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Synthesis and Structural Characterization of Organoindium–Phosphorus Complexes Containing a Four-Membered In–P–In–Cl or In–P–In–P Ring: Crystal Structures of $(Me_3SiCH_2)_2InP(SiMe_3)_2In(CH_2SiMe_3)_2Cl$ and $[(Me_3SiCH_2)_2InP(SiMe_3)_2]_2$

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The first example of an In–P–In–Cl-ring-containing compound, $(Me_3SiCH_2)_2InP(SiMe_3)_2In(CH_2SiMe_3)_2Cl$ (1), was prepared by the reaction of $(Me_3SiCH_2)_2InCl$ and $(Me_3Si)_3P$ in a 2:1 mole ratio. Similarly, the dimer containing an In–P–In–P core, $[(Me_3SiCH_2)_2InP(SiMe_3)_2]_2$ (2), was prepared by reaction in a 1:1 mole ratio. X-ray crystallographic analyses showed the In–P–In–Cl ring of 1 to be nonplanar while the In–P–In–P ring of 2 is planar. Compound 1 belongs to the triclinic system, space group $P\bar{1}$ (C_i^1), with two molecules in a unit cell of dimensions $a = 12.581$ (1) Å, $b = 19.470$ (2) Å, $c = 9.643$ (1) Å, $\alpha = 89.75$ (1)°, $\beta = 112.91$ (1)°, and $\gamma = 100.68$ (1)°. Compound 2 crystallizes in the orthorhombic system, space group *Pbcn* (D_{2h}^{14}), with four molecules in a unit cell of dimensions $a = 12.782$ (2) Å, $b = 21.482$ (3) Å, and $c = 18.651$ (3) Å. Compound 2 reacts with 2 equiv of $(Me_3SiCH_2)_2InCl$ to yield 1 as a major product, as evidenced by ^1H and $^{13}C\{^1H\}$ NMR and melting point data.

Introduction

Recently, there has been heightened interest concerning the production of crystalline nanometer-size particles (nanocrystals) of semiconductor materials,[1-4] because they possess the important feature of exhibiting quantum confinement effects not seen in the bulk material.[5-8] Indeed, Alivisatos and co-workers recently reported the first proven example of the formation of nanocrystals of GaAs in polar organic solvents[3] utilizing a dehalosilylation reaction (viz., $GaCl_3$ with $(Me_3Si)_3As$) reported by us.[9,10] For some time, in our laboratory we have been applying this dehalosilylation methodology to the syntheses of novel group III–V compounds[11-17] for, in part, possible conversion to group III–V materials. Thus, reaction between an organo group III halide and a silylarsine proceeds readily and, in a number of cases, the core fragments of these complexes are composed of four-membered rings containing two group III metals bridged either by two arsenic atoms or by one arsenic and one halogen atom. For example, compounds of the formula $R_2MAs(SiMe_3)_2M(R)_2Cl$ and $[R_2MAs(SiMe_3)_2]_2$ (R = Ph,[13,14] Me_3SiCH_2,[16] M = Ga; R = Me_3SiCH_2,[17] M = In) have been synthesized by us. In an effort to expand these fundamental investigations to include possible indium phosphide (InP) precursors, reactions were carried out with $(Me_3SiCH_2)_2InCl$ and $(Me_3Si)_3P$. Herein, we report the isolation and crystal structure of the first example of an In–P–In–Cl-ring-containing compound, $(Me_3SiCH_2)_2InP(SiMe_3)_2In(CH_2SiMe_3)_2Cl$ (1), as well as the recently reported dimer $[(Me_3SiCH_2)_2InP(SiMe_3)_2]_2$ (2).[4] The syntheses of compounds 1 and 2 from reactions of $(Me_3SiCH_2)_2InCl$ and $(Me_3Si)_3P$ in a 2:1 and 1:1 mole ratio, respectively, are described. Additionally, the conversion of 2 to 1 is reported.

Experimental Section

General Considerations. All manipulations were performed using Schlenk techniques in a Vacuum Atmospheres HE-493 Dri-Lab containing an argon atmosphere. Toluene was distilled from sodium/benzophenone ketyl under dry dinitrogen. Benzene-d_6 was dried over sodium/benzophenone ketyl and vacuum-transferred from the flask containing the latter. Hexane was distilled over $LiAlH_4$ under dry dinitrogen. Indium(III) chloride was purchased from Alfa Products, Ward Hill, MA, and used as received. $(Me_3Si)_3P$ was purchased from Quantum Design Inc., Austin, TX, and was also used without further purification. $(Me_3SiCH_2)_3In$ and $(Me_3SiCH_2)_2InCl$[18] were prepared by literature procedures. ^1H, ^{31}P, and ^{13}C NMR spectra were obtained on a Varian XL-300 (300.0, 121.4, and 75.4 MHz, respectively) spec-

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trometer using 5-mm tubes. ^1H and ^{13}C spectra were referenced to TMS using the residual protons or carbons of deuterated benzene at δ 7.15 and 128 ppm, respectively. ^{31}P spectra were referenced externally to H_3PO_4 at δ 0.00 ppm. NMR tubes were flame-sealed under vacuum, and all spectra were run in C_6D_6. All melting points were obtained from sealed capillaries with a Thomas-Hoover Uni-melt apparatus and are uncorrected. Crystals used in X-ray analyses were flame-sealed under argon in 0.7-mm thin-walled glass capillaries. Elemental analyses were performed by E+R Microanalytical Laboratory, Inc., Corona, NY.

Preparation of $(Me_3SiCH_2)_2\overline{InP(SiMe_3)_2In(CH_2SiMe_3)_2Cl}$ (1). In the drybox, $(Me_3SiCH_2)_2InCl$ (0.709 g, 2.18 mmol) in 15 mL of hexane and $(Me_3Si)_3P$ (0.273 g, 1.09 mmol) in 10 mL of hexane were combined in a 100-mL one-necked round-bottomed flask equipped with a Teflon valve and a microstirbar. After the resulting clear solution was removed from the box and stirred at room temperature for 24 h, the volatiles were removed in vacuo to yield a white residue. Dissolving the residue in approximately 3 mL of warm toluene followed by cooling to −15 °C for 5 days afforded colorless crystals of 1 suitable for single-crystal X-ray analysis (0.657 g, 76% yield); mp 60–63 °C. Anal. Calcd (found) for $C_{22}H_{62}ClIn_2PSi_6$: C, 33.30 (33.54); H, 8.01 (7.74); P, 3.91 (3.70). ^1H NMR: δ 0.16 (s, 8 H, CH_2), 0.26 (s, 36 H, $SiMe_3$), 0.33 (d, 18 H, $PSiMe_3$ (J_{P-H} = 5.6 Hz)). $^{13}C\{^1H\}$ NMR: δ 2.89 (s, $SiMe_3$), 4.62 (d, $PSiMe_3$ (J_{P-C} = 8.6 Hz)), 7.28 (d, CH_2 (J_{P-C} = 8.7 Hz)). $^{31}P\{^1H\}$ NMR: δ −218.99 (s).

Preparation of $[(Me_3SiCH_2)_2InP(SiMe_3)_2]_2$ (2). Reaction of $(Me_3SiCH_2)_2InCl$ (0.628 g, 1.93 mmol) in 15 mL of hexane and $(Me_3Si)_3P$ (0.484 g, 1.93 mmol) in 10 mL of hexane was carried out in a fashion analogous to that for 1. After the resulting solution was stirred at room temperature for 24 h, the volatiles were removed in vacuo to yield a white solid. The crude product was dissolved in approximately 20 mL of warm toluene, and when the solution was cooled for 48 h at −15 °C, a multitude of clear, colorless, and *extremely air-sensitive* crystals of 2 suitable for single-crystal X-ray analysis resulted. Removal of approximately 80% of the toluene by evaporation afforded a second crop of 2 (0.767 g total, 85% yield), mp 240 °C (lit.[4] mp 245 °C). Anal. Calcd (found) for $C_{28}H_{80}In_2P_2Si_8$: C, 36.02 (36.23); H, 8.64 (8.21); P, 6.63 (6.42). ^1H NMR: δ 0.20 (s, 8 H, CH_2), 0.33 (s, 36 H, $SiMe_3$), 0.46 (t, 36 H, $PSiMe_3$ (J_{P-H} = 2.4 Hz)). $^{13}C\{^1H\}$ NMR: δ 3.70 (s, $SiMe_3$), 4.11 (s, CH_2), 5.30 (t, $PSiMe_3$ (J_{P-C} = 4.2 Hz)). $^{31}P\{^1H\}$ NMR: δ −227.36 (s).

Reaction of 2 with $(Me_3SiCH_2)_2InCl$. $(Me_3SiCH_2)_2InCl$ (12.5 mg, 0.038 mmol) and 2 (18.0 mg, 0.019 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 dinitrogen, the tube was flame-sealed and warmed to ambient temperature. When the mixture stood for 3 h, the ^1H NMR spectrum obtained for it corresponded to that of an authentic sample of 1. The NMR tube was then opened in the drybox and the solvent evaporated to yield a colorless solid which melted at 63 °C, a melting point comparable to that found for authentic 1 (vide ante).

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 were also applied. The structure of 1 was solved by the heavy-atom approach. Approximate coordinates for the indium atoms were derived from a Patterson map. The remaining non-hydrogen atoms were located in a series of weighted F_o and difference Fourier syntheses. For 2, non-hydrogen atom coordinates of its isomorphous indium–arsenic analogue[17] were used as initial values. 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, except for those at the somewhat disordered C(32′) and C(33′) methyl groups in 1, 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 19.

Table I. Crystallographic Data and Measurements[a] for $(Me_3SiCH_2)_2\overline{InP(SiMe_3)_2In(CH_2SiMe_3)_2Cl}$ (1) and $[(Me_3SiCH_2)_2InP(SiMe_3)_2]_2$ (2)

	1	**2**
mol formula	$C_{22}H_{62}PClIn_2Si_6$	$C_{28}H_{80}P_2In_2Si_8$
fw	791.32	933.23
cryst syst	triclinic	orthorhombic
space group	$P\bar{1}$ (C_i^1)	$Pbcn$ (D_{2h}^{14})
a, Å	12.581 (1)	12.782 (2)
b, Å	19.470 (2)	21.482 (3)
c, Å	9.643 (1)	18.651 (3)
α, deg	89.75 (1)	90.00
β, deg	112.91 (1)	90.00
γ, deg	100.68 (9)	90.00
no. of orientation rflns; θ range, deg	25; 27–35	25; 35–40
V, Å^3	2132.1 (9)	5121 (2)
Z	2	4
D_{calcd}, g cm^{-3}	1.233	1.210
temp, °C	23	23
cryst dimens, mm	0.14 × 0.19 × 0.45	0.32 × 0.40 × 0.44
$T_{max}:T_{min}$	1.00:0.55	1.00:0.46
radiation (wavelength, Å)	Cu Kα (1.5418)	Cu Kα (1.5418)
μ, cm^{-1}	115.2	99.2
scan type	$\omega-2\theta$	$\omega-2\theta$
scan width, deg	0.80 + 0.14 tan θ	0.80 + 0.14 tan θ
θ_{max}, deg	65	75
intens control rflns	222, 312, 151, 141	115, 223, $2\bar{2}3$, $1\bar{1}5$
variation, %; repeat time, h	<2; 2	<1; 2
no. of rflns recorded	8061 ($+h,\pm k,\pm l$)	5261 ($+h,+k,+l$)
no. of rflns retained, $I > 3.0\sigma(I)$	4077	2081
no. of params refined	290	183
extinction cor	6.6 (5) × 10^{-7}	2.8 (1) × 10^{-7}
R, R_w[b]	0.046, 0.058	0.047, 0.062
goodness of fit[c]	1.16	1.15
max shift/esd in final least-squares cycle	0.02	0.02
final max, min $\Delta\rho$, e Å^{-3}	0.82, −0.58	0.79, −1.12

[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 computers by use of the Enraf-Nonius Structure Determination Package (SDP). [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_0 - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. $\sum w\Delta^2$ ($w = 1/\sigma^2(|F_o|)$, $\Delta = (|F_o| - |F_c|)$) was minimized. [c] Goodness of fit = $[\sum w\Delta^2/(N_{observs} - N_{params})]^{1/2}$.

Results and Discussion

The ambient-temperature reaction of $(Me_3SiCH_2)_2InCl$ and $(Me_3Si)_3P$ in a 2:1 mole ratio in hexane yields 1 via a dehalosilylation reaction (eq 1). In that 1 contains an $\overline{In-P-In-Cl}$ ring, it is the first reported example of a compound with the two indium atoms being bridged by both a phosphorus atom and a chlorine atom and is yet another example of what we refer to as a "mixed-bridge" complex/compound.[13-17] Compound 1 is the phosphorus analogue of our recently reported complex $(Me_3SiCH_2)_2\overline{InAs(SiMe_3)_2In(CH_2SiMe_3)_2Cl}$ (3), which, as indicated, contains both an arsenic and chlorine bridge.[17] Interestingly, 3 undergoes gradual decomposition at ambient temperature, whereas 1 is quite stable for extended periods of time.

$$2(Me_3SiCH_2)_2InCl + (Me_3Si)_3P \rightarrow \underset{\mathbf{1}}{(Me_3SiCH_2)_2\overline{InP(SiMe_3)_2In(CH_2SiMe_3)_2Cl}} + Me_3SiCl \qquad (1)$$

Reaction of $(Me_3SiCH_2)_2InCl$ with $(Me_3Si)_3P$ in a 1:1 mole ratio afforded compound 2 (eq 2), the phosphorus analogue of the dimer $[(Me_3SiCH_2)_2InAs(SiMe_3)_2]_2$ (4).[17] Dimer 2 contains an $\overline{In-P-In-P}$ core. Similarly, Douglas

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

$$(Me_3SiCH_2)_2InCl + (Me_3Si)_3P \rightarrow \tfrac{1}{2}\underset{\mathbf{2}}{[(Me_3SiCH_2)_2InP(SiMe_3)_2]_2} + Me_3SiCl \quad (2)$$

and Theopold also have isolated **2** and, while they provide no detailed synthesis or complete structural characterization, it was reported that conversion of **2** to InP particles via an alcoholysis reaction was achieved.[4]

Previous studies in our laboratory have demonstrated quite clearly that dehalosilylation reactions between an organogallium or -indium halide and a silylarsine to form species containing metal–arsenic bonds occur readily under mild conditions and in relatively high yields.[11-17] Although such reactions involving silylphosphines to form indium–phosphorus bonds have not been developed to the same extent, Barron and co-workers did report the isolation of InP from the thermolysis of the product obtained by the reaction of InX_3 (X = Cl, Br) with $(Me_3Si)_3P$ and, similarly, used a dehalosilylation reaction to form $(Me_2InPPh_2)_2$.[20,21]

The syntheses of **1** and **2** are clearly dependent upon the stoichiometry of the reagents used, and each is prepared in good yield. In the case of **1**, this is in marked contrast to the case for its arsenic analogue (i.e., **3**), since the latter mixed-bridge complex was produced in only 16% yield. Both **1** and **2** are very soluble in nonpolar organic solvents, but **2** is significantly less soluble than **1**. Also, it is interesting to note that for the reactions involving $(Me_3SiCH_2)_2GaCl$ with $(Me_3Si)_3As$ in either a 1:1 or 2:1 mole ratio, only the mixed-bridge compound was observed as the major product.[16] Additionally, compound **1** can be produced easily by the reaction of **2** with $(Me_3SiCH_2)_2InCl$ in a 1:2 mole ratio (eq 3).

$$\underset{\mathbf{2}}{[(Me_3SiCH_2)_2InP(SiMe_3)_2]_2} + 2(Me_3SiCH_2)_2InCl \rightarrow \underset{\mathbf{1}}{(Me_3SiCH_2)_2\overline{InP(SiMe_3)_2In(CH_2SiMe_3)_2Cl}} \quad (3)$$

The ^1H NMR spectra of both **1** and **2** show there is coupling of the ^{31}P nuclei with the methyl protons of the adjacent trimethylsilyl groups. The former exhibits a doublet while the latter gives a triplet. As Douglas and Theopold noted,[4] the triplet resonance for **2** reveals the dimeric nature of the complex in solution. Thus, it would follow that complex **1** should exhibit a doublet, since there is only one phosphorus atom in the ring. It is from the inherent differences between the two ^1H NMR spectra that the conversion of **2** to **1** can be easily monitored from the reaction of **2** and additional $(Me_3SiCH_2)_2InCl$.

In the ^{13}C NMR spectra, it is noteworthy that for both **1** and **2** coupling is again observed between the ^{31}P nuclei and the adjacent trimethylsilyl groups. However, for complex **1**, coupling is also seen with the adjacent methylene protons in the (trimethylsilyl)methyl groups. As for the ^{31}P NMR spectra of **1** and **2**, each exhibits one sharp resonance, indicating that each compound exists as a single species. This behavior for **2** differs substantially from that of $[(Me_3SiCH_2)_2InPPh_2]_2$, which was shown to exist as an equilibrium mixture of monomer and dimer in solution.[22]

Crystals of **1** suitable for X-ray analysis were obtained by recrystallization from a toluene solution. Crystallographic data are summarized in Table I. Figure 1 presents an ORTEP diagram showing the atom-numbering scheme for **1**. Table II lists the non-hydrogen atom fractional coordinates and equivalent isotropic thermal parameters; selected bond lengths and angles are reported in Table IV.

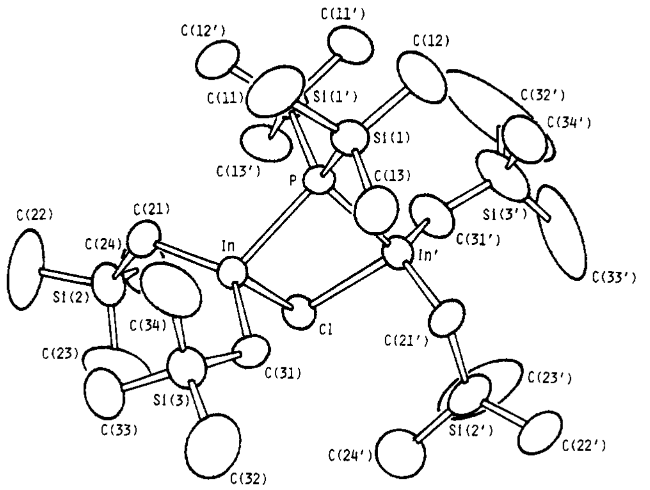

Figure 1. ORTEP diagram (40% probability ellipsoids) showing the structure and atom-numbering scheme of $(Me_3SiCH_2)_2\overline{InP(SiMe_3)_2In(CH_2SiMe_3)_2Cl}$ (**1**). Hydrogen atoms have been omitted for clarity.

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
P	0.0584 (2)	0.3070 (1)	0.3304 (2)	3.92 (4)
In	−0.11679 (4)	0.20821 (3)	0.16724 (6)	4.15 (1)
In′	0.19445 (4)	0.26442 (3)	0.21818 (6)	4.47 (1)
Cl	−0.0007 (2)	0.2094 (1)	−0.0084 (2)	5.04 (5)
Si(1)	0.1128 (2)	0.3083 (1)	0.5825 (3)	4.83 (6)
Si(2)	−0.3588 (2)	0.2204 (2)	−0.1570 (3)	6.81 (8)
Si(3)	−0.2105 (2)	0.0633 (2)	0.3245 (3)	6.36 (7)
Si(1′)	0.0193 (2)	0.4111 (1)	0.2456 (3)	5.75 (7)
Si(2′)	0.2914 (3)	0.1105 (2)	0.2264 (3)	7.89 (8)
Si(3′)	0.4265 (3)	0.3903 (3)	0.2248 (4)	13.1 (1)
C(11)	−0.0083 (9)	0.3288 (7)	0.6312 (11)	9.5 (3)
C(12)	0.2509 (10)	0.3762 (7)	0.6785 (12)	8.9 (4)
C(13)	0.1390 (9)	0.2204 (5)	0.6403 (10)	6.7 (3)
C(11′)	0.1511 (10)	0.4826 (5)	0.3324 (13)	8.1 (4)
C(12′)	−0.1017 (9)	0.4329 (6)	0.2911 (14)	8.8 (4)
C(13′)	−0.0270 (11)	0.4027 (5)	0.0352 (12)	8.4 (4)
C(21)	−0.2749 (7)	0.2476 (5)	0.0485 (9)	5.4 (2)
C(22)	−0.5130 (11)	0.2282 (13)	−0.2145 (15)	16.8 (7)
C(23)	−0.3598 (17)	0.1286 (8)	−0.2013 (16)	14.2 (7)
C(24)	−0.2956 (11)	0.2733 (8)	−0.2742 (13)	10.6 (5)
C(31)	−0.0993 (7)	0.1067 (4)	0.2547 (9)	5.1 (2)
C(32)	−0.1781 (11)	−0.0234 (7)	0.3926 (16)	12.3 (4)
C(33)	−0.3602 (9)	0.0426 (7)	0.1638 (15)	9.3 (4)
C(34)	−0.2183 (11)	0.1196 (8)	0.4709 (14)	12.5 (4)
C(21′)	0.2608 (7)	0.1768 (5)	0.3336 (10)	6.0 (2)
C(22′)	0.4006 (9)	0.0631 (6)	0.3554 (14)	9.3 (4)
C(23′)	0.3289 (14)	0.1453 (9)	0.0734 (15)	19.9 (5)
C(24′)	0.1528 (15)	0.0437 (9)	0.1306 (20)	18.7 (6)
C(31′)	0.2801 (8)	0.3410 (6)	0.1140 (10)	8.0 (3)
C(32′)	0.4452 (22)	0.4814 (12)	0.1737 (23)	40.5 (8)
C(33′)	0.5314 (13)	0.3414 (16)	0.2033 (25)	48 (1)
C(34′)	0.4576 (12)	0.3963 (8)	0.4283 (17)	11.5 (5)

Compound **1** crystallizes in the triclinic system with the two molecules in the unit cell occupying the general positions of the centrosymmetric space group $P\bar{1}$. It is of interest that the $\overline{In–P–In–Cl}$ ring in **1** is distinctly nonplanar, whereas in the As analogue **3**, the As and Cl atoms lie on a crystallographic C_2 symmetry axis and thus the $\overline{In–As–In–Cl}$ ring is flat.[17] The mean of the In–Cl bond lengths (2.630 (3), 2.611 (2) Å) at 2.621 Å in **1** is virtually identical to the In–Cl distance of 2.619 (2) Å in **3**. The Cl atom is displaced by 1.020 Å from the In–P–In′ plane in **1**, giving rise to a dihedral angle of 33.3 (1)° between the

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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
P	0.1411 (2)	0.1854 (1)	0.2382 (1)	3.01 (4)
In(1)	0.0000 (-)[a]	0.27559 (3)	0.2500 (-)[a]	3.23 (1)
In(2)	0.0000 (-)[a]	0.09537 (3)	0.2500 (-)[a]	3.04 (1)
Si(1)	0.2355 (2)	0.1746 (1)	0.1368 (2)	4.47 (6)
Si(2)	0.2589 (2)	0.1895 (2)	0.3280 (2)	4.53 (6)
Si(11)	0.0388 (3)	0.3885 (1)	0.1151 (2)	4.45 (6)
Si(21)	−0.0846 (3)	−0.0219 (1)	0.1310 (2)	5.20 (7)
C(11)	0.1468 (12)	0.1906 (6)	0.0608 (6)	6.3 (3)
C(12)	0.3503 (10)	0.2281 (6)	0.1338 (8)	7.0 (3)
C(13)	0.2859 (10)	0.0928 (6)	0.1295 (7)	6.3 (3)
C(21)	0.3309 (10)	0.2656 (6)	0.3285 (8)	7.3 (4)
C(22)	0.3581 (10)	0.1257 (6)	0.3195 (7)	6.8 (3)
C(23)	0.1871 (10)	0.1812 (6)	0.4157 (6)	6.2 (3)
C(111)	−0.0392 (10)	0.3241 (5)	0.1513 (6)	5.7 (3)
C(112)	0.0290 (16)	0.3892 (10)	0.0162 (10)	14.8 (8)
C(113)	0.1804 (12)	0.3845 (8)	0.1387 (11)	10.6 (5)
C(114)	−0.0162 (19)	0.4620 (6)	0.1416 (16)	16.7 (9)
C(211)	−0.0028 (10)	0.0476 (4)	0.1472 (16)	4.6 (2)
C(212)	−0.0011 (13)	−0.0911 (6)	−0.1090 (11)	9.7 (5)
C(213)	−0.1740 (12)	−0.0407 (6)	0.2065 (8)	8.1 (4)
C(214)	−0.1701 (13)	−0.0114 (8)	0.0523 (9)	9.3 (5)

[a] Fixed by symmetry.

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

	Bond Lengths		
P–In	2.605 (2)	In′–Cl	2.611 (2)
P–In′	2.601 (3)	In–C(21)	2.15 (1)
P–Si(1)	2.253 (3)	In′–C(21′)	2.15 (1)
P–Si(1′)	2.250 (3)	In–C(31)	2.16 (1)
In–Cl	2.630 (3)	In′–C(31′)	2.15 (1)
	Bond Angles		
In–P–In′	90.6 (1)	Cl–In–C(31)	99.5 (3)
In–P–Si(1)	116.8 (1)	Cl–In′–C(31′)	102.4 (2)
In–P–Si(1′)	108.8 (1)	C(21)–In–C(31)	128.8 (3)
In′–P–Si(1)	117.7 (1)	C(21′)–In′–C(31′)	126.9 (4)
In′–P–Si(1′)	110.2 (1)	In–Cl–In′	89.8 (1)
Si(1)–P–Si(1′)	111.1 (1)	P–Si(1)–C(11)	109.2 (3)
P–In–Cl	84.9 (1)	P–Si(1′)–C(11′)	111.2 (3)
P–In′–Cl	85.3 (1)	P–Si(1)–C(12)	109.6 (4)
P–In–C(21)	112.2 (2)	P–Si(1′)–C(12′)	110.5 (4)
P–In′–C(21′)	110.1 (3)	P–Si(1)–C(13)	107.8 (3)
P–In–C(31)	112.2 (2)	P–Si(1′)–C(13′)	106.9 (3)
P–In′–C(31′)	116.6 (3)	In–C(21)–Si(2)	118.3 (5)
Cl–In–C(21)	108.7 (3)	In–C(21′)–Si(2′)	118.1 (5)
Cl–In′–C(21′)	105.3 (2)	In–C(31)–Si(3)	117.5 (5)
		In–C(31′)–Si(3′)	119.5 (5)

In–P–In′ and In–Cl–In′ planes (mean endocyclic torsion angle about the ring bonds 22.9°), and thus the ring is considerably puckered. The departure from coplanarity in **1** aids in relieving nonbonded intramolecular steric overcrowding of the bulky ring substituents. These effects are more severe in **1** than in **3** as a consequence of the shorter distances for bonds involving phosphorus (mean In–P = 2.603 Å, mean P–Si = 2.252 Å) in contrast to the longer In–As and As–Si distances of 2.677 (1) and 2.356 (2) Å, respectively, in **3**. The In–P–In′, In–Cl–In′, and mean P–In–Cl bond angles are 90.6 (1), 89.8 (1), and 85.1°, respectively.

Previous structural studies in our laboratory have shown that the Si–As–Si angle at 103.66 (4)° in $[(Me_3Si)_2AsGa(CH_2SiMe_3)_2]_2$[16] lies close to the essentially equal C–As–C angles of 104.3 (2)° subtended at the ring As atoms in $\{[(Me_3SiCH_2)_2As]_2GaBr\}_2$[12] and 104.4 (2)° in $[(Me_3SiCH_2)_2AsGaPh_2]_2$,[23] thereby indicating that the Me_3Si and Me_3SiCH_2 ring substituents have comparable steric demands. The mean C–In–C bond angle at 127.9° in **1** is similar to the C–In–C angle of 126.3 (3)° in **3**, and although steric effects may make some contribution to the very significant enlargement over tetrahedral geometry (109.5°), the principal factors must be electronic in nature.

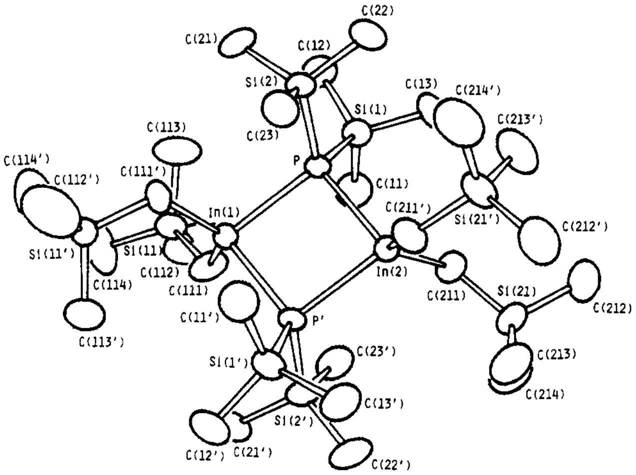

Figure 2. ORTEP diagram (40% probability ellipsoids) showing the structure and atom-numbering scheme of $[(Me_3SiCH_2)_2InP(SiMe_3)_2]_2$ (**2**). Hydrogen atoms have been omitted for clarity.

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

	Bond Lengths		
P–In(1)	2.656 (2)	In(1)–C(111)	2.174 (11)
P–In(2)	2.654 (2)	In(2)–C(211)	2.175 (9)
P–Si(1)	2.255 (4)		
P–Si(2)	2.254 (4)		
	Bond Angles		
In(1)–P–In(2)	93.6 (1)	P–Si(2)–C(22)	111.1 (4)
In(1)–P–Si(1)	120.5 (1)	P–Si(2)–C(23)	108.4 (4)
In(1)–P–Si(2)	111.3 (1)	P–In(1)–C(111′)	105.3 (3)
In(2)–P–Si(1)	111.0 (1)	P–In(1)–P′	86.3 (1)
In(2)–P–Si(2)	114.8 (1)	C(111)–In(1)–C(111′)	122.7 (4)
Si(1)–P–Si(2)	105.7 (2)	P–In(2)–C(211)	106.4 (3)
P–In(1)–C(111)	115.9 (3)	P–In(2)–P′	86.4 (1)
P–Si(1)–C(11)	107.2 (5)	P–In(2)–C(211′)	113.9 (3)
P–Si(1)–C(12)	112.5 (5)	C(211)–In(2)–C(211′)	123.7 (3)
P–Si(1)–C(13)	109.9 (4)	In(1)–C(111)–Si(11)	123.2 (6)
P–Si(2)–C(21)	111.4 (5)	In(2)–C(211)–Si(21)	122.3 (5)

Recrystallization of **2** from toluene provided crystals suitable for an X-ray structural study. Crystal data are reported in Table I along with data collection and refinement parameters. An ORTEP diagram, with the atom-numbering scheme, is provided in Figure 2. Non-hydrogen atom fractional coordinates are listed in Table III; Table V contains selected bond lengths and angles.

Compound **2** crystallizes in the orthorhombic system, space group *Pbcn*, with four formula units per unit cell. It is isomorphous with $[(Me_3SiCH_2)_2InAs(SiMe_3)_2]_2$ (**4**)[17] as well as $[(Me_3SiCH_2)_2GaAs(SiMe_3)_2]_2$,[16] and thus accordingly it also lies on a crystallographic C_2 axis which passes through the group III centers. The four-membered ring is required by symmetry to be strictly planar. The In–P bonds (2.656 (2), 2.654 (2) Å) are essentially equal, and their mean at 2.655 Å is significantly greater (Δ = 0.052 Å) than the mean of 2.603 Å in **1**; a similar difference of 0.051 Å, in the same sense, is found between the In–As bonds of **3** and **4**, indicating that group III–group V bond strain is greater in the dimers than in the mixed-bridge species. The bond angle pattern in the ring P–In–P ≪ In–P–In (Δ = 7.2°) in **2** is also similar to that in the As analogue **4** (Δ = 9.3°). The mean C–In–C angle at 123.2° in **2** is slightly smaller than that of 125.4° in **4**; the Si–P–Si

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(23) Wells, R. L.; Purdy, A. P.; McPhail, A. T.; Pitt, C. G. *J. Organomet. Chem.* **1986**, *308*, 281.

angles (105.2 (2)° in **2**, 105.4 (2)° in **4**) are equal.

The literature contains numerous examples of compounds containing $\overline{\text{In–P–In–P}}$ units.[2,4,21,22,24,25] However, only two such structures contain similar alkyl substituents (i.e., Me_3SiCH_2 or Me_3Si) and therefore warrant comparison with **2**. As was previously noted, Beachley et al. reported the structure of $[(Me_3SiCH_2)_2InPPh_2]_2$ (**5**).[22] Compound **5** was prepared via two routes: an alkane elimination involving $HPPh_2$ and $In(Me_3SiCH_2)_3$ or a salt elimination between $KPPh_2$ and $(Me_3SiCH_2)_2InBr$. As found for **2**, compound **5** contains a planar $\overline{\text{In–P–In–P}}$ core and the average In–P length of 2.65 (1) Å compares favorably to that of **2** (vide ante). Conversely, the mean In–P–In and P–In–P bond angles in **5** differ significantly from those in **2** (97.49 (11) and 82.52 (10)° for **5** and 93.6 (1) and 86.4 (1)° for **2**, respectively). These differences can be explained sterically, where less demanding phenyl groups allow the In–P–In angle to open up somewhat. It then follows that, with these smaller phenyl substituents, the Me_3SiCH_2 groups are able to move further apart, thus causing the P–In–P angle to decrease accordingly.

The only other published structural example of a compound containing an $\overline{\text{In–P–In–P}}$ ring with trimethylsilyl substituents on phosphorus was first reported in 1989 and then again in 1991 by Theopold and co-workers.[2,4] This compound, $[Cp^*(Cl)InP(SiMe_3)_2]_2$ (**6**; $Cp^* = C_5Me_5$), is apparently produced by three different pathways: by the novel reaction of Cp^*_2InCl with $LiP(SiMe_3)_2$ to eliminate $LiCp^*$[2] and by reaction of Cp^*InCl_2 with either $LiP(SiMe_3)_2$ or $P(SiMe_3)_3$ to yield LiCl and Me_3SiCl, respectively.[4] Compound **6** has an average In–P bond length of 2.62 Å, which is slightly shorter than those in **2**, and it contains In–P–In and P–In–P bond angles (92.2 (1) and 87.8 (1)°, respectively) which are quite similar to those found in **2** (vide ante).

Conclusions

The work described here demonstrates that, in addition to being a facile route to compounds containing the $\overline{\text{In–P–In–P}}$ ring, the use of the dehalosilylation methodology allows for the ready preparation of the $\overline{\text{In–P–In–Cl}}$ moiety. As has been shown by Theopold and co-workers,[2,4] organoindium compounds containing the $(Me_3Si)_2P$ group can be converted to InP by alcoholysis and, in the case of **2**, there is evidence for nanometer-size particles being formed.[4] Thus, mixed-bridge complex **1** and some of its derivatives appear to be likely single-source InP precursors. In addition, the ease with which dimer **2** can be converted to the mixed-bridge species **1** underscores the possible synthetic usefulness of this type of complex to the preparation of other related species. We will use this investigation as another benchmark for future studies into the formation of suitable precursors to InP and other In-containing group III–V alloys.

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Registry No. 1, 136806-13-8; 2, 132080-11-6; $(Me_3SiCH_2)_2InCl$, 132080-07-0; $(Me_3Si)_3P$, 15573-38-3.

Supplementary Material Available: Tables of hydrogen atom coordinates and isotropic thermal parameters, anisotropic temperature factors, and all interatomic distances and angles, including torsion angles, for 1 and 2 and equations of least-squares planes through groups of atoms for 1 (13 pages); listings of observed and calculated structure amplitudes for 1 and 2 (42 pages). Ordering information is given on any current masthead page.

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