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SYNTHESIS AND CHARACTERIZATION OF A DIMERIC
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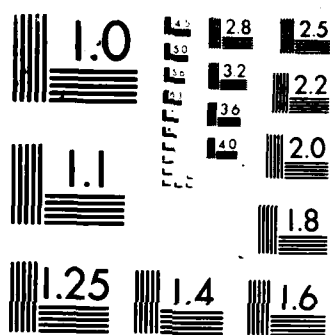
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ring of alternating four-coordinate Ga and As atoms.

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by

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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
 $\{[(\text{Me}_3\text{SiCH}_2)_2\text{As}]_3\text{Ga}\}_2$ [†]

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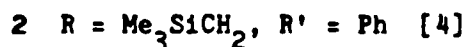
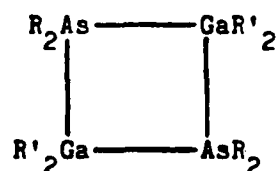
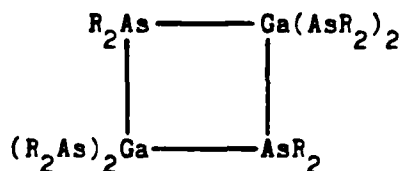
Summary

The dimer $\{[(\text{Me}_3\text{SiCH}_2)_2\text{As}]_3\text{Ga}\}_2$, only the second tris(arsino)gallane to be completely characterized, has been prepared from the reaction of $(\text{Me}_3\text{SiCH}_2)_2\text{AsLi}$ 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

[†]Dedicated to Professor G. E. Coates on the occasion of his 70th birthday.

the first example of a tris(arsino)gallane, monomeric $(\text{Mes}_2\text{As})_3\text{Ga}$, which X-ray analysis [2] has shown to contain three-coordinate gallium and arsenic. Subsequently, $(\text{Bu}^t_2\text{As})_3\text{Ga}$ 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 $[(\text{Me}_3\text{SiCH}_2)_2\text{As}]_3\text{Ga}$ (1), prepared by the lithium arsenide method. Interestingly, as noted previously, the reaction of $(\text{Me}_3\text{SiCH}_2)_2\text{AsSiMe}_3$ 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 $(\text{Ga-As})_2$ units in $[(\text{Me}_3\text{SiCH}_2)_2\text{AsGaPh}_2]_2$ (2) [4], the first dimeric mono(arsino)gallane for which the structure was reported, and in $(\text{Bu}^t_2\text{AsGaMe}_2)_2$ (3) [3], and the nearly planar unit in $(\text{Bu}^t_2\text{AsGaBu}^n_2)_2$ (4) [3], but is similar to, although less puckered than, the novel nonplanar $(\text{Ga-S})_2$ form found in $(\text{Pr}^i\text{SGaI}_2)_2$ which contains two four-coordinate Ga atoms and two three-coordinate S atoms [5].



A suspension of $(\text{Me}_3\text{SiCH}_2)_2\text{AsLi}$ [6] (2.03 g, 7.9 mmol) in hexane when added [7] to a hexane solution of GaCl_3 (0.46 g, 2.6 mmol) at -78°C gave, after 18 h at room temperature, a brown mixture which, following filtration and solvent removal, redissolved in hexane. Crystallization (-78°C) and

cold filtration, followed by solvent removal, recrystallization, hexane washings, and drying in vacuo afforded $\{[(\text{Me}_3\text{SiCH}_2)_2\text{As}]_3\text{Ga}\}_2$ (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 Figure 1. Several features of this dimer attest to its highly strained nature. Thus, the Ga-As1-Ga'-As1' ring, with a dihedral angle of 13.6° [vs. 36.7(2)° in the (Ga-S)₂ ring of $(\text{Pr}^1\text{SGaI}_2)_2$] between the As1-Ga-As1' and As1-Ga'-As1' planes (mean endocyclic dihedral angle about the ring bonds = 10.2°) is, as shown in Figure 2, distinctly non-planar. Two of the ring bonds, Ga-As1' and Ga'-As1' 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 $[(\text{PhAsH})(\text{R}_2\text{Ga})(\text{PhAs})_6(\text{RGa})_4]$ (R = Me_3SiCH_2) cluster [10]. All of 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 $(\text{Me}_2\text{As})_3\text{Ga}$. The mean ring bond angles in 1 (84.81° at Ga, 95.30° at As) are similar to those encountered 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)^o] indicating the greater resistance of the As centers to bond angle deformation.

Based on the cryoscopic molecular weight, **1** remains intact as a dimer in solution at low temperatures. It appears, however, 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 ¹³C NMR signals as the temperature is increased. Also, compound **1** is thermally unstable in solution at ambient temperatures and above, and slowly decomposes to the diarsine [(Me₃SiCH₂)₂As]₂ [1] and unknown products.

Acknowledgement. We thank the Office of Naval Research for financial support.

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- 6 $(\text{Me}_3\text{SiCH}_2)_2\text{AsLi}$ was produced by the reaction of $(\text{Me}_3\text{SiCH}_2)_2\text{AsH}$ [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 a dry nitrogen atmosphere.
- 8 Found: C, 35.34; H, 8.29%; mol. wt., 1582 ± 65 (cryoscopic, 0.268 g in 12.22 g cyclohexane). $\text{C}_{48}\text{H}_{132}\text{As}_6\text{Ga}_2\text{Si}_{12}$ 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, $^2J_{\text{HH}}$ 13.8 Hz, exo- CH_2), 1.71 (endo- CH_2); $^{13}\text{C}\{^1\text{H}\}$ 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: $\text{C}_{48}\text{H}_{132}\text{As}_6\text{Ga}_2\text{Si}_{12}$ (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) $^\circ$, V 4400.5 Å³, $Z = 2$, D_c 1.234 g cm⁻³, $\mu(\text{Cu-K}\alpha \text{ radiation}) = 50.7 \text{ cm}^{-1}$. 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 $R = 0.064$ [$R_w = 0.097$; $w = 1/\sigma^2(|F_o|)$] over 8504 absorption-corrected reflections [$I > 3.0\sigma(I)$] recorded on an Enraf-Nonius CAD-4 diffractometer (Cu-K α radiation, $\lambda = 1.5418$ Å; incident-beam graphite monochromator; ω - 2θ scans, $\theta_{\text{max}} = 57^\circ$). Tables of coordinates, bond lengths and angles, thermal parameters, torsion angles, and observed and calculated structure amplitudes are available from the authors (R.L.W.).
- 10 R.L. Wells, A.P. Purdy, A.T. McPhail, and C.G. Pitt, J. Chem. Soc., Chem. Commun., (1986) 487.

Legends For Figures

Figure 1. Molecular structure of $\{[(\text{Me}_3\text{SiCH}_2)_2\text{As}]_3\text{Ga}\}_2$ (1). Selected distances ($\text{\AA}$) and angles ($^\circ$) are: Ga-As1 2.581(1), Ga-As2 2.478(2), Ga-As3 2.476(2), Ga-As1' 2.540(1), Ga'-As1' 2.540(1), Ga'-As2' 2.470(1), Ga'-As3' 2.474(2), Ga'-As1 2.559(1), As1-Ga-As1' 83.58(4), As1-Ga'-As1' 84.04, Ga-As1-Ga' 94.57(4), Ga-As1'-Ga' 96.02(4), As2-Ga-As3 122.37(5), As2'-Ga'-As3' 113.68(5), C111-As1-C121 103.0(4), C111'-As1'-C121' 104.7(4).

Figure 2. The nonplanar $(\text{Ga-As})_2$ ring of compound 1.

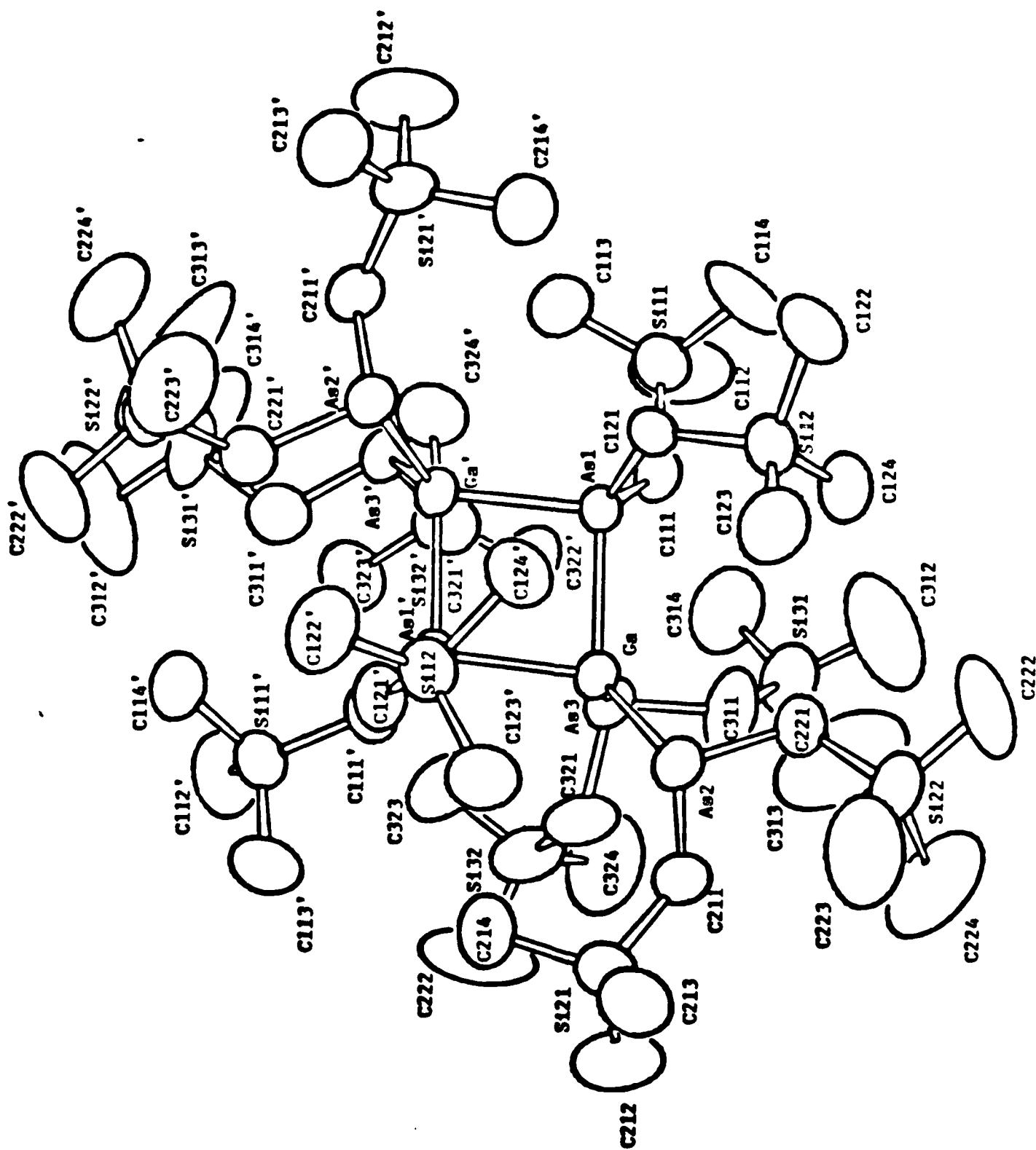
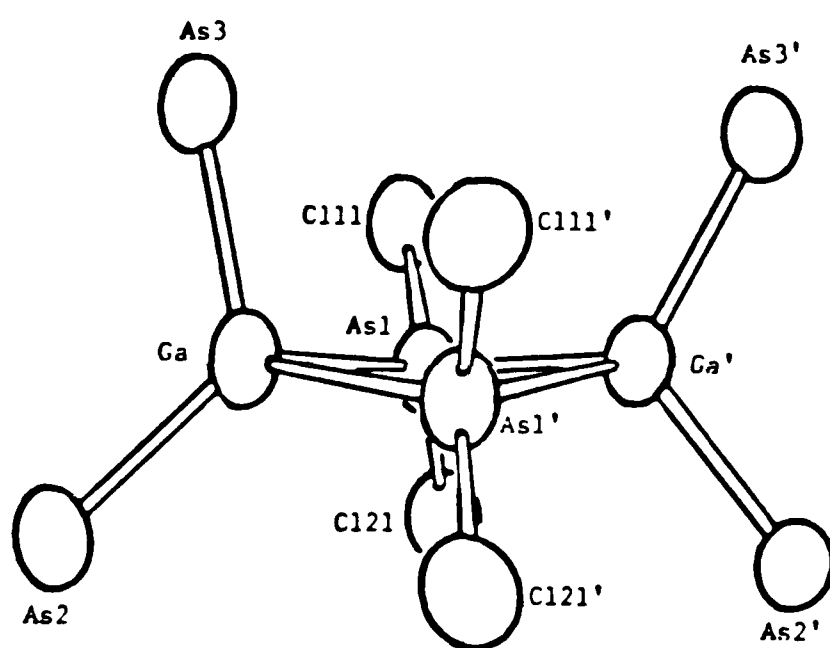


Figure 1



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