$[Ga_2Cl_4(dioxane)_2]_x$: molecular structure and reactivity of a polymeric gallium(II) halide containing two five-coordinate gallium atoms about a Ga–Ga bond

Pingrong Wei, Xiao-Wang Li and Gregory H. Robinson*

Department of Chemistry, The University of Georgia, Athens, GA 30602-2556, USA.
E-mail: robinson@SUNCHEM.uga.edu

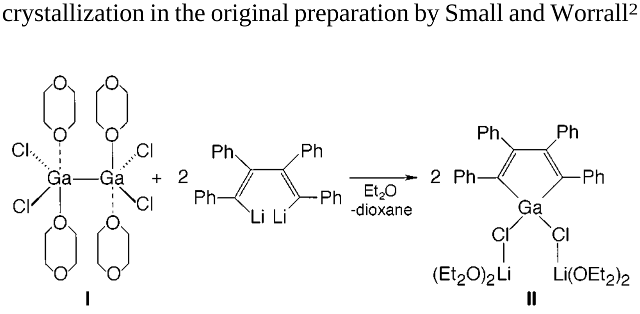
Received (in Columbia, MO, USA) 20th April 1999, Accepted 21st May 1999

A polymeric 1,4-dioxane adduct of gallium(II) chloride, $[Ga_2Cl_4(dioxane)_2]_x$, containing two five-coordinate gallium atoms about a Ga–Ga bond [Ga–Ga 2.3825(9) Å], reacts with 1,4-dilithiotetraphenylbutadiene affording an unusual Ga(II)–tetraphenylbutadiene complex.

The first organometallic compound unambiguously shown to contain a Ga–Ga bond, $[(Me_3Si)_2HC]_2Ga–Ga[CH(SiMe_3)_2]_2$ [Ga–Ga 2.541(1) Å], isolated from reaction of $LiCH(SiMe_3)_2$ with gallium(II) bromide bis(dioxane), $Ga_2Br_4(dioxane)_2$, was reported only a decade ago.[1] In the solid state, $Ga_2Br_4(dioxane)_2$ resides in a *trans* geometry about a Ga–Ga bond of 2.395(6) Å.[2] The solid state structure of the corresponding bis(dioxane) adduct of gallium(II) chloride, $Ga_2Cl_4(dioxane)_2$, assumes a similar *trans* geometry about a comparable Ga–Ga bond of 2.406(1) Å.[3] In both $Ga_2Br_4(dioxane)_2$ and $Ga_2Cl_4(dioxane)_2$, the gallium atoms are four-coordinate tetrahedral—each bonding to two halide atoms, one dioxane adduct, and the remaining gallium atom. Herein, we report a polymeric 1,4-dioxane adduct of gallium(II) chloride, $[Ga_2Cl_4(dioxane)_2]_x$ **I**,[4] wherein both gallium atoms reside in five-coordinate trigonal bipyramidal environments about a Ga–Ga bond. The polymeric structure of **I** is interesting as it is notably different from previously reported Ga(II) halides. Moreover, **I** is shown to react with 1,4-dilithiotetraphenylbutadiene affording $[(PhC{=}CPhPhC{=}CPh)]Ga[(Cl)Li(OEt_2)_2]_2$[5] **II** (Scheme 1).

Compound **I** is significant as it represents a rare example of two five-coordinate gallium atoms about a Ga–Ga bond. Compound **II** involves cleavage of the Ga–Ga bond affording a Ga(II)–tetraphenylbutadiene complex.

From the discovery of cyclogallenes,[6–8] metalloaromatic Ga_3^{2-} ring systems, to reports of a gallyne,[9,10] a Ga_2^{2-} organometallic analog of acetylene, this laboratory has been interested in the dynamics of the Ga–Ga bond. These discoveries notwithstanding, this laboratory remained intrigued by the chemistry of the simple bis(dioxane) adducts of gallium halides, $Ga_2X_4(dioxane)_2$ (X = Cl, Br) and their well documented ability to stabilize both the Ga(II) oxidation state and the Ga–Ga bond. To this end, we sought to isolate triclinic crystals of $Ga_2Cl_4(dioxane)_2$ and explore its reactivity. To our great surprise, we obtained orthorhombic crystals of $[Ga_2Cl_4(dioxane)_2]_x$ **I** (Fig. 1).[11] It is possibly noteworthy that **I** was crystallized in our laboratory at room temperature while crystallization in the original preparation by Small and Worrall[2] took place at 0 °C. While **I** has a number of similarities with $Ga_2Cl_4(dioxane)_2$ and $Ga_2Br_4(dioxane)_2$ (*i.e.* the dioxane adducts are in the chair form), the differences are quite remarkable. Most striking about **I** is the five-coordinate, almost idealized trigonal bipyramidal coordination about both gallium atoms [O–Ga–O 179.10(10)°] while maintaining a Ga–Ga bond. It is particularly noteworthy that **I** is a rare example of a dimeric gallane consisting of two five-coordinate gallium atoms about a Ga–Ga bond. The trigonal bipyramidal coordination notwithstanding, it is also surprising that the Ga–Ga bond distance of 2.3825(9) Å in **I** is shorter than the values reported for both $Ga_2Br_4(dioxane)_2$ [2.395(6) Å] and $Ga_2Cl_4(dioxane)_2$ [2.406(1) Å]. Indeed, the Ga–Ga bond in **I** is considerably shorter than the cyclogallene Ga–Ga bond distances of 2.441(1) and 2.4187(5) Å reported for $Na_2[(Mes_2C_6H_3)Ga]_3$ and $K_2[(Mes_2C_6H_3)Ga]_3$, respectively, involving trigonal planar coordinated gallium atoms. The independent Ga–O bond distance of 2.4087(19) Å in **I** is considerably longer than the mean values of 2.03(2) and 2.027(2) Å reported for $Ga_2Br_4(dioxane)_2$ and $Ga_2Cl_4(dioxane)_2$, respectively. However, the Ga–O bond length of **I** compares well with the Ga–O(axial)



Scheme 1

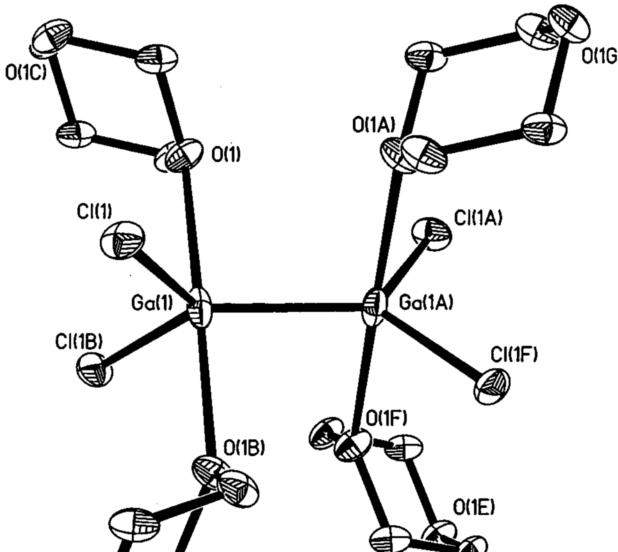


Fig. 1 Molecular structure of $[Ga_2Cl_4(dioxane)_2]_x$ **I**. Bond distances (Å) and angles (°): Ga(1)–Ga(1a) 2.3825(9), Ga(1)–Cl(1) 2.1721(7), Ga(1)–O(1) 2.4087(19), O(1)–C(2) 1.439(3), Cl(1b)–Ga(1)–Cl(1) 112.75(5), Cl(1b)–Ga(1)–Ga(1a) 123.62(2), Cl(1)–Ga(1)–Ga(1a) 123.62(2), Cl(1b)–Ga(1)–O(1) 89.46(5), Cl(1)–Ga(1)–O(1) 90.05(5), Ga(1a)–Ga(1)–O(1) 90.45(5), Cl(1b)–Ga(1)–O(1b) 90.05(5), Cl(1)–Ga(1)–O(1b) 89.46(5), Ga(1a)–Ga(1)–O(1b) 90.45(5), O(1)–Ga(1)–O(1b) 179.10(10). (Symmetry codes: a: $-x + 1/2, -y + 1/2, z$; b: $x, -y + 1/2, -z + 1/2$; c: $-x, -y + 1, -z + 1$; d: $-x, y - 1.2, z - 1/2$; e: $x + 1/2, -y + 1, z - 1/2$; g: $x + 1/2, y - 1/2, -z + 1$).

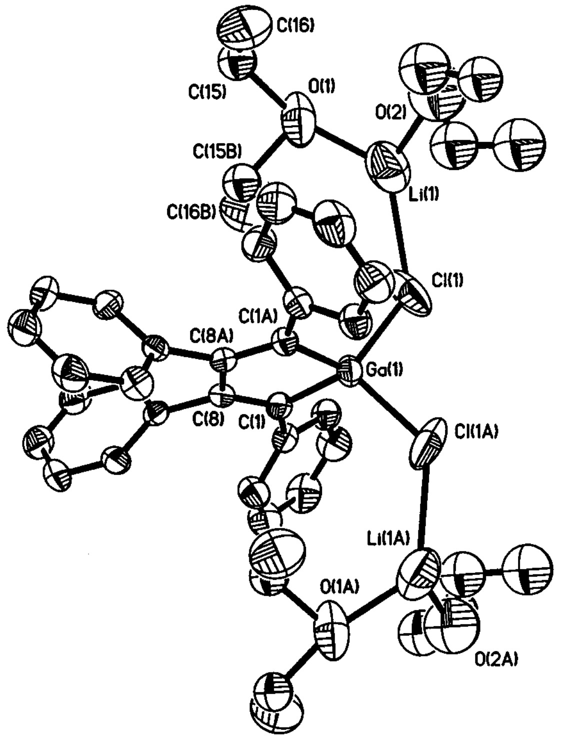


Fig. 2 Molecular structure of [(PhC=CPhPhC=CPh)]Ga[(Cl)Li(OEt$_2$)$_2$]$_2$ **II**. Bond distances (Å) and angles (°): Ga(1)–C(1a) 1.966(4), Ga(1)–C(1) 1.966(4), Ga(1)–Cl(1a) 2.2306(18), Ga(1)–Cl(1) 2.2305(18), Cl(1)–Li(1) 2.625(18), Li(1)–O(1) 2.07(2), Li(1)–O(2) 2.31(2); C(1a)–Ga(1)–C(1) 91.4(3), (1a)–Ga(1)–Cl(1a) 115.56(15), C(1)–Ga(1)–Cl(1a) 116.17(13), C(1a)–Ga(1)–Cl(1) 116.17(13), C(1)–Ga(1)–Cl(1) 115.57(15), Cl(1a)–Ga(1)–Cl(1) 102.68(14), (1)–Cl(1)–Li(1) 125.8(4). (Symmetry codes: a, $y + 1/3$, $x - 1/3$, $-z + 1.6$; b: $y + 1/3$, $x - 1/3$, $-z + 7/6$).

distances of 2.450(5) and 2.278(5) Å reported for the trigonal bipyramidal coordinated gallium atom in the azacrown ether complexation of the dimethylgallium fragment of [(Me$_2$Ga)-(diaza-18-crown-6)[GaMe$_3$]$_2$.[12] Also noteworthy, a view of the unit cell of **I** reveals an extended array stabilized by Cl···H(dioxane) interactions at contacts of 2.836 Å. Effectively, these interactions allow the dioxane moieties to loosely associate Ga$_2$Cl$_4$(dioxane)$_2$ units in infinite chains within the unit cell.

The tetraphenylbutadiene ligand is potentially useful in organogallium chemistry. Indeed, this ligand was utilized in the stabilization of the recently reported spirogallane anion, [(PhC=CPhPhC=CPh)$_2$Ga]$^-$.[13] Reaction of **I** with 1,4-dilithiotetraphenylbutadiene yields the interesting gallium(II) product **II** (Fig. 2).[11] **II** resides about a two fold mirror plane passing through the Ga(1) atom and bisecting the C(8)–C(8a) bond. The coordination about the gallium atom is distorted tetrahedral. The Ga–C bonds in **II** are a little shorter than those reported for the spirogallane. Although the mechanism which affords **II** remains unclear, Ga–Ga bond cleavage was clearly involved. Moreover, it is interesting that instead of the system eliminating LiCl, the lithium atoms, stabilized by diethyl ether, remained in the coordination sphere *via* bridging chlorine atoms [Li(1)–Cl(1)–Ga(1) bond angle is 125.8(4)°]. The Ga–Cl bond distance of 1.966(4) Å in **II** is considerably shorter than the values of 2.177(5) and 2.201(5) Å for (Mes$_2$C$_6$H$_3$)$_2$GaCl[14] and [(Pr$^i{}_3$C$_6$H$_2$)$_2$C$_6$H$_3$GaCl$_2$]$_2$,[15] respectively.

We are grateful to the National Science Foundation (G. H. R.: CHE-95-9520162) and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

Notes and references

1 W. Uhl, M. Layh and T. Hildenbrand, *J. Organomet. Chem.*, 1989, **364**, 289.

2 R. W. H. Small and I. J. Worrall, *Acta Crystallogr., Sect. B*, 1982, **38**, 250.

3 J. C. Beamish, R. W. H. Small and I. J. Worrall, *Inorg. Chem.*, 1979, **18**, 220.

4 Inside the drybox (M. Braun Labmaster 130) Ga$_2$Cl$_4$ (Aldrich Chemical Co.) (17.8 mmol, 5 g) was dissolved in 1,4-dioxane (25 mL). The resulting mixture was filtered and the solution was allowed to stand at room temperature for several days resulting in colorless cubic crystals (4 g, 62% yield). Mp 158–159 °C. Anal. (E + R Microanalytical Laboratories, Parispanny, NY) Calc. (found) Ga$_2$Cl$_4$(dioxane)$_2$: C, 21.00 (21.17); H, 3.50 (2.90%). The less than ideal hydrogen analysis may be due to the loosely associated solvent molecules. ^{1}H NMR (300 MHz, 298 K, THF-d$_8$): δ 3.52 (m, 2H, –OCH$_2$); ^{13}C NMR (300 MHz, 298 K, THF-d$_8$): δ 72.7 (–OCH$_2$).

5 A suspension of 1,4-dilithiotetraphenylbutadiene in diethyl ether (50 mL), obtained from reaction of diphenylacetylene (Aldrich Chemical Co.) (10 mmol, 1.78 g) and lithium (10 mmol, 0.071 g), was added to a diethyl ether solution of **I** (2.5 mmol, 1.14 g) at −78 °C. After stirring for 3 h at −78 °C, the system was allowed to slowly warm to room temperature, stirring continued overnight. The resulting solution was separated from the precipitate by filtration, and concentrated to about a half of its volume, and then kept at −20 °C for several days. Yellow crystals were obtained (1.0 g, 31%). Mp 92 °C. Anal. Calc. (found) Ph$_4$C$_4$GaCl$_2$Li$_2$(Et$_2$O)$_3$: C, 65.50 (65.07); H, 6.82 (6.54%). ^{1}H NMR (300 MHz, 298 K, THF-d$_8$): δ 1.07 (m, 18H, –OCH$_2$CH$_3$), 3.35 (m, 12H, –OCH$_2$CH$_3$), 6.68–7.15 (br, m, 20H, Ph H); ^{13}C NMR (300 MHz, 298 K, THF-d$_8$): δ 15.7 (–OCH$_2$CH$_3$), 66.3 (–OCH$_2$CH$_3$), 123.7, 125.1, 127.4, 127.5, 130.2, 131.5, 141.6, 143.6, 148.8, 149.6.

6 X.-W. Li, W. T. Pennington and G. H. Robinson, *J. Am. Chem. Soc.*, 1995, **117**, 7578.

7 X.-W. Li, Y. Xie, P. R. Schreiner, K. D. Gripper, R. C. Crittendon, C. F. Campana, H. F. Schaefer, III and G. H. Robinson, *Organometallics*, 1996, **15**, 3798.

8 Y. Xie, P. R. Schreiner, H. F. Schaefer, III, X.-W. Li and G. H. Robinson, *J. Am. Chem. Soc.*, 1996, **118**, 10 635.

9 J. Su, X.-W. Li, R. C. Crittendon and G. H. Robinson, *J. Am. Chem. Soc.*, 1997, **119**, 5471.

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

11 X-Ray intensity data were measured at room temperature on a Bruker SMART TM CCD-based X-ray diffractometer system with graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å). *Crystallographic data*: For **I**: orthorhombic, space group *Pnnn* (no. 48) with unit cell parameters a = 8.2481(1), b = 8.277(1), c = 11.385(1) Å, V = 777.4(2) Å^3, Z = 8. Refinement converged at $R1$ = 0.024 and wR_2 = 0.059.

For **II**: trigonal, space group $R\bar{3}c$ (no. 167) with unit cell parameters a = 45.008(4), c = 10.413(1) Å, V = 18.268(3) Å^3, Z = 36. Refinement converged at $R1$ = 0.052 and wR_2 = 0.131.

CCDC 182/1272.

12 B. Lee, W. T. Pennington and G. H. Robinson, *Organometallics*, 1990, **9**, 1709.

13 J. Su, S. D. Goodwin, X.-W. Li and G. H. Robinson, *J. Am. Chem. Soc.*, 1998, **120**, 12 994.

14 X.-W. Li, W. T. Pennington and G. H. Robinson, *Organometallics*, 1995, **14**, 2109.

15 J. Su, X.-W. Li and G. H. Robinson, *Chem. Commun.*, 1998, 2015.

Communication 9/03166I