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[19. ABSTRACT]

The dimers $[\text{Ph}(\text{Me}_3\text{SiCH}_2)\text{InAs}(\text{SiMe}_3)_2]_2$ (1), $[\text{Me}(\text{Me}_3\text{SiCH}_2)\text{InAs}(\text{SiMe}_3)_2]_2$ (2), $[\text{Me}(\text{Me}_3\text{SiCH}_2)\text{InP}(\text{SiMe}_3)_2]_2$ (3), and $[\text{Cl}(\text{Me}_3\text{SiCH}_2)\text{InP}(\text{SiMe}_3)_2]_2$ (4) are reported. These compounds are produced *via* ligand exchange reactions involving the migration of either alkyl groups, for 1 - 3, or a chlorine atom, in the case of 4, from various group 13 species. Additionally, 3 and 4 can be prepared utilizing alternate routes involving a novel Si-C bond cleavage and reaction of $(\text{Me}_3\text{SiCH}_2)\text{InCl}_2$ with $\text{P}(\text{SiMe}_3)_3$, respectively. Compound 1 crystallizes in a *trans* configuration in the triclinic space group $P\bar{1}$ with unit cell parameters a 11.859(2), b 12.222(2), c 10.021(2) Å, α 107.59(1), β 110.47(1), γ 66.54(1)°, V 1225.6(7) Å³ and $Z = 1$. Crystals of isostructural compounds 2 - 4 are isomorphous. These compounds also crystallize in a *trans* configuration in the monoclinic space group $P2_1/c$ with unit cell parameters: a 9.928(1), b 19.882(1), c 11.513(1) Å, β 111.21(1)°, V 2118.6(6) Å³ and $Z = 2$ for 2; a 9.858(1), b 19.662(1), c 11.456(1) Å, β 110.88(1)°, V 2074.7(6) Å³ and $Z = 2$ for 3; a 9.845(1), b 19.349(1), c 11.442(1) Å, β 110.63(1)°, V 2039.8(6) Å³ and $Z = 2$ for 4.

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Synthesis, Isolation, and Characterization of Dimeric Compounds
Containing Two Different Exocyclic Ligands on the Group 13 Center. X-Ray Crystal Structures of
 $[R(\text{Me}_3\text{SiCH}_2)\text{InE}(\text{SiMe}_3)_2]_2$ (R = Ph, E = As; R = Me, E = As, P; R = Cl, E = P).

by

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**SYNTHESIS, ISOLATION, AND CHARACTERIZATION OF DIMERIC
COMPOUNDS CONTAINING TWO DIFFERENT EXOCYCLIC LIGANDS ON
THE GROUP 13 CENTER. X-RAY CRYSTAL STRUCTURES OF
[R(Me₃SiCH₂)InE(SiMe₃)₂]₂ (R = Ph, E = As; R = Me, E = As, P; R = Cl, E = P).**

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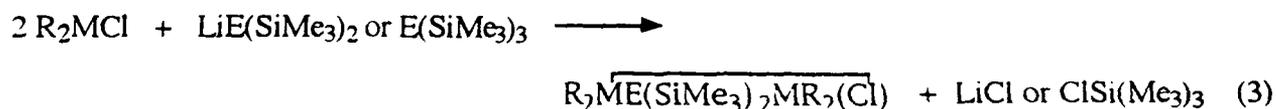
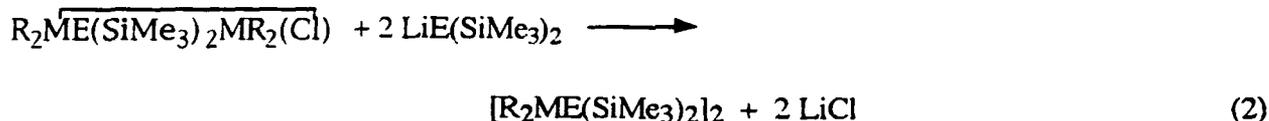
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Abstract

The dimers [Ph(Me₃SiCH₂)InAs(SiMe₃)₂]₂ (**1**), [Me(Me₃SiCH₂)InAs(SiMe₃)₂]₂ (**2**), [Me(Me₃SiCH₂)InP(SiMe₃)₂]₂ (**3**), and [Cl(Me₃SiCH₂)InP(SiMe₃)₂]₂ (**4**) are reported. These compounds are produced *via* ligand exchange reactions involving the migration of either alkyl groups, for **1** - **3**, or a chlorine atom, in the case of **4**, from various group 13 species. Additionally, **3** and **4** can be prepared utilizing alternate routes involving a novel Si-C bond cleavage and reaction of (Me₃SiCH₂)InCl₂ with P(SiMe₃)₃, respectively. Compound **1** crystallizes in a *trans* configuration in the triclinic space group $P\bar{1}$ with unit cell parameters a 11.859(2), b 12.222(2), c 10.021(2) Å, α 107.59(1), β 110.47(1), γ 66.54(1)°, V 1225.6(7) Å³ and $Z = 1$. Crystals of isostructural compounds **2** - **4** are isomorphous. These compounds also crystallize in a *trans* configuration in the monoclinic space group $P2_1/c$ with unit cell parameters: a 9.928(1), b 19.882(1), c 11.513(1) Å, β 111.21(1)°, V 2118.6(6) Å³ and $Z = 2$ for **2**; a 9.858(1), b 19.662(1), c 11.456(1) Å, β 110.88(1)°, V 2074.7(6) Å³ and $Z = 2$ for **3**; a 9.845(1), b 19.349(1), c 11.442(1) Å, β 110.63(1)°, V 2039.8(6) Å³ and $Z = 2$ for **4**.

Introduction

Fundamental research in the area of single-source precursors to 13-15 materials has received wide attention in the past decade [1,2]. These compounds typically contain a 1:1 mole ratio of a group 13 and group 15 element [1-5], hence they could prove useful in the production of binary semiconductors. Of late, we have reported the formation of four-membered ring compounds such as the dimeric species $[\text{R}_2\text{ME}(\text{SiMe}_3)_2]_2$ and the mixed-bridge species $\overline{\text{R}_2\text{ME}(\text{SiMe}_3)_2\text{MR}_2(\text{Cl})}$ ($\text{M} = \text{Ga}$, $\text{E} = \text{As}$, $\text{R} = \text{Ph}$ [6,7], Me_3SiCH_2 [8], Me_3CCH_2 [9]; $\text{M} = \text{In}$, $\text{E} = \text{As}$ [10], P [11], $\text{R} = \text{Me}_3\text{SiCH}_2$). Typically, these type of compounds can be prepared in high yields from the reactions shown in equations (1 - 4).



A natural extension of this methodology would be the formation of mixed group 13 systems such that compounds with cores of formula $\overline{\text{MEM}'\text{E}}$ or $\overline{\text{MEM}'\text{Cl}}$, where $\text{M} \neq \text{M}'$ and both are a group 13 metal, could be produced. Earlier attempts to prepare such species resulted in unusual ligand transfer reactions where symmetrization about the metal centers occurred [i.e., the formation of such compounds as $(\text{Me}_3\text{SiCH}_2)_3\text{In}$ and Ph_3Ga] [12]. Presented here are our latest efforts in which compounds with non-symmetrical metal centers are produced. Additionally, through these

investigations, we have observed an apparent Si-C bond cleavage reaction resulting in a Me group migration. Herein, we report the synthesis, isolation, and characterization (including X-ray analysis) of the dimers $[\text{Ph}(\text{Me}_3\text{SiCH}_2)\text{InAs}(\text{SiMe}_3)_2]_2$ (1), $[\text{Me}(\text{Me}_3\text{SiCH}_2)\text{InAs}(\text{SiMe}_3)_2]_2$ (2), $[\text{Me}(\text{Me}_3\text{SiCH}_2)\text{InP}(\text{SiMe}_3)_2]_2$ (3), and $[\text{Cl}(\text{Me}_3\text{SiCH}_2)\text{InP}(\text{SiMe}_3)_2]_2$ (4). Of note, Beachley *et al.* recently reported the mixed-ligand dialkylindium halides, $(\text{Me}_3\text{CCH}_2)(\text{Me}_3\text{SiCH}_2)\text{InCl}$ (including the X-ray structure) and $\text{Ph}(\text{Me}_3\text{CCH}_2)\text{InCl}$ [13]. In the same article, synthesis of the dimer, $(\text{Me}_3\text{CCH}_2)(\text{Me}_3\text{SiCH}_2)\text{InPEt}_2$ (5), was described, but due to its oily nature an X-ray analysis could not be performed. Thus, the X-ray crystallographic characterizations of compounds 1 - 3 are the first for 13-15 dimeric species containing differing organic substituents on the metal atom.

Experimental

General Considerations

All manipulations were performed using Schlenk techniques or in a Vacuum/Atmospheres HE-493 Dri-Lab containing an argon atmosphere. Toluene and benzene were distilled from sodium benzophenone ketyl under dry dinitrogen. Benzene- d_6 was dried over sodium benzophenone ketyl and vacuum transferred to another flask. Pentane was distilled over LiAlH_4 under dry dinitrogen. The dimeric compounds, $[\text{R}_2\text{ME}(\text{SiMe}_3)_2]_2$ (M = Ga, E = As, R = Ph [6,7], Me_3SiCH_2 [8], Me_3CCH_2 [9]; M = In, E = As [10], P [11], R = Me_3SiCH_2), Ph_2GaCl [14], $(\text{Me}_3\text{SiCH}_2)_2\text{InCl}$ [15], $(\text{Me}_3\text{SiCH}_2)\text{InCl}_2$ [15], and $(\text{Me}_3\text{SiCH}_2)_2\text{GaCl}$ [16] were prepared by literature procedures. $\text{LiP}(\text{SiMe}_3)_2$ [17] was prepared *via* the 1:1 mole reaction of MeLi with $\text{P}(\text{SiMe}_3)_3$ [18]. Me_3Ga was generously donated by Professor G. H. Robinson of Clemson University. The integrity of all materials utilized was confirmed *via* melting point and ^1H NMR spectra prior to reaction. ^1H and ^{13}C NMR spectra were obtained on a Varian XL-300 spectrometer operating at 300 and 75.4 MHz, respectively. All spectra were referenced to TMS by using the residual protons or carbons of deuterated benzene at δ 7.15 or 128 ppm. NMR samples were prepared in 5-mm tubes which were flame sealed under vacuum. All melting points (uncorrected) were obtained on a Thomas-Hoover Uni-melt apparatus, and capillaries were flame-

sealed under argon. Elemental analyses were performed by E+R Microanalytical Laboratory, Inc., Corona, NY.

Synthesis of [Ph(Me₃SiCH₂)InAs(SiMe₃)₂]₂ (1) from [(Me₃SiCH₂)₂In-As(SiMe₃)₂]₂ and Ph₂GaCl

A one-neck 200 ml round-bottom flask equipped with a Teflon valve and a micro-stirbar was charged with 0.200 g (0.196 mmol) of [(Me₃SiCH₂)₂InAs(SiMe₃)₂]₂ dissolved in 25 ml of benzene. Ph₂GaCl (0.103 g, 0.397 mmol) in 15 ml of benzene was then added and the solution was stirred at room temperature overnight. The volatiles were removed *in vacuo* from the resulting light yellow solution, leaving a viscous yellow oil. This oil was dissolved in pentane and upon storing at -15 °C for 1 week, colorless crystals of **1** suitable for single-crystal X-ray analysis were recovered (0.017 g, 8.7 % yield based on indium); m.p. decomposed to a black solid above 125 °C which then melted to a black liquid above 159 °C. Anal. Calcd. for C₃₂H₆₈As₂In₂Si₆: C, 38.40; H, 6.85 %. Found: C, 38.44; H, 6.86 %. ¹H NMR: δ 0.18 (s, 8 H), 0.20 (s, 7.4 H), 0.28 (s, 7.1 H), 0.33 (s, 10 H), 0.43 (s, 18.8 H), 0.54 (s, 7.4 H), 7.16-7.22 (m, partially obscured by solvent, Ph), 7.25-7.36 (m, 4 H, Ph), 7.78-7.77(m, 4 H, Ph). ¹³C{¹H} NMR: δ 2.75, 2.87, 3.76, 4.91, 5.06, 5.28, 127.58 (s, Ph), 127.86 (s, Ph), 128.19 (s, Ph), 128.54 (s, Ph), 128.60 (s, Ph).

Synthesis of [Ph(Me₃SiCH₂)InAs(SiMe₃)₂]₂ (1) from [Ph₂GaAs(SiMe₃)₂]₂ and (Me₃SiCH₂)₂InCl

In a similar arrangement to that described above, [Ph₂GaAs(SiMe₃)₂]₂ (0.233 g, 0.261 mmol, in 15 ml of benzene) and (Me₃SiCH₂)₂InCl (0.170 g, 0.523 mmol, in 5 ml of benzene) were combined. After stirring overnight at ambient temperature, the volatiles were removed *in vacuo* from the yellow solution. The resulting glassy, yellow residue was dissolved in pentane and cooled to -15 °C. After several days, fine needle-like crystals formed (0.022 g, 7.8% yield based on indium). The identity of these crystals as **1** was confirmed by ¹H and ¹³C{¹H} NMR spectra, melting point, and X-ray intensity data recorded on an Enraf-Nonius CAD-4 diffractometer.

Synthesis of [Me(Me₃SiCH₂)InAs(SiMe₃)₂]₂ (2) from [(Me₃SiCH₂)₂In-As(SiMe₃)₂]₂ and Me₃Ga

Me₃Ga (0.025 g, 0.218 mmol, 11% excess) in 10 ml of pentane was placed in the top bulb of a two-bulbed flask. [(Me₃SiCH₂)₂InAs(SiMe₃)₂]₂, 0.100 g (0.098 mmol), was dissolved in 15 ml of pentane and placed in the bottom bulb equipped with a micro-stir bar. The Me₃Ga solution was added dropwise over a 0.5 h period while the reaction was stirred at room temperature. The resulting colorless solution was frozen and the flask evacuated. The solution was then warmed to 40° C in an oil bath and allowed to stir for 5 days. The volatiles were removed *in vacuo* leaving a powdery white residue. The residue was dissolved in hexane and cooled to -15 °C for several days, after which time colorless crystals of **2** suitable for single-crystal X-ray analysis were recovered (0.057 g, 66.0% yield based on indium); m.p. decomposed to a black solid above 125 °C which then melted to a black liquid above 159 °C. Anal. Calcd. for C₂₂H₆₄As₂In₂Si₆: C, 30.14; H, 7.36; Si, 19.22%. Found: C, 29.61; H, 7.25; Si, 19.09%. ¹H NMR: δ 0.115 (s, 4 H, *cis*-CH₃), 0.145 (s, 4 H, *trans*-CH₃), 0.253 (s, 22 H, *trans*-CH₂SiCH₃), 0.260 (s, 22 H, *cis*-CH₂SiCH₃), 0.388 (s, 18 H, *cis*-SiCH₃), 0.421 (s, 36 H, *trans*-SiCH₃), 0.447 (s, 18 H, *cis*-SiCH₃). ¹³C{¹H} NMR: δ 3.30 (s, *cis*- and *trans*-CH₃), 2.50 (s, *cis*-CH₂SiCH₃), 2.73 (s, *cis*-CH₂SiCH₃), 4.69 (s, *cis*-SiCH₃), 4.98 (s, *trans*-SiCH₃), 5.25 (s, *cis*-SiCH₃).

Synthesis of [Me(Me₃SiCH₂)InP(SiMe₃)₂]₂ (3) from (Me₃SiCH₂)InCl₂ and LiP(SiMe₃)₂

A one-neck 200 ml round-bottom flask equipped with a Teflon valve was charged with 0.100 g (0.366 mmol) of (Me₃SiCH₂)InCl₂ dissolved in 40 ml of toluene. LiP(SiMe₃)₂ (0.135 g, 0.733 mmol) in 10 ml of toluene was then added and the solution was placed in a sonicating water bath at room temperature for 48 h. The volatiles were removed *in vacuo* from the resulting cloudy yellow solution, leaving a milky yellow oil. The oil was dissolved in pentane and allowed to evaporate slowly at room temperature for 1 day, after which time colorless platelets of **3** suitable for single-crystal X-ray analysis were recovered (0.094 g, 65.3% yield based on indium); m.p. 153 - 160 °C decomposes to a brown oil. Anal. Calcd. for C₂₂H₆₄In₂P₂Si₆: C, 33.49; H, 8.18; In, 29.11%. Found: C, 33.32; H, 8.03; In, 29.29%. ¹H NMR: δ 0.079 (s, 12 H, *cis*- and *trans*-

CH₃), 0.250 (s, 22 H, *trans*-CH₂SiCH₃), 0.259 (s, 22 H, *cis*-CH₂SiCH₃), 0.341 (t, 18 H, *cis*-SiCH₃, J_{P-H} = 2.70 Hz), 0.373 (s, 36 H, *trans*-SiCH₃, J_{P-H} = 2.60), 0.398 (t, 18 H, *cis*-SiCH₃, J_{P-H} = 2.69). ¹³C{¹H} NMR: δ 1.63 (s, *cis*-CH₂), 1.85 (s, *trans*-CH₂), 2.61 (s, *cis*-CH₂SiCH₃), 2.65 (s, *trans*-CH₂SiCH₃), 2.83 (s, *trans*-CH₃), 3.47 (s, *cis*-CH₃), 4.413 - 4.716 (bm, *cis*- and *trans*-SiCH₃). ³¹P{¹H} NMR: δ -234.67 (s, *trans*), -234.32 (s, *cis*)

Synthesis of [Me(Me₃SiCH₂)InP(SiMe₃)₂]₂ (3) from [(Me₃SiCH₂)₂InP(SiMe₃)₂]₂ and Me₃Ga

In a similar arrangement to that described for (2) above, (Me₃SiCH₂)₂InP(SiMe₃)₂ (0.250 g, 0.268 mmol, dissolved in 20 ml of pentane) and Me₃Ga (0.068 g, 0.595 mmol, 11% excess, in 20 ml of pentane) were combined and stirred at room temperature for 48 h. The volatiles were removed *in vacuo* from the resulting clear solution, leaving a clear semi-solid. This was dissolved in pentane and cooled to -15 °C for 3 days, following which colorless crystals of 3 (confirmed *via* ¹H and ¹³C NMR and melting point) were recovered from a clear viscous oil (0.133 g, 63.1% yield based on indium).

Synthesis of [Me(Me₃SiCH₂)InP(SiMe₃)₂]₂ (3) from [Cl(Me₃SiCH₂)InP(SiMe₃)₂]₂ and LiP(SiMe₃)₂

In a similar arrangement to that used previously, [Cl(Me₃SiCH₂)InP(SiMe₃)₂]₂ (4) (0.052 g, 0.062 mmol, dissolved in 25 ml of pentane) and LiP(SiMe₃)₂ (0.012 g, 0.125 mmol, in 25 ml of pentane) were combined and placed in a sonicating water bath at room temperature for 48 h. The volatiles were removed *in vacuo* from the resulting turbid yellow solution, leaving a yellow semi-solid. This was extracted with 25 ml of pentane which was then cooled to -15 °C for 3 days, after which time colorless crystals of 3 (confirmed *via* ¹H and ¹³C NMR and melting point) were recovered from a yellow tacky oil (0.026 g, 52.2% yield based on indium).

Synthesis of [Cl(Me₃SiCH₂)InP(SiMe₃)₂]₂ (4) from [(Me₃SiCH₂)₂InP(SiMe₃)₂]₂ and Ph₂GaCl

A Schlenk flask was charged with 0.113 g (0.435 mmol) of Ph₂GaCl dissolved in 10 ml of toluene. To this was added 0.203 g (0.218 mmol) of [(Me₃SiCH₂)₂InP(SiMe₃)₂]₂. The solution was stirred overnight, yielding a colorless solution. The volatiles were removed *in vacuo*, leaving a tacky oil which produced no crystalline material from toluene when cooled to -15 °C for several days. Upon adding pentane, a transient white suspension formed, which quickly redissolved and

yielded small colorless crystals at room temperature. After 24 h, a large number of these crystals which were later identified as **4** had formed coincident with a viscous oil. Attempts to isolate the crystalline material from the oil by washing with cold pentane resulted in their dissolution along with the oily residue (0.097 g, 54% yield with slight contamination of oily residue). Anal. Calcd for $C_{20}H_{58}Cl_2In_2P_2Si_6$: C, 28.95; H, 7.05%. Found: C, 27.55; H, 6.67%. 1H NMR: δ 0.318 (s, 4 H, CH_2), 0.322 (s, 18 H, $SiCH_3$), 0.45 (t, 36 H, $PSiCH_3$, $J_{P-H} = 2.50$ Hz). $^{13}C\{^1H\}$ NMR: δ 2.44 (s, $SiCH_3$), 3.98 (d, $PSiCH_3$, $J_{P-C} = 4.0$ Hz), 6.28 (s, CH_2). $^{31}P\{^1H\}$ NMR: δ -241.43 (s). Additionally, an X-ray analysis of this product confirmed its structure to be that of **4**, but the crystals contained a disordered structure[19].

*Synthesis of $[Cl(Me_3SiCH_2)InP(SiMe_3)_2]_2$ (**4**) from $(Me_3SiCH_2)InCl_2$ and $P(SiMe_3)_3$*

A one-neck 200 ml round-bottom flask equipped with a Teflon valve and micro stir-bar was charged with 0.500 g (1.832 mmol) of $(Me_3SiCH_2)InCl_2$ dissolved in 25 ml of pentane. $P(SiMe_3)_3$ (0.459 g, 1.832 mmol) in 25 mL of pentane was then added and the solution was stirred at room temperature for 24 h. The volatiles were removed *in vacuo* from the resulting pale yellow solution, leaving a clear yellow oil. The oil was dissolved in pentane and cooled to $-15^\circ C$ for 1 week following which colorless crystals of **4** suitable for X-ray analysis were recovered (0.653 g, 86% yield); mp = $150-153^\circ C$ (decomposed to brown liquid). 1H , $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR identical to that of a previously prepared sample.

X-ray crystal structure analyses of 1, 2, 3, and 4

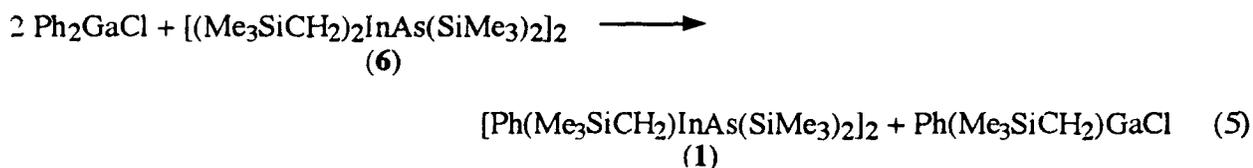
Crystallographic measurements. Crystals of each of the four compounds were sealed inside thin-walled glass capillaries under an argon atmosphere. Crystal data and data collection parameters are summarized in Table 1. All measurements were performed on an Enraf-Nonius CAD-4 diffractometer equipped with a graphite monochromator. Intensity data were corrected for the usual Lorentz and polarization effects. An empirical absorption correction, based on the ϕ -dependency of the intensities of several reflections with χ ca. 90° , was applied to each data set. The Laue symmetry indicated that the space group for **1** was either $P1$ or $P\bar{1}$; the latter was assumed initially and confirmed by the structure analysis and refinement. The space group $P2_1/c$

for **2** - **4** was established unambiguously by the Laue symmetry and systematic absences: $0k0$ when k is odd, $h0l$ when l is odd.

Structural analysis. The crystal structures of **1** and **3** were both solved by the heavy-atom approach whereas for **2** and **4** advantage was taken of the fact that they are isomorphous with **3**. Approximate In and As coordinates for **1** and **3** were derived from Patterson maps. The remaining non-hydrogen atoms were located in difference Fourier syntheses phased by these heavier atoms. Positional and thermal parameters (at first isotropic, then anisotropic) were then adjusted by means of several rounds of full-matrix least-squares calculations. Hydrogen atoms were incorporated at their calculated positions [$C(ar)-H = 1.0 \text{ \AA}$, $C(sp^3)-H = 1.05 \text{ \AA}$] for both compounds and an extinction correction was also included as a variable for **1** during the later iterations. For **2** and **4**, the refined non-hydrogen atom positional parameters of **3** were used as initial input into the least-squares cycles. Parameter refinement then proceeded as for **1**. Difference Fourier syntheses evaluated following convergence of the least-squares refinement revealed no unusual features. For all structure-factor calculations, neutral atom scattering factors and their anomalous dispersion corrections were taken from ref. 20. In the least-squares iterations, $\sum w\Delta^2$ [$w = 1/\sigma^2(|F_O|)$, $\Delta = (|F_O| - |F_C|)$] was minimized. Crystallographic calculations were performed on PDP11/44 and MicroVAX computers by use of the Enraf-Nonius Structure Determination Package (SDP 3.0) [21]. Non-hydrogen atom fractional coordinates for **1** - **4** are provided in Tables 2 - 5, respectively. Bond lengths and angles for **1** are given in Table 6 while corresponding values for **2**, **3**, and **4** are listed alongside each other in Table 7. Tables of anisotropic temperature factor parameters, hydrogen atom parameters, torsion angles, and observed and calculated structure amplitudes for **1** - **4** are available from the authors (RLW).

Results and Discussion

The reaction of Ph_2GaCl with the dimer $[(\text{Me}_3\text{SiCH}_2)_2\text{InAs}(\text{SiMe}_3)_2]_2$ (**6**) does not yield a mixed-metal, mixed-bridge compound (i.e., $\overline{\text{MEM}'\text{Cl}}$) but results instead in the formation of a viscous oil from which **1** is isolated, equation (5).



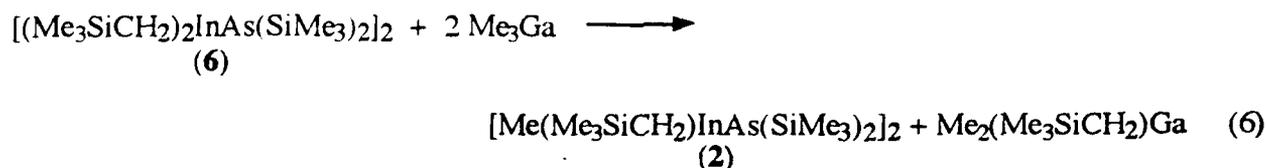
Compound **1** results from a ligand redistribution reaction in which phenyl and Me_3SiCH_2 groups are transferred from one group 13 metal center to another and although not isolated, $\text{Ph}(\text{Me}_3\text{SiCH}_2)\text{GaCl}$ is indicated by mass balance. Colorless, crystalline **1** is extremely air sensitive, decomposing rapidly to a dark red liquid. Also, it appears that **1** is thermally unstable. Upon standing at room temperature under an atmosphere of argon, for several days, **1** becomes an orange solid. A ^1H NMR sample solution of this solid exhibits additional resonances at δ 0.405 and 0.521 ppm. Similarly, stored solutions of **1** demonstrate the same characteristics after several days or upon heating to 60°C for several minutes. Nevertheless, **1** can be stored in the dark at -15°C with no apparent decomposition.

The ambient temperature ^1H and ^{13}C NMR spectra of **1** are complex, somewhat undecipherable and inconsistent with those expected for the solid state structure of **1**. However, the fact that no resonance has a chemical shift identical with any observed for **6** indicates that a mixture of **6** and $[\text{Ph}_2\text{InAs}(\text{SiMe}_3)_2]_2$ (**7**) [22] is not present. As was postulated by Beachley *et al.* for **5**, the complex NMR spectra suggest a fluxional process possibly between *cis* and *trans* isomers, multiple ring conformations, varying degrees of oligimerization or a combination of the above.

Compound **1** crystallizes in the centrosymmetric space group $P\bar{1}$ with one formula unit per unit cell. A view of the solid-state structure is presented in Figure 1. The dimeric molecule lies

on a crystallographic center of symmetry and thus the $\overline{\text{InAsInAs}}$ core is required to be strictly planar. In accord with the general situation in group 13-15 dimers, the endocyclic bond angle at the group 15 center is larger than that at the group 13 center [In-As-In = 92.89(2)°; As-In-As = 87.11(2)°]. The mean of the essentially equal In-As bond lengths at 2.679 Å is close to that of 2.686 Å in **7** but distinctly shorter than the value of 2.728 Å in **6**. The shorter distances in **1** and **7** can be attributed to the smaller steric demands of their phenyl groups versus those of the bulkier Me₃SiCH₂ substituents in **6**. Significant differences in the exocyclic bond angles subtended at indium [108.2(3)° and 108.9(3)° in **7**, 118.1(3)° in **1**, and 125.8(5)° in **6**] are consistent with this view. The In-C(ar) and In-C(sp³) bond lengths of 2.157(7) Å and 2.178(5) Å, respectively, are similar to each other as well as to the mean In-C distances of 2.18 Å in **7** and 2.19 Å in **6**. The mean As-Si bond lengths [2.355 Å in **7**, 2.350 Å in **1**, 2.348 Å in **6**] do not differ significantly, and the Si-As-Si angles [108.46(5)° in **1**, 106.2° (mean) in **7**, 105.4(2)° in **6**] show only a small variation.

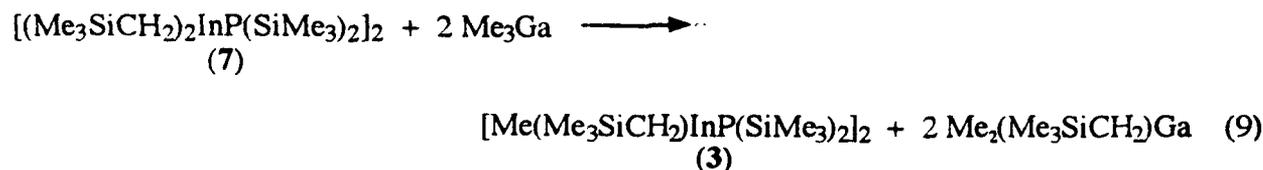
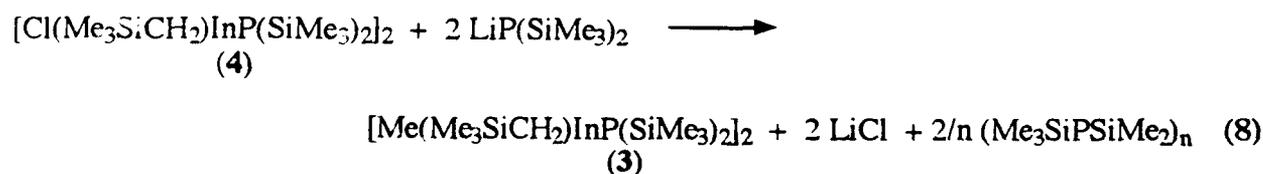
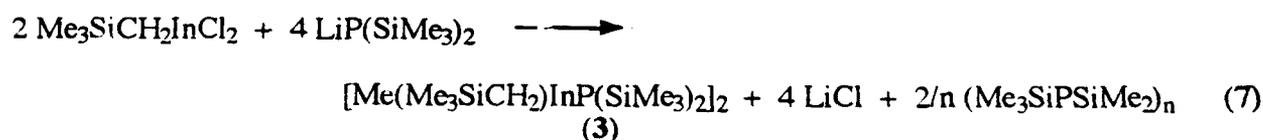
The reaction of Me₃Ga with **6** in a 2:1 mole ratio results in the formation of **2**, equation (6).



As was the case for **1**, the possible by-product, Me₂(Me₃SiCH₂)Ga, was not isolated but is inferred only by mass balance. Compound **2**, is a colorless crystalline material which is similarly unstable like that of **1**. Unlike **1**, the room temperature ¹H and ¹³C NMR spectra of **2** are clean, easily decipherable, and demonstrate clearly the existence of both *cis* and *trans* isomers in solution. No other fluxional processes or oligomerizations were observed. It is interesting that only the *trans* isomer is observed in the solid state whereas in solution both are present.

Compound **2** crystallizes in the centrosymmetric space group $P2_1/c$ with each of the two molecules in the unit cell lying on centers of symmetry and thus the $\overline{\text{InAsInAs}}$ core is planar. The solid-state structure is illustrated in Figure 2. The In-As-In and As-In-As angles in **2** [$94.30(2)^\circ > 85.70(2)^\circ$, respectively] differ in the usual manner for group 13-15 dimers [1,2] and are similar to corresponding values in **6** [$94.57(2)^\circ > 85.43^\circ$ (mean)]. The mean of the In-As bond lengths at 2.706 Å is intermediate between those of 2.679 Å in **1** and 2.728 Å and **6**, reflecting the different steric demands of the indium atom substituents. That the exocyclic bond angle subtended at indium [$119.9(3)^\circ$] in **2** is only very slightly larger than that of $118.1(3)^\circ$ in **1** but much smaller than that of $125.8(5)^\circ$ in **6** is also indicative of the different steric requirements of the substituents. The mean As-Si and As-C bond lengths in **2** at 2.344 and 2.186 Å, respectively, are essentially the same as corresponding distances in **6** [2.348, 2.19 Å]

The preparation of **3** has been accomplished *via* three different reaction pathways, equations (7 - 9).



Though the exact mechanism responsible for the formation of **3** in equations (7) and (8) is not known, it is obvious that several key factors are involved. The first of these is that **4**, eq. (7), is a probable intermediate to **3** since the latter can be prepared from the former. Secondly, the

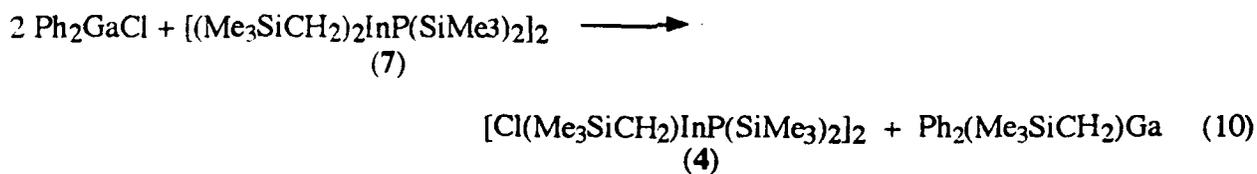
appearance of the Me group in **3** probably was the result of a cleavage reaction involving a Si-C bond in the phosphide species. Naturally, such a reaction would leave behind some unit of $(\text{Me}_3\text{SiPSiMe}_2)$ of unknown oligomerization. Although this by-product was not completely isolated, its probable existence can be inferred from the intractable oily residue isolated concomitant with **3** (**3** could not be fully separated from the oil). The ^1H NMR spectrum of this contaminated oily material exhibits a broad set of resonances ranging from δ 0.078 - 0.496 and also exhibits the overlapping spectrum of **3**. The ^{31}P NMR spectrum displays both a resonance associated with **3** and one other located at δ -153.47. Both the ^1H and ^{31}P NMR spectra indicate the presence of another phosphorus species and the values of these are within the range reported for other similarly formulated $(\text{RPSiR}'_2)_n$ oligomers [24 - 26]. As for equation (9), the formation of **3** was the result of a ligand transfer reaction involving the Me groups of Me_3Ga and the Me_3SiCH_2 groups of $[(\text{Me}_3\text{SiCH}_2)_2\text{InP}(\text{SiMe}_3)_2]_2$ (**7**). Again, the possible by-product, $\text{Me}_2(\text{Me}_3\text{SiCH}_2)\text{Ga}$, was not isolated but is inferred only by mass balance.

Compound **3**, is also a colorless crystalline material, but it is stable under an inert atmosphere at room temperature. However, like that of the previous compounds, it is extremely air-sensitive and undergoes appreciable decomposition upon standing in solution. The room temperature ^1H and ^{13}C NMR spectra of **3**, like those of its isostructural compound **2**, are easily interpretable and demonstrate the existence of both *cis* and *trans* isomers in solution. The virtual coupling of the ring phosphorus atoms allows the identification of the two isomers to be quickly made in the ^1H NMR (i.e., for the SiMe_3 protons a triplet resonance for the *trans* configuration and two triplets for the *cis*). The ^{31}P NMR spectrum exhibits two sharp resonances corresponding to the two isomers. As with **2**, no other fluxional processes were observed. The isolation of only the *trans* isomer in the solid state may be due to a combination of packing interactions and lattice considerations.

Crystals of compound **3** belong to the centrosymmetric space group $P2_1/c$ and are isomorphous with those of **2**; accordingly, the $\overline{\text{InPInP}}$ core is planar. Figure 3 provides a view of the solid-state structure. It is informative to compare the core geometry of **3** not only with that in

8, which differs in the nature of only one organic substituent, but also with those of their arsenic analogs **2** and **6**. Selected bond lengths and angles are recorded in Table 8. The bond distances quoted are similar within each pair [**2/6** and **3/8**] as are the endocyclic bond angles. Highly significant differences occur in the exocyclic bond angles subtended at the indium centers [$125.8(5)^\circ$ in **6** \gg $119.9(3)^\circ$ in **2**; $122.7(4)^\circ$ in **8** \gg $118.3(2)^\circ$ in **3**] where the larger value in each case is associated with the sterically more demanding geminal Me_3SiCH_2 groups in **6** and **8** in contrast to the situation in **2** and **3** where one of these bulky groups at each indium atom is replaced by the much smaller Me group. These differences are relayed to the exocyclic bond angles at the As and P centers where the Si-As-Si and Si-P-Si values differ to a smaller extent in the opposite sense [$105.4(2)^\circ$ in **6** $<$ $107.4(1)^\circ$ in **2**; $105.7(2)^\circ$ in **8** $<$ $108.0(1)^\circ$ in **3**]. The endocyclic In-P-In and P-In-P bond angles in **3** [$93.35(6)^\circ$ and $86.65(5)^\circ$, respectively] are similar to the corresponding values in **8** [$93.6(1)^\circ$, mean 86.3°], and show a similar bond angle pattern in the ring [P-In-P \ll In-P-In] in accord with the usual trend [1,2].

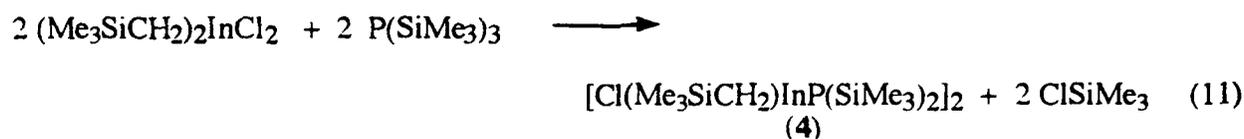
The reaction of Ph_2GaCl with **7** at ambient temperature in a 2:1 mole ratio affords **4** in a 54 % yield along with a viscous intractable oil, equation (10).



Nither the complete separation of **4** from this oily residue nor the reverse was possible as both are very soluble in hydrocarbon solvents and co-precipitate. Though not confirmed, this oily material could possibly be $\text{Ph}_2(\text{Me}_3\text{SiCH}_2)\text{Ga}$ since its ^1H NMR spectrum exhibits resonances at δ 0.102 and 0.150 (possibly Me_3SiCH_2) and 7.01 (indicating Ph). Again, this transformation was accomplished *via* a ligand transfer reaction involving the Cl atoms of Ph_2GaCl and Me_3SiCH_2 groups of **7**. It is intriguing that in the case of an indium phosphorus containing compound, a

chlorine atom was transferred whereas in the analogous indium arsenic reaction [eq. (5)] a Ph group was transferred.

As was noted earlier, it was our original contention that **4** was a possible intermediate in the preparation of **3**, however, the product obtained in equation (10) is difficult to purify. Therefore, an alternate preparation was sought. Douglas and Theopold reported that **4** could be prepared by the reaction of $(\text{Me}_3\text{SiCH}_2)\text{InCl}_2$ with $\text{P}(\text{SiMe}_3)_3$, equation (11), but did not give any experimental or characterization data [5].



The product obtained from equation (11) is easily purifiable and as was shown by experiment, subsequent reaction [eq. (8)] does yield **3**.

Compound **4** is a clear colorless crystalline material which decomposes rapidly in air to an orange brown material, is unstable in solution decomposing to an orange oil upon which it, surprisingly, liberates $\text{P}(\text{SiMe}_3)_3$, as evidenced by ^1H and ^{31}P NMR, but is quite stable in the solid form under an inert atmosphere at -15°C . Contrary to **1** - **3**, at room temperature, the solution ^1H , ^{13}C , and ^{31}P NMR spectra of **4** shows no evidence of both *cis* and *trans* species or any other oligomerization. Only the spectra consistent with the *trans* form is observed. It is possible that upon dissolution at room temperature, conversion from a *cis* to *trans* configuration is too rapid to detect.

Monoclinic crystals of compound **4** belong to the centrosymmetric space group $P2_1/c$, are isomorphous with those of **2** and **3**, and likewise contain a planar $\overline{\text{InPInP}}$ core. A view of the solid-state structure is provided in Figure 4. The mean In-P bond length at 2.593 \AA in **4** is substantially shorter than that found in either **3** [mean 2.635 \AA] or **8** [2.655 \AA] due in part to the more electronegative nature of the exocyclic Cl atom versus either Me or Me_3SiCH_2 substituents as well as its smaller steric size and larger covalent radius [$\text{In-Cl} = 2.405(2) \text{ \AA} \gg \text{In-C}(31) =$

2.165(5) Å in **4**). The distance in **4** lies close to the mean In-P distance of 2.62 Å in [h⁵-C₅Me₅(Cl)InP(SiMe₃)₂]₂ (**9**) [5,27]. Endocyclic In-P-In and P-In-P bond angles in **4** are 91.00(6)° and 89.00(5)°, respectively; in **9**, the corresponding values are 92.2(1)° and 87.8(1)°. In contrast to the situation for **3** or **8**, the difference of only 2.0° in the P-In-P and In-P-In bond angles for **4** is much less than those of 6.7° in **3**, 7.2° in **8**, resulting in **4** having a nearly square ring; for **9**, the difference is intermediate at 4.4°. The Cl-In-C angle of 112.1(2)° in **4** is significantly smaller than the C-In-C angle of 118.3(2)° in **3** whereas the opposite is the case, but to a smaller extent, for the Si-P-Si angles [110.1(1)° in **4**, 108.0(1)° in **3**] as noted above for **6** and **8** versus **2** and **3**, respectively.

The preparation of **1** - **4** by ligand exchange reactions gives clear precedent these exchanges can occur between group 13 centers. Also, their isolation proves that relatively stable, dimeric hetero-dialkylindium species are accessible. With this knowledge, it may eventually be possible to fabricate 13-15 compounds with varied functionalities about the metal atom, each designed to react in a very specific manner. Additionally, future attempts to prepare compounds containing mixed group 13 centers will have to take into account the fact that ligand redistribution reactions can readily occur under mild conditions.

Acknowledgement

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Captions to Figures

Fig. 1. ORTEP diagram (40% probability ellipsoids) showing the atom numbering scheme and solid-state conformation of **1**; primed atoms are related to the unprimed atoms by a crystallographic center of symmetry. Hydrogen atoms have been omitted for clarity.

Fig. 2. ORTEP diagram (40% probability ellipsoids) showing the atom numbering scheme and solid-state conformation of **2**; primed atoms are related to the unprimed atoms by a crystallographic center of symmetry. Hydrogen atoms have been omitted for clarity.

Fig. 3. ORTEP diagram (40% probability ellipsoids) showing the atom numbering scheme and solid-state conformation of **3**; primed atoms are related to the unprimed atoms by a crystallographic center of symmetry. Hydrogen atoms have been omitted for clarity.

Fig. 4. ORTEP diagram (40% probability ellipsoids) showing the atom numbering scheme and solid-state conformation of **4**; primed atoms are related to the unprimed atoms by a crystallographic center of symmetry. Hydrogen atoms have been omitted for clarity.

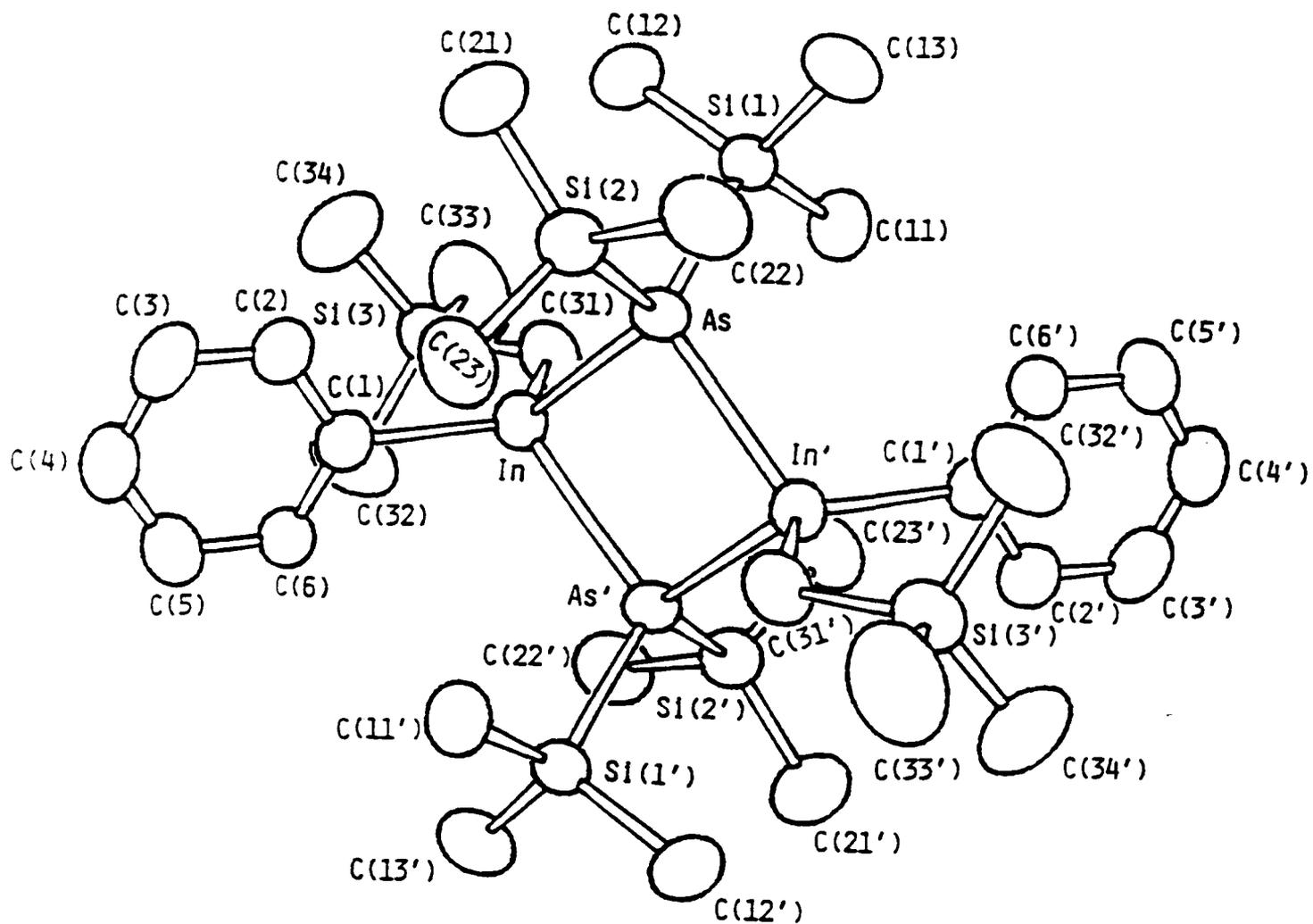


Figure 1.

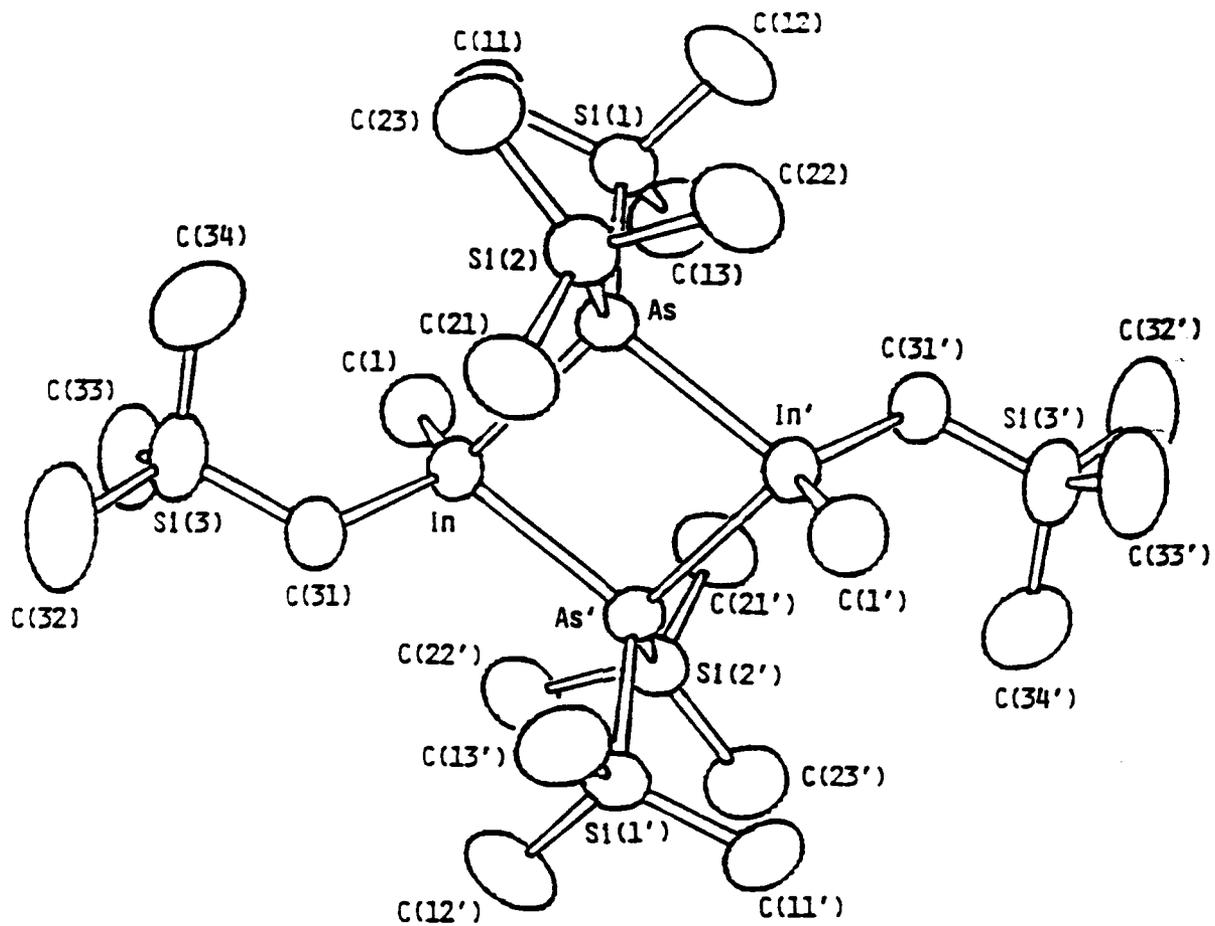


Figure 2.

Table 1

Crystal data and summary of analyses

Compound	1	2	3	4
Formula weight	C ₃₂ H ₆₈ As ₂ In ₂ Si ₆	C ₂₂ H ₆₄ As ₂ In ₂ Si ₆	C ₂₂ H ₆₄ In ₂ P ₂ Si ₆	C ₂₀ H ₅₈ Cl ₂ In ₂ P ₂ Si ₆
Crystal system	triclinic	monoclinic	monoclinic	monoclinic
Space group	$P\bar{1}(C_1)$ -No.2	$P2_1/c(C_{2h}^5)$ -No.14	$P2_1/c(C_{2h}^5)$ -No.14	$P2_1/c(C_{2h}^5)$ -No.14
a(Å)	11.859(2)	9.928(1)	9.858(1)	9.845(1)
b(Å)	12.222(2)	19.882(1)	19.662(1)	19.349(1)
c(Å)	10.021(2)	11.513(1)	11.456(1)	11.442(1)
α (°)	107.59(1)	90.0(-)	90.0(-)	90.0(-)
β (°)	110.47(1)	111.21(1)	110.88(1)	110.63(1)
γ (°)	66.54(1)	90.0(-)	90.0(-)	90.0(-)
V(Å ³)	1225.6(7)	2118.6(6)	2074.7(6)	2039.8(6)
Z	1	2	2	2
D _{calc}	1.356	1.374	1.263	1.351
Radiation	Cu-K α ($\lambda = 1.5418\text{Å}$)	Cu-K α ($\lambda = 1.5418\text{Å}$)	Cu-K α ($\lambda = 1.5418\text{Å}$)	Cu-K α ($\lambda =$
1.5418Å)				
μ (cm ⁻¹)	107.8	123.9	116.1	130.5
Temp(°C)	25	25	25	25
Crystal size (mm)	0.20 x 0.30 x 0.80	0.09 x 0.14 x 0.50	0.11 x 0.17 x 0.80	0.30 x 0.30 x 0.34
T _{max} ·T _{min}	1.00:0.32	1.00:0.035	1.00:0.43	1.00:0.56
Scan type	ω -2 θ	ω -2 θ	ω -2 θ	ω -2 θ
Scanwidth (°)	1.25 + 0.14tan θ	0.80 + 0.14tan θ	1.00 + 0.14tan θ	0.80 + 0.14tan θ
θ_{max} (°)	75	75	75	75

Table 1 (continued)

Compound	1	2	3	4
Intensity control refls.	1 1 2, 1 2 2̄,	0 4 1, 1 2 3,	1 2 3, 2 1 3̄,	1 3 2̄, 2 1 3̄,
Variation	1 2 1̄, 1 2 1	2 1 3̄, 3 1 1̄	3 1 1, 0 2 2	1 4 1, 1 2 3
Repeat time (h)	-3%	<1%	<1%	<2%
Total no. of refls. recorded	2	2	2	2
No. of non-equiv. refls.	5439(+h, ±k, ±l)	4599(+h, +k, ±l)	4497(+h, +k, ±l)	4433(+h, +k, ±l)
R_{merge} (on I)	5047	4353	4250	4191
No. of refls. retained [$I > 3.0\sigma(I)$]	0.023	0.025	0.033	0.033
No. of parameters refined	3979	2733	2952	2991
Extinction correction	191	146	145	146
R^a	$8(1) \times 10^{-7}$	$4.5(4) \times 10^{-7}$	none	$4.2(6) \times 10^{-7}$
R_w^b	0.044	0.038	0.043	0.044
GOF ^c	0.061	0.048	0.059	0.059
Max. shift: esd in final cycle	1.53	1.14	1.30	1.36
Final $\Delta\rho(e/\text{Å}^3)$ max.; min.	0.03	0.01	0.01	0.02
	0.15; -1.13	0.75; -0.76	0.71; -0.94	0.87; -1.49

$aR = \Sigma |F_o| - |F_c| / \Sigma |F_o|$. $bR_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w |F_o|^2]^{1/2}$. $cGOF = [\Sigma w \Delta^2 / N_{\text{observations}} - N_{\text{parameters}}]^{1/2}$. ^dLocated in the vicinity of the indium atom.

Table 2

Non-hydrogen atom fractional coordinates and equivalent isotropic thermal parameters for **1**, with estimated standard deviations in parentheses

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} (Å ²)
As	-0.14815(4)	0.12368(4)	-0.05755(5)	3.66(1)
In	-0.09797(3)	-0.10766(3)	-0.04592(3)	4.09(1)
Si(1)	-0.2478(1)	0.1483(1)	-0.2999(2)	4.46(3)
Si(2)	-0.2710(2)	0.2778(1)	0.0903(2)	4.96(4)
Si(3)	-0.2098(2)	-0.3300(1)	-0.2905(2)	5.69(4)
C(11)	-0.1306(6)	0.0523(6)	-0.4072(6)	5.9(2)
C(12)	-0.3906(6)	0.0972(6)	-0.3637(8)	6.8(2)
C(13)	-0.3017(8)	0.3096(6)	-0.3188(8)	7.5(2)
C(21)	-0.4442(7)	0.2965(8)	0.0094(9)	7.8(2)
C(22)	-0.2418(8)	0.4230(5)	0.1106(9)	7.1(2)
C(23)	-0.2183(8)	0.2344(6)	0.2725(7)	7.0(2)
C(31)	-0.1323(6)	-0.2179(5)	-0.2625(6)	5.5(1)
C(32)	-0.1200(10)	-0.4344(6)	-0.1612(11)	9.8(3)
C(33)	-0.2240(11)	-0.4212(7)	-0.4783(10)	11.3(3)
C(34)	-0.3722(8)	-0.2531(9)	-0.2669(13)	10.4(3)
C(1)	-0.1731(4)	-0.1249(4)	0.1113(6)	4.4(1)
C(2)	-0.2966(5)	-0.0581(5)	0.1215(7)	5.5(2)
C(3)	-0.3488(6)	-0.0767(7)	0.2149(8)	6.7(2)
C(4)	-0.2780(6)	-0.1648(6)	0.2977(8)	6.9(2)
C(5)	-0.1561(7)	-0.2317(6)	0.2901(7)	6.5(2)
C(6)	-0.1056(5)	-0.2138(5)	0.1946(6)	5.2(1)

Table 3

Non-hydrogen atom fractional coordinates and equivalent isotropic thermal parameters for **2**, with estimated standard deviations in parentheses

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} (Å ²)
As	0.48398(7)	0.07672(3)	0.58347(5)	3.51(1)
In	0.37997(5)	0.04177(2)	0.33939(3)	3.81(1)
Si(1)	0.6377(2)	0.1701(1)	0.6186(2)	4.33(4)
Si(2)	0.3247(2)	0.0962(1)	0.6884(2)	4.46(4)
Si(3)	0.0398(2)	0.1007(1)	0.1733(2)	5.97(5)
C(1)	0.4920(8)	0.1016(4)	0.2444(7)	5.6(2)
C(11)	0.5338(9)	0.2425(3)	0.5293(7)	6.3(2)
C(12)	0.7105(10)	0.1920(5)	0.7856(7)	7.4(2)
C(13)	0.7896(8)	0.1490(4)	0.5671(8)	6.6(2)
C(21)	0.1683(8)	0.0391(4)	0.6167(7)	6.3(2)
C(22)	0.4160(9)	0.0774(5)	0.8566(7)	6.4(2)
C(23)	0.2612(9)	0.1852(4)	0.6744(8)	7.3(2)
C(31)	0.1448(7)	0.0282(3)	0.2546(7)	4.9(2)
C(32)	-0.1570(10)	0.0798(6)	0.1014(10)	9.7(3)
C(33)	0.0984(10)	0.1299(5)	0.0459(8)	8.2(3)
C(34)	0.0618(12)	0.1705(5)	0.2860(11)	9.7(3)

Table 4

Non-hydrogen atom fractional coordinates and equivalent isotropic thermal parameters for **3**, with estimated standard deviations in parentheses

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} (Å ²)
P	0.4853(2)	0.0761(1)	0.5833(1)	3.57(3)
In	0.38352(4)	0.04142(2)	0.34521(3)	3.82(1)
Si(1)	0.6347(2)	0.1664(1)	0.6162(2)	4.31(3)
Si(2)	0.3312(2)	0.0945(1)	0.6855(2)	4.39(3)
Si(3)	0.0428(2)	0.1015(1)	0.1748(2)	5.80(5)
C(1)	0.4957(7)	0.1032(3)	0.2479(6)	4.9(1)
C(11)	0.5323(8)	0.2406(3)	0.5254(7)	6.3(2)
C(12)	0.7107(9)	0.1888(4)	0.7849(7)	6.8(2)
C(13)	0.7869(8)	0.1453(4)	0.5639(7)	6.5(2)
C(21)	0.1728(8)	0.0364(4)	0.6141(7)	6.2(2)
C(22)	0.4252(9)	0.0751(5)	0.8543(6)	6.4(2)
C(23)	0.2643(8)	0.1846(4)	0.6693(8)	7.0(2)
C(31)	0.1493(7)	0.0268(3)	0.2557(6)	5.0(2)
C(32)	-0.1538(9)	0.0799(6)	0.1035(9)	9.4(3)
C(33)	0.1007(10)	0.1301(5)	0.0464(8)	8.4(3)
C(34)	0.0674(12)	0.1735(6)	0.2867(10)	9.7(3)

Table 5

Non-hydrogen atom fractional coordinates and equivalent isotropic thermal parameters for **4**, with estimated standard deviations in parentheses

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} (Å ²)
P	0.4843(1)	0.0766(1)	0.5863(1)	2.51(2)
In	0.37030(3)	0.03797(2)	0.35536(3)	2.66(1)
Si(1)	0.6270(2)	0.1714(1)	0.6116(2)	3.20(3)
Si(2)	0.3319(2)	0.0892(1)	0.6934(2)	3.35(3)
Si(3)	0.0417(2)	0.1064(1)	0.1710(2)	4.56(4)
Cl	0.4948(2)	0.1085(1)	0.2520(2)	4.62(4)
C(11)	0.5166(9)	0.2431(4)	0.5198(8)	5.1(2)
C(12)	0.6989(10)	0.1943(5)	0.7801(8)	6.1(2)
C(13)	0.7799(7)	0.1515(5)	0.5577(8)	5.0(2)
C(21)	0.1803(7)	0.0278(5)	0.6220(9)	5.5(2)
C(22)	0.4327(9)	0.0677(5)	0.8614(7)	5.0(2)
C(23)	0.2595(9)	0.1790(5)	0.6776(9)	5.9(2)
C(31)	0.1417(6)	0.0273(4)	0.2460(6)	4.1(1)
C(32)	-0.1590(9)	0.0877(7)	0.1031(10)	8.0(3)
C(33)	0.1050(10)	0.1371(6)	0.0438(9)	6.9(3)
C(34)	0.0724(12)	0.1755(6)	0.2911(11)	7.3(3)

Table 6. Bond distances (Å) and angles (°) for **1**, with estimated standard deviations in parentheses

(a) Bond lengths			
As-In	2.678(1)	Si(2)-C(23)	1.879(8)
As-In'	2.680(1)	Si(3)-C(31)	1.841(8)
As-Si(1)	2.353(2)	Si(3)-C(32)	1.842(9)
As-Si(2)	2.346(2)	Si(3)-C(33)	1.863(9)
In-C(1)	2.157(7)	Si(3)-C(34)	1.842(10)
In-C(31)	2.178(5)	C(1)-C(2)	1.387(7)
Si(1)-C(11)	1.857(7)	C(1)-C(6)	1.381(8)
Si(1)-C(12)	1.874(8)	C(2)-C(3)	1.399(13)
Si(1)-C(13)	1.862(8)	C(3)-C(4)	1.373(11)
Si(2)-C(21)	1.871(8)	C(4)-C(5)	1.365(10)
Si(2)-C(22)	1.879(8)	C(5)-C(6)	1.398(12)
(b) Bond angles			
In-As-In'	92.89(2)	As-Si(2)-C(23)	108.2(2)
In-As-Si(1)	108.19(3)	C(21)-Si(2)-C(22)	110.4(4)
In-As-Si(2)	118.35(6)	C(21)-Si(2)-C(23)	109.3(5)
In'-As-Si(1)	117.53(5)	C(22)-Si(2)-C(23)	109.8(4)
In'-As-Si(2)	111.15(5)	C(31)-Si(3)-C(32)	111.5(4)
Si(1)-As-Si(2)	108.46(5)	C(31)-Si(3)-C(33)	110.7(5)
As-In-As'	87.11(2)	C(31)-Si(3)-C(34)	110.5(4)
As-In-C(1)	113.1(1)	C(32)-Si(3)-C(33)	108.6(4)
As-In-C(31)	111.3(2)	C(32)-Si(3)-C(34)	108.2(6)
As'-In-C(1)	112.7(1)	C(33)-Si(3)-C(34)	107.2(5)
As'-In-C(31)	110.6(2)	In-C(31)-Si(3)	116.6(4)

Table 6 (continued)

C(1)-In-C(31)	118.1(3)	In-C(1)-C(2)	122.0(5)
As-Si(1)-C(11)	107.4(2)	In-C(1)-C(6)	121.1(4)
As-Si(1)-C(12)	107.9(3)	C(2)-C(1)-C(6)	116.5(6)
As-Si(1)-C(13)	112.1(2)	C(1)-C(2)-C(3)	121.9(6)
C(11)-Si(1)-C(12)	110.9(3)	C(2)-C(3)-C(4)	119.9(6)
C(11)-Si(1)-C(13)	110.0(4)	C(3)-C(4)-C(5)	119.4(9)
C(12)-Si(1)-C(13)	108.5(3)	C(4)-C(5)-C(6)	120.2(7)
As-Si(2)-C(21)	110.8(2)	C(1)-C(6)-C(5)	122.0(5)
As-Si(2)-C(22)	108.3(3)		

Table 7. Bond lengths (Å) and angles (°) for **2**, **3**, and **4**, with estimated standard deviations in parentheses

	2	3	4
	E = As	E = P	E = P
	X = C(Me)	X = C(Me)	X = Cl
(a) Bond distances			
E-In	2.710(1)	2.638(1)	2.591(1)
E'-In	2.701(1)	2.632(2)	2.595(2)
E-Si(1)	2.344(2)	2.251(3)	2.266(3)
E-Si(2)	2.344(3)	2.253(3)	2.260(3)
In-X	2.174(9)	2.195(7)	2.405(2)
In-C(31)	2.197(6)	2.186(6)	2.165(5)
Si(1)-C(11)	1.851(7)	1.866(6)	1.845(8)
Si(1)-C(12)	1.845(8)	1.860(8)	1.858(9)
Si(1)-C(13)	1.857(10)	1.850(9)	1.857(9)
Si(2)-C(21)	1.858(8)	1.871(7)	1.857(8)
Si(2)-C(22)	1.855(8)	1.862(7)	1.873(8)
Si(2)-C(23)	1.866(8)	1.876(8)	1.863(10)
Si(3)-C(31)	1.826(6)	1.851(6)	1.858(7)
Si(3)-C(32)	1.872(9)	1.864(9)	1.886(9)
Si(3)-C(33)	1.856(11)	1.845(11)	1.871(12)
Si(3)-C(34)	1.858(12)	1.867(12)	1.864(12)

Table 7 (continued)

	2	3	4
	E = As	E = P	E = P
	X = C(Me)	X = C(Me)	X = Cl
(b) Bond angles			
In-E-In'	94.30(2)	93.35(6)	91.00(6)
In-E-Si(1)	111.2(1)	111.2(1)	113.0(1)
In-E-Si(2)	120.1(1)	120.0(1)	116.9(1)
In'-E-Si(1)	114.7(1)	114.9(1)	113.4(1)
In'-E-Si(2)	109.0(1)	109.1(1)	111.4(1)
Si(1)-E-Si(2)	107.4(1)	108.0(1)	110.1(1)
E-In-E'	85.70(2)	86.65(5)	89.00(5)
E-In-X	108.0(2)	107.9(2)	103.01(6)
E-In-C(31)	115.9(2)	117.9(2)	127.3(2)
E'-In-X	110.9(2)	111.3(2)	106.30(6)
E'-In-C(31)	111.3(2)	110.5(2)	115.7(2)
X-In-C(31)	119.9(3)	118.3(2)	112.1(2)
E-Si(1)-C(11)	108.8(2)	109.4(2)	108.8(3)
E-Si(1)-C(12)	110.6(3)	111.0(3)	108.5(3)
E-Si(1)-C(13)	108.6(3)	109.1(3)	109.2(3)
C(11)-Si(1)-C(12)	109.0(4)	109.4(3)	110.1(4)
C(11)-Si(1)-C(13)	110.6(4)	109.6(4)	110.5(4)
C(12)-Si(1)-C(13)	109.2(4)	108.5(4)	109.7(4)
E-Si(2)-C(21)	106.3(3)	106.7(3)	106.1(3)
E-Si(2)-C(22)	109.8(3)	109.2(3)	108.6(3)
E-Si(2)-C(23)	112.5(3)	112.2(3)	110.6(4)

Table 7 (continued)

	2	3	4
	E = As X = C(Me)	E = P X = C(Me)	E = P X = Cl
C(21)-Si(2)-C(22)	110.8(4)	111.0(4)	111.3(4)
C(21)-Si(2)-C(23)	109.8(4)	108.9(3)	109.5(4)
C(22)-Si(2)-C(23)	107.7(4)	108.9(4)	110.7(4)
C(31)-Si(2)-C(32)	111.2(4)	110.7(4)	109.9(5)
C(31)-Si(3)-C(33)	111.6(4)	111.1(4)	110.7(4)
C(31)-Si(3)-C(34)	109.3(4)	110.3(4)	109.2(4)
C(32)-Si(3)-C(33)	107.2(5)	106.8(4)	109.2(5)
C(32)-Si(3)-C(34)	108.4(5)	109.5(5)	108.4(6)
C(33)-Si(3)-C(34)	109.1(5)	108.4(5)	109.5(5)
In-C(31)-Si(3)	116.7(3)	116.5(3)	117.5(4)

Table 8. Comparison of bond lengths (\AA) and selected angles ($^\circ$) involving the core atoms of **2**, **3**, **6**, and **8**

Compound	2	6		3	8
(a) Bond lengths					
As-In(mean)	2.706	2.728	P-In(mean)	2.635	2.655
As-Si(mean)	2.344	2.348	P-Si(mean)	2.252	2.255
In-C(mean)	2.186	2.19	P-C(mean)	2.191	2.175
(b) Bond angles					
In-As-In	94.30(2)	94.57(5)	In-P-In	93.35(6)	93.6(1)
Si-As-Si	107.4(1)	107.4(2)	Si-P-Si	108.0(1)	105.7(2)
As-In-As	85.70(2)	85.43(mean)	P-In-P	86.65(5)	86.4(mean)
C-In-C	119.9(3)	125.8(5)	C-In-C	118.3(2)	122.7(4)

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