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THE FIRST ORGANOGALLIUM FOUR-MEMBERED RING COMPOUND WITH  
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STRUCTURE OF  $\text{Ph}_2\text{GaAs}(\text{SiMe}_3)_2\text{Ga}(\text{Ph})_2\text{Cl}$

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*Gallium Arsenide, 1971*

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The First Organogallium Four-Membered Ring Compound with Arsenic, Halogen  
Mixed Bridging: Synthesis and Crystal Structure of  $\text{Ph}_2\text{GaAs}(\text{SiMe}_3)_2\text{Ga}(\text{Ph})_2\text{Cl}$

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A. T. McPhail, and C. G. Pitt

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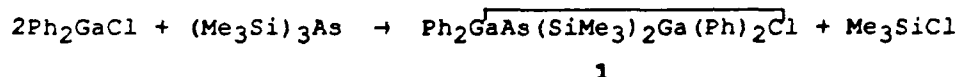
INTRODUCTION

In gallium chemistry, four-membered ring formation is known to occur via bridging of gallium centers by two arsenic atoms<sup>1</sup> or two halogen atoms<sup>2</sup>, but the literature contains no references to this occurring through one of each of these atoms. Here we report the synthesis and crystal structure of  $\text{Ph}_2\text{GaAs}(\text{SiMe}_3)_2\text{Ga}(\text{Ph})_2\text{Cl}$  (1), the first organogallium four-membered ring compound resulting from arsenic, halogen mixed bridging. We also report the synthesis of  $[\text{Ph}_2\text{GaAs}(\text{SiMe}_3)_2]_2$  (2). The fact that 1 can be prepared from  $\text{Ph}_2\text{GaCl}$  and  $(\text{Me}_3\text{Si})_3\text{As}$  again exemplifies the utility of

dehalosilylation between a silylarsine and a halogallane in preparing novel gallium-arsenic systems.<sup>1,3</sup>

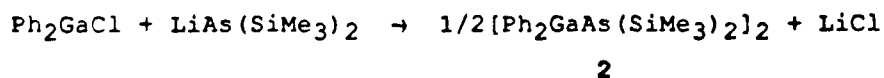
#### RESULTS AND DISCUSSION

Combining C<sub>6</sub>H<sub>6</sub> solutions of Ph<sub>2</sub>GaCl<sup>4</sup> and (Me<sub>3</sub>Si)<sub>3</sub>As<sup>5</sup> (2:1 mole ratio), followed by stirring at room temperature and removal of solvent and Me<sub>3</sub>SiCl, gave a white solid. A ligroin extract of the solid afforded **1** as white crystals [mp 145-146 °C (dec), 55.3% yield]. A satisfactory molecular weight was obtained by cryoscopic measurements. NMR: <sup>13</sup>C{<sup>1</sup>H} (C<sub>6</sub>D<sub>6</sub>) δ 3.14 (s, Me<sub>3</sub>Si), 128.30, 128.72, 135.81, 146.57 (m, Ph).



Likewise, mixing solutions of Ph<sub>2</sub>GaCl and (Me<sub>3</sub>Si)<sub>3</sub>As (3:1 mole ratio) resulted in the formation of **1** as the predominant product (53.5% yield).

A mixture of **1** and **2**, Me<sub>3</sub>SiCl and other unidentified products were isolated after heating (76 °C) a 1:1 mole ratio combination of Ph<sub>2</sub>GaCl and (Me<sub>3</sub>Si)<sub>3</sub>As in C<sub>6</sub>H<sub>6</sub>. Compounds **1** and **2** were identified as the components of the mixture by comparison of the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of the mixture with those of authentic samples of **1** and **2**. The latter was prepared from Ph<sub>2</sub>GaCl and LiAs(SiMe<sub>3</sub>)<sub>2</sub><sup>5</sup> (1:1 mole ratio) in benzene and isolated as white crystals [mp 229-230 °C (dec), 33.3% yield], and it was determined to be a dimer in solution by cryoscopic molecular weight measurements. NMR: <sup>13</sup>C{<sup>1</sup>H} (C<sub>6</sub>D<sub>6</sub>) δ 4.82 (s, Me<sub>3</sub>Si), 127.75, 128.02, 137.62, 149.55 (m, Ph).



The production of **1** was also accomplished by allowing Ph<sub>2</sub>GaCl and **2** (2:1 mole ratio in C<sub>6</sub>D<sub>6</sub>) to react in a sealed NMR tube.

# RING COMPOUND WITH ARSENIC, HALOGEN MIXED BRIDGING

Heating a sample of 1 in C<sub>6</sub>D<sub>6</sub> in a sealed NMR tube for one month at 80 °C resulted in the formation of 2, Me<sub>3</sub>SiCl and other unidentified products.

An X-ray crystal structure analysis of 1 revealed that the asymmetric unit comprises a discrete molecule (Figure 1) containing the heretofore unknown As- and Cl-bridged four-membered Ga-As-Ga'-Cl ring. That this ring is not strictly planar, and thus

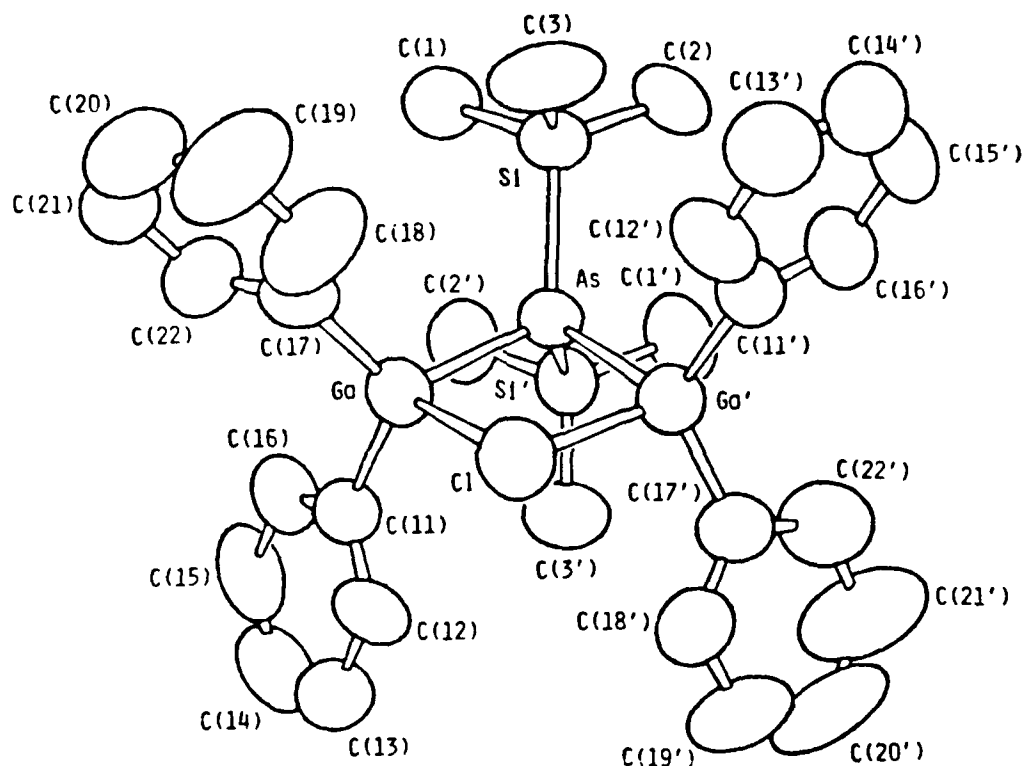


FIGURE 1 Molecular structure of  $\text{Ph}_2\text{GaAs}(\text{SiMe}_3)_2\text{Ga}(\text{Ph})_2\text{Cl}$  (1) (hydrogen atoms omitted for clarity). Selected distances (Å) and angles (°): Ga-As 2.469(2), Ga'-As 2.463(2), Ga-Cl 2.412(3), Ga'-Cl 2.409(4), Si-As 2.359(4), Si'-As 2.367(4), Ga-As-Ga' 88.70(7), Ga-Cl-Ga' 91.3(1), As-Ga-Cl 89.5(1), As-Ga'-Cl 89.8(1), Si-As-Si' 111.0(2), C(11)-Ga-C(17) 120.0(5), C(11')-Ga'-C(17') 122.6(5).

the molecule deviates from exact  $C_{2v}$  symmetry presumably to relieve unfavorable non-bonded intramolecular interactions between substituents in such a symmetric form, is manifested by the Cl atom displacement of 0.256 Å from the Ga-As-Ga' plane (the associated angle between the Ga-As-Ga' and Ga-Cl-Ga' planes is  $8.8^\circ$  and the mean endocyclic dihedral angle about the ring bonds is  $6.2^\circ$ ). The extent of the departure from exact planarity in **1** is somewhat less than in the (Ga-As)<sub>2</sub> ring of  $\{[(Me_3SiCH_2)_2As]_3Ga\}_2$ <sup>6</sup> where more severe overcrowding of the bulkier ring substituents leads to corresponding interplanar and dihedral angles of  $13.6^\circ$  and  $10.2^\circ$ , respectively. In contrast to the situation in (Ga-As)<sub>2</sub> rings where the endocyclic angles subtended at As and Ga differ significantly [range:  $94.57(4) - 96.02(4)^\circ$  and  $83.58(4) - 85.02(2)^\circ$ , respectively],<sup>1</sup> those in **1** are almost equal [ $88.70(7)^\circ$  at As;  $89.5(1)$  and  $89.8(1)^\circ$  at Ga]. The bond angle at the bridging Cl atom [ $91.3(1)^\circ$ ] is nearly the same as that of  $91.4(1)^\circ$  in  $[Ga(C_5H_5)Cl_2]_2$ (**3**)<sup>7</sup> and lies in the middle of the range of  $86(2)^\circ$  in  $(GaCl_3)_2$ (**4**)<sup>8</sup> and the mean of  $97.4(2)^\circ$  in  $[Ga(C_5Me_5)_2Cl]_2$  (**5**).<sup>7</sup> The mean C-Ga-C angle at  $121.3(5)^\circ$  is close to the corresponding value of  $120.8(2)^\circ$  in  $[(Me_3SiCH_2)_2AsGaPh_2]_2$ .<sup>9</sup> A significantly larger Si-As-Si' angle [ $111.0(2)^\circ$ ] is present in **1** than in  $[(Me_3Si)_2AsLi \cdot DME]_2$  (DME = 1, 2-dimethoxyethane) (**6**) [ $103.2(4)^\circ$ ].<sup>10</sup> The mean Ga-As bond length in **1** [2.466(2) Å] is shorter than any found within (Ga-As)<sub>2</sub> rings [range: 2.513(1) - 2.581(1) Å],<sup>1</sup> whereas the mean Ga-Cl distance at 2.411(4) Å is longer than the corresponding length in **4** [2.29(9) Å] as well as the mean of those in **3** [2.363(3) Å], but it is shorter than the mean in **5** [2.448(7) Å]. The mean Si-As distance at 2.363(4) Å is significantly longer than in **6** [2.307(7) Å].

Finally, the <sup>13</sup>C NMR spectrum and the experimentally determined molecular weight of **1** indicate it has the same molecular structure in solution as in the solid state.

# RING COMPOUND WITH ARSENIC, HALOGEN MIXED BRIDGING

## ACKNOWLEDGEMENT

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