Journal of Organometallic Chemistry, 308 (1986) 281–288
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

SYNTHESIS AND CRYSTAL STRUCTURE OF THE DIMER BIS{[BIS(TRIMETHYLSILYLMETHYL)ARSINO]DIPHENYLGALLANE}

RICHARD L. WELLS*, ANDREW P. PURDY, ANDREW T. McPHAIL, and COLIN G. PITT*

Department of Chemistry, Paul M. Gross Chemical Laboratory, Duke University, Durham, NC 27706 (U.S.A.)

(Received January 6th, 1986)

Summary

The dimer $[(Me_3SiCH_2)_2AsGaPh_2]_2$, obtained from the reaction of $(Me_3SiCH_2)_2AsH$ with Ph_3Ga, has been characterized by partial elemental analysis, NMR spectroscopy, cryoscopic molecular weight determination, and complete single-crystal X-ray analysis. Crystals of the dimer are triclinic, space group $P\bar{1}$, with a 10.541(1), b 11.939(1), c 10.539(1) Å, α 99.72(1), β 83.00(1), γ 114.55(1)°, U 1187.1 Å^3 and $Z = 1$. The bond lengths (Ga–As 2.518(1) and Ga–As′ 2.530(1) Å) and bond angles (As–Ga–As′ 85.08(2) and Ga–As–Ga′ 94.92(2)°) in the centrosymmetric, and consequently planar, four-membered ring indicate a significant degree of strain.

Introduction

The organometallic chemistry of gallium is dominated by its tendency to expand its coordination number from 3 to 4 or 5 [1]. This is particularly true of gallium compounds containing Groups 15 and 16 elements, where intramolecular p–π bonding is thermodynamically unfavorable relative to intermolecular association. For example, amino-, phosphino-, arsino-, and thiogallanes generally exist as oligomers and polymers, rather than as monomers [1a]. We have been interested in the extent to which the oligomerization of organogallium-arsenic compounds can be controlled by introducing bulky substituents such as the trimethylsilylmethyl [2,3] and mesityl [4] groups. As reported by others, the use of these and the sterically hindered bisyl and trisyl groups, $(Me_3Si)_nCH_{3-n}$ ($n = 2$ and 3), have permitted the isolation of a number of unusual transition and Main Group organometallics [5]. In our laboratories, the novel cluster $[(PhAsH)(R_2Ga)(PhAs)_6(RGa)_4]$ has been isolated as a product of the reaction of $PhAsH_2$ with R_3Ga ($R = Me_3SiCH_2$) [3]. Also, the first monomeric trisarsinogallane, $(R_2As)_3Ga$, has been synthesized by the reaction of R_2AsLi with $GaCl_3$ (R = mesityl) [4].

0022-328X/86/$03.50

Efforts to obtain a monomeric arsinogallane from hindered gallanes and arsines were not successful using the alkane elimination reaction [6,7] (eq. 1); however, in the course of these studies, the dimer $[(Me_3SiCH_2)_2AsGaPh_2]_2$ was isolated. One

$$R_2AsH + R'_3Ga \rightarrow 1/n(R_2AsGaR'_2)_n + R'H \qquad (1)$$

other arsinogallane, $Ph_2AsGaMe_2$, has been reported to be dimeric on the basis of its cryoscopic molecular weight [6]. Here we report the synthesis of $[(Me_3SiCH_2)_2AsGaPh_2]_2$ by the reaction of $(Me_3SiCH_2)_2AsH$ with Ph_3Ga, and its characterization, including a complete crystal structure which is the first reported for a dimeric gallium-arsenic compound [2].

Experimental

General comments

All manipulations and reactions were carried out under vacuum, or under an atmosphere of N_2 in I^2R glove bags, a Vacuum/Atmospheres HE-43 Dri-Lab, or standard Schlenk apparatus. Except for Ph_3Ga, which was recrystallized from a $CHCl_3$/hexane mixture, commercially available reagents were not further purified. Organic solvents were distilled from CaH_2, sodium benzophenone ketyl, or P_2O_5. An Et_2O solution of Me_3SiCH_2MgCl was prepared by a literature method [8]; Zn amalgam was prepared from Zn dust, $HgCl_2$, and $CuSO_4$ in a manner similar to a reported procedure for preparing a two component amalgam [9]. The types of reactions used in this study to prepare $(Me_3SiCH_2)_2AsCl$ [10] and $(Me_3SiCH_2)_2AsH$ have been reported previously [9,11]. Proton (80 MHz) and ^{13}C (22.5 MHz) NMR spectra were recorded on IBM NR-80 and JEOL FX-90Q spectrometers, respectively, and the IR spectrum was recorded on a Perkin-Elmer 297 spectrometer. A Normag No. 2029 apparatus was used to determine the molecular weight cryoscopically in C_6H_6. Elemental analyses were carried out at the Schwarzkopf Microanalytical Laboratory, Woodside, NY.

Preparation of $(Me_3SiCH_2)_2AsCl$

Arsenic trioxide (10.1 g, 0.0511 mol) and Et_2O (50 ml) were combined in a 500 ml 3-necked flask equipped with a magnetic stir bar, a reflux condenser, an N_2 gas inlet tube connected to a manifold with a bubbler, and an addition funnel containing Me_3SiCH_2MgCl (0.20 mol in 100 ml of Et_2O) (manipulations performed in a glove bag). A mildly exothermic reaction occurred as the Grignard reagent was added dropwise over a 2 h period to the stirred solution. The resulting mixture was hydrolyzed with a large excess of concentrated HCl, and the Et_2O layer was separated and combined with a hexane/Et_2O extract of the acid layer. Following filtration of the organic extracts (performed in a glove bag) and removal of solvents under vacuum distillation afforded $(Me_3SiCH_2)_2AsCl$ as a colorless liquid (24 g, 84% yield), b.p. 58–62°C/0.3–0.5 Torr; ^1H NMR (C_6D_6) δ 0.08 (s, Me_3Si), 1.02 and 1.46 (AB pattern ($^2J(HH)$ 13.5 Hz), CH_2); ^{13}C NMR ($CDCl_3$) (decoup.) δ 0.40 (s, Me_3Si), 27.32 (s, CH_2).

Preparation of $(Me_3SiCH_2)_2AsH$

Chlorobis(trimethylsilylmethyl)arsine (10.3 g, 0.0360 mol) was added to a 500 ml 3-necked flask containing H_2O (75 ml), thf (75 ml) and conc. HCl (150 ml), and equipped with a magnetic stir bar, a stopper, an N_2 gas inlet tube connected to a manifold with a bubbler, and a length of Tygon tubing (stoppered at the top end and closed with a pinch clamp near the bottom end) containing Zn amalgam (Zn (29 g, 0.45 mol); Hg (2.2 g, 0.011 mol); Cu (0.83 g, 0.013 mol)) (manipulations performed in a glove bag). Small quantities of amalgam were added periodically over a 2 day period to the vigorously stirred mixture. The HCl layer was separated and extracted three times with pentane. Following removal of solvent from the combined extracts, distillation afforded $(Me_3SiCH_2)_2AsH$ as a colorless liquid (7.8 g, 86% yield), b.p. 39–43°C/0.05 Torr, (Found: C, 38.61; H, 9.43%. $C_8H_{23}Si_2As$ calcd.: C, 38.38; H, 9.26%); ^1H NMR (C_6D_6) δ 0.065 (s, Me_3Si), 0.53 and 0.76, 2.57 (AA′BB′X pattern (^2J(HH) 13.2, ^3J(HH) 5.1, ^3J(HH) 10.0, ^4J(HH) 0 Hz), CH_2 and AsH); ^{13}C NMR (C_6D_6) δ -0.50 (q (J(CH) 118.7 Hz), Me_3Si), 7.2 (t (J(CH) 120.9 Hz), CH_2); IR (liq.) ν2950(s), 2875(m), 2050(m, AsH), 1250(m), 1240(s), 1060(w, br), 830(vs), 710(m), 690(m) cm^{-1}.

Preparation of $[(Me_3SiCH_2)_2AsGaPh_2]_2$

Bis(trimethylsilylmethyl)arsine (0.25 g, 1.0 mmol) and Ph_3Ga (0.30 g, 1.0 mmol) were transferred with ca. 5 ml of hexane into a 50 ml bulb equipped with a Teflon stopcock and a magnetic stir bar. The bulb was attached to a vacuum line, cooled to −196°C, and degassed. Stirring the mixture for 3 days at 50°C, followed by removal of the solvent in vacuo, gave a viscous liquid containing As–H species as indicated by its ^1H NMR spectrum. The residue was redissolved in hexane. Heating and stirring for 3 days at 75°C, followed by solvent removal, afforded a wet solid. Recrystallization from ligroin (b.p. 95°C), washing with pentane, and drying under vacuum gave $[(Me_3SiCH_2)_2AsGaPh_2]_2$ as colorless crystals (0.18 g, 38% yield) m.p. 181–183°C (dec., slightly transparent at 159°C) (Found: C, 50.48; H, 6.90%; mol. wt., 976 (cryoscopic, C_6H_6, 0.0251 m). $C_{40}H_{64}As_2Ga_2Si_4$ calcd.: C, 50.75; H, 6.81%; mol. wt., 947); ^1H NMR (C_6D_6, 0.073 M; 28, 58, and 91°C) δ − 0.13 (s, Me_3Si), 1.43 (s, CH_2), 7.2–7.4 and 7.9–8.0 (m, Ph), ((C_7D_8, 0.076 M; −62 and −78°C) same peaks, but with line broadening); ^{13}C NMR (C_6D_6, 0.073 M, 25°C) (dec.) δ 0.91 (s, Me_3Si), 4.9 (s, CH_2), 128.2, 128.3, 138.1 and 147.3 (s, Ph). Proton spectra were run at four other concentrations (0.0021, 0.0061, 0.014, and 0.019 M). A second species increased with decreasing concentration, but it was identified as $(Me_3SiCH_2)_2AsH$ from hydrolysis of the dimer by the following (a) a plot of ln of the integral fraction (Me_3Si peaks from ^1H NMR spectra) of the second species times the total concentration (in monomeric units) versus the same for the primary species gave a line with zero slope which indicated a constant, concentration-independent, amount of the second species, (b) the chemical shifts of the peaks of the second species are the same as those for $(Me_3SiCH_2)_2AsH$, and (c) drying the C_7D_8 over $LiAlH_4$ resulted in a very substantial decrease in the amount of the second species observed in the ^1H NMR spectrum run at a concentration of 0.0037 M.

Crystal data. $C_{40}H_{64}As_2Ga_2Si_4$, $M = 946.58$, triclinic, a 10.541(1), b 11.939(1), c 10.539(1) Å, α 99.72(1), β 83.00(1), γ 114.55(1)°, U 1187.1 Å^3, $Z = 1$, D_c 1.324 g cm^{-3}, μ(Cu-K_α, λ 1.5418 Å) 41.1 cm^{-1}. Space group $P1$ (C_i^1) or $P\bar{1}$(C_i^1) from Laue symmetry; proved to be the latter by structure solution and refinement. Sample dimensions: 0.16 × 0.20 × 1.1 mm (sealed inside a thin-walled glass capillary).

Crystallographic measurements. Preliminary unit-cell parameters and space group information were obtained from precession, oscillation, and Weissenberg photo-

TABLE 1

NON-HYDROGEN ATOM FRACTIONAL COORDINATES ($\times 10^4$), WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	x	y	z
As	849.1(4)	1048.7(3)	1253.5(4)
Ga	1027.5(4)	1138.0(4)	−1134.5(4)
Si(1)	4112(1)	3060(1)	1941(1)
Si(2)	−301(1)	2380(1)	3938(1)
C(1)	2806(4)	1108(4)	−1948(4)
C(2)	3340(5)	299(4)	−1623(5)
C(3)	4555(5)	237(6)	−2240(7)
C(4)	5246(6)	963(8)	−3180(7)
C(5)	4787(7)	1776(9)	−3491(7)
C(6)	3557(6)	1869(6)	−2886(5)
C(7)	401(4)	2413(3)	−1436(4)
C(8)	1320(5)	3637(4)	−1479(5)
C(9)	923(6)	4550(4)	−1641(6)
C(10)	−488(5)	4266(4)	−1721(6)
C(11)	−1432(5)	3077(5)	−1677(6)
C(12)	−1006(5)	2155(4)	−1539(5)
C(13)	2583(4)	1527(4)	2141(4)
C(14)	5045(6)	3584(7)	3469(6)
C(15)	5334(6)	2858(7)	606(7)
C(16)	3594(7)	4295(5)	1600(7)
C(17)	32(4)	2203(4)	2130(4)
C(18)	−977(9)	897(6)	4604(6)
C(19)	1299(8)	3464(10)	4741(7)
C(20)	−1676(6)	3000(6)	4292(7)

graphs. Intensity data for a hemisphere of reciprocal space, recorded on an Enraf–Nonius CAD-4 automated diffractometer (Cu-K_α radiation, incident-beam graphite monochromator; $\omega - 2\theta$ scans, $\theta_{max.}$ 67°) yielded a total of 4238 independent reflections out of which those 3575 with $I > 3.0\sigma(I)$ were retained for the structure analysis and corrected for the usual Lorentz and polarization effects. The variation of the intensities of four reference reflections, monitored periodically throughout the data collection, was insignificant (−0.9% over 33.2 h). Empirical absorption corrections, based on the ϕ-dependence of the intensities of 4 reflections with χ ca. 90°, were also applied to the data. Refined unit-cell parameters were derived by least-squares treatment of the diffractometer setting angles for 25 reflections ($57° < \theta < 67°$) widely separated in reciprocal space.

Structural analysis. The structure was solved by the heavy-atom approach. Full-matrix least-squares adjustment of non-hydrogen atom positional and thermal parameters, with hydrogen atoms included at their idealized calculated positions in the later iterations, converged to $R = 0.055$ ($R = \Sigma \| F_0 | - | F_c \| / \Sigma | F_0 |$). Atomic scattering factors used in the structure-factor calculations were taken from ref. 12. In the least-squares iterations, $\Sigma w\Delta^2[(w = 1/\sigma^2(| F_0 |), \Delta = \| F_0 | - | F_c \|]$ was minimized. All crystallographic calculations were performed on a PDP11/44 computer by use of the Enraf–Nonius SDP suite of programs. Final non-hydrogen atom positional parameters are in Table 1, bond lengths and angles are in Table 2, selected torsion angles are in Table 3, and displacements of selected atoms from

TABLE 2. INTERATOMIC DISTANCES (Å) AND ANGLES (deg.), WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

(a) Bond lengths [a]			
Ga–As	2.518(1)	Si(2)–C(20)	1.859(8)
Ga–As′	2.530(1)	C(1)–C(2)	1.406(8)
Ga–C(1)	1.976(5)	C(1)–C(6)	1.394(7)
Ga–C(7)	1.976(5)	C(2)–C(3)	1.389(8)
As–C(13)	1.977(5)	C(3)–C(4)	1.361(10)
As–C(17)	1.964(5)	C(4)–C(5)	1.349(15)
Si(1)–C(13)	1.894(4)	C(5)–C(6)	1.412(10)
Si(1)–C(14)	1.867(6)	C(7)–C(8)	1.382(5)
Si(1)–C(15)	1.844(7)	C(7)–C(12)	1.398(7)
Si(1)–C(16)	1.870(8)	C(8)–C(9)	1.361(9)
Si(2)–C(17)	1.887(4)	C(9)–C(10)	1.391(9)
Si(2)–C(18)	1.840(7)	C(10)–C(11)	1.358(6)
Si(2)–C(19)	1.844(8)	C(11)–C(12)	1.384(9)
(b) Bond angles [a]			
As–Ga–As′	85.08(2)	C(18)–Si(2)–C(19)	109.0(4)
As–Ga–C(1)	111.6(2)	C(18)–Si(2)–C(20)	106.9(4)
As–Ga–C(7)	108.7(1)	C(19)–Si(2)–C(20)	110.0(4)
As′–Ga–C(1)	109.9(1)	Ga–C(1)–C(2)	121.2(3)
As′–Ga–C(7)	115.0(1)	Ga–C(1)–C(6)	121.0(5)
C(1)–Ga–C(7)	120.8(2)	C(2)–C(1)–C(6)	117.8(5)
Ga–As–Ga′	94.92(2)	C(1)–C(2)–C(3)	121.1(5)
Ga–As–C(13)	118.7(1)	C(2)–C(3)–C(4)	120.0(7)
Ga–As–C(17)	108.3(1)	C(3)–C(4)–C(5)	120.6(6)
Ga′–As–C(13)	121.3(1)	C(4)–C(5)–C(6)	121.2(7)
Ga′–As–C(17)	108.6(1)	C(1)–C(6)–C(5)	119.3(7)
C(13)–As–C(17)	104.4(2)	Ga–C(7)–C(8)	121.9(4)
C(13)–Si(1)–C(14)	107.1(3)	Ga–C(7)–C(12)	122.3(3)
C(13)–Si(1)–C(15)	110.6(3)	C(8)–C(7)–C(12)	115.7(5)
C(13)–Si(1)–C(16)	113.8(3)	C(7)–C(8)–C(9)	123.7(5)
C(14)–Si(1)–C(15)	108.4(3)	C(8)–C(9)–C(10)	119.2(4)
C(14)–Si(1)–C(16)	109.5(3)	C(9)–C(10)–C(11)	119.3(6)
C(15)–Si(1)–C(16)	107.3(4)	C(10)–C(11)–C(12)	120.7(5)
C(17)–Si(2)–C(18)	113.2(2)	C(7)–C(12)–C(11)	121.4(4)
C(17)–Si(2)–C(19)	110.9(3)	As–C(13)–Si(1)	120.3(3)
C(17)–Si(2)–C(20)	106.7(3)	As–C(17)–Si(2)	121.1(3)

[a] Primed atoms are related to unprimed atoms in Table 1 by the transformation: $-x$, $-y$, $-z$.

TABLE 3. SELECTED TORSION ANGLES [a,b] (deg.)

As′–Ga–As–Ga′	0.0	As–Ga–As′–Ga′	0.0
As′–Ga–As–C(13)	129.9	As–Ga–As′–C(13′)	128.0
As′–Ga–As–C(17)	−111.5	As–Ga–As′–C(17′)	−111.2
C(1)–Ga–As–Ga′	−109.5	C(1)–Ga–As′–Ga′	111.2
C(1)–Ga–As–C(13)	20.4	C(1)–Ga–As′–C(13′)	−120.8
C(1)–Ga–As–C(17)	139.1	C(1)–Ga–As′–C(17′)	0.0
C(7)–Ga–As–Ga′	114.8	C(7)–Ga–As′–Ga′	−108.4
C(7)–Ga–As–C(13)	−115.3	C(7)–Ga–As′–C(13′)	19.6
C(7)–Ga–As–C(17)	3.3	C(7)–Ga–As′–C(17′)	140.4
As–Ga–C(1)–C(2)	42.8	As′–Ga–C(1)–C(2)	−49.8
As′–Ga–C(7)–C(12)	8.0	C(7)–Ga–C(1)–C(6)	−9.0

[a] The torsion angle A–B–C–D is defined as positive if, when viewed along the B–C bond, atom A must be rotated clockwise to eclipse atom D. [b] Primed atoms are related to the unprimed atoms in Table 1 by the transformation: $-x$, $-y$, $-z$.

TABLE 4

EQUATIONS OF LEAST-SQUARES PLANES THROUGH GROUPS OF ATOMS [a,b], IN THE FORM: $PX + QY + RZ - S = 0$ [b], WITH, IN PARENTHESES, DISPLACEMENTS (Å) OF SELECTED ATOMS FROM THESE PLANES

Plane A: Ga, As, Ga′, As′
$0.9284X - 0.3514Y - 0.1212Z = 0$
(Ga 0.000, As 0.000, Ga′ 0.000, As′ 0.000, C(1) 1.732, C(7) −1.699, C(13) 1.331, C(17) −1.735)

Plane B: C(1)–C(6)
$-0.3552X - 0.6219Y - 0.6979Z + 0.2838 = 0$
(Ga 0.107, As −1.415, Ga′ 0.460, As′ 1.983, C(1) 0.013, C(2) −0.006, C(3) −0.008, C(4) 0.014, C(5) −0.007, C(6) −0.007, C(7) −0.088)

Plane C: C(7)–C(12)
$0.0884X - 0.0654Y - 0.9939Z - 1.2096 = 0$
(Ga −0.098, As −2.518, Ga′ −2.321, As′ 0.098, C(1) 0.893, C(7) 0.002, C(8) −0.010, C(9) 0.012, C(10) −0.006, C(11) −0.002, C(12) 0.004)

Dihedral angles (deg.) between planes: A/B 91.5; A/C 77.0; B/C 45.3

---

[a] Primed atoms are related to the unprimed atoms in Table 1 by the transformation: $-x$, $-y$, $-z$.
[b] Cartesian coordinates (X, Y, Z) are related to the fractional atomic coordinates (x, y, z) in Table 1 by the transformations: $X = xa + yb\cos\gamma + zc\cos\beta$, $Y = yb\sin\gamma + zc[\cos\alpha - \cos\beta.\cos\gamma]/\sin\gamma$, $Z = zc\{\sin^2\beta - [(\cos\alpha - \cos\beta.\cos\gamma)/\sin\gamma]^2\}^{1/2}$.

various least-squares planes are in Table 4. A view of the atomic arrangement (hydrogen atoms omitted for clarity) in the centrosymmetric dimer is in Fig. 1. Tables of thermal parameters, hydrogen atom parameters, torsion angles, and observed and calculated structure factors are available from the authors (R.L.W.)

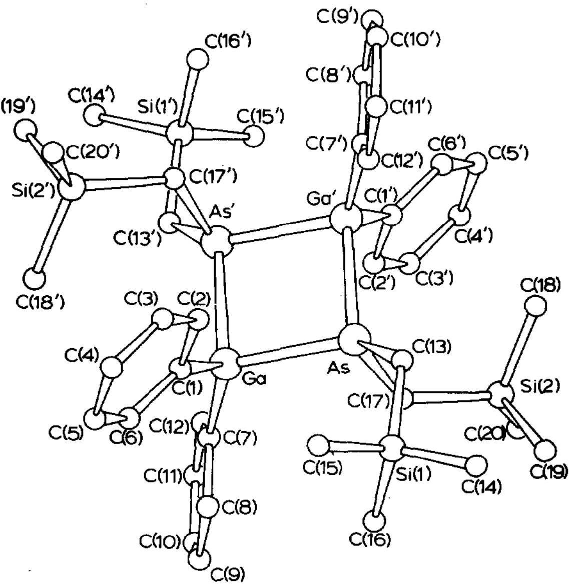

Fig. 1. Atomic arrangement in $[(Me_3SiCH_2)_2AsGaPh_2]_2$ (hydrogen atoms omitted for clarity).

Discussion

The complete crystal structure, and molecular weight and NMR data, demonstrate $(Me_3SiCH_2)_2AsGaPh_2$ is dimeric in both the solid state and in solution. Thus the trimethylsilylmethyl and phenyl groups as positioned do not provide the steric bulk required to allow isolation of a monomeric arsinogallane. The X-ray analysis of $[(Me_3SiCH_2)_2AsGaPh_2]_2$ shows the four-membered Ga–As ring is strained in the solid state; however, dissociation does not occur in solution for the cryoscopic molecular weight in benzene was determined to be 976, consistent with a dimeric structure (calcd. mol. wt., 947). In addition, the ^1H NMR spectra of $[(Me_3SiCH_2)_2AsGaPh_2]_2$ in benzene and toluene showed resonances attributable to a single species, independent of the temperature and concentration. Initially, some ^1H spectra indicated the presence of a small amount of a second species in solution [2], but it was subsequently shown to be a hydrolysis product of the dimer which is extremely sensitive to water and oxygen.

Crystals of the arsinogallane contain centrosymmetric dimers separated by normal Van der Waals distances. Although the Ga–As–Ga′–As′ ring is constrained to be planar by crystallographic symmetry, it departs significantly from a square planar geometry (Ga–As 2.518(1), Ga–As′ 2.530(1) Å; Ga...Ga′ 3.719(1), As...As′ 3.413(1) Å; As–Ga–As′ 85.08(2), Ga–As–Ga′ 94.92(2)°). The Ga–As bonds in the dimer are both longer than the three (2.470(1), 2.498(1), 2.508(1) Å) found in $(R_2As)_3Ga$ (R = mesityl), which contains a trigonal planar Ga atom [4], but lie within the range (2.450(1) to 2.553(1) Å) found in the cluster $[(PhAsH)(R_2Ga)(PhAs)_6(RGa)_4]$ ($R = Me_3SiCH_2$) which contains four-coordinate Ga atoms [3].

The largest bond angle about the Ga, C(1)–Ga–C(7) at 120.8(2)°, lies opposite the small ring angle (85.08(2)°). The Ga atom is displaced significantly from both phenyl ring planes (Δ 0.107 and 0.098 Å, respectively, from the C(1)–C(6) and C(7)–C(12) planes (Table 4)). One phenyl ring is oriented such that its plane is in an approximately bisecting orientation with respect to the $(Ga-As)_2$ ring (torsion angles As–Ga–C(1)–C(2) 42.8, As′–Ga–C(1)–C(2) −49.8°), while the other almost eclipses one of the Ga–As ring bonds (torsion angle As′–Ga–C(7)–C(12) 8.0°). The second largest bond angle at Ga (As–Ga–C(7) 115.0(1)°) is associated with the latter conformation. Torsion angles about the Ga–As bonds (C(1)–Ga–As–C(13) 20.4, C(1)–Ga–As′–C(17′) 0.0, C(7)–Ga–As–C(17) 3.3, C(7)–Ga–As′–C(13′) 19.6°) reveal that the As–C bonds are not symmetrically disposed with respect to the Ga–C bonds but rather adopt a form which minimizes non-bonded interactions between the C(7)–C(12) phenyl ring and the C(13′) methylene group. Enlargement of the Ga–As–C(13) and Ga′–As–C(13) bond angles (118.7(1) and 121.3(1)°, respectively) is also associated with these interactions.

Acknowledgement

We thank the Office of Naval Research and the Duke University Research Council for financial support.

References

1 (a) For a general discussion and some examples, see I. Haiduc and J.J. Zuckerman, Basic Organometallic Chemistry, Walter de Gruyter, Berlin, Germany, and New York, NY, 1985; (b) for examples of organogallium compounds containing five-coordinate gallium, see I. Pattison and K. Wade, J. Chem. Soc. A, (1968) 2618; K. Dymock and G.J. Palenik, J. Chem. Soc., Chem. Commun., (1973) 884; S.J. Rettig, A. Storr, and J. Trotter, Can. J. Chem., 53 (1975) 753; S.J. Rettig, A. Storr, and J. Trotter, ibid., 54 (1976) 1278; and A.T. McPhail, R.W. Miller, C.G. Pitt, G. Gupta, and S.C. Srivastava, J. Chem. Soc., Dalton Trans., (1976) 1657.

2 R.L. Wells, A.P. Purdy, A.T. McPhail, and C.G. Pitt, Abstr. Papers, 189th Nat. Meeting Am. Chem. Soc., Miami Beach, FL (April, 1985) INOR 26.

3 R.L. Wells, A.P. Purdy, A.T. McPhail, and C.G. Pitt, J. Chem. Soc., Chem. Commun., (1986) 487.

4 C.G. Pitt, K.T. Higa, A.T. McPhail, and R.L. Wells, Inorg. Chem., submitted for publication; and C.G. Pitt, K.T. Higa, A.T. McPhail, and R.L. Wells, Abstr. Papers, 191st Nat. Meeting Am. Chem. Soc., New York, NY (April, 1986) INOR 347.

5 See for example: C.S. Cundy, B.M. Kingston, and M.F. Lappert, Adv. Organomet. Chem., 11 (1973) 253; P.J. Davidson, M.F. Lappert and R. Pearce, Acc. Chem. Res., 7 (1974) 209; O.T. Beachley and R.G. Simmons, Inorg. Chem., 19 (1980) 1021; R. West, Science, 225 (1984) 1109; A.H. Cowley, J.E. Kildruff, J.G. Lasch, S.K. Mehrotra, N.C. Norman, M. Pakulski, B.R. Whittlesey, J.L. Atwood, and W.E. Hunter, Inorg. Chem., 23 (1984) 2582; C. Eaborn, M.N.A. El-Kheli, P.B. Hitchcock, and J.D. Smith, J. Organomet. Chem., 272 (1984) 1; and N.H. Buttrus, C. Eaborn, P.B. Hitchcock, J.D. Smith, and A.C. Sullivan, J. Chem. Soc., Chem. Commun., (1985) 1380.

6 G.E. Coates and J. Graham, J. Chem. Soc., (1963) 233.

7 O.T. Beachley and G.E. Coates, J. Chem. Soc. (1965) 3241.

8 R.A. Anderson and G. Wilkinson, Inorg. Synth., 19 (1979) 262.

9 E.J. Cragoe, R.J. Andres, R.F. Coles, B. Elpern, J.F. Morgan, and C.S. Hamilton, J. Am. Chem. Soc., 69 (1947) 925.

10 D. Seyferth, U.S. Patent 2964550 (1960).

11 F.F. Blicke and F.D. Smith, J. Am. Chem. Soc., 51 (1929) 1558; F.F. Blicke and G.L. Webster, ibid., 59 (1937) 536; and G.O. Doak and L.D. Friedman, Organometallic Compounds of Arsenic, Antimony, and Bismuth, Wiley-Interscience Division of John Wiley and Sons, Inc., New York, NY, 1970.

12 International Tables for X-ray Crystallography, Vol. IV, The Kynoch Press, Birmingham, England, 1974.