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Isolation and Characterization of an Indium–Mixed-Pnicogen Four-Membered-Ring Compound: Crystal Structure of $(Me_3SiCH_2)_2InAs(SiMe_3)_2In(CH_2SiMe_3)_2P(SiMe_3)_2$

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Summary: The first four-membered ring containing two indium atoms with bridging by two different group 15 elements, $(Me_3SiCH_2)_2InAs(SiMe_3)_2In(CH_2SiMe_3)_2P(SiMe_3)_2$ *(1), to be characterized completely was prepared by the equilibration of* $[(Me_3SiCH_2)_2InP(SiMe_3)_2]_2$ *(2) with* $[(Me_3SiCH_2)_2InAs(SiMe_3)_2]_2$ *(3) in a 1:1 mole ratio. X-ray crystallographic analysis showed the In–As–In–P ring of 1 to be planar. Crystals of 1 belong to the orthorhombic system, space group* $Pbcn$ (D_{2h}^{14})*, with four molecules in a unit cell of dimensions* a = *12.848(1) Å,* b = *21.558(1) Å, and* c = *18.736(1) Å and are isomorphous with those of 2 and 3. The electron ionization (20 eV) mass spectrum of 1 shows a fragmentation pattern indicative of this compound and no peaks above m/z 510 consistent with either 2 or 3. Clusters assigned to specific ions in the mass spectrum show appropriate isotopic patterns as calculated for the atoms present.*

Introduction

The search for single-source precursors to semiconducting materials has resulted in the synthesis of a large number of new compounds[1,2] and several new classes of compounds.[3-7] Numerous adducts[8] as well as monomeric and oligomeric compounds containing group 13–15 elements have been prepared,[9-11] many of which have been utilized to prepare group 13–15 binary semiconductors.[9,12,13] To our knowledge, no single-source precursors to the heavier ternary group 13–15 materials containing two different pnicogens have been synthesized. Our past attempts to prepare compounds containing a group 13 metal and two different group 15 elements have resulted in unusual rearrangements. For example, the reaction of $LiAs(SiMe_3)_2$ with $(Me_3SiCH_2)_2InP(SiMe_3)_2In(CH_2SiMe_3)_2Cl$ resulted in the formation of the adduct $(Me_3SiCH_2)_3In{\cdot}As(SiMe_3)_3$ rather than the desired salt elimination reaction product, $(Me_3SiCH_2)_2InAs(SiMe_3)_2In(CH_2SiMe_3)_2P(SiMe_3)_2$ (1).[14]

Most group 13–15 compounds characterized by X-ray diffraction studies as dimeric in the solid state also have an association of 2 in solution, although several have been shown to exhibit a monomer–dimer equilibrium in solution.[12,15] The compound $[(Me_3SiCH_2)_2InP(SiMe_3)_2]_2$ (2)[16] was found to be dimeric both as a solid and in solution, but the ^1H NMR spectrum of a $<8 \times 10^{-4}$ M (<0.5 mg in 0.75 mL of benzene-d_6) solution indicated a monomer–dimer equilibrium, as evidenced by the presence of both a doublet (monomer) and a triplet (dimer) arising from the virtual coupling of the trimethylsilyl protons with phosphorus.[17] This prompted us to attempt an equilibration reaction between two dimeric compounds. Herein, we report the synthesis and complete characterization, including X-ray crystallographic analysis, of compound 1 from the reaction of 2 with $[(Me_3SiCH_2)_2InAs(SiMe_3)_2]_2$ (3)[18] in a 1:1 mole ratio.

Experimental Section

General Considerations. All manipulations were performed by Schlenk techniques or in a Vacuum Atmospheres HE-493 Dri-Lab under argon. Benzene, benzene-d_6, and toluene-d_8 were distilled from sodium/benzophenone under dry nitrogen. Pentane was distilled over $LiAlH_4$ under dry nitrogen. Compounds 2[16] and 3[18] were prepared by literature methods.

^1H, ^{13}C, and ^{31}P NMR spectra were obtained on a Varian XL-300 (300, 75.4, and 121.4 MHz, respectively) spectrometer using 5-mm tubes. ^1H and ^{13}C spectra were referenced to TMS using the residual protons or carbons of deuterated benzene at δ 7.15 or 128 ppm or the residual protons of deuterated toluene at δ 2.09 ppm. ^{31}P NMR spectra were referenced externally to H_3PO_4 at δ 0.00 ppm. NMR tubes were flame-sealed under vacuum. All melting points (uncorrected) were obtained with a Thomas-Hoover Uni-melt apparatus, and capillaries were flame-sealed

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(1) Cowley, A. H.; Jones, R. A. *Angew. Chem., Int. Ed. Engl.* **1989,** *28,* 1208.

(2) Wells, R. L. *Coord. Chem. Rev.* **1992,** *112,* 273.

(3) Cowley, A. H.; Harris, P. R.; Jones, R. A.; Nunn, C. M. *Organometallics* **1991,** 10, 652.

(4) Atwood, D. A.; Cowley, A. H.; Harris, P. R.; Jones, R. A.; Koschmieder, S. U.; Nunn, C. M. *J. Organomet. Chem.* **1993,** *449,* 61.

(5) Wells, R. L.; McPhail, A. T.; Pasterczyk, J. W.; Alvanipour, A. *Organometallics* **1992,** *11,* 226.

(6) Wells, R. L.; McPhail, A. T.; Alvanipour, A. *Polyhedron* **1992,** *11,* 839.

(7) Wells, R. L.; Aubuchon, S. R.; Self, M. F.; Jasinski, J. P.; Woudenberg, R. C. *Organometallics* **1992,** *11,* 3370.

(8) Zaouk, A.; Salvetat, E.; Sakaya, J.; Maury, F.; Constant, G. *J. Cryst. Growth* **1981,** *55,* 135.

(9) Higa, K. T.; George, C. *Organometallics* **1990,** *9,* 275.

(10) Wells, R. L.; McPhail, A. T.; Jones, L. J.; Self, M. F. *Polyhedron* **1993,** *12,* 141.

(11) Miller, J. E.; Mardones, M. A.; Nail, J. W.; Cowley, A. H.; Jones, R. A.; Ekerdt, J. G. *Chem. Mater.* **1992,** *4,* 447.

(12) Wells, R. L.; Self, M. F.; McPhail, A. T.; Aubuchon, S. R.; Jasinski, J. P.; Woudenberg, R. C. *Organometallics* **1993,** *12,* 2832.

(13) Cowley, A. H.; Jones, R. A.; Mardones, M. A.; Atwood, J. L.; Bott, S. G. *Angew. Chem., Int. Ed. Engl.* **1990,** *29,* 1409.

(14) Wells, R. L.; McPhail, A. T.; Jones, L. J.; Self, M. F. *Organometallics* **1992,** *11,* 2694.

(15) Beachley, O. T.; Kopasz, J. P.; Zhang, H.; Hunter, W. E.; Atwood, J. L. *J. Organomet. Chem.* **1987,** *325,* 69.

(16) Wells, R. L.; McPhail, A. T.; Self, M. F. *Organometallics* **1992,** *11,* 221.

(17) Wells, R. L.; Self, M. F., unpublished results.

(18) Wells, R. L.; Jones, L. J.; McPhail, A. T.; Alvanipour, A. *Organometallics* **1991,** *10,* 2345.

0276-7333/94/2313-2504$04.50/0

under argon. Crystals used in the X-ray analysis were flame-sealed in 0.7-mm glass capillaries. Elemental analysis was performed by E+R Microanalytical Laboratory, Inc., Corona, NY.

Preparation of $\overline{(Me_3SiCH_2)_2InAs(SiMe_3)_2In(CH_2SiMe_3)_2P}(SiMe_3)_2$ (1). A one-neck round-bottom flask equipped with a micro-stirbar and a Teflon valve was charged with 0.196 g (0.211 mmol) of 2 in 20 mL of benzene and 0.215 g (0.211 mmol) of 3 in 20 mL of benzene. The solution was stirred at room temperature overnight, during which time the solution became light yellow. The volatiles were removed *in vacuo*, and the solid residue was dissolved in pentane and cooled to −15 °C. After 1 h, colorless crystals suitable for X-ray diffraction analysis were recovered (0.180 g, 75.3% yield), mp 107–212 °C (decomposed to a red liquid which ultimately turned black). Anal. Calcd (found) for $C_{28}H_{80}AsIn_2PSi_8$: C, 34.42 (34.24); H, 8.25 (7.58); As, 7.67 (7.96); P, 3.17 (2.95). ^1H NMR (C_6D_6): δ 0.22 (s, 4 H, CH_2), 0.24 (s, 4 H, CH_2), 0.32 (s, 36 H, Me_3CH_2), 0.45 (d, 18 H, Me_3SiP (J_{P-H} = 4.8 Hz)), 0.50 (s, 18 H, Me_3SiAs). ^{13}C NMR (C_6D_6): δ 3.03 (s, CH_2), 3.68 (s, Me_3SiCH_2), 5.09 (d, Me_3SiP (J_{P-C} = 9.7 Hz)), 5.32 (s, Me_3SiAs). ^{31}P NMR (C_6D_6): δ −230.72 (s), −229.84 (s). The electron ionization (20 eV) mass spectrum shows a cluster for $(C_{24}H_{69}AsIn_2PSi_7)^+$ at m/z 889, a cluster for $(C_{20}H_{58}AsInPSi_6)^+$ at m/z 687, and a cluster for $(C_{16}H_{47}AsInPSi_5)^+$ at m/z 600. These ions correspond to the fragments formed by the elimination of a single (trimethylsilyl)methyl group, the elimination of $In(CH_2SiMe_3)_2$, and the elimination of both of these moieties from 1, respectively.

The above reaction was investigated over a range of temperatures in NMR tubes. Solids 2 (8.4 mg, 0.0090 mmol) and 3 (9.2 mg, 0.0090 mmol) were placed in each of two NMR tubes. The tubes were evacuated, and 0.6 mL of toluene-d_8 was distilled onto the mixtures. Before each experiment was run, the solvent in each tube was thawed in a −78 °C bath and the tubes were placed in the NMR probe which was equilibrated at −40 °C. Spectra were recorded from −40 to +20 °C at 10 °C increments, with 10 min allowed for equilibration at each temperature. The first tube was used to record ^1H NMR spectra and the second to record ^{31}P NMR spectra. In both cases, only minimal amounts of the starting materials had dissolved, even after approximately 20 min at room temperature. This low solubility at reduced temperature prevented the acquisition of adequate spectra. After each experiment, the NMR sample was shaken at room temperature until all solid had dissolved. The ^1H and ^{31}P NMR spectra were then recorded. ^1H NMR (C_7D_8): δ 0.19 (bs, 4 H, CH_2), 0.21 (bs, 4 H, CH_2), 0.31 (s, 36 H, Me_3CH_2), 0.45 (d, 18 H, Me_3SiP (J_{P-H} = 3.3 Hz)), 0.50 (s, 18 H, Me_3SiAs). ^{31}P NMR (C_7D_8): δ −227.86 (s), −222.91 (s).

Structural Analysis of 1. Crsytallographic data and measurements are presented in Table 1. Intensity data were corrected for the usual Lorentz and polarization effects; empirical absorption corrections were also applied. Coordinates for the non-hydrogen atoms of isomorphous 2 were used as initial parameters with the modification that the average scattering factor $(f_{As} + f_P)/2$ was substituted for that of As in the structure-factor calculations. Positional and thermal parameters of these atoms (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 and an extinction correction was included as a variable. A final difference Fourier synthesis contained no unusual features. For structure-factor calculations, neutral atom scattering factors and their anomalous dispersion corrections were taken from ref 19.

Table 1. Crystallographic Data and Measurements^a for $\overline{(Me_3SiCH_2)_2InAs(SiMe_3)_2In(CH_2SiMe_3)_2P}(SiMe_3)_2$ (1)

molecular formula	$C_{28}H_{80}AsIn_2PSi_8$
fw	977.17
cryst syst	orthorhombic
space group	*Pbcn*
a (Å)	12.848(1)
b (Å)	21.558(1)
c (Å)	18.736(1)
V (Å^3)	5189(1)
Z	4
D_{calcd} (g cm^{-3})	1.251
radiation (wavelength)	Cu Kα (1.5418 Å)
μ (cm^{-1})	102.1
temp (°C)	23
cryst dimens (mm)	0.18 × 0.18 × 0.24
T_{max}:T_{min}	1.00:0.59
scan type	ω–2θ
scan width (deg)	0.60 + 0.14 tan θ
θ_{max}	60
intensity control rflns	041, 154, 261, 113
Variation (%); repeat time (h)	<1; 2
no. of rflns (+h,+k,+l) recorded	4099
no. of rflns retained ($I > 3.0\sigma(I)$)	1607
no. of params refined	183
extinction correction	4(1) × 10^{-8}
R (R_w)^b	0.048 (0.061)
goodness of fit^c	1.12
max shift: esd in final least-squares cycle	0.03
final $\Delta\rho$ (e/Å^3): max; min	+0.95; −0.76

^{a} An Enraf-Nonius CAD-4 diffractometer equipped with a graphite monochromator was used for all measurements. Crystallographic calculations were performed on PDP11/44 and MicroVAX II computers by use of the Enraf-Nonius Structure Determination Package (SDP). ^{b} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $\Sigma w\Delta^2$ ($w = 1/\sigma^2(|F_o|)$, $\Delta = (|F_o| - |F_c|)$) was minimized. ^{c} Goodness of fit = $[\Sigma w\Delta^2/(N_{observations} - N_{parameters})]^{1/2}$.

Results and Discussion

The reaction of equimolar amounts of 2 and 3 at room temperature in benzene yields a colorless crystalline material, which was ultimately found to be the mixed-pnicogen compound 1 (eq 1). X-ray diffraction quality

$$\underset{2}{[(Me_3SiCH_2)_2InP(SiMe_3)_2]_2} + \underset{3}{[(Me_3SiCH_2)_2InAs(SiMe_3)_2]_2} \rightarrow \underset{1}{\overline{(Me_3SiCH_2)_2InAs(SiMe_3)_2In(CH_2SiMe_3)_2P}(SiMe_3)_2} \quad (1)$$

crystals of 1, grown from pentane, were found to be isomorphous with those for isostructural compounds 2[16] and 3,[18] as would be expected. In fact, the unit cell parameters are almost the average of those for 2 and 3. X-ray analysis revealed that the crystals contain a four-membered $\overline{In–E–In–E}$ ring (E = P, As). The pnicogen sites exhibited a 50:50 occupancy for phosphorus and arsenic, but by its nature, X-ray crystallographic analysis is unable to distinguish whether the crystals contain discrete mixed-pnicogen molecules or cocrystallized starting materials.

It should be noted that although Cowley and co-workers have reported the six mixed-metal compounds of the series $\overline{Me_2ME(^tBu)_2M'Me_2E}(^tBu)_2$ (M, M′ = Al, Ga, In; E = P, As), no detailed structural information was given.[20] This series of compounds may be useful for the preparation of ternary group 13–15 semiconductors composed of two group 13 metals and a single pnicogen.

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

(20) Arif, A. M.; Benac, B. L.; Cowley, A. H.; Jones, R. A.; Kidd, K. B.; Nunn, C. M. *New J. Chem.* **1988**, *12*, 553.

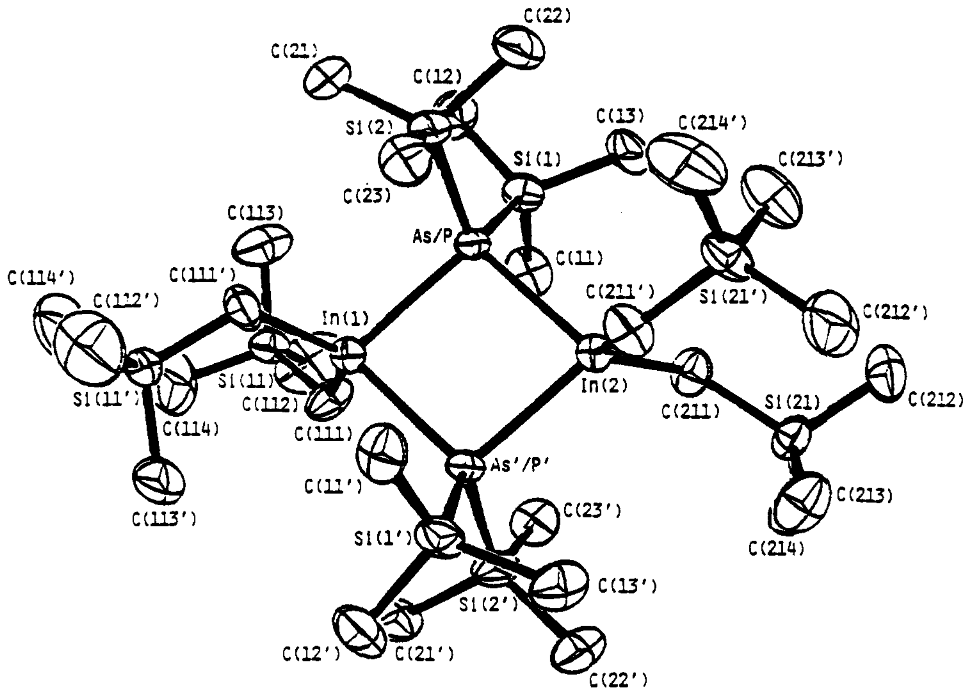

Figure 1. ORTEP diagram showing the solid-state structure of $(Me_3SiCH_2)_2InAs(SiMe_3)_2In(CH_2SiMe_3)_2P(SiMe_3)_2$ (1), with thermal ellipsoids at the 30% probability level. Hydrogen atoms have been omitted for clarity. Primed atoms are related to the unprimed atoms by a crystallographic 2-fold axis of symmetry passing through the In atoms.

Table 2. Non-Hydrogen Atom Fractional Coordinates and Equivalent Isotropic Thermal Parameters for 1, with Estimated Standard Deviations in Parentheses

atom	x	y	z	B_{eq} (Å^2)
As/P	0.1415(1)	0.1860(1)	0.2375(1)	3.83(3)
In(1)	0.0000 (–)[a]	0.27734(5)	0.2500(–)[a]	4.24(2)
In(2)	0.0000(–)[a]	0.09457(5)	0.2500(–)[a]	4.02(2)
Si(1)	0.2369(3)	0.1746(2)	0.1342(2)	5.53(9)
Si(2)	0.2615(3)	0.1905(2)	0.3290(2)	5.72(8)
Si(11)	0.0391(3)	0.3888(2)	0.1151(2)	5.29(8)
Si(21)	–0.0849(3)	–0.0220(2)	0.1310(2)	6.3(1)
C(11)	0.1497(13)	0.1905(7)	0.0583(7)	7.3(4)
C(12)	0.3481(12)	0.2206(7)	0.1282(9)	8.4(5)
C(13)	0.2889(11)	0.0934(7)	0.1285(8)	7.4(4)
C(21)	0.3306(12)	0.2661(7)	0.3280(8)	8.1(4)
C(22)	0.3596(12)	0.1276(8)	0.3210(8)	8.2(4)
C(23)	0.1940(12)	0.1818(7)	0.4155(7)	7.1(4)
C(111)	–0.0404(11)	0.3248(6)	0.1524(8)	6.8(4)
C(112)	0.0338(18)	0.3869(11)	0.0156(11)	15.6(8)
C(113)	0.1734(14)	0.3856(8)	0.1404(11)	10.5(6)
C(114)	–0.0158(19)	0.4628(8)	0.1417(18)	18(1)
C(211)	–0.0053(11)	0.0473(6)	0.1457(7)	6.1(3)
C(212)	–0.0027(14)	–0.0905(7)	0.1131(14)	11.9(7)
C(213)	–0.1733(15)	–0.0402(8)	0.2040(9)	9.6(5)
C(214)	–0.1667(15)	–0.0126(9)	0.0511(9)	11.0(6)

[a] Fixed by symmetry.

Table 3. Selected Bond Distances (Å) and Angles (deg) for 1, with Estimated Standard Deviations in Parentheses

	Bond Lengths		
(As,P)–In(1)	2.690(2)	(As,P)–Si(2)	2.308(4)
(As,P)–In(2)	2.692(2)	In(1)–C(111)	2.159(15)
(As,P)–Si(1)	2.304(4)	In(2)–C(211)	2.205(13)
	Bond Angles		
In(1)–(As,P)–In(2)	94.1(1)	(As,P)–In(1)–(As′,P′)	85.9(1)
In(1)–(As,P)–Si(1)	120.7(1)	(As,P)–In(1)–C(111′)	105.0(4)
In(1)–(As–P)–Si(2)	110.9(1)	C(111)–In(1)–C(111′)	123.4(5)
In(2)–(As,P)–Si(1)	110.8(1)	(As,P)–In(2)–C(211)	106.4(4)
In(2)–(As,P)–Si(2)	114.7(1)	(As,P)–In(2)–(As′,P′)	85.8(1)
Si(1)–(As,P)–Si(2)	105.9(1)	(As,P)–In(2)–C(211′)	113.3(4)
(As,P)–In(1)–C(111)	115.8(4)	C(211)–In(2)–C(211′)	125.0(5)

Details of the crystallographic analysis of 1 are summarized in Table 1. An ORTEP diagram showing the solid-state conformation and atom-numbering scheme is presented in Figure 1. Table 2 lists the non-hydrogen atom fractional coordinates and equivalent isotropic thermal parameters, while Table 3 contains bond distances and angles with estimated standard deviations.

In common with its isomorphous starting materials, 2 and 3, the four-membered ring of 1 lies on a crystallographic C_2 symmetry axis, and thus it is planar. The essentially equal pnicogen–indium bonds at 2.690(2) and 2.692(2) Å are almost the average of 2.692 Å for those found in 2 and 3 (2.655 and 2.728 Å, respectively). As expected on the basis of similar four-membered-ring systems,[16,18] the In–(As,P)–In angles (94.1(1)°) are larger than the (As,P)–In–(As′,P′) angles (85.9(1) and 85.8(1)°). The angles subtended at the pnicogen centers (105.9(1)°) and the average exocyclic angle at the indium centers (125.2°) in 1 are close to the averages at 105.6 and 124.3° for the corresponding angles in 2 and 3.

The ^{1}H NMR spectrum of 1 clearly indicates that neither of the starting dimers are present in solution. The most striking feature of this spectrum is the absence of the triplet which would be expected if two chemically equivalent phosphorus atoms were present in the ring. That both the ^{1}H and ^{13}C NMR spectra exhibit doublets for the protons and carbons of the trimethylsilyl groups on phosphorus points to the presence of a single phosphorus atom in the ring. The ^{31}P NMR spectrum exhibits a major peak at δ –230.7 and a smaller peak at δ –229.8; neither of these correspond to that of 2. An attempt to determine the relative rate of this equilibration reaction involving variable-temperature NMR studies was inconclusive, as no peaks corresponding to the reagents or product could be assigned. Apparently, the minimal solubility of the starting dimers at reduced temperatures prevented the acquisition of suitable spectra. The ^{1}H and ^{31}P NMR spectra run immediately after all of the starting materials had dissolved showed spectraconsistent with only 1. The melting range for 1 was large (105°) and included the range over which a mixture of pure **2** and **3** melted.

The electron ionization (20 eV) mass spectrum of 1 shows ion clusters arising from the loss of a single (Me_3SiCH_2) ligand at *m/z* 889 as well as the loss of the $In(CH_2SiMe_3)_2$ group at *m/z* 687. An ion cluster resulting from the loss of both of these moieties is observed at *m/z* 600. Hence, the mass spectrum shows the presence of indium, arsenic, and phosphorus in a single gas-phase ion. This augments the results of the single-crystal X-ray analysis. No peaks corresponding to ionic species containing two arsenic or two phosphorus atoms were observed in the mass spectrum.

Conclusions

The work described herein demonstrates that the reaction of dimeric species, each containing two different pnicogens and the same group 13 metal, can potentially lead to a mixed-pnicogen compound. Compound 1 is the first example of a four-membered ring containing two indium atoms bridged by both an arsenic and a phosphorus. Further applications of a straightforward equilibration reaction between existing dimeric compounds of the group 13 metals and pnicogens as well as the utility of 1 and similar compounds as single-source precursors to ternary group 13–15 materials are currently being investigated in our laboratories.

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Supplementary Material Available: Tables of hydrogen atom coordinates and isotropic thermal parameters, anisotropic temperature factors, and all interatomic bond distances, bond angles, and torsion angles for 1 (6 pages). Ordering information is given on any current masthead page.

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