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Preliminary communication

SYNTHESIS AND CHARACTERIZATION OF A DIMERIC TRIS(ARSINO)GALLANE CONTAINING A NONPLANAR $(Ga–As)_2$ RING: CRYSTAL STRUCTURE OF $\{[(Me_3SiCH_2)_2As]_3Ga\}_2$ *

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Summary

The dimer $\{[(Me_3SiCH_2)_2As]_3Ga\}_2$, only the second tris(arsino)gallane to be completely characterized, has been prepared by the reaction of $(Me_3SiCH_2)_2AsLi$ with $GaCl_3$; X-ray crystallographic analysis shows it to be the first example of a compound containing a distinctly nonplanar four-membered ring of alternating four-coordinate Ga and As atoms.

Recently, we applied two new synthetic methods to the preparation of compounds containing a gallium–arsenic bond, viz., dehalosilylation between a silylarsine and a halogallane [1], and coupling using a lithium arsenide and a chlorogallane [2]. Among the compounds prepared by both methods is the first example of a tris(arsino)gallane, monomeric $(Mes_2As)_3Ga$, which X-ray analysis [2] has shown to contain three-coordinate gallium and arsenic. Subsequently, $(Bu^t_2As)_3Ga$ was reported by others, but data for a crystal structure were not obtainable [3]. We now report the structure of a second tris(arsino)gallane, dimeric $[(Me_3SiCH_2)_2As]_3Ga$ (**1**), prepared by the lithium arsenide method. Interestingly, as noted previously, the reaction of $(Me_3SiCH_2)_2AsSiMe_3$ with $GaCl_3$ did not yield **1** [1]. Compound **1** has a solid state structure containing a distinctly nonplanar four-membered ring of alternating four-coordinate Ga and As atoms. This form contrasts with the planar, centrosymmetric $(Ga–As)_2$ units in $[(Me_3SiCH_2)_2AsGaPh_2]_2$ (**2**) [4], the first dimeric mono(arsino)gallane for which the structure was reported, and in $(Bu^t_2AsGaMe_2)_2$ (**3**) [3], and the nearly planar unit in $(Bu^t_2AsGaBu^n_2)_2$ (**4**) [3], but is similar to, although less puckered than, the novel nonplanar $(Ga–S)_2$ form found

* Dedicated to Professor G.E. Coates on the occasion of his 70th birthday.

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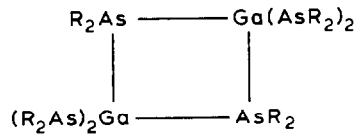
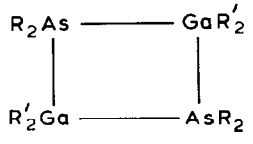
in $(Pr^iSGaI_2)_2$ which contains two four-coordinate Ga atoms and two three-coordinate S atoms [5].





1 : R = Me_3SiCH_2

2 : R = Me_3SiCH_2, R′ = Ph [4]
3 : R = Bu^t, R′ = Me [3]
4 : R = Bu^t, R′ = Bu^n [3]

A suspension of $(Me_3SiCH_2)_2AsLi$ [6] (2.03 g, 7.9 mmol) in hexane was added [7] to a hexane solution of $GaCl_3$ (0.46 g, 2.6 mmol) at −78°C. After 18 h at room

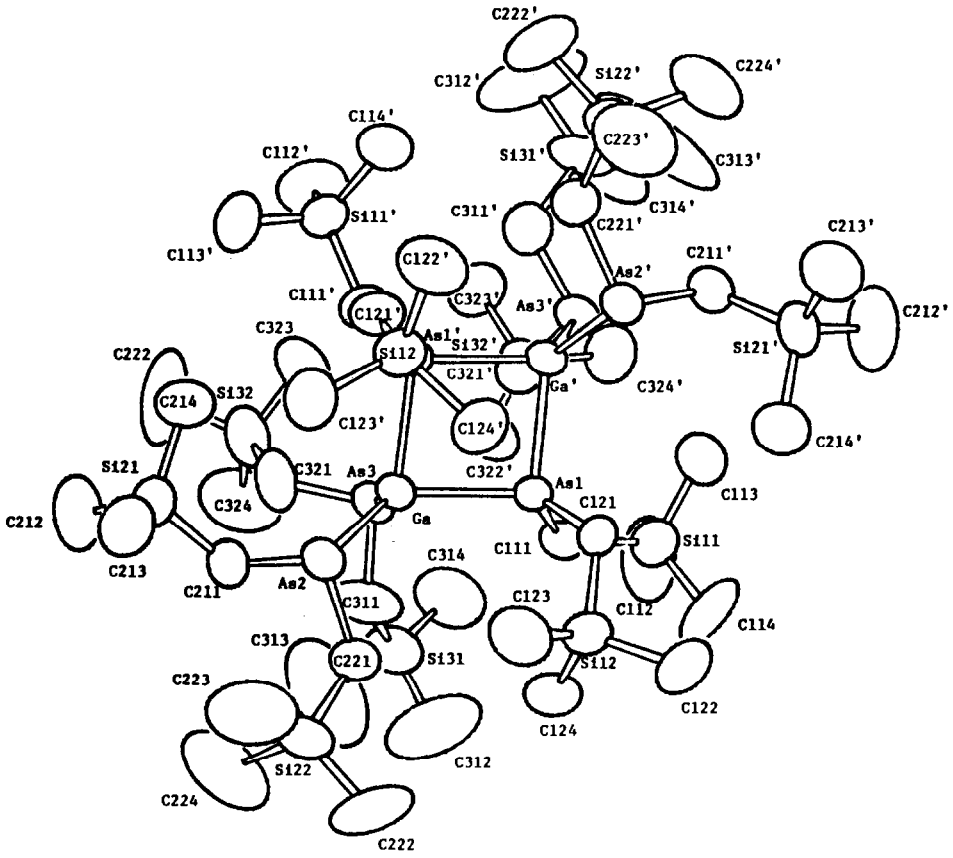


Fig. 1. Molecular structure of $\{[(Me_3SiCH_2)_2As]_3Ga\}_2$ (**1**). Selected distances (Å) and angles (°) are: Ga–As(1) 2.581(1), Ga–As(2) 2.478(2), Ga–As(3) 2.476(2), Ga–As(1′) 2.540(1), Ga′–As(1′) 2.540(1), Ga′–As(2′) 2.470(1), Ga′–As(3′) 2.474(2), Ga′–As(1) 2.559(1), As(1)–Ga–As(1′) 83.58(4), As(1)–Ga′–As(1′) 84.04, Ga–As(1)–Ga′ 94.57(4), Ga–As(1′)–Ga′ 96.02(4), As(2)–Ga–As(3) 122.37(5), As(2′)–Ga′–As(3′) 113.68(5), C(111)–As(1)–C(121) 103.0(4), C(111′)–As(1′)–C(121′) 104.7(4).

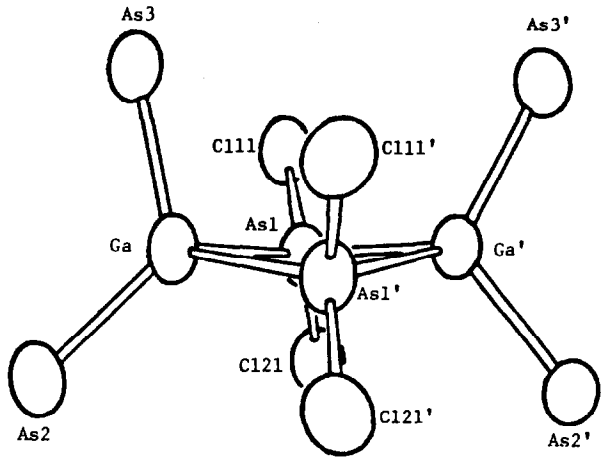


Fig. 2. The nonplanar $(Ga–As)_2$ ring of compound **1**.

temperature, the brown mixture formed was filtered, and the filtrate was evaporated and the residue dissolved in hexane. Crystallization (−78°C) and cold filtration, followed by solvent removal, recrystallization, hexane washings, and finally drying in vacuo afforded $\{[(Me_3SiCH_2)_2As]_3Ga\}_2$ (**1**) as a pale yellow solid (0.46 g, 22% yield) m.p. 71–149°C (dec.) [8]. Crystals suitable for an X-ray structure determination were grown from a C_6F_6 solution [9].

Crystals of **1** comprise discrete centrosymmetrically-related dimers having the structure illustrated in Fig. 1. Several features of this dimer attest to its highly strained nature. Thus, the Ga–As(1)–Ga′–As(1′) ring, with a dihedral angle of 13.6° (vs. 36.7(2)° in the $(Ga–S)_2$ ring of $(Pr^iSGaI_2)_2$) between the As(1)–Ga–As(1′) and As(1)–Ga′–As(1′) planes (mean endocyclic dihedral angle about the ring bonds 10.2°) is, as shown in Fig. 2, distinctly non-planar. Two of the ring bonds, Ga–As(1′) and Ga′–As(1′) at 2.540(1) Å, are equal, and significantly shorter than the other pair, 2.559(1) and 2.581(1) Å, of which the latter is the longest distance yet reported for such a bond and contrasts with the corresponding longest values of 2.530(1), 2.558(1), 2.557(3), and 2.553(1) Å, respectively, for four-coordinate Ga in dimers **2**, **3**, and **4**, and the unusual $[(PhAsH)(R_2Ga)(PhAs)_6(RGa)_4]$ (R = Me_3SiCH_2) cluster [10]. All the ring bonds of **1** are longer than the mean of the essentially equal exocyclic Ga–As bonded distances to three-coordinate As atoms, which, at 2.475 Å, is slightly shorter than the mean Ga–As distance for trigonal planar Ga in monomeric $(Mes_2As)_3Ga$. The mean ring bond angles in **1** (84.81° at Ga, 95.30° at As) are similar to those in dimers **2**, **3**, and **4** (range: 84.31–85.08° at Ga; 94.92–95.69° at As), but the exocyclic As–Ga–As angles involving the three-coordinate As atoms (122.37(5), 113.68(5)°) differ significantly in response to the different intramolecular interactions involving substituents at each of the Ga centers. Corresponding exocyclic C–As–C angles show much less variation (103.0(4), 104.7(4)°), indicating the greater resistance of the As centers to bond angle deformation.

Cryoscopic molecular weight determinations indicate that **1** remains intact as a dimer in solution at low temperatures. It appears, however, that the dimer is

fluxional in solution (the fluxional properties of a dimeric bis(arsino)gallane have been reported) [1], as indicated by broadening and eventual coalescence of ^{13}C NMR signals as the temperature is increased. Also, compound **1** is thermally unstable in solution at ambient temperature and above, and slowly decomposes to the diarsine $[(Me_3SiCH_2)_2As]_2$ [1] and unknown products.

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6 $(Me_3SiCH_2)_2AsLi$ was produced by the reaction of $(Me_3SiCH_2)_2AsH$ [4] and Bu^nLi in hexane for 2 days at 60 °C, and isolated as an off-white powder.

7 All manipulations were performed under dry nitrogen.

8 Found: C, 35.34; H, 8.29; mol. wt., 1582±65 (cryoscopic, 0.268 g in 12.22 g cyclohexane). $C_{48}H_{132}As_6Ga_2Si_{12}$ calcd.: C, 35.25; H, 8.13%; mol. wt., 1636. ^1H NMR (300 MHz) (C_6D_6, 21 °C): δ 0.32 (s, *exo*-Me_3Si), 0.37 (s, *endo*-Me_3Si), 1.32 and 1.79 (AB Pattern, ^2J(HH) 13.8 Hz, *exo*-CH_2), 1.71 (*endo*-CH_2); $^{13}C\{^1H\}$ NMR (75.4 MHz) (C_6D_6, 21 °C): δ 0.98 (s, *exo*-Me_3Si), 2.02 (s, *endo*-Me_3Si), 6.69 (s, *exo*-CH_2), 10.59 (s, *endo*-CH_2).

9 Crystal data: $C_{48}H_{132}As_6Ga_2Si_{12}$ (**1**), M = 1635.59, triclinic, space group $P\bar{1}$, a 15.050(3), b 25.417(8), c 12.621(4) Å, α 93.73(3), β 110.68(2), γ 77.00(2)°, U 4400.5 Å^3, Z = 2, D_c 1.234 g cm^{-3}, μ(Cu-K_α radiation) 50.7 cm^{-1}. The crystal structure was solved by direct methods. Full-matrix least-squares refinement of atomic positional and thermal parameters (anisotropic As, C, Ga, Si; fixed methylene H contributions) converged to R = 0.064 (R_w = 0.097; $w = 1/\sigma^2(|F_0|)$) over 8504 absorption-corrected reflections ($I > 3.0\sigma(I)$) recorded on an Enraf–Nonius CAD-4 diffractometer (Cu-K_α radiation, λ 1.5418 Å; incident-beam graphite monochromator; $\omega - 2\theta$ scans, θ_{max} 57°). A table of atomic coordinates and a full list of bond lengths and angles has been deposited with the Cambridge Crystallographic Data Centre.

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