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Combining $P(SiMe_3)_3$ or $As(SiMe_3)_3$ with $(Me_3CCH_2)_3In$ in a 1:1 mole ratio yields simple adducts $(Me_3CCH_2)_3In{\cdot}P(SiMe_3)_3$ (I) and $(Me_3CCH_2)_3In{\cdot}As(SiMe_3)_3$ (II), respectively. Addition of $(Me_3CCH_2)_2InCl$ to a diethyl ether solution of $LiP(SiMe_3)_2$ results in the formation of $Me(Me_3CCH_2)_2In{\cdot}P(SiMe_3)_3$ (III). Isomorphous I and II crystallize in the trigonal system, space group $P3(C_3^1)$, with $a = b$ = 16.278(1), c = 11.496(1) Å, V = 2638(1) Å^3, Z = 3, $D_{calc.}$ = 1.093 g cm^{-3} for I, and $a = b$ = 16.304(1), c = 11.579(1) Å, V = 2665.6(6) Å^3, Z = 3, $D_{calc.}$ = 1.164 g cm^{-3} for II . Full-matrix least-squares refinement based on 2859 (I) and 2920 (II) reflections with $I > 3\sigma(I)$, respectively, converged at R = 0.049 (R_w = 0.065) and R = 0.042 (R_w = 0.055), respectively. Monoclinic crystals of III belong to space group $P2_1/c(C_{2h}^5)$, with a = 16.047(2), b = 12.641(2), c = 31.576(4) Å, β= 102.92(1)°, V = 6243(3) Å^3, Z = 8, $D_{calc.}$ = 1.112 g cm^{-3} for . Full-matrix least-squares refinement converged at R = 0.069 (R_w = 0.087) over 4611 reflections with $I > 3\sigma(I)$.

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Abstract — Combining $P(SiMe_3)_3$ or $As(SiMe_3)_3$ with $(Me_3CCH_2)_3In$ in a 1:1 mole ratio yields simple adducts $(Me_3CCH_2)_3In{\cdot}P(SiMe_3)_3$ (I) and $(Me_3CCH_2)_3In{\cdot}As(SiMe_3)_3$ (II), respectively. Addition of $(Me_3CCH_2)_2InCl$ to a diethyl ether solution of $LiP(SiMe_3)_2$ produces $Me(Me_3CCH_2)_2In{\cdot}P(SiMe_3)_3$ (III). Isomorphous I and II crystallize in the trigonal system, space group $P3(C_3^1)$, with $a = b = 16.278(1)$, $c = 11.496(1)$ Å, $V = 2638(1)$ Å^3, $Z = 3$, $D_{calc.} = 1.093$ g cm^{-3} for I, and $a = b = 16.304(1)$, $c = 11.579(1)$ Å, $V = 2665.6(6)$ Å^3, $Z = 3$, $D_{calc.} = 1.164$ g cm^{-3} for II. Full-matrix least-squares refinement based on 2859 (I) and 2920 (II) reflections with $I > 3\sigma(I)$ converged at $R = 0.049$ ($R_w = 0.065$) and $R = 0.042$ ($R_w = 0.055$), respectively. Monoclinic crystals of III belong to space group $P2_1/c(C_{2h}^5)$, with $a = 16.047(2)$, $b = 12.641(2)$, $c = 31.576(4)$ Å, $\beta = 102.92(1)°$, $V = 6243(3)$ Å^3, $Z = 8$, $D_{calc.} = 1.112$ gcm^{-3}. Full-matrix least-squares refinement converged at $R = 0.069$ ($R_w = 0.087$) over 4611 reflections with $I > 3\sigma(I)$.

For a considerable time, research in our laboratory has focused on the use of silylpnictides with organo group III reagents to facilitate the formation of III-V bonds.

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These transformations are typically accomplished *via* dehalosilylation reactions or lithium chloride elimination.[1] Through these investigations, the majority of compounds produced contain either an $\overline{\text{MEME}}$ (M = Ga, E = As;[2-5] M = In, E = P[6] or As[7]) or $\overline{\text{MEMC}}$ (M = Ga, E = As[2,4,5] or P;[8] M = In, E = P[6] or As[7]) core. Additionally, adducts of the type $R_3M{\cdot}E(SiMe_3)_3$ (R = Me_3SiCH_2, M = In, E = As;[9] R = Ph[9] or C_6F_5,[10] M = Ga, E = As) and $R_2(Cl)M{\cdot}E(SiMe_3)_3$ (R = Me_3CCH_2, M = Ga, E = As;[5] R = Ph, M = Ga, E = P;[8] R = Me_2CHCH_2, M = Al, E = As,[11] P[12]) have been isolated. We report herein the synthesis and characterization, including single crystal X-ray analysis, of three new main group adducts, $(Me_3CCH_2)_3In{\cdot}P(SiMe_3)_3$ (**I**), $(Me_3CCH_2)_3In{\cdot}As(SiMe_3)_3$ (**II**), and $Me(Me_3CCH_2)_2In{\cdot}P(SiMe_3)_3$ (**III**).

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 dinitrogen, and degassed prior to use. Literature methods were used to prepare $(Me_3CCH_2)_3In$,[13] $P(SiMe_3)_3$,[14] and $As(SiMe_3)_3$.[15] $LiP(SiMe_3)_2$[16] was prepared *via* the 1:1 mole reaction of MeLi with $P(SiMe_3)_3$. In(III) chloride was purchased from Alfa Products, Ward Hill, MA, and purified by sublimation. $(Me_3CCH_2)_2InCl$ was prepared *via* the equilibration of $(Me_3CCH_2)_3In$ and In(III) chloride in refluxing toluene in a 2:1 mole ratio and purified by recrystallization. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were obtained on a Varian XL-300 instrument at 300.0, 75.4, and 121.4 MHz, respectively; ^1H and ^{13}C spectra were referenced to TMS *via* the residual protons or carbons of C_6D_6. ^{31}P 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, N Y. Single crystal X-ray diffraction data were recorded on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Cu-Kα radiation.

(1) $(Me_3CCH_2)_3In{\cdot}P(SiMe_3)_3$ (I)

Inside the dry-box, a one necked 250 cm^3 round-bottom flask equipped with a Teflon valve was charged with toluene (15 cm^3) and $(Me_3CCH_2)_3In$ (0.743 g, 2.26 mmol) furnishing a clear solution to which was added dropwise $P(SiMe_3)_3$ (0.567 g, 2.26 mmol) in toluene (20 cm^3). The resulting clear solution was stirred for 24 h at room temperature. Following removal of the volatiles *in vacuo*, the crude product was dissolved in warm pentane (5 cm^3). Upon cooling to -15 °C for several days, colourless, air-sensitive crystals of I formed; 1.284 g, 98% yield, mp. 118 - 119 °C (dec). Found: C, 49.70; H, 10.19. Calc. for $C_{24}H_{60}InPSi_3$: C, 49.80; H, 10.45. ^1H NMR: δ 0.30 [d, 27 H, Si*Me₃* ($J_{P\text{-}H}$ = 4.6 Hz)], 1.17 (s, 6 H, C*H*₂), 1.27 (s, 27H, C*Me₃*). $^{13}C\{^1H\}$ NMR: δ 4.00 [d, Si*Me₃* ($J_{P\text{-}C}$ = 9.6 Hz)], 33.41 (s, *C*H₂), 35.30 (s, *Me₃*), 42.42 (s, *C*). $^{31}P\{^1H\}$ NMR: δ -246.60 (s).

(2) $(Me_3CCH_2)_3In{\cdot}As(SiMe_3)_3$ (II)

Inside the dry box, a one necked 100 cm^3 round-bottom flask was charged with pentane (2 cm^3) and $As(SiMe_3)_3$ (0.250 g, 0.84 mmol) producing a clear solution to which was added dropwise $(Me_3CCH_2)_3In$ (0.279 g, 0.84 mmol) in toluene (10 cm^3). Upon addition of the organoindium species, immediate formation of colourless crystals of II occurred. The solvent was allowed to evaporate from the resulting mixture, yielding a second crop of II; 0.505 g total, 96% yield, mp. 115 - 116 °C. Found: C, 46.05; H, 9.50. Calc. for $C_{24}H_{60}AsInSi_3$: C, 46.29; H, 9.71. ^1H NMR: δ 0.33 (s, 27 H, Si*Me₃*), 1.18 (s, 6 H, C*H*₂), 1.26 (s, 27H, C*H*₃). $^{13}C\{^1H\}$ NMR: δ 4.04 (s, Si*Me₃*), 33.35 (s, *C*H₂), 35.29 (s, *Me₃*), 41.84 (s, *C*).

(2) $Me(Me_3CCH_2)_3In{\cdot}P(SiMe_3)_3$ (III)

Inside the dry-box, a one necked 250 cm^3 round-bottom flask equipped with a Teflon valve was charged with diethyl ether (15 cm^3) and $LiP(SiMe_3)_2$ (0.362 1.99 mmol). $(Me_3CCH_2)_2InCl$ (0.614g, 1.99 mmol) in toluene (20 cm^3) was added dropwise. The reulting clear solution was stirred for 24 h at room temperature folowing which the volatiles were removed *in vacuo* and the crude product was dissolved in warm pentane (5 cm^3). Upon cooling to -15 °C for several days, colourless, air-sensitive crystals of III formed; 0.431 g, 44% yield (based on mass balance, total of 0.976 g), mp. 82 - 83 °C (dec). Found: C, 45.80; H, 10.16. Calc. for $C_{20}H_{52}InPSi_3$: C, 45.96; H, 10.03. ^1H NMR: δ 0.26 [d, 27 H, Si*Me₃* ($J_{P\text{-}H}$ = 3.25 Hz)], 1.08 (s, 3 H, $InCH_3$), 1.21 (s, 4 H, CH_2), 1.32 (s, 18H, CMe_3). ^{13}C {^1H} NMR: δ 3.55 [d, $SiMe_3$ ($J_{P\text{-}C}$ = 9.8 Hz)], 33.51 (s, CH_2), 35.21 (s, Me_3), 37.80 (s, *C*). ^{31}P {^1H} NMR: δ -245.16 (s).

X-ray structural solution and refinement

Colourless crystals of I, II, and III were mounted inside flame-sealed 0.6 mm thin-walled glass capillaries under an inert argon atmosphere. Laue symmetry and the lack of any systematic absences indicated that I and II belonged to the trigonal space group $P3$ or $P\bar{3}$; only the former was consistent with an odd number of molecules in the unit cell. For III, the monoclinic space group $P2_1/c$ was established unequivocally from the Laue symmetry and systematic absences: $0k0$ when $k \neq 2n$, $h0l$ when $l \neq 2n$. Crystallographic data are summarized in Table 1. Intensity data ($+h,\pm k,+l$; 5913 reflections, θ_{max} = 75° for I; $\pm h,+k,+l$; 5949 reflections, θ_{max} = 75° for II; $+h,+k,\pm l$; 11493 reflections, θ_{max} = 67° for III), recorded on an Enraf-Nonius CAD-4 diffractometer (Cu-Kα radiation, λ = 1.5418 Å, graphite monochromator), were corrected for the usual Lorentz and polarization effects; ψ-scan derived empirical absorption corrections were also applied. Equivalent reflections were averaged, leaving 3641(I), 3653(II), and 11066(III) out of which 2859, 2920, and 4611, respectively, with $I > 3.0\sigma(I)$ were retained for the analyses. The asymmetric unit in crystals of I and II consists of three independent molecules occupying Wyckoff positions *a*, *b*, and *c*, with their indium and phosphorus(I)/arsenic(II) atoms lying on C_3 axes while two independent molecules situated in general positions define the asymmetric unit in crystals of III. The crystal structures of I and III were solved by direct methods (MULTAN11/82). Initial indium, phosphorus, and silicon atom coordinates were derived from an *E*-map. For II, coordinates for the indium, arsenic, and silicon atoms of the isomorphous phosphorus analogue, I, were used as initial input to the structure-factor calculations. Carbon atoms in I-III were located in weighted F_o and difference Fourier syntheses phased by the heavier atoms. Atomic positional and thermal parameters (at first isotropic, then anisotropic) were adjusted by means of several rounds of full-matrix least-squares calculations. 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 correct enantiomer for each of the crystals of I and II used for data collection was established by use of anomalous scattering effects. Parameter refinements converged at $R = 0.0485$ ($R_w = 0.0671$) for I and $R = 0.0399$ ($R_w = 0.0521$) for II when the imaginary contributions to the anomalous scattering corrections were omitted. Introduction of the imaginary contributions into the structure-factor calculations for I then gave $R = 0.0558$ ($R_w = 0.0787$) for the (hkl) reflections as recorded versus $R' =$ 0.0566 ($R_w' = 0.0821$) for the Friedel pairs ($\bar{h}\bar{k}\bar{l}$); corresponding values for II were $R =$ 0.0527 ($R_w = 0.0761$) and $R' = 0.0527$ ($R'_w = 0.0772$). The R_w'/R_w ratios (1.0432 for I, 1.0145 for II) indicated that the parameters employed in each case corresponded to those for the correct choice of enantiomer.[17] Verification of these assignments was derived by remeasuring the intensity differences for several Friedel pairs of enantiomer-sensitive reflections. Continuation of the least-squares iterations led to convergance at $R = 0.049$ ($R_w = 0.067$) for I and $R = 0.042$ ($R_w = 0.055$) for II. Least-squares parameter refinement for centrosymmetric crystal III converged at $R = 0.069$ ($R_w = 0.087$). Final difference Fourier syntheses revealed no unusual features [max. $\Delta\rho$(e/Å^3): 1.00 (I), 1.25

(**II**), and 1.4 (**III**), all in the vicinity of the In atoms]. Crystallographic calculations were performed using the Enraf-Nonius Structure Determination Package[18] on PDP11/44 and MicroVAX computers. For all structure-factor calculations, neutral atom scattering factors and their anomalous dispersion corrections were taken from ref. 19. In the least-squares iterations, $\Sigma w\Delta^2$ [$w = 1/\sigma^2(|F_o|)$, $\Delta = (|F_o| - |F_c|)$] 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

The 1:1 mole ratio reaction of $(Me_3CCH_2)_3In$ with $E(SiMe_3)_3$ (E = P or As) at room temperature does not undergo an intermolecular elimination but affords instead adducts **I** and **II**, respectively. Addition of a diethyl ether solution of $(Me_3CCH_2)_2InCl$ to $LiP(SiMe_3)_2$ in a 1:1 mole ratio yields **III** {in the reverse addition, $[Me(Me_3CCH_2)InP(SiMe_3)_2]_2$ is produced}.[20] Compound **III** presumably results from a methyl group elimination akin to that observed in analogous indium-phosphorus systems.[21] Compounds **I**, **II**, and **III** are colourless crystalline materials which, in contrast to their starting materials, do not decompose to any appreciable extent under an inert atmosphere at room temperature over extended periods of time. Although there are three crystallographically distinct and conformationally different molecules of **I** and **II** in the solid-state (*vide infra*), the room temperature ^1H, ^{13}C, and ^{31}P NMR spectra of both adducts are clean, simple, and indicative of only one solution conformation; no fluxional processes or dissociations are observed.

A literature review reveals no previous structural reports of simple organoindium-phosphorus adducts. The asymmetric unit in crystals of **I** consists of three independent molecules each of which has its In-P bond lying on a crystallographic C_3 symmetry axis. The In-P bond vector in molecules 1 and 2 points along the negative direction of the *c*-axis whereas that in molecule 3 is directed in the opposite sense. This mode of packing is similar to those found in a number of triphenylphosphine complexes which also crystallize in the space group *P*3: Pt(CO)[P(C_6H_5)$_3$]$_3$,[22] Ir(NO)[P(C6H5)3]3,[23] Cu(BF_4)-[P(C_6H_5)$_3$]$_3$,[24] Rh(NO)[P(C_6H_5)$_3$]$_3$,[25] and Cu(Cl)[P(C_6H_5)$_3$]$_3$.[26] Solid-state conformations of each of the crystallographically independent molecules of I, with their atom numbering schemes, are illustrated in Fig. 1. Selected bond lengths, bond angles and torsion angles are listed in Table 2; Newman projections down the In-P bonds are provided in Fig. 2. The conformations about the In-P bonds, classified using the smaller of the pair of C-In-P-Si torsion angles in each case to define the chirality, correspond overall to an (*SRS*) configuration. Further differences occur in the conformations adopted about the In-C bonds as indicated by the C1'-In-C1-C2 torsion angles of 43(1), 46(1), and -39.2(9)° in molecules 1 - 3, respectively. In-P bond lengths associated with each of these conformations [2.890(5), 2.806(4), 2.944(4) Å] differ significantly, attesting to their sensitivity to variations in intramolecular non-bonded substituent interactions. Enlargement of the mean C-In-C bond angle to 119.1° and concomitant decrease in the mean C-In-P angle to 95.5° from an ideal tetrahedral geometry may be ascribed to the considerable steric requirements of the neopentyl substituents. Mean bond angles at the P atom [In-P-Si = 113.0° > Si-P-Si = 105.7°] reflect the relayed effect of the steric compressions resulting from the angular deformations around In.

There has been only one previous structural report of an indium-arsenic adduct, *viz.* (Me_3SiCH_2)$_3$In•As($SiMe_3$)$_3$ (IV),[9] which crystallizes in the trigonal space group *R*3 with one molecule in the asymmeteric unit lying on a crystallographic C_3 symmetry axis. In contrast, the asymmetric unit in crystals of adduct II, as in the case of isomorphous I, consists of three non-equivalent molecules which also have significantly different conformations enantiomeric to those found in the crystal of I (*vide supra*); accordingly, the overall configuration in the crystal used is (*RSR*). The In-As bond lengths [3.018(1), 2.948(2), 2.888(2) Å] in II, like their counterparts in I, are unequal and all exceed that of 2.778(4) Å in IV. Moreover, the mean As-Si and In-C bond lengths at 2.365 and 2.22 Å, respectively, are longer than the As-Si [2.298(5) Å] and In-C [2.18(1) Å] bonded distances in **IV**. Whereas bond angles at the As atoms in **II** [mean values: In-As-Si = 113.8°, Si-As-Si = 104.8°] lie close to those in **IV** [In-As-Si = 112.9(1)°, Si-As-Si = 105.8(2)°] the angles around the In atoms [As-In-C = 94.3°, C-In-C = 119.3° for the mean values in **II**; As-In-C = 101.2(3)°, C-In-C = 116.3(6)° in **IV**] differ significantly. These observed bond length and bond angle variations can be directly related to the fact that C-C distances in Me_3CCH_2 groups are substantially shorter than Si-C bonds in Me_3SiCH_2 moieties thereby increasing the severity of the steric crowding in **II** versus **IV**.

The asymmetric unit in crystals of **III** consists of two independent molecules with similar conformations and, accordingly, the solid-state structure of only one, with the atom numbering scheme, is illustrated in Fig. 3. Selected bond lengths and angles are listed in Table 3. The mean In-P bond length at 2.799 Å is close to the In-P distance of 2.806(4) Å in that molecule of **I** (molecule 2) which has a similar conformation about the In-P bond. Replacement of one of the neopentyl (Np) groups in **I** by a methyl group in **III** reduces substituent overcrowding, and this is reflected in moderation of the departure of the bond angles at In and P from tetrahedral. Thus, although the mean C(Np)-In-C(Me) bond angle at 119.2° in **III** is essentially the same as the mean C(Np)-In-C(Np) angle of 119.1° in **I**, the mean C(Np)-In-C(Np) angle at 112.1° in **III** is considerably smaller, and the mean C-In-P bond angle at 100.4° in **III** is larger than that of 95.5° in **I**. Moreover, the mean In-P-Si and Si-P-Si bond angles at 111.9° and 107.0°, respectively, in **III** are both closer to tetrahedral than corresponding means of 113.0° and 105.7° in **I**.

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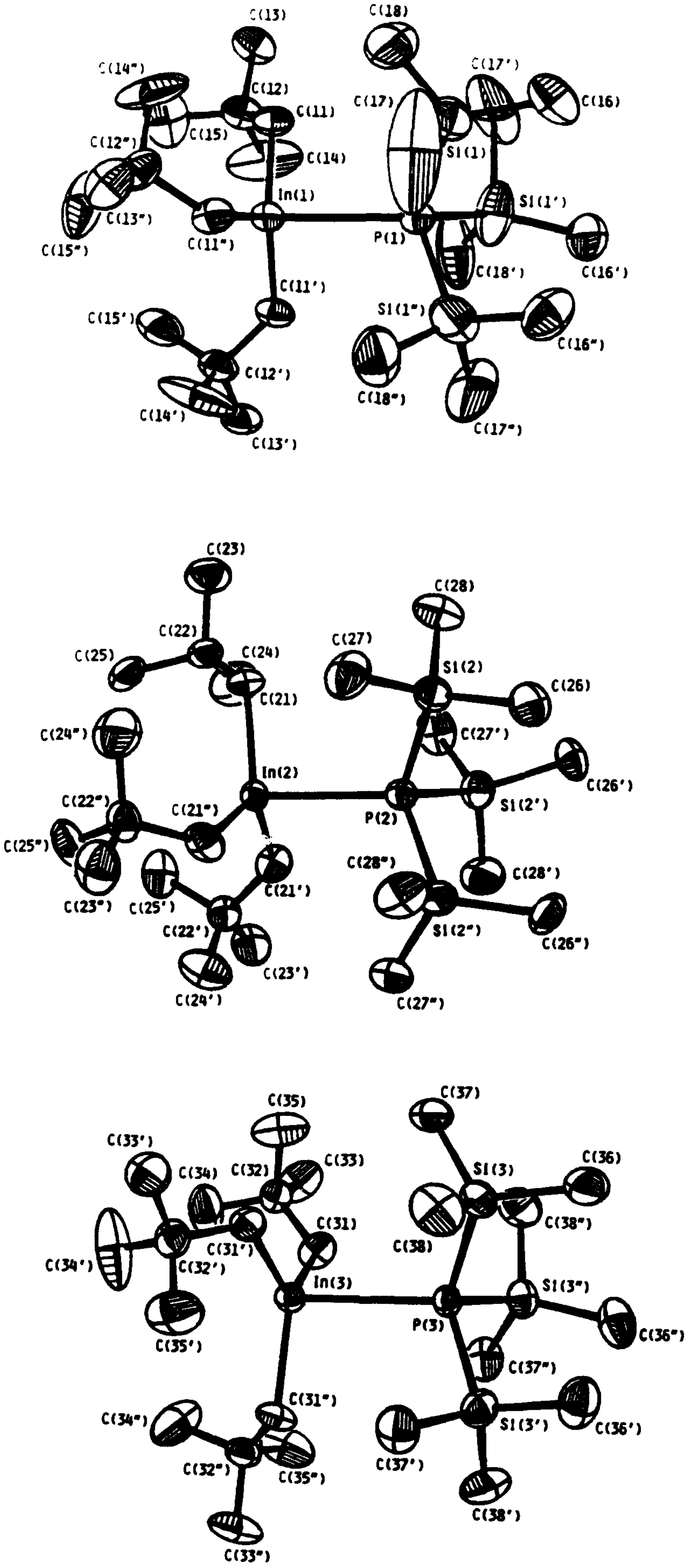
Captions to Figures

Fig. 1. ORTEP diagram (30% probability ellipsoids) showing the solid-state conformations and atom numbering schemes of each of the three $(Me_3CCH_2)_3In{\cdot}P(SiMe_3)_3$ (**I**) molecules in the asymmetric crystal unit; primed and double primed atoms are related to the unprimed atoms by a crystallographic C_3 axis of symmetry. Hydrogen atoms have been omitted for clarity.

Fig. 2. Newman projections along the In-P bonds (torsion angles ±0.3°) in the three $(Me_3CCH_2)_3In{\cdot}P(SiMe_3)_3$ (**I**) molecules in the asymmetric crystal unit.

Fig. 3. ORTEP diagram (40% probability ellipsoids) showing the solid-state conformation and atom numbering scheme of one of the two $Me(Me_3CCH_2)_2In{\cdot}P(SiMe_3)_3$ (**III**) molecules in the asymmetric crystal unit. Hydrogen atoms have been omitted for clarity.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In(1)
Si(1')
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P(1)
C(15")
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C(18')
C(16')
C(11')
C(15')
Si(1")
C(16")
C(12')
C(18")
C(14')
C(17")
C(13')
C(23)
C(28)
C(22)
C(27)
C(25)
C(24)
Si(2)
C(26)
C(21)
C(24")
C(27')
In(2)
C(26')
C(22")
C(21")
P(2)
Si(2')
C(25")
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C(28')
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C(25')
C(21')
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C(35)
C(33')
C(36)
C(34)
C(32)
C(33)
Si(3)
C(31)
C(38")
C(31')
C(38)
C(34')
C(32')
In(3)
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P(3)
C(35')
C(36")
C(37")
C(31")
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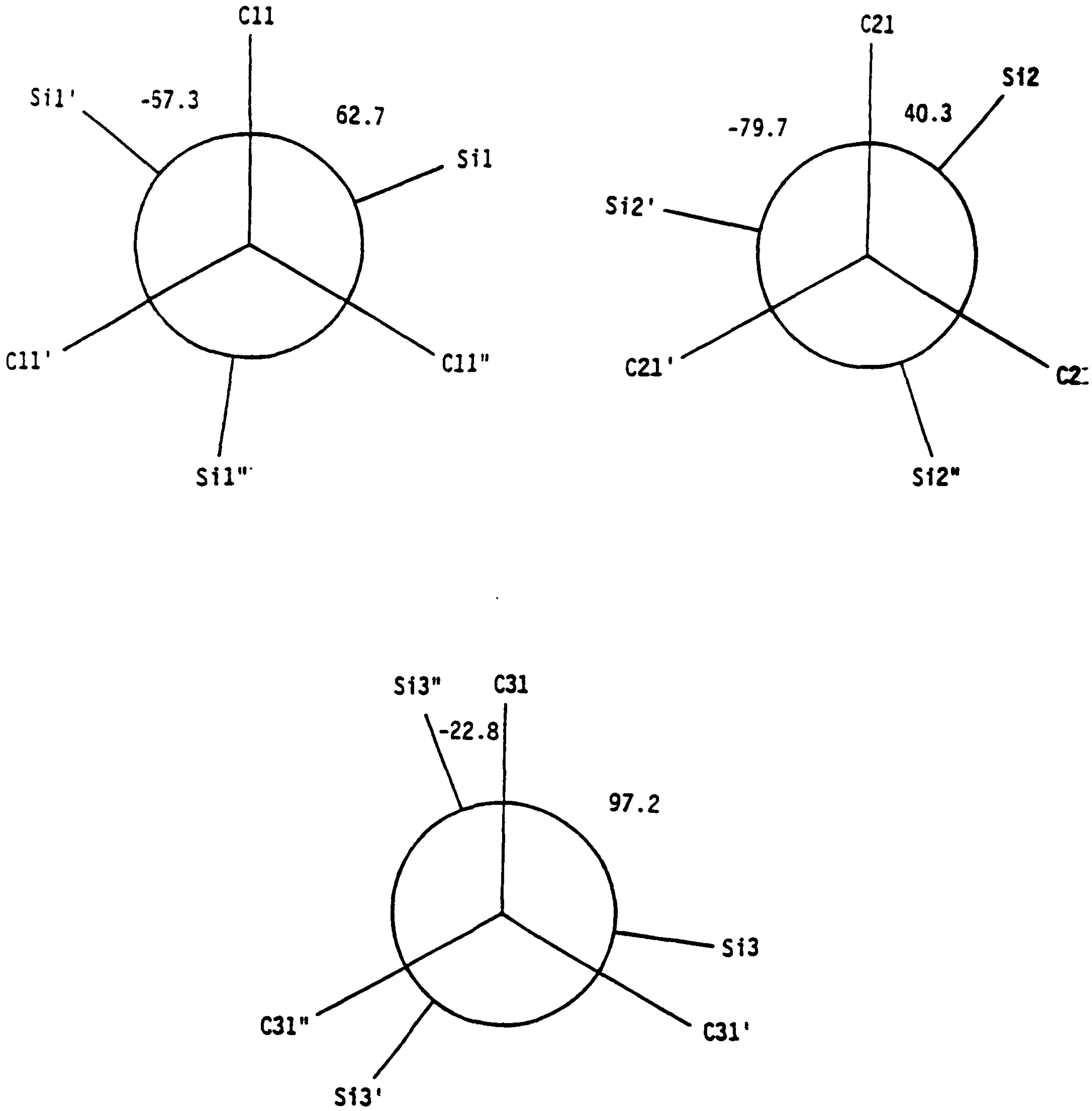
Si(3')
C(36')
C(37')
C(32")
C(35")
C(38')
C(33")

Fig. 1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Si1'
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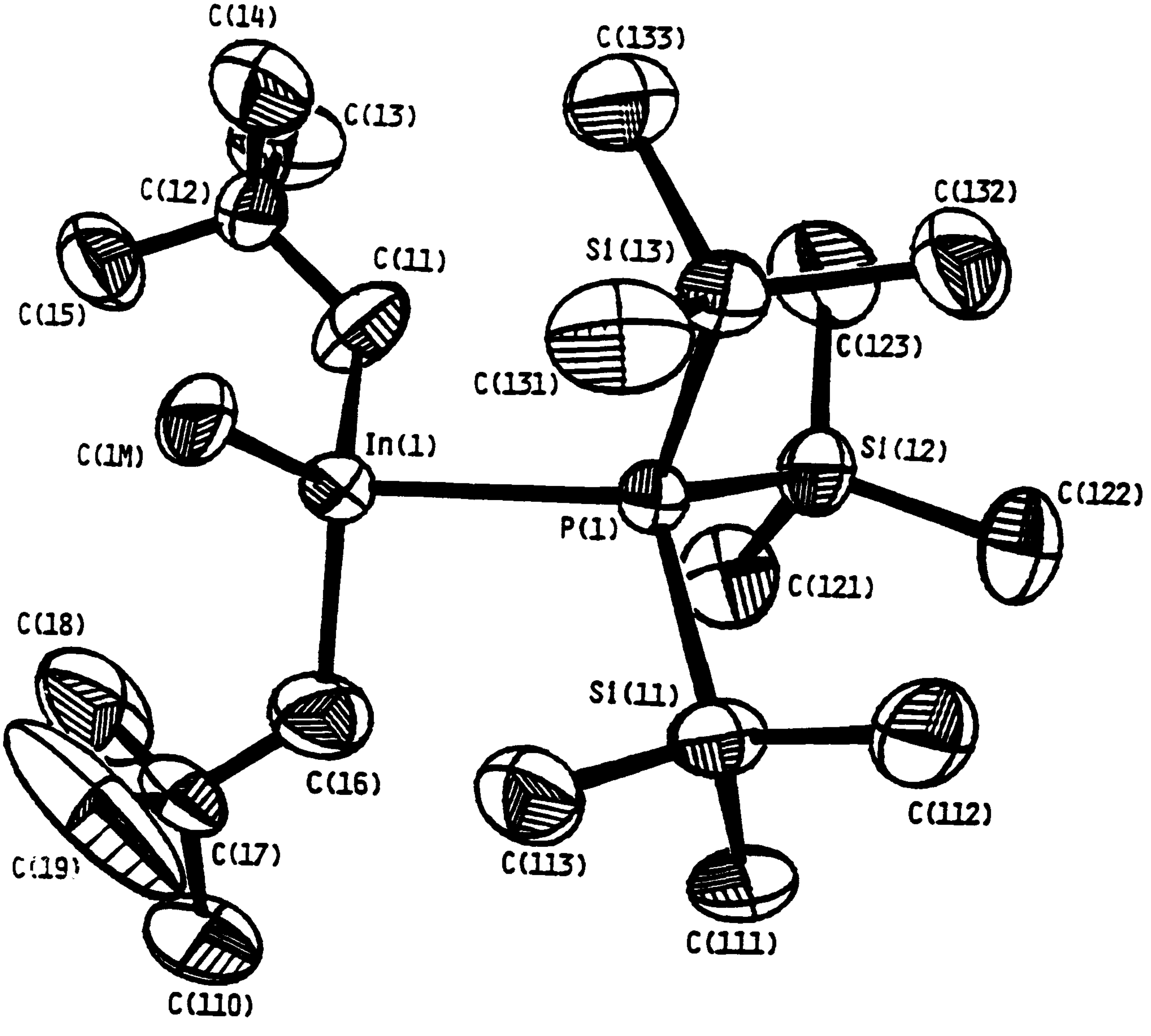
62.7
Si1
C11'
C11"
Si1"
C21
Si2
40.3
-79.7
Si2'
C21'
C2
Si2"
Si3"
C31
-22.8
97.2
Si3
C31"
C31'
Si3'

Fig. 2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C(122)
P(1)
C(121)
C(18)
Si(11)
C(16)
C(112)
C(19)
C(17)
C(113)
C(111)
C(110)

Fig. 3

Table 1. Crystallographic data and summary of data collection and refinement for $(Me_3CCH_2)_3In{\cdot}P(SiMe_3)_3$ (I), $(Me_3CCH_2)_3In{\cdot}As(SiMe_3)_3$ (II), and $Me(Me_3CCH_2)_2In{\cdot}P(SiMe_3)_3$ (III)

	(I)	(II)	(III)
Molecular formula	$C_{24}H_{60}InPSi_3$	$C_{24}H_{60}AsInSi_3$	$C_{20}H_{52}InPSi_3$
Formula weight	578.80	622.75	522.69
Crystal system	trigonal	trigonal	monoclinic
Space group	$P3(C_3^1)$	$P3(C_3^1)$	$P2_1/n(C_{2h}^5)$
a (Å)	16.278(1)	16.304(1)	16.047(2)
b (Å)	16.278(1)	16.304(1)	12.641(2)
c (Å)	11.496(1)	11.579(1)	31.576(4)
β (°)	90.0(-)	90.00(-)	102.92(1)
No. of orient. refls; θ, range (°)	25; 35-40	25; 35-40	25; 33-40
V (Å^3)	2638(1)	2665.6(6)	6243(3)
Z	3	3	8
D_{calc} (g cm^{-3})	1.093	1.164	1.112
Temperature (K)	296	296	296
Crystal dimensions (mm)	0.30 x 0.30 x 0.44	0.40 x 0.40 x 0.40	0.20 x 0.36 x 0.46
$T_{max}:T_{min}$	1.00:0.60	1.00:0.62	1.00:0.27
Radiation (wavelength)	Cu-$K\alpha$ (1.5418 Å)	Cu-$K\alpha$ (1.5418 Å)	Cu-$K\alpha$ (1.5418 Å)
μ (cm^{-1})	69.7	75.1	78.1
Scan type	ω-2θ	ω-2θ	ω-2θ
Scan width (°)	0.60 + 0.14tanθ	0.70 + 0.14tanθ	0.80 + 0.14tanθ
θ_{max} (°)	75	75	67
Intensity control reflns	$21\bar{2}$,$31\bar{1}$,122,113	$21\bar{2}$,$\bar{3}51$,123,$\bar{3}13$	113,232,$2\bar{3}2$,$1\bar{1}3$

Table 1(cont)

Variation; repeat time (h)	<2%; 2	<1%; 2	<1%; 2
No. of rflns recorded	5913 ($+h,\pm k,+l$)	5949 ($\pm h,+k,-l$)	11493 ($+h,+k,\pm l$)
No. of non-equiv refls	3541	3653	11066
R(merge)	0.047 on I	0.039 on I	0.052 on I
No. of rflns retained, $I > 3.0\sigma(I)$	2859	2920	4611
No. of parameters refined	262	262	452
Extinction correction	$1.5(1) \times 10^{-6}$	$2.7(1) \times 10^{-6}$	$3.0(1) \times 10^{-7}$
$R(F)$, $R_w(F)$[a]	0.049, 0.065	0.042, 0.055	0.069, 0.087
Goodness-of-fit[b]	1.35	1.31	1.68
Max shift: esd in final least-squares cycle	0.03	0.03	0.02
Final $\Delta\rho$(e/Å^3) max; min	1.00; -0.91	1.25; -0.68	1.4; -1.5

---

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}\Sigma w\Delta^2[w = 1/\sigma^2(|F_o|), \Delta = (|F_o| - |F_c|)]$ was minimized.

[b] Goodness-of-fit = $[\Sigma w\Delta^2 / (N_{obs} - N_{para})]^{1/2}$.

Table 2. Selected bond lengths (Å) and bond angles (°), with ESD's in parentheses, for $(Me_3CCH_2)_3In{\cdot}P(SiMe_3)_3$ (I).

	m = 1	m = 2	m = 3
(a) Bond Lengths			
In(m)-P(m)	2.890(5)	2.806(4)	2.944(4)
In(m)-C(m1)	2.22(1)	2.21(1)	2.21(1)
P(m)-Si(m)	2.272(4)	2.277(3)	2.265(3)
Si(m)-C (mean)	1.84	1.86	1.86
(b) Bond Angles			
P(m)-In(m)-C(m1)	96.4(3)	96.0(3)	94.0(3)
C(m1)-In(m)-C(m1')	118.8(3)	118.9(4)	119.5(3)
In(m)-P(m)-Si(m)	113.8(2)	113.1(1)	112.2(1)
Si(m)-P(m)-Si(m')	104.9(3)	105.6(2)	106.6(2)
In-C(m1)-C(m2)	125.1(6)	123.5(6)	121.8(7)
P(m)-Si(m)-C (mean)	109.6	109.9	110.1
C-Si(m)-C (mean)	109	109	109
(c) Torsion angles[a]			
C(m1)-In(m)-P(m)-Si(m)	62.7(3)	40.3(3)	97.2(2)
C(m1)-In(m)-P(m)-Si(m')	-57.3(3)	-79.7(3)	-142.8(2)
C(m1)-In(m)-P(m)-Si(m")	-177.3(3)	160.3(3)	-22.8(2)
P(m)-In(m)-C(m1)-C(m2)	143(1)	147(1)	-136.1(7)
C(m1')-In(m)-C(m1)-C(m2)	43(1)	46(1)	-39.2(9)
C(m1")-In(m)-C(m1)-C(m2)	-116(1)	-113(1)	127.1(7)
In(m)-P(m)-Si(m)-C(m6)	-163(1)	160.9(4)	-165.4(6)
In(m)-P(m)-Si(m)-C(m7)	81(1)	41.1(5)	-44.0(5)
In(m)-P(m)-Si(m)-C(m8)	-30(1)	-74.4(5)	75.6(5)
Si(m')-P(m)-Si(m)-C(m6)	-38(1)	-74.9(4)	71.4(6)
Si(m')-P(m)-Si(m)-C(m7)	-154(1)	165.3(5)	-167.3(4)
Si(m')-P(m)-Si(m)-C(m8)	95(1)	49.9(5)	-47.6(5)

Table 2 (continued)

	m = 1	m = 2	m = 3
Si(m")-P(m)-Si(m)-C(m6)	72(1)	36.7(5)	-42.2(6)
Si(m")-P(m)-Si(m)-C(m7)	-44(1)	-83.1(5)	79.2(5)
Si(m")-P(m)-Si(m)-C(m8)	-155(1)	161.5(5)	-161.2(5)
In(m)-C(m1)-C(m2)-C(m3)	-179(1)	178(1)	-172(1)
In(m)-C(m1)-C(m2)-C(m4)	-61(1)	-63(1)	-54(1)
In(m)-C(m1)-C(m2)-C(m5)	59(1)	59(1)	65(1)

[a] The torsion angle A-B-C-D is defined as positive if, when viewed along the B-C bond, atom A must be rotated clockwise to eclipse atom D.

Table 3. Selected bond lengths (Å) and bond angles (°), with ESD's in parentheses, for $(Me_3CCH_2)_3In\cdot As(SiMe_3)_3$ (II).

	m = 1	m = 2	m = 3
(a) Bond Lengths			
In(m)-As(m)	3.018(1)	2.948(2)	2.888(2)
In(m)-C(m1)	2.214(7)	2.230(9)	2.204(7)
As(m)-Si(m)	2.371(3)	2.364(2)	2.360(3)
Si(m)-C (mean)	1.86	1.88	1.86
(b) Bond Angles			
As(m)-In(m)-C(m1)	93.4(3)	92.6(2)	97.0(3)
C(m1)-In(m)-C(m1')	119.7(4)	119.8(3)	118.5(4)
In(m)-As(m)-Si(m)	114.3(1)	113.7(1)	113.5(1)
Si(m)-As(m)-Si(m')	104.2(1)	104.9(1)	105.2(1)
In-C(m1)-C(m2)	120(1)	119(1)	123(1)
As(m)-Si(m)-C (mean)	109.2	108.8	109.5
C-Si(m)-C (mean)	109	110	110
(c) Torsion angles[a]			
C(m1)-In(m)-As(m)-Si(m)	57.5(3)	-40.2(3)	21.0(3)
C(m1)-In(m)-As(m)-Si(m')	-62.5(3)	79.8(3)	-99.1(3)
C(m1)-In(m)-As(m)-Si(m")	177.5(3)	-160.2(3)	141.0(3)
As(m)-In(m)-C(m1)-C(m2)	-136(1)	-148(1)	135(1)
C(m1')-In(m)-C(m1)-C(m2)	-40(1)	-53(1)	33(1)
C(m1")-In(m)-C(m1)-C(m2)	128(1)	118(1)	-124(1)
In(m)-As(m)-Si(m)-C(m6)	161.8(5)	-164.0(4)	162.2(5)
In(m)-As(m)-Si(m)-C(m7)	36.3(6)	-42.2(4)	45.0(4)
In(m)-As(m)-Si(m)-C(m8)	-79.9(6)	76.4(4)	-73.7(5)
Si(m')-As(m)-Si(m)-C(m6)	36.3(5)	-39.1(5)	37.6(6)
Si(m')-As(m)-Si(m)-C(m7)	154.7(6)	-158.7(4)	161.7(5)
Si(m')-As(m)-Si(m)-C(m8)	-89.2(6)	82.7(4)	-79.7(4)

Table 3 (continued)

	m = 1	m = 2	m = 3
Si(m")-As(m)-Si(m)-C(m6)	-72.7(5)	71.2(4)	-73.2(6)
Si(m")-As(m)-Si(m)-C(m7)	45.6(6)	-48.5(4)	51.0(5)
Si(m")-As(m)-Si(m)-C(m8)	161.8(6)	-167.1(4)	169.6(4)
In(m)-C(m1)-C(m2)-C(m3)	-178(1)	-176(1)	178(1)
In(m)-C(m1)-C(m2)-C(m4)	-63(1)	66(1)	-68(1)
In(m)-C(m1)-C(m2)-C(m5)	56(1)	-58(1)	52(1)

[a] The torsion angle A-B-C-D is defined as positive if, when viewed along the B-C bond, atom A must be rotated clockwise to eclipse atom D.

Table 4. Selected bond lengths (Å) and bond angles (°), with ESD's in parentheses, for $Me(Me_3CCH_2)_2In{\cdot}P(SiMe_3)_3$ (III).

	m = 1	m = 2
(a) Bond Lengths		
In(m)-P(m)	2.802(3)	2.796(3)
In(m)-C(m1)	2.24(2)	2.22(2)
In(m)-C(m6)	2.20(1)	2.16(1)
In(m)-C(mM)	2.17(1)	2.18(1)
P(m)-Si(m1)	2.268(6)	2.273(6)
P(m)-Si(m2)	2.259(5)	2.266(4)
P(m)-Si(m3)	2.273(5)	2.253(5)
Si-C (mean)	1.87	1.86
(b) Bond Angles		
P(m)-In(m)-C(m1)	101.4(4)	98.5(4)
P(m)-In(m)-C(m6)	99.7(4)	99.4(4)
P(m)-In(m)-C(mM)	101.6(4)	101.8(6)
C(m1)-In(m)-C(m6)	112.2(5)	112.0(5)
C(m1)-In(m)-C(mM)	119.2(6)	121.8(6)
C(m6)-In(m)-C(mM)	118.1(5)	117.5(7)
In(m)-P(m)-Si(m1)	110.2(2)	111.8(1)
In(m)-P(m)-Si(m2)	111.5(2)	111.1(2)
In(m)-P(m)-Si(m3)	113.5(2)	113.3(2)
Si(m1)-P(m)-Si(m2)	108.0(2)	106.9(2)
Si(m1)-P(m)-Si(m3)	106.3(2)	106.3(2)
Si(m2)-P(m)-Si(m3)	107.2(2)	107.1(2)
In(m)-C(m1)-C(m2)	121(1)	120(1)
In(m)-C(m6)-C(m7)	125(1)	125(1)

Table 4 (continued)

(c) Torsion angles[a]

C(m1)-In(m)-P(m)-Si(m1)	-155.6(4)	-158.5(4)
C(m1)-In(m)-P(m)-Si(m2)	-35.8(4)	-39.2(4)
C(m1)-In(m)-P(m)-Si(m3)	85.4(4)	81.4(4)
C(m6)-In(m)-P(m)-Si(m1)	-40.4(5)	-44.4(5)
C(m6)-In(m)-P(m)-Si(m2)	79.4(5)	74.9(5)
C(m6)-In(m)-P(m)-Si(m3)	-159.5(5)	-164.5(5)
C(mM)-In(m)-P(m)-Si(m1)	81.1(4)	76.4(5)
C(mM)-In(m)-P(m)-Si(m2)	-159.1(5)	-164.3(5)
C(mM)-In(m)-P(m)-Si(m3)	-38.0(5)	-43.7(5)
P(m)-In(m)-C(m1)-C(m2)	-134(1)	-149(1)
C(m6)-In(m)-C(m1)-C(m2)	121(1)	107(1)
C(mM)-In(m)-C(m1)-C(m2)	-24(1)	-40(1)
P(m)-In(m)-C(m6)-C(m7)	153(1)	144(1)
C(m1)-In(m)-C(m6)-C(m7)	-100(1)	-113(1)
C(mM)-In(m)-C(m6)-C(m7)	45(1)	35(2)
In(m)-P(m)-Si(m1)-C(m11)	77.8(5)	75.5(5)
In(m)-P(m)-Si(m1)-C(m12)	-162.1(5)	-161.8(6)
In(m)-P(m)-Si(m1)-C(m13)	-42.6(5)	-43.2(5)
In(m)-P(m)-Si(m2)-C(m21)	-38.5(6)	-40.1(6)
In(m)-P(m)-Si(m2)-C(m22)	-158.4(8)	-162.8(8)
In(m)-P(m)-Si(m2)-C(m23)	80.4(8)	78.8(5)
In(m)-P(m)-Si(m3)-C(m31)	71.8(6)	77.3(5)
In(m)-P(m)-Si(m3)-C(m32)	-165.4(6)	-162.6(6)
In(m)-P(m)-Si(m3)-C(m33)	-44.2(6)	-41.0(6)

[a] The torsion angle A-B-C-D is defined as positive if, when viewed along the B-C bond, atom A must be rotated clockwise to eclipse atom D.

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