

# Synthesis, Structural Characterization, and Reactivity of $(\text{Me}_3\text{CCH}_2)_2\text{GaAs}(\text{SiMe}_3)_2\text{Ga}(\text{CH}_2\text{CMe}_3)_2\text{Cl}$ , $[(\text{Me}_3\text{CCH}_2)_2\text{GaAs}(\text{SiMe}_3)_2]_2$ , and $(\text{Me}_3\text{CCH}_2)_2\text{Ga}(\text{Cl})\cdot\text{As}(\text{SiMe}_3)_3$

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Reaction of 2 equiv of  $(\text{Me}_3\text{CCH}_2)_2\text{GaCl}$  with  $(\text{Me}_3\text{Si})_3\text{As}$  affords  $(\text{Me}_3\text{CCH}_2)_2\text{GaAs}(\text{SiMe}_3)_2\text{Ga}(\text{CH}_2\text{CMe}_3)_2\text{Cl}$  (1), the fourth example of a compound containing the Ga-As-Ga-X (X = Cl, Br) core, but the first wherein the organogallium four-membered ring with arsenic/halogen mixed bridging is not puckered. Compound 1, as well as  $(\text{Me}_3\text{CCH}_2)_2\text{GaCl}$ , reacts with  $\text{LiAs}(\text{SiMe}_3)_2\cdot 2\text{THF}$  (1:1 mole ratio) to produce the common product  $[(\text{Me}_3\text{CCH}_2)_2\text{GaAs}(\text{SiMe}_3)_2]_2$  (2), which on reaction with  $(\text{Me}_3\text{CCH}_2)_2\text{GaCl}$  (1:2 mole ratio) gives 1 quantitatively. Mixing  $(\text{Me}_3\text{CCH}_2)_2\text{GaCl}$  and  $(\text{Me}_3\text{Si})_3\text{As}$  in a 1:1 mole ratio yields the adduct  $(\text{Me}_3\text{CCH}_2)_2\text{Ga}(\text{Cl})\cdot\text{As}(\text{SiMe}_3)_3$  (3). Thermolysis of 3 did not afford 2, nor did its reaction with an additional 1 equiv of  $(\text{Me}_3\text{CCH}_2)_2\text{GaCl}$  lead to 1 as the predominate product. Various physical and spectroscopic characterization data are presented for compounds 1-3, as well as the results of their X-ray crystal structure determinations. Crystal data: 1, monoclinic, space group  $P2_1/c$  ( $C^5_{2h}$ ),  $a = 12.412$  (1) Å,  $b = 17.306$  (1) Å,  $c = 20.238$  (2) Å,  $\beta = 119.34$  (1)°,  $V = 3790$  (1) Å<sup>3</sup>,  $Z = 4$ ; 2, monoclinic, space group  $P2_1/c$  ( $C^4_{2h}$ ),  $a = 12.180$  (1) Å,  $b = 12.744$  (1) Å,  $c = 19.618$  (2) Å,  $\beta = 128.43$  (1)°,  $V = 2386$  (1) Å<sup>3</sup>,  $Z = 2$ ; 3, monoclinic, space group  $P2_1/c$  ( $C^5_{2h}$ ),  $a = 12.486$  (1) Å,  $b = 12.544$  (1) Å,  $c = 19.985$  (2) Å,  $\beta = 101.73$  (1)°,  $V = 3065$  (1) Å<sup>3</sup>,  $Z = 4$ .

## Introduction

Recent work in our research group involving the formation of gallium-arsenic bonds has resulted in the preparation of the novel ring compounds  $\text{Ph}_2\text{GaAs}(\text{SiMe}_3)_2\text{Ga}(\text{Ph}_2)\text{X}$  (X = Cl (4),<sup>1,2</sup> Br (5)<sup>2</sup>) and  $(\text{Me}_3\text{SiCH}_2)_2\text{GaAs}(\text{SiMe}_3)_2\text{Ga}(\text{CH}_2\text{SiMe}_3)_2\text{Cl}$  (6),<sup>3</sup> as well as the dimers  $[\text{Ph}_2\text{GaAs}(\text{SiMe}_3)_2]_2$  (7)<sup>1,2</sup> and  $[(\text{Me}_3\text{SiCH}_2)_2\text{GaAs}(\text{SiMe}_3)_2]_2$  (8).<sup>3</sup> In addition, we very recently reported the isolation of the indium-arsenic<sup>4</sup> and indium-phosphorus<sup>5</sup> analogues of 6 and 8,  $(\text{Me}_3\text{SiCH}_2)_2\text{InAs}(\text{SiMe}_3)_2\text{In}(\text{CH}_2\text{SiMe}_3)_2\text{Cl}$  and  $[(\text{Me}_3\text{SiCH}_2)_2\text{InAs}(\text{SiMe}_3)_2]_2$ , and  $(\text{Me}_3\text{SiCH}_2)_2\text{InP}(\text{SiMe}_3)_2\text{In}(\text{CH}_2\text{SiMe}_3)_2\text{Cl}$  and  $[(\text{Me}_3\text{SiCH}_2)_2\text{InP}(\text{SiMe}_3)_2]_2$ , respectively. As part of a continuing effort to expand the scope of the gallium-arsenic series, the neopentyl group was chosen as the alkyl substituent on the gallium atoms with the expectation that its different steric bulk might manifest itself in a different ring conformation or size in comparison to that of the previously studied (trimethylsilyl)methyl group. We also sought to investigate more fully the reactivity and interconvertibility of these types of compounds. We present herein our results obtained with the neopentyl ligand system.

## Experimental Section

**General Considerations.** All manipulations and reactions were performed under vacuum, under argon in a Vacuum Atmospheres HE-493 Dri-Lab, or under N<sub>2</sub> in standard Schlenk apparatus. Solvents were distilled from sodium/benzophenone ketyl under dry N<sub>2</sub> and degassed by several freeze-pump-thaw

cycles.  $(\text{Me}_3\text{CCH}_2)_2\text{GaCl}$ ,<sup>6</sup>  $(\text{Me}_3\text{Si})_3\text{As}$ ,<sup>7</sup> and  $\text{LiAs}(\text{SiMe}_3)_2\cdot 2\text{THF}$ <sup>7</sup> were prepared by literature procedures. <sup>1</sup>H (300 MHz) and <sup>13</sup>C{<sup>1</sup>H} (75.4 MHz) NMR spectra were recorded on a Varian XL-300 spectrometer at ambient temperatures using C<sub>6</sub>D<sub>6</sub> or C<sub>7</sub>D<sub>8</sub> solutions in 5-mm tubes which were flame-sealed under vacuum and were referenced to TMS using the residual protons or the carbons of deuterated benzene at  $\delta$  7.15 or 128 ppm, respectively, or the upfield pentet of C<sub>7</sub>D<sub>8</sub> at  $\delta$  2.09 ppm for <sup>1</sup>H NMR spectra. Melting points (uncorrected) were obtained with a Thomas-Hoover Uni-melt apparatus, and capillaries were flame-sealed under argon. Crystals used in the X-ray analyses were flame-sealed in 0.7-mm thin-walled glass capillaries. Elemental analyses were performed by E+R Microanalytical Laboratory, Inc., Corona, NY.

**Preparation of  $(\text{Me}_3\text{CCH}_2)_2\text{GaAs}(\text{SiMe}_3)_2\text{Ga}(\text{CH}_2\text{CMe}_3)_2\text{Cl}$  (1).** Reaction of  $(\text{Me}_3\text{CCH}_2)_2\text{GaCl}$  with  $(\text{Me}_3\text{Si})_3\text{As}$  (2:1 Mole Ratio).  $(\text{Me}_3\text{CCH}_2)_2\text{GaCl}$  (0.247 g, 1.00 mmol) in 20 mL of benzene and  $(\text{Me}_3\text{Si})_3\text{As}$  (0.147 g, 0.500 mmol) in 5 mL of benzene were combined in a 100-mL one-necked round-bottomed flask equipped with a Teflon valve and a magnetic stirbar. After one freeze-pump-thaw cycle of the solution, followed by stirring at room temperature for 5 days, removal of the volatiles in vacuo afforded a crude product which was dissolved in a small amount of pentane. When the solution stood overnight at -15 °C, a very small amount of white material (mp 170 °C dec; <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  0.53 (s, 18 H, SiMe<sub>3</sub>), 1.32 (s, 9 H, CMe<sub>3</sub>), 1.42 (s, 2 H, CH<sub>2</sub>) precipitated from the pentane solution, and after filtration and concentration, cooling the mother liquor to -15 °C afforded colorless crystals of 1 suitable for X-ray analysis (0.14 g, 41% yield; mp 70-110 °C dec. Anal. Calcd (found) for C<sub>26</sub>H<sub>62</sub>AsClGa<sub>2</sub>Si<sub>2</sub>: C, 45.87 (45.74); H, 9.17 (9.27). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  0.45 (s, 18 H, SiMe<sub>3</sub>), 1.27 (s, 36 H, CMe<sub>3</sub>), 1.38 (s, 8 H, CH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  4.71 (SiMe<sub>3</sub>), 32.92 (Me<sub>3</sub>C), 34.50 (Me<sub>3</sub>C), 40.57 (CH<sub>2</sub>).

**Preparation of  $[(\text{Me}_3\text{CCH}_2)_2\text{GaAs}(\text{SiMe}_3)_2]_2$  (2).** (a) Reaction of  $(\text{Me}_3\text{CCH}_2)_2\text{GaCl}$  with  $\text{LiAs}(\text{SiMe}_3)_2\cdot 2\text{THF}$ . Addition of a solution of  $\text{LiAs}(\text{SiMe}_3)_2\cdot 2\text{THF}$  (0.283 g, 0.800 mmol) in 10 mL of benzene to a solution of  $(\text{Me}_3\text{CCH}_2)_2\text{GaCl}$  (0.200 g, 0.800 mmol) in 20 mL of benzene contained in a 100-mL one-necked round-bottomed flask equipped with a Teflon valve and a microstirbar gave a light brown reaction mixture which was stirred at room temperature for 24 h. Removal of the benzene

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Table I. Crystallographic Data and Measurements<sup>a</sup> for  $(\text{Me}_3\text{CCH}_2)_2\text{GaAs}(\text{SiMe}_3)_2\text{Ga}(\text{CH}_2\text{CMe}_3)_2\text{Cl}$  (1),  $(\text{Me}_3\text{CCH}_2)_2\text{GaAs}(\text{SiMe}_3)_2$  (2), and  $(\text{Me}_3\text{CCH}_2)_2\text{Ga}(\text{Cl})\cdot\text{As}(\text{SiMe}_3)_3$  (3)

	1	2	3
mol formula	$\text{C}_{26}\text{H}_{62}\text{AsClGa}_2\text{Si}_2$	$\text{C}_{32}\text{H}_{80}\text{As}_2\text{Ga}_2\text{Si}_4$	$\text{C}_{19}\text{H}_{49}\text{AsClGaSi}_3$
fw	685.97	866.62	541.96
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$ ( $C_2^2h$ )	$P2_1/c$ ( $C_2^2h$ )	$P2_1/c$ ( $C_2^2h$ )
a, Å	12.412 (1)	12.180 (1)	12.486 (1)
b, Å	17.306 (1)	12.744 (1)	12.544 (2)
c, Å	20.238 (2)	19.618 (2)	19.985 (1)
$\beta$ , deg	119.34 (1)	128.43 (1)	101.73 (1)
no. of orientn rflns; $\theta$ range, deg	25; 42–48	25; 42–48	25; 45–48
V, Å <sup>3</sup>	3790 (1)	2386 (1)	3065 (1)
Z	4	2	4
$D_{\text{calcd}}$ , g cm <sup>-3</sup>	1.202	1.206	1.174
temp, °C	25	25	25
cryst dimens, mm	0.40 × 0.50 × 0.60	0.40 × 0.40 × 0.60	0.40 × 0.50 × 0.60
$T_{\text{max}}:T_{\text{min}}$	1.00:0.68	1.00:0.51	1.00:0.61
radiation (wavelength, Å)	Cu K $\alpha$ (1.5418)	Cu K $\alpha$ (1.5418)	Cu K $\alpha$ (1.5418)
$\mu$ , cm <sup>-1</sup>	43.0	40.4	44.1
scan type	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$
scan width, deg	1.10 + 0.14 tan $\theta$	1.10 + 0.14 tan $\theta$	1.10 + 0.14 tan $\theta$
$\theta_{\text{max}}$ , deg	75	75	75
intens control rflns	151, 341, 126, 208	355, 522, 333, 262	224, 224, 224, 224
variation, %; repeat time, h	<2; 2	-36; 1	<2; 2
no. of rflns recorded	8216 (+h,+k, $\pm$ l)	5138 (+h,k, $\pm$ l)	6594 (+h,+k, $\pm$ l)
no. of nonequiv rflns recorded	7775	4906	6299
$R_{\text{merge}}$ (on I)	0.026	0.043	0.036
no. of rflns retained, $I > 3.0\sigma(I)$	6153	2496	4351
no. of params refined	290	183	227
extinction cor	[8.1 (3)] × 10 <sup>-7</sup>	[1.55 (5)] × 10 <sup>-6</sup>	[2.44 (3)] × 10 <sup>-6</sup>
R ( $R_w$ ) <sup>b</sup>	0.045 (0.065)	0.054 (0.072)	0.045 (0.060)
goodness of fit <sup>c</sup>	2.36	1.48	1.39
max shift/esd in final least-squares cycle	0.02	0.02	0.02
final max, min $\Delta\rho$ , e Å <sup>-3</sup>	0.75, -0.69	1.05, -0.70	0.45, -0.62

<sup>a</sup> An Enraf-Nonius CAD-4 diffractometer equipped with a graphite monochromator was used for all measurements. Crystallographic calculations were performed on PDP11/44 and MicroVAX computers by use of the Enraf-Nonius Structure Determination Package (SDP). <sup>b</sup>  $R = \sum |F_o| - |F_c| / \sum |F_o|$ ;  $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ .  $\sum w\Delta^2$  ( $w = 1/\sigma^2(|F_o|)$ ,  $\Delta = |F_o| - |F_c|$ ) was minimized. <sup>c</sup> Goodness of fit =  $[\sum w\Delta^2 / (N_{\text{observns}} - N_{\text{params}})]^{1/2}$ .

in vacuo was followed by addition of 30 mL of pentane to the brownish white residue; filtration and subsequent removal in vacuo of the pentane from the filtrate afforded crude product (2; 0.28 g, 82% yield). Cooling a pentane (5 mL) solutions of the latter to -15 °C gave colorless crystals suitable for X-ray analysis; mp 160–170 °C. Anal. Calcd (found) for  $\text{C}_{32}\text{H}_{80}\text{As}_2\text{Ga}_2\text{Si}_4$ : C, 44.35 (44.49); H, 9.30 (9.26). <sup>1</sup>H NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  0.60 (s, 36 H,  $\text{SiMe}_3$ ), 1.30 (s, 36 H,  $\text{CMe}_3$ ), 1.47 (s, 8 H,  $\text{CH}_2$ ).

(b) Reaction of 1 with  $\text{LiAs}(\text{SiMe}_3)_2\cdot 2\text{TTHF}$ . Addition of a solution of  $\text{LiAs}(\text{SiMe}_3)_2\cdot 2\text{TTHF}$  (0.018 g, 0.050 mmol) in toluene- $d_6$  (1 mL) to a solution of 1 (0.034 g, 0.050 mmol) in toluene- $d_6$  (1 mL) contained in a 50-mL one-necked round-bottomed flask equipped with a Teflon valve resulted in the formation of a white precipitate (presumably LiCl). After the solution stood in the drybox for 12 h, followed by removal of the toluene- $d_6$  in vacuo and replacement with pentane (15 mL), the insoluble white solid was separated by filtration. Cooling the concentrated filtrate to -15 °C afforded 2 in nearly quantitative yield (melting point and <sup>1</sup>H NMR spectrum same as those of an authentic sample of 2; vide supra).

**Preparation of  $(\text{Me}_3\text{CCH}_2)_2\text{GaAs}(\text{SiMe}_3)_2\text{Ga}(\text{CH}_2\text{CMe}_3)_2\text{Cl}$  (1).** Reaction of  $(\text{Me}_3\text{CCH}_2)_2\text{GaCl}$  with 2 (2:1 Mole Ratio). Ten minutes after  $(\text{Me}_3\text{CCH}_2)_2\text{GaCl}$  (7 mg,  $3 \times 10^{-2}$  mmol) and 2 (12 mg,  $1.4 \times 10^{-2}$  mmol) were combined in  $\text{C}_6\text{D}_6$  (1 mL) in an NMR tube, the <sup>1</sup>H NMR spectrum of the reaction mixture was identical with that of an authentic sample of 1, thereby indicating there was complete conversion of the starting materials to 1. The subsequently obtained <sup>13</sup>C[<sup>1</sup>H] NMR spectrum was also identical with that of an authentic sample of 1.

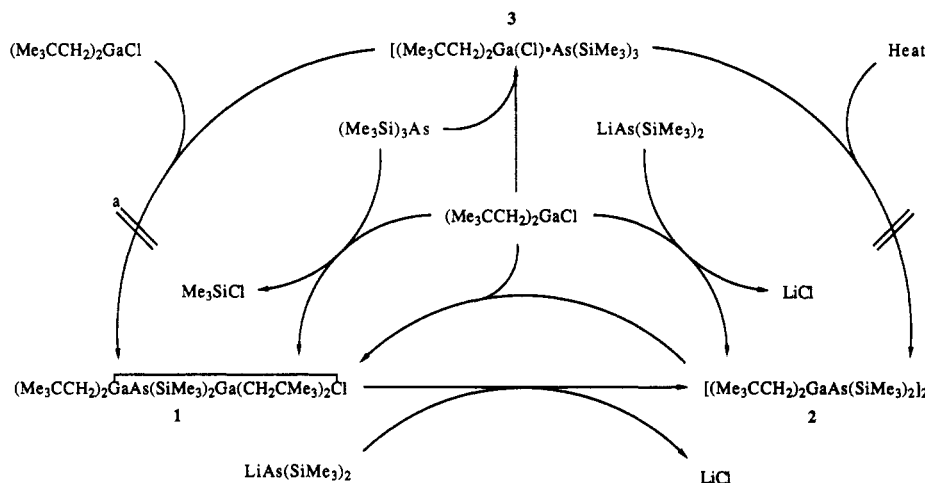
**Preparation of  $(\text{Me}_3\text{CCH}_2)_2\text{Ga}(\text{Cl})\cdot\text{As}(\text{SiMe}_3)_3$  (3).** Reaction of  $(\text{Me}_3\text{CCH}_2)_2\text{GaCl}$  with  $(\text{Me}_3\text{Si})_3\text{As}$  (1:1 Mole Ratio).  $(\text{Me}_3\text{CCH}_2)_2\text{GaCl}$  (0.247 g, 1.00 mmol) in 20 mL of benzene and  $(\text{Me}_3\text{Si})_3\text{As}$  (0.295 g, 1.00 mmol) in 5 mL of benzene were combined in a 100-mL one-necked round-bottomed flask equipped with a Teflon valve and a magnetic stirbar. After one freeze-pump-thaw

cycle of the solution, followed by stirring at room temperature for 5 days, removal of the solvent in vacuo afforded a white solid, which was dissolved in a small amount of pentane. When this solution was stored at -15 °C, large colorless crystals of 3 suitable for X-ray analysis were deposited (0.20 g, 40% yield); mp 78 °C (decomposes at 130 °C to a red material). Anal. (satisfactory analysis could not be obtained due to decomposition of sample) Calcd (found) for  $\text{C}_{19}\text{H}_{49}\text{AsClGaSi}_3$ : C, 42.11 (37.97); H, 9.11 (8.08); Cl, 6.54 (3.32). <sup>1</sup>H NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  0.34 (s, 27 H,  $\text{SiMe}_3$ ), 1.23 (s with shoulder, 22 H,  $\text{CH}_2\text{CMe}_3$ ). <sup>13</sup>C[<sup>1</sup>H] NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  3.49 ( $\text{Me}_3\text{Si}$ ), 34.14 ( $\text{Me}_3\text{C}$ ) (the methylene ( $\text{CH}_2$ ) and tertiary ( $\text{Me}_3\text{C}$ ) carbons were not observed).

**Thermolysis of  $(\text{Me}_3\text{CCH}_2)_2\text{Ga}(\text{Cl})\cdot\text{As}(\text{SiMe}_3)_3$  (3).** A flame-sealed NMR tube containing 3 (10 mg) dissolved in  $\text{C}_7\text{D}_8$  was heated at 110–120 °C over a period of 43 h with <sup>1</sup>H NMR spectra being recorded at various intervals. The resonance in the initial ambient-temperature spectrum associated with 3 at  $\delta$  1.20 was replaced by one at  $\delta$  1.09 and a series of other peaks at  $\delta$  0.19 (possibly due to  $\text{Me}_3\text{SiCl}$ ), 0.45, 0.54, and 1.03; however, the one at  $\delta$  0.35 remained as a major peak. No resonances that could be attributed to 2 were evident.

**Reaction of  $(\text{Me}_3\text{CCH}_2)_2\text{Ga}(\text{Cl})\cdot\text{As}(\text{SiMe}_3)_3$  (3) with  $(\text{Me}_3\text{CCH}_2)_2\text{GaCl}$  (1:1 Mole Ratio).**  $(\text{Me}_3\text{CCH}_2)_2\text{GaCl}$  (5 mg, 0.02 mmol) and 3 (95 mg, 0.02 mmol) were dissolved in  $\text{C}_7\text{D}_8$  in an NMR tube. The ambient-temperature <sup>1</sup>H NMR spectrum recorded immediately after the reactants were combined and the tube was flame-sealed, as well as that obtained 19 h later, was relatively simple with three major peaks at  $\delta$  0.35, 1.17, 1.23, which correspond to those associated with the adduct. By integration, the  $(\text{Me}_3\text{CCH}_2)_2\text{GaCl}$  protons appeared to be degenerate with those of the adduct. After the mixture was heated at 80 °C for 5 h and very little change was observed in its spectrum, the mixture was heated at 100 °C for 29 h and new major resonances were observed at  $\delta$  1.09, 1.03, 0.54, 0.45, and 0.19 (possibly due to  $\text{Me}_3\text{SiCl}$ ), with minor peaks being observed at  $\delta$  1.27 and 1.38.

**Scheme I. Reaction Summary: Synthesis and Reactivity of  $(\text{Me}_3\text{CCH}_2)_2\text{GaAs}(\text{SiMe}_3)_2\text{Ga}(\text{CH}_2\text{CMe}_3)_2\text{Cl}$  (1),  $[(\text{Me}_3\text{CCH}_2)_2\text{GaAs}(\text{SiMe}_3)_2]_2$  (2), and  $(\text{Me}_3\text{CCH}_2)_2\text{Ga}(\text{Cl})\cdot\text{As}(\text{SiMe}_3)_3$  (3)**



<sup>a</sup> Complex <sup>1</sup>H NMR spectrum of reaction mixture contains peaks which could be attributed to 1.

The last two peaks along with the one at  $\delta$  0.45 can be assigned to 1, but the relative areas are not correct for that compound.

**Structural Analyses of 1–3.** Crystallographic data and data collection parameters are presented in Table I. Intensity data were corrected for the usual Lorentz and polarization effects; empirical absorption corrections, and for 2 a linear decay correction, were also applied. Each crystal structure was solved by direct methods (MULTAN11/82). For 1, approximate non-hydrogen atom positions were obtained in part from an *E* map and completed by a series of difference Fourier syntheses phased successively by an increasing number of atoms. In the case of 2, with only two formula units in the unit cell of space group *P2/c*, the dimer is required to lie on either a center of symmetry or a *C*<sub>2</sub> axis. An *E* map yielded Ga, As, and Si atom coordinates and, moreover, established that the As atoms lay on a crystallographic *C*<sub>2</sub> symmetry axis; C atoms were subsequently located in a difference Fourier synthesis. Approximate As, Ga, Cl, and Si atom positions for 3 were derived routinely from an *E* map, and a weighted *F*<sub>o</sub> Fourier synthesis phased by these atoms revealed C atom locations. Positional and thermal parameters (at first isotropic, then anisotropic) for each compound were adjusted by means of several rounds of full-matrix least-squares calculations. Hydrogen atoms were incorporated at their calculated positions (C–H = 1.05 Å), and an extinction correction was included as a variable during the final least-squares iterations. For structure-factor calculations, neutral atom scattering factors and their anomalous dispersion corrections were taken from ref 8.

### Results and Discussion

Tris(trimethylsilyl)arsine,  $(\text{Me}_3\text{Si})_3\text{As}$ , reacts with 2 equiv of  $(\text{Me}_3\text{CCH}_2)_2\text{GaCl}$  in benzene at room temperature to produce the mixed-bridge compound  $(\text{Me}_3\text{CCH}_2)_2\text{GaAs}(\text{SiMe}_3)_2\text{Ga}(\text{CH}_2\text{CMe}_3)_2\text{Cl}$  (1) in 41% crystalline yield (see Scheme I for a summary of this and the other reactions investigated in this study). This result is in accord with those obtained when the aryl/alkyl groups on the gallium starting material are phenyl or (trimethylsilyl)methyl, furnishing 4 and 6, respectively. Compound 1 was characterized by <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy, partial elemental analysis, and single-crystal X-ray analysis (vide infra).

On the other hand, in stark contrast to the  $\text{Ph}_2\text{GaCl}$  and  $(\text{Me}_3\text{SiCH}_2)_2\text{GaCl}$  cases, the reaction of  $(\text{Me}_3\text{Si})_3\text{As}$  with 1 equiv of  $(\text{Me}_3\text{CCH}_2)_2\text{GaCl}$  produces the 1:1 adduct  $(\text{Me}_3\text{CCH}_2)_2\text{Ga}(\text{Cl})\cdot\text{As}(\text{SiMe}_3)_3$  (3) in 40% crystalline yield.

The corresponding equimolar reaction with  $\text{Ph}_2\text{GaCl}$  leads to a mixture of mixed-bridge 4 and dimer 7,<sup>1</sup> whereas the 1:1 reaction between the silylarsine and  $(\text{Me}_3\text{SiCH}_2)_2\text{GaCl}$  affords mixed-bridge 6 and other uncharacterized products, but not dimer 8.<sup>3</sup> These results led us to consider the possibility that 3 may be an intermediate in the synthesis of 1 or in the synthesis of the dimer  $[(\text{Me}_3\text{CCH}_2)_2\text{GaAs}(\text{SiMe}_3)_2]_2$  (2). To investigate this hypothesis, a toluene-*d*<sub>8</sub> solution of 3 sealed in an NMR tube was heated in an effort to eliminate  $\text{Me}_3\text{SiCl}$  and produce 2; however, on the basis of the NMR spectra obtained, only a small amount of what appeared to be  $\text{Me}_3\text{SiCl}$  and other products was present but, significantly, there was no evidence for 2 or 1. A similar NMR-tube reaction between 3 and 1 equiv of  $(\text{Me}_3\text{CCH}_2)_2\text{GaCl}$  at elevated temperatures gave what appeared to be the same products plus a trace of 1, but no evidence for 2. It thus appears that adduct 3 is not an intermediate in the preparation of 2 and it is not likely that it is the predominate intermediate in the preparation of 1. By inference, analogous hypothetical adducts may not be intermediates in the synthesis of 4, 6, 7, or 8. Interestingly, it was eventually possible to characterize adduct 3 by <sup>1</sup>H NMR spectroscopy, and an X-ray crystallographic analysis (vide infra), but it was too unstable to allow a satisfactory elemental analysis to be obtained.

In a manner completely analogous to that previously reported by us to prepare 7<sup>2</sup> and 8,<sup>3</sup> dimer 2 was synthesized in 82% yield from the reaction of  $(\text{Me}_3\text{CCH}_2)_2\text{GaCl}$  with  $\text{LiAs}(\text{SiMe}_3)_2\cdot 2\text{THF}$ , and it was characterized by <sup>1</sup>H NMR spectroscopy, partial elemental analysis, and a single-crystal X-ray analysis (vide infra). This dimer can also be prepared by reaction of mixed-bridge 1 with 1 equiv of the same lithium arsenide. Conversely, 2 reacts with 2 equiv of  $(\text{Me}_3\text{CCH}_2)_2\text{GaCl}$  to produce mixed-bridge 1. The aforementioned conversion of 1 to 2 is the first reported example of the replacement of the chlorine atom in the Ga–As–Ga–Cl ring species by a salt-elimination reaction. The facile manner in which this reaction occurred indicates that other replacements may be possible, and efforts are being made to prepare compounds which contain two gallium centers bridged by two different group V elements, another class of mixed-bridge compounds not yet reported.

For X-ray structural characterization of 1–3, crystals were grown from pentane solutions. Crystallographic data and data collection parameters are summarized in Table

(8) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

**Table II. Non-Hydrogen Atom Fractional Coordinates and Equivalent Isotropic Thermal Parameters for  $(\text{Me}_3\text{CCH}_2)_2\text{GaAs}(\text{SiMe}_3)_2\text{Ga}(\text{CH}_2\text{CMe}_3)_2\text{Cl}$  (1), with Estimated Standard Deviations in Parentheses**

atom	x	y	z	$B_{\text{eq}}, \text{\AA}^2$
As	0.33519 (3)	0.26603 (2)	0.29967 (2)	3.68 (1)
Ga(1)	0.55433 (3)	0.24109 (3)	0.40315 (2)	4.24 (1)
Ga(2)	0.29019 (4)	0.12380 (3)	0.29344 (2)	4.04 (1)
Cl	0.50217 (8)	0.10515 (7)	0.39309 (6)	5.45 (2)
Si(1)	0.33287 (9)	0.33054 (8)	0.19622 (6)	5.05 (3)
Si(2)	0.19465 (9)	0.33408 (7)	0.32466 (6)	4.93 (2)
C(1)	0.4319 (5)	0.4180 (4)	0.2337 (3)	7.8 (1)
C(2)	0.3991 (4)	0.2663 (4)	0.1504 (2)	7.4 (1)
C(3)	0.1722 (4)	0.3586 (4)	0.1244 (3)	7.1 (1)
C(4)	0.2149 (5)	0.4408 (3)	0.3198 (3)	7.8 (2)
C(5)	0.0349 (4)	0.3043 (3)	0.2511 (3)	6.6 (1)
C(6)	0.2196 (4)	0.3105 (4)	0.4211 (3)	7.1 (1)
C(11)	0.6711 (3)	0.2577 (3)	0.3635 (2)	5.6 (1)
C(12)	0.7764 (3)	0.2014 (3)	0.3805 (2)	5.8 (1)
C(13)	0.8403 (5)	0.1732 (5)	0.4620 (4)	9.1 (2)
C(14)	0.8676 (5)	0.2401 (5)	0.3616 (4)	10.7 (2)
C(15)	0.7250 (5)	0.1310 (5)	0.3297 (4)	9.7 (2)
C(16)	0.5838 (4)	0.2598 (3)	0.5071 (2)	5.8 (1)
C(17)	0.6402 (4)	0.3368 (3)	0.5457 (2)	6.0 (1)
C(18)	0.5726 (6)	0.4042 (4)	0.4921 (4)	8.9 (2)
C(19)	0.7727 (6)	0.3450 (5)	0.5641 (4)	10.1 (2)
C(20)	0.6279 (7)	0.3472 (5)	0.6165 (3)	13.9 (2)
C(21)	0.3024 (4)	0.0693 (3)	0.2117 (2)	5.5 (1)
C(22)	0.1839 (5)	0.0490 (3)	0.1373 (3)	6.9 (1)
C(23)	0.1077 (6)	0.1226 (4)	0.1034 (4)	8.9 (2)
C(24)	0.1072 (7)	-0.0101 (4)	0.1494 (4)	11.6 (3)
C(25)	0.2214 (7)	0.0179 (5)	0.0802 (3)	10.7 (2)
C(26)	0.1759 (3)	0.1010 (3)	0.3336 (2)	5.3 (1)
C(27)	0.2070 (4)	0.0387 (3)	0.3950 (3)	6.2 (1)
C(28)	0.3013 (5)	0.0697 (4)	0.4732 (3)	8.0 (2)
C(29)	0.2570 (6)	-0.0341 (3)	0.3774 (3)	8.4 (2)
C(30)	0.0889 (5)	0.0181 (4)	0.3977 (4)	9.7 (2)

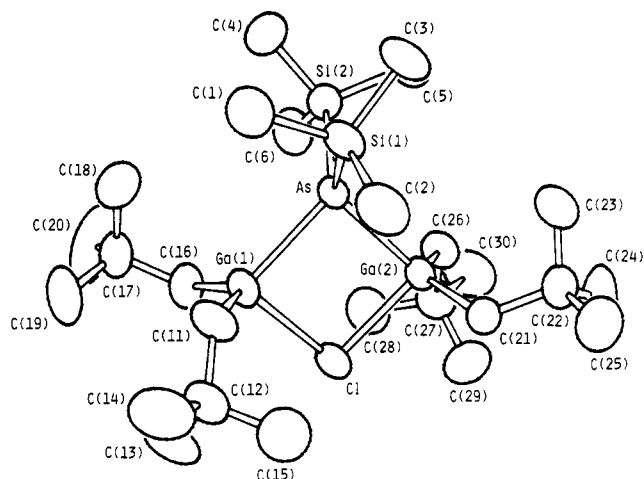
**Table III. Non-Hydrogen Atom Fractional Coordinates and Equivalent Isotropic Thermal Parameters for  $[(\text{Me}_3\text{CCH}_2)_2\text{GaAs}(\text{SiMe}_3)_2]_2$  (2), with Estimated Standard Deviations in Parentheses**

atom	x	y	z	$B_{\text{eq}}, \text{\AA}^2$
As(1)	0.00000 (-) <sup>a</sup>	0.11924 (7)	0.25000 (-) <sup>a</sup>	3.73 (2)
As(2)	0.00000 (-) <sup>a</sup>	0.39360 (7)	0.25000 (-) <sup>a</sup>	3.60 (2)
Ga	-0.03287 (5)	0.25610 (6)	0.14143 (3)	3.95 (2)
Si(1)	-0.18629 (14)	0.00320 (14)	0.20167 (9)	5.02 (4)
Si(2)	-0.19277 (14)	0.50923 (14)	0.18669 (9)	4.59 (4)
C(1)	0.1440 (5)	0.2395 (6)	0.1566 (3)	5.5 (2)
C(2)	0.1675 (5)	0.2798 (5)	0.0939 (3)	5.2 (2)
C(3)	0.3247 (6)	0.2788 (9)	0.1384 (5)	9.9 (3)
C(4)	0.0968 (7)	0.2115 (8)	0.0154 (4)	8.6 (3)
C(5)	0.1145 (7)	0.3917 (7)	0.0678 (4)	8.5 (3)
C(6)	-0.2349 (6)	0.2767 (6)	0.0400 (4)	5.7 (2)
C(7)	-0.3127 (6)	0.2270 (6)	-0.0503 (3)	5.5 (2)
C(8)	-0.4731 (8)	0.2336 (7)	-0.0961 (5)	8.8 (3)
C(9)	-0.2701 (7)	0.1127 (7)	-0.0422 (5)	8.1 (3)
C(10)	-0.2872 (8)	0.2871 (9)	-0.1054 (5)	9.1 (3)
C(11)	-0.3564 (6)	0.0765 (7)	0.1373 (4)	6.7 (5)
C(12)	-0.1968 (6)	-0.1020 (6)	0.1327 (4)	7.3 (2)
C(13)	-0.1630 (6)	-0.0595 (6)	0.2959 (4)	7.0 (2)
C(21)	-0.2307 (6)	0.5764 (6)	0.0898 (4)	6.0 (2)
C(22)	-0.1545 (6)	0.6126 (6)	0.2666 (4)	7.2 (2)
C(23)	-0.3542 (6)	0.4355 (7)	0.1490 (4)	7.1 (2)

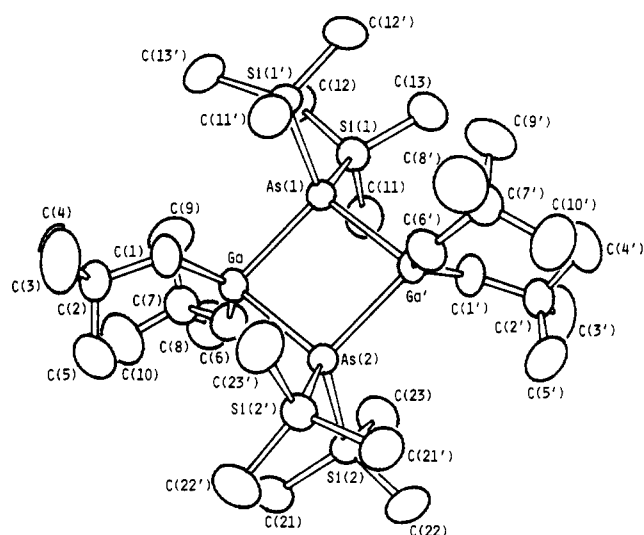
<sup>a</sup>Fixed by symmetry.

I. ORTEP diagrams showing the atom-numbering schemes for 1-3 are presented in Figures 1-3, respectively. Tables II-IV list the non-hydrogen atom fractional coordinates and equivalent isotropic thermal parameters, while selected bond lengths for 1-3 are provided in Tables V-VII, respectively.

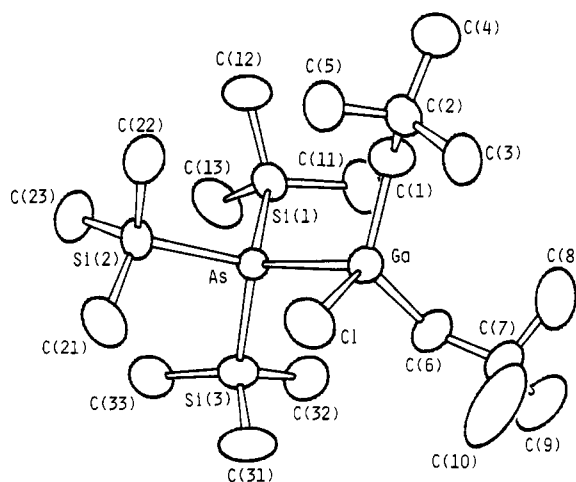
Compound 1 crystallizes in the monoclinic system with four molecules occupying the general positions of the centrosymmetric space group  $P2_1/c$ . Atoms of the Ga-



**Figure 1.** ORTEP diagram (40% probability ellipsoids) showing the atom-numbering scheme and solid-state conformation of  $(\text{Me}_3\text{CCH}_2)_2\text{GaAs}(\text{SiMe}_3)_2\text{Ga}(\text{CH}_2\text{SiMe}_3)_2\text{Cl}$  (1). Hydrogen atoms have been omitted for clarity.



**Figure 2.** ORTEP diagram (40% probability ellipsoids) showing the atom-numbering scheme and solid-state conformation of  $[(\text{Me}_3\text{CCH}_2)_2\text{GaAs}(\text{SiMe}_3)_2]_2$  (2). Hydrogen atoms have been omitted for clarity. Primed atoms are related to the unprimed atoms by a crystallographic  $C_2$  symmetry axis, which passes through As(1) and As(2).



**Figure 3.** ORTEP diagram (40% probability ellipsoids) showing the atom-numbering scheme and solid-state conformation of  $(\text{Me}_3\text{CCH}_2)_2\text{Ga}(\text{Cl})\text{As}(\text{SiMe}_3)_3$  (3). Hydrogen atoms have been omitted for clarity.

**Table IV. Non-Hydrogen Atom Fractional Coordinates and Equivalent Isotropic Thermal Parameters for  $(\text{Me}_3\text{CCH}_2)_2\text{Ga}(\text{Cl})\cdot\text{As}(\text{SiMe}_3)_3$  (3), with Estimated Standard Deviations in Parentheses**

atom	x	y	z	$B_{\text{eq}}, \text{\AA}^2$
As	0.18503 (3)	0.26048 (3)	0.40668 (2)	3.60 (1)
Ga	0.28703 (4)	0.10447 (4)	0.35816 (2)	4.18 (1)
Si(1)	0.24582 (11)	0.27807 (11)	0.52610 (6)	5.13 (3)
Si(2)	0.00773 (9)	0.24102 (10)	0.38670 (7)	4.95 (3)
Si(3)	0.21298 (12)	0.42719 (10)	0.35757 (7)	5.31 (3)
Cl	0.16634 (12)	0.07974 (12)	0.25979 (6)	6.78 (3)
C(1)	0.2965 (4)	-0.0119 (4)	0.4277 (2)	5.3 (1)
C(2)	0.2584 (3)	-0.1261 (3)	0.4099 (2)	4.7 (1)
C(3)	0.3082 (4)	-0.1695 (4)	0.3515 (2)	5.8 (1)
C(4)	0.2941 (5)	-0.1976 (4)	0.4719 (3)	6.4 (1)
C(5)	0.1338 (4)	-0.1312 (4)	0.3888 (3)	6.2 (1)
C(6)	0.4209 (4)	0.1806 (5)	0.3445 (3)	6.4 (1)
C(7)	0.5009 (4)	0.1322 (5)	0.3055 (3)	6.9 (1)
C(8)	0.5974 (6)	0.2048 (8)	0.3079 (4)	12.5 (2)
C(9)	0.5500 (6)	0.0339 (7)	0.3449 (5)	12.4 (2)
C(10)	0.4492 (7)	0.1047 (13)	0.2362 (4)	19.8 (5)
C(11)	0.3955 (5)	0.2535 (5)	0.5423 (3)	7.9 (2)
C(12)	0.1788 (5)	0.1734 (5)	0.5695 (3)	7.9 (2)
C(13)	0.2163 (6)	0.4139 (5)	0.5565 (3)	8.6 (2)
C(21)	-0.0634 (5)	0.2701 (5)	0.2959 (3)	8.0 (2)
C(22)	-0.0401 (4)	0.1024 (4)	0.4057 (3)	7.0 (1)
C(23)	-0.0671 (4)	0.3329 (4)	0.4422 (3)	7.8 (1)
C(31)	0.1989 (6)	0.4074 (5)	0.2641 (3)	8.2 (2)
C(32)	0.3533 (5)	0.4741 (5)	0.3958 (3)	7.6 (1)
C(33)	0.1115 (5)	0.5289 (4)	0.3736 (3)	6.9 (1)

**Table V. Selected Bond Distances ( $\text{\AA}$ ) and Angles ( $\text{deg}$ ) for  $(\text{Me}_3\text{CCH}_2)_2\text{GaAs}(\text{SiMe}_3)_2\text{Ga}(\text{CH}_2\text{CMe}_3)_2\text{Cl}$  (1), with Estimated Standard Deviations in Parentheses**

Bond Lengths			
As-Ga(1)	2.528 (1)	Ga(1)-C(11)	1.992 (5)
As-Ga(2)	2.514 (1)	Ga(1)-C(16)	1.977 (4)
As-Si(1)	2.360 (1)	Ga(2)-C(21)	1.974 (5)
As-Si(2)	2.356 (1)	Ga(2)-C(26)	1.990 (5)
Ga(1)-Cl	2.422 (1)		
Ga(2)-Cl	2.428 (1)		
Bond Angles			
Ga(1)-As-Ga(2)	89.82 (2)	Cl-Ga(1)-C(11)	108.9 (2)
Ga(1)-As-Si(1)	110.87 (3)	Cl-Ga(1)-C(16)	98.7 (2)
Ga(1)-As-Si(2)	121.12 (3)	C(11)-Ga(1)-C(16)	127.8 (2)
Ga(2)-As-Si(1)	120.85 (4)	Ga(2)-As-Si(2)	109.30 (4)
As-Ga(2)-Cl	87.98 (3)	As-Ga(2)-C(21)	113.8 (2)
Si(1)-As-Si(2)	105.39 (5)	As-Ga(2)-C(26)	111.0 (2)
As-Ga(1)-Cl	87.79 (2)	Cl-Ga(1)-C(11)	110.0 (1)
Cl-Ga(2)-C(21)	97.8 (1)	Cl-Ga(2)-C(26)	109.5 (1)
As-Ga(1)-C(16)	114.6 (1)	C(21)-Ga(2)-C(26)	127.6 (2)
		Ga(1)-Cl-Ga(2)	94.41 (4)

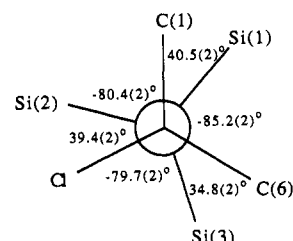
**Table VI. Selected Bond Distances ( $\text{\AA}$ ) and Angles ( $\text{deg}$ ) for  $[(\text{Me}_3\text{CCH}_2)_2\text{GaAs}(\text{SiMe}_3)_2]_2$  (2), with Estimated Standard Deviations in Parentheses**

Bond Lengths			
As(1)-Ga	2.584 (1)	Ga-C(1)	1.994 (7)
As(1)-Si(1)	2.358 (2)	Ga-C(6)	1.999 (5)
As(2)-Ga	2.590 (1)		
As(2)-Si(2)	2.367 (2)		
Bond Angles			
Ga-As(1)-Ga'	95.11 (4)	As(1)-Ga-C(1)	101.9 (2)
Ga-As(1)-Si(1)	118.32 (4)	As(1)-Ga-C(6)	111.9 (3)
Ga'-As(1)-Si(1)	111.84 (5)	As(2)-Ga-C(1)	110.4 (2)
Si(1)-As(1)-Si(1')	102.32 (7)	As(2)-Ga-C(6)	101.3 (2)
Ga-As(2)-Ga'	94.84 (4)	C(1)-Ga-C(6)	135.2 (3)
As(1)-Ga-As(2)	85.02 (3)		

As-Ga-Cl ring deviate by only  $\pm 0.001 \text{ \AA}$  from their least-squares plane, and thus they are coplanar. This geometry contrasts with the puckered forms encountered in the other previously reported gallium-arsenic-halogen mixed-bridge compounds 4,<sup>1,2</sup> 5,<sup>2</sup> and 6,<sup>3</sup> in all three of which the halogen atom is displaced significantly ( $\Delta =$

**Table VII. Selected Bond Distances ( $\text{\AA}$ ) and Angles ( $\text{deg}$ ) for  $(\text{Me}_3\text{CCH}_2)_2\text{Ga}(\text{Cl})\cdot\text{As}(\text{SiMe}_3)_3$  (3), with Estimated Standard Deviations in Parentheses**

Bond Lengths			
As-Ga	2.626 (1)	Ga-Cl(1)	2.242 (1)
As-Si(1)	2.363 (1)	Ga-C(1)	2.002 (5)
As-Si(2)	2.371 (1)	Ga-C(6)	1.991 (6)
As-Si(3)	2.366 (1)		
Bond Angles			
Ga-As-Si(1)	111.24 (4)	As-Ga-Cl	97.87 (4)
Ga-As-Si(2)	114.40 (4)	As-Ga-C(1)	104.6 (1)
Ga-As-Si(3)	112.46 (4)	As-Ga-C(6)	100.2 (2)
Si(1)-As(1)-Si(2)	106.64 (5)	Cl-Ga-C(1)	116.2 (1)
Si(1)-As-Si(3)	106.99 (3)	Cl-Ga-C(6)	112.3 (2)
Si(2)-As-Si(3)	104.56 (5)	C(1)-Ga-C(6)	120.8 (2)

**Figure 4. Newman projection down the Ga-As bond in  $(\text{Me}_3\text{CCH}_2)_2\text{Ga}(\text{Cl})\cdot\text{As}(\text{SiMe}_3)_3$ .**

0.256, 0.293, and 0.860  $\text{\AA}$ , respectively) from the Ga-As-Ga' plane. The mean Ga-As bond distance at 2.521  $\text{\AA}$  in the planar ring of 1 is longer than the mean of 2.466  $\text{\AA}$  in slightly puckered 4 but only slightly longer than the value of 2.504  $\text{\AA}$  in the very puckered ring of 6. Less variation is apparent in the mean Ga-Cl distances in these same compounds (2.425  $\text{\AA}$  in 1, 2.411  $\text{\AA}$  in 4, 2.432  $\text{\AA}$  in 6). The Ga-Cl-Ga angle at 94.41 (4) $^\circ$  in 1 is considerably greater than the essentially equal values in 4 (91.3 (1) $^\circ$ ) and 6 (91.33 (4) $^\circ$ ). The mean exocyclic C-Ga-C bond angle of 127.7 $^\circ$  in 1 is also much enlarged over the corresponding angles in either 4 (121.3 $^\circ$ ) or 6 (123.6 $^\circ$ ).

Crystals of dimer 2 belong to the monoclinic system, space group  $P2_1/c$ , with the As atoms lying on a crystallographic  $C_2$  axis of symmetry, and thus the Ga-As-Ga-As ring is strictly planar. The mean Ga-As bond length at 2.587  $\text{\AA}$  in 2 is only slightly longer than that of 2.567  $\text{\AA}$  in 8. The Ga-As distances in dimeric 2 and 8 exceed those in the corresponding halogen-bridged species by comparable amounts ( $\Delta = 0.066 \text{ \AA}$  for 2 vs 1;  $\Delta = 0.063 \text{ \AA}$  for 8 vs 6), reflecting the more severe nature of the bond strain in group III-group V dimers vs their chloro-bridged counterparts. Moreover, the Si-As-Si angle at 102.32 (7) $^\circ$  in dimeric 2 is smaller than that of 105.39 (5) $^\circ$  in chloro-bridged 1, indicating the increased steric compression present in the former. Like differences in corresponding bond lengths ( $\Delta = 0.051, 0.052 \text{ \AA}$ ) and angles ( $\Delta = 3.3, 5.4^\circ$ ) have also been found recently in pairs of In-As and In-P analogues  $[(\text{Me}_3\text{SiCH}_2)_2\text{InM}(\text{SiMe}_3)_2]_2$  and  $(\text{Me}_3\text{SiCH}_2)_2\text{InM}(\text{SiMe}_3)_2\text{In}(\text{CH}_2\text{SiMe}_3)_2\text{Cl}$  (M = As,<sup>4</sup> P<sup>5</sup>).

Adduct 3 crystallizes in the centrosymmetric space group  $P2_1/c$  with the four molecules in the unit cell lying in general positions. In the solid state, this molecule adopts the staggered conformation depicted in Figure 4. Surprisingly, a search of the literature revealed that although a number of gallium-arsenic adducts have been reported,<sup>9</sup> no complete crystal structure analysis has yet appeared.

Consequently, the only Ga-As bond length comparison possible is with those found in cyclic species containing four-coordinate Ga and As atoms; the distance in **3** at 2.626 (1) Å is longer than any of the Ga-As lengths in such compounds (see preceding discussion and cited references). The mean As-Si bond length at 2.367 Å lies close to the essentially equal values of 2.358 Å in **1** and 2.363 Å in **2**, whereas the mean Ga-C bond length at 1.997 Å is identical with that of 1.997 Å in **2** but longer than that of 1.966 Å in **1**. The Ga-Cl bond length at 2.242 (1) Å is significantly shorter than the means of 2.411-2.432 Å in the Ga-As-Ga-Cl rings of **1**, **4**, and **6**. Intramolecular nonbonded interactions between substituents at As and Ga are minimized by a combination of bond angle deformation and rotation around the As-Ga bond. Thus, enlargement of the Cl-Ga-C and C-Ga-C angles (mean 116.4°), due at least in part to electronic effects, results in steric compression at the arsenic atom (mean Si-As-Si angle 106.06° < mean Ga-As-Si angle 112.70°). Rotation around the Ga-As bond aids in producing approximately equidistant C...C separations of ca. 4.0 Å between the carbon atoms in each of the CH<sub>2</sub> groups at Ga and those in pairs of Me groups of the SiMe<sub>3</sub> substituents at As.

### Conclusions

The facile preparation of compound **1** adds another member to the growing list of mixed-bridge compounds

involving the heavier elements of groups III and V. In addition, we believe it is significant that it has been clearly demonstrated that the Ga-As-Ga-Cl ring of **1** is easily converted to the Ga-As-Ga-As ring of **2**. This demonstrates the feasibility of using the same methodology to prepare compounds containing the Ga-As-Ga-E ring (E = N, P, Sb). Moreover, the fact that adduct **3** was isolated from the 1:1 mole ratio reaction between (Me<sub>3</sub>CCH<sub>2</sub>)<sub>2</sub>GaCl and (Me<sub>3</sub>Si)<sub>3</sub>As and that it could not be readily converted to **1** or **2** give some indication that as the bulk of the ligands on gallium increases, dehalosilylation occurs less readily and the adduct is not necessarily an intermediate in the formation of **1** and **2**.

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**Registry No.** **1**, 137396-24-8; **2**, 137396-25-9; **3**, 137396-26-0; (Me<sub>3</sub>CCH<sub>2</sub>)<sub>2</sub>GaCl, 113976-09-3; (Me<sub>3</sub>Si)<sub>3</sub>As, 17729-30-5; LiAs(SiMe<sub>3</sub>)<sub>2</sub>, 76938-15-3.

**Supplementary Material Available:** Tables of hydrogen atom coordinates and isotropic thermal parameters, anisotropic temperature factors, and complete lists of interatomic distances and angles, including torsion angles, for **1-3**, as well as equations of least-squares planes through groups of atoms for **1** (18 pages); listings of observed and calculated structure amplitudes for **1-3** (87 pages). Ordering information is given on any current masthead page.

## Synthesis, Characterization, and Reaction Chemistry of New Trifluoromethanesulfonato Complexes of Rhodium and Iridium: Formation of Cationic Rh-Pt and Ir-Pt Heterobinuclear Complexes with Bridging Chloride Ligands

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Reactions of ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)M(PMe<sub>3</sub>)(Cl)<sub>2</sub> (M = Rh, **1**; M = Ir, **2**) with excess AgOTf in CH<sub>2</sub>Cl<sub>2</sub> give bis(triflate) complexes ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)M(PMe<sub>3</sub>)(OTf)<sub>2</sub> (M = Rh, **3**; M = Ir, **4**). Complexes **3** and **4** undergo facile reactions with CH<sub>3</sub>CN affording bis(acetonitrile) complexes [( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)M(PMe<sub>3</sub>)(CH<sub>3</sub>CN)<sub>2</sub>]<sup>2+</sup>[OTf]<sub>2</sub><sup>-</sup> (M = Rh, **5**; M = Ir, **6**). Reactions of ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)Rh(PMe<sub>3</sub>)(OTf)<sub>2</sub> (**3**) with *cis*-Pt(Cl)<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub> ((PR<sub>3</sub>)<sub>2</sub> = Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>3</sub>PPh<sub>2</sub>, **7**; PR<sub>3</sub> = PPh<sub>3</sub>, **8**) generate heterobinuclear Rh-Pt complexes [( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)(PMe<sub>3</sub>)Rh( $\mu$ -Cl)<sub>2</sub>Pt(PR<sub>3</sub>)<sub>2</sub>]<sup>2+</sup>[OTf]<sub>2</sub><sup>-</sup> (**9**, **11**). Likewise, reactions of ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)Ir(PMe<sub>3</sub>)(OTf)<sub>2</sub> (**4**) with *cis*-Pt(Cl)<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub> (**7**, **8**) result in the formation of heterobinuclear Ir-Pt complexes [( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)(PMe<sub>3</sub>)Ir( $\mu$ -Cl)<sub>2</sub>Pt(PR<sub>3</sub>)<sub>2</sub>]<sup>2+</sup>[OTf]<sub>2</sub><sup>-</sup> (**10**, **12**). An unambiguous structural assignment for the heterobinuclear bridging chloride complexes **9-12** has been established by an X-ray diffraction study on complex [( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)(PMe<sub>3</sub>)Ir( $\mu$ -Cl)<sub>2</sub>Pt(Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>3</sub>PPh<sub>2</sub>)]<sup>2+</sup>[OTf]<sub>2</sub><sup>-</sup> (**10**).

### Introduction

Transition-metal complexes containing a coordinated triflate ligand have been studied extensively during the past two decades and are a subject of current interest.<sup>1</sup> It

is only in the past ten years that the utilization of coordinated triflate precursors in synthesis has become prevalent. Although many triflate complexes of rhodium and iridium are known, to the best of our knowledge, rhodium and iridium triflate complexes involving the pentamethylcyclopentadienyl ligand or its analogues have not yet been reported. This relatively late development of these types of rhodium and iridium triflate complexes is surprising in view of the established value of triflate complexes as versatile and important reagents in mechanistic studies and organometallic synthesis. Therefore, we undertook the design and synthesis of new complexes with the anticipation that newly developed triflate complexes of rhodium and iridium might serve as potentially valuable

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