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The reaction of (Me ₃) simple adducts (Me ₃ SiCl Combining (Me ₃ SiC (Me ₃ SiCH ₂) ₃ In•P(SiMe ₃ The solid-state structu and 3 crystallize in the tri	SiCH ₂) ₃ Ga with P(SiMe ₃) ₄ (1) an H ₂) ₃ Ga•P(SiMe ₃) ₃ (1) an CH ₂) ₃ In with P(SiMe ₃) ₃ (3), in a nearly quantita res of 1 and 3 were estab gonal system, space group	3)3 or As(SiMe ₃) ₃ in a 1:1 d (Me ₃ SiCH ₂) ₃ Ga•As(SiMe ₃) ₃ in a 1:1 mole rat tive yield. blished by X-ray crystallog $p P3_1$, with a = 16.027(3), or	mole ratio affords the $Me_3)_3$ (2), respectively. io yields the adduct raphy. Isomorphous 1 c = 11.9928(18) Å, V =	
2667.9(7) Å ³ , Z = 3, $D_{calc.} = 1.087$ g cm ⁻³ for 1, and a = 16.061(8), c = 12.0913(19) Å, V = 2701.0(13) Å ³ , Z = 3, $D_{calc.} = 1.156$ g cm ⁻³ for 3. Full-matrix least-quares refinement based on 3397				
(1) and 4156 (3) reflection 0.044), respectively. Me 2.771 Å. The thermal dec indicated that compound compound 3 decomposed	is with $I > 2.5\sigma$ converge tal-pnicogen bond length composition behavior of I s 1 and 2 eliminated the in a single-step process.	d at R = 0.059 ($R_w = 0.062$ s were found to be: Ga-P 1 - 3 was examined by TG. eir organic ligands in a st	2) and R = 0.039 ($R_w = 2.646$ Å, and In-P = A-DTA. These studies epwise manner, while	
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SYNTHESIS AND CHARACTERIZATION OF (Me₃SiCH₂)₃M·E(SiMe₃)₃, (M = Ga, E = P or As; M = In, E = P). X-RAY CRYSTAL STRUCTURES OF (Me₃SiCH₂)₃Ga·P(SiMe₃)₃ AND (Me₃SiCH₂)₃In·P(SiMe₃)₃.

by

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SYNTHESIS AND CHARACTERIZATION OF (Me₃SiCH₂)₃M•E(SiMe₃)₃, (M = Ga, E = P or As; M = In, E = P). X-RAY CRYSTAL STRUCTURES OF (Me₃SiCH₂)₃Ga•P(SiMe₃)₃ AND (Me₃SiCH₂)₃In•P(SiMe₃)₃.

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Summary—The reaction of $(Me_3SiCH_2)_3Ga$ with $P(SiMe_3)_3$ or $As(SiMe_3)_3$ in a 1:1 mole ratio affords the simple adducts $(Me_3SiCH_2)_3Ga \cdot P(SiMe_3)_3(1)$ and $(Me_3SiCH_2)_3Ga \cdot As(SiMe_3)_3(2)$, respectively. Combining $(Me_3SiCH_2)_3In$ with $P(SiMe_3)_3$ in a 1:1 mole ratio yields the adduct $(Me_3SiCH_2)_3In \cdot P(SiMe_3)_3(3)$, in a nearly quantitative yield.

The solid-state structures of 1 and 3 were established by X-ray crystallography. Isomorphous 1 and 3 crystallize in the trigonal system, space group P3₁, with a = 16.027(3), ____ c = 11.9928(18) Å, V = 2667.9(7) Å³, Z = 3, D_{calc.} = 1.087 g cm⁻³ for 1, and a = 16.061(8), ____ c = 12.0913(19) Å, V = 2701.0(13) Å³, Z = 3, D_{calc.} = 1.156 g cm⁻³ for 3. Full-matrix least-



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*Author for correspondence

squares refinement based on 3397 (1) and 4156 (3) reflections with $I > 2.5\sigma$ converged at R = 0.059 ($R_w = 0.062$) and R = 0.039 ($R_w = 0.044$), respectively. Metal-pnicogen bond lengths were found to be: Ga-P = 2.646 Å, and In-P = 2.771 Å. The thermal decomposition behavior of 1 - 3 was examined by TGA-DTA. These studies indicated that compounds 1 and 2 eliminated their organic ligands in a stepwise manner, while compound 3 decomposed in a single-step process.

INTRODUCTION

Recent investigations in our laboratory have centered on the facile formation of the 13-15 bond by reactions of organo-group 13 reagents with either the silylpnicogen compounds $E(SiMe_3)_3$ (E = P or As) or their monolithium salts in solution¹. As a result of our efforts, we have isolated several new compounds containing the 13-15 covalent bond. Included in our results are compounds which exhibit dimeric structures in the solid-state² and those in which two group 13 centers are bridged by a halogen atom and a group 15 atom². In addition, adducts of the type $R_3M \cdot E(SiMe_3)_3$ (R = Me_3SiCH₂, M = In, E = As³; R = Ph³ or C₆F₅⁴, M = Ga, E = As or P) have been isolated in our laboratory. Adducts of this type may find utility as potential singlesource precursors to binary 13-15 semiconductors⁵; however, a review of the literature finds limited structural and thermal analysis data for adducts of this type. We report herein the synthesis, characterization, and thermal analysis of three new main group adducts,

 $(Me_3SiCH_2)_3Ga \cdot P(SiMe_3)_3$ (1), $(Me_3SiCH_2)_3Ga \cdot As(SiMe_3)_3$ (2), and

 $(Me_3SiCH_2)_3In \cdot P(SiMe_3)_3$ (3).

EXPERIMENTAL

General Considerations

All manipulations of air- and moisture-sensitive materials were performed in a Vacuum Atmospheres HE-493 Dri-Lab containing an argon atmosphere or by general Schlenk techniques. Pentane was distilled over LiAlH₄ under dry dinitrogen. Literature procedures were used to prepare and purify $P(SiMe_3)_3^6$, $As(SiMe_3)_3^7$, $(Me_3SiCH_2)_3Ga^8$ and $(Me_3SiCH_2)_3In^9$. The

integrity of all materials used was confirmed via ¹H NMR spectra. ¹H, ¹³C{¹H}, and ³¹P{¹H} NMR spectra were recorded on a Varian XL-300 spectrometer operating at 300, 75.4, and 121.4 MHz, respectively and a Varian Unity 500 spectrometer operating at 500, 125.7, and 202.3 MHz, respectively. ¹H and ¹³C{¹H} spectra were referenced to TMS by using the residual protons or carbons of deuterated benzene at δ 7.15 or 128 ppm. ³¹P{¹H} spectra were referenced externally to H₃PO₄ at δ 0.00 ppm. All NMR samples were prepared in 5-mm tubes which were septum-sealed under argon. All melting points (uncorrected) were obtained on a Thomas-Hoover Unimelt apparatus and the melting point capillaries were flame-sealed under argon. Thermo-Gravimetric Analysis/Differential Thermal Analysis data were collected on a TA Instruments SDT 2960 simultaneous TGA-DTA instrument. Elemental analyses were performed by E+R Microanalytical Laboratory. Inc., Corona, NY. X-ray crystallographic analyses were conducted in the Single Crystal X-ray Structure Center at the University of North Carolina at Čhapel Hill.

Preparation of (Me₃SiCH₂)₃Ga•P(SiMe₃)₃ (1)

Inside the dry-box, a one-necked 250 mL round-bottomed flask equipped with a Teflon valve was charged with pentane (30 mL) and (Me₃SiCH₂)₃Ga (0.331 g, 0.999 mmol) furnishing a clear solution to which was added dropwise P(SiMe₃)₃ (0.250 g, 0.998 mmol) in pentane (30 mL). The resulting clear solution was stirred outside of the dry-box for 48 h at room temperature. Following removal of the volatiles *in vacuo*, the crude crystalline product was dissolved in warm pentane (5 mL). Upon cooling to -15 °C for several days, colorless, air-sensitive crystals of 1 formed; 0.564 g, 97% yield, mp. 48 - 53 °C. Anal. Calcd. for C₂₁H₆₀GaPSi₆: C, 43.34 H, 10.39. Found: C, 43.02 H, 10.23. ¹H NMR: δ 0.272 [d, SiMe₃ (J_{P-H} =4.5 Hz)], 0.078 (s, CH₂), 0.109 (s, C-SiMe₃). ¹³C {¹H} NMR: δ 4.066 [d, SiMe₃ (J_{P-C} = 10.9 Hz)], 2.543 (s, CH₂), 12.247 (s, Me₃). ³¹P {¹H} NMR: δ -248.98 (s).

Preparation of (Me₃SiCH₂)₃Ga•As(SiMe₃)₃ (2)

[Compound (2) was synthesized in the manner described for (1).] Reactants: (Me₃SiCH₂)₃Ga (0.331 g, 0.999 mmol), As(SiMe₃)₃ (0.294 g, 0.998 mmol). Product: 0.501 g, 80% yield. mp. 43 - 50 °C. Anal. Calcd. for C₂₁H₆₀GaAsSi₆: C, 40.30 H. 9.66. Found: C, 39.91 H. 9.54. ¹H NMR: δ 0.343 (s, SiMe₃) , 0.120 (s, CH₂), 0.132 (s, C-SiMe₃). ¹³C {¹H} NMR: δ 4.066 (s, SiMe₃), 2.543 (s, CH₂), 12.247 (s, Me₃).

Preparation of (Me₃SiCH₂)₃In•P(SiMe₃)₃ (3)

[Compound (3) was synthesized in the manner described for (1).]

Reactants: (Me₃SiCH₂)₃In (0.376 g, 0.999 mmol), P(SiMe₃)₃ (0.250 g, 0.998 mmol).

Product: 0.613 g, 98% yield, mp. 125 - 127 °C. Anal. Calcd. for $C_{21}H_{60}InPSi_{6}$: C, 40.23; H, 9.65. Found: C, 39.97; H, 9.43. ¹H NMR: δ 0.244 [d, SiMe₃ (J_{P-H} =5.0 Hz)], -0.112 (s, CH₂), 0.295 (s, C-SiMe₃). ¹³C {¹H} NMR: δ 3.538 [d, SiMe₃ (J_{P-C} = 9.1 Hz)], 3.239 (s, CH₂), 5.235 (s, Me₃). ³¹P {¹H} NMR: δ -241.80 (s).

X-ray structural solution and refinement

Crystallographic data are summarized in Table 1. Colorless crystals of 1 and 3 were mounted on a glass fiber with a viscous oil under a stream of cold dinitrogen. X-ray intensity data were recorded at -135 °C on a Rigaku AFC6/S diffractometer utilizing graphitemonochromated Mo-K α radiation ($\lambda = 0.71073$ Å), and the structures were solved by direct methods. Full-matrix least-squares refinement with weights based upon counting-statistics was performed. Hydrogen atoms were incorporated at their calculated positions using a riding model in the later iterations of refinement which converged at R = 0.059 (R_w = 0.062) for 1, and R = 0.039 (R_w = 0.044) for 3. A final difference-Fourier synthesis revealed no unusual features. Crystallographic calculations were performed using the NRCVAX¹⁰ suite of structure determination programs. For all structure-factor calculations, neutral atom scattering factors and their anomalous dispersion corrections were taken from ref. 11. Interatomic distances and angles are given in Tables 2 - 4. ORTEP¹² diagrams showing the solid-state conformations and atom numbering schemes of **1** and **3** are presented in Figures 1 and 2. Full information concerning conditions for crystallographic data collection and structure refinement, atomic coordinates, thermal and positional parameters, and observed and calculated structure factors has been deposited with the Cambridge Crystallographic Data Centre.

RESULTS and DISCUSSION

The 1:1 mole ratio reaction of $(Me_3SiCH_2)_3Ga$ with $E(SiMe_3)_3$ (E = P or As) at room temperature affords the simple adducts 1 and 2 in high yields. Similarly, compound 3 results from the 1:1 mole reaction of $(Me_3SiCH_2)_3In$ and $P(SiMe_3)_3$ in pentane solution. Compounds 1 and 3 are white crystalline materials which are stable over long periods of time under inert atmosphere. Compound 2, however, decomposes from a white crystalline solid to an orange liquid upon long standing. All three compounds are extremely sensitive to air and moisture and decompose rapidly upon exposure. The ¹H and ¹³C NMR spectra of 1 - 3 confirm that these compounds do not dissociate in solution at room temperature and are pure prior to recrystallization.

The solid-state structures of 1 and 3 were determined by single-crystal X-ray analysis. The inability to isolate a suitable crystal of 2 precluded its structural determination. Compound 1 is one of a few crystallographically characterized 1:1 Ga-P adducts. Those whose structures have been determined are: $(Me_3CCH_2)_3Ga \cdot P(H)Ph_2$ (4)¹³, Ph₃Ga \cdot P(SiMe_3)_3 (5)¹⁴, Ph₂(Cl)Ga · P(SiMe_3)_3 (6)¹⁴, Me₂(Cl)Ga · PPh₂CH₂PPh₂ (7)¹⁵, Cl₃Ga · PMe₃ (8)¹⁶, and I₃Ga · PPh₃ (9)¹⁷. In addition, the 2:1 complex (Me₃Ga)₂ · (PPh₂CH₂)₂ (10)¹⁸ was also characterized in this manner. The Ga-P bond length of 2.646 Å in 1 is within the established range of lengths previously observed [the shortest being 2.353 (2) Å in 8 and the longest being 2.6853 (5) Å in 4]. The elongated bond length in 1 is most likely due to the steric repulsions between the trimethylsilyl groups and the bulky trimethylsilylmethyl ligands. These repulsions

are also evidenced by the staggered conformation between the Me₃SiCH₂ and Me₃Si moieties. The coordination geometry about the gallium center is that of a distorted tetrahedron with a mean C-Ga-C angle of 116.7° and a mean C-Ga-P angle of 100.3°. Mean bond angles at the P atom $[Ga-P-Si = 113.4^\circ > Si-P-Si = 105.3^\circ]$ reflect the relayed effect of the steric compressions resulting from the angular deformations around Ga.

Crystallographic information on simple organoindium-phosphorus adducts is scant and is limited to $(Me_3CCH_2)_3In \cdot P(SiMe_3)_3$ (11)¹⁹, Me $(Me_3CCH_2)_2In \cdot P(SiMe_3)_3$ (12)¹⁹, and $(Me_3In)_2 \cdot (PPh_2CH_2)_2$ (13)¹⁷. The unit cell in 3 consists of discrete monomeric units with the In-P bond length being 2.771 Å. This is within range of the lengths previously observed in compounds 11 - 13 [the shortest being 2.755 (4) Å in 13 and the longest being 2.944 (4) Å in 11]. The mean P-Si and In-C bond lengths at 2.276 Å and 2.210 Å, respectively in 3 are nearly identical to the average P-Si [2.271 Å] and In-C [2.213 Å] in 11, whereas the angles around the In atoms [P-In-C = 101.43°, C-In-C = 116.18° for the mean values in 3; P-In-C = 95.5°, C-In-C = 119.1° in 11] differ significantly. These observed bond angle variations may be directly related to the fact that the C-C distances in Me_3CCH₂ groups are substantially shorter than Si-C bonds in Me_3SiCH₂ moieties thereby increasing the severity of the steric crowding in 11 vs 3; although, the bond lengths should reflect this steric difference as well.

The potential for compounds 1 - 3 to serve as single-source precursors to 13-15 semiconductor materials motivated our study of their thermal decomposition behavior. Ideally, we desired that these adducts would completely eliminate their organic substituents at moderate thermal conditions (< 450 °C) with the resultant formation of the desired 13-15 material. Subsequently, we performed Thermo-Gravimetric Analysis studies on milligram quantities of 1 -**3**. Samples were heated at a rate of 5 °C/min. under a stream of nitrogen. The resulting TGA-DTA plots for each adduct 1 - 3 are given in the supplementary material. From these data, we concluded that compounds 1 and 2 undergo stepwise elimination of the organic ligands, while compound 3 decomposes in a single-step process. For each decomposition, it is important to note that weight percentages correponding to GaP, GaAs, and InP, respectively were observed for the remaining decomposition residues, however, no further analysis was done to characterize these residues.

The results seen in the small-scale decompositions of 1 - 3 prompted us to attempt largescale decompositions utilizing the thermal information gained from the TGA-DTA data. First, the adducts were placed in a vacuum sublimator and heated from 30 - 300 °C in ten degree increments under dynamic vacuum. Each of the adducts sublimed onto the sublimator coldfinger at temperatures less than 125 °C, and no decomposition was seen. Under argon atmosphere, adduct sublimation was somewhat hindered and the adducts changed phase from solid to liquid at 200 °C. The result at 300 °C was refluxing of the adducts on the sublimator cold finger and a small amount of oily residue at the bottom of the sublimator. No material which could be characterized as GaP, GaAs, or InP was obtained. These decomposition experiments were followed by attempts to decompose the adducts in a high-temperature tube furnace. Each of the adducts was sealed in a thick-walled glass tube and placed into the tube furnace under atmospheric pressure. The samples were heated to 400 °C for eight hours. In each case, the result was an oily residue which did not yield any viable product.

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Captions to Figures

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Figure 1. ORTEP diagram (30% probability ellipsoids) showing the solid-state structure and atom numbering scheme of 1. Hydrogen atoms are omitted for clarity.

Figure 2. ORTEP diagram (30% probability ellipsoids) showing the solid-state structure and atom numbering scheme of **3**. Hydrogen atoms are represented by small circles.



Figure 1



	1	3	
molecular formula	$C_{21}H_{60}Ga_1P_1Si_6$	$C_{21}H_{60}In_1P_1Si_6$	
formula weight	581.91	627.01	
crystal system	trigonal	trigonal	
space group	P3 1	P3 1	
a, Å	16.027(3)	16.061(8)	
c. Å	11.9928(18)	12.0913(2)	
V, A ³	2667.8(7)	2701.0(1)	
Z	3	3	
Radiation	Μο Κα (0.71073)	Mo Ka (0.71073)	
(wavelength, \hat{A})			
μ, cm ⁻¹	10.2	8.9	
temp. C	-135	-135	
D _{calcd} , g cm ⁻³	1.087	1.156	
crystal dimens mm	0.40 x 0.30 x 0.25	0.38 x 0.32 x0.25	
T _{max} : T _{min}	0.782:0.626	0.804:0.727	
scan type	ω	ω	
scan width, deg	1.00	1.00	
Θ_{\max} , deg	50	60	
No. of rflns rec.	5284	5466	
No. of non-equiv.	5284	5224	
rflns recorded			
No. of rflns retained,	3397	4156	
$I > 2.5 \sigma(I)$			
No. of parameters			
refined	261	262	
$R: R_w^a$	0.059; 0.062	0.039: 0.044	
goodness-of-fit ^b	1.32	1.08	
Max shift / esd.			
in final least-squares	0.013	0.001	
cycle			

Table 1. Crystallographic Data and Measurements for $(Me_3SiCH_2)_3Ga\bullet P(SiMe_3)_3(1)$, and $(Me_3SiCH_2)_3In\bullet P(SiMe_3)_3(3)$

Table 1 (continued)

	1	3	<u> </u>		
Final max, min کې, e/Å ⁻³	0.830: -0.780	0.890; -0.760			
${}^{a}R = \Sigma(F_{o} - F_{c})/\Sigma F_{o} ; R_{w} = [\Sigma_{w} (F_{o} - F_{c})^{2}/\Sigma_{w} F_{o} ^{2}]^{1/2}.$ bGoodness-of-fit = [$\Sigma_{w}\Delta^{2}/(N_{o}bservations - N_{parameters})]^{1/2}.$					

		Bond	Lengths	5	
Ga1-P(1)	2.646(3)	Gal-0	C(31)	2.019(15)	
Ga1-C(11)	2.014(14)	P(1)-	Si(5)	2.284(5)	
Gal-C(21)	2.025(14)				
		Bond	Angles		
P(1) - Ga(1)	- C(11)	98.4(4)	C(11)	- Ga(1) - C(31)	116.5(6)
Ga(1) - P(1)	- Si(5)	113.54(19)	Si(4)	- P(1) - Si(5)	106.25(21)
P(1) - Si(4) -	- C(42)	109.8(5)	C(11)	- Si(1) - C(14)	112.9(7)
C(13) - Si(1) - C(14)	108.0(8)	Ga(1)	- C(31) - Si(3)	119.7(8)

Table 2. Selected bond distances (Å) and bond angles (°) for 1. with Estimated StandardDeviations in Parentheses

	Dudt		
	Bond L	engths	
In1-P(1) 2.7713(15)	In1-C(3	1) 2.207(6)	
In1-C(11) 2.206(6)	P(1)-Si	(5) 2.2809(23)	
In1-C(21) 2.218(6)			
	Bond A	ngles	
P(1) - In(1) - C(11)	98.45(16)	P(1) - Si(4) - C(42)	109.39(20)
C(11) - In(1) - C(31)	117.53(22)	C(11) - Si(1) - C(14)	111.1(3)
In(1) - P(1) - Si(5)	112.73(7)	C(13) - Si(1) - C(14)	108.6(3)
Si(4) - P(1) - Si(5)	107.56(8)	In(1) - C(31) - Si(3)	117.7(3)

Table 3. Selected bond distances (Å) and bond angles (°) for **3**, with Estimated Standard Deviations in Parentheses

Atom	x	У	Z	B _{iso} (Å ²) ^a
Ga	-0.32356(11)	-0.33654(13)	-0.82776(-)	0.93(8)
Р	-0.3380(3)	-0.3255(3)	-0.6091(3)	1.11(18)
Si(1)	-0.0930(3)	-0.2016(3)	-0.9218(4)	1.58(21)
Si(2)	-0.4372(3)	-0.2556(3)	-0.9888(4)	2.05(23)
Si(3)	-0.4041(3)	-0.5558(3)	-0.9407(4)	1.82(23)
Si(4)	-0.3518(3)	-0.1957(3)	-0.5596(4)	1.56(22)
Si(5)	-0.2086(3)	-0.3119(3)	-0.5133(4)	1.50(22)
Si(6)	-0.4678(3)	-0.4539(3)	-0.5306(4)	1.70(21)
C11	-0.1992(10)	-0.2119(10)	-0.8509(12)	1.4(8)
C12	-0.0401(10)	-0.2621(11)	-0.8364(14)	2.3(8)
C13	-0.0009(11)	-0.0717(13)	-0.9359(15)	3.0(9)
C14	-0.1205(12)	-0.2559(13)	-1.0637(14)	3.0(10)
C21	-0.4449(10)	-0.3378(10)	-0.8774(12)	1.4(7)
C22	-0.3938(11)	-0.1348(13)	-0.9304(14)	2.7(10)
C23	-0.3510(13)	-0.2428(12)	-1.1022(14)	3.6(11)
C24	-0.5578(10)	-0.2968(10)	-1.0546(13)	1.5(7)
C31	-0.3178(10)	-0.4589(10)	-0.8449(13)	1.8(8)
C32	-0.4099(14)	-0.5104(13)	-1.0815(17)	4.1(11)
C33	-0.3708(12)	-0.6522(11)	-0.9636(14)	2.7(9)
C34	-0.5307(12)	-0.6203(12)	-0.8830(15)	3.0(10)
C41	-0.3321(10)	-0.1678(11)	-0.4105(12)	2.0(8)
C42	-0.2620(11)	-0.0869(10)	-0.6387(13)	2.0(8)
C43	-0.4776(12)	-0.2216(12)	-0.5921(14)	2.8(9)
C51	-0.1050(11)	-0.1871(11)	-0.5340(13)	2.2(8)
C52	-0.2311(10)	-0.3360(10)	-0.3609(12)	1.4(7)
C53	-0.1787(12)	-0.3994(12)	-0.5727(14)	2.8(9)
C61	-0.5752(11)	-0.4870(11)	-0.6195(16)	2.8(9)
C62	-0.4466(11)	-0.5566(11)	-0.5258(15)	3.1(9)
C63	-0.4927(11)	-0.4288(13)	-0.3851(16)	3.7(10)

Table 4. Non-Hydrogen Atom Fractional Coordinates and Equivalent Isotropic Thermal Parameters for 1. with Estimated Standard Deviations in Parentheses

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 ${}^{a}B_{iso}$ = the mean of the principal axes of the thermal ellipsoid

Atom	x	у	Z	$B_{iso}(Å^2)^a$
In	0.32963(3)	0.31798(2)	0.20454(-)	0.985(2)
Р	0.34260(1)	0.34696(1)	0.43129(1)	1.01(6)
Si(1)	0.47458(1)	0.22386(1)	0.11329(1)	1.41(8)
Si(2)	0.40727(1)	0.51762(1)	0.03687(2)	1.60(8)
Si(3)	0.10208(1)	0.17049(1)	0.09229(2)	1.60(7)
Si(4)	0.47110(1)	0.49332(1)	0.47400(1)	1.29(7)
Si(5)	0.36011(1)	0.23342(1)	0.52505(1)	1.32(7)
Si(6)	0.21244(1)	0.34570(1)	0.50542(2)	1.51(8)
C11	0.4689(4)	0.3251(4)	0.1779(5)	1.40(2)
C12	0.4101(5)	0.1120(5)	0.1983(6)	2.0(3)
C13	0.6034(5)	0.2539(5)	0.1005(6)	2.3(3)
C14	0.4189(5)	0.1969(5)	-0.0285(6)	2.3(3)
C21	0.3187(4)	0.4424(4)	0.1435(5)	1.5(3)
C22	0.5293(5)	0.5930(5)	0.0995(7)	2.1(3)
C23	0.4172(5)	0.4410(5)	-0.0740(5)	2.5(3)
C24	0.3711(5)	0.5996(6)	-0.0317(6)	2.9(4)
C31	0.1981(4)	0.1769(4)	0.1842(5)	1.7(3)
C32	0.1512(5)	0.2247(6)	-0.0456(6)	2.8(3)
C33	0.0048(5)	0.0423(5)	0.0687(6)	2.1(3)
C34	0.0422(5)	0.2339(5)	0.1564(7)	2.8(4)
C41	0.4416(5)	0.5876(5)	0.4350(6)	2.4(3)
C42	0.5783(4)	0.5116(5)	0.3936(5)	1.8(3)
C43	0.5004(5)	0.5065(5)	0.6243(5)	2.1(3)
C51	0.4848(5)	0.2575(5)	0.5019(6)	2.0(3)
C52	0.3392(5)	0.2346(5)	0.6760(6)	2.3(3)
C53	0.2719(5)	0.1128(5)	0.4659(6)	2.0(3)
C61	0.2352(5)	0.3948(6)	0.6498(6)	2.7(4)
C62	0.1107(5)	0.2188(5)	0.5081(7)	2.6(3)
C63	0.1782(5)	0.4177(5)	0.4149(6)	2.2(3)

Table 5. Non-Hydrogen Atom Fractional Coordinates and Equivalent Isotropic Thermal Parameters for **3**. with Estimated Standard Deviations in Parentheses

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 ${}^{a}B_{iso}$ = the mean of the principal axes of the thermal ellipsoid

Abstract for inclusion in ChemAbstracts

Abstract—The reaction of $(Me_3SiCH_2)_3Ga$ with $P(SiMe_3)_3$ or $As(SiMe_3)_3$ in a 1:1 mole ratio affords the simple adducts $(Me_3SiCH_2)_3Ga \cdot P(SiMe_3)_3(1)$ and $(Me_3SiCH_2)_3Ga \cdot As(SiMe_3)_3(2)$, respectively. Combining $(Me_3SiCH_2)_3In$ with $P(SiMe_3)_3$ in a 1:1 mole ratio yields the adduct $(Me_3SiCH_2)_3In \cdot P(SiMe_3)_3(3)$, in a nearly quantitative yield.

The solid-state structures of 1 and 3 were established by X-ray crystallography. Isomorphous 1 and 3 crystallize in the trigonal system, space group P3₁, with a = 16.027(3), c = 11.9928(18) Å, V = 2667.9(7) Å³, Z = 3, D_{calc.} = 1.087 g cm⁻³ for 1, and a = 16.061(8), c = 12.0913(19) Å, V = 2701.0(13) Å³, Z = 3, D_{calc.} = 1.156 g cm⁻³ for 3. Full-matrix leastsquares refinement based on 3397 (1) and 4156 (3) reflections with I > 2.5 σ converged at R = 0.059 (R_w = 0.062) and R = 0.039 (R_w = 0.044), respectively. Metal-pnicogen-bond lengths were found to be: Ga-P = 2.646 Å, and In-P = 2.771 Å. The thermal decomposition behavior of 1 - 3 was examined by TGA-DTA. These studies indicated that compounds 1 and 2 eliminated their organic ligands in a stepwise manner, while compound 3 decomposed in a single-step process.

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