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Synthesis and Characterization of Indium–Arsenic Compounds Containing a Four-Membered $\overline{\text{In–As–In–As}}$ or $\overline{\text{In–As–In–Cl}}$ Ring: Crystal Structures of $[(Me_3SiCH_2)_2InAs(SiMe_3)_2]_2$ and $(Me_3SiCH_2)_2\overline{InAs(SiMe_3)_2In(CH_2SiMe_3)_2Cl}$

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The first four-membered ring compounds with bridging of the indium atoms by two arsenic atoms and with mixed bridging of the indium centers by one arsenic and one chlorine, $[(Me_3SiCH_2)_2InAs(SiMe_3)_2]_2$ (1) and $(Me_3SiCH_2)_2\overline{InAs(SiMe_3)_2In(CH_2SiMe_3)_2Cl}$ (2), to be characterized completely were prepared by the reaction of $(Me_3SiCH_2)_2InCl$ and $(Me_3Si)_3As$ in 1:1 and 2:1 mol ratios, respectively. X-ray crystallographic analyses showed both the $\overline{\text{In–As–In–As}}$ ring of 1 and the $\overline{\text{In–As–In–Cl}}$ ring of 2 to be planar. Compound 1 belongs to the orthorhombic system, space group *Pbcn* (D^{14}_{2h}), with four molecules in a unit cell of dimensions *a* = 12.920 (1) Å, *b* = 21.618 (2) Å, and *c* = 18.797 (2) Å. Compound 2 crystallizes in the monoclinic system, space group *C*2/*c* (C^6_{2h}), with four molecules in a unit cell of dimensions *a* = 19.233 (3) Å, *b* = 10.798 (2) Å, *c* = 20.819 (3) Å, and *β* = 105.91 (1)°. Compound 1 reacts with 2 equiv of $(Me_3SiCH_2)_2InCl$ to yield 2 as a major product, as evidenced by ^1H and $^{13}C\{^1H\}$ NMR and melting point data.

Introduction

Recently, organogallium–arsenic compounds containing four-membered rings consisting of mixed bridging of the gallium atoms by one arsenic atom and one halogen atom have been synthesized via dehalosilylation between an organogallium halide and a silylarsine.[1-4] Thus, compounds formulated as $R_2\overline{GaAs(SiMe_3)_2Ga(R)_2Cl}$ (R = Ph,[1,2] Me_3SiCH_2[3]) and $Ph_2\overline{GaCl(Ph)_2Ga(Me_3Si)As}(CH_2)_3\overline{As(SiMe_3)Ga(Ph)_2ClGa}Ph_2$[4] have been described by us. Until now, our studies regarding the formation of such mixed-bridge systems involving the heavier elements of groups III and V have focused only on gallium and arsenic. In order to investigate the generality of this behavior, analogous reactions utilizing an organoindium halide were carried out. Here we report the isolation of $[(Me_3SiCH_2)_2InAs(SiMe_3)_2]_2$ (1) from the reaction of $(Me_3SiCH_2)_2InCl$ and $(Me_3Si)_3As$ in a 1:1 mol ratio, whereas the reaction in a 2:1 mol ratio afforded $(Me_3SiCH_2)_2\overline{InAs(SiMe_3)_2In(CH_2SiMe_3)_2Cl}$ (2). In addition to describing the synthesis and complete characterization of 1 and 2, including their crystal structures, the conversion of 1 to 2 is reported.

Experimental Section

General Considerations. All manipulations were performed by using Schlenk techniques in an I^2R glovebag under dry nitrogen or in a Vacuum/Atmospheres HE-493 Dri-Lab containing an argon atmosphere. Aromatic solvents were distilled from sodium/benzophenone ketyl under dry nitrogen. Benzene-d_6 was dried over sodium/benzophenone ketyl and vacuum-transferred from the same. Pentane was distilled over $LiAlH_4$ under dry nitrogen. Indium(III) chloride was purchased from Alfa Products, Ward Hill, MA, and was not further purified. $(Me_3SiCH_2)_3In$, $(Me_3SiCH_2)_2InCl$,[5] and $(Me_3Si)_3As$[6] were prepared by literature procedures. ^1H and ^{13}C NMR spectra were obtained on a Varian XL-300 (300 and 75.4 MHz, respectively) spectrometer using 5-mm tubes. All spectra were referenced to TMS by using the residual protons or carbons of deuterated benzene at δ 7.15 or 128 ppm. NMR tubes were flame-sealed under vacuum. All 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 $[(Me_3SiCH_2)_2InAs(SiMe_3)_2]_2$ (1). $(Me_3SiCH_2)_2InCl$ (0.500 g, 1.54 mmol) in 30 mL of benzene and $(Me_3Si)_3As$ (0.454 g, 1.54 mmol) in 5 mL of benzene were combined in a 100-mL one-necked round-bottomed flask equipped with a Teflon valve and a microstirbar. The solution, which was freeze–pump–thawed once and left to stir at room temperature, became light yellow within 1 h. Continuation of the stirring at room temperature for 3 days, followed by removal of volatiles in vacuo, afforded a yellow solid. The crude product was dissolved in a small amount of warm pentane and after one day at −15 °C, the solution afforded colorless crystals of 1 suitable for single-crystal X-ray analysis. Removal of pentane by evaporation afforded a white powder, which when redissolved in hot pentane followed by cooling to −15 °C, gave a second crop of 1 (0.578 g total, 75.5% yield) [mp not observed (sample decomposed to a black solid above 210 °C)]. Anal. Calcd (found) for $C_{28}H_{80}As_2In_2Si_8$: C, 32.94 (32.95); H, 7.90 (7.91); Cl, 0.00 (0.31). ^1H NMR: δ 0.24 (s, 8 H, C*H*$_2$), 0.32 (s, 36 H, Si*Me*$_3$), 0.49 (s, 36 H, Si*Me*$_3$). $^{13}C\{^1H\}$ NMR: δ 3.60 ($SiMe_3$), 3.91 (CH_2), 5.32 ($SiMe_3$).

Preparation of $(Me_3SiCH_2)_2\overline{InAs(SiMe_3)_2In(CH_2SiMe_3)_2Cl}$ (2). $(Me_3SiCH_2)_2InCl$ (0.500 g, 1.54 mmol) in 30 mL of benzene and $(Me_3Si)_3As$ (0.227 g, 0.771 mmol) in 5 mL of benzene were combined in a one-necked round-bottomed flask equipped with a Teflon valve and a microstirbar. The solution was freeze–pump–thawed, and on stirring at room temperature, became yellow within 1 h. After the reaction mixture was stirred at room temperature for 3 days, the volatiles were removed in vacuo. Dissolution of the resulting solid yellow residue in pentane, followed by cooling to −15 °C for 5 days, afforded colorless crystals of 2 suitable for single-crystal X-ray analysis (0.103 g, 16.2% yield), mp 68–71 °C. Anal. Calcd (found) for $C_{22}H_{62}AsClIn_2Si_6$: C, 31.64 (31.39); H, 7.48 (7.39); Cl, 4.24 (4.57). ^1H NMR: δ 0.27 (s, 44 H,

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Table I. Crystallographic Data and Measurements[a] for $[(Me_3SiCH_2)_2InAs(SiMe_3)_2]_2$ (1) and $(Me_3SiCH_2)_2InAs(SiMe_3)_2In(CH_2SiMe_3)_2Cl$ (2)

	1	2
molecular formula	$C_{28}H_{80}As_2In_2Si_8$	$C_{22}H_{62}AsClIn_2Si_6$
fw	1021.12	835.27
cryst syst	orthorhombic	monoclinic
space group	*Pbcn* (D^{14}_{2h})	*C*2/*c* (C^6_{2h})
a, Å	12.920 (1)	19.233 (3)
b, Å	21.618 (2)	10.798 (2)
c, Å	18.797 (2)	20.819 (3)
β, deg		105.91 (1)
no. of orient reflns; *θ* range, deg	25; 40–45	25; 40–46
V, Å^3	5250 (1)	4158 (2)
Z	4	4
D_{calcd}, g cm^{-3}	1.292	1.334
temp, °C	25	25
cryst dimens, mm	0.20 × 0.20 × 0.26	0.30 × 0.40 × 0.70
T_{max}:T_{min}	1.00:0.70	1.00:0.25
radiation (λ, Å)	Cu Kα (1.5418)	Cu Kα (1.5418)
μ, cm^{-1}	105.1	123.4
scan type	ω–2θ	ω–2θ
scan width, deg	0.80 + 0.14 tan θ	1.00 + 0.14 tan θ
θ_{max}, deg	75	75
intens control reflns	441, 443, $\bar{4}43$, $\bar{4}41$	313, 531, 53$\bar{1}$, 31$\bar{3}$
variation; repeat time, *h*	−37%; 2	<2%; 2
no. of rflns recorded	5386 (+*h*,+*k*,+*l*)	4388 (+*h*,+*k*,±*l*)
no. of rflns retained, $I > 3.0\sigma(I)$	1877	3252
no. of params refined	183	147
extinction corrn	1.5 (1) × 10^{-7}	2.1 (1) × 10^{-6}
R, R_w[b]	0.054, 0.071	0.067, 0.088
goodness-of-fit[c]	1.3	2.1
max shift; esd in final least-squares cycle	0.01	0.03
final $\Delta\rho$, e/Å^3 (max; min)	0.87; −1.57	2.5; −1.9

[a] 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 II computers by use of the Enraf-Nonius Structure Determination Package (SDP). [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $\sum w\Delta^2$ [$w = 1/\sigma^2(|F_o|)$, $\Delta = (|F_o| - |F_c|)$] was minimized. [c] Goodness-of-fit = $[\sum w\Delta^2/(N_{obsns} - N_{params})]^{1/2}$.

C*H*$_2$Si*Me*$_3$), 0.39 (s, 18 H, Si*Me*$_3$); an individual methylene resonance was not observed. $^{13}C\{^1H\}$ NMR: δ 2.83 (SiMe$_3$), 7.75 (CH$_2$), 4.69 (SiMe$_3$).

Reaction of 1 with $(Me_3SiCH_2)_2InCl$. $(Me_3SiCH_2)_2InCl$ (13.1 mg, 0.040 mmol) and 1 (20.4 mg, 0.020 mmol) were combined in an NMR tube, into which was vacuum-distilled 0.75 mL of benzene-d_6. After the contents of the tube were frozen with liquid nitrogen, the tube was flame-sealed and allowed to warm to room temperature. After thawing, the ^1H NMR spectrum of the solution contained three singlets at δ 0.17, 0.26 and 0.39, the first of which corresponded to the SiMe$_3$ protons of $(Me_3SiCH_2)_2InCl$ (the methylene proton resonance at δ 0.27 is under the peak at δ 0.26). No peaks attributable to 1 were observed, even though the NMR tube still contained solid that was presumed to be 1. After 1.5 h, all of the solid in the tube had disappeared, and the ^1H and $^{13}C\{^1H\}$ NMR spectra of the resulting solution corresponded to those obtained for 2. After the tube was opened, the solvent was removed and a colorless solid was isolated, the melting point of which was the same as that recorded for an authentic sample of 2.

Structural Analyses of 1 and 2. Crystallographic data and measurements are presented in Table I. Intensity data were corrected for the usual Lorentz and polarization effects; empirical absorption corrections (and in the case of 1, a linear decay correction) were also applied. For 1, non-hydrogen atom coordinates of its isomorphous gallium analogue[3] were used as initial values, whereas the crystal structure of 2 was solved by direct methods. Positional and thermal parameters (at first isotropic, then anisotropic) for both compounds were adjusted by means of several rounds of full-matrix least-squares calculations. Hydrogen atoms were included at their calculated positions during the final least-squares iterations, which also included refinement of an extinction correction. For structure-factor calculations, neutral-atom scattering factors and their anomalous dispersion corrections were taken from ref 7.

Results and Discussion

The reaction of $(Me_3SiCH_2)_2InCl$ and $(Me_3Si)_3As$ in a 1:1 mol ratio at room temperature in benzene yields 1 (eq 1), the indium analogue of $[(Me_3SiCH_2)_2GaAs(SiMe_3)_2]_2$ (3).[3] The ^1H NMR spectrum of 1 is consistent with expectations based on its solid-state structure. Compound 1 is stable at room temperature over a period of at least 10 days, as evidenced by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy.

$$2(Me_3SiCH_2)_2InCl + 2(Me_3Si)_3As \rightarrow \underset{\textbf{1}}{[(Me_3SiCH_2)_2InAs(SiMe_3)_2]_2} + 2Me_3SiCl \quad (1)$$

When $(Me_3SiCH_2)_2InCl$ is treated with $(Me_3Si)_3As$ in a 2:1 mol ratio at room temperature in benzene compound 2, the indium analogue of $(Me_3SiCH_2)_2GaAs(SiMe_3)_2Ga(CH_2SiMe_3)_2Cl$ (4),[3] is produced (eq 2). The ^1H NMR spectrum of 2 shows only one type of trimethylsilyl and (trimethylsilyl)methyl group, with the methylene signal of the latter degenerate with its methyl signal. The $^{13}C\{^1H\}$ NMR spectrum contains three signals that can be assigned to methylene or methyl carbons on the basis of intensities. Compound 2 is unstable at room temperature, decomposing to an orange/brown solid within a few hours.

$$2(Me_3SiCH_2)_2InCl + (Me_3Si)_3As \rightarrow \underset{\textbf{2}}{(Me_3SiCH_2)_2InAs(SiMe_3)_2In(CH_2SiMe_3)_2Cl} + Me_3SiCl \quad (2)$$

Dehalosilylation between an organogallium halide and a silylarsine to form gallium–arsenic bonds now has ample precedent;[1–4,8,9] however, analogous reactions utilizing organoindium halides to form indium–arsenic bonds have until now been unknown. The synthesis of 1 and 2 is clearly dependent on the stoichiometry of organoindium halide and silylarsine. Thus, whereas compound 1 is prepared in good yield from the reaction of $(Me_3SiCH_2)_2InCl$ and $(Me_3Si)_3As$ in a 1:1 mol ratio, 2 is formed in significantly lower yield when a 2:1 mol ratio is employed. The low yield of the latter is, in part, due to its high solubility in all solvents from which recrystallization was attempted (pentane, toluene, ligroin, and benzene). This dependence on reagent stoichiometry to prepare 1 and 2 is interesting, since it contrasts with the behavior observed in the reaction of $(Me_3SiCH_2)_2GaCl$ with $(Me_3Si)_3As$, where both 1:1 and 2:1 mol ratios yield only mixed-bridge compound 4.

Crystals of 1 suitable for X-ray diffraction were obtained by recrystallization from a pentane solution. Crystallographic details are summarized in Table I. An ORTEP diagram showing the atom-numbering scheme of 1 is presented in Figure 1. Table II gives the non-hydrogen atom fractional coordinates and equivalent isotropic thermal parameters, while Table IV gives selected bond lengths and angles.

In accord with its isomorphous gallium analogue, compound 1 contains a planar four-membered ring with

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Table II. Non-Hydrogen Atom Fractional Coordinates and Equivalent Isotropic Thermal Parameters for 1, with Estimated Standard Deviations in Parentheses

atom	*x*	*y*	*z*	B_{eq}, Å^2
As	0.14199 (10)	0.18627 (6)	0.23718 (7)	3.97 (3)
In(1)	0.00000 (–)[a]	0.27933 (5)	0.25000 (–)[a]	4.23 (3)
In(2)	0.00000 (–)[a]	0.09393 (5)	0.25000 (–)[a]	4.09 (2)
Si(1)	0.2386 (3)	0.1749 (2)	0.1321 (3)	5.5 (1)
Si(2)	0.2644 (3)	0.1908 (2)	0.3292 (3)	5.8 (1)
Si(11)	0.0391 (4)	0.3900 (2)	0.1150 (3)	5.3 (1)
Si(21)	–0.0858 (4)	–0.0211 (2)	0.1307 (3)	6.7 (1)
C(11)	0.1501 (14)	0.1895 (8)	0.0567 (9)	7.7 (5)
C(12)	0.3506 (13)	0.2304 (8)	0.1292 (11)	8.4 (5)
C(13)	0.2933 (12)	0.0938 (7)	0.1272 (10)	7.3 (5)
C(21)	0.3332 (13)	0.2661 (8)	0.3283 (11)	9.0 (6)
C(22)	0.3595 (14)	0.1262 (8)	0.3202 (10)	8.6 (5)
C(23)	0.1939 (14)	0.1823 (8)	0.4163 (9)	7.9 (5)
C(111)	–0.0366 (13)	0.3249 (6)	0.1507 (10)	6.9 (4)
C(112)	0.0324 (20)	0.3903 (13)	0.0185 (12)	16 (1)
C(113)	0.1780 (14)	0.3866 (8)	0.1405 (14)	12.8 (7)
C(114)	–0.0123 (19)	0.4614 (8)	0.1433 (21)	20 (1)
C(211)	–0.0036 (12)	0.0468 (6)	0.1459 (8)	5.9 (4)
C(212)	–0.0039 (15)	–0.0910 (8)	0.1122 (17)	12.7 (8)
C(213)	–0.1751 (15)	–0.0366 (8)	0.2085 (12)	10.6 (6)
C(214)	–0.1683 (18)	–0.0101 (10)	0.0496 (11)	11.5 (7)

[a] Fixed by symmetry.

Table III. Non-Hydrogen Atom Fractional Coordinates and Equivalent Isotropic Thermal Parameters for 2, with Estimated Standard Deviations in Parentheses

atom	*x*	*y*	*z*	B_{eq}, Å^2
As	0.00000 (–)[a]	0.0313 (1)	0.25000 (–)[a]	2.77 (2)
In	0.09994 (2)	0.20343 (5)	0.24914 (2)	3.12 (1)
Cl	0.0000 (–)[a]	0.3677 (3)	0.2500 (–)[a]	4.69 (6)
Si	0.0419 (1)	–0.0958 (2)	0.3447 (1)	3.58 (4)
Si(1)	0.1009 (1)	0.3459 (3)	0.0973 (1)	4.45 (5)
Si(2)	0.2302 (1)	0.3679 (3)	0.3624 (1)	5.27 (6)
C(1)	–0.0122 (6)	–0.2397 (10)	0.3378 (6)	7.0 (3)
C(2)	0.0352 (6)	–0.0065 (13)	0.4184 (5)	7.0 (3)
C(3)	0.1373 (5)	–0.01350 (10)	0.3532 (5)	5.6 (2)
C(11)	0.1294 (4)	0.2160 (8)	0.1563 (4)	4.1 (2)
C(12)	0.1315 (7)	0.4968 (12)	0.1382 (6)	7.0 (3)
C(13)	0.1429 (7)	0.3273 (15)	0.0270 (5)	7.9 (3)
C(14)	0.0018 (6)	0.3467 (13)	0.0638 (6)	7.4 (3)
C(21)	0.1716 (5)	0.2281 (10)	0.3485 (3)	4.8 (2)
C(22)	0.1743 (7)	0.5104 (13)	0.3513 (8)	9.0 (4)
C(23)	0.2954 (9)	0.3655 (20)	0.4465 (7)	13.3 (5)
C(24)	0.2833 (6)	0.3674 (13)	0.3005 (7)	7.5 (3)

[a] Fixed by symmetry.

Table IV. Selected Bond Distances (Å) and Angles (deg) for 1, with Estimated Standard Deviations in Parentheses

	Bond Lengths		
As–In(1)	2.733 (2)	In(1)–C(111)	2.16 (2)
As–In(2)	2.722 (2)	In(2)–C(211)	2.21 (1)
As–Si(1)	2.349 (5)		
As–Si(2)	2.346 (5)		
	Bond Angles		
In(1)–As–In(2)	94.57 (5)	As–In(1)–As′	85.21 (4)
In(1)–As–Si(1)	120.5 (1)	As–In(1)–C(111′)	105.3 (4)
In(1)–As–Si(2)	110.9 (1)	C(111)–In(1)–C(111′)	125.8 (5)
In(2)–As–Si(1)	110.8 (2)	As–In(2)–C(211)	105.9 (4)
In(2)–As–Si(2)	114.8 (1)	As–In(2)–As′	85.65 (4)
Si(1)–As–Si(2)	105.4 (2)	As–In(2)–C(211′)	113.8 (4)
As–In(1)–C(111)	113.9 (4)	C(211)–In(2)–C(211′)	125.0 (5)

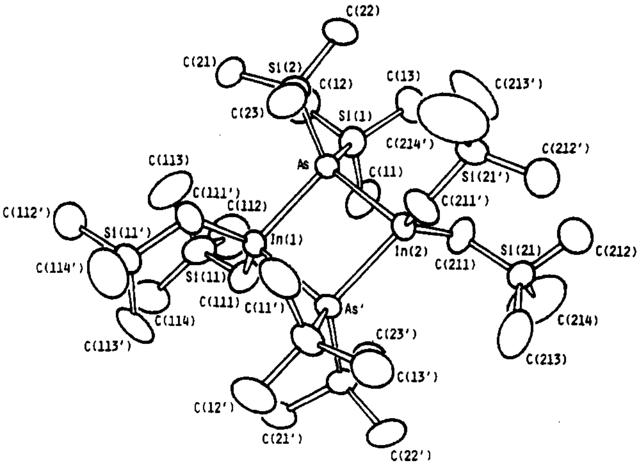

Figure 1. ORTEP diagram of the solid-state structure of $[(Me_3SiCH_2)_2InAs(SiMe_3)_2]_2$ (1), with thermal ellipsoids at the 40% probability level. Hydrogen atoms have been omitted for clarity.

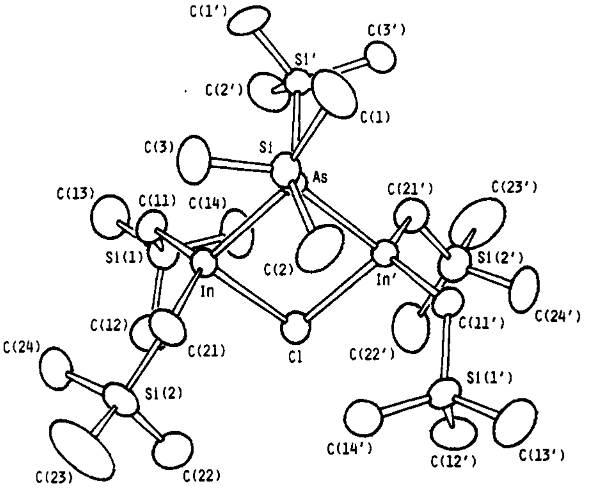

Figure 2. ORTEP diagram of the solid-state structure of $(Me_3SiCH_2)_2\overline{InAs(SiMe_3)_2In(CH_2SiMe_3)_2Cl}$ (2), with thermal ellipsoids at the 40% probability level. Hydrogen atoms have been omitted for clarity.

slightly unequal bond lengths [In–As = 2.733 (2), 2.722 (2) Å]. The In–As–In angle is 94.57 (5)° and As–In–As angles are 85.21 (4) and 85.65 (4)°. The mean of the In–As bond lengths in 1 (2.728 Å) is considerably greater than that at 2.676 Å in $[Me_2InAsMe_2]_3$ (5),[10] the only other compound containing In–As bonds to have its structure completely elucidated by single-crystal X-ray analysis. Such bond length variation appears to be a general phenomenon among many group III–V dimers and trimers.[11] The planar nature of 1 and the pattern of exocyclic bond angles subtended at the arsenic and indium centers [Si–As–Si′ = 105.4 (2) ≪ C–In–C = 125.8 (5), 125.0 (5)°] are similar to those of the gallium analogue, 3 [Si–As–Si = 103.66 (6) ≪ C–Ga–C′ = 123.2 (3), 124.6 (3)°].

Cowley, Jones, et al. have reported an indium-arsenic dimer of formula $[Me_2InAsBu^t_2]_2$ (6),[12] but no detailed crystallographic data have appeared. Both compounds 1 and 6 are colorless, crystalline materials that decompose at elevated temperatures (1 decomposes to a black solid above 210 °C, whereas, 6 is reported to melt with decomposition at 250–252 °C).

Recrystallization of 2 from pentane provided crystals of 2 suitable for an X-ray structural study. Crystal data and data collection and refinement parameters are given in Table I. An ORTEP diagram of 2, with the atom-numbering

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Table V. Selected Bond Distances (Å) and Angles (deg) for 2, with Estimated Standard Deviations in Parentheses

	Bond Lengths		
As–In	2.677 (1)	In–C(11)	2.162 (9)
As–Si	2.356 (2)	In–C(21)	2.165 (6)
In–Cl	2.619 (2)		
	Bond Angles		
In–As–In′	92.07 (4)	Cl–In–C(21)	100.7 (3)
In–As–Si	109.18 (5)	C(11)–In–C(21)	126.3 (3)
In–As–Si′	118.71 (6)	In–Cl–In′	94.7 (1)
Si–As–Si′	108.73 (8)	As–Si–C(1)	111.6 (3)
As–In–Cl	86.59 (6)	As–Si–C(2)	107.8 (4)
As–In–C(11)	114.5 (2)	As–Si–C(3)	108.5 (3)
As–In–C(21)	110.4 (3)	In–C(11)–Si(1)	122.7 (4)
Cl–In–C(11)	109.6 (2)	In–C(21)–Si(2)	116.7 (4)

scheme, is illustrated in Figure 2. Table III lists the non-hydrogen atom fractional coordinates and equivalent isotropic thermal parameters; Table V contains bond lengths and angles.

In 2, the As and Cl atoms lie on a crystallographic C_2 symmetry axis and thus the $\overline{In–As–In–Cl}$ ring is strictly planar. This ring geometry contrasts with that adopted in 4, its gallium analogue, as well as in $Ph_2\overline{GaAs(SiMe_3)_2GaPh_2Cl}$ (7), both of which have the Cl atom displaced from the Ga–As–Ga′ plane. The In–As bond distance at 2.677 (1) Å in 2 is virtually identical with the mean In–As bond length at 2.676 Å in trimer 5.[10] The In–Cl–In′ angle at 94.7 (1)° is larger than the Ga–Cl–Ga′ bond angle in either 4 or 7 [91.33 (4) or 91.3 (1)°, respectively]. Although 2 does not have the steric constraints associated with the additional trimethylsilyl ligands of 1, the exocyclic C–In–C′ bond angle at 126.3 (3)° in 2 is similar to the C–In–C′ angles [125.8 (5), 125.0 (5)°] in 1.

It was observed by us that $[Ph_2GaAs(SiMe_3)_2]_2$ reacts cleanly with 2 mol equiv of Ph_2GaCl to afford 7,[2] and more recently, we reported a similar conversion of 3 to its corresponding mixed-bridge species, 4, via reaction of 3 with 2 equiv of $(Me_3SiCH_2)_2GaCl$.[3] Likewise, 1 reacts with 2 equiv of $(Me_3SiCH_2)_2InCl$ to afford **2** as the only product (eq 3). As evidenced by the ^1H NMR spectrum of the

$$2(Me_3SiCH_2)_2InCl + 1 \rightarrow 2(Me_3SiCH_2)_2\underset{\mathbf{2}}{\overline{InAs(SiMe_3)_2In(CH_2SiMe_3)_2Cl}} \quad (3)$$

reaction mixture, compound 1 reacts very quickly with $(Me_3SiCH_2)_2InCl$. Before all of compound 1 had dissolved completely, the only signals observed were those that resulted from $(Me_3SiCH_2)_2InCl$ and 2. This method of preparing 2 is preferable to dehalosilylation, since the product is cleaner and can thus be recovered in greater yield.

Conclusions

The fact that 2 can be prepared readily by two routes provides additional evidence that mixed-bridge compounds may become a common species in the area of chemistry involving the heavier elements of groups III and V. In addition, we believe it is significant that the specific methodology wherein a gallium–arsenic mixed-bridge compound results from reaction between a gallium–arsenic dimer and a dialkylgallium halide can be applied to the preparation of a like indium–arsenic compound from analogous indium reactants. Further applications of this methodology, including efforts to prepare mixed-metal mixed-bridge compounds for use in subsequent studies, are being investigated in our laboratories.

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Supplementary Material Available: Tables of hydrogen atom coordinates and isotropic thermal parameters, anisotropic temperature factors, complete lists of interatomic distances and angles, including torsion angles, and equations of least-squares planes through groups of atoms for 1 and 2 (10 pages); listings of observed and calculated structure amplitudes for 1 and 2 (35 pages). Ordering information is given on any current masthead page.