ORGANOMETALLICS

Reaction of LiE(SiMe3)2 with compounds containing four-membered cores of the general formula [cyclic] MEM(Cl) (M = In, E = As, P; M = Ga, E = As): novel rearrangement reactions to form the adducts R3M.cntdot.As(SiMe3)3 (R = Me3SiCH2, M = In; R = Ph, M = Ga)

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Reaction of $LiE(SiMe_3)_2$ with Compounds Containing Four-Membered Cores of the General Formula $\overline{MEM(Cl)}$ (M = In, E = As, P; M = Ga, E = As): Novel Rearrangement Reactions To Form the Adducts $R_3M{\cdot}As(SiMe_3)_3$ ($R = Me_3SiCH_2$, M = In; R = Ph, M = Ga)

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Summary: The 1:1 reactions of $R_2\overline{ME(SiMe_3)_2M(R)_2Cl}$ with $LiE(SiMe_3)_2$ ($R = Me_3SiCH_2$, M = In, E = P; $R = Me_3SiCH_2$, M = In, E = As; $R = Me_3SiCH_2$, M = Ga, E = As; R = Ph, M = Ga, E = As) result in the formation of species containing $\overline{MEME}$ core structures as verified by comparison of ^{13}C and ^1H NMR spectra, and melting points, to those obtained for authentic samples prepared previously. When reactions were carried out involving $R_2\overline{ME(SiMe_3)_2M(R)_2Cl}$ and $LiE'(SiMe_3)_2$ ($R = Me_3SiCH_2$, M = In, E = P, E′ = As; R = Ph, M = Ga, E = As, E′ = P), novel rearrangements resulted to form $R_3M{\cdot}As(SiMe_3)_3$ [$R = Me_3SiCH_2$, M = In (**1**) or R = Ph, M = Ga (**2**)]. Both **1** and **2** are formed via the homoleptic redistribution of the substituents on both the metal center and the pnictide. Compound **1** belongs to the rhombohedral system, space group $R3$ with cell constants a = 16.185 (5) Å, c = 12.265 (4) Å, V = 2782 (2) Å^3, and Z = 3. Compound **2** crystallizes in the monoclinic system, space group $P2_1/c$ with cell constants a = 18.867 (5) Å, b = 19.307 (2) Å, c = 20.926 (6) Å, β = 123.27 (1)°, V = 6373 (5) Å^3, and Z = 8.

The last decade has seen considerable attention focused on the formation of suitable precursors to III–V compound semiconductors.[1-6] As a part of our research in this area, we recently reported the isolation of "mixed-bridge" compounds of the heavier group III elements [i.e., four-membered ring systems of the type $\overline{MEM(Cl)}$, where M = In, E = P[7] or As[8] and M = Ga, E = As[9-12]], whose chlorine atom should allow introduction of other functional groups within these systems. From these precursors, the isolation of mixed III–V compound semiconductors may be possible. Herein we report the reactions of several mixed-bridge compounds with $LiAs(SiMe_3)_2$ and $LiP(SiMe_3)_2$ to produce dimeric compounds and the reactions of $(Me_3SiCH_2)_2\overline{InP(SiMe_3)_2In(CH_2SiMe_3)_2Cl}$[7] and $Ph_2\overline{GaAs(SiMe_3)_2Ga(Ph)_2Cl}$[10] with $LiAs(SiMe_3)_2$ and $LiP(SiMe_3)_2$, respectively, to give the arsine adducts $(Me_3SiCH_2)_3In{\cdot}As(SiMe_3)_3$ (**1**) and $Ph_3Ga{\cdot}As(SiMe_3)_3$ (**2**). Both **1** and **2** can be prepared by direct 1:1 reaction of R_3M ($R = Me_3SiCH_2$, M = In; R = Ph, M = Ga) with $As(SiMe_3)_3$.

Experimental Section

General Considerations. All manipulations were performed using general Schlenk, drybox, or high-vacuum techniques. Solvents (including those for NMR spectra) were appropriately dried and distilled under argon prior to use. Literature methods were used to prepare $R_2\overline{ME(SiMe_3)_2M(R)_2Cl}$ ($R = Me_3SiCH_2$, M = In, E = P;[7] $R = Me_3SiCH_2$, M = In, E = As;[8] $R = Me_3SiCH_2$, M = Ga, E = As;[11] R = Ph, M = Ga, E = As),[10] $LiAs(SiMe_3)_2$, and $LiP(SiMe_3)_2$.[13] ^1H and $^{13}C\{^1H\}$ NMR spectra were obtained on a Varian XL-300 at 300.0 and 75.4 MHz, respectively, and referenced to TMS via the residual protons or carbons of the solvent. Melting points (uncorrected) were taken in sealed capillaries. Elemental analyses were performed by E+R Microanalytical Laboratory, Inc., Corona, NY.

Synthesis of $[(Me_3SiCH_2)_2InP(SiMe_3)_2]_2$,[7] $[(Me_3SiCH_2)_2InAs(SiMe_3)_2]_2$,[8] $[(Me_3SiCH_2)_2GaAs(SiMe_3)_2]_2$,[11] and $[Ph_2GaAs(SiMe_3)_2]_2$.[10] All reactions were carried out similarly as follows: 0.01 mmol of the mixed-bridge species was placed in a 5-mm NMR tube in the drybox. Next, 0.01 mmol of the appropriate lithium salt was added (eq 1). The tube was immersed into liquid dinitrogen, and to it approximately 1 mL of benzene-d_6 was vacuum distilled. The reaction mixture was maintained at −196 °C and the NMR tube flame sealed. The mixture was allowed to thaw to room temperature, and the progress of the reaction was monitored at 10-min intervals via ^1H NMR spectroscopy until no resonances corresponding to the starting materials were evident, usually after 40 min. Upon completion of the reaction, the ^{13}C NMR spectrum was obtained (for $[(Me_3SiCH_2)_2InP(SiMe_3)_2]_2$, a ^{31}P NMR spectrum was also recorded), the tube was returned to the drybox, the material was recovered, and a melting point was taken for comparison to an authentic sample of the respective dimer.

Synthesis of $(Me_3SiCH_2)_3In{\cdot}As(SiMe_3)_3$ (1) from $(Me_3SiCH_2)_2\overline{InP(SiMe_3)_2In(CH_2SiMe_3)_2Cl}$ and $LiAs(SiMe_3)_2$. In the drybox, $(Me_3SiCH_2)_2\overline{InP(SiMe_3)_2In(CH_2SiMe_3)_2Cl}$ (0.587 g, 0.741 mmol) was dissolved in 50 mL of toluene in a 100-mL one-necked round-bottomed flask equipped with a Teflon valve and a microstirbar. $LiAs(SiMe_3)_2$ (0.180 g, 0.771 mmol) in 15 mL of hexane and 5 mL of tetrahydrofuran was slowly added dropwise. Initially the reaction mixture was clear. However, after the solution was sealed and stirred at room

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(1) Cowley, A. H.; Jones, R. A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1208.

(2) Byrne, E. K.; Douglas, T.; Theopold, K. H. *Mater. Res. Symp. Proc.* **1989**, *131*, 59.

(3) Olshavsky, M. A.; Goldstein, A. N.; Alivisatos, A. P. *J. Am. Chem. Soc.* **1990**, *112*, 9438.

(4) Douglas, T.; Theopold, K. H. *Inorg. Chem.* **1991**, *30*, 596.

(5) Glass, A. M. *Science* **1987**, *235*, 1003.

(6) Wells, R. L. *Coord. Chem. Rev.* **1992**, *112*, 273.

(7) Wells, R. L.; McPhail, A. T.; Self, M. F. *Organometallics* **1992**, *11*, 221.

(8) Wells, R. L.; Jones, L. J.; McPhail, A. T.; Alvanipour, A. *Organometallics* **1991**, *10*, 2345.

(9) Wells, R. L.; Holley, W. K.; Shafieezad, S.; McPhail, A. T.; Pitt, C. G. *Phosphorus, Sulfur, Silicon Relat. Elem.* **1989**, *41*, 15.

(10) Holley, W. K.; Wells, R. L.; Shafieezad, S.; McPhail, A. T.; Pitt, C. G. *J. Organomet. Chem.* **1990**, *381*, 15.

(11) Wells, R. L.; Pasterczyk, J. W.; McPhail, A. T.; Johansen, J. D.; Alvanipour, A. *J. Organomet. Chem.* **1991**, *407*, 17.

(12) Wells, R. L.; McPhail, A. T.; Pasterczyk, J. W.; Alvanipour, A. *Organometallics* **1992**, *11*, 226.

(13) Becker, G.; Gutekunst, G.; Wessely, H. J. *Z. Anorg. Allg. Chem.* **1980**, *462*, 113.

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Table I. Crystallographic Data and Measurements for $(Me_3SiCH_2)_3In \bullet As(SiMe_3)_3$ (1) and $Ph_3Ga \bullet As(SiMe_3)_3$ (2)

	1	2
molecular formula	$C_{21}H_{60}AsInSi_6$	$C_{27}H_{42}AsGaSi_3$
formula weight	671.0	595.54
crystal system	rhombohedral	monoclinic
space group	$R3$	$P2_1/c$
a, Å	16.185 (5)	18.867 (5)
b, Å	16.185 (5)	19.307 (2)
c, Å	12.265 (4)	20.926 (6)
α, deg	90.00	90.00
β, deg	90.00	123.27 (1)
γ, deg	120.00	90.00
no. of orient. rflns; θ, deg, range	25; 13–17	25; 36–40
V, Å^3	2782 (2)	6373 (5)
Z	3	8
d_{calcd}, g cm^{-3}	1.201	1.241
temp, °C	−49	25
crystal dimens, mm	0.42 × 0.66 × 0.54	0.30 × 0.30 × 0.75
$T_{max}:T_{min}$	0.863:0.655	1.00:0.86
radiation (wavelength)	Mo Kα (0.710 73 Å)	Cu Kα (1.54 18 Å)
μ, cm^{-1}	17.09	35.2
scan type	ω–2θ	ω–2θ
scan width, deg	$1.0 + \Delta_{a1,a2}$	$1.00 + 0.14 \tan \theta$
θ_{max}, deg	22.5	75
intensity control rflns	$\bar{9}00$, 090, 009	$4,3,\overline{12}$, $12,\bar{3},\bar{4}$, $12,\bar{3},4$
variation; repeat time	<1%; every 97 rfln	<2%; every 2 h
no. of rflns recorded	1838 ($-h,+k,\pm l$)	13 499 ($+h,+k,\pm l$)
no. of rflns retained, $I > 3\sigma(I)$	1549	8565
no. of params refined	88	578
extinction correction	6.6 (5) × 10^{-7}	2.9 (3) × 10^{-7}
R, R_w[a]	0.067, 0.097	0.090, 0.144
goodness of fit[b]	0.78	3.0
max shift; esd in final least-squares cycle	0.02	0.03

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w\ |F_o|^2]^{1/2}$; $\sum w\Delta^2[w = 1/\sigma^2(|F_o|), \Delta = (|F_o| - |F_c|)]$ was minimized. [b] Goodness of fit, $[\sum w\Delta^2/(N_{observns} - N_{params})]^{1/2}$.

temperature for 3 days, it became quite orange. LiCl was filtered off, and the volatiles were removed in vacuo to yield a thick sticky orange oil. Addition of approximately 10 mL of warm hexane to this oil, followed by cooling to −15 °C for 30 min, afforded an intractable orange oil and, based on As, a quantitative yield of pale yellow crystals of 1 (0.156 g, slightly contaminated by the oily residue) suitable for X-ray analysis, mp 210–223 °C (dec to brown liquid). Anal. Calcd (Found) for $C_{21}H_{60}AsInSi_6$: C, 37.60 (37.27); H, 9.01 (9.18); As, 3.91 (3.70). ^{1}H NMR: δ −0.06 (s, 6 H, CH_2), 0.30 (s, 27 H, SiMe_3), 0.31 (s, 27 H, AsSiMe_3). ^{13}C{^{1}H} NMR: δ 3.21 (s, SiMe_3), 4.00 (s, ArSiMe_3), 6.18 (s, CH$_2$).

Synthesis of $Ph_3Ga{\cdot}As(SiMe_3)_3$ (2) from $Ph_2GaAs(SiMe_3)_2Ga(Ph)_2Cl$ and $LiP(SiMe_3)_2$. By use of the above procedure, $Ph_2GaAs(SiMe_3)_2Ga(Ph)_2Cl$ (0.100 g, 0.142 mmol) dissolved in 20 mL of benzene was allowed to react with $LiP(SiMe_3)_2$ (0.032 g, 0.142 mmol) in 8 mL of benzene and 0.5 mL of THF to give a pale yellow solution. LiCl was filtered off, and the volatiles were removed in vacuo. Dissolving the off-white thick tacky residue in 4 mL of warm toluene followed by cooling to −15 °C afforded colorless crystals of 2, from an intractable oil, suitable for X-ray analysis in 29.2% yield (0.035 g, based on As), mp 173–185 °C. Anal. Calcd (Found) for $C_{27}H_{42}AsGaSi_3$: C, 54.46 (54.36); H, 7.11 (7.14). ^{1}H NMR: δ 0.13 (s, 27 H, SiMe_3), 7.29 (m, 3 H, Ph), 7.38 (m, 6 H, Ph), 8.10 (m, 6 H, Ph). ^{13}C{^{1}H} NMR: δ 3.22 (s, SiMe_3), 127.81 (partially obscured by solvent, s, Ph), 138.99 (br s, Ph).

Direct Synthesis of 1 and 2. Compounds 1 and 2 can be prepared by the 1:1 reaction of the trialkylmetal with $As(SiMe_3)_3$. R_3M (R = Me_3SiCH_2, M = In; R = Ph, M = Ga) (0.250 mmol) was dissolved in 15 mL of toluene, and $As(SiMe_3)_3$ (0.250 mmol) in 15 mL of toluene was added slowly dropwise. The clear solution was stirred at room temperature for 12 h. Then the volatiles were removed in vacuo to yield the adduct quantitatively as colorless crystals.

Table II. Non-Hydrogen Atom Fractional Coordinates and Equivalent Isotropic Thermal Parameters for 1[a]

atom	x	y	z	U(eq)
In	0	0	0.2554	0.040 (1)
As	0	0	0.0282 (3)	0.080 (1)
Si(1)	0.1386 (3)	0.2218 (3)	0.3794 (4)	0.073 (2)
Si(2)	0.0110 (3)	0.1360 (2)	−0.0447 (3)	0.055 (2)
C(1)	0.1343 (9)	0.1294 (9)	0.2899 (11)	0.050 (3)
C(11)	0.0763 (17)	0.2781 (14)	0.3060 (22)	0.114 (12)
C(12)	0.0869 (20)	0.1740 (19)	0.5137 (20)	0.123 (15)
C(13)	0.2630 (13)	0.3194 (13)	0.4070 (18)	0.094 (9)
C(21)	−0.0747 (12)	0.1602 (11)	0.0301 (18)	0.079 (8)
C(22)	0.1303 (12)	0.2354 (11)	−0.0209 (16)	0.085 (8)
C(23)	−0.0197 (18)	0.1195 (14)	−0.1981 (14)	0.090 (11)

[a] Estimated standard deviations in parentheses.

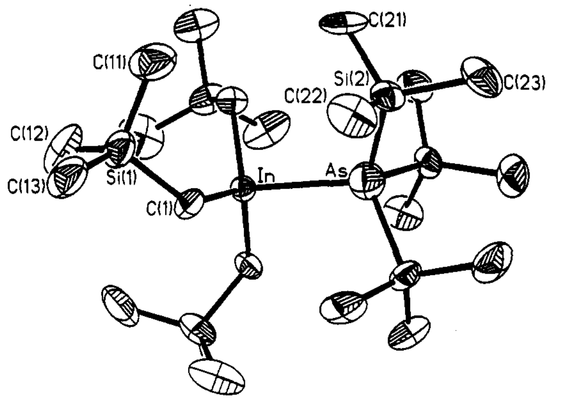

Figure 1. Thermal ellipsoid diagram (40% probability ellipsoids) showing the solid-state conformation and atom-numbering scheme for the unique fraction of $(Me_3SiCH_2)_3In{\cdot}As(SiMe_3)_3$ (1). Hydrogen atoms have been omitted for clarity.

X-ray Crystallography. Single crystals of 1 and 2 were mounted in 0.6-mm thin-walled-glass capillaries under an inert atmosphere of argon and flame sealed. Relevant crystallographic data are given in Table I. For 1, data were collected on a Siemens R3m/V diffractometer (Laboratory for the Structure of Matter, Naval Research Laboratory, Washington, DC). Cell constants and an orientation matrix for data collection corresponded to a rhombohedral cell. The space group was determined by a combination of extinctions and the successful solution and refinement of the structure. Intensity data were corrected for the usual Lorentz and polarization effects. An empirical absorption correction was applied, and equivalent reflections were averaged [R_{merge} = 0.050 on (I)] to yield 1838 reflections out of which 1549 with $F > 3\sigma(F)$ were retained. The structure was solved by direct methods and refined to convergence using SHELXTL PLUS.[14] Non-hydrogen atoms were refined using anisotropic thermal parameters; hydrogen atoms, in calculated positions, were included in structure factor calculations. The weighting scheme was based on counting statistics and included a factor (p = 0.0140) to downweight the intense reflections. The final difference map contained maxima and minima of 1.80 and −2.61 e/Å^3, respectively, located in close proximity to the In atom. Final fractional atomic coordinates are given in Table II. Selected bond distances and angles are given in Table IV. A thermal ellipsoid diagram showing the atom labeling scheme for the unique part of 1 is presented in Figure 1.

For 2, oscillation and Weissenberg photographs provided preliminary unit cell parameters and space group information. The space group was established unequivocally from the Laue symmetry and systematic absences ($0k0$ when k is odd, $h0l$ when l is odd). Reflections hkl were systematically weak when $h+l$ was odd, indicating that Ga and As atoms were related by an approximate B lattice centering. Intensity data, recorded on an Enraf-Nonius CAD-4 diffractometer (Crystal Structure Center, Duke University), were corrected for the usual Lorentz and po-

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(14) Sheldrick, G. M. SHELXTL PLUS, *Crystallographic Computing System, Revision 3.42*; Nicolet Instrument Corp.: Madison, WI, 1986.

Table III. Non-Hydrogen Atom Fractional Coordinates and Equivalent Isotropic Thermal Parameters for 2[a]

atom	*x*	*y*	*z*	B_{eq}, Å^2
As	0.22363 (6)	0.05619 (6)	0.46852 (5)	4.79 (2)
Ga	0.35749 (5)	0.06523 (5)	0.60435 (5)	3.54 (2)
Si(11)	0.1614 (1)	−0.0531 (1)	0.4365 (1)	3.83 (5)
Si(12)	0.2540 (1)	0.0840 (2)	0.3777 (1)	4.37 (5)
Si(13)	0.1156 (1)	0.1310 (1)	0.4453 (1)	4.05 (5)
C(11)	0.3128 (6)	0.1047 (5)	0.6665 (5)	4.7 (2)
C(12)	0.2519 (6)	0.0729 (6)	0.6710 (5)	6.3 (2)
C(13)	0.2262 (7)	0.0981 (8)	0.7166 (6)	8.7 (3)
C(14)	0.2642 (8)	0.1572 (8)	0.7600 (6)	9.1 (3)
C(15)	0.3232 (7)	0.1913 (7)	0.7542 (6)	7.8 (3)
C(16)	0.3485 (6)	0.1658 (6)	0.7071 (6)	5.8 (3)
C(21)	0.4025 (5)	−0.0314 (5)	0.6307 (5)	4.1 (2)
C(22)	0.4353 (6)	−0.0659 (5)	0.5947 (6)	5.3 (2)
C(23)	0.4714 (6)	−0.1307 (6)	0.6184 (7)	6.3 (3)
C(24)	0.4750 (8)	−0.1634 (6)	0.6760 (8)	7.4 (4)
C(25)	0.4400 (8)	−0.1324 (7)	0.7133 (7)	7.1 (4)
C(26)	0.4048 (6)	−0.0680 (6)	0.6895 (6)	5.6 (3)
C(31)	0.4333 (5)	0.1300 (5)	0.5958 (5)	4.3 (2)
C(32)	0.5085 (5)	0.1103 (6)	0.6073 (5)	5.1 (2)
C(33)	0.5643 (7)	0.1543 (7)	0.6052 (6)	7.1 (3)
C(34)	0.5396 (8)	0.2263 (7)	0.5891 (8)	9.8 (4)
C(35)	0.4676 (7)	0.2468 (6)	0.5805 (8)	7.8 (4)
C(36)	0.4138 (6)	0.2002 (6)	0.5788 (7)	6.5 (3)
C(111)	0.0492 (6)	−0.0503 (6)	0.3522 (6)	5.6 (3)
C(112)	0.2236 (8)	−0.1117 (6)	0.4132 (6)	7.0 (3)
C(113)	0.1642 (6)	−0.0871 (6)	0.5218 (5)	5.1 (2)
C(121)	0.2654 (7)	0.1784 (7)	0.3730 (6)	7.5 (3)
C(122)	0.3538 (5)	0.0413 (7)	0.4059 (5)	6.1 (3)
C(123)	0.1747 (8)	0.0554 (8)	0.2815 (6)	7.5 (4)
C(131)	0.1654 (5)	0.2137 (5)	0.4941 (5)	5.0 (2)
C(132)	0.0582 (6)	0.0942 (6)	0.4846 (6)	6.4 (3)
C(133)	0.0414 (6)	0.1477 (6)	0.3425 (6)	6.0 (3)
As′	0.27163 (7)	−0.05857 (7)	0.03520 (6)	5.39 (3)
Ga′	0.13900 (5)	−0.07283 (5)	−0.09992 (5)	3.42 (2)
Si(11′)	0.2656 (1)	0.0347 (1)	0.1018 (1)	4.12 (5)
Si(12′)	0.3908 (1)	−0.0414 (2)	0.0321 (1)	5.50 (6)
Si(13′)	0.2994 (2)	−0.1538 (2)	0.1129 (2)	4.97 (7)
C(11′)	0.0663 (4)	−0.1416 (5)	−0.0911 (4)	3.8 (2)
C(12′)	0.0405 (5)	−0.1366 (5)	−0.0411 (5)	4.8 (2)
C(13′)	−0.0126 (7)	−0.1817 (7)	−0.0385 (6)	6.9 (3)
C(14′)	−0.0457 (7)	−0.2381 (6)	−0.0904 (6)	7.2 (3)
C(15′)	−0.0180 (7)	−0.2466 (6)	−0.1395 (6)	6.4 (3)
C(16′)	0.0331 (5)	−0.1978 (5)	−0.1409 (5)	4.8 (2)
C(21′)	0.0891 (4)	0.0217 (5)	−0.1278 (4)	3.5 (2)
C(22′)	0.1241 (6)	0.0785 (6)	−0.1406 (5)	5.0 (3)
C(23′)	0.0850 (7)	0.1426 (6)	−0.1634 (6)	6.4 (3)
C(24′)	0.0088 (7)	0.1542 (5)	−0.1726 (6)	6.3 (3)
C(25′)	−0.0224 (6)	0.1015 (6)	−0.1562 (6)	6.3 (3)
C(26′)	0.0142 (5)	0.0351 (5)	−0.1340 (5)	4.3 (2)
C(31′)	0.1816 (5)	−0.1105 (5)	−0.1628 (4)	4.1 (2)
C(32′)	0.1765 (6)	−0.0709 (5)	−0.2208 (5)	5.7 (2)
C(33′)	0.2050 (8)	−0.0985 (8)	−0.2650 (6)	8.5 (3)
C(34′)	0.2210 (8)	−0.1639 (8)	−0.2637 (6)	8.9 (3)
C(35′)	0.2255 (7)	−0.2051 (7)	−0.2076 (6)	7.4 (3)
C(36′)	0.2063 (6)	−0.1786 (6)	−0.1576 (5)	5.5 (2)
C(111′)	0.3418 (7)	0.0292 (6)	0.2060 (5)	5.8 (3)
C(112′)	0.2899 (10)	0.1181 (6)	0.0693 (7)	9.0 (4)
C(113′)	0.1580 (6)	0.0345 (7)	0.0844 (5)	6.9 (3)
C(121′)	0.4164 (6)	−0.1249 (9)	0.0077 (7)	8.7 (4)
C(122′)	0.3654 (6)	0.0203 (8)	−0.0419 (6)	7.6 (3)
C(123′)	0.4797 (6)	−0.0048 (8)	0.1248 (7)	7.5 (3)
C(131′)	0.2712 (10)	−0.2327 (6)	0.0530 (7)	9.2 (5)
C(132′)	0.2338 (7)	−0.1472 (7)	0.1565 (6)	7.0 (3)
C(133′)	0.4181 (8)	−0.1570 (7)	0.1932 (7)	7.5 (4)

[a] Estimated standard deviations in parentheses.

Table IV. Selected Bond Distances (Å) and Angles (deg) for 1[a]

Bond Lengths	
In–As	2.778 (4)
As–Si(2)	2.298 (5)
In–C(1)	2.177 (10)
Bond Angles[b]	
As–In–C(1)	101.2 (3)
In–As–Si(2)	112.9 (1)
C(1)–In–C(1)a	116.3 (6)
Si(2)–As–Si(2)a	105.8 (2)
Torsion Angle[c]	
Si(2)–As–In–C(1)	57.7 (4)

[a] Estimated standard deviations in parentheses. [b] Numbered atoms denoted with a lettered postscript are symmetry equivalents to similarly numbered nonpostscripted atoms by the transformation (−*y*, *x* − *y*, *z*) or (*y* − *x*, −*x*, *z*). [c] 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.

Table V. Selected Bond Distances (Å) and Angles (deg) for 2[a]

	unprimed molecule	primed molecule
Bond Lengths		
As–Ga	2.571 (1)	2.563 (1)
As–Si(11)	2.327 (3)	2.318 (3)
As–Si(12)	2.329 (3)	2.308 (3)
As–Si(13)	2.321 (3)	2.316 (3)
Ga–C(11)	2.05 (1)	1.99 (1)
Ga–C(21)	2.00 (1)	1.99 (1)
Ga–C(31)	1.98 (1)	2.02 (1)
Bond Angles		
Ga–As–Si(11)	114.45 (7)	113.98 (7)
Ga–As–Si(12)	110.74 (7)	111.15 (8)
Ga–As–Si(13)	113.98 (7)	113.41 (8)
Si(11)–As–Si(12)	106.6 (2)	106.0 (2)
Si(11)–As–Si(13)	104.9 (1)	105.1 (2)
Si(12)–As–Si(13)	105.5 (1)	106.6 (1)
As–Ga–C(11)	103.3 (2)	106.0 (2)
As–Ga–C(21)	104.6 (2)	104.1 (1)
As–Ga–C(31)	105.3 (2)	105.1 (2)
C(11)–Ga–C(21)	115.7 (4)	113.6 (4)
C(11)–Ga–C(31)	113.1 (4)	111.2 (4)
C(21)–Ga–C(31)	113.3 (4)	115.7 (4)
Torsion Angles[b]		
Si(11)–As–Ga–C(21)	24.6 (3)	24.4 (3)
Si(12)–As–Ga–C(31)	23.8 (3)	26.8 (3)
Si(13)–As–Ga–C(11)	23.9 (3)	24.6 (3)

[a] Estimated standard deviations in parentheses. [b] 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.

larization effects. An empirical absorption correction was applied, and equivalent reflections were averaged [R_{merge} = 0.026 on (I)] to yield 13 098 reflections out of which those 8565 with $I > 3\sigma(I)$ were retained for the analysis. The crystal structure was solved by the heavy-atom approach. The asymmetric unit contains two crystallographically independent molecules of 2. Approximate coordinates for the Ga and As atoms were derived from a Patterson map. The remaining non-hydrogen atoms were located in a series of difference and weighted F_0 Fourier syntheses, and their distributions distinguished the Ga and As atoms. Several rounds of full-matrix least-squares adjustment of non-hydrogen atom positional and thermal parameters (at first isotropic and then anisotropic) followed. Hydrogen atoms were incorporated at their calculated positions, and an extinction correction was included as a variable in the later iterations. A final difference Fourier synthesis revealed no unusual features (maximum, 1.4 e/Å^3, minimum −2.6 e/Å^3, located ca. 0.2–0.5 Å from the Ga and As atoms). Crystallographic calculations were performed using the Enraf-Nonius Structure Determination Package (SDP).[15] For all structure factor calculations, neutral atom scattering factors and their anomalous dispersion corrections were taken from ref 16. Fractional atomic coordinates are listed in Table III. Selected distances and angles are given in Table V. A thermal ellipsoid diagram showing the atom labeling scheme and solid-state con-

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(15) Enraf-Nonius Structure Determination Package (SDP 3.0). Enraf-Nonius, Delft, The Netherlands, 1985.

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

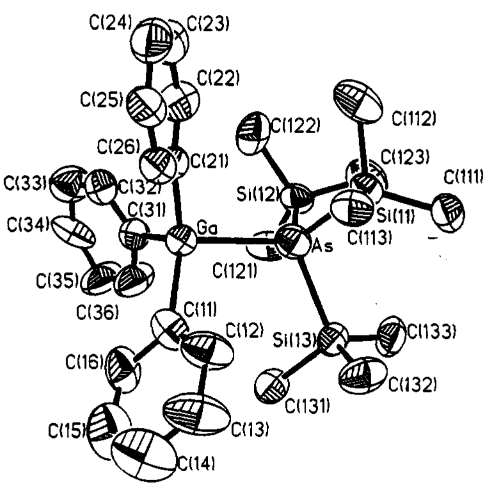

Figure 2. Thermal ellipsoid diagram (40% probability ellipsoids) showing the solid-state conformation of one of the molecules in the asymmetric crystal unit and atom-numbering scheme of $Ph_3Ga{\cdot}As(SiMe_3)_3$ (**2**). Hydrogen atoms have been omitted for clarity.

formation of one of the molecules in the asymmetric crystal unit of **2** is presented in Figure 2.

Results and Discussion

Currently, our laboratory is investigating the potential use of mixed-bridge-type compounds for the synthesis of further III–V oligomeric units. As part of an earlier study, it was shown by us that the reaction of $(Me_3CCH_2)_2\overline{GaAs(SiMe_3)_2Ga(CH_2CMe_3)_2Cl}$ with $LiAs(SiMe_3)_2$ yields $[(Me_3CCH_2)_2GaAs(SiMe_3)_2]_2$,[12] and we decided to explore whether this reactivity could be generally applied to similar mixed-bridge systems. The following transformations were accomplished according to

$$R_2\overline{ME(SiMe_3)_2M(R)_2Cl} + LiE(SiMe_3)_2 \rightarrow [R_2ME(SiMe_3)_2]_2 + LiCl \quad (1)$$

$$R = Me_3SiCH_2,\ M = In,\ E = P, As$$

$$R = Me_3SiCH_2, Ph,\ M = Ga,\ E = As$$

These facile and clean reactions result in the formation of dimeric systems where the bridging chlorine has been replaced by the pnictide of the lithium salt.

Similarly, the introduction of two different pnictide atoms into these systems to give rings of the formula $\overline{MEME'}$ (E = As, E′ = P) was investigated. Interestingly, when $R_2\overline{ME(SiMe_3)_2M(R)_2Cl}$ and $LiE'(SiMe_3)_2$ (R = Me_3SiCH_2, M = In, E = P, E′ = As; R = Ph, M = Ga, E = As, E′ = P) are allowed to react, rearrangements occur to form $(Me_3SiCH_2)_3In{\cdot}As(SiMe_3)_3$ (**1**) and $Ph_3Ga{\cdot}As(SiMe_3)_3$ (**2**). No indium–phosphorus or gallium–phosphorus compounds were isolated. Reagent purity was verified through spectroscopic (NMR) and physical (melting point) measurements prior to, and after, use and no contamination was detected. Though the precise pathway of these transformations is not known, the fact that substituent transfer occurred at both the metal and the arsenic centers in each is quite remarkable. The subtle combination of both an arsenic and phosphorus atom in these systems substantially changes their reaction pathways. These reactions are apparently much more complicated than was originally envisioned.

A literature review reveals no structural reports of indium–arsenic adducts. Compound **1** has a threefold axis of symmetry coincidental with the indium arsenic bond. The As–In–C and C–In–C angles are 101.2 (4)° and 116.3 (3)°, respectively. Undoubtedly, the large C–In–C angle is indicative of seric repulsions from the Me_3SiCH_2 groups. The In–As–Si and Si–As–Si bond angles are 112.9 (1)° and 105.8 (1)°, respectively. The large In–As–Si angle is interesting and may be due to electronic repulsions between the arsenic atom and $SiMe_3$ groups or repulsions between the $SiMe_3$ groups and neighboring Me_3SiCH_2 groups. In sharp contrast to either $As(SiMe_3)_3$ or $(Me_3SiCH_2)_3In$, **1** is quite stable and will not undergo appreciable decomposition even upon exposure to air for over 10 h or undergo further reaction (via ^1H NMR spectroscopy and melting point) when heated in chlorobenzene at 140 °C for 3 days in a sealed pressure tube.

There have been three structural reports of gallium–arsenic adducts, viz. $Cl_3Ga{\cdot}AsMe_3$ (**4**) (only the unit cell parameters were given),[17] $(Me_3CCH_2)_2(Cl)Ga{\cdot}As(SiMe_3)_3$ (**5**),[12] and $(C_6F_5)_3Ga{\cdot}As(SiMe_3)_3$ (**6**).[18] Compounds **6** and **2** crystallize in the monoclinic space group $P2_1/c$, and although they are isostructural, they are not isomorphous. In **6**, one molecule occupies each of the four general positions of the space group while the asymmetric unit of **2** consists of two structurally identical, but crystallographically independent, molecules that lie in general positions. Values for mean bond angles in **2** and **6** [Ga–As–Si = 113.0°, Si–As–Si = 105.8°, As–Ga–C = 104.7°, C–Ga–C = 113.8°, smallest Si–As–Ga–C torsion angle, 24.7° in **2**; Ga–As–Si = 113.2°, Si–As–Si = 105.5°, As–Ga–C = 106.8°, C–Ga–C = 112.0°, smallest Si–As–Ga–C torsion angle, 17.1° in **6**] are very alike. The mean Ga–As bond length of 2.567 Å in **2** is slightly longer than that of 2.550 (4) Å in **6**, but both are significantly shorter than the value of 2.626 (1) Å in **5**. The mean Ga–C(ar) bond distance in **2** (2.01 Å) is the same as in **6** (2.012 Å) whereas the mean As–Si bond lengths in **2** at 2.320 Å is significantly shorter than the corresponding value of 2.403 Å in **6**, reflecting differences in nonbonded intramolecular steric interactions (H···H < F···H) between substituents on the Ga and As centers. As with **1**, compound **2** is similarly unreactive under refluxing conditions.

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Supplementary Material Available: Tables of hydrogen atom coordinates and isotropic thermal parameters, anisotropic temperature factors, and complete lists of bond distances and angles, including torsion angles, for **1** and **2** (16 pages). Ordering information is given on any current masthead page.

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[17] Carter, J. C.; Jugie, G.; Enjalbert, R.; Galy, J. *Inorg. Chem.* **1978**, *17*, 1248.

[18] Wells, R. L.; McPhail, A. T.; Hallock, R. B.; Johansen, J. D. *J. Organomet. Chem.*, submitted for publication.