

Preliminary communication

Hybrid inorganic–organometallic compounds
with gallium–gallium bondsAlan H. Cowley^{*}, Andreas Decken¹, Claudia A. Olazábal

Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin, TX 78712, USA

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Abstract

The first examples of digallium compounds that feature both organo and halo substituents, $[\text{Li}(\text{THF})_4][\text{Ar}'(\text{Cl})\text{GaGaCl}_3]$ (**1**) and $\text{Ar}'(\text{Cl})\text{GaGa}(\text{Cl})\text{Ar}'$ (**2**), have been prepared by reaction of $\text{Ga}_2\text{Cl}_4 \cdot 2$ dioxane with LiAr' ($\text{Ar}' = 2,4,6\text{-}^i\text{Bu}_3\text{C}_6\text{H}_2$). The Ga_2Cl_2 skeleton of **2** is planar with a dihedral angle of 180° .

Keywords: Gallium; Digallium compounds; X-ray crystal structures

1. Introduction

Interest in the lower oxidation states of the heavier Group 13 elements is emerging, and promises a rich harvest of unusual derivatives with metal–metal bonds (for a review see Ref. [1]). In the context of gallium chemistry, the simplest such species comprise bimetallic compounds of the type R_2GaGaR_2 and $[\text{R}_3\text{GaGaR}_3]^{2-}$. The currently available examples of these classes of compound are either fully organo-substituted neutral molecules ($\text{R} = (\text{Me}_3\text{Si})_2\text{CH}$ [2], $2,4,6\text{-}^i\text{Pr}_3\text{C}_6\text{H}_2$ [3], $2,4,6\text{-}(\text{CF}_3)_3\text{C}_6\text{H}_2$ [4]; $\text{R}_2 = \text{carborane}$ [5] or completely halo-substituted (see Ref. [2] for bibliography; for an interesting cage-amido derivative, see Ref. [6]). We report the first examples of digallium compounds that feature both organo and halo substituents.

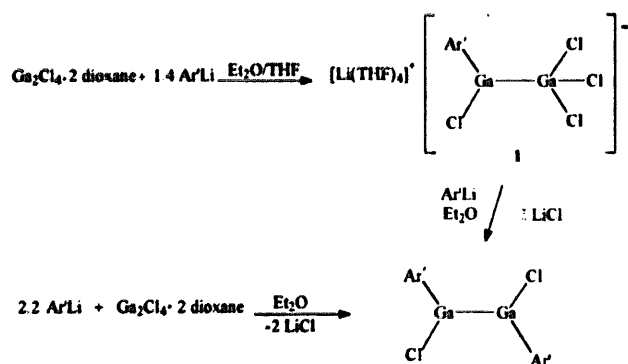
The reaction of 1 equivalent of $\text{Ga}_2\text{Cl}_4 \cdot 2$ dioxane with 1.4 equivalents of LiAr' ($\text{Ar}' = 2,4,6\text{-}^i\text{Bu}_3\text{C}_6\text{H}_2$) in Et_2O solution at -78°C afforded, after work-up, a 54% yield of the salt **1** (Scheme 1). If the number of equivalents of LiAr' was increased to 2.2, and the order of addition was reversed, a different product, **2**, was obtained in 51% yield. Moreover, **1** could be converted to **2** by treatment with 1.0 equivalent of LiAr' in Et_2O solution at -78°C , albeit in low yield (12%). Com-

pounds **1** and **2** are both air-sensitive, colorless crystalline solids. The preliminary identification of **1** was based on a satisfactory elemental analysis and ^1H and ^{13}C (^1H) NMR evidence for the presence of an Ar' moiety. Compound **2** was characterized initially in a similar fashion; however, in this case it was also possible to secure a satisfactory high-resolution mass spectral value for the molecular ion (Found 698.2424; Calc. 698.2427).

For a more definitive characterization of **1** and **2** it was necessary to appeal to X-ray crystallography. [Crystal data for **1**: $\text{C}_{34}\text{H}_{61}\text{Cl}_4\text{Ga}_2\text{LiO}_4$, $M = 822.0$, monoclinic, $P2_1/c$, $a = 19.531(3)$, $b = 9.902(2)$, $c = 22.770(3)$ Å, $\beta = 101.61(1)^\circ$, $V = 4313(2)$ Å³, $Z = 4$, $\rho_{\text{calc}} = 1.266$ g cm⁻³, Mo K α 0.71073 Å, $\mu = 15.28$ cm⁻¹. 5876 unique data were collected at 298 K on an Enraf–Nonius CAD4 diffractometer (θ – 2θ scan technique, $4.0 < 2\theta < 45^\circ$). Of these, 1996 had $F > 4\sigma(F)$ and were used for structure solution (direct methods) and refinement, $R = 8.40\%$. Crystal data for **2**: $\text{C}_{34}\text{H}_{58}\text{Cl}_2\text{Ga}_2$, $M = 701.2$, orthorhombic, $Cmca$, $a = 12.839(3)$, $b = 13.553(3)$, $c = 25.890(5)$ Å, $V = 4506(2)$ Å³, $Z = 4$, $\rho_{\text{calc}} = 1.033$ g cm⁻³, Mo K α 0.71073 Å, $\mu = 13.32$ cm⁻¹. 1538 unique data were collected at 298 K on an Enraf–Nonius CAD4 diffractometer (θ – 2θ scan technique, $4.0 < 2\theta < 45^\circ$). Of these, 843 had $F > 4\sigma(F)$ and were used for structure solution (direct methods) and refinement, $R = 10.26\%$.] Compound **1** crystallizes in the $P2_1/c$ space group

^{*} Corresponding author.

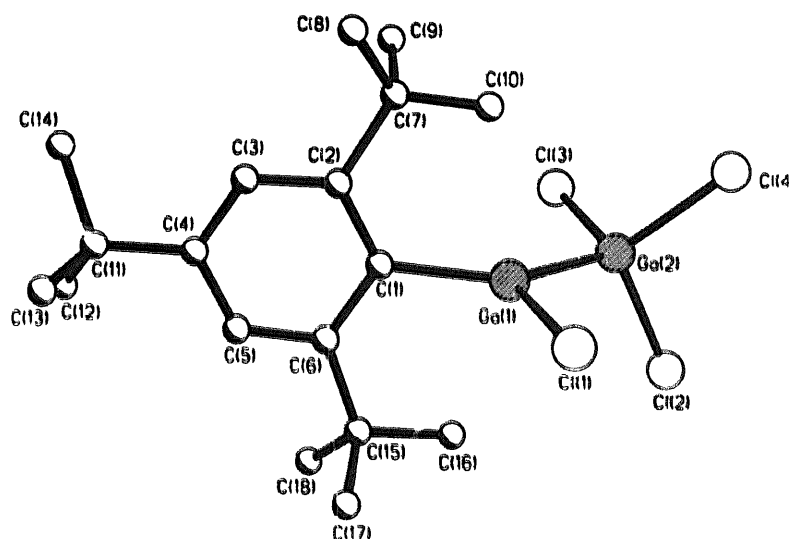
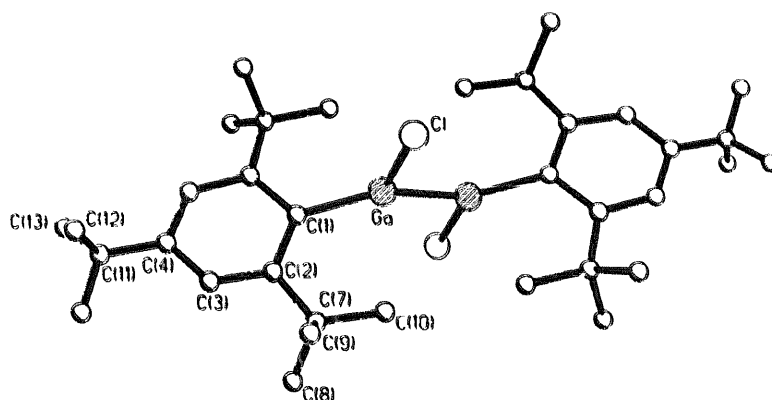
¹ Present address: Department of Chemistry, University of New Brunswick, Fredericton, NB E3B 5A6, Canada.



Scheme 1.

with four molecules per unit cell. There are no unusually short interionic contacts and the $[\text{Ar}'(\text{Cl})\text{GaGaCl}_3]^-$ and $[\text{Li}(\text{THF})_4]^+$ ions reside on general positions; neither ion has crystallographically imposed symmetry. The anion of **1** features both three- and four-coordinate gallium atoms which are united by a gallium–gallium bond (Fig. 1). The geometry at the Ga(1) center is

trigonal planar (sum of angles $359.0(5)^\circ$); however, owing to the steric demands of the bulky aryl group, the C(1)–Ga(1)–Ga(2) angle ($136.9(5)^\circ$) is appreciably more obtuse than the ideal value. This is not true of the C(1)–Ga(1)–Cl(1) angle, because the aryl and C(1)–Ga(1)–Ga(2) planes are almost orthogonal. The geometry of Ga(2) is tetrahedral and the departures from the ideal values can be understood on the basis of the steric influence of the Ar' moiety. Specifically, the Ga(1)–Ga(2)–Cl(2) ($112.4(2)^\circ$), Ga(1)–Ga(2)–Cl(3) ($111.4(2)^\circ$), and Ga(1)–Ga(2)–Cl(4) ($115.0(2)^\circ$) angles are larger than the remaining three bond angles at Ga(2). The gallium–gallium bond length in **1** is $2.422(3) \text{ \AA}$. In terms of this metrical parameter, the closest analogues of **1** are the salts $[\text{NMe}_4]_2[\text{Cl}_3\text{Ga-GaCl}_3]$ [7] and $[\text{Ph}_3\text{PH}]_2[\text{Cl}_3\text{Ga-GaCl}_3]$ [8] for which the gallium–gallium bond lengths are $2.390(2)$ and $2.404(2) \text{ \AA}$ respectively. It might be expected that the gallium–gallium bond length in **1** would be shorter than that in the $[\text{Ga}_2\text{Cl}_6]^{2-}$ anion, since the former features one sp^2 and one sp^3 rather than two sp^3 hybridized

Fig. 1. View and numbering scheme for **1**. Hydrogen atoms are omitted for clarity.Fig. 2. View and numbering scheme for **2**. Hydrogen atoms are omitted for clarity.

gallium atoms. The longer bond length in the mono-anion **1** is presumably due to steric effects.

Compound **2** crystallizes in the orthorhombic space group *Cmca* with four molecules per unit cell. There are no unusually short intermolecular contacts and molecules of **2** reside on a mirror plane that includes Cl, Ga, and C(1), and the other half of the molecule is generated by a center of symmetry located at the midpoint of the Ga–Ga bond (Fig. 2). As a consequence, the C(1)ClGa–Ga(A)Cl(A)C(1A) skeleton is required to be planar and the aryl rings are perpendicular to this plane. For comparison, the dihedral angles between the GaC₂ planes in organo-substituted digallanes are around 0°, 43.8°, and around 90° for Ga₂{CH(SiMe₃)₂}₄ (**3**) [2], Ga₂(2,4,6-ⁱPr₃C₆H₂)₄ (**4**) [3], and Ga₂(2,4,6-(CF₃)₃C₆H₂)₄ (**5**) [4] respectively.

The gallium–gallium bond length in **2** (2.438(6) Å) is shorter than those in **3** (2.541(1) Å) [2], **4** (2.513(3) Å) [3], and **5** (2.479(1) Å) [4]. Presumably, the reason for this shortening stems from the fact that **2** features two rather than four bulky substituents. However, although the geometry of gallium is trigonal planar, the C(1)–Ga–Ga(A) angle (142.7(8)°) is considerably larger than the other two, thus indicating the operation of steric effects.

2. Experimental section

1: A solution of (2,4,6-ⁱBu₃C₆H₂)Li (1.31 g, 5.18 mmol) in 30 ml of Et₂O was added to a solution of Ga₂Cl₄ · 2 dioxane (1.68 g, 3.7 mmol) in 30 ml of Et₂O at –78 °C. The reaction mixture was allowed to warm to ambient temperature and was stirred for an additional 19 h. The colorless mixture was filtered and the solvent was removed under reduced pressure. The white residue was washed with 15 ml of hexane, following which it was dissolved in 70 ml of a 1:1 mixture of Et₂O and THF. Colorless crystals of **1** (m.p. 160–162 °C) formed in 54% yield upon cooling the saturated solution to –20 °C. ¹H NMR (THF-*d*₈): δ 1.31 (s, 9H, (s, *p*-(CH₃)₃C), 1.58 (s, 18H, (s, *o*-(CH₃)₃C), 7.46 (s, 2H, H-aryl); ¹³C{¹H}NMR (C₆D₆): δ 31.38 (s, *p*-(CH₃)₃C), 34.93 (s, *p*-(CH₃)₃C), 33.71 (s, *o*-(CH₃)₃C), 38.44 (s, *o*-(CH₃)₃C), 122.14 (s, *m*-C aryl), 128.66 (s, *ipso*-C), 151.39 (s, *p*-C aryl), 157.94 (s, *o*-C aryl). Anal. Found: C, 49.47; H, 7.30. C₃₄H₆₁Cl₄Ga₂LiO₄ Calc.: C, 49.68; H, 7.48%.

2: A solution of Ga₂Cl₄ · dioxane (1.25 g, 2.7 mmol) in 30 ml of Et₂O was added to a stirred solution of (2,4,6-ⁱBu₃C₆H₂)Li (1.5 g, 6.0 mmol) in 30 ml of Et₂O at –78 °C. The reaction mixture was allowed to warm slowly to ambient temperature and was stirred for a

further 4.5 h. Following filtration, the resulting white powder was washed with 10 ml of hexane, then dissolved in 30 ml of toluene. Colorless crystals of **2** (m.p. 109–110 °C) formed in 51% yield upon cooling the saturated solution to –20 °C. ¹H NMR (C₆D₆): δ 1.26 (s, 18H, (s, *p*-(CH₃)₃C), 1.52 (s, 36H, (s, *o*-(CH₃)₃C), 7.48 (s, 4H, H-aryl); ¹³C{¹H}NMR (C₆D₆): δ 31.36 (s, *p*-(CH₃)₃C), 34.90 (s, *p*-(CH₃)₃C), 33.54 (s, *o*-(CH₃)₃C), 38.48 (s, *o*-(CH₃)₃C), 122.30 (s, *m*-C aryl), 141.74 (s, *ipso*-C), 151.43 (s, *p*-C aryl), 156.49 (s, *o*-C aryl). Anal. Found: C, 60.91; H, 8.10. C₃₆H₅₈Ga₂Cl₂ Calc.: C, 61.66; H, 8.34%.

As an alternative (but lower yield) synthesis of **2**, a solution of (2,4,6-ⁱBu₃C₆H₂)Li (0.40 g, 1.6 mmol) in 15 ml of Et₂O was added to a solution of **1** (1.31 g, 1.6 mmol) in 15 ml of Et₂O at –78 °C. The reaction mixture was allowed to warm slowly to ambient temperature and was stirred for a further 3 h. Work-up of the reaction mixture as described above afforded a 12% yield of **2**.

3. Note added in proof

Since the submittal of this manuscript, a communication has appeared in which the (dimeric) tris(trimethylsilyl)silyl analogue of **2** is described: G. Linti and W. Kostler, *Angew. Chem., Int. Ed. Engl.*, 35 (1996) 550.

Acknowledgements

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References

- [1] W. Uhl, *Angew. Chem., Int. Ed. Engl.*, 32 (1993) 1386.
- [2] W. Uhl, M. Layh and T. Hildenbrand, *J. Organomet. Chem.*, 364 (1989) 289.
- [3] X. He, R.A. Bartlett, M.M. Olmstead, K.R. Senge, B.E. Sturgeon and P.P. Power, *Angew. Chem., Int. Ed. Engl.*, 32 (1993) 717.
- [4] R.D. Schluter, A.H. Cowley, D.A. Atwood, R.A. Jones, M.R. Bond and C.J. Carrano, *J. Am. Chem. Soc.*, 115 (1993) 2070.
- [5] A.K. Saxena, H. Zhang, J.A. Maguire, N.S. Hosmane and A.H. Cowley, *Angew. Chem., Int. Ed. Engl.*, 34 (1995) 332.
- [6] M. Veith, F. Goffing, S. Becker and V. Huch, *J. Organomet. Chem.*, 406 (1991) 105; M. Veith and J. Pöhlmann, *Z. Naturforsch. B*, 43 (1988) 505.
- [7] K.L. Brown and D. Hall, *J. Chem. Soc., Dalton Trans.*, (1973) 1843.
- [8] M. Khan, C. Oldham, M.J. Taylor and D.C. Tuck, *Inorg. Nucl. Chem. Lett.*, 16 (1980) 469.