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The use of silylarsines to prepare gallium–arsenic compounds

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CONTENTS

A. INTRODUCTION

In recent years, after a hiatus of approximately two decades, there has been a noticeable spate of activity in the area of gallium-arsenic chemistry, some of which was prompted by the search for new gallium arsenide (GaAs) precursors [1]. As a result, a number of new compounds containing this elemental combination have been reported, some of which were prepared by the method wherein a secondary or a primary arsine reacts with a tri(organo)gallium compound to afford a hydrocarbon with concomitant formation of the gallium–arsenic bond. First utilized by Coates and co-workers to prepare two mono(arsino)gallanes (eqn. (1)) [2,3] and substances described by them as polymers (eqn. (2)) [3], this mode of preparation is now often

$$R_2AsH + Me_3Ga \rightarrow \frac{1}{n}(R_2AsGaMe_2)_n + CH_4 \tag{1}$$

$$R = Me;\ n = 3 \text{ (from mol. wt.)}$$

$$R = Ph;\ n = 2 \text{ (from mol. wt.)}$$

$$RAsH_2 + Me_3Ga \rightarrow \text{polymers} + CH_4 \tag{2}$$

$$R = Me, Ph$$

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referred to as the 'Coates method' or the 'alkane/arene elimination reaction'. Among the new compounds prepared by this method in the 1980s are two which were isolated in our laboratories, $[(Me_3SiCH_2)_2AsGaPh_2]_2$ (eqn. (3)) [4] and $\{(PhAsH)[(Me_3SiCH_2)_2Ga](PhAs)_6(Me_3SiCH_2Ga)_4\}$ (eqn. (4)) [5], the first dimeric

$$(Me_3SiCH_2)_2AsH + Ph_3Ga \rightarrow \frac{1}{2} [(Me_3SiCH_2)_2AsGaPh_2]_2 + C_6H_6 \quad (3)$$

$$PhAsH_2 + (Me_3SiCH_2)_3Ga \rightarrow (PhAs)_6 + Me_4Si + H_2$$
$$+ \{(PhAsH)[(Me_3SiCH_2)_2Ga](PhAs)_6(Me_3SiCH_2Ga)_4\} \quad (4)$$

mono(arsino)gallane and gallium–arsenic cluster, respectively, to be structurally characterized by single-crystal X-ray analysis. Nevertheless, in our hands, this method became impractical (eqn. (5)), and eventually failed (eqn. (6)) [6], as the steric bulk of the substituents on the gallium and arsenic was increased. Moreover, the fact that

$$Ph_2AsH + (Me_3SiCH_2)_3Ga \rightarrow \text{impure } [Ph_2AsGa(CH_2SiMe_3)_2]_n + (PhAs)_2$$
$$+ Me_4Si + H_2 + \text{unreacted } (Me_3SiCH_2)_3Ga \quad (5)$$

$$(Me_3SiCH_2)_2AsH + (Me_3SiCH_2)_3Ga \nrightarrow (Me_3SiCH_2)_2AsGa(CH_2SiMe_3)_2 \quad (6)$$

bis- and tris(arsino)gallanes, $[(R_2As)_{3-x}GaR_x]_n$ ($x = 1, 0$, respectively) were inaccessible by this route (eqn. (7)) [6] led us to examine alternative preparative methods.

$$2Ph_2AsH + Me_3Ga \rightarrow \frac{1}{n} (Ph_2AsGaMe_2)_n + CH_4 + Ph_2AsH \quad (7)$$

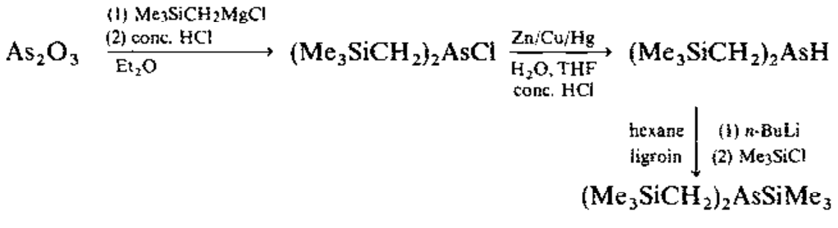
To this end, in 1986, we reported the initial use of dehalosilylation between a silylarsine and a halogallane to form the gallium–arsenic bond [6] and, during ensuing years, we have exploited the utility of this type of reaction (eqn. (8)) to prepare a number of novel gallium–arsenic systems.

$$R_2AsSiMe_3 + R'_2GaX \rightarrow \frac{1}{n} (R_2AsGaR'_2)_n + Me_3SiX \quad (8)$$

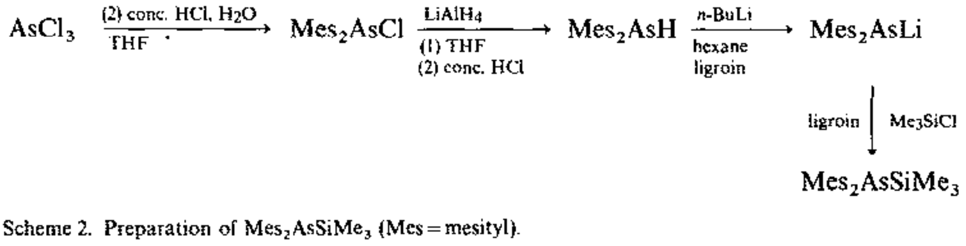
In this review, there will be an emphasis on this specific use of silylarsines and the compounds derived therefrom; however, some attention will be given to another method of synthesis pioneered in our laboratories, viz. lithium halide elimination between a lithium arsenide and a halogallane (eqn. (9)) [7].

$$R_2AsLi + R'_2GaX \rightarrow \frac{1}{n} (R_2AsGaR'_2)_n + LiX \quad (9)$$

Our research involving the preparation of gallium–arsenic compounds has required a variety of specific new organoarsenic starting materials, including primary and secondary arsines which, when necessary, could be converted to silylarsines. Thus, certain synthetic procedures had to be developed to meet these needs. Of course, all of the attempts to synthesize desired materials were not productive and, at times, side reactions were significant. For example, reduction of $(Me_3SiCH_2)_2AsCl$ with Zn amalgam in refluxing MeOH resulted in an extremely poor yield of $(Me_3SiCH_2)_2AsH$, but gave $(Me_3SiCH_2)_2AsAs(CH_2SiMe_3)_2$ in a 60% yield [6]. On the other hand, reduction of the same chloride with a Zn/Cu amalgam in an $HCl_{(aq)}$/THF solution at room temperature afforded the secondary arsine in 86% yield [4]. In the case of $Me_3SiCH_2AsH_2$, we were successful in designing a satisfactory overall scheme for its preparation (47% yield) [8] only after trying other much less rewarding procedures. For example, reaction of Me_3SiCH_2MgCl with As_2O_3 (2:1 mole ratio) in ether, followed by reduction with Zn/Cu amalgam, produced $Me_3SiCH_2AsH_2$ in only 4% yield and $(Me_3SiCH_2)_2AsH$ in 60% yield [9]. The routes developed by us to prepare $(Me_3SiCH_2)_2AsSiMe_3$, $Mes_2AsSiMe_3$ (Mes = mesityl) [6], $Me_3SiCH_2As(SiMe_3)_2$ [8], and $(Me_3Si)_2As(CH_2)_3As(SiMe_3)_2$ [10] are presented in Schemes 1–4, respectively. References to precedence for these routes may be found in the papers where the syntheses first appeared [6,8,10]. The methods used in our laboratories to prepare $As(SiMe_3)_3$ and $LiAs(SiMe_3)_2$ are those reported by Becker et al. [11] and are shown in Scheme 5 and as part of Scheme 4, respectively. ***Caution: tris(trimethylsilyl)arsine (TTMSA), $As(SiMe_3)_3$, is a pyrophoric liquid with a very disagreeable***



Scheme 1. Preparation of $(Me_3SiCH_2)_2AsSiMe_3$.



Scheme 2. Preparation of $Mes_2AsSiMe_3$ (Mes = mesityl).

$$\begin{tikzcd}[column sep=small]
AsCl_3 \arrow[r, "Et_3N"] & ClAs(NEt_2)_2 \arrow[r, "Me_3SiCH_2MgCl", "Et_2O"'] & Me_3SiCH_2As(NEt_2)_2 \arrow[r, "conc.\ HCl"] & Me_3SiCH_2AsCl_2 \arrow[d, "LiAlH_4", "Et_2O"'] \\
 & & Me_3SiCH_2As(SiMe_3)_2 & Me_3SiCH_2AsH_2 \arrow[l, "(1)\ n\text{-}BuLi \\ (2)\ Me_3SiCl"', "THF"]
\end{tikzcd}$$

Scheme 3. Preparation of $Me_3SiCH_2As(SiMe_3)_2$.

$$As(SiMe_3)_3 \xrightarrow[THF]{MeLi} LiAs(SiMe_3)_2 \cdot 2THF \xrightarrow[pentane]{Cl(CH_2)_3Cl} (Me_3Si)_2As(CH_2)_3As(SiMe_3)_2$$

Scheme 4. Preparation of $(Me_3Si)_2As(CH_2)_3As(SiMe_3)_2$.

$$As \xrightarrow[DME]{Na/K\ alloy} \text{“}Na_3As/K_3As\text{”} \xrightarrow{Me_3SiCl} As(SiMe_3)_3$$

Scheme 5. Preparation of $As(SiMe_3)_3$.

odor and should be handled with the assumption that it is toxic. In general, it is best to assume that all arsines and lithium arsenides are, to some extent, air-sensitive and toxic; thus, they should be handled with extreme care using appropriate equipment.

C. REACTIONS OF $(Me_3SiCH_2)_2AsSiMe_3$ AND $Mes_2AsSiMe_3$ (Mes = MESITYL)

Reactions of halogallanes with secondary trimethylsilylarsines, $R_2AsSiMe_3$, proceed readily in hydrocarbon solvents to produce oligomeric mono- and bis (arsino)gallanes and, in one case, a monomeric tris(arsino)gallane (eqns. (10)–(14)) [6,9,12]. Most of these reactions occur readily at room temperature, and the only

$$R_2AsSiMe_3 + GaX_3 \rightarrow \frac{1}{n}(R_2AsGaX_2)_n + Me_3SiCl \tag{10}$$

$$R = Me_3SiCH_2;\ X = Cl\ (\mathbf{1}),\ Br\ (\mathbf{2});\ n = 3$$

$$R = Mes;\ X = Cl\ (\mathbf{3});\ n = ?$$

$$(Me_3SiCH_2)_2AsSiMe_3 + RGaCl_2 \rightarrow \frac{1}{2,3}[(Me_3SiCH_2)_2AsGa(Cl)R]_{2,3} + Me_3SiCl \tag{11}$$

$$R = Me\ (\mathbf{4}),\ Ph\ (\mathbf{5})$$

$$(Me_3SiCH_2)_2AsSiMe_3 + Me_2GaCl \rightarrow \frac{1}{2,3}\underset{\mathbf{6}}{[(Me_3SiCH_2)_2AsGaMe_2]_{2,3}}$$

$$+ Me_3SiCl \tag{12}$$

$$2R_2AsSiMe_3 + GaX_3 \rightarrow \frac{1}{n}[(R_2As)_2GaX]_n + 2Me_3SiCl \qquad (13)$$

$R = Me_3SiCH_2$; $X = Cl$ (**7**), Br (**8**); $n = 2$

$R = Mes$; $X = Cl$ (**9**); $n = ?$

$$\underset{\mathbf{9}}{Mes_2AsSiMe_3 + \frac{1}{n}[(Mes_2As)_2GaCl]_n} \rightarrow \underset{\mathbf{10}}{(Mes_2As)_3Ga} + Me_3SiCl \qquad (14)$$

by-product of such dehalosilylation reactions, Me_3SiCl, is easily removed in vacuo, a considerable advantage when handling these air-sensitive materials. Lack of suitable crystals and the very low solubility of **3** and **9**, also prepared from Mes_2AsLi and $GaCl_3$ [7], prohibited determination of their degree of oligomerization.

The trimeric formulation of **1** and **2** is based on cryoscopic molecular weight determinations and, in the case of **2**, a crystal structure which showed this trimeric mono(arsino)gallane contains a $(Ga–As)_3$ ring (Fig. 1, *i*) in the twist-boat conformation [13]. Recently, some of the structural features of **2** have been compared with other trimers containing various combinations of elements from Groups III and V [1]. The cryoscopic molecular weights of white, crystalline (mono)arsinogallanes **4–6** revealed that each has a degree of association between 2 and 3. For **4** and **5**, the concentration dependence of the ^1H NMR spectra at 25°C confirmed the presence of dimer–trimer equilibria (eqn. (15)) [12].

$$3[(Me_3SiCH_2)_2AsGa(Cl)R]_2 \xrightleftharpoons{C_6D_5CD_3} 2[(Me_3SiCH_2)_2AsGa(Cl)R]_3 \qquad (15)$$

4, $\Delta G = -8.5 \pm 0.1$ kcal mol^{-1}
5, $\Delta G = -6.4 \pm 0.1$ kcal mol^{-1}

The predominant species for both compounds is the *trans* trimer (**4**, $\Delta G_{cis-trans} = -1.6 \pm 0.2$ kcal mol^{-1}; **5**, $\Delta G_{cis-trans} = -1.5 \pm 0.1$ kcal mol^{-1}); for the dimers, the *cis–trans* equilibrium constants equal 1 within experimental error.

The dimeric nature of the bis(arsino)gallanes **7** and **8** was also established by cryoscopic molecular weight determinations. In addition, a single-crystal X-ray analysis of **8** revealed the centrosymmetric, dimeric molecule (Fig. 1, *ii*) crystallizes in the *trans* configuration, with unequal endocyclic Ga–As distances [2.513(1) and 2.521(1) Å] and very significantly different bond angles [84.37(1) and 95.63(2)° at Ga and As, respectively] in the planar $(Ga–As)_2$ ring [12] (for a comparison of these structural features with those of other gallium–arsenic dimers, as well as related III–V dimers, see Table 1, below, and reference 1). In addition, we demonstrated that molecules of dimers **7** and **8** are fluxional and undergo an exchange of the endocyclic and exocyclic $(Me_3SiCH_2)_2As$ groups [6,12]. For compound **8**, a $^{13}C\{^1H\}$ dynamic NMR study revealed that, in addition to the interchange of the $(Me_3SiCH_2)_2As$

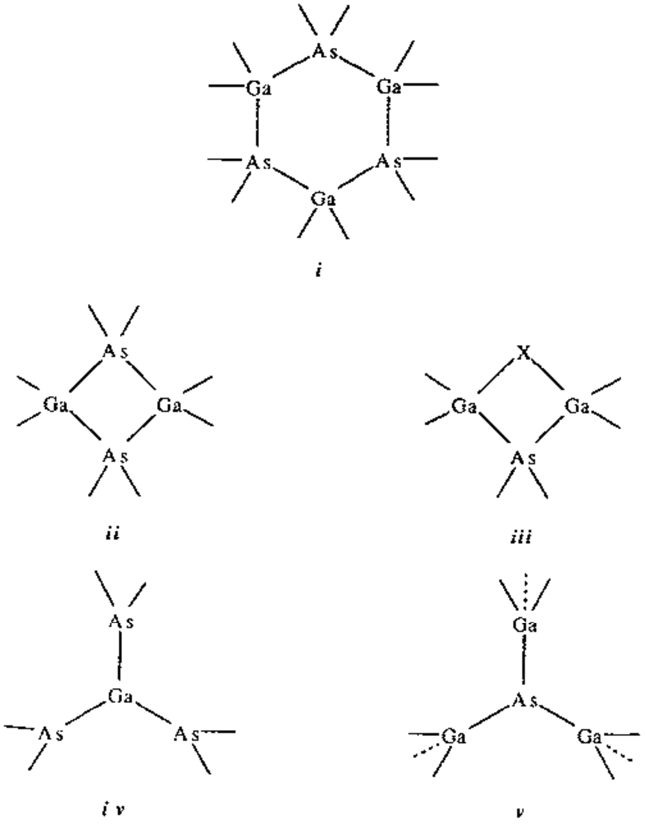
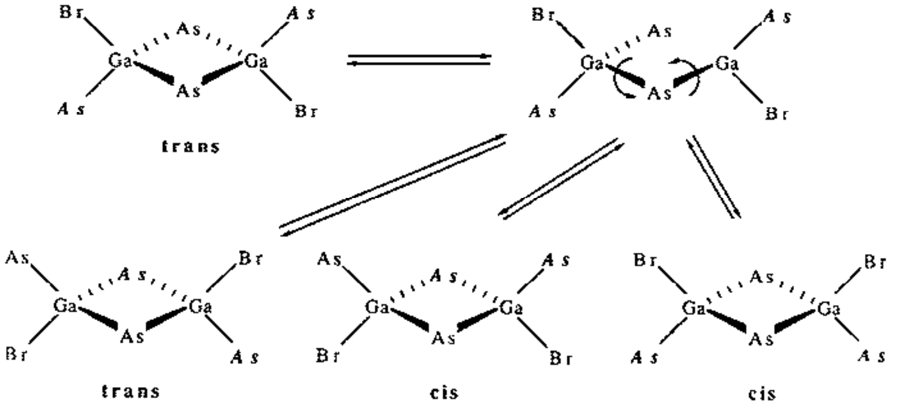


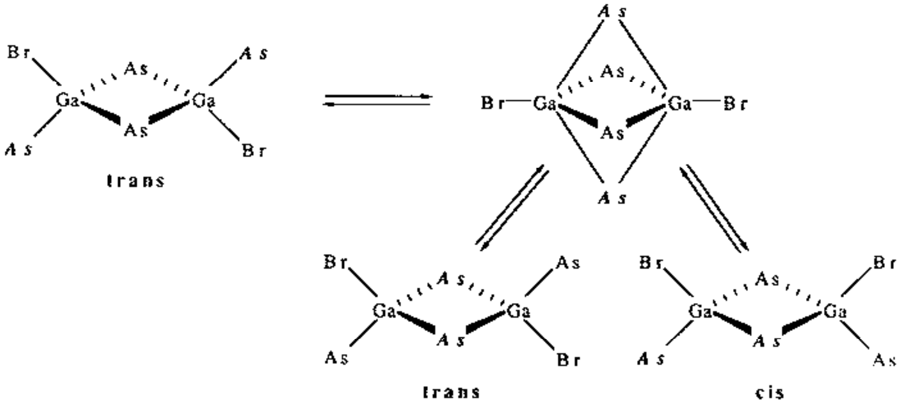
Fig. 1. Various cores of compounds which can be prepared using silylarsines. *i*, $(Ga–As)_3$ ring found in the twist-boat conformation in $[(Me_3SiCH_2)_2AsGaBr_2]_3$ (**2**). *ii*, $(Ga–As)_2$ ring found in the planar form in, for example, $\{[(Me_3SiCH_2)_2As]_2GaBr\}_2$ (**8**). *iii*, $\overline{Ga–As–Ga–X}$ ring found in the non-planar form in, for example, $Ph_2GaAs(SiMe_3)_2Ga(Ph)_2Cl$ (**20**); also found in the planar form (within experimental error) in $(Me_3CCH_2)_2GaAs(SiMe_3)_2Ga(CH_2CMe_3)_2Cl$ (**23**). *iv*, As_3Ga unit found in a nearly trigonal-planar configuration in $(Mes_2As)_3Ga$ (**10**). *v*, Ga_3As unit found in a pyramidal configuration in $As[GaBr_2(THF)]_3$ (**19**).

groups ($\Delta H^{\ddagger} = 18.7 \pm 0.3$ kcal mol^{-1}; $\Delta S^{\ddagger} = 4.5 \pm 1.0$ cal mol^{-1} K^{-1}), a *trans–cis* isomerization takes place ($\Delta H^{\ddagger} = 17.4 \pm 0.7$ kcal mol^{-1}; $\Delta S^{\ddagger} = -2.2 \pm 2.1$ cal mol^{-1} K^{-1}). Schemes 6 and 7 show possible mechanisms for these fluxional processes in **8** [12].

As indicated by eqn. (14), a dehalosilylation reaction also afforded compound **10**, a sterically hindered tris(arsino)gallane which was first prepared by us from Mes_2AsLi and $GaCl_3$ and shown to be monomeric by single-crystal X-ray analysis [7]. The gallium atom is bonded to the three arsenic atoms in a nearly trigonal-planar configuration and is positioned 0.149 Å out of the plane formed by the three arsenic atoms (Fig. 1, *iv*). The mean Ga–As bond length at 2.492(1) Å is somewhat



Scheme 6. Possible one-bond dissociative mechanism for the fluxional processes in $\{[(Me_3SiCH_2)_2As]_2GaBr\}_2$ (**8**).



Scheme 7. Possible associative mechanism for the fluxional processes in $\{[(Me_3SiCH_2)_2As]_2GaBr\}_2$ (**8**).

longer than the Ga–As distances at 2.433(4) and 2.466(3) Å, respectively, in the monomeric mono(arsino)gallanes $(Me_3Si)_2AsGa(C_5Me_5)_2$ (**11**) [14] and $(t\text{-}Bu)_2AsGa(t\text{-}Bu)_2$ (**12**) [15].

Interestingly, the dehalosilylation method did not yield the tris(arsino)gallane $\{[(Me_3SiCH_2)_2As]_3Ga\}_2$ (**13**); however, it was prepared using a lithium chloride elimination reaction and shown by single-crystal X-ray analysis to exist as the dimer (i.e. $n=2$) [16]. The mean ring bond angles in **13** (83.81° at Ga, 95.30° at As) are similar to those in other gallium–arsenic dimers (see Table 1, below); however, it differs in that it contains a distinctly non-planar four-membered ring of alternating four-coordinate gallium and arsenic atoms (mean dihedral angle about the ring bonds of 10.2° (Table 1); dihedral angle of 13.6° between the As(1)–Ga–As(1′) and As(1)–

Ga′–As(1′) planes [16]). Cryoscopic molecular weight determinations indicated that **13** remains intact as a dimer in solution at low temperatures; however, it is fluxional in solution as indicated by broadening and eventual coalescence of ^{13}C NMR signals as the temperature is increased [16].

It is also of interest to note here that only four bis(arsino)gallanes and three tris(arsino)gallanes have been prepared and studied, even though there is considerable evidence that compounds of these two types have quite interesting properties. The former are compounds **7–9**, and $\{[(Me_3SiCH_2)_2As]_2GaPh\}_2$ (**14**) (prepared from $(Me_3SiCH_2)_2AsLi$ and $PhGaCl_2$ [9]); the latter are compounds **10**, **13**, and $(t\text{-}Bu_2As)_3Ga$ (**15**) (prepared by Cowley and co-workers from $t\text{-}Bu_2AsLi$ and $GaCl_3$ [17]). In addition to the fluxionality of three of the seven (**7**, **8** and **13**, see below), five of them (**7**, **8**, **10**, **13** and **14**) are known to be unstable in solution at room temperature and above, and each decomposes to a diarsine as well as other products [6,9,12,16]. The thermal decomposition of the dimeric bis(arsino)gallanes **7**, **8** and **14** affords $(Me_3SiCH_2)_2AsAs(CH_2SiMe_3)_2$ in each case along with the trimeric mono(arsino)gallanes **1**, and **2** and the dimer $[(MeSiCH_2)_2AsGaPh_2]_2$, respectively (eqn. (16)). For dimeric tris(arsino)gallane **13**, decomposition results in a dark red solution containing the same diarsine and some other unidentified product(s); whereas, monomer **10** decomposes to a dark red solution containing $Mes_2AsAsMes_2$, as well as a yellow-brown precipitate (eqn. (17)). Furthermore, it has been shown that two of the tris(arsino)gallanes, **13** and **15**, can be converted at room temperature to dimeric mono(arsino)gallanes as exemplified by eqns. (18) and (19) [9,18]. Significantly, Cowley and Jones have also shown that this method can be utilized to prepare

$$\{[(Me_3SiCH_2)_2As]_2GaX\}_2 \rightarrow [(Me_3SiCH_2)_2As]_2 + \text{gray/black powder} + \frac{1}{n}[(Me_3SiCH_2)_2AsGaX_2]_n \qquad (16)$$

$X = Cl$ (**7**) $\qquad X = Cl, n = 3$ (**1**)

$X = Br$ (**8**) $\qquad X = Br, n = 3$ (**2**)

$X = Ph$ (**14**) $\qquad X = Ph, n = 2$

$$\frac{1}{n}[(R_2As)_3Ga]_n \rightarrow (R_2As)_2 + \text{other unidentified product(s)} \qquad (17)$$

$R = Mes, n = 1$ (**10**)

$R = Me_3SiCH_2, n = 2$ (**13**)

$$\{[(Me_3SiCH_2)_2As]_3Ga\}_2 + 4R_3Ga \rightarrow 3[(Me_3SiCH_2)_2AsGaR_2]_2 \qquad (18)$$

13 $\qquad R = Ph, Me_3SiCH_2$

$$2(t\text{-}Bu_2As)_3Ga + 4R_3Ga \rightarrow 3(t\text{-}Bu_2AsGaR_2)_2 \qquad (19)$$

15 $\qquad R = Me, Et$

some mixed-metal four-membered ring compounds, for example, $Me_2Ga(\mu\text{-}As\text{-}t\text{-}Bu_2)_2AlMe_2$ [1].

D. REACTIONS OF $Me_3SiCH_2As(SiMe_3)_2$ AND $(Me_3Si)_2As(CH_2)_3As(SiMe_3)_2$

Reactions of halogallanes with primary trimethylsilylarsines, $RAs(SiMe_3)_2$, also proceed quite readily in hydrocarbon solvents (eqns. (20) and (21)) [9,8]; however, in most cases, the isolation and characterization of the resulting gallium–arsenic

$$Me_3SiCH_2As(SiMe_3)_2 + GaCl_3 \rightarrow \frac{1}{n}\,(Me_3SiCH_2AsGaCl)_n + 2Me_3SiCl \qquad (20)$$

16

$$Me_3SiCH_2As(SiMe_3)_2 + PhGaCl_2 \rightarrow \frac{1}{n}\,(Me_3SiCH_2AsGaPh)_n + 2Me_3SiCl \qquad (21)$$

17

compounds/species has proven to be much more difficult than was found in the preceding studies. Although a completely 'satisfactory elemental analysis' (C, H, Cl) was not obtained for yellow compound **16**, and its ^1H NMR is complex, the available data strongly support the formula shown in eqn. (20). All attempts to obtain single crystals met with failure. Similarly, we were unable to satisfactorily/completely characterize compound **17**, a colorless sticky material. Nevertheless, its ^1H NMR spectrum compared favorably with that obtained for the apparently impure yellow solid which was produced by heating $[Me_3SiCH_2(H)AsGaPh_2]_3$ to eliminate C_6H_6 [8].

In analogy to our synthesis of mono-mixed-bridge compounds (discussed in Sect. E, below), we found that reaction of a specific bisarsine with four equivalents of Ph_2GaCl in benzene yields a bis-mixed-bridge compound (**18**) (eqn. (22)) [10]. Along with the stoichiometric amount of Me_3SiCl, unique compound **18** was obtained

$$(Me_3Si)_2As(CH_2)_3As(SiMe_3)_2 + 4Ph_2GaCl$$

$$\rightarrow Ph_2\overline{GaCl(Ph)_2Ga(Me_3Si)As}(CH_2)_3\overline{As(SiMe_3)Ga(Ph)_2ClGa}Ph_2 + 2Me_3SiCl \qquad (22)$$

18

as very fine, whisker-like colorless crystals from ligroin and as a solvate from toluene, neither of which has yet proved suitable for structural characterization by X-ray crystallography. However, a number of pieces of convincing evidence attest to the fact that it is a pure single compound and its correct formulation is that shown in eqn. (22) and Fig. 2. Compound **18** melts at 181–182°C with decomposition, gave a satisfactory elemental analysis (C, H), and its NMR spectra are readily interpreted.

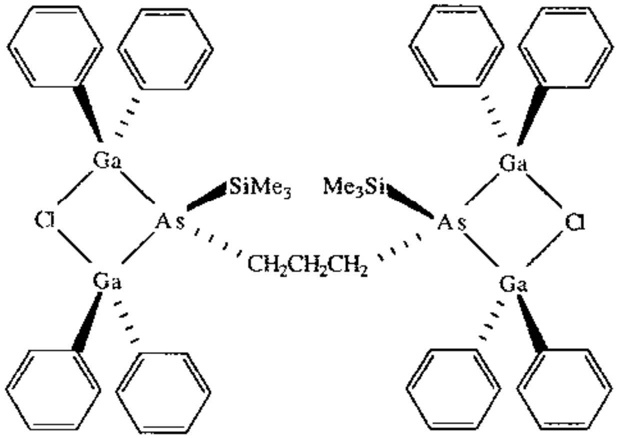


Fig. 2. Proposed structure for compound 18.

Briefly stated, the positions and corresponding integrations of the ^1H NMR signals argue for a proton stoichiometry as formulated, and the $^{13}C\{^1H\}$ NMR spectrum, particularly the fact that eight phenyl carbon signals are observed, is consistent with the proposed idealized C_{2v} symmetry structure shown in Fig. 2. In this structure there are two types of phenyl groups, those proximal and those distal to the trimethylsilyl groups, each of which has four different types of carbons, assuming that there is free rotation about the Ga–C_{ipso} bonds.

E. REACTIONS OF $As(SiMe_3)_3$

One of the processes commonly used for the epitaxial growth of GaAs is organometallic chemical vapor deposition (OMCVD) and, in this process, it has been the general practice to utilize an alkane elimination reaction, as exemplified by eqn. (23). However, concerns regarding the use of AsH_3 and high reaction temperatures have prompted the evaluation of other sources of arsenic, as well as various single-source precursors [1,14,15]. Having demonstrated that dehalosilylation reactions are a facile route to the formation of the Ga–As covalent bond, we subsequently applied this method of synthesis to the preparation of GaAs using tris(trimethylsilyl)arsine (TTMSA), $As(SiMe_3)_3$ (eqn. (24)) [19,20]. We indeed found that

$$AsH_3 + Me_3Ga \xrightarrow[\sim 700\,^\circ C]{H_2} GaAs + 3CH_4 \tag{23}$$

$$As(SiMe_3)_3 + GaX_3 \rightarrow GaAs + 3Me_3SiX \quad (X = Cl, Br) \tag{24}$$

reactions between TTMSA and either $GaCl_3$ or $GaBr_3$ in hydrocarbon solvents proceed at relatively low temperatures (the latter less readily) to eliminate Me_3SiX with the concurrent formation of GaAs. This viable route allowed the isolation of GaAs in 88–96% purity (based on elemental analyses) from very crude experiments with no attempts to optimize the reaction conditions. Significantly, there is a low incorporation of silicon relative to carbon and halogen in the GaAs so produced.

Properly sized clusters/crystallites of the semiconductor GaAs are expected to exhibit a range of interesting and useful properties, among them being superior non-linear optical qualities [21–23]. Notwithstanding this potential, schemes for the facile synthesis and isolation of such particulates had not been forthcoming until recently. In 1990, Alivisatos and co-workers reported [24] that GaAs nanocrystals are, in fact, produced by the dehalosilylation reaction (eqn. (24)) as initially carried out in our laboratories. Furthermore, in some very important experiments, they demonstrated that the same reaction carried out in quinoline afforded somewhat smaller crystallites which are soluble in pyridine as well as in quinoline [24].

Although the transformation described by eqn. (24) affords a relatively straightforward route to GaAs, both reactants must be manipulated in an inert atmosphere using appropriate equipment and laboratory techniques. Thus, safer, less moisture- and air-sensitive precursors could well prove more useful and facilitate investigation of microcrystalline GaAs by those who may otherwise have to forego such studies due to the hazards and handling difficulties intrinsic to many gallium and arsenic compounds. Recently, we showed that $GaCl_3$ and TTMSA mixed in either a 2:1 or a 3:1 mole ratio react at room temperature to yield, in each case, the same relatively stable yellow solid product having the empirical formula $AsCl_3Ga_2$ (eqn. (25)) [25]. Upon heating, new single-source precursor $(AsCl_3Ga_2)_n$ eliminates $GaCl_3$ via a novel

$$As(SiMe_3)_3 + 2GaCl_3 \rightarrow \frac{1}{n}(AsCl_3Ga_2)_n + 2Me_3SiCl \tag{25}$$

reaction pathway to give microcrystalline GaAs (eqn. (26)) [25].

$$\frac{1}{n}(AsCl_3Ga_2)_n \rightarrow GaAs + GaCl_3 \tag{26}$$

Furthermore, we have now reported that CVD experiments using TTMSA with either $GaCl_3$ or Me_3Ga at ambient pressure have produced films of GaAs on Si and semi-conducting GaAs substrates [26]. The films were characterized by X-ray diffraction and Auger electron spectroscopy, and each has small amounts of carbon and oxygen impurities with no evidence for silicon or chlorine being found. Note that for the Me_3Ga reaction, the other product is tetra(methyl)silane; thus, we have demonstrated that a gas-phase dealkylsilylation can also be used to produce GaAs.

Finally, it should be noted that, as a part of all of these studies, we also demonstrated that other arsenic-containing III–V alloys could be produced via dehalosilylation reactions; thus, reaction of TTMSA with MCl_3 (M = Al, In) affords MAs [19,20].

As mentioned in Sects. A and C, there were no published examples of compounds containing a single As_3Ga unit prior to 1986. Our search of the literature revealed this also to be true for compounds containing the opposite formulation, i.e. Ga_3As. However, during that year, two compounds of the first type having three-coordinate gallium and three-coordinate arsenic were reported (compounds **10** and **15**). It was not until the following year that we were able to isolate and structurally characterize a compound of the second type having, in this initial case, four-coordinate gallium and three-coordinate arsenic as shown by a complete crystal structure, $As[GaBr_2(THF)]_3$ (**19**) (eqn. (27)), Fig. 1, *v*) [27].

$$As(SiMe_3)_3 + 3GaBr_3 \xrightarrow[(2)\,THF]{(1)\,Toluene} \underset{\mathbf{19}}{As[GaBr_2(THF)]_3} + 3Me_3SiBr \qquad (27)$$

Interestingly, this reaction was actually the first reported use of a tris(silyl)arsine to form the Ga As linkage, yet **19** is the only known example of a tris(gallyl)arsine.

Our considerable efforts to prepare another unknown class of gallium–arsenic compounds, bis(gallyl)arsines of general formula $RAs(GaR'_2)_2$, have been as yet unsuccessful. Nevertheless, these particular studies have been very fruitful in that we have found routes to what now appears to be another general class of gallium–arsenic compounds, viz. arsenic, halogen mixed-bridge compounds. Although four-membered ring formation is known to occur via bridging of gallium centers by two arsenic atoms [1] or two halogen atoms (for a general discussion, see ref. 28) (Table 1), there were no reports of this occurring through one of each of these atoms prior to our communications in 1989 and 1990 [29,30]. We reported the complete characterization, including crystal structures, of two compounds containing four-membered rings with arsenic, halogen mixed bridging of gallium centers, $Ph_2\overline{GaAs(SiMe_3)_2Ga(Ph)_2X}$ {X = Cl (**20**) [29,30], Br (**21**) [30]} (Fig. 1, *iii*), obtained by dehalosilylation reactions between $As(SiMe_3)_3$ and Ph_2GaCl or Ph_2GaBr, respectively. Subsequently, we used the same method to prepare the trimethylsilylmethyl (Me_3SiCH_2) [31] (Fig. 3), and the *neo*-pentyl (Me_3CCH_2) [32] analogs of **20** (eqn. (28)).

$$As(SiMe_3)_3 + 2R_2GaX \rightarrow R_2\overline{GaAs(SiMe_3)_2Ga(R)_2X} + Me_3SiCl \qquad (28)$$

R = Ph; X = Cl (**20**), Br (**21**)

R = Me_3SiCH_2 (**22**), Me_3CCH_2 (**23**); X = Cl

As indicated in eqn. (28) when TTMSA reacts with the halogallanes in a 1 : 2 mole ratio at room temperature, mixed-bridge species are produced, each corresponding to the elimination of only one equivalent of Me_3SiX. Even the reaction of TTMSA

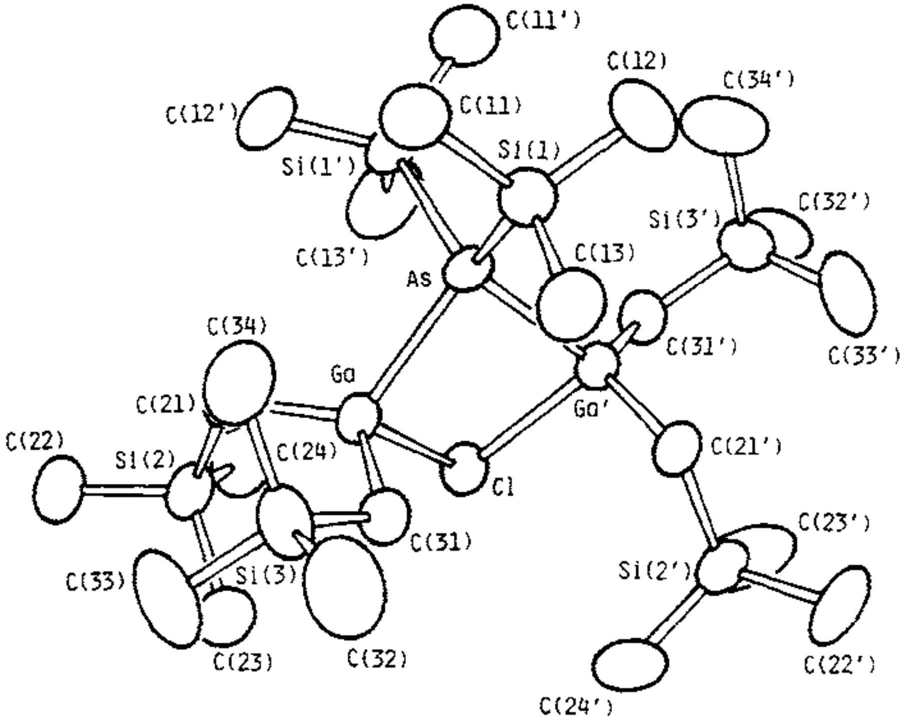


Fig. 3. ORTEP diagram of $(\mathrm{Me_3SiCH_2})_2\overline{\mathrm{GaAs(SiMe_3)_2Ga(CH_2SiMe_3)_2Cl}}$ (22) showing the solid state configuration. (Hydrogen atoms have been omitted for clarity.)

with $\mathrm{Ph_2GaCl}$ in a 1:3 mole ratio at room temperature affords **20** as the predominant product. This latter behavior is interesting since it contrasts with that involved in the formation of **19**, which corresponds to elimination of three equivalents of $\mathrm{Me_3SiBr}$. That compounds **20–23** do not eliminate a second equivalent of $\mathrm{Me_3SiX}$ at room temperature to produce the bis(gallyl) compounds, $\mathrm{(R_2Ga)_2AsSiMe_3}$, can be rationalized by assigning formal charges to the ring atoms. A positive formal charge on the arsenic atom is expected to increase the reactivity of the attached silicon atoms toward negatively charged species. A halogen atom bridging two gallium centers is assigned a positive formal charge and therefore would not be expected to react with the silicon. This reasoning must rule out the possible ionic solution species, $\mathrm{(R_2Ga)_2As(SiMe_3)_2^+X^-}$, since the $\mathrm{X^-}$ ion would be expected to attack the silicon atoms easily through its unoccupied 3d orbitals. An intermediate in the formation of the tris(gallyl) compound **19** with a structure analogous to that found in compounds **20–23**, but having R groups replaced by bromine atoms, appears reasonable. This intermediate would contain singly coordinate bromine atoms activated for attack on the silicon atoms by the negative formal charges on the gallium atoms, leading to formation of $\mathrm{(Br_2Ga)_2AsSiMe_3}$. Attack of the latter by another mole of $\mathrm{GaBr_3}$ to create another mixed-bridge intermediate, followed by elimination of the last equivalent of Me_3SiBr, could give **19**. In order to produce singly coordinate halogen atoms out of compounds **20–23**, breaking of the bridging Ga–X–Ga′ bonds must occur, an event which would be endoenergic. Alternatively, dissociation of compounds **20–23** to give Ph_2GaX and $Ph_2GaAs(SiMe_3)_2$, followed by formation of Me_3SiX, may require an activation energy which is not overcome at room temperature.

Mixing TTMSA and the halogallane in a 1 : 1 mole ratio did not give the same results with each of the above three alkyl groups. For the case of Ph_2GaCl, a mixture of **20** and dimer $[(Me_3Si)_2AsGaPh_2]_2$ (**24**) was isolated after heating the 1 : 1 mole ratio combination of reactants at 76°C [29]. The presence of **24** is consistent with the observation that prolonged heating of **20** at 80°C produced a mixture of **24**, Me_3SiCl and unidentified products. On the other hand, for $(Me_3SiCH_2)_2GaCl$, the only gallium–arsenic species isolated was **22** after allowing this combination of reactants to stand at room temperature [31]; whereas, mixing $(Me_3CCH_2)_2GaCl$ and TTMSA in a 1 : 1: mole ratio gave the adduct $(Me_3CCH_2)_2Ga(Cl)\cdot As(SiMe_3)_3$ [32].

It has also been shown that the dimers **24**, **25** (Fig. 4), and **26**, prepared by

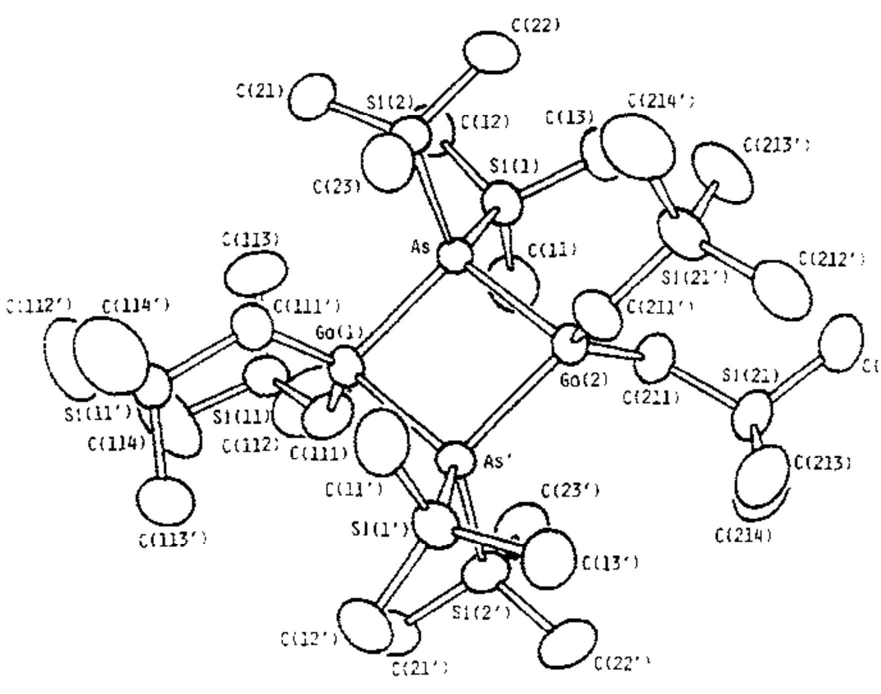


Fig. 4. ORTEP diagram of $[(Me_3Si)_2AsGa(CH_2SiMe_3)_2]_2$ (**25**) showing the solid state configuration. (Hydrogen atoms have been omitted for clarity.)

lithium halide elimination reactions (eqn. (29)) [29–32], react with their respective

$$\mathrm{LiAs(SiMe_3)_3 + R_2GaCl \rightarrow \frac{1}{2}\,[(Me_3Si)_2AsGaR_2]_2 + LiCl} \tag{29}$$

$\mathrm{R = Ph}$ (**24**)

$\mathrm{R = Me_3SiCH_2}$ (**25**)

$\mathrm{R = Me_3CCH_2}$ (**26**)

halogallanes (eqn. (30)) [29–32] to yield compounds **20**, **22** and **23**.

$$\mathrm{[(Me_3Si)_2AsGaR_2]_2 + 2R_2GaCl \rightarrow 2R_2\overline{GaAs(SiMe_3)_2Ga(R)_2Cl}} \tag{30}$$

(**24**) $\mathrm{R = Ph}$ (**20**)

(**25**) $\mathrm{R = Me_3SiCH_2}$ (**22**)

(**26**) $\mathrm{R = Me_3CCH_2}$ (**23**)

In addition, mixed-bridge **23** can be reconverted to dimer **26** by a lithium chloride elimination reaction (eqn. (31)) [32]. Also, in an effort to explore further the

$$\underset{\mathbf{23}}{\mathrm{(Me_3CCH_2)_2\overline{GaAs(SiMe_3)_2Ga(CH_2CMe_3)_2Cl}}} + \mathrm{LiAs(SiMe_3)_3}$$

$$\rightarrow \underset{\mathbf{26}}{\mathrm{[(Me_3Si)_2AsGa(CH_2CMe_3)_2]_2}} + \mathrm{LiCl} \tag{31}$$

method of preparing gallium–arsenic mixed-bidge compounds illustrated by eqn. (30), the reactions depicted in eqns. (32) and (33) were carried out in sealed NMR tubes and monitored by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy. In both cases,

$$\underset{\mathbf{24}}{\mathrm{[(Me_3Si)_2AsGaPh_2]_2}} + \mathrm{2(Me_3SiCH_2)_2GaCl}$$

$$\rightarrow \underset{\mathbf{27}}{\mathrm{Ph_2\overline{GaAs(SiMe_3)_2Ga(CH_2SiMe_3)_2Cl}}} + ? \tag{32}$$

$$\underset{\mathbf{25}}{\mathrm{[(Me_3Si)_2AsGa(CH_2SiMe_3)_2]_2}} + \mathrm{2Ph_2GaCl}$$

$$\rightarrow \underset{\mathbf{27}}{\mathrm{Ph_2\overline{GaAs(SiMe_3)_2Ga(CH_2SiMe_3)_2Cl}}} + ? \tag{33}$$

complete disappearance of the starting materials was observed within one hour of preparing the samples, and in neither reaction were the starting materials for the complementary reaction observed. Mixtures of products appeared to have formed and, while the available data were not conclusive, they nevertheless suggested that reactions (32) and (33) gave a common product believed to be that indicated as **27** [31].

X-ray crystallographic analyses showed that each of the compounds **20–22** contains a non-planar $\overline{\mathrm{Ga{-}As{-}Ga{-}X}}$ ring [29–31], whereas the ring of **23** is not puckered (within experimental error) [32], as exemplified by the mean dihedral angle about ring bonds for each compound. On the other hand, in common with most compounds containing the $\overline{\mathrm{Ga{-}As{-}Ga{-}As}}$ core, dimers **25** and **26** contain planar rings. Bond lengths, bond distances and, where appropriate, mean dihedral angles about ring bonds for these and selected compounds, are presented in Table 1. A list of all numbered compounds (**1–27**) appearing throughout this review is given in Table 2.

F. CONCLUDING COMMENTS

A number of gallium–arsenic compounds/systems have been realized by applying the general method of synthesis referrred to as dehalosilylation between a silylarsine and a halogallane. Among those prepared are bis- and tris(arsino)gallanes, with one of the latter being isolated as the monomer, a compound containing a single Ga_3As unit, and compounds containing rings with arsenic, halogen mixed bridging of gallium centers. Also, this method has been utilized to prepare gallium arsenide.

The methodologies developed in these studies are currently being applied to the synthesis of additional new gallium–arsenic compounds/systems, and they are finding much practicality in the synthesis of other related III–V species. For example, we have recently isolated and characterized the indium–arsenic compound $(Me_3SiCH_2)_2\overline{InAs(SiMe_3)_2In(CH_2SiMe_3)_2Cl}$ [36], as well as its phosphorus analog [37]. The fact that these two indium compounds can be prepared adds credence to our suggestion that mixed-bridge compounds may be common species in the area of chemistry involving the heavier elements of Groups III and V.

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TABLE 1

Bond lengths (Å), bond angles (deg), and dihedral angles about ring bonds (deg) for selected compounds

Compound	Mean endocyclic As–Ga bond length	Mean endocyclic Cl–Ga, Br–Ga bond length	Mean As–Si bond length	Mean dihedral angle about ring bonds	Endocyclic Ga–As–Ga angle(s)	Endocyclic Ga–Cl–Ga, Ga–Br–Ga angle(s)	Endocyclic As–Ga–Cl, As–Ga–As angle(s)	Exocyclic Si–As–Si angle	Ref.
$Ph_2\overline{GaAs(SiMe_3)_2Ga(Ph)_2Cl}$ (**20**)	2.466(2)	2.411(4)	2.363(4)	6.2	88.70(7)	91.3(1)	89.5(1) 89.8(1)	111.0(2)	29, 30
$Ph_2\overline{GaAs(SiMe_3)_2Ga(Ph)_2Br}$ (**21**)	2.465(1)	2.566(1)	2.365(2)	6.6	91.62(4)	87.10(4)	90.35(4) 90.21(4)	110.22(8)	30
$(Me_3SiCH_2)_2\overline{GaAs(SiMe_3)_2Ga(CH_2SiMe_3)_2Cl}$ (**22**)	2.504(1)	2.432(1)	2.348(2)	21.1	87.96(2)	91.33(4)	86.40(3) 85.53(3)	108.64(6)	31
$(Me_3CCH_2)_2\overline{GaAs(SiMe_3)_2Ga(CH_2CMe_3)_2Cl}$ (**23**)	2.521(1)	2.425(1)	2.358(1)	0.05	89.82(2)	94.41(4)	87.79(2) 87.98(3)	105.39(5)	32
$[(Me_3Si)_2AsGa(CH_2SiMe_3)_2]_2$ (**25**)	2.567(1)		2.357(2)		93.91(2)		85.85(3) 86.32(3)	103.66(6)	31
$[(Me_3Si)_2AsGa(CH_2CMe_3)_2]_2$ (**26**)	2.587(1)		2.363(2)		95.11(4) 94.84(4)		85.02(3)	102.32(7) 102.99(7)	32
$[(Me_3SiCH_2)_2AsGaPh_2]_2$	2.524(1)				94.92(2)		85.08(2)		4
$\{[(Me_3SiCH_2)_2As]_2GaBr\}_2$ (**8**)	2.517(1)				95.63(2)		84.37(2)		12
$\{[(Me_3SiCH_2)_2As]_3Ga\}_2$ (**13**)	2.555(1)			10.2	94.57(4) 96.02(4)		84.04(4) 83.58(4)		16
$[(Me_3Si)_2AsLi\cdot DME]$			2.307(7)					103.2(4)	33
$[Ga(C_5Me_5)_2Cl]_2$		2.448(7)				97.4(2)			34
$[Ga(C_5Me_5)Cl_2]_2$		2.363(3)				94.1(1)			34
$(GaCl_3)_2$		2.29(9)				86(2)			35

TABLE 2

Numbered compounds **1**–**27**

No.	Compound	Ref.
1	$[(\mathrm{Me_3SiCH_2})_2\mathrm{AsGaCl_2}]_3$	6
2	$[(\mathrm{Me_3SiCH_2})_2\mathrm{AsGaBr_2}]_3$	12
3	$(\mathrm{Mes_2AsGaCl_2})_n$	6
4	$[(\mathrm{Me_3SiCH_2})_2\mathrm{AsGa(Cl)Me}]_{2,3}$	12
5	$[(\mathrm{Me_3SiCH_2})_2\mathrm{AsGa(Cl)Ph}]_{2,3}$	12
6	$[(\mathrm{Me_3SiCH_2})_2\mathrm{AsGaMe_2}]_{2,3}$	9
7	$\{[(\mathrm{Me_3SiCH_2})_2\mathrm{As}]_2\mathrm{GaCl}\}_2$	6
8	$\{[(\mathrm{Me_3SiCH_2})_2\mathrm{As}]_2\mathrm{GaBr}\}_2$	12
9	$[(\mathrm{Mes_2As})_2\mathrm{GaCl}]_n$	6
10	$(\mathrm{Mes_2As})_3\mathrm{Ga}$	6
11	$(\mathrm{Me_3Si})_2\mathrm{AsGa(C_5Me_5)_2}$	14
12	$(t\text{-}\mathrm{Bu})_2\mathrm{AsGa}(t\text{-}\mathrm{Bu})_2$	15
13	$\{[(\mathrm{Me_3SiCH_2})_2\mathrm{As}]_3\mathrm{Ga}\}_2$	16
14	$\{[(\mathrm{Me_3SiCH_2})_2\mathrm{As}]_2\mathrm{GaPh}\}_2$	9
15	$(t\text{-}\mathrm{Bu_2As})_3\mathrm{Ga}$	17
16	$(\mathrm{Me_3SiCH_2AsGaCl})_n$	9
17	$(\mathrm{Me_3SiCH_2AsGaPh})_n$	8
18	$\mathrm{Ph_2\overline{GaCl(Ph)_2Ga(Me_3Si)As}(CH_2)_3\overline{As(SiMe_3)Ga(Ph)_2ClGa}Ph_2}$	10
19	$\mathrm{As[GaBr_2(THF)]_3}$	27
20	$\mathrm{Ph_2\overline{GaAs(SiMe_3)_2Ga(Ph)_2Cl}}$	29, 30
21	$\mathrm{Ph_2\overline{GaAs(SiMe_3)_2Ga(Ph)_2Br}}$	30
22	$\mathrm{(Me_3SiCH_2)_2\overline{GaAs(SiMe_3)_2Ga(CH_2SiMe_3)_2Cl}}$	31
23	$\mathrm{(Me_3CCH_2)_2\overline{GaAs(SiMe_3)_2Ga(CH_2CMe_3)_2Cl}}$	32
24	$[(\mathrm{Me_3Si})_2\mathrm{AsGaPh_2}]_2$	29, 30
25	$[(\mathrm{Me_3Si})_2\mathrm{AsGa(CH_2SiMe_3)_2}]_2$	31
26	$[(\mathrm{Me_3Si})_2\mathrm{AsGa(CH_2CMe_3)_2}]_2$	32
27	$\mathrm{Ph_2\overline{GaAs(SiMe_3)_2Ga(CH_2SiMe_3)_2Cl}}$	31

James W. Pasterczyk, Mark F. Self, and Soheila Shafieezad; graduate students, James D. Johansen, Leonidas J. Jones, Chong-Yun Kwag, and Andrew P. Purdy.

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