workers reduced  $[(\text{Me}_3\text{Si})_2\text{HC}]_2\text{Ga}–\text{Ga}[\text{CH}(\text{SiMe}_3)_2]_2$  with ethyllithium to afford red-black crystals of the corresponding radical anion,  $[(\text{Me}_3\text{Si})_2\text{HC}]_2\text{Ga}–\text{Ga}[\text{CH}(\text{SiMe}_3)_2]_2^{\bullet-}$ ,<sup>18</sup> to yield a ‘one electron  $\pi$ -bond’. Both EPR and single crystal X-ray diffraction were in support of this description. The Ga–Ga bond distance of 2.301(1) Å in  $[(\text{Me}_3\text{Si})_2\text{HC}]_2\text{Ga}–\text{Ga}[\text{CH}(\text{SiMe}_3)_2]_2^{\bullet-}$  represents a decrease of 0.240 Å from the neutral gallane.

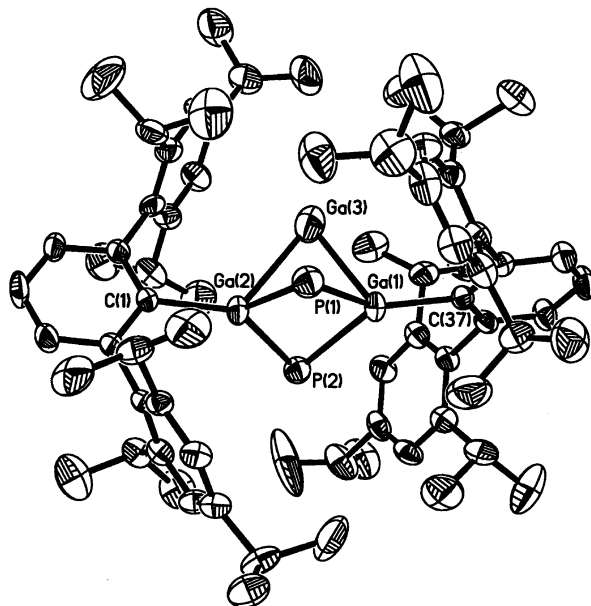


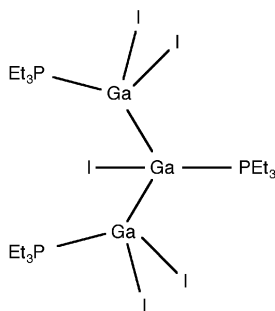
Fig. 3 Crystal structure of  $[(\text{Pr}_3\text{C}_6\text{H}_2)_2\text{C}_6\text{H}_3]\text{Ga}\{\text{H}_2\text{PGa}(\text{H})\text{PH}_2\}-\text{Ga}[\text{C}_6\text{H}_3(\text{C}_6\text{H}_2\text{Pr}_3)_2]$ .

Although *m*-terphenyl ligands have been shown by this laboratory to be effective in the stabilization of compounds containing Ga–Ga bonds, their general reactivity had not been examined relative to Lewis bases. Recently we explored the reaction of  $[(\text{Pr}_3\text{C}_6\text{H}_2)_2\text{C}_6\text{H}_3]\text{GaCl}_2$  with the sterically demanding Lewis base tris(trimethylsilyl)phosphine,  $\text{P}(\text{SiMe}_3)_3$ . This reaction affords the unusual organometallic compound  $[(\text{Pr}_3\text{C}_6\text{H}_2)_2\text{C}_6\text{H}_3]\text{Ga}\{\text{H}_2\text{PGa}(\text{H})\text{PH}_2\}\text{Ga}[\text{C}_6\text{H}_3(\text{C}_6\text{H}_2\text{Pr}_3)_2]$  (Fig. 3).<sup>19</sup>

The isolation of this compound was as unexpected as it was interesting. Noteworthy is the fact that the compound contains a –Ga–Ga– linkage. Just as striking is the *m*-terphenyl ligand stripping from the central gallium atom (being replaced by a hydrogen atom) and the stripping of the tris(trimethylsilyl) groups from the two phosphorus atoms (being replaced by two hydrogen atoms each). While it may be reasonable to dismiss the five hydrogen atoms, two on each of the two phosphorus atoms and one on the central gallium atom, as having originated from the stripped *m*-terphenyl ligand, there are other possibilities. For example, it is also reasonable that the ligand stripping may have initiated hydride abstraction from the solvent (or *vice versa*). The phosphine hydrogen atoms and the gallium hydride were prominently manifested in IR and NMR spectroscopy. Moreover, theoretical calculations of IR bands on the model molecule  $\text{MeGa}\{\text{H}_2\text{PGa}(\text{H})\text{PH}_2\}\text{GaMe}$  are in good agreement with the experimental IR spectrum.<sup>19</sup> The asymmetric nature of the Ga(1)–Ga(3)–Ga(2) linkage, at distances of 2.5145(13) and 2.7778(14) Å for Ga(1)–Ga(3) and Ga(2)–Ga(3), respectively, is interesting. It should be noted, however, that this compound is not strictly governed by a symmetry element (*i.e.*, mirror plane or two-fold axis) which would impose a symmetrical –Ga–Ga– linkage. Even as the Ga–Ga bond distances in  $[(\text{Pr}_3\text{C}_6\text{H}_2)_2\text{C}_6\text{H}_3]\text{Ga}\{\text{H}_2\text{PGa}(\text{H})\text{PH}_2\}\text{Ga}[\text{C}_6\text{H}_3(\text{C}_6\text{H}_2\text{Pr}_3)_2]$  are somewhat elongated, they compare well with other Ga–Ga bond distances observed in tetrahedra or heteronuclear trigonal bipyramids (*vide infra*).

The literature reveals another compound containing a Ga–Ga–Ga linkage in  $\text{Ga}_3\text{I}_5\cdot 3\text{PET}_3$  (below), isolated from ultrasonic irradiation of gallium and diiodine in the presence of triethylphosphine.<sup>20</sup>

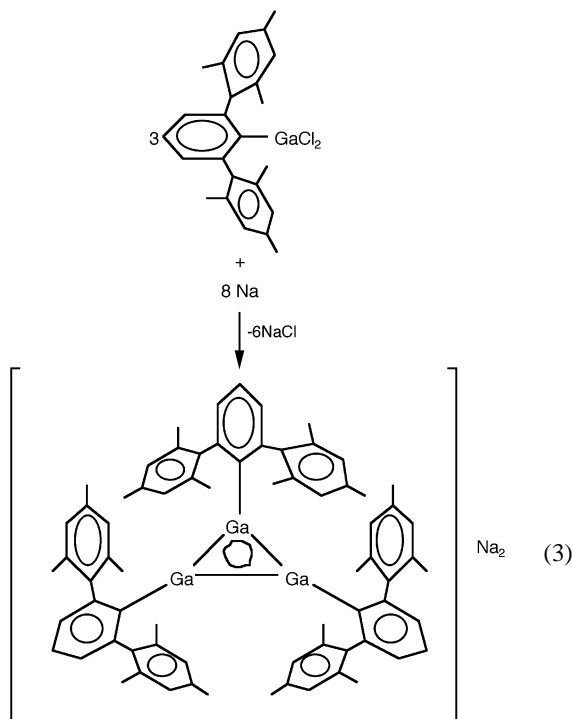
In this mixed-valent compound, a Ga(I) centre is the bridging moiety for two Ga(II) units with Ga–Ga distances of 2.451(1) and 2.4560(1) Å. The Ga–I bond distances in the two terminal  $\text{GaI}_2$  units [2.610(1) Å] are slightly shorter than the central Ga–I [2.627(1) Å]. The Ga–Ga–Ga bond angle is 121.9(1)°. This



value is compared with  $69.68^\circ$  for the corresponding Ga–Ga–Ga bond angle observed in  $[(\text{Pr}^i_3\text{C}_6\text{H}_2)_2\text{C}_6\text{H}_3]\text{Ga}\{\text{H}_2\text{P-Ga(H)PH}_2\}\text{Ga}[\text{C}_6\text{H}_3(\text{C}_6\text{H}_2\text{Pr}^i_2)_2]$ , a striking difference of almost  $50^\circ$ .

### Cyclogallenes: metalloaromatic compounds

Even though gallium has demonstrated limited catenation abilities, as evidenced by the synthesis of (previously discussed) compounds containing –Ga–Ga–Ga– linkages, reports of an entirely new class of organogallium compounds are perhaps more substantial. Sodium metal reduction of the *m*-terphenylgallium dichloride  $[(\text{Me}_3\text{C}_6\text{H}_2)_2\text{C}_6\text{H}_3]\text{GaCl}_2$  in diethyl ether has been shown by this laboratory (below) to afford dark red crystals of  $\text{Na}_2[(\text{Me}_3\text{C}_6\text{H}_2)_2\text{C}_6\text{H}_3\text{Ga}]_3$  [eqn. (3)].<sup>21</sup>



The X-ray crystal structure of  $\text{Na}_2[(\text{Me}_3\text{C}_6\text{H}_2)_2\text{C}_6\text{H}_3\text{Ga}]_3$  (Fig. 4) reveals a perfectly planar gallium three-membered ring, Ga–Ga bond distances of 2.441(1) Å, and Ga–Ga–Ga bond angles within the ring of  $60.01^\circ$ .

Upon closer examination a more intriguing aspect of the  $\text{Na}_2[(\text{Me}_3\text{C}_6\text{H}_2)_2\text{C}_6\text{H}_3\text{Ga}]_3$  compound began to emerge. The gallium atoms are taken to be  $\text{sp}^2$  hybridized along with one unhybridized p orbital on each gallium atom. Moreover, the three p orbitals are populated by two electrons, one from each of the two sodium atoms. Thus, this first example of a gallium ring compound, a cyclogallene, is also a  $2\pi$  aromatic system. The synthesis and molecular structure of a potassium based cyclogallene,  $\text{K}_2[(\text{Me}_3\text{C}_6\text{H}_2)_2\text{C}_6\text{H}_3\text{Ga}]_3$ , was subsequently reported (similar bond distances and angles were observed).<sup>22</sup> The Ga–Ga bonds within these rings are shorter than most of the

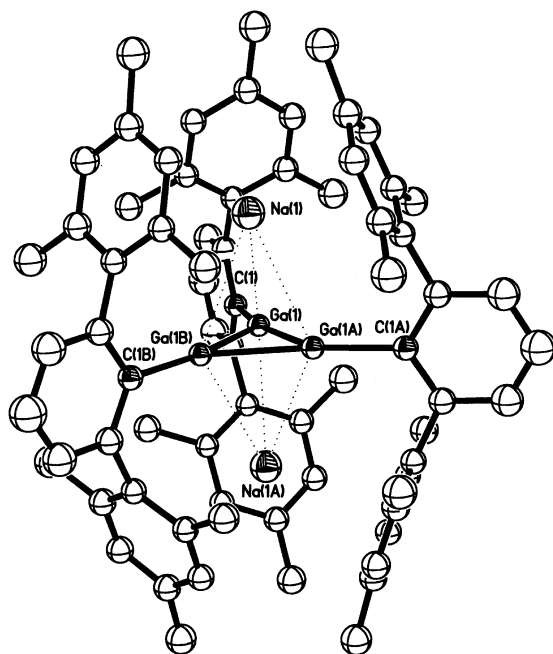
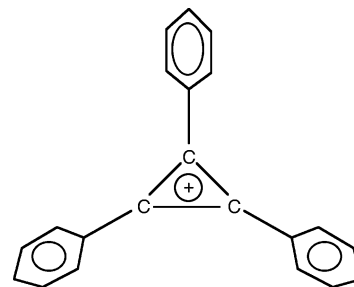


Fig. 4 Crystal structure of  $\text{Na}_2[(\text{Me}_3\text{C}_6\text{H}_2)_2\text{C}_6\text{H}_3\text{Ga}]_3$ .

reported gallanes. In addition, these ring compounds bear a striking resemblance to the smallest aromatic moiety—the triphenylcyclopropenium cation reported by Breslow more than four decades ago.<sup>23</sup>



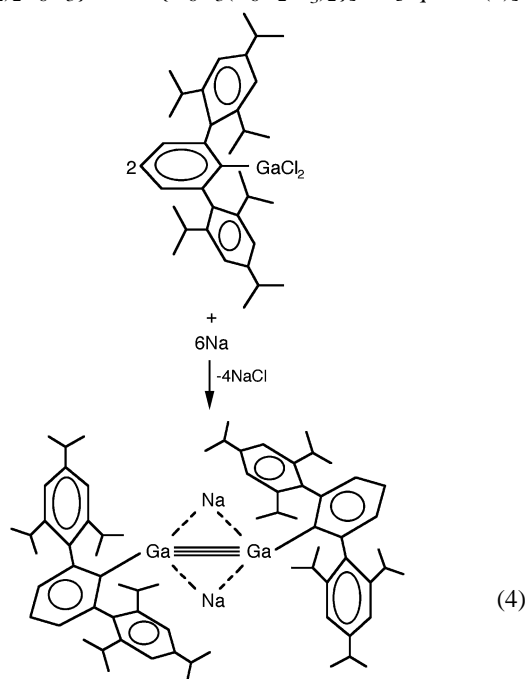
The nucleus independent chemical shifts (NICS) values<sup>24</sup> calculated for cyclogallenes<sup>25</sup> were supportive of aromatic behavior. Thus, the term *metalloaromaticity*,<sup>22</sup> intended to denote traditional aromatic behavior derived from a metallic ring system, was deemed warranted for these novel compounds. Metallic ring systems demonstrating traditional aromatic behavior present a serious challenge to borazine's long held position as the most important inorganic aromatic system.<sup>26</sup>

### The gallium–gallium triple bond: a provocative compound, a vigorous debate

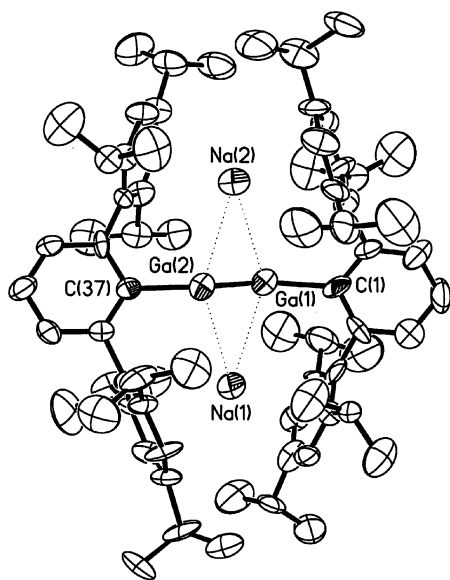
Even as it is the simplest of all alkynes, it is generally accepted that acetylene is also the most important compound possessing the iconic carbon–carbon triple bond. Moreover, the chemical bonding in acetylene is elegantly simplistic as interpreted by valence bond theory: a perfectly linear H–C–C–H molecular structure, as a consequence of  $\text{sp}$  hybridized carbon atoms, coupled with a tubular-shaped electron density. To be sure, the concept of a main group metal compound being analogous to acetylene would prove formidable.

In an effort to ascertain the extent to which slight modifications in the *m*-terphenyl ligand would affect the nature of the resulting organometallic compound we sought to modify the ligand. We slightly modified the peripheral substituents on the *m*-terphenyl ligand from methyl groups (in the case of cyclogallenes) to isopropyl groups. Thus, we prepared the  $[(\text{Pr}^i_3\text{C}_6\text{H}_2)_2\text{C}_6\text{H}_3]\text{Li}$  lithium salt and allowed it to react with gallium chloride. Sodium metal reduction of the resulting

sterically demanding gallium based *m*-terphenyl,  $[(\text{Pr}^i_3\text{C}_6\text{H}_2)_2\text{C}_6\text{H}_3]\text{GaCl}_2$ , which is dimeric in the solid state, bridging through two chlorine atoms,<sup>27</sup> affords  $\text{Na}_2\text{-}[\{(\text{Pr}^i_3\text{C}_6\text{H}_2)_2\text{C}_6\text{H}_3\}\text{Ga}\equiv\text{Ga}\{\text{C}_6\text{H}_3(\text{C}_6\text{H}_2\text{Pr}^i_3)_2\}]^{2-}$  [eqn. (4)].



The article which reported the synthesis and molecular structure of this reaction product, entitled *How Short is a  $-\text{Ga}\equiv\text{Ga}-$ Triple Bond?*<sup>28</sup> made a most provocative claim: that the  $[\{(\text{Pr}^i_3\text{C}_6\text{H}_2)_2\text{C}_6\text{H}_3\}\text{Ga}\equiv\text{Ga}\{\text{C}_6\text{H}_3(\text{C}_6\text{H}_2\text{Pr}^i_3)_2\}]^{2-}$  dianion represented a digallium analog of acetylene, or a *gallyne*, the first moiety claiming to contain a  $\text{Ga}\equiv\text{Ga}$  triple bond. The molecular structure of  $\text{Na}_2[\{(\text{Pr}^i_3\text{C}_6\text{H}_2)_2\text{C}_6\text{H}_3\}\text{Ga}\equiv\text{Ga}\{\text{C}_6\text{H}_3(\text{C}_6\text{H}_2\text{Pr}^i_3)_2\}]$  is shown in Fig. 5.



**Fig. 5** Crystal structure of  $\text{Na}_2[\{(\text{Pr}^i_3\text{C}_6\text{H}_2)_2\text{C}_6\text{H}_3\}\text{Ga}\equiv\text{Ga}\{\text{C}_6\text{H}_3(\text{C}_6\text{H}_2\text{Pr}^i_3)_2\}]^{2-}$ .

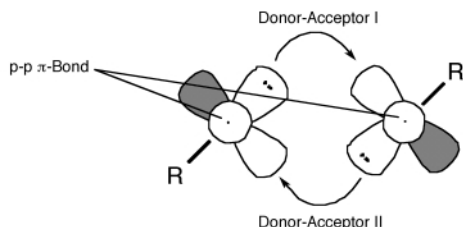
The inherent significance of such a claim is evidenced by the fact that it resulted in two highly publicized reports in *Chemical & Engineering News*.<sup>29,30</sup> The  $\text{Ga}-\text{Ga}$  bond distance in the dianion of 2.341 Å is among the shortest distances reported for a compound containing a gallium–gallium bond. However, the decidedly nonlinear  $\text{C}-\text{Ga}-\text{Ga}-\text{C}$  core linkage of 127 and 134° was most *unacetylenic*. Our justification in describing the metal–metal bonding as a gallium–gallium triple bond goes far

beyond the short  $\text{Ga}-\text{Ga}$  bond distance. Indeed, *where heavier main group element compounds (beyond carbon) are concerned, short bond distances are neither necessary nor sufficient to constitute multiple bonding*. Essentially, the nature of a chemical bond is first and foremost determined by the electronic structure, not by the molecular geometry. Theoreticians and computational quantum chemists have been predicting for years (prior to the gallyne report) that if such a main group metal compound could be synthesized possessing a homonuclear diatomic triple bond, its structure would *not* be linear (as in the case of acetylene), but rather it would possess a non-linear *trans*-bent structure,<sup>31</sup> as in the gallyne. Perhaps most informative, workers such as Kobayashi and Nagase<sup>32</sup> (and references cited therein) have long predicted that, at the expense of the linear disilyne model  $\text{H}-\text{Si}\equiv\text{Si}-\text{H}$  ( $D_{\infty h}$ ), the *trans*-bent disilyne model  $\text{H}-\text{Si}\equiv\text{Si}-\text{H}$  ( $C_{2h}$ ) would be favored.

Opposition to the gallium–gallium triple bond was swift and vigorous.<sup>30</sup> Utilizing density functional theory (DFT) Cotton, Cowley, and Feng (CCF)<sup>33</sup> examined a number of main group element moieties containing multiple bonds including  $\text{P}_2$ ,  $\text{P}=\text{C}-\text{R}$ ,  $\text{R}-\text{P}=\text{P}-\text{R}$ ,  $\text{R}_2-\text{Ge}=\text{Ge}-\text{R}_2$ . These results were compared with calculations on the closely related (2,6-diphenyl)-phenyl gallyne model,  $\text{Na}_2[(\text{Ph}_2\text{C}_6\text{H}_3)\text{Ga}\equiv\text{Ga}(\text{C}_6\text{H}_3\text{Ph}_2)]$ . The principal conclusion put forth by CCF (beyond a discussion on the presence and/or absence of a gallium hydride in the gallyne): ‘With or without hydrogen atoms, there can only be a  $\text{Ga}=\text{Ga}$  double bond [one  $\sigma$  bond and one  $\pi$  bond which may be described by two canonical molecular orbitals], namely,  $\text{Na}_2[\text{R}-\text{Ga}=\text{Ga}-\text{R}]$ , rather than  $\text{Na}_2[\text{R}-\text{Ga}\equiv\text{Ga}-\text{R}]$  for the case of no hydrogen atoms.’ Importantly, the CCF effort, in posing an argument against a  $\text{Ga}\equiv\text{Ga}$  triple bond, failed to address the concept of bond orders, an obvious and puzzling omission. Allen, Fink and Power<sup>34</sup> also argued against the gallium–gallium triple bond in the gallyne. These workers simply, if pejoratively, stated (among other things) that ‘there is no  $\text{GaGa}$   $\sigma$  bond [in the gallyne].’ Furthermore, these workers proceeded to address bond orders *without providing or calculating a bond order for the  $\text{Ga}-\text{Ga}$  interaction in question*. Allen, Fink and Power summarily stated, ‘The results of these studies provide strong evidence that the  $\text{Ga}-\text{Ga}$  or  $\text{Ge}-\text{Ge}$  bond orders in such molecules are significantly less than three and, in the case of the gallium species, *very probably between one and two*.’ Our calculated bond orders of 2.36 and 3.02 [for  $[\text{HGa}\equiv\text{GaH}]^{2-}$  ( $C_{2h}$ )] and 2.79 for  $\text{Na}_2[(\text{Ph}_2\text{C}_6\text{H}_3)\text{Ga}\equiv\text{Ga}(\text{C}_6\text{H}_3\text{Ph}_2)]$  would appear to refute this work (*vide infra*).

Offering a rebuttal to the more credible CCF position, we also published a detailed DFT study firmly in support of the gallyne model and the  $\text{Ga}\equiv\text{Ga}$  triple bond, entitled ‘*The Nature of the Gallium–Gallium Triple Bond*’.<sup>35</sup> Our position is unambiguous: the  $\text{Na}_2[\{(\text{Pr}^i_3\text{C}_6\text{H}_2)_2\text{C}_6\text{H}_3\}\text{Ga}\equiv\text{Ga}\{\text{C}_6\text{H}_3(\text{C}_6\text{H}_2\text{Pr}^i_3)_2\}]$  gallyne consists of two donor–acceptor bonds and one  $\pi$  bond, thus resulting in a gallium–gallium triple bond, albeit a *weak triple bond*. Klinkhammer,<sup>36</sup> utilizing the Natural Bond Orbitals technique (NBO), states that the bonding (of the gallyne) bears a striking similarity to that put forth by Lappert<sup>37</sup> in 1976 for the distannene  $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Sn}=\text{Sn}[\text{CH}(\text{SiMe}_3)_2]_2$ : namely, the  $\text{Sn}=\text{Sn}$  double bond is constituted by two donor–acceptor bonds resulting in ‘a “bent” and weak  $\text{Sn}-\text{Sn}$  double bond.’ Specifically, one may interpret the bonding in the gallyne, writes Klinkhammer, as two donor–acceptor bonds (as in the distannene) which are ‘augmented by an additional  $\pi$  bond to yield a  $\text{Ga}\equiv\text{Ga}$  triple bond (below).’

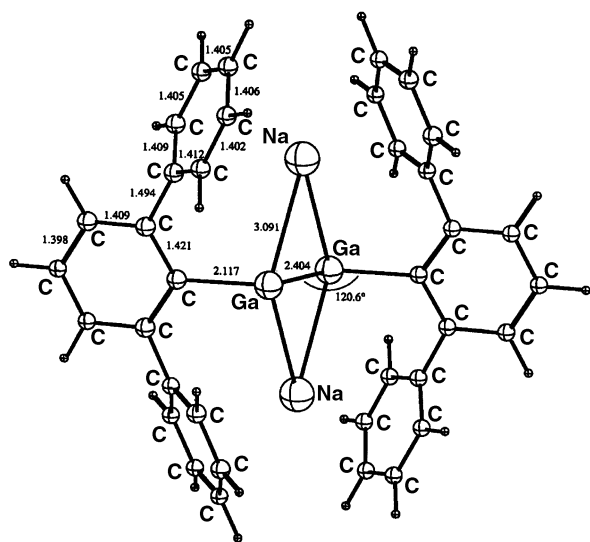
Indeed, Power and Brothers,<sup>38</sup> describing  $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Sn}=\text{Sn}[\text{CH}(\text{SiMe}_3)_2]_2$  as ‘a tin analogue of a substituted ethene,’ prophetically opined: ‘The discovery of such compounds [as  $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Sn}=\text{Sn}[\text{CH}(\text{SiMe}_3)_2]_2$ ] 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.’



Thus, an interesting dichotomy emerges most unlike the case for multiple bonds involving carbon: even as the bonding in the gallyne is described as a triple bond, this interaction is admittedly *weak*. Indeed, a recent study examining force constants given by DFT frequency calculations shows that the gallium–gallium bond in  $\text{Ga}_2\text{H}_2^{2-}$  is only slightly strengthened with respect to the Ga–Ga single bond in  $\text{Ga}_2\text{H}_6^{2-}$ .<sup>39</sup> Another recently published work entitled ‘*How Strong is the Gallium  $\equiv$  Gallium Triple Bond?*’, found that the gallium–gallium bond strength in the  $\text{Na}_2[\text{H}-\text{GaGa}-\text{H}]$  gallyne model is weaker than the gallium=gallium double bond in the  $\text{Na}_2[\text{H}_2\text{Ga}=\text{GaH}_2]$  model gallene.<sup>40</sup> The fact that these workers conclude that the gallium–gallium bond is weak is perfectly consistent with our original position. Other workers have also referred to the gallyne as having a weak Ga $\equiv$ Ga triple bond.<sup>41</sup>

Relative to bond orders, there are a number of ways in which they may be defined and calculated. Nonetheless, if the same method is applied to a series of moieties, logical trends should emerge. Thus, in this work we calculated the bond orders by the Wiberg Bond Index (WBI)<sup>42</sup> and the Natural Localized Molecular Orbital Natural Population Analysis (NLMO/NPA)<sup>43</sup> obtaining values of 2.36 and 3.02, respectively, for the *trans*-bent  $[\text{H}-\text{Ga}\equiv\text{Ga}-\text{H}]^{2-}$  ( $C_{2h}$ ) gallyne model. These bond orders are, at minimum, supportive of a multiple bond considerably beyond that of a double bond. The bond order of 3.02 is clearly deserving of the triple bond label.

Earlier this year we published a second detailed theoretical examination of the gallyne in a more realistic model: we used the same gallyne model that Cotton had used, namely  $\text{Na}_2[(\text{Ph}_2\text{C}_6\text{H}_3)\text{Ga}\equiv\text{Ga}(\text{C}_6\text{H}_3\text{Ph}_2)]$ .<sup>44</sup> A cursory examination of the optimized  $\text{Na}_2[(\text{Ph}_2\text{C}_6\text{H}_3)\text{Ga}\equiv\text{Ga}(\text{C}_6\text{H}_3\text{Ph}_2)]$  gallyne model (Fig. 6) reveals that this molecule is very similar to the experimentally prepared gallyne, differing only in the absence of the six isopropyl substituents.



**Fig. 6** Geometry ( $C_{2h}$ ) of the  $\text{Na}_2[(\text{Ph}_2\text{C}_6\text{H}_3)\text{Ga}\equiv\text{Ga}(\text{C}_6\text{H}_3\text{Ph}_2)]$  molecule optimized at the B3LYP level of theory with a basis set of 836 contracted Gaussian functions.

The  $\text{Na}_2[(\text{Ph}_2\text{C}_6\text{H}_3)\text{Ga}\equiv\text{Ga}(\text{C}_6\text{H}_3\text{Ph}_2)]$  structure was fully optimized with the B3LYP method utilizing a substantial basis set of 836 contracted Gaussian functions. In this work we

obtained a NLMO/NPA bond order of 2.79 for  $\text{Na}_2[(\text{Ph}_2\text{C}_6\text{H}_3)\text{Ga}\equiv\text{Ga}(\text{C}_6\text{H}_3\text{Ph}_2)]$ , thus offering support for a weak Ga $\equiv$ Ga triple bond in the model compound and in the experimental gallyne.

The associated bond distances and angles are similar to the experimental values. The calculated Ga–Ga bond distance of 2.404 Å, although similar to, is somewhat shorter than that reported for the simplest gallyne model,  $\text{Na}_2[\text{H}-\text{Ga}\equiv\text{Ga}-\text{H}]$  (2.441 Å), and considerably shorter than the methyl gallyne derivative,  $\text{Na}_2[\text{Me}-\text{Ga}\equiv\text{Ga}-\text{Me}]$  (2.508 Å). There should be little cause for concern with this trend, however. A similar trend is observed in the disilyne model series  $\text{H}-\text{Si}\equiv\text{Si}-\text{H}$  (2.111 Å),  $\text{Me}-\text{Si}\equiv\text{Si}-\text{Me}$  (2.123 Å) and  $\text{R}-\text{Si}\equiv\text{Si}-\text{R}$  (2.095 Å) (R = large substituent).<sup>32</sup> As suggested by CCF, we also observed that the optimized structure allows for twisting of the four substituent phenyl rings toward the sodium atoms at a distance of 2.8 Å. This has the effect of shortening the Ga–Ga distance (as compared to those simpler gallyne models which do not have aryl substituents). It is important to point out, however, that our optimized Ga–Ga distance is longer than that reported in the CCF study. We believe that this is due to the relatively small basis sets used by these workers (6-31G and 6-311G, without polarization and diffuse functions).

Relative to the Ga–Ga bond distances, our calculated bond distance of 2.404 Å is 0.085 Å longer than the experimental value of 2.319(3) Å. We view this as an indication that the gallium–gallium bond in the experimental compound may be a bit more substantial than for the gallyne model. The experimental Ga–C bond distance of 2.044 Å compares to a calculated value of 2.117 Å. In contrast, the experimental Ga–Na (3.081 Å) distances compare well to the calculated value (3.091 Å). Finally, a NLMO/NPA bond order of 2.79 was obtained for  $\text{Na}_2[(\text{Ph}_2\text{C}_6\text{H}_3)\text{Ga}\equiv\text{Ga}(\text{C}_6\text{H}_3\text{Ph}_2)]$ .

An elegantly detailed examination of homonuclear multiple bonding between main group elements was recently put forth by Grützmacher and Fässler.<sup>45</sup> While presenting an informative historical perspective on chemical bonding and the development of the symbols used to denote bonding, these workers utilized electron localization function (ELF) to examine and interpret the bonding in the gallyne and other heavier main group moieties involving multiple bonds. Grützmacher and Fässler reached an unambiguous conclusion regarding the heavier main group elements:

“The classical multiple bond indicators—bond lengths and bond strengths—have no meaning for multiple bonds in which elements from the higher periods are involved. However, they are valid for an exceptional element: carbon.”

This striking position, also put forth by Klinkhammer,<sup>36</sup> underscores the awkward reality that most of our theories of structure and bonding are based upon the element carbon. The resulting implication: What holds for carbon need not necessarily hold for the heavier main group elements. The conclusion of Grützmacher and Fässler relative to the gallyne: these workers refer to the Ga–Ga interaction as a ‘slipped triple bond’ as compared to an ‘unslipped triple bond’ in the case of acetylene. Grützmacher and Fässler<sup>45</sup> further add, ‘Clearly this compound [the gallyne] has a [Ga $\equiv$ Ga] triple bond.’

## Concluding remarks

The synthesis and molecular structure of organogallium compounds are an interesting area of study. A number of novel compounds have been prepared in recent years. Few topics in organogallium chemistry have generated more interest than the report of a compound containing a Ga $\equiv$ Ga triple bond.<sup>46</sup> The fact that this compound has served as a substrate upon which fundamental questions of structure and bonding may be pondered and debated is most significant. It would appear that

some of our long-standing theories of structure and bonding may be inadequate to describe sufficiently novel organometallic compounds.

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