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[19. ABSTRACT]

**Reactions of  $\text{GaX}_3$  ( $\text{X} = \text{Br}, \text{I}$ ) with  $\text{As}(\text{SiMe}_3)_3$ ;  
Crystal Structures of  
 $\text{I}_3\text{Ga}\cdot\text{As}(\text{SiMe}_3)_3$  and  $[\text{I}_2\text{GaAs}(\text{SiMe}_3)_2]_2$**

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**ABSTRACT**

Reactions of  $\text{GaX}_3$  ( $\text{X} = \text{Br}, \text{I}$ ) with  $\text{As}(\text{SiMe}_3)_3$  in 1:1 and 2:1 mole ratios were investigated. For the latter reactant stoichiometry, substances having the empirical formulae  $\text{AsBr}_3\text{Ga}_2$  (1) and  $\text{AsI}_3\text{Ga}_2$  (2), the analogs of the previously reported single-source GaAs precursor  $(\text{AsCl}_3\text{Ga}_2)_n$ , were isolated as yellow insoluble powders. Low temperature reactions in a 1:1 mole ratio resulted in the isolation of the adducts  $\text{Br}_3\text{Ga}\cdot\text{As}(\text{SiMe}_3)_3$  (3) and  $\text{I}_3\text{Ga}\cdot\text{As}(\text{SiMe}_3)_3$  (4). On the other hand, at room temperature, the  $\text{GaBr}_3$  reaction resulted in a complex mixture from which no characterizable compounds were isolated, whereas the  $\text{GaI}_3$  reaction afforded the crystalline compound  $[\text{I}_2\text{GaAs}(\text{SiMe}_3)_2]_2$  (5). The structures of 4 and 5 were elucidated by complete single crystal X-ray analyses (crystal data: 4, monoclinic, space group  $P2_1/c$ ,  $a = 16.497(2) \text{ \AA}$ ,  $b = 9.629(1) \text{ \AA}$ ,  $c = 16.658(2) \text{ \AA}$ ,  $\beta = 113.21(1)^\circ$ ,  $V = 2432(1) \text{ \AA}^3$ ,  $Z = 4$ ; 5, orthorhombic, space group  $Pbca$ ,  $a = 14.279(2) \text{ \AA}$ ,  $b = 17.509(2) \text{ \AA}$ ,  $c = 13.818(2) \text{ \AA}$ ,  $V = 3455(1) \text{ \AA}^3$ ,  $Z = 4$ ).

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## Introduction

Since our introduction in 1986<sup>1</sup> of the use of the silyl halide elimination reaction for forming the Ga-As bond, we have found it to be a versatile tool for the synthesis of interesting compounds. Using reagents of the general form  $R_n\text{As}(\text{SiMe}_3)_{3-n}$  and  $R'_n\text{GaX}_{3-n}$  ( $n = 0, 1, 2$ ), a number of monomeric, dimeric, trimeric, and mixed-bridge arsinogallanes have been prepared.<sup>2</sup> However, some of the most basic reactions in this series, viz. those between  $\text{As}(\text{SiMe}_3)_3$  and  $\text{GaX}_3$ , remained largely unexplored.

Previously, we reported that reaction of  $\text{GaX}_3$  ( $X = \text{Cl}, \text{Br}$ ) and  $\text{As}(\text{SiMe}_3)_3$  in a 1:1 mole ratio yields products which, upon being heated with a cool flame, give microcrystalline GaAs.<sup>3</sup> Others have shown that GaAs made in this way consists of particles small enough to be expected to exhibit quantum confinement effects. In fact, Alivisatos and coworkers have obtained soluble nanocrystalline GaAs by combining these reagents in refluxing quinoline.<sup>4</sup> Moreover, we recently published the results of our investigation of the reaction of  $\text{GaCl}_3$  and  $\text{As}(\text{SiMe}_3)_3$  in a 2:1 mole ratio; we reported that thermal decomposition of the sole solid product from this reaction,  $(\text{AsCl}_3\text{Ga}_2)_n$ , also yields microcrystalline GaAs.<sup>5</sup>

In this paper, we describe the isolation of five new compounds from 2:1 and 1:1 mole ratio reactions of  $\text{GaX}_3$  ( $X = \text{Br}, \text{I}$ ) with  $\text{As}(\text{SiMe}_3)_3$ . Materials with the empirical formula  $\text{AsX}_3\text{Ga}_2$  [ $X = \text{Br}$  (1), or  $\text{I}$  (2)], analogs

of the above mentioned single-source precursor  $(\text{AsCl}_3\text{Ga}_2)_n$ , have been obtained from 2:1 mole ratio reactions of the corresponding gallium halides. The respective 1:1 mole ratio reactions at low temperature afforded the adducts  $\text{X}_3\text{Ga}\cdot\text{As}(\text{SiMe}_3)_3$  [ $\text{X} = \text{Br}$  (3),  $\text{I}$  (4)]. In addition, the reaction of  $\text{GaI}_3$  with  $\text{As}(\text{SiMe}_3)_3$  at room temperature yielded  $[\text{I}_2\text{GaAs}(\text{SiMe}_3)_2]_2$  (5). Preliminary decomposition studies have shown that some, if not all, of these new materials, can be heated to afford GaAs.

### Experimental

**General.** All operations were carried out under vacuum, dry nitrogen or argon in a Vacuum/Atmospheres HE-493 Dri-Lab, an I<sup>2</sup>R glove bag, or in custom-made high vacuum glassware. All of the solvents were distilled from sodium benzophenone ketyl under dry dinitrogen.  $\text{As}(\text{SiMe}_3)_3$  was prepared according to the published procedure.<sup>6</sup>  $\text{GaBr}_3$  and  $\text{GaI}_3$  were obtained from Alfa Products, and Roc-Ric Inc., respectively. Crystals for X-ray diffraction studies and melting point samples were flame-sealed in glass capillaries. NMR samples were flame sealed under vacuum in standard 5 mm NMR tubes.  $^1\text{H}$  (300 MHz) spectra were obtained on a Varian XL 300 spectrometer, and chemical shifts were referenced to TMS, using the residual protons of  $\text{C}_6\text{D}_6$  ( $\delta = 7.15$ ) and  $\text{C}_6\text{D}_5\text{CD}_3$  ( $\delta = 2.09$ ). Melting points (uncorrected) were obtained on a Thomas Hoover Uni-Melt apparatus. Elemental analyses were performed by E+R Microanalytical Laboratory, Inc., Corona, NY.

**Preparation of  $(\text{AsBr}_3\text{Ga}_2)_n$  (1).** In an argon-filled Dri-Lab,  $\text{GaBr}_3$  (0.126 g, 0.408 mmol) was combined with ~6 mL of hexane in a sample vial.  $\text{As}(\text{SiMe}_3)_3$  (0.060 g, 0.203 mmol) was added, and the mixture

was refluxed for 10 min. Yield: 0.093 g (100%) as a fine yellow powder. Anal. Calcd for  $\text{AsBr}_3\text{Ga}_2$ : As, 16.50; Br, 52.79; Ga, 30.71. Found: As, 15.94; Br, 51.60; Ga, 29.92; (0.99:3.00:1.99 As:Br:Ga ratio). A previous preparation, in which the reagents were mixed in pentane and the product isolated after 1 month at room temp, yielded the same product. Anal. Calcd for  $\text{AsBr}_3\text{Ga}_2$ : As, 16.50; Br, 52.79; Ga, 30.71. Found: As, 15.26; Br, 49.91; Ga, 29.90; C, 3.34; H, 0.49; Si, 0.80; (0.98:3.00:2.06 As:Br:Ga ratio).

**Preparation of  $(\text{AsI}_3\text{Ga}_2)_n$  (2).** In an argon-filled Dri-Lab,  $\text{GaI}_3$  (1.503 g, 3.337 mmol) and 25 mL of pentane were placed in a two-necked collection flask equipped with a Teflon valve.  $\text{As}(\text{SiMe}_3)_3$  (0.491 g, 1.67 mmol) was added, and the mixture was allowed to sit undisturbed for 16 days. A very small amount of an unidentified yellow crystalline product was removed, and the solvent was stripped off of the remainder. The residual yellow powder was washed successively with pentane, benzene, and toluene. Two crystalline products were isolated from these washes; the unidentified product mentioned above, and  $[\text{I}_2\text{GaAs}(\text{SiMe}_3)_3]_2$  (5). The insoluble powder that remained was confirmed by elemental analysis to be 2. Anal. Calcd for  $\text{AsGa}_2\text{I}_3$ : As, 12.59; Ga, 23.43; I, 63.98. Found: As, 12.09; Ga, 22.58; I, 61.87; C, 3.25; H, 0.57; Si, 0.0; (1:2.01:3.00 As:Ga:I ratio).

**Preparation of  $\text{Br}_3\text{Ga} \cdot \text{As}(\text{SiMe}_3)_3$  (3).** In an argon-filled Dri-Lab,  $\text{GaBr}_3$  (0.455 g, 1.29 mmol) was dissolved in toluene and pipetted into the small addition bulb of a custom-made, two-bulb, greaseless reaction flask.  $\text{As}(\text{SiMe}_3)_3$  (0.434 g, 1.47 mmol) was added to the main reaction bulb of the flask, along with ~10 mL of toluene. The  $\text{As}(\text{SiMe}_3)_3$  solution was degassed on a high vacuum line, and chilled in a  $-50^\circ\text{C}$  bath. The contents of the addition bulb were then chilled, and allowed to drip slowly into the main reaction bulb. The resulting mixture consisted of a fine, white powder and a clear,

colorless solution. This mixture was filtered through a medium frit while still cool, and the solvent was stripped under high vacuum, either at or below room temperature. The apparatus was then immediately brought into the glove-box, where the products were placed in a  $-15\text{ }^{\circ}\text{C}$  freezer. The white powder which was scraped off the frit was washed once with pentane and sent for analysis. Toluene solutions of this powder yielded colorless crystals, which are apparently a toluene solvate of 3. Note, all manipulations of this compound must be carried out at reduced temperatures, since the compound decomposes slowly at room temperature, both neat and in solution. Due to the tendency of this reactive compound towards decomposition and/or the loss of solvent, all attempts to obtain a complete single-crystal X-ray analysis have failed. Yield: 0.494 g (56%) white powder. Anal. Calcd for  $\text{C}_9\text{H}_{27}\text{AsBr}_3\text{GaSi}_3$ : C, 17.90; H, 4.51; As, 12.40; Br, 39.69; Ga, 11.55. Found: C, 17.80; H, 4.24; As, 12.58; Br, 39.65; Ga, 11.46.  $^1\text{H}$  NMR (toluene- $d_8$ ):  $\delta$  0.339 (s,  $\text{Me}_3\text{Si}$ ).

**Reaction of  $\text{Br}_3\text{Ga}\cdot\text{As}(\text{SiMe}_3)_3$  (3) with excess  $\text{GaBr}_3$ .**  $\text{Br}_3\text{Ga}\cdot\text{As}(\text{SiMe}_3)_3$  (0.041 g, 0.067 mmol) was placed in a sample vial along with 3 mL of toluene.  $\text{GaBr}_3$  (0.03 g, 0.1 mmol) was added neat, and the mixture was shaken. A beige solid resulted, which turned yellow as the vial was heated to  $69\text{ }^{\circ}\text{C}$  for 5 min. Yield: 0.033 g (107%). Anal. Calcd for  $\text{AsBr}_3\text{Ga}_2$ : Br, 52.79; Ga, 30.71. Found: Br, 51.79; Ga, 29.89; C, 3.34; H, 0.49; Si, 0.80; (3.02:2.00 Br:Ga ratio).

**Preparation of  $\text{I}_3\text{Ga}\cdot\text{As}(\text{SiMe}_3)_3$  (4).** In an argon-filled Dri-Lab,  $\text{GaI}_3$  (0.076 g, 0.17 mmol), was added to a sample vial containing  $\text{As}(\text{SiMe}_3)_3$  (0.05 g, 0.17 mmol) and 3 mL of toluene. Reagents, solvents, and vials were all chilled to  $-15\text{ }^{\circ}\text{C}$  before beginning the reaction. Reagents were combined, and the mixture was placed back in the  $-15\text{ }^{\circ}\text{C}$  freezer for



20 h before the solvent was pipetted off of the pale yellow crystals which had formed. A single crystal X-ray analysis confirmed that the product was indeed the monomeric adduct **4** (*vide infra*). Yield: 0.074 g (59%). Anal. Calcd for  $C_9H_{27}AsGaI_3Si_3$ : C, 14.51; H, 3.65; I, 51.11. Found: C, 14.47; H, 3.54; I, 50.91.  $^1H$  NMR (toluene- $d_8$ ):  $\delta$  0.347 (s,  $SiMe_3$ ), 0.386 (s,  $SiMe_3$ ). Note that upon heating neat **4** in the dry-box, large, clear crystals which formed on the surface of the material were shown to be **5**, from X-ray diffraction data.

**Original Preparation of  $[I_2GaAs(SiMe_3)_2]_2$  (**5**).** In an argon-filled Dri-Lab,  $GaI_3$  (0.804 g, 1.79 mmol) and 30 mL of pentane were placed in a custom two-necked collection flask.  $As(SiMe_3)_3$  (0.526 g, 1.79 mmol) was added to the mixture, resulting in a yellow solution and a yellow powder. The appearance of the products changed from yellow to orange over the course of a few hours. Three days later, colorless crystals were noted on the upper walls of the flask. The volatiles were removed *in vacuo* to yield an orange powder and a few colorless crystals, which were then loaded into capillaries for X-ray analysis. These crystals were confirmed to be **5**.  $^1H$  NMR (benzene- $d_6$ ):  $\delta$  0.543 (m,  $Me_3Si$ ), 0.311 (m,  $Me_3Si$ ), 0.114 (m,  $Me_3Si$ ).

**High Yield Preparation of  $[I_2GaAs(SiMe_3)_2]_2$  (**5**).** In an argon-filled Dri-Lab,  $GaI_3$  (0.499 g, 1.11 mmol) was dissolved in 5 mL of toluene, with the addition of six drops of ether, and added to a toluene solution of  $As(SiMe_3)_3$  (0.326 g, 1.107 mmol) in a sample vial. A white crystalline product was produced as the addition was carried out. These crystals were confirmed to be **5** by elemental analysis. Yield: 0.510 g (84.5%). Anal. Calcd for  $C_{12}H_{36}As_2Ga_2I_4Si_4$ : C, 13.23; H, 3.33; I, 46.58. Found: C, 13.42; H, 3.61; I, 46.25.

**Thermal Decomposition of  $(AsBr_3Ga_2)_n$  (**1**).**  $(AsBr_3Ga_2)_n$  (~0.3 g) was placed in a 25 mL, one-necked reaction flask, which was equipped

with a Teflon valve. The flask was evacuated and placed in an oil bath maintained at 340 °C for 16 h. The broad lines observed in the powder pattern of the resulting red/brown powder compared favorably with those obtained from a *bona fide* sample of GaAs. However, the elemental analysis shows this to be a very impure sample containing GaAs. Anal. Calcd for GaAs: As, 51.80; Ga, 48.20. Found: As, 23.09; Ga, 32.20; Br, 42.55; C, 1.79; H, 0.88; Si, 0.0.

**Thermal Decomposition of  $[\text{I}_2\text{GaAs}(\text{SiMe}_3)_2]_2$  (5).**  $[\text{I}_2\text{GaAs}(\text{SiMe}_3)_3]_2$  (0.379 g, 0.696 mmol) was placed in a 25 ml, one-necked reaction flask, which was equipped with a Teflon valve. The flask was evacuated and placed in a 340 °C oil bath for 16 h. The resulting reddish-grey powder was loaded into a glass capillary for X-ray powder pattern analysis. No distinct lines were observed in the resulting powder pattern. The remaining product was heated in the dry-box, to ~400 °C, using a heating mantle. The resulting grey powder was loaded into a glass capillary for X-ray powder pattern analysis. The broad lines observed in the powder pattern compared favorably with those obtained from a *bona fide* sample of GaAs. However, the elemental analysis shows this also to be a very impure sample containing GaAs. Anal. Calcd. for GaAs: As, 51.80; Ga, 48.20. Found: As, 33.27; Ga, 30.38; I, 33.87; C, 1.54; H, 0.79; Si, 0.0.

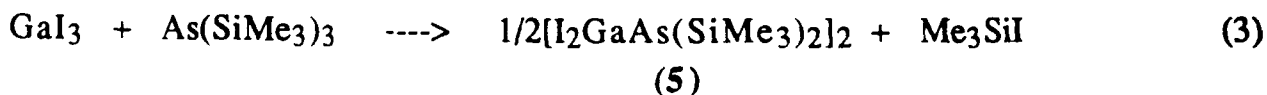
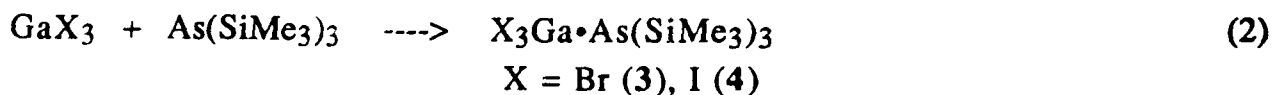
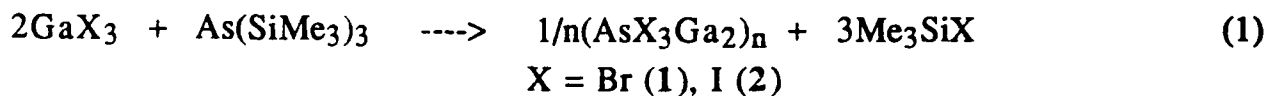
**X-Ray Crystal Structure Analysis of  $\text{I}_3\text{Ga}\cdot\text{As}(\text{SiMe}_3)_3$  (4) and  $[\text{I}_2\text{GaAs}(\text{SiMe}_3)_2]_2$  (5).** For X-ray measurements, crystals of 4 and 5) were sealed inside thin-walled glass capillaries under an argon atmosphere. Preliminary unit cell parameters and space group information were derived from oscillation and Weissenberg photographs which revealed that the crystals of both compounds diffracted poorly. Intensity data (+*h*, +*k*, ±*l*,  $\theta_{\text{max}} = 55^\circ$  for 4; +*h*, +*k*, +*l*;  $\theta_{\text{max}} = 67^\circ$  for 5),

recorded on an Enraf-Nonius CAD-4 diffractometer (Cu-K $\alpha$  radiation,  $\lambda = 1.5418$  Å; incident-beam graphite monochromator), were corrected for the usual Lorentz and polarization effects. Empirical absorption corrections, based on the  $\phi$ -dependency of the intensities of several reflections measured at  $\psi$  ca. 90°, were also applied. From totals of 3042 (4) and 3073 (5) non-equivalent measurements, only those 1254 and 1010 reflections, respectively, with  $I > 3.0\sigma(I)$  were retained for the analyses. The space groups,  $P2_1/c$  for 4 and  $Pbca$  for 5, were established unequivocally from the Laue symmetry and systematic absences:  $0k0$  when  $k \neq 2n$ ,  $h0l$  when  $l \neq 2n$  for 4;  $0kl$  when  $k \neq 2n$ ,  $h0l$  when  $l \neq 2n$ , and  $hk0$  when  $h \neq 2n$  for 5. Both crystal structures were solved by direct methods (MULTAN11/82). For 4, approximate coordinates for the arsenic, gallium, and iodine atoms were derived from an  $E$ -map. A difference Fourier synthesis phased by these atoms yielded silicon and carbon atom coordinates. In the case of 5, an  $E$ -map furnished initial coordinates for the arsenic, gallium, iodine, and silicon atoms, and carbon atom positions were obtained routinely from a difference Fourier synthesis phased by these heavier atoms. Positional and thermal parameters [anisotropic As, Ga, I, Si; isotropic C for 4; anisotropic As, Ga, I, Si, C for 5] were adjusted by means of several rounds of full-matrix least-squares calculations. Hydrogen atoms in both compounds were incorporated at their idealized positions (C-H = 1.05 Å) in the later least-squares iterations. Final difference Fourier syntheses contained no unusual features. Crystallographic calculations were performed on PDP11/44 and MicroVAX computers by use of the Enraf-Nonius Structure Determination Package (SDP). For all structure-factor calculations, neutral atom scattering factors and their anomalous dispersion corrections were taken from *International*

*Tables for X-Ray Crystallography*, Vol. IV, The Kynoch Press, Birmingham, U.K. In the least-squares iterations,  $\Sigma w\Delta^2$  [ $w = 1/\sigma^2(|F_o|)$ ,  $\Delta = (|F_o| - |F_c|)$ ] was minimized. Further details pertaining to these analyses are summarized in Table I. Non-hydrogen atom fractional coordinates and equivalent isotropic thermal parameters for **4** are listed in Table II while corresponding parameters for **5** are in Table III. Tables IV and V contain selected bond lengths and angles for **4** and **5**, respectively. Supplementary material: Tables of anisotropic temperature factor parameters, hydrogen atom parameters, bond lengths and angles for **4** and **5** have been deposited at the Cambridge Crystallographic Data Centre.

### Results and Discussion

The 2:1 mole ratio reactions of the respective gallium halides with  $\text{As}(\text{SiMe}_3)_3$  at room temperature afford substances with the empirical formula  $\text{AsX}_3\text{Ga}_2$  [ $\text{X} = \text{Br}$  (**1**),  $\text{I}$  (**2**)] (eq 1). The adducts  $\text{X}_3\text{Ga}\cdot\text{As}(\text{SiMe}_3)_3$  [ $\text{X} = \text{Br}$  (**3**),  $\text{I}$  (**4**)] can be isolated from the 1:1 mole ratio reactions of the same reagents at low temperature (eq 2) but, on the other hand, the equimolar reaction of  $\text{GaI}_3$  with  $\text{As}(\text{SiMe}_3)_3$  at room temperature produces  $[\text{I}_2\text{GaAs}(\text{SiMe}_3)_2]_2$  (**5**) (eq 3).



Crystals of **4** and **5** suitable for X-ray diffraction studies were sealed inside thin-walled glass capillaries under an argon atmosphere. Crystallographic data are summarized in Table I. ORTEP diagrams showing the atom numbering schemes and solid-state conformations are presented in Figures 1 and 2. Non-hydrogen atom fractional coordinates for **4** and **5** are provided in Tables II and III, respectively; selected bond lengths and angles are listed in Tables III and IV.

Adduct **4** crystallizes in the monoclinic space group  $P2_1/c$  with one molecule occupying each of the general positions. The Ga-As distance of 2.423(7) Å in **4** is distinctly shorter than the corresponding distances in other previously structurally characterized adducts of  $\text{As}(\text{SiMe}_3)_3$  all of which involve aryl or alkyl substituents at Ga [2.550(4) Å in  $(\text{C}_6\text{F}_5)_3\text{Ga}\cdot\text{As}(\text{SiMe}_3)_3$  (**6**),<sup>7</sup> a mean of 2.567 Å in two crystallographically independent molecules of  $(\text{C}_6\text{H}_5)_3\text{Ga}\cdot\text{As}(\text{SiMe}_3)_3$  (**7**),<sup>8</sup> and 2.626(1) Å in  $(\text{Me}_3\text{CCH}_2)(\text{Cl})\text{Ga}\cdot\text{As}(\text{SiMe}_3)_3$  (**8**)<sup>9</sup>]. The mean Ga-I length at 2.535 Å in **4** is virtually equal to that of 2.538 Å in **5** (*vide infra*). Bond angles at Ga and As in **4** lie in the fairly narrow range of 108.8(2)°-110.2(6)° and thus the coordination about both centers approximates more closely to a regular tetrahedral geometry than do those in the symmetrically substituted adduct **6** and its isostructural analogue **7** where substituent steric effects produce a greater amount of bond angle distortion from a regular arrangement [e.g., mean values for **6** : Si-As-Si = 105.5°, Ga-As-Si = 113.2°, Al-Ga-C = 106.8°, C-Ga-C = 112.0°]. The As-Si bond is rotated around the As-Ga bond by a mean of 45.4° from an orientation in which it would eclipse the Ga-I bond. The magnitude of this torsion angle is greater than the corresponding means of 17.1° in **6**, 24.7° in (**7**), and 38.2° in **8** (which has one halogen substituent at Ga), and its wide variation reflects the role

played by intramolecular non-bonded steric interactions associated with the different Ga substituents in dictating the overall conformations of such adducts.

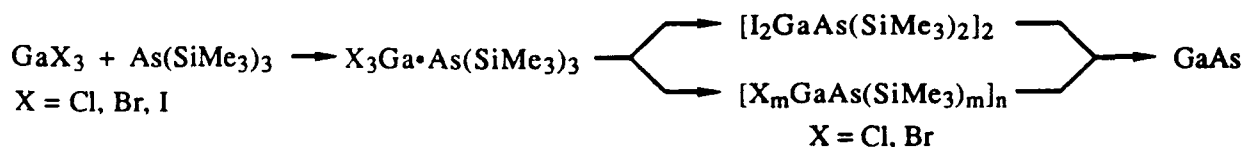
Crystals of **5** belong to the orthorhombic system, space group *Pbca*. The unit cell contains four discrete dimers situated on crystallographic centers of symmetry and, accordingly, the (AsGa)<sub>2</sub> ring is constrained to be planar. The mean As-Si distance at 2.379 Å lies in the 2.363-2.400 Å range found in [(Me<sub>3</sub>CCH<sub>2</sub>)<sub>2</sub>GaAs(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (**9**),<sup>9</sup> [(Me<sub>3</sub>SiCH<sub>2</sub>)<sub>2</sub>GaAs(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (**10**),<sup>10</sup> and [(Me<sub>3</sub>C)<sub>2</sub>GaAs(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (**11**),<sup>11</sup> but the mean As-Ga bond length at 2.471 Å is shorter than the corresponding means of 2.567-2.630 Å in these same dimers where ring substituent crowding is more severe. As stated above, the mean Ga-I bond length of 2.538 Å in **5** is essentially the same as that of 2.535 Å in (**4**). In contrast to the situation in **9-11** in which the Ga-As-Ga angle is consistently larger than the As-Ga-As angle (by 7.8°-10.0°), the Ga-As-Ga angle of 88.0(1)° is smaller than the As-Ga-As angle 92.0(1)° in (**5**); to our knowledge, this represents the first instance in which this feature has been observed in (GaAs)<sub>2</sub> rings. The Si-As-Si angle of 111.4(3)° is much enlarged over those of 95.67(6)°-103.66(6)° in **9-11** whereas the I-Ga-I angle of 105.4(1)° is significantly smaller than any of the C-Ga-C angles for compounds **9-11** wherein they vary widely [114.3(3)°-135.2(3)°].

The reactions of As(SiMe<sub>3</sub>)<sub>3</sub> with GaBr<sub>3</sub> and the products therefrom, closely mimic those with GaCl<sub>3</sub>, while those involving GaI<sub>3</sub> appear to differ substantially. For example, a white crystalline compound which was isolated in the equimolar GaCl<sub>3</sub> reaction could never be fully characterized, as it decomposed in less than a minute at room temperature.<sup>3</sup> However, adduct **3**, isolated from the analogous GaBr<sub>3</sub> reaction, shows no observable

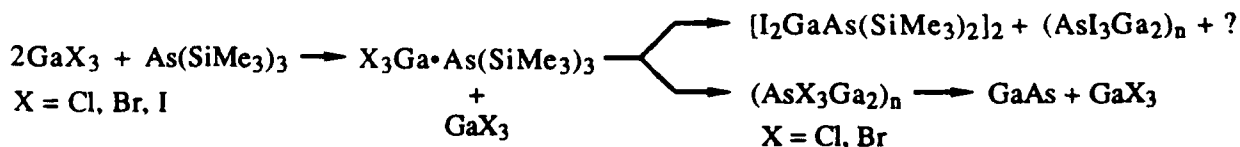
signs of decomposition after an hour at room temperature, and adduct **4** is stable for days at 25 °C. Similarly, in the synthesis of  $(\text{AsCl}_3\text{Ga}_2)_n$ , the white precipitate which forms first turns bright yellow in less than a minute at room temperature.<sup>4</sup> In the  $(\text{AsBr}_3\text{Ga}_2)_n$  synthesis, this transition can take hours but, in the reaction with  $\text{GaI}_3$ , alternative reactions appear to dominate.

The observations above, along with the fact that **3** is converted to **1** by the addition of  $\text{GaBr}_3$ , lead us to propose the following reaction schemes (Schemes I and II). The proposed pathways also are reasonably consistent with vague elemental analysis data we obtained from partially decomposed samples of the white intermediate obtained in the  $\text{GaCl}_3$  reactions.

**Scheme I. Reaction of  $\text{GaX}_3$  and  $\text{As}(\text{SiMe}_3)_3$  in a 1:1 Mole Ratio.**



**Scheme II. Reaction of  $\text{GaX}_3$  and  $\text{As}(\text{SiMe}_3)_3$  in a 2:1 Mole Ratio.**



In Scheme II, it is assumed that the 1:1 adduct is formed first, and then  $(\text{AsX}_3\text{Ga}_2)_n$  is formed, either by an intermolecular reaction with the second equivalent of  $\text{GaX}_3$  or by the formation of a 2:1 adduct, and

followed by an intramolecular silyl halide elimination. However, the formation of **5** dominates in the  $\text{GaI}_3$  2:1 mole ratio reaction. We propose two reasons for this phenomenon: (a) either the intermolecular elimination is slow enough to allow the adduct formed to undergo an intramolecular reaction, or (b) the steric bulk of the  $\text{GaI}_3$  does not allow the formation of the 2:1 adduct.

Most, if not all, of the compounds described herein are new single-source GaAs precursors; however we believe that their use as synthetic reagents is an even more promising potential application. All of them are potentially reactive at all available sites, and various reaction schemes can be envisioned which could add substituents selectively, at the gallium or at the arsenic, thereby facilitating the controlled synthesis of additional new single-source precursors, as well as other compounds of interest. We see these compounds as potentially useful reagents for the synthesis of III-V clusters, rings, and polymers, as well as for the preparation of mixed metal and mixed pnictide compounds.

Substances **1** and **5** have been thermally decomposed to yield impure GaAs. In addition, **4** is also a GaAs precursor, since **5** is a resultant product when **4** is heated. Compound **2** was produced in such small quantity as to render its decomposition of minimal importance. The same reaction which produced **3** at low temperature was shown to yield GaAs, when carried out at room temperature and the product mixture subsequently pyrolyzed.<sup>3</sup> Therefore, we assume that **3** is also a single-source GaAs precursor.

These relatively low temperature decompositions were not optimized, nor were the products purified. Therefore, the large amount of impurities shown by the analysis is not surprising. These reactions serve



only to demonstrate conclusively that GaAs can be obtained from this class of compounds, under relatively mild conditions.

### Conclusion

Considering the potential utility of GaAs nanocrystals in optical and optoelectronic devices, investigation of reactions which produce such materials are desperately needed. In this study, not only has the only proven method for producing nanocrystalline GaAs been further clarified, but five new compounds have been isolated from related reactions. These compounds hold promise as useful reagents as well as single-source precursors themselves. It is hoped that through a better understanding of the trimethylsilyl halide elimination reaction in general, and the availability of these selectively reactive new reagents, the great potential of GaAs can be further realized.

**Acknowledgment.** The financial support for this work by the Office of Naval Research is gratefully acknowledged.

**Supplementary Materials Available.** Tables of hydrogen atom coordinates and isotropic thermal parameters, anisotropic temperature factors, and complete lists of interatomic distances and angles for **4** and **5**, equations of least-squares planes through groups of atoms for **5** (8 pages); listings of observed and calculated structure amplitudes for **4** and **5** (16 pages).

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**Table I. Crystallographic Data and Measurements  
for  $\text{I}_3\text{Ga}\cdot\text{As}(\text{SiMe}_3)_3$  (4) and  $[\text{I}_2\text{GaAs}(\text{SiMe}_3)_2]_2$  (5).**

|                                                      | 4                                                  | 5                                                                       |
|------------------------------------------------------|----------------------------------------------------|-------------------------------------------------------------------------|
| Molecular formula                                    | $\text{C}_9\text{H}_{27}\text{AsGaI}_3\text{Si}_3$ | $\text{C}_{12}\text{H}_{36}\text{As}_2\text{Ga}_2\text{I}_4\text{Si}_4$ |
| Formula weight                                       | 744.93                                             | 1089.66                                                                 |
| Crystal system                                       | monoclinic                                         | orthorhombic                                                            |
| Space group                                          | $P2_1/c$                                           | $Pbca$                                                                  |
| $a(\text{\AA})$                                      | 16.497(2)                                          | 14.279(2)                                                               |
| $b(\text{\AA})$                                      | 9.629(1)                                           | 17.509(2)                                                               |
| $c(\text{\AA})$                                      | 16.658(2)                                          | 13.818(2)                                                               |
| $\beta(^{\circ})$                                    | 113.21(1)                                          |                                                                         |
| No. of orient. refls.                                | 25                                                 | 25                                                                      |
| $\theta(^{\circ})$ range                             | 30-36                                              | 30-35                                                                   |
| $V(\text{\AA}^3)$                                    | 2432(1)                                            | 3455(1)                                                                 |
| $Z$                                                  | 4                                                  | 4                                                                       |
| $D$ calcd. ( $\text{g cm}^{-3}$ )                    | 2.034                                              | 2.095                                                                   |
| Temp. ( $^{\circ}\text{C}$ )                         | 25                                                 | 25                                                                      |
| Crystal dims. (mm)                                   | 0.07x0.08x0.20                                     | 0.12x0.14x0.40                                                          |
| $T_{\text{max.}}:T_{\text{min.}}$                    | 1.00:0.20                                          | 1.00:0.49                                                               |
| Radiation                                            | $\text{Cu-K}\alpha$ (1.5418 $\text{\AA}$ )         | $\text{Cu-K}\alpha$ (1.5418 $\text{\AA}$ )                              |
| $\mu$ ( $\text{cm}^{-1}$ )                           | 347                                                | 338.5                                                                   |
| Scan type                                            | $\omega$ -2 $\theta$                               | $\omega$ -2 $\theta$                                                    |
| Scan width ( $^{\circ}$ )                            | $0.80 + 0.14\tan\theta$                            | $0.80 + 0.14\tan\theta$                                                 |
| $\theta_{\text{max.}}$ ( $^{\circ}$ )                | 55                                                 | 67                                                                      |
| Intensity cntl. refls.                               | 222, 411, 132, 542                                 | 111, 312, 312, 111                                                      |
| Variation; repeat time (hr)                          | <1%;2                                              | <1%;2                                                                   |
| No. of reflections recorded                          | 3168                                               | 3073                                                                    |
| No. of refls. retained                               | 3042                                               | 1010                                                                    |
| No. of parameters refined                            | 109                                                | 109                                                                     |
| $R$ ( $R_w$ ) <sup>a</sup>                           | 0.097 (0.121)                                      | 0.055 (0.069)                                                           |
| Goodness of fit <sup>a</sup>                         | 2.3                                                | 1.21                                                                    |
| Max shift: esd in final<br>least-squares cycle       | 0.07                                               | 0.04                                                                    |
| Final $\Delta\rho(\text{e}/\text{\AA}^3)$ max.; min. | 1.5; -1.5                                          | 0.88; -1.03                                                             |

**Table I. (continued)**

$$^aR = \Sigma||F_o| - |F_c||/\Sigma|F_o|; R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2};$$
$$\text{Goodness of fit} = [\Sigma w(|F_o| - F_c)^2/N_{\text{obsns}} - N_{\text{params}})]^{1/2}$$

**Table II. Non-hydrogen Atom Fractional Coordinates and Equivalent Isotropic Thermal Parameters<sup>a</sup> for I<sub>3</sub>Ga·As(SiMe<sub>3</sub>)<sub>3</sub> (4), with Estimated Standard Deviations in Parentheses**

| Atom  | <i>x</i>  | <i>y</i>  | <i>z</i>  | <i>B</i> <sub>eq</sub> (Å <sup>2</sup> ) |
|-------|-----------|-----------|-----------|------------------------------------------|
| As    | 0.2582(3) | 0.5548(5) | 0.2326(2) | 6.4(1)                                   |
| Ga    | 0.2129(3) | 0.3630(5) | 0.2996(3) | 5.5(1)                                   |
| I(1)  | 0.3456(2) | 0.2057(4) | 0.3761(2) | 9.0(1)                                   |
| I(2)  | 0.0935(2) | 0.2264(4) | 0.1829(4) | 14.3(2)                                  |
| I(3)  | 0.1564(2) | 0.4564(5) | 0.4097(2) | 10.4(1)                                  |
| Si(1) | 0.392(1)  | 0.642(2)  | 0.332(1)  | 17.1(5)                                  |
| Si(2) | 0.276(1)  | 0.474(2)  | 0.106(1)  | 12.1(4)                                  |
| Si(3) | 0.148(1)  | 0.731(2)  | 0.193(1)  | 15.6(5)                                  |
| C(11) | 0.409(6)  | 0.825(12) | 0.303(6)  | 25(4)                                    |
| C(12) | 0.390(4)  | 0.645(9)  | 0.448(5)  | 19(3)                                    |
| C(13) | 0.491(3)  | 0.522(7)  | 0.345(4)  | 12(2)                                    |
| C(21) | 0.357(4)  | 0.597(9)  | 0.083(5)  | 17(3)                                    |
| C(22) | 0.328(2)  | 0.302(5)  | 0.130(2)  | 7(1)                                     |
| C(23) | 0.162(4)  | 0.470(8)  | 0.010(4)  | 16(2)                                    |
| C(31) | 0.170(5)  | 0.854(12) | 0.120(5)  | 24(4)                                    |
| C(32) | 0.042(5)  | 0.644(10) | 0.144(5)  | 19(3)                                    |
| C(33) | 0.160(3)  | 0.835(7)  | 0.297(3)  | 12(2)                                    |

<sup>a</sup>Carbon atoms were refined isotropically.

**Table III. Non-hydrogen Atom Fractional Coordinates and Equivalent Isotropic Thermal Parameters for  $[\text{I}_2\text{GaAs}(\text{SiMe}_3)_2]_2$  (5), with Estimated Standard Deviations in Parentheses**

| Atom  | <i>x</i>   | <i>y</i>  | <i>z</i>   | <i>B</i> <sub>eq</sub> (Å <sup>2</sup> ) |
|-------|------------|-----------|------------|------------------------------------------|
| As    | -0.0820(2) | 0.0734(1) | 0.0266(2)  | 2.87(5)                                  |
| Ga    | 0.0398(2)  | 0.0520(1) | -0.0970(2) | 2.96(6)                                  |
| I(1)  | 0.1721(1)  | 0.1487(1) | -0.0960(2) | 5.90(5)                                  |
| I(2)  | -0.0198(2) | 0.0496(1) | -0.2700(2) | 5.67(5)                                  |
| Si(1) | -0.2364(5) | 0.0772(4) | -0.0389(6) | 4.1(2)                                   |
| Si(2) | -0.0511(6) | 0.1821(3) | 0.1242(6)  | 4.8(2)                                   |
| C(11) | -0.321(2)  | 0.078(2)  | 0.063(3)   | 8(1)                                     |
| C(12) | -0.249(2)  | -0.005(2) | -0.115(2)  | 5(1)                                     |
| C(13) | -0.245(3)  | 0.164(2)  | -0.111(2)  | 8(1)                                     |
| C(21) | -0.055(2)  | 0.266(1)  | 0.043(3)   | 8(1)                                     |
| C(22) | -0.145(3)  | 0.186(2)  | 0.216(3)   | 9(1)                                     |
| C(23) | 0.067(2)   | 0.172(1)  | 0.180(3)   | 7(1)                                     |

**Table IV. Selected Bond Lengths (Å) and Angles (°) for  $\text{I}_3\text{Ga}\cdot\text{As}(\text{SiMe}_3)_3$  (4), with Estimated Standard Deviations in Parentheses**

---

| <b>Bond Lengths</b> |          |              |          |
|---------------------|----------|--------------|----------|
| As-Ga               | 2.423(7) | Ga-I(1)      | 2.552(6) |
| As-Si(1)            | 2.33(2)  | Ga-I(2)      | 2.524(6) |
| As-Si(2)            | 2.37(2)  | Ga-I(3)      | 2.528(6) |
| As-Si(3)            | 2.38(2)  |              |          |
| <b>Bond Angles</b>  |          |              |          |
| Ga-As-Si(1)         | 109.0(5) | As-Ga-I(1)   | 108.8(2) |
| Ga-As-Si(2)         | 109.2(5) | As-Ga-I(2)   | 109.3(2) |
| Ga-As-Si(3)         | 109.3(5) | As-Ga-I(3)   | 109.4(2) |
| Si(1)-As-Si(2)      | 109.6(6) | I(1)-Ga-I(2) | 109.3(2) |
| Si(1)-As-Si(3)      | 110.2(6) | I(1)-Ga-I(3) | 109.8(2) |
| Si(2)-As-Si(3)      | 109.6(6) | I(2)-Ga-I(3) | 110.2(3) |

---

**Table V. Selected Bond Lengths (Å) and Angles (°) for [I<sub>2</sub>GaAs(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (5), with Estimated Standard Deviations in Parentheses**

---

| <b>Bond Lengths</b> |          |         |          |
|---------------------|----------|---------|----------|
| As-Ga               | 2.466(4) | As-Ga'  | 2.476(3) |
| As-Si(1)            | 2.384(8) | Ga-I(1) | 2.537(3) |
| As-Si(2)            | 2.374(7) | Ga-I(2) | 2.538(4) |

| <b>Bond Angles</b> |          |              |          |
|--------------------|----------|--------------|----------|
| Ga-As-Ga'          | 88.0(1)  | As-Ga-As'    | 92.0(1)  |
| Si(1)-As-Si(2)     | 111.4(3) | I(1)-Ga-I(2) | 105.4(1) |
| Ga-As-Si(1)        | 113.2(2) | Ga-As-Si(2)  | 112.6(2) |
| Ga'-As-Si(1)       | 113.5(2) | Ga'-As-Si(2) | 116.3(2) |
| As-Ga-I(1)         | 114.8(1) | As-Ga-I(2)   | 114.7(1) |
| As'-Ga-I(1)        | 114.1(1) | As'-Ga-I(2)  | 115.9(1) |

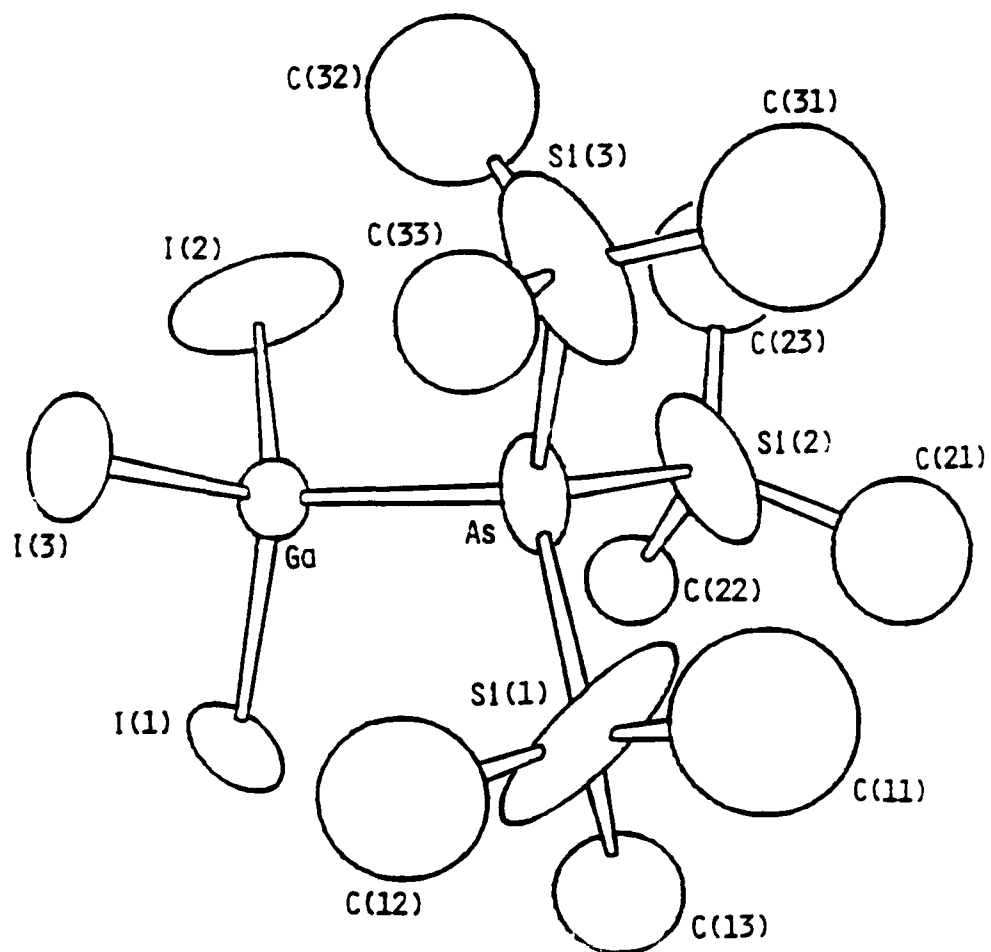
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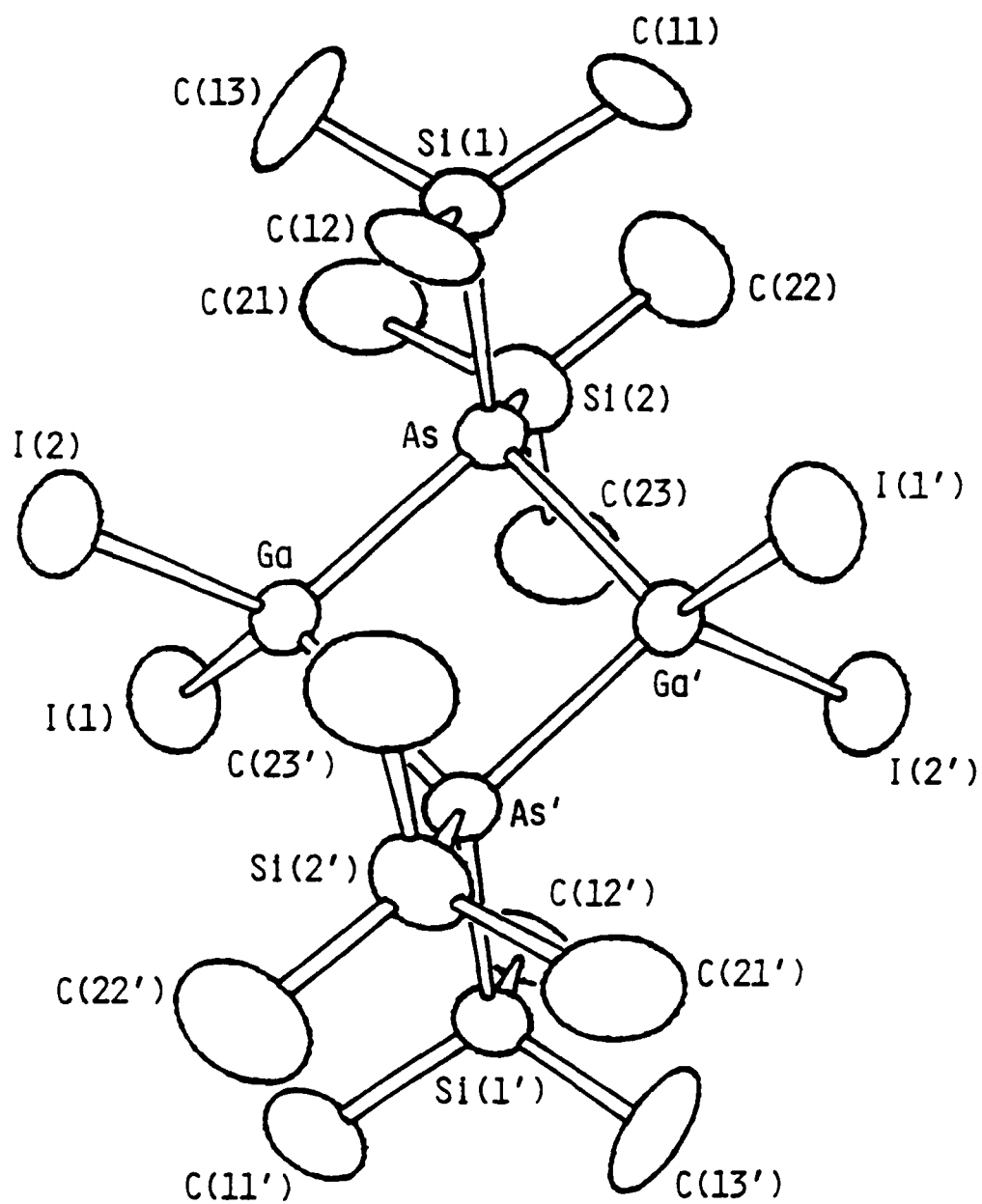


### Captions to Figures

**Figure 1. ORTEP diagram (40% probability ellipsoids) showing the atom numbering scheme and solid-state conformation of  $\text{I}_3\text{Ga}\cdot\text{As}(\text{SiMe}_3)_3$ ; hydrogen atoms have been omitted for clarity.**

**Figure 2. ORTEP diagram (50% probability ellipsoids) showing the atom numbering scheme and solid-state conformation of  $[\text{I}_2\text{GaAs}(\text{SiMe}_3)_3]_2$  (5); primed atoms are related to unprimed atoms by a crystallographic center of symmetry. Hydrogen atoms have been omitted for clarity.**





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