

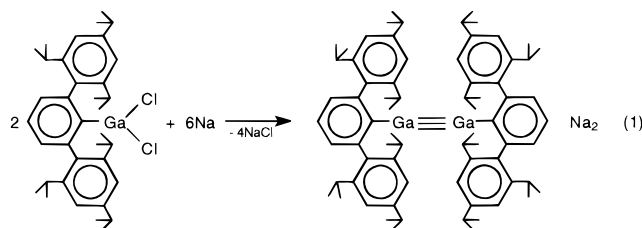
**How Short is a -Ga≡Ga- Triple Bond?
Synthesis and Molecular Structure of
Na₂[Mes*₂C₆H₃-Ga≡Ga-C₆H₃Mes*₂]
(Mes* = 2,4,6-*i*-Pr₃C₆H₂):
The First Gallyne**

Jianrui Su, Xiao-Wang Li, R. Chad Crittendon, and
Gregory H. Robinson*

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

Received January 7, 1997

Owing to its highly unsaturated nature, the C≡C triple bond is one of the most fascinating fragments in chemistry. Possessing characteristic two-coordinate sp-hybridized carbon atoms, acetylene, the simplest yet most important alkyne, is exceptional as it may be utilized to prepare a wide variety of important organic compounds. Even as there are few inorganic or organometallic congeners which offer a convenient comparison with acetylene, herein we report the synthesis¹ and molecular structure² of Na₂[Mes*₂C₆H₃-Ga≡Ga-C₆H₃Mes*₂] (Mes* = 2,4,6-*i*-Pr₃C₆H₂), isolated as deep red (almost black) crystals from the sodium metal reduction of (Mes*₂C₆H₃)GaCl₂ (eq 1). In addition to being the first organometallic compound



containing two-coordinate gallium atoms, the title compound,

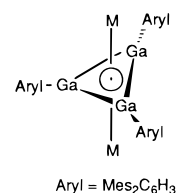
(1) (a) Synthesis of Na₂[Mes*₂C₆H₃-Ga≡Ga-C₆H₃Mes*₂]: Inside the drybox (M Braun Labmaster 130) a reaction vessel was charged with Mes*₂C₆H₃GaCl₂^{1b} (4.9 mmol), diethyl ether (25 mL), and finely cut sodium metal (43 mmol). Upon returning to the bench top, the system was allowed to stir (at room temperature) undisturbed for 2 weeks. Although the mixture initially turned green, it ultimately took on a dark brown color. An intensely dark red color was observed upon allowing the reaction vessel to stand undisturbed for 2 hours. Filtration and cooling to -20 °C for 1 week resulted in deposition of a multitude of dark red (almost black) crystals along the walls of the flask (1.62 g, 27% yield): mp 188 °C. The crystalline compound contains one molecule of diethyl ether per asymmetric unit. Anal. (E + R Microanalytical Laboratories, Corona, NY). Calcd (Found) for C₇₆H₁₀₈Ga₂Na₂O: C, 74.63 (73.68); H, 8.90 (8.90). ¹H NMR (300 MHz, 297 K, C₂D₅OC₂D₅): δ 0.90 (m, 6H, -CH₃ (ether)), 3.25 (q, 4H, -CH₂- (ether)), 0.81 (d, 12H, -CH₃ (*i*-Pr)), 0.95 (d, 12H, -CH₃ (*i*-Pr)), 1.00 (d, 12H, -CH₃ (*i*-Pr)), 1.13 (d, 12H, -CH₃ (*i*-Pr)), 1.18 (d, 12H, -CH₃ (*i*-Pr)), 1.34 (d, 12H, -CH₃ (*i*-Pr)), 2.73 (m, 12H, -CH (*i*-Pr)), 6.54–7.28 (m, 6H, -CH (aromatic)), 6.86 (s, 4H, -CH (aromatic)), 6.92 (s, 4H, -CH (aromatic)). ¹³C NMR (300 MHz, 297 K, C₂D₅OC₂D₅): δ 24.69, 30.57, 31.00, 31.13, 34.85, 35.31 (carbon atoms of *i*-Pr), 120.3, 120.9, 127.0, 128.3, 128.6, 147.1, 147.3, 148.7 (aromatic carbon atoms). IR (Nujol mull): 718 s, 802 s, 873 s, 939 w, 1014 m, 1169 w, 1258 m, 1315 m, 1568 m, 1606 s. (b) Mes*₂C₆H₃-GaCl₂ was prepared by reaction of gallium chloride with (Mes*₂C₆H₃)Li.¹⁴ The solid-state structure of Mes*₂C₆H₃GaCl₂ has been determined by this laboratory to be a chloro-bridged dimer. Su, J.; Li, X.-W.; Robinson, G. H. *Chem. Commun.* In press.

(2) (a) A number of crystals of Na₂[Mes*₂C₆H₃-Ga≡Ga-C₆H₃Mes*₂] were mounted in glass capillaries under an atmosphere of nitrogen inside the drybox. X-ray intensity data on an appropriate sample were collected on a Siemens P4 single-crystal diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å) at 21 °C. Cell parameters and an orientation matrix for data collection, obtained from a least-squares analysis of the setting angles of 25 carefully centered reflections in the range 15.0° < 2 θ < 30.0°, corresponded to the monoclinic space group P2₁/c (No. 14) with unit cell parameters $a = 14.912(7)$ Å, $b = 18.435(7)$ Å, $c = 27.316(10)$ Å, $\beta = 96.40(1)^\circ$, $D_{\text{calcd}} = 1.089$ g cm⁻³, and $V = 7462(5)$ Å³ for $Z = 4$. Full-matrix F^2 refinement, based upon 2379 observed reflections, $I > 2\sigma(I)$, using the SHELXTL 5.0^{2b} system of computer programs, converged at $R1 = 0.086$, $wR2 = 0.226$. (b) Sheldrick, G. M. *SHELXTL 5.0, Crystallographic Computing System*; Siemens Analytical X-ray Instruments: Madison, WI, 1995.

characterized by ¹H and ¹³C NMR, elemental analyses, IR spectroscopy, and single-crystal X-ray diffraction, is most significant as it is the first example of a Ga≡Ga triple bond.

Although much of the activity in the organometallic chemistry of the group 13 elements of the past decade has been driven by a quest for group 13–15 (III–V) single-source molecular precursors, fundamental issues of structure and bonding remain relevant. Recent advances in the stabilization of the organometallic group 13 M–M (M = Al, Ga, In) bond provide an illustrative example.³ Relative to gallium, the literature reveals only a few relevant organometallic gallanes, the first example of which was reported in 1989 with [(Me₃Si)₂HC]₂Ga–Ga[CH–(SiMe₃)₂]₂.⁴ A Ga₄-tetrahedral gallane, [Ga{C(SiMe₃)₃}]₄,⁵ and a radical anionic gallane, [(*i*-Pr₃C₆H₂)₂Ga–Ga(*i*-Pr₃C₆H₂)₂]^{•-},⁶ were reported in 1992 and 1993, respectively (*vide infra*).

Largely concerning 2,6-dimesitylphenyl, Mes₂C₆H₃ (Mes = 2,4,6-Me₃C₆H₂), this laboratory has had an interest in the organometallic chemistry of aryl-substituted sterically demanding ligands for some time.^{7–10} Particularly significant is the fact that alkali metal reduction of (Mes₂C₆H₃)GaCl₂ has recently been shown by this laboratory to afford sodium¹¹ and potassium-based¹² M₂[(Mes₂C₆H₃)Ga]₃ (M = Na, K) cyclogallenes—novel Ga₃²⁻ dianionic, formal 2 π -electron, aromatic systems (below)—thereby constituting experimental realization of metalloaromaticity.¹³



In an effort to approach the structural and electronic extremes of gallanes as a function of ligand steric loading, we endeavored to examine the organometallic chemistry of the exceedingly bulky iso propyl derivative of Mes₂C₆H₃, Mes*₂C₆H₃ (Mes* = 2,4,6-*i*-Pr₃C₆H₂).¹⁴

The molecular structure of Na₂[Mes*₂C₆H₃-Ga≡Ga-C₆H₃Mes*₂], given in Figure 1, consists of two Mes*₂C₆H₃ ligands bridged by a pair of gallium atoms with the core being completed by a pair of sodium atoms residing on either side of the Ga–Ga bond constituting a nearly planar Ga₂Na₂ four-membered ring (Ga \cdots Na_(mean), 3.08 Å; a Ga \cdots Na contact of 3.220(2) Å was observed for the sodium-based cyclogallene¹¹). The Ga–Ga bond distance of 2.319(3) Å in Na₂[Mes*₂C₆H₃-Ga≡Ga-C₆H₃Mes*₂] is particularly noteworthy. In order to

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

(4) Uhl, W.; Layh, M.; Hildenbrand, T. *J. Organomet. Chem.* **1989**, 364, 289.

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

(6) 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.

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

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

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

(10) Li, X.-W.; Su, J.; Robinson, G. H. *Organometallics* **1997**, 16, 2443.

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

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

(13) Xie, Y.; Schreiner, P. R.; Schaefer, H. F., III; Li, X.-W.; Robinson, G. H. *J. Am. Chem. Soc.* **1996**, 118, 10635.

(14) Schiemenz, B.; Power, P. P. *Organometallics* **1996**, 15, 958.

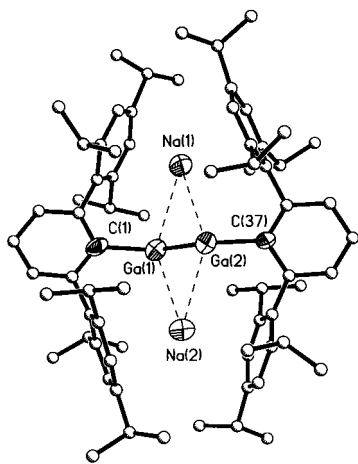


Figure 1. Molecular structure of $\text{Na}_2[\text{Mes}^*_2\text{C}_6\text{H}_3\text{-Ga}\equiv\text{Ga-C}_6\text{H}_3\text{Mes}^*_2]$ (thermal ellipsoids are shown at 35% probability levels). Selected bond distances (Å) and angles (deg): Ga(1)–Ga(2), 2.319(3); Ga(1)–C(1), 2.06(2); Ga(2)–C(37), 2.028(14); Ga(1)–Na(1), 3.085(7); Ga(1)–Na(2), 3.056(6); Ga(2)–Na(1), 3.078(6); Ga(2)–Na(2), 3.106(7); C(1)–Ga(1)–Ga(2), 128.5(4); C(37)–Ga(2)–Ga(1), 133.5(4); C(1)–Ga(1)–Na(1), 102.1(5); C(1)–Ga(1)–Na(2), 107.0(6); C(37)–Ga(2)–Na(1), 101.7(5); C(37)–Ga(2)–Na(2), 106.5(6); Ga(1)–Ga(2)–Na(1), 68.1(2); Ga(1)–Ga(2)–Na(2), 66.76(13).

place this distance in perspective, note the significantly longer Ga–Ga single-bond distances observed in $[\text{Ga}_4\{\text{C}(\text{SiMe}_3)_3\}_4]$,⁵ 2.688 Å, and $[(\text{Me}_3\text{Si})_2\text{HC}]_2\text{Ga-Ga}[\text{CH}(\text{SiMe}_3)_2]_2$,⁴ 2.541(1) Å. These values are compared with Ga–Ga distances of 2.441(1) and 2.4255 Å for the sodium-¹¹ and potassium-based¹² cyclogallanes, respectively. The radical anionic gallane $[(i\text{-Pr}_3\text{C}_6\text{H}_2)_2\text{Ga-Ga}(i\text{-Pr}_3\text{C}_6\text{H}_2)_2]^-$ has a Ga–Ga distance of 2.343(2) Å as compared to 2.515(3) Å for the neutral digallane, $[(i\text{-Pr}_3\text{C}_6\text{H}_2)_2\text{Ga-Ga}(i\text{-Pr}_3\text{C}_6\text{H}_2)_2]$.⁶ The shortening of the Ga–Ga bond, coupled with a decrease in the torsion angle between the two GaC_2 planes, was taken as evidence of π -bonding in the radical anion as a consequence of a one-electron alkali metal reduction of the neutral digallane. Thus, the Ga–Ga bond distance of 2.319(3) Å in $\text{Na}_2[\text{Mes}^*_2\text{C}_6\text{H}_3\text{-Ga}\equiv\text{Ga-C}_6\text{H}_3\text{Mes}^*_2]$ is the shortest on record.¹⁵

(15) Although not particularly germane to the title compound or the associated discussion, the literature reveals a few other Ga–Ga gallanes: (a) $\text{Ga}_2[\text{I}_3\text{Ga-GaI}_3]$, 2.388(5) Å: Gerlach, G.; Honle, W.; Simon, A. *Z. Anorg. Allg. Chem.* **1982**, *486*, 7. (b) $(\text{tmp})_2\text{Ga-Ga}(\text{tmp})_2$ (tmp = 2,2,6,6-tetramethylpiperidino), 2.541(1) Å: Linti, G.; Frey, R.; Schmidt, M. *Z. Naturforsch.* **1994**, *49B*, 958. (c) $[(t\text{-Bu})\text{NCHCHN}(t\text{-Bu})]\text{Ga-Ga}[(t\text{-Bu})\text{NCHCHN}(t\text{-Bu})]$, 2.333(1) Å: Brown, D. S.; Decken, A.; Cowley, A. H. *J. Am. Chem. Soc.* **1995**, *117*, 5421. (d) $[(\text{Me}_3\text{Si})_3\text{Si}]_2\text{Ga-Ga}[(\text{Si}(\text{SiMe}_3)_3)_2]$, 2.599(4) Å: Linti, G.; Köster, W. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 550.

The degree of nonlinearity about the Ga–Ga–C fragment in $\text{Na}_2[\text{Mes}^*_2\text{C}_6\text{H}_3\text{-Ga}\equiv\text{Ga-C}_6\text{H}_3\text{Mes}^*_2]$, at bond angles of 128.5(4)° and 133.5(4)°, is intriguing. The possibility of a hydrogen atom bonding to each gallium atom, thereby contributing to the observed nonlinearity, appears unlikely as evidenced by the ¹H NMR spectrum of the title compound which shows no resonances in the expected range for gallium hydrides.¹⁶ Although it is compelling to consider a number of contributing factors giving rise to this nonlinearity (*i.e.*, steric interaction of the ligands), it is important to note that several theoretical studies have addressed heavier main group model compounds such as Si_2H_2 , Ge_2H_2 , Al_2H_2 , and Ga_2H_2 , concluding that, unlike acetylene, the linear structure is not a minimum on the potential energy hypersurface, but rather a nonlinear trans orientation is often favored.¹⁷ The H–Ge≡Ge–H molecule is informative as it is isoelectronic with the title compound. Theoretical studies H–Ge≡Ge–H have predicted Ge–Ge–H bond angles of 125.2°, 125.5°, and 124.8° at the SCF/B1, SCF/B2, and CISD/B1 levels of theory, respectively.^{17a} Indeed, preliminary *ab initio* examination of the $\text{Na}_2[\text{CH}_3\text{-Ga}\equiv\text{Ga-CH}_3]$ model predicts a Ga–Ga–C bond angle of 126.9°, very comparable to the values observed in the title compound.¹⁸

The short Ga–Ga bond, coupled with the unprecedented two-coordinate status of the gallium atoms and the overall sterically crowded geometry, is consistent with $\text{Na}_2[\text{Mes}^*_2\text{C}_6\text{H}_3\text{-Ga}\equiv\text{Ga-C}_6\text{H}_3\text{Mes}^*_2]$ being the first example of a Ga≡Ga triple bond and, by consequence, the first experimental confirmation of a group 13 metal engaging in triple bond formation: *the first Ga≡Ga gallyne*.

Acknowledgment. We are grateful to the National Science Foundation (G.H.R., CHE-9520162) and to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for support of this work. The authors also thank one of the referees for useful discussions during the review of this manuscript. In addition, we are grateful to Professor H. F. Schaefer, III, and Dr. Yaoming Xie, of the Center for Computational Quantum Chemistry of The University of Georgia, for their assistance.

Supporting Information Available: Summary of data collection and refinement and tables of crystal data, bond distances and angles, final fractional coordinates, thermal parameters, and observed and calculated structure factors (15 pages). See any current masthead page for ordering and Internet access instructions.

JA9700562

(16) (a) The gallium hydride ¹H NMR resonances for $[o\text{-}(\text{Me}_2\text{-NCH}_2)\text{C}_6\text{H}_4]\text{GaH}_2$ and $[o\text{-}(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]_2\text{GaH}$ were observed at δ 5.49 and 5.12, respectively.^{16b} (b) Isom, H. S.; Cowley, A. H.; Decken, A.; Sissingh, F.; Corbelin S.; Lagow, R. *J. Organometallics* **1995**, *14*, 2400.

(17) (a) Grev, R. S.; Deleuw, B. J.; Schaefer, H. F., III *Chem. Phys. Lett.* **1990**, *165*, 257. (b) Laane, J., Ed. *Structures and Conformations of Non-Rigid Molecules*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1993; pp 325–342. (c) Pala'gyi, Z.; Schaefer, H. F., III; Kapuy, E. *Chem. Phys. Lett.* **1993**, *203*, 195. (d) Pala'gyi, Z.; Schaefer, H. F., III; Kapuy, E. *J. Am. Chem. Soc.* **1993**, *115*, 6901.

(18) Xie, Y.; Schaefer, H. F., III, Li, X.-W.; Robinson, G. H. Unpublished results.