DEHALOSILYLATION REACTIONS INVOLVING $E(SiMe_3)_3$ AND $Ph_2InCl.$ SYNTHESIS AND X-RAY STRUCTURES OF $[Ph_2InE(SiMe_3)_2]_2$ (E = P OR As)

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(Received 24 July 1992; accepted 1 October 1992)

Abstract—Combining $P(SiMe_3)_3$ or $As(SiMe_3)_3$ with Ph_2InCl in a 1:1 mole ratio results in the elimination of Me_3SiCl via a dehalosilylation reaction to yield $[Ph_2InP(SiMe_3)_2]_2$ (I) and $[Ph_2InAs(SiMe_3)_2]_2$ (II), respectively. X-ray structures were determined for I and II. The $(InP)_2$ core of dimer I is planar, whereas in dimer II the $(InAs)_2$ ring is slightly puckered.

The quest for suitable single-source precursors to ceramic and/or electronic III-V materials in previous years has resulted in a large number of fundamental reports concerning the structural aspects and reactivities of these compounds.^{1,2} Elucidation of this basic chemistry is paramount to the understanding of the nature of the factors that influence the correct design and fabrication of such materials. Research in our laboratory has primarily centred on the use of silvlarsines and, of late, silvlphosphines in dehalosilylation reactions with a dialkyl group III halide or group III trihalide. These reactions eliminate a silvl halide thus forming a III-V bond.^{1,3} This line of investigation has proven to be very fruitful in that a variety of compounds containing MEME (M = Ga, E = As; $^{4-7}$ M = In, E = P⁸ or As⁹) and MEMCl (M = Ga, E = As^{4,6,7} or P;¹⁰ $M = In, E = P^8$ or As^9) cores have been isolated. From the latter compounds, the possibility of replacing the chlorine atom with other functionalities exists.¹¹ Currently, for the case of compounds with cores consisting of MEME (M = In, E = P or As) rings, we have only employed this dehalosilylation methodology to (Me₃SiCH₂)₂InCl.^{8,9} Herein we report our further explorations into this area with the synthesis and structural characterization of $[Ph_2InP(SiMe_3)_2]_2$ (I) and $[Ph_2InAs(SiMe_3)_2]_2$ (II).

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EXPERIMENTAL

Synthesis

All manipulations were performed using general Schlenk, dry-box and/or high vacuum techniques. Solvents (including those for NMR spectra) were appropriately dried, distilled under argon and degassed prior to use. Literature methods were used to prepare Ph_3In , ¹² P(SiMe_3)₃¹³ and As(SiMe_3)₃.¹⁴ Indium(III) chloride was purchased from Alfa Products, Ward Hill, MA, and purified by sublimation. Ph₂InCl was prepared via the equilibration of Ph₃In and indium(III) chloride in refluxing toluene in a 2:1 mole ratio and purified by recrystallization. ${}^{1}H$, ${}^{13}C{}^{1}H$ and ${}^{31}P{}^{1}H$ NMR spectra were obtained on a Varian XL-300 at 300.0. 75.4 and 121.4 MHz, respectively. ¹H and ¹³C spectra were referenced to TMS via the residual protons or carbons of $C_6 D_6$. ³¹P spectra were referenced to external 80% H_3PO_4 at δ 0.00 ppm. Melting points (uncorrected) were taken in sealed capillaries (Thomas-Hoover Uni-melt). Elemental analyses were performed by E+R Microanalytical Laboratory, Inc., Corona, NY. Single-crystal X-ray data were collected on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Cu- K_{α} radiation.

 $[Ph_2InP(SiMe_3)_2]_2 (I)$

Inside the dry-box a one-necked 250 cm³ roundbottomed flask equipped with a Teflon valve was charged with pentane (15 cm³) and Ph₂InCl (0.250 g, 0.82 mmol), furnishing a white suspension to which was added dropwise P(SiMe₃)₃ (0.206 g, 0.82 mmol) in pentane (20 cm³). The resulting milky mixture was placed in a sonicating water bath and allowed to react for 48 h after which it became pale yellow. The volatiles were removed in vacuo and the crude product was dissolved in warm pentane (15 cm³). Upon cooling to -15° C for several days, colourless air-sensitive crystals of I formed; 0.224 g, 61.2% yield; m.p. 205-240°C (dec). Found: C, 48.4; H, 6.3%. Calc. for $C_{36}H_{56}In_2P_2Si_4$: C, 48.6; H, 6.3%. ¹H NMR: δ 0.34 (t, 36 H, SiMe₃ [J(P-H) = 2.7 Hz], 7.17 (t, 4H, para-C₆H₅), 7.26 (t, 8H, meta- C_6H_5), 7.80 (d, 8H, ortho- C_6H_5). ¹³C{¹H} NMR: δ 4.79 (t, SiMe₃ [J(P-C) = 4.7 Hz]), [127.63-129.17 (m, C₆H₅) partially obscured by solvent], 139.23 (s, C_6H_5). ³¹P{¹H} NMR: δ -221.59 (s).

$[Ph_2InAs(SiMe_3)_2]_2$ (II)

In a manner similar to that employed for the preparation of I, Ph₂InCl (0.250 g, 0.82 mmol) in pentane (15 cm³) and As(SiMe₃)₃ (0.243 g, 0.82 mmol) in pentane (20 cm^3) were combined. The resulting milky mixture was stirred for 48 h at room temperature giving a yellow solution. The volatiles were removed in vacuo and the crude product was dissolved in warm pentane (15 cm³). Upon cooling to -15° C for several days, colourless air-sensitive crystals of II formed; 0.141 g, 35.0% yield; m.p. 185–190°C (dec. to orange liquid). Found : C, 44.5; H, 6.1%. Calc. for $C_{36}H_{56}As_2In_2Si_4$: C, 44.1; H, 5.8%. ¹H NMR : δ 0.35 (s, 36H, SiMe₃), 7.18 (t, 4 H, para-C₆ H_5), 7.29 (t, 8H, meta-C₆ H_5), 7.85 (d, 8H, ortho- C_6H_5). ¹³C{¹H} NMR : δ 5.00 (s, SiMe₃), $[127.80 (s, C_6H_5), 128.12 (s, C_6H_5) \text{ partially}$ obscured by solvent], 139.00 (s, C_6H_5).

X-ray structural solution and refinement

Colourless crystals of I and II were mounted inside flame-sealed 0.6 mm thin-walled glass capillaries under an inert argon atmosphere. Oscillation and Weissenberg photographs provided preliminary unit cell parameters and space groups $P2_1/c$ for I and $P2_1/n$ (alternative setting of $P2_1/c$) for II were established unequivocally from the Laue symmetry and systematic absences. Crystallographic data are summarized in Table 1. Intensity data (+h, +k, $\pm l$; 4832 reflections, $\theta_{max} = 75^{\circ}$ for I; 8025 reflections, $\theta_{max} = 65^{\circ}$ for II), recorded on an Enraf-Nonius CAD-4 diffractometer (Cu- K_{α} radiation, $\lambda = 1.5418$ Å, graphite monochromator), were cor-

rected for the usual Lorentz and polarization effects; empirical absorption corrections (derived from ψ -scans) were also applied. Equivalent reflections were averaged leaving 4598 (I) and 7734 (II) out of which 2765 and 3625, respectively, with $I > 3.0\sigma(I)$, were retained for the analyses. With two formula units per unit cell, dimer I must lie on a crystallographic centre of symmetry. For II, on the other hand, the unit cell contains four dimers that may either occupy general positions or two crystallographically independent dimers must lie on centres of symmetry. Initial indium atom coordinates for I were derived from a Patterson map. Approximate indium and arsenic coordinates for II, obtained from an E-map (MULTAN11/82), indicated that the molecules lay in general positions with no crystallographically-imposed symmetry. The remaining non-hydrogen atoms of I and II were located in a series of weighted F_{0} and difference Fourier syntheses phased successively by an increasing number of atoms. Several rounds of fullmatrix least-squares adjustment of atomic positional and thermal parameters (at first isotropic, then anisotropic) followed. In the later iterations, hydrogen atoms were incorporated at their calculated positions (C—H = 1.05 Å) and an extinction correction was included as a variable. The parameter refinements converged at R = 0.038 $(R_{\rm w} = 0.050)$ for I and R = 0.040 $(R_{\rm w} = 0.048)$ for II. Final difference-Fourier syntheses revealed no unusual features [max. $\Delta \rho$ (e Å⁻³): 0.54 (I) and 0.56 (II), both in the vicinity of the indium atom]. The solid-state structures of I and II, with their atom numbering schemes, are illustrated in Figs 1 and 2, respectively. Selected bond lengths and bond angles are listed in Tables 2 and 3. Crystallographic calculations were performed using the Enraf-Nonius structure determination package¹⁵ on PDP11/44 and MicroVAX computers. For all structure-factor calculations, neutral atom scattering factors and their anomalous dispersion corrections were taken from ref. 16. In the least-squares iterations, $\Sigma w \Delta^2$ $[w = 1/\sigma^2(|F_0|), \Delta = (|F_0| - |F_c|)]$ was minimized. Supplementary material: atomic coordinates, thermal parameters, bond lengths and angles and crystal data have been deposited with the Cambridge Crystallographic Data Centre.

RESULTS AND DISCUSSION

We have previously demonstrated the utility of dehalosilylation reactions between an organogroup III halide and a silylarsine¹ or silylphosphine^{8,10} to form III–V bonds. Our initial efforts in pursuit of compounds possessing In—E bonds (E = As or P) involved only the reaction of organoindium species

	Ι	П	
Molecular formula	C ₃₆ H ₅₆ In ₂ P ₂ Si ₄	C ₃₆ H ₅₆ As ₂ In ₂ Si ₄	
Formula weight	892.78	980.68	
Crystal system	Monoclinic	Monoclinic	
Space group	$P2_{1}/c (C_{2h}^{5})$	$P2_{1}/n (C_{2h}^{5})$	
<i>a</i> (Å)	10.691(1)	16.248(1)	
<i>b</i> (Å)	19.821(2)	20.285(1)	
<i>c</i> (Å)	11.512(1)	13.887(1)	
β (°)	113.34(1)	90.12(1)	
No. of orient. reflections; θ , range (°)	25; 36–40	25; 36-40	
$V(Å^3)$	2239.8(8)	4577.0(8)	
Z	2	4	
$D_{\rm calc}$ (g cm ⁻³)	1.324	1.423	
Temperature (K)	296	296	
Crystal dimensions (mm)	$0.18 \times 0.18 \times 0.40$	$0.21 \times 0.23 \times 0.28$	
$T_{\max}: T_{\min}$	1.00:0.68	1.00:0.76	
Radiation (wavelength)	$Cu-K_{\alpha}$ (1.5418 Å)	Cu- <i>K</i> _a (1.5418 Å)	
μ (cm ⁻¹)	103.1	110.4	
Scan type	ω –2 θ	ω –2 θ	
Scan width (°)	$0.80 \pm 0.14 \tan \theta$	$0.70 + 0.14 \tan \theta$	
θ_{\max} (°)	75	65	
Intensity control reflections	131, 232, 33 2 , 421	132, 212, 331, 412	
Variation; repeat time (h)	< 2%; 2	< 1%; 2	
No. of reflections recorded	$4832(+h, +k, \pm l)$	$8025(+h, +k, \pm l)$	
No. of non-equivalent reflections	4598	7734	
R(merge)	0.029 on I	0.034 on <i>I</i>	
No. of reflections retained, $I > 3.0\sigma(I)$	2765	3625	
No. of parameters refined	200	398	
Extinction correction	$6.8(4) \times 10^{-7}$	$1.7(1) \times 10^{-7}$	
$R(F), R_w(F)^a$	0.038, 0.050	0.040, 0.048	
Goodness-of-fit ^b	1.25	1.17	
Max. shift; e.s.d. in final least-squares cycle	0.02	0.01	
Final $\Delta \rho$ (e Å ⁻³) max.; min.	0.54; -0.55	0.56; -0.56	

Table 1. Crystallographic data and summary of data collection and refinement for $[Ph_2InP(SiMe_3)_2]_2$ (I) and $[Ph_2InAs(SiMe_3)_2]_2$ (II)

 ${}^{a}R = \Sigma ||F_{o}| - |F_{c}|| / \Sigma |F_{o}|; R_{w} = [\Sigma w(|F_{o}| - |F_{c}|)^{2} / \Sigma w|F_{o}|^{2}]^{1/2}; \Sigma w\Delta^{2}[w = 1/\sigma^{2}(|F_{o}|), \Delta = (|F_{o}| - |F_{c}|)] \text{ was minimized.}$ ${}^{b}\text{ Goodness-of-fit} = [\Sigma w\Delta^{2} / (N_{obs} - N_{para})]^{1/2}.$

bearing the Me₃SiCH₂ group,^{8,9} an organic substituent that was chosen because of its steric bulk and relative stability. In an effort to ascertain the viability of our methodology for other systems, we have begun to explore the use of different organic substituents at the organoindium centre. We now report the synthesis, characterization and X-ray structures of two new compounds containing the In—E bond (E = P or As), [Ph₂InP(SiMe₃)₂]₂ (I) and [Ph₂InAs(SiMe₃)₂]₂ (II).

The 1:1 mole ratio reaction of Ph_2InCl with $E(SiMe_3)_3$ (E = P or As) at room temperature in pentane affords I and II, respectively, via a dehalosilylation reaction [eq. (1)].

$$2Ph_2InCl + 2E(SiMe_3)_3 \longrightarrow$$

$$[Ph_2InE(SiMe_3)_2]_2 + 2Me_3SiCl \quad (1)$$

Compounds I and II are the second examples of dimeric In-P or In-As species to be prepared in our laboratory through the elimination of Me₃SiCl, $[(Me_3SiCH_2)_2InP(SiMe_3)_2]_2$ (III)⁸ and with [(Me₃SiCH₂)₂InAs(SiMe₃)₂]₂ (IV)⁹ constituting the first. Subsequent to III and IV being reported, Theopold and co-workers demonstrated that $[C_5Me_5(Cl)InP(SiMe_3)_2]_2$ (V)¹⁷ results from a similar reaction. As with III, IV and V the core fragment of I consists of a planar four-membered (InP)₂ ring, whereas in II the $(InAs)_2$ ring is slightly puckered (vide infra). The ¹H, ¹³C and for I, ³¹P room-temperature NMR spectra for each compound are consistent with their solid-state structures. The dimeric nature of I is clearly demonstrated by the virtual coupling of the ring phosphorus atoms with the hydrogen and carbon atoms of the trimethylsilyl



Fig. 1. ORTEP diagram (30% probability ellipsoids) of the solid-state structure of [Ph₂InP(SiMe₃)₂]₂
 (I); primed atoms are related to the unprimed atoms by a crystallographic centre of symmetry. Hydrogen atoms have been omitted for clarity.



Fig. 2. ORTEP diagram (30% probability ellipsoids) of the solid-state structure of $[Ph_2InAs(SiMe_3)_2]_2$ (II). Hydrogen atoms have been omitted for clarity.

(a) Bond lengths P—In P'—In	2.612(1) 2.612(1)	InC(31) InC(41)	2.178(6) 2.185(5)
P—Si(1) P—Si(2)	2.262(2) 2.261(3)		
(b) Bond angles			
In - P - In' In - P - Si(1) In - P - Si(2) In' - P - Si(2) In' - P - Si(2) Si(1) - P - Si(2) Si(1) - P - Si(2) P - In - P' P - In - C(31) P - In - C(31) P - In - C(31)	92.97(4) 107.30(7) 120.62(8) 112.32(8) 114.64(7) 108.26(8) 87.03(4) 118.1(2) 114.3(2) 112.7(1)	$\begin{array}{l} C(31) & - In - C(41) \\ P - Si(1) - C(12) \\ P - Si(1) - C(12) \\ P - Si(1) - C(13) \\ P - Si(2) - C(21) \\ P - Si(2) - C(22) \\ P - Si(2) - C(23) \\ In - C(31) - C(32) \\ In - C(31) - C(36) \\ In - C(41) - C(42) \\ \end{array}$	105.7(2) 107.9(2) 111.0(3) 108.8(3) 107.1(3) 108.5(3) 110.2(4) 118.2(5) 125.3(5) 127.9(5)
P'InC(41)	118.8(2)	In— $C(41)$ — $C(46)$	114.5(5)

Table 2. Selected bond lengths (Å) and angles (°), with e.s.d.s in parentheses, for $[Ph_2InP(SiMe_3)_2]_2$ (I)

Table 3. Selected bond lengths (Å) and angles (°), with e.s.d.s in parentheses, for $[Ph_2InAs(SiMe_3)_2]_2$ (II)

(a) Bond lengths			
As(1)-In(1) 2.68	9(1)	As(2)—In(1)	2.689(1)
As(1)—In(2) 2.68	3(1)	As(2)-In(2)	2.682(1)
As(1)—Si(11) 2.34	4(4)	As(2)-Si(21)	2.370(4)
As(1)-Si(12) 2.35	2(2)	As(2)-Si(22)	2.353(2)
In(1)—C(1) 2.19	(1)	In(2)—C(13)	2.17(1)
In(1)—C(7) 2.17	(1)	In(2)—C(19)	2.17(1)
(b) Bond angles			
In(1)As(1)In(2)	93.47(4)	In(1)As(2)In	.(2) 93.48(4)
In(1)—As(1)—Si(11)	119.8(1)	In(1)—As(2)—Si	(21) 121.6(1)
In(1) - As(1) - Si(12)	110.3(1)	In(1)As(2)Si	(22) 107.8(1)
In(2)—As(1)—Si(11)	118.2(1)	In(2)As(2)Si	(21) 116.6(1)
In(2) - As(1) - Si(12)	107.5(1)	In(2)As(2)Si	(22) 111.3(1)
Si(11)— $As(1)$ — $Si(12)$	106.7(1)	Si(21)—As(2)—S	i(22) 105.6(1)
As(1)— $In(1)$ — $As(2)$	86.22(4)	As(1)— $In(2)$ — $As(1)$	s(2) 86.49(3)
As(1) - In(1) - C(1)	112.5(2)	As(1)-In(2)-C	(13) 115.8(3)
As(1) - In(1) - C(7)	117.4(3)	As(1)-In(2)-C	(19) 116.4(2)
As(2) - In(1) - C(1)	115.2(3)	As(2)-In(2)-C	(13) 114.5(2)
As(2) - In(1) - C(7)	115.4(3)	As(2)In(2)C	(19) 114.3(3)
C(1)— $In(1)$ — $C(7)$	108.9(3)	C(13)—In(2)—C	(19) 108.2(3)
As(1)Si(11)C(111)	109.8(4)	As(2)-Si(21)-C	2(211) 111.3(5)
As(1)-Si(11)-C(112)	108.8(5)	As(2)-Si(21)-C	2(212) 106.6(5)
As(1)-Si(11)-C(113)	106.5(5)	As(2)—Si(21)—C	2(213) 107.7(5)
As(1) - Si(12) - C(121)	106.3(4)	As(2) - Si(22) - C	2(221) 108.7(4)
As(1) - Si(12) - C(122)	111.0(4)	As(2)-Si(22)-C	2(222) 110.6(4)
As(1) - Si(12) - C(123)	109.6(4)	As(2) - Si(22) - C	2(223) 107.7(4)
In(1) - C(1) - C(2)	123(1)	In(2) - C(13) - C	(14) 126(1)
In(1) - C(1) - C(6)	119(1)	In(2)-C(13)-C	(18) 119(1)
In(1) - C(7) - C(8)	117(1)	In(2)—C(19)—C	(20) 119(1)
$\ln(1) - C(7) - C(12)$	125(1)	In(2)C(19)C	(24) 125(1)

substituents at the phosphorus centre. This coupling gives rise to a triplet for these groups in the ¹H and ¹³C NMR spectra. At room temperature no evidence of solution fluxionality has been observed for either I or II.

Compound I crystallizes in the monoclinic space group $P2_1/c$ with the two dimers in the unit cell lying on crystallographic centres of symmetry and accordingly the $(InP)_2$ ring is required to be strictly planar. The In-P bond lengths are both 2.612(1) Å, a distance which is distinctly shorter than the mean of 2.655 Å in **III**, reflecting the less sterically demanding nature of the phenyl substituents in I versus the much bulkier Me_3SiCH_2 moieties in III. The mean P-Si bond length of 2.262 Å in I is similar to the mean of 2.255 Å in III. Bond angles in the $(InP)_2$ core of I $[In-P-In = 92.97(4)^\circ >$ $P-In-P = 87.03(4)^{\circ}$ are similar to and differ in the same sense as corresponding angles in III $[93.6(1)^{\circ}, 86.4^{\circ} \text{ (mean)}]$ and V $[92.2(1)^{\circ}, 87.8(1)^{\circ}]$. The C—In—C angle at $105.7(2)^{\circ}$ in I is very much smaller that the mean of 123.2° in III where the considerable enlargement from an approximately tetrahedral value may be ascribed at least in part to the greater steric crowding by the geminal Me₃SiCH₂ substituents. It is relevant to note that the larger the exocyclic bond angle subtended at an opposite pair of ring atoms in four-membered rings, the greater the steric compression exerted on substituents at the other ring centres. It is, therefore, not surprising to find that the Si-P-Si angle of $108.3(1)^{\circ}$ in I is slightly larger than that of $105.7(2)^{\circ}$ in III. In contrast to the situations in [In(2,4,6trimethylphenyl)₂I]₂,¹⁸ (Ph₂InOSiMe₃)₂¹⁹ and $[Ph_2GaAs(CH_2SiMe_3)_2]$,⁵ where one of the phenyl ring planes approximately eclipses one of the fourmembered ring bonds while the other is in a bisecting orientation, or in Ph₂GaAs(SiMe₃)₂Ga(Ph)₂Cl⁶ where all are in approximately eclipsing orientations, both of the phenyl rings in I are rotated moderately away from either the eclipsing or the bisecting orientation [torsion angles: P-In- $C(31)-C(36) = 36.4(6)^{\circ}, P'-In-C(31)-C(32) =$ $-49.5(5)^{\circ}$; P'-In-C(41)-C(42) = $-22.5(6)^{\circ}$, $P-In-C(41)-C(42) = 78.1(6)^{\circ}$ minimize to intramolecular non-bonded interactions with the proximal SiMe₃ substituents. The indium atom lies close to the C(41)—C(46) least-squares plane $(\Delta = 0.013 \text{ Å})$, but is displaced significantly $(\Delta = 0.108 \text{ Å})$ from that through the other phenyl ring atoms [C(31)—C(36)]. Substituent crowding is also indicated in the highly significant differences between the exocyclic bond angles at the ipso carbon [In-C(31)-C(36)]atoms = 125.3(5)° > In--C(31)-C(32) = $118.2(5)^{\circ}$; In--C(41)-C(42) $= 127.9(5)^{\circ} > \text{In}-C(41) - C(46) = 114.5(5)^{\circ}$].

Crystals of dimer Π also belong to the monoclinic system but they are not isomorphous with those of I. Compound II crystallizes in the space group $P2_1/n$ with four molecules occupying the general positions. In contrast to the planar (InAs)₂ ring in I, in II the ring is very slightly puckered [As(1)-In (1)—As(2)/As(1)—In(2)—As(2) dihedral angle = 6.0°]. The mean In-As bond length at 2.686 Å in **II** is significantly shorter than the value of 2.728 Å in the planar ring of IV; the difference between these distances ($\Delta = 0.042$ Å), which is essentially the same as that between the corresponding bonds ($\Delta = 0.043$ Å) in the phosphorus analogues I and III, again may be ascribed principally to the different steric demands of the geminal substituents, Ph « Me₃SiCH₂. Endocyclic angles $[In-As-In = 93.48^{\circ}(mean)]$ bond > As—In—As = 86.36° (mean)] in II lie close to the corresponding values for IV [94.57(5)°, 85.43°(mean)]. The mean As—Si bond length [2.355 Å] and the mean Si—As—Si bond angle [106.2°] in II do not differ significantly from those in IV $[As-Si = 2.348 \text{ Å}(mean), Si-As-Si = 105.4(2)^{\circ}].$ In addition, the mean In-C bond length at 2.18 Å in II is the same as that in I (2.182 Å). The mean of the C-In-C angles at 108.5° in II is slightly larger than that of $105.7(2)^{\circ}$ in I, whereas it is much smaller than the mean of 125.4° in IV which has the bulky Me₃SiCH₂ substituents at indium. With the reduced symmetry of II versus I, the dispositions of the phenyl rings with respect to the As—In bonds show more variation [torsion angles: As(2)- $In(1) - C(1) - C(2) = -27(1)^{\circ}, As(1) - In(1) -$ $C(1)-C(6) = 58(1)^{\circ}; As(1)-In(1)-C(7)-C(12) =$ $41(1)^{\circ}$, As(2)—In(1)—C(7)—C(2) = -59(1)^{\circ}; As(1)-In(2)-C(13)-C(14) = 15(1)°; As(2)- $In(2) - C(13) - C(18) = -72(1)^{\circ}; As(2) - In(2) - C(18) = -72(1)^{\circ}; As(2) - C(18) - C(18$ C(19)-C(24) = -25(1), As(1)-In(2)-C(19)- $C(24) = 73(1)^{\circ}$]. The indium atom lies out of each of the phenyl ring planes [$\Delta = 0.070, 0.108, 0.151$] and 0.156 Å, respectively, from the C(1)—C(6), C(7)-C(12), C(13)-C(18) and C(19)-C(24) leastsquares planes]. In common with I, exocyclic bond angle deformation at the ipso carbon centres is also present in II $[In(1)-C(1)-C(2) = 123(1)^{\circ} >$ In(1)—C(1)—C(6) = $119(1)^{\circ}$; In(1)—C(7)—C(12) $= 125(1)^{\circ} > In(1) - C(7) - C(8) = 117(1)^{\circ}; In(2) = 117(1)^{\circ}; In(2$ $C(13)-C(14) = 126(1)^{\circ} > In(2)-C(13)-C(18) =$ $119(1)^{\circ}$; In(2)--C(19)--C(24) = $125(1)^{\circ} > In(2)$ --C(19)— $C(20) = 119(1)^{\circ}$] to aid in the minimization of intramolecular non-bonded interactions.

Acknowledgement—We are grateful to the Office of Naval Research for their financial support.

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