A Metallic System with Aromatic Character. Synthesis and Molecular Structure of $Na_2[(Mes_2C_6H_3)Ga]_3$ (Mes = 2,4,6-$Me_3C_6H_2$): The First Cyclogallane

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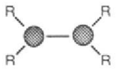
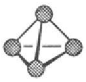
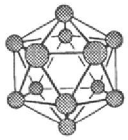
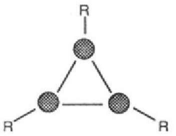
Homonuclear metal−metal bonding involving the heavier group 13 elements, despite a rather substantial latent period,[1] is now showing signs of being a fertile, if still emerging, area of organo−main group chemistry.[2] Seminal reports have appeared wherein an alane (R = C_5Me_5),[3] a gallane (R = $C(SiMe_3)_3$),[4] and an indane (R = $C(SiMe_3)_3$),[5] $[RM]_4$, have been shown to contain M_4 tetrahedral cores. Indeed, an interesting alane containing an Al_{12} icosahedral core, $K_2[Al_{12}(i\text{-Bu})_{12}]$,[6] has also been reported. These reports notwithstanding, the majority of compounds containing homonuclear metal−metal bonds of the group 13 metals have typically taken the simpler R_2M-MR_2 form.[7] Thus, only the dimeric, tetrahedral, and icosahedral structural frameworks have been observed in this area of group 13 organometallic chemistry while simple cyclic frameworks such as $[RM]_3$ (below) are noteworthy in their absence.



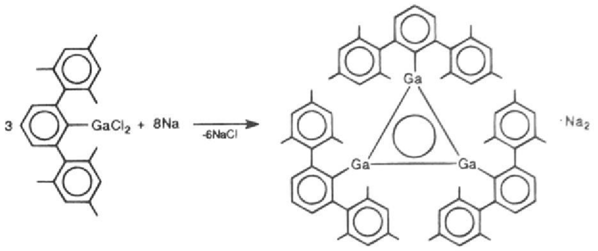






In an effort to assess the ramifications of the sterically demanding ligand system 2,6-dimesitylphenyl on group 13 organometallic chemistry we prepared (2,6-dimesitylphenyl)gallium dichloride, $(Mes_2C_6H_3)GaCl_2$ (Mes = 2,4,6-$Me_3C_6H_2$), and allowed it to undergo alkali metal reduction. Herein, we report the synthesis and molecular structure of $Na_2[(Mes_2C_6H_3)Ga]_3$, isolated from the sodium metal reduction of $(Mes_2C_6H_3)GaCl_2$ in diethyl ether (eq 1).[8]

In addition to being the first *cyclogallane*, $Na_2[(Mes_2C_6H_3)Ga]_3$ is at once both promising and intriguing as the concept of *metalloaromaticity*—a metallic ring system possessing aromatic character—is brought to the fore.



(1)

X-ray intensity data were collected on a Rigaku AFC-7R diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å) at −140 °C. It is of interest that the color of the title compound reversibly changes from red to light orange in the nitrogen cold stream. Cell parameters and an orientation matrix for data collection, obtained from a least-squares analysis of the setting angles of 24 carefully centered reflections in the range $49.47° < 2\theta < 49.97°$, corresponded to the hexagonal space group $P6_3/m$ (No. 176) with unit cell parameters $a = 13.712(2)$ Å, $c = 21.919(5)$ Å, $V = 3569(1)$ Å^3, and $D_{\text{calcd}} = 1.25$ g cm^{-3} for $Z = 2$. The molecule resides about a $\bar{6}$− site ($^1/_3$, $^2/_3$, $^1/_4$). In addition to the molecule the lattice contains two badly disordered ether molecules: one situated about a 6− site ($^2/_3$, $^1/_3$, $^1/_4$) and the other about a 3− site (0, 0, $^1/_2$). The structure was solved by direct methods and refined, based upon 1787 observed reflections, using the TEXSAN[9] and SHELXTL[10] systems of computer programs. Refinement converged at $R = 0.032$, $R_w = 0.049$.[11] The molecular structure of $Na_2[(Mes_2C_6H_3)Ga]_3$ is given in Figure 1a while a view of the title compound along the Na−Na vector is given in Figure 1b.

We recently endeavored to explore the coordination chemistry of aryl-substituted phenyl-based ligands in organogallium chemistry. The sterically demanding ligand system 2,6-dimesitylphenyl[12] has proven to be very interesting as we utilized it to prepare bis(2,6-dimesitylphenyl)gallium chloride, $(Mes_2C_6H_3)_2$-

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(1) The initial reports of organometallic compounds containing M−M bonding of the group 13 metals, although now generally viewed as being mischaracterized alkali metal adducts of organoaluminum moieties,[2] were first reported almost 30 years ago: (a) Schram, E. P. *Inorg. Chem.* **1966**, *5*, 1291. (b) Schram, E. P.; Hall, R. E.; Glore, J. D. *J. Am. Chem. Soc.* **1969**, *91*, 6643.

(2) For a review of this area, please see: Uhl, W. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1386.

(3) Dohmeier, C.; Robl, C.; Tacke, M.; Schnöckel, H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 564.

(4) Uhl, W.; Hiller, W.; Layh, M.; Schwarz, W. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1364.

(5) Uhl, W.; Graupner, R.; Layh, M.; Schütz, U. *J. Organomet. Chem.* **1995**, *493*, C1.

(6) Hiller, W.; Klinkhammer, K.-W.; Uhl, W.; Wagner, J. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 179.

(7) (a) M = Al; R = $CH(SiMe_3)_2$: Uhl, W. *Z. Naturforsch B* **1988**, *43*, 1113. (b) M = Ga; R = $CH(SiMe_3)_2$: Uhl, W.; Layh, M.; Hildenbrand, T. *J. Organomet. Chem.* **1989**, *364*, 289. (c) M = In; R = $CH(SiMe_3)_2$: Uhl, W.; Layh, M.; Hiller, W. *J. Organomet. Chem.* **1989**, *368*, 139. (d) M = Ga, In; R = $(CF_3)_3C_6H_2$: Schluter, R. D.; Cowley, A. H.; Atwood, D. A.; Jones, R. A.; Bond, M. R.; Carrano, C. J. *J. Am. Chem. Soc.* **1993**, *115*, 2070.

(8) Synthesis of $Na_2[(Mes_2C_6H_3)Ga]_3$: Inside a drybox a 100 mL Schlenk flask was charged with $GaCl_3$ (4 mmol) and diethyl ether (30 mL). A solution of $(Mes_2C_6H_3)Li$ (ref 12) (1.28 g; 4 mmol) was slowly added at −78 °C. The system was stirred for 3 h at −78 °C, allowed to slowly warm to room temperature, and stirred for an additional 24 h. The resulting slightly yellow solution containing $(Mes_2C_6H_3)GaCl_2$ was filtered to another flask containing ether and freshly cut pieces of sodium metal (0.50 g; 22 mmol) and stirred for 4 days, resulting in a dark red solution. Removal of solvent afforded an orange solid, which was recrystallized from an ether/hexane mixture (1:2). The title compound was isolated as large ruby red crystals (0.80 g; 50% yield): mp 217 °C. The crystalline compound contains two molecules of diethyl ether per asymmetric unit. Anal. (E + R Microanalytical Laboratories, Corona, NY). Calcd (found) for $C_{80}H_{95}Ga_3Na_2O_2$: C, 71.50 (67.45); H, 7.13 (7.22). Elemental analyses for this compound were carried out no fewer than five times (on five separate samples, on five separate occasions). In these analyses the found value for carbon proved problematic while that for hydrogen was consistently in good agreement with the calculated value. Such, we have concluded, appears to be an unfortunate artifact of $Na_2[(Mes_2C_6H_3)Ga]_3{\cdot}(Et_2O)_n$. ^{1}H NMR (300 MHz, 297 K, $C_2D_5OC_2D_5$): δ 0.96, t, 12H, CH_3 (ether); 3.25, q, 8H, CH_2 (ether); 1.91, s, 18H, o'-CH_3; 1.94, s, 18H, o'-CH_3; 2.16, s, 9H, p'-CH_3; 2.49, s, 9H, p'-CH3; 6.64−6.71, m, 3H, p-CH (aromatic); 6.76, s, 6H, m'-CH (aromatic); 6.77, s, 6H, m'-H (aromatic); 6.83−7.33, m, 6H, m-CH (aromatic). ^{13}C NMR (300 MHz, 297K, $C_2D_5OC_2D_5$): δ 19.59, 19.61, 20.73, 20.75, 20.75, 124.95, 126.08, 126.45, 126.83, 127.37, 127.77, 129.94, 133.40, 134.80, 135.50, 136.90, 144.10. IR (Nujol mull): 675 w, 743 w, 850 m, 1510 m, 1545 m, 1563 m, 1675 m, 1700 m, 1750 w, 1784 w, 1862 w, 1890 w, 2320 vs, 2330 vs, 2720 w, 2862 s, 3625 w, 3750 w, 3830 w.

(9) Swepston, P. N. *TEXSAN; Structure Analysis Software*; Molecular Structure Corporation: The Woodlands, TX, 1993.

(10) Sheldrick, G. M. *SHELXTL, Crystallographic Computing System*; Nicolet Instruments Division: Madison, WI, 1986.

(11) X-ray data of this compound were attempted on four different samples. While the same unit cell was consistently obtained, the crystal quality was insufficient to afford successful refinement. Only upon a number of recrystallizations did we obtain adequate crystals for successful refinement.

(12) Both 2,6-dimesityl-1-iodobenzene, $(Mes_2C_6H_3)I$,[12a] and its lithium salt, $(Mes_2C_6H_3)Li$,[12b] were prepared by published procedures: (a) Du, C.-J.; Hart, H.; Ng, K.-K. D. *J. Org. Chem.* **1986**, *51*, 3162. (b) Ruhland-Senge, K.; Ellison, J. J.; Wehmschulte, R. J.; Pauer, F.; Power, P. P. *J. Am. Chem. Soc.* **1993**, *115*, 11353.

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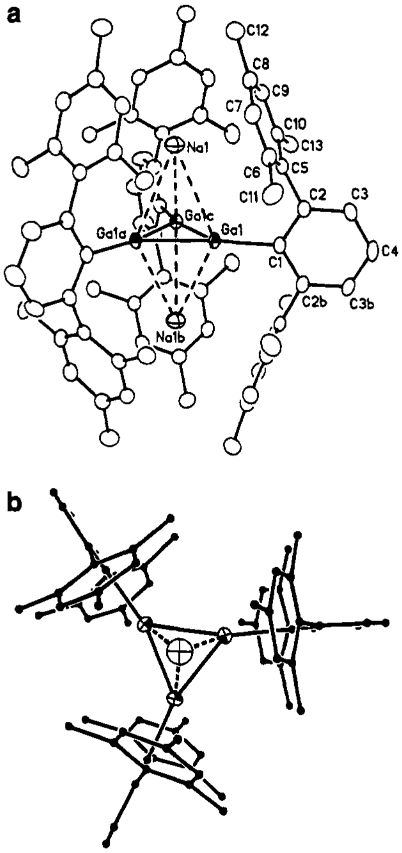
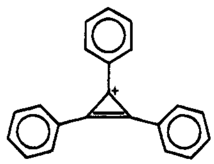


Figure 1. (a) Molecular structure of $Na_2[(Mes_2C_6H_3)Ga]_3$ (thermal ellipsoids are shown at 35% probability levels). Selected bond distances (Å) and angles (deg): Ga(1)–Na(1), 3.229(2); Ga(1)–C(1), 2.037(3); Ga(1)–Ga(1a), 2.441(1); Ga(1)–Na(1b), 3.229(2); C(1)–Ga(1)–Ga(1a), 166.3(1); C(1)–Ga(1)–Ga(1c), 133.7(1); Ga(1a)–Ga(1)–Ga(1c), 60.0(1); Na(1)–Ga(1)–Na(1b), 128.2(1); Ga(1)–Na(1)–Ga(1a), 44.4 (1). (b) View of $Na_2[(Mes_2C_6H_3)Ga]_3$ along the Na–Na vector.

GaCl, a rare example of a gallium atom residing in a T-shaped environment.[13] Indeed, this laboratory has also utilized this ligand to prepare the chlorine-bridged organoindium dimer bis[(2,6-dimesitylphenyl)indium dichloride], $[(Mes_2C_6H_3)InCl_2]_2$.[14]

The title compound resides about an inherently planar three-membered Ga_3 core with Ga–Ga–Ga angles of 60.0(1)°. The metallic core of $Na_2[(Mes_2C_6H_3)Ga]_3$ is completed by two sodium atoms perfectly centered above and beneath the centroid of the Ga_3 plane (Ga··Na: 3.220(2) Å) thus constituting a Na_2-Ga_3 metallic trigonal bipyramid somewhat similar to the Pb_5^{2-} and Sn_5^{2-} Zintl ions.[15] The independent Ga–Ga bond distance of 2.441(1) Å in $Na_2[(Mes_2C_6H_3)Ga]_3$ is particularly noteworthy. For perspective, the mean Ga–Ga bond distance in the $[Ga_4\{C(SiMe_3)_3\}_4]^4$ tetramer is 2.688 Å while the Ga–Ga distance in $[(Me_3Si)_2HC]_2GaGa[CH(SiMe_3)_2]_2$[6b] is 2.541(1) Å. By contrast, the shortest Ga–Ga bond distance reported for an organometallic compound is 2.343(2) Å given for the radical anion $[(Trip)_2GaGa(Trip)_2]^{\bullet-}$ (Trip = 2,4,6-*i*-$Pr_3C_6H_2$),[16] wherein the metal–metal bond was taken to possess π character. These Ga–Ga bond distances are compared to a value of 2.70 Å for gallium metal.[17] The Ga–C distance found in the title compound of 2.037(3) Å compares with values of 1.956(16) and 2.001(16) Å observed in $(Mes_2C_6H_3)_2GaCl$.[13]

Although traditional boundaries between inorganic and organic chemistry are ever becoming less rigid, the concept of aromaticity remains a steadfast beacon of demarcation. In general, aromatic compounds are taken to be planar (or nearly planar) cyclic molecules with shorter inter-ring bonds. In addition, aromatic species generally obey the Hückel $4n + 2$ rule of π electrons. Consequently, borazine, $B_3N_3H_6$, occupies a unique, if largely historical, position as the *inorganic analog of benzene*, even though borazine bears little resemblance to benzene in terms of its reactivity. The correspondingly smaller three-membered aromatic ring system possessing two π electrons, the cyclopropenium cation, is noteworthy as salts of its triphenyl derivative, the triphenylcyclopropenium cation (below), often display great stability.



The Ga_3 three-membered ring core of $Na_2[(Mes_2C_6H_3)Ga]_3$ possesses inherent planarity while the Ga–Ga bonds are among the shortest reported. In terms of π electrons, it is our position that the two Na atoms donate one electron each to the unoccupied p orbitals of the three sp^2-hybridized Ga atoms thereby providing the requisite two π electrons for delocalization and making the core of the title compound isoelectronic with the triphenylcyclopropenium species, thus affording an aromatic *cyclogallene* Ga_3^{2-} species.

The novel cyclogallane $Na_2[(Mes_2C_6H_3)Ga]_3$ represents a fundamental contribution to the chemistry of main group ring systems. Furthermore, $Na_2[(Mes_2C_6H_3)Ga]_3$ fulfills the usual requirements that are normally employed to ascertain the presence of aromatic character, thus constituting a rare example of metalloaromaticity. The synthesis and structure of $Na_2[(Mes_2C_6H_3)Ga]_3$ will be used as a bench mark as we continue to explore this area.

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Supporting Information Available: Textual summary of data collection and refinement and tables of crystal data, bond distances and angles, final fractional coordinates, and thermal parameters (8 pages); observed and calculated structure factors (8 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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[15] (a) Edwards, P.; Corbett, J. D. *Inorg. Chem.* **1977**, *16*, 903. (b) Corbett, J. D. *Chem. Rev.* **1985**, *85*, 383.

[16] He, X.; Barlett, R. A.; Olmstead, M. M.; Ruhlandt-Senge, K.; Sturgeon, B. E.; Power, P. P. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 717.

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