Cyclogallanes and Metalloaromaticity. Synthesis and Molecular Structure of Dipotassium Tris((2,6-dimesitylphenyl)cyclogallene), $K_2[(Mes_2C_6H_3)Ga]_3$ (Mes = 2,4,6-$Me_3C_6H_2$): A Structural and Theoretical Examination

Xiao-Wang Li,[†] Yaoming Xie,[†] Peter R. Schreiner,[†] Kevin D. Gripper,[†]
R. Chad Crittendon,[†] Charles F. Campana,[‡] Henry F. Schaefer,[†] and
Gregory H. Robinson*[,†]

Department of Chemistry and Center for Computational Quantum Chemistry, The University of Georgia, Athens, Georgia 30602-2556, and Analytical X-Ray Instrumentation Division, Siemens Energy and Automation, Inc., 6300 Enterprise Lane, Madison, Wisconsin 53719-1173

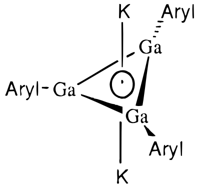
Received June 24, 1996[⊗]

The cyclogallane dipotassium tris((2,6-dimesitylphenyl)cyclogallene), $K_2[(Mes_2C_6H_3)Ga]_3$ (Mes = 2,4,6-$Me_3C_6H_2$), has been prepared by either of two distinct synthetic routes. Disproportionation of gallium(II) chloride, Ga_2Cl_4, in the presence of (2,6-dimesitylphenyl)-lithium, $(Mes_2C_6H_3)Li$, followed by potassium metal reduction in Et_2O affords the title compound as large ruby red crystals. Alternatively, $K_2[(Mes_2C_6H_3)Ga]_3$ may readily be approached by direct alkali metal reduction of $(Mes_2C_6H_3)GaCl_2$. The title compound was characterized by ^1H and ^{13}C NMR, elemental analyses, IR spectroscopy, and single-crystal X-ray diffraction. The cyclogallane resides about the planar Ga_3 triangle constituted by extremely short Ga−Ga bonds: 2.4260(5), 2.4317(5), and 2.4187(5) Å. Theoretical examination of the Ga_3^{2-} anionic core in $[GaH]_3^{2-}$, $Na_2[GaH]_3$, and $K_2[GaH]_3$ suggests a well-defined π-molecular orbital. Both experimental and theoretical results strongly support the cyclogallene dianion, $[(Mes_2C_6H_3)Ga]_3^{2-}$, as a well-defined metalloaromatic system—a metallic ring system exhibiting aromatic behavior.

Introduction

From an inorganic perspective, the concept of aromaticity has been the predominant, if largely historical, domain of borazine—the boron−nitrogen six-membered ring compound often referred to as *inorganic benzene*. Although benzene and its boron−nitrogen congener share a number of similar physical properties, the two compounds display markedly divergent chemical behaviors as benzene readily undergoes electrophilic aromatic substitution reactions while in similar systems borazine exclusively yields addition products. Nonetheless, the realm of inorganic chemistry in general, and that of organometallic chemistry in particular, has witnessed few other examples to which the concept of aromaticity is relevant.

This laboratory recently endeavored to examine the group 13 organometallic chemistry of the sterically demanding aryl-substituted 2,6-dimesitylphenyl ligand, $Mes_2C_6H_3$ (Mes = 2,4,6-$Me_3C_6H_2$). The steric demands of this ligand have been shown by this laboratory to be sufficiently substantial so as to afford rare T-shaped three-coordinate organogallium[1] and organoindium[2] compounds, $(Mes_2C_6H_3)_2MX$ (M = Ga, In; X = Cl, Br), while the indium dichloride derivative has been shown to be an asymmetric dimer, $[(Mes_2C_6H_3)_2InCl_2]_2$,[3] residing about a distorted In_2Cl_2 four-membered ring. Herein we report the synthesis and molecular structure of the cyclogallane[4] dipotassium tris((2,6-dimesitylphenyl)cyclogallene), $K_2[(Mes_2C_6H_3)Ga]_3$, **II**.



Aryl = $Mes_2C_6H_3$

II

An interesting disproportionation of gallium(II) chloride, Ga_2Cl_4, in the presence of (2,6-dimesitylphenyl)-lithium, $(Mes_2C_6H_3)Li$, followed by potassium metal reduction in Et_2O affords the title compound as large ruby red crystals. Alternatively, **II** may readily be approached by direct alkali metal reduction of $(Mes_2C_6H_3)GaCl_2$. Although a recent preliminary report from this laboratory described the synthesis and molecular structure of $Na_2[(Mes_2C_6H_3)Ga]_3$, **I**,[5] herein we

---

[†] The University of Georgia.

[‡] Siemens Energy and Automation, Inc.

[⊗] Abstract published in *Advance ACS Abstracts,* August 15, 1996.

(1) Li, X.-W.; Pennington, W. T.; Robinson, G. H. *Organometallics* **1995**, *14*, 2109.

(2) Li, X.-W.; Pennington, W. T.; Robinson, G. H. *Main Group Chem.* **1996**, *1*, 301.

(3) Robinson, G. H.; Li, X.-W.; Pennington, W. T. *J. Organomet. Chem.* **1995**, *501*, 399.

(4) Consistent with alkane and alkene nomenclature, the term *cyclogallane* is utilized to describe a ring system composed exclusively of gallium atoms while the corresponding term *cyclogallene* is used to denote a situation involving double bonding.

(5) Li, X.-W.; Pennington, W. T.; Robinson, G. H. *J. Am. Chem. Soc.* **1995**, *117*, 7578.

S0276-7333(96)00508-0 CCC: $12.00

offer a more detailed examination of only the second example of a cyclogallane. The title compound has been characterized by ^{1}H and ^{13}C NMR, elemental analyses, IR spectroscopy, and single-crystal X-ray diffraction. In addition to these data, we offer theoretical studies in support of the proposition that the $[(Mes_2C_6H_3)Ga]_3^{2-}$ metallic ring dianion presents a measure of aromaticity—thereby constituting an example of *metalloaromaticity*.

Experimental Section

General Comments. Standard Schlenk techniques were employed in conjunction with an inert-atmosphere drybox (M Braun Labmaster 30). Solvents were distilled from sodium benzophenone under an atmosphere of argon prior to use. Argon was passed through copper-based purification and molecular sieve columns prior to use. Gallium(III) chloride, gallium(II) chloride, and 2-bromomesitylene were purchased from Aldrich Chemical Co. (Milwaukee, WI) while 2,6-dibromoaniline was purchased from Lancaster Synthesis Inc. (Windham, NH); all reagents were used as received. Both 2,6-dimesityl-1-iodobenzene, $(Mes_2C_6H_3)I$,[6] and 2,6-dimesitylphenyllithium, $(Mes_2C_6H_3)Li$,[7] were prepared as previously noted. Elemental analyses were performed by E + R Microanalytical Laboratories (Corona, NY). IR spectra were recorded on a Perkin-Elmer 1500 spectrometer while NMR spectra were recorded on a Bruker AMX-400 NMR spectrometer. X-ray intensity data were collected at −120 °C on a Siemens SMART CCD area detector system equipped with a normal focus X-ray tube at 2.0 kW (50 kV/40 mA).

Synthesis of $K_2[(Mes_2C_6H_3)Ga]_3$. Method A. A solution of $(Mes_2C_6H_3)Li$ (1.60 g, 5 mmol) in diethyl ether (40 mL) was added over a period of 10 min to a diethyl ether (50 mL) suspension of Ga_2Cl_4 (1.41 g, 5 mmol) at −78 °C. The reaction mixture was stirred for 3 h and then allowed to warm to 0 °C over a period of 10 h. A yellow solution resulted along with a precipitate (LiCl). As the system continued to warm to room temperature over a period of 2 h, a minute amount of metallic gallium deposited in the reaction vessel. The mixture was stirred for an additional 30 h and filtered. The yellow solution was transferred, *via* cannula, to a flask charged with potassium metal (0.70 g, 18 mmol). The mixture stirred for 5 days (in the absence of light). The solution gradually took on a deep ruby red color as a fine precipitate formed (KCl). The solid was separated by filtration and the red solution was concentrated. Upon cooling of the concentrated solution to −25 °C for 1 week, dark red—nearly black—crystals of $K_2[(Mes_2C_6H_3)Ga]_3\cdot(Et_2O)_2$ (0.65 g, 0.47 mmol) formed in the reaction vessel. X-ray-quality crystals were grown from an ether−hexane (1:2) mixture. Yield: 28% (based on $(Mes_2C_6H_3)Li$). Mp: 190 °C (dec). Calcd (found) for $C_{80}H_{95}Ga_3K_2O_2$: C, 69.83 (69.37); H, 6.96 (6.51). ^{1}H NMR (400 MHz, 298 K, $C_2D_5OC_2D_5$), δ): 1.02, t, C$\boldsymbol{H}_3$ (ether); 1.90, s, 18H, o′-C$\boldsymbol{H}_3$; 2.00, s, 18H, o′-C$\boldsymbol{H}_3$; 2.16, s, 9H, p′-C$\boldsymbol{H}_3$; 2.41, s, 9H, p′-C$\boldsymbol{H}_3$; 3.29, q, C$\boldsymbol{H}_2$ (ether); 6.67−6.70, m, 3H, p-C***H*** (aromatic); 6.71, s, 6H, m′-C***H*** (aromatic); 6.75, m, 6H, m′-C***H*** (aromatic); 6.77−6.84, m, 3H, m-C***H*** (aromatic); 6.94−7.00, m, 3H, m-C***H*** (aromatic). ^{13}C NMR (400 MHz, 298 K, $C_2D_5OC_2D_5$): δ 19.65, 19.84, 20.50, 20.54, 20.96, 124.29, 125.25, 126.29, 126.88, 127.36, 127.93, 129.71, 132.66, 134.33, 135.40, 137.84, 144.43. Unfortunately, the quardrapolar nature of the ^{71}Ga nucleus, coupled with the relatively asymmetric environment about the ^{71}Ga nuclei, proved problematic in our efforts to obtain informative ^{71}Ga spectra. IR (Nujol mull, KBr, cm^{-1}): 680 w, 720 m, 722 w, 745 w, 797 m, 849 m, 1401 w, 1512 w, 1540 w, 1565 w, 1654, 1721 w, 1755 w, 1784 w, 1890 w, 2723 w, 2865 s, 3630 m, 3755 w.

Method B. A solution of $(Mes_2C_6H_3)Li$ (1.60 g, 5 mmol) in diethyl ether (30 mL) was added over a period of 10 min to a diethyl ether (40 mL) solution of $GaCl_3$ (0.88 g, 5 mmol) at −78 °C. The reaction mixture was stirred for 3 h and allowed to warm to room temperature over a period of 2 h. It was then stirred for an additional 30 h. The mixture was filtered, and the resulting yellow solution was transferred directly to a flask, *via* cannula, charged with potassium metal (0.80 g, 20 mmol). After 5 days of stirring at room temperature (in the absence of light), the solution became dark ruby red in color accompanied by the formation of a precipitate (KCl). The solid was separated by filtration, and the red solution was concentrated to about a 20 mL volume. Cooling this concentrated solution to −25 °C for 1 week afforded dark red crystals of $K_2[(Mes_2C_6H_3)Ga]_3\cdot(Et_2O)_2$ (0.70 g, 0.51 mmol). Yield: 31% (based on $(Mes_2C_6H_3)Li$). Mp: 190 °C (dec). Spectroscopic characterization of **I** was consistent with data presented in method A.

Theoretical Methods. The structures of the model species $[GaH]_3$, $[GaH]_3^{2-}$, $Na_2[GaH]_3$, and $K_2[GaH]_3$ were fully optimized by quantum mechanical self-consistent field, SCF, and density functional theory, DFT, methods. In our study, the DFT method is B3LYP, that is, employing the three-parameter Becke's exchange functional[8] and the Lee−Yang−Parr nonlocal correlation functional.[9] The basis set is of the TZ2P quality (triple-ζ plus two sets of polarization functions). Diffuse basis functions were also augmented to the elements in the $[GaH]_3^{2-}$ dianion part (*i.e.*, for Ga and H). For gallium, Dunning's 14s11p5d primitive basis set[10] was contracted to 10s8p2d and then augmented with one s and one p diffuse functions [α_s(Ga) = 0.01838, α_p(Ga) = 0.01472] and two sets of d polarization functions [α_d(Ga) = 0.216, 0.068]. For hydrogen, Huzinaga's 5s primitive set[11] was contracted to 3s and then augmented with one s diffuse function [α_p(H) = 0.03016] and two set of p polarization functions [α_p(H) = 1.50, 0.375]. For potassium, Wachters's basis set (14s9p/10s6p) was augmented with two sets of p diffuse functions (α_p(K) = 0.085202, 0.031737), which may be regarded as describing the 4p orbital, and two sets of d polarization functions (α_d(K) = 0.20, 0.05).[12] For sodium, McLean and Chandler's basis set (12s9p/6s5p)[13] was augmented with two d polarization functions (α_d(Na) = 0.350, 0.0875). The above described basis sets are thus designated as Ga(15s12p7d/11s9p4d), H(6s2p/4s2p), K(14s11p2d/8s7p2d), and Na(12s9p2d/6s5p2d). As a comparison, we also studied a similar species cyclopropenium cation, $[CH]_3^+$, in parallel. The latter basis set is of TZ2P quality and may be designated as C(10s6p2d/5s3p2d) and H(5s2p/3s2p).[14] For hydrogen in $[CH]_3^+$, the basis set is the same as that specified earlier except for the lack of the diffuse function. For carbon, the orbital exponents of the polarization functions are α_d(C) = 1.50 and 0.375.

X-ray Structural Determination. Inside the drybox a crystal of the title compound was taken from the reaction vessel, placed in a glass capillary, and flame sealed upon leaving the box. The crystalline sample was placed on the diffractometer goniometer head and optically aligned. A total of 1321 frames of data were collected using a narrow-frame method with scan widths of 0.3° in ω and 30 s exposure times using a crystal-to-detector distance of 4.983 cm (maximum 2θ angle of 56.35°). The total data collection time was approximately 13.5 h. Frames were integrated with the Siemens SAINT program to yield a total of 36 237 reflections, of which 15 011 were independent (R_{int} = 4.33%, R_{sig} = 4.80%) and $4\sigma(F)$. The monoclinic primitive unit cell parameters of a = 16.3439(3) Å, b = 19.5981(3) Å, c = 15.4433(3) Å, and β =

---

(6) Du, C.-J.; Hart, H.; Ng, K.-K. D. *J. Org. Chem.* **1986**, *51*, 3162.

(7) Ruhlandt-Senge, K.; Ellison, J. J. ; Wehmschulte, R. J.; Pauer, F.; Power, P. P. *J. Am. Chem. Soc.* **1993**, *115*, 11353.

(8) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(9) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B*, **1988**, *37*, 785.

(10) Dunning, T. H. *J. Chem. Phys.* **1977**, *66*, 1382.

(11) Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293.

(12) (a) Wachters, A. J. H. *J. Chem. Phys.* **1970**, *52*, 1033. (b) Ma, B.; Meredith, C.; Schaefer, H. F. *J. Phys. Chem.* **1994**, *98*, 8216.

(13) McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639.

(14) Dunning, T. H. *J. Chem. Phys.* **1971**, *55*, 716.

Table 1. Crystallographic Data for $K_2[(Mes_2C_6H_3)Ga]_3 \cdot 2Et_2O$, II

Crystal Data	
empirical formula	$C_{80}H_{95}Ga_3K_2O_2$
fw	1375.98
color; habit	red, prism
size (mm)	$0.24 \times 0.44 \times 0.16$
space group	monoclinic, $P2_1/n$ (No. 14)
unit cell dimens	
a (Å)	16.3439(3)
b (Å)	19.5981(3)
c (Å)	20.7553(4)
β (deg)	92.97(1)
formula units/cell	4
V (Å^3)	6639.2(2)
D_{calc} (g/cm^3)	1.27
F(000)	2636
Data Collection	
unit cell reflns	8192
maximum 2θ angle (deg)	56.35
frames collcd	1321
exposure times (s)	30
no. of reflns collcd	36 237
no. of reflns unique	15 011
power	50 kV/40 mA
scan width (ω)	0.3
abs coeff (mm^{-1})	1.375
min/max transm	0.686/0.822
Refinement	
refinement method	full-matrix least squares on F^2
final R indices [$I > 2\sigma(I)$]	$R = 0.056$; $R_w = 0.119$
R indices (all data)	$R = 0.073$; $R_w = 0.128$
goodness of fit	$S = 1.130$
no. of obs reflns	12 164
no of params refined	736
largest diff peak and hole (e$^-$/Å^3)	0.838/−0.595

92.97(1)° were based upon least-squares refinement of the three-dimensional centroids of 8192 reflections. A semiempirical absorption correction was applied to the data using an ellipsoidal model with transmission coefficients ranging from 0.686 to 0.822. The structure was solved in the monoclinic space group $P2_1$/n (No. 14) with four molecules per unit cell. The unit cell was found to contain two disordered Et_2O molecules. The final refinement of this model using full-matrix F^2 refinement with SHELXTL 5.0[15] converged at $R = 0.056$ and $R_w = 0.128$. Crystallographic data are found in Table 1 while the molecular structure of **II** is given in Figure 1.

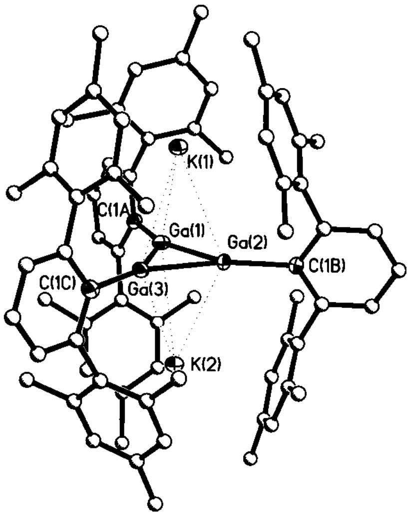
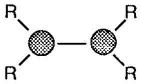
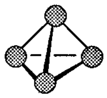


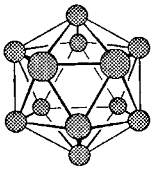
Figure 1. Molecular structure of $K_2[(Mes_2C_6H_3)Ga]_3$, **II** (thermal ellipsoids are shown at 35% probability levels). Selected bond distances (Å) and angles (deg): Ga(1)−Ga(2), 2.4260(5); Ga(1)−Ga(3), 2.4187(5); Ga(2)−Ga(3): 2.4317(5); Ga(1)−C(1a), 2.040(3); Ga(2)−C(1b), 2.050(3); Ga(3)−C(1c), 2.043(3); Ga(1)−K(1), 3.5294(8); Ga(1)−K(2), 3.5777(8); Ga(2)−K(1), 3.5289(8); Ga(2)−K(2), 3.5567(8); Ga(3)−K(1), 3.5817(8); Ga(3)−K(2), 3.5488(8); Ga(1)−Ga(2)−Ga(3), 59.73(2); Ga(3)−Ga(1)−Ga(2), 60.26(2); Ga(1)−Ga(3)−Ga(2), 60.02(2); C(1a)−Ga(1)−Ga(3), 143.03 (10); C(1a)−Ga(1)−Ga(2), 156.69(10); C(1b)−Ga(2)−Ga(3), 154.97(10).

Results and Discussion

The chemistry of boron exists in stark contrast to that of the heavier metallic members of group 13. This disparity is particularly pronounced where the chemistry of the group 13 element−element bond is concerned. While the chemistry of the B−B bond has been extensively developed over decades, the M−M (Al, Ga, In) bond has proven to be an exceedingly elusive synthetic/structural fragment.[16] Nonetheless, recent years have witnessed seminal discoveries wherein the synthesis and structure of a number of interesting organometallic compounds containing M−M bonds have been reported. Although the majority of these complexes, generally employing silyl-, isobutyl-, or cyclopentadienyl-based sterically demanding ligands, have assumed a simple dimeric structural framework,[17] reports have also appeared describing M_4 tetrahedral frameworks,[18−20] while one report has described an Al_{12} icosahedral skeleton:[21]







The fact that simple ring compounds were (until very recently) conspicuously absent from this collection of structural frameworks of the group 13 metals is intriguing. Furthermore, it seemed reasonable that the steric and electronic nature of the given ligand would play a critical role if such group 13 metallic ring compounds were to be successfully approached. To this end, this laboratory endeavored to examine the group 13 organometallic chemistry of the sterically demanding 2,6-dimesitylphenyl ligand. Utilizing this ligand, this laboratory recently prepared the first cyclogallane in disodium tris((2,6-dimesitylphenyl)cyclogallene), Na_2-

---

(15) Sheldrick, G. M. *SHELXTL 5.0, Crystallographic Computing System*; Siemens Analytical X-Ray Instruments: Madison, WI, 1995.

(16) For review of this area please see: (a) Dohmeier, C.; Loos, D.; Schnockel, H. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 129. (b) Uhl, W. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1386. (c) Robinson, G. H. *Main Group Chem. News* **1996**, *4*, 4.

(17) (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. (e) M = In; R = Si(t-Bu)$_3$: Wiberg, N.; Amelunxen, K.; Noth, H.; Schmidt, M.; Schwenk, H. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 65. (f) M = Ga; R = $CH(SiMe_3)_2$: Uhl, W.; Schutz, U.; Kaim W.; Waldhor, E. *J. Organomet. Chem.* **1995**, *501*, 79.

(18) M = Al, R = C_5Me_5: Dohmeier, C.; Robl, C.; Tacke, M.; Schnöckel, H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 564.

(19) M = Ga, R = $C(SiMe_3)_3$: Uhl, W.; Hiller, W.; Layh, M. Schwarz, W. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1364.

(20) M = In, R = $C(SiMe_3)_3$: Uhl, W.; Graupner, R.; Layh, M.; Schütz, U. *J. Organomet. Chem.* **1995**, *493*, C1.

(21) M = Al, R = i-Bu: Hiller, W.; Klinkhammer, K.-W.; Uhl, W.; Wagner, J. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 179.

Table 2. Ga–Ga Bond Distances (Å) in Organometallic Gallanes

compd	Ga–Ga
$[Ga\{C(SiMe_3)_3\}]_4$[a]	2.688
$[(Me_3Si)_2HC]_2Ga-Ga[CH(SiMe_3)_2]_2$[b]	2.541(1)
$(tmp)_2Ga-Ga(tmp)_2$[c]	2.525(1)
$[(i\text{-}Pr_3C_6H_2)_2Ga-Ga(i\text{-}Pr_3C_6H_2)_2]^{\bullet -}$ [d]	2.343(2)
$[(t\text{-}Bu)NCHCHN(t\text{-}Bu)]Ga-Ga[(t\text{-}Bu)\text{-}NCHCHN(t\text{-}Bu)]$[e]	2.333(1)
$Na_2[(Mes_2C_6H_3)Ga]_3$[f]	2.441(1)
$K_2[(Mes_2C_6H_3)Ga]_3$[g]	2.4260(5)
	2.4317(5)
	2.4187(5)

[a] Reference 19. [b] Reference 17b. [c] Reference 24b. tmp = 2,2,6,6-tetramethylpiperidino. [d] Reference 28. [e] Reference 24a. [f] Reference 5. [g] This study.

$[(Mes_2C_6H_3)Ga]_3$, **I**,[5] isolated from the alkali metal reduction of $(Mes_2C_6H_3)GaCl_2$ in ether. The planarity of the Ga_3 ring and the very short Ga–Ga bonds (2.441(1) Å), coupled with the premise that the metallic ring is proposed to be a 2π-electron system, led us to suggest that this metallic moiety constituted an aromatic system–an example of *metalloaromaticity*.[22] Along with an alternative synthesis of **II**, we offer additional crystallographic data, coupled with theoretical studies, in support of the concept of a metallic ring exhibiting aromatic behavior. Although the structural parameters of **I** and **II** are quite comparable to each other (Table 2), as are the ^1H and ^{13}C NMR and the IR spectra, the most notable structural difference between the two compounds is found in the orientation of the phenyl rings bound to gallium. In **I** each of the three rings is perfectly orthogonal to the Ga_3 ring, while in **II** the three rings are tilted in a propeller fashion (9.1, 8.9, and 9.6° for the rings attached to Ga1, Ga2, and Ga3, respectively).

II has been approached by either of two synthetic routes. The most straightforward approach, and that employed for the preparation of **I**, concerns the alkali metal reduction of (2,6-dimesitylphenyl)gallium dichloride in ether (eq 1).

$$3(Mes_2C_6H_3)GaCl_2 + 8K \xrightarrow[-6KCl]{} \underset{\textbf{II}}{K_2[(Mes_2C_6H_3)Ga]_3} \qquad (1)$$

Distinct from the preparation described in eq 1, which was initiated with gallium(III) chloride in the formation of $(Mes_2C_6H_3)GaCl_2$, **II** may also be approached by an interesting disproportionation involving gallium(II) chloride, Ga_2Cl_4, followed by potassium metal reduction. In this preparation, gallium(II) chloride interacts with (2,6-dimesitylphenyl)lithium, $(Mes_2C_6H_3)Li$, affording a yellow solution containing $[(Mes_2C_6H_3)ClGa-GaCl_2]\cdot nEt_2O$. It is our position that this species disproportionated affording the gallium(III) species, $(Mes_2C_6H_3)GaCl_2$, in addition to a mixture of other (uncharacterized) low-valent gallium species: 2Ga(II) → Ga(III) + "Ga(I)". Such a process could readily afford the desired Ga(III) species while the gallium(I) species could, in turn, undergo a similar disproportionation yielding a more stable gallium(II) species and gallium metal: 2Ga(I) → Ga(II) + Ga(0). Although such a disproportionation is somewhat unusual, it has been suggested by this laboratory[3] and others[23] where indium(II) species are concerned. It is important to note that the direct disproportionation of a Ga(II) species to Ga(0) and Ga(III) is also a possibility and, indeed, has been suggested in another Ga_2Cl_4 system.[24] That a minute amount of gallium metal was observed in the reaction vessel during the preparation of **II** (method A) is consistent with either of these hypotheses.

Even as 1996 marks the 70th anniversary of its initial preparation by Stock and Pohland,[25] borazine remains, arguably, the most infamous of all main group compounds. This notoriety is due, at least in part, to the fact that with borazine the π-bonding capability of group 13 elements was first brought to the fore coupled with the realization that group 13 elements could engage in the formation of interesting ring compounds. These two tenets remain relevant in contemporary group 13 organometallic chemistry: the π-bonding in group 13 organometallic compounds is still being debated[22] while the syntheses of ring compounds, as evidenced by the trimeric aminoalane $[MeAlN(i\text{-}Pr_2C_6H_3)]_3$[26] and the dimeric phosphinogallane $[(Me_3Si)_2P\{Me_2Ga\}_2PMe]_2$,[27] continue to be an active area of research. Thus, the preparation of a simple organometallic ring compound–where the ring is constituted exclusively by group 13 metals–with the concomitant possibility of π-bonding *within* the ring is indeed a novel concept.

Consideration of the Ga–Ga bonds in the silyl-based tetrahedral gallane, 2.688 Å, and those in the silyl-based dimeric gallane, 2.541(1) Å (Table 2), as metal–metal single bonds affords a measure of perspective. Although the shortest Ga–Ga distance is found in the nitrogen heterocycle-based gallane $[(t\text{-}Bu)NCHCHN(t\text{-}Bu)]Ga-Ga[(t\text{-}Bu)NCHCHN(t\text{-}Bu)]$,[22] 2.333(1) Å, π-bonding in this complex is precluded as a consequence of the orthogonality of the p orbitals on the two sp^2-hybridized gallium atoms (rather, the short Ga–Ga bond distance was ascribed to diminished steric demands within the complex). Multiple bonding was suggested in the radical anion $[(i\text{-}Pr_3C_6H_2)_2Ga-Ga(i\text{-}Pr_3C_6H_2)_2]^{\bullet -}$, where a substantially shorter Ga–Ga bond distance of 2.343(2) Å was reported.[28] The preparation of this radical anion is significant as it resulted from the lithium metal reduction of the neutral gallane $[(i\text{-}Pr_3C_6H_2)_2Ga-Ga(i\text{-}Pr_3C_6H_2)_2]$, with a considerably longer Ga–Ga bond distance of 2.515(3) Å, in the presence of 12-crown-4–thus offering a convenient single bond/double bond comparison within the same complex. In addition, the torsion angle between the two GaC_2 planes decreased considerably from 43.8 to 15.5° for the neutral digallane and radical anion, respectively. The decrease of the Ga–Ga bond by 0.17 Å (7%) found in the radical anion

---

[22] The term metalloaromaticity was used previously to describe some early transition metal metallocyclobutadiene complexes: (a) Bursten, B. E.; Fenske, R. F. *Inorg. Chem.* **1979**, *18*, 1760. (b) Bursten, B. E. *J. Am. Chem. Soc.* **1983**, *105*, 121. The term is utilized herein in a different context as we are referring to a metallic ring which mimics traditional aromatic behavior.

[23] 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.

[24] (a) Brown, D. S.; Decken, A.; Cowley, A. H. *J. Am. Chem. Soc.* **1995**, *117*, 5421. (b) Linti, G.; Frey, R.; Schmidt, M. *Z. Naturforsch.* **1994**, *49B*, 958.

[25] Stock, A.; Pohland, E. *Chem. Ber.* **1926**, *59B*, 2215.

[26] Waggoner, K. M.; Hope, H.; Power, P. P. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1699.

[27] Burns, J. A.; Pennington, W. T.; Robinson, G. H. *Organometallics* **1995**, *14*, 1533.

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

[29] Breslow, R. *J. Am. Chem. Soc.* **1957**, *79*, 5318.

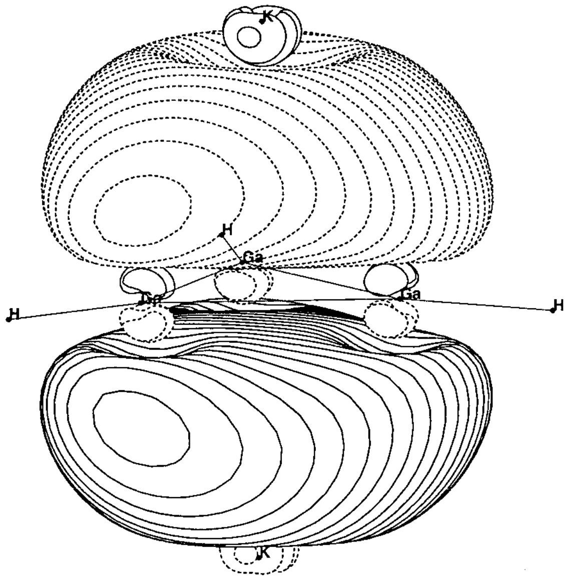


Figure 2. π–Molecular orbital of $K_2[GaH]_3$.

coupled with the reduction of the GaC_2 torsion angles was cited as being consistent with a one-electron π bond between the gallium atoms. In light of the distances noted for the previously reported compounds containing Ga–Ga bonds, the mean Ga–Ga bond distance in **II** of 2.4255 Å must be considered quite short.

The chemist's definition of aromaticity has evolved over time in parallel with society's technological advances. Thus, from such humble beginnings as "sweet smelling" to the more quantitative "planar rings obeying Hückel's $4n + 2$ rule of π electrons", almost without exception aromaticity has remained the domain of ring compounds of carbon. The simplest and smallest traditional aromatic moiety is the triphenylcyclopropenium cation, a three-membered 2π electron system, prepared for the first time by Breslow.[29] It is our contention that the $[(Mes_2C_6H_3)Ga]_3^{2-}$ dianion of **II** is valence isoelectronic with the triphenylcyclopropenium cation as the requisite 2π electrons are provided by the two potassium atoms (one electron each) to the unhybridized p orbitals of the three sp^2-hybridized gallium atoms. Theoretical studies are in agreement with this position as evidenced by the well-defined π molecular orbital of the $K_2[GaH]_3$ model species (Figure 2), a close approximation of the title compound (the K_2Ga_3 cores of the two species should be electronically very similar). It is important to note that the π electron cloud plot of $K_2[GaH]_3$ is very similar to that which we predicted for $[CH]_3^+$.

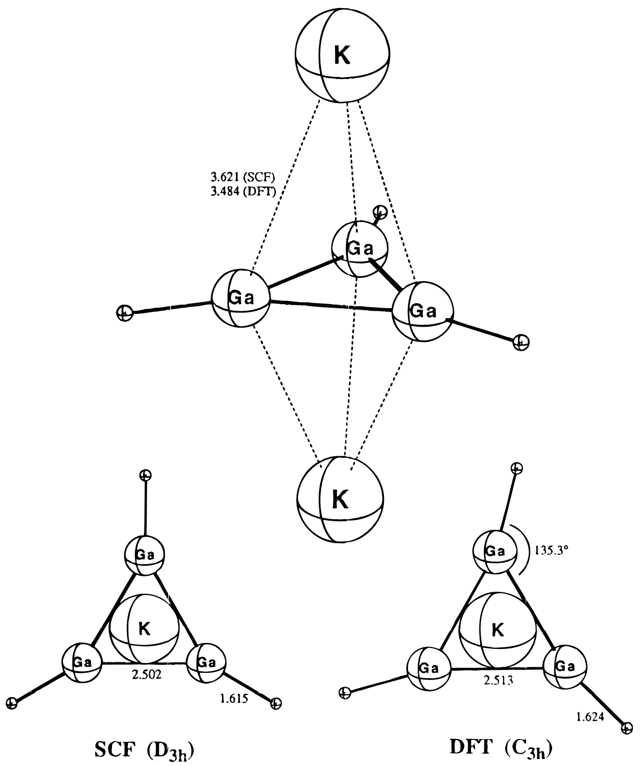


Figure 3. Theoretical structures of $K_2[GaH]_3$. The two lower structures are viewed down the K···K vector.

Although both SCF and DFT methods were utilized in this study, the DFT method was consistently in better agreement with the experimental results. Theoretical structures of $K_2[GaH]_3$ were determined using both methods (Figure 3). It is interesting that the SCF method predicts an idealized structure with D_{3h} symmetry with the Ga–H bond perfectly bisecting the Ga–Ga–Ga triangle (Ga–Ga–H: 150°), while the DFT model predicts C_{3h} symmetry (Ga–Ga–H: 135.3°). The predictions of the DFT model are in better agreement with our experimental results from the X-ray crystal structure of **II** as the Ga–Ga–C bond angle ranged from 143.03(10) to 146.60(10)° affording approximate C_{3h} symmetry. While both SCF and DFT models predict similar Ga–Ga bond distances, these values are somewhat longer that those found crystallographically in **II**. The mean Ga···K found in **II** (3.554 Å) nears the mean of the values predicted by SCF (3.621 Å) and DFT (3.484 Å). The same trends are observed for **I** relative to its theoretical structure. The experimental structures derived from X-ray diffraction results of **I** and **II** are compared with the corresponding theoretical structural parameters of $[GaH]_3$, $[GaH]_3^{2-}$, $Na_2[GaH]_3$, and $K_2[GaH]_3$ in Table 3.

The syntheses and structures of **I** and **II** coupled with

Table 3. Comparison of Theoretical and Experimental Structural Parameters of Cyclogallanes

	bond dists (Å)			bond angles (deg)		
cyclogallane	Ga–Ga	Ga–Na/K	Ga–H/C	Ga–Ga–H/C	core symmetry	method
$[GaH]_3$	2.6228		1.5918	150.0	D_{3h}	SCF
	2.8463		1.6250	134.0	C_{3h}	DFT
$[GaH]_3^{2-}$	2.5070		1.6420	150.0	D_{3h}	SCF
	2.4927		1.6737	145.6	C_{3h}	DFT
$Na_2[GaH]_3$	2.5280	3.1366	1.6073	150.0	D_{3h}	SCF
	2.5316	3.0258	1.6174	145.0	C_{3h}	DFT
$K_2[GaH]_3$	2.5023	3.6205	1.6153	150.0	D_{3h}	SCF
	2.5134	3.4835	1.6242	135.3	C_{3h}	DFT
$Na_2[(Mes_2C_6H_3Ga)]_3$, **I**	2.441(1)	3.229(2)	2.037(3)	133.7(1)	C_{3h}	X-ray[a]
$K_2[(Mes_2C_6H_3Ga)]_3$, **II**	2.4255	3.5539	2.044	145.0(10)	C_{3h}	X-ray[a]

[a] Mean Value.

the theoretical studies are in agreement with the proposition that the three-membered cyclogallane $[(Mes_2C_6H_3)Ga]_3^{2-}$ dianion is valence isoelectronic with the triphenylcyclopropenium cation and possess a measure of aromatic character—metalloaromaticity. The synthesis, structure, and reactivity of cyclogallanes are continuing in this laboratory.

Acknowledgment. We are grateful to the National Science Foundation (G.H.R., CHE-9520162; H.F.S., CHE-9527468) and to the donors of the Petroleum Research Fund, administered American Chemical Society, for support of this work (G.H.R.). We also thank Quency Teng (The University of Georgia) and Alex Kitaygorodskiy (Clemson University) for assistance with the ^{39}K and ^{71}Ga NMR experiments. R.S.Q.

Supporting Information Available: Tables of crystallographic data, atomic coordinates, positional parameters, and bond distances and angles (15 pages). Ordering information is given on any current masthead page.

OM9605084