Thermally-Induced Transformations of Gallium and Indium Alkyl Phosphido Complexes: Dealkylsilylation Routes to MP (M = Ga, In)

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The dehalosilylation reaction of $^{n}Bu_2GaCl$ with 1 equiv of $P(SiMe_3)_3$ provided $[^{n}Bu_2GaP(SiMe_3)_2]_2$ (**1**) in good yield. A similar reaction between $^{n}BuGaCl_2$ and $P(SiMe_3)_3$ gave $[^{n}Bu(Cl)GaP(SiMe_3)_2]_2$ (**2**). Compound **1** was characterized by X-ray crystallography and possesses an approximately square planar Ga_2P_2 molecular core. Both the P and the Ga centers are in distorted tetrahedral environments. Thermolysis of **1**, at 400 °C, produced GaP and $BuSiMe_3$ and no other crystalline products, as confirmed by thermogravimetric and spectroscopic analysis. The indium analogue of **1**, $[(^{n}Bu)_2InP(SiMe_3)_2]_2$ (**3**), was prepared from the reaction of $(^{n}Bu)_2InCl$ with $P(SiMe_3)_3$. The thermolysis of **3** at 400 °C under nitrogen produced butene, butane, and butyltrimethylsilane as organic products and a dark grey solid. Powder X-ray diffraction of this solid revealed it to consist of InP and metallic indium. Combination of $In(^{n}Bu)_3$ with $P(SiMe_3)_3$ produced the monomeric adduct $(^{n}Bu)_3In{\cdot}P(SiMe_3)_3$ (**4**). The thermal reactivity of complex **4** was investigated at various temperatures. At 130 °C in a sealed tube, the products of thermolysis are $[(^{n}Bu)_2InP(SiMe_3)_2]_2$ (**3**) and In^0. While complex **1** is a potential precursor to GaP via a dealkylsilylation mechanism, the indium analogue **3** and the adduct **4** appear to have a more facile β-hydrogen elimination pathway which makes them less suitable for the production of pure InP.

Introduction

The considerable recent interest and effort toward the preparation of complexes of Al, Ga, and In bearing group 15 ligands (N, P, As) has as one of its primary motivations the preparation of single-source precursors to binary solids of the formula MPn (M = Al, Ga, In; Pn = N, P, As).[1] These materials exhibit a range of optoelectronic properties that are of practical and potential technological importance.[2] Molecular-precursor-based synthesis may offer several advantages over bulk solid state methodologies. Among these are the possibility of preparing thin films on complex surfaces via chemical vapor deposition (CVD) techniques, developing low-temperature routes to metastable phases, and investigating the detailed mechanisms for the aggregation of molecular species on route to extended solids. Since bulk group 13/15 solids are available in high purity by simple routes, our interests in this area and the major focus of our studies are directed toward the fundamental investigation of molecular synthetic routes to solids and not toward the optimization of the preparation of the group 13/15 product.

In general, the transformation of the molecular species to the solid state material is thermally induced and several pathways have been explored. Perhaps the most thoroughly studied thermolysis reaction for both the synthesis of molecular precursors and their conversion to extended solids has been the binuclear elimination of a trialkylsilyl moiety and a halogen group (i.e., dehalosilylation).[3−8] The facility of this method is based on the formation of a strong Si−X bond. The elimination of a trialkylsilyl group from one center with an alkyl ligand on the other (dealkylsilylation) has been investigated to a lesser extent.[9−14]

With these facts in mind, we have prepared a family of dialkyl gallium and indium phosphido compounds

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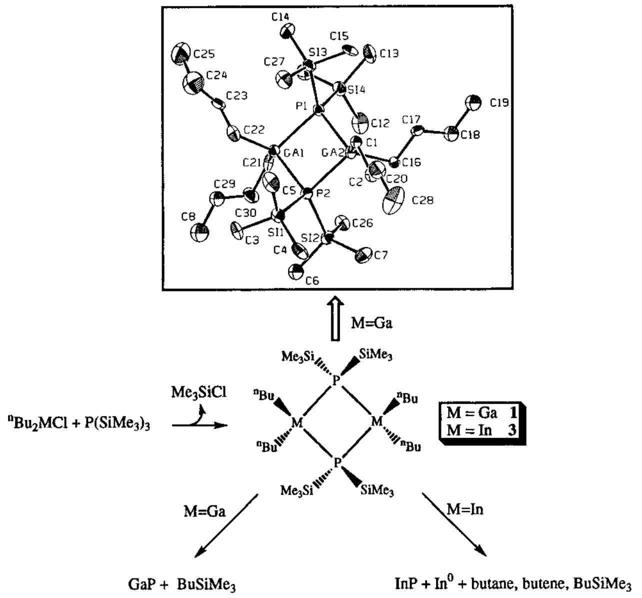
Scheme 1



bearing P$-$SiMe$_3$ groups. This series includes a pair of analogous base-free dimers [^{n}Bu$_2$MP(SiMe$_3$)$_2$]$_2$, a mixed alkylhalo complex [(^{n}Bu)(Cl)GaP(SiMe$_3$)$_2$]$_2$, and the Lewis base adduct ^{n}Bu$_3$In·P(SiMe$_3$)$_3$. In addition to the synthesis and characterization of these species, we have explored the thermal transformations of these compounds, specifically their susceptibility to dealkylsilylation reactions, as part of an investigation of their potential as precursors to MP (M = Ga, In).

Results and Discussion

The phosphido complex [^{n}Bu$_2$GaP(SiMe$_3$)$_2$]$_2$ (**1**) was easily synthesized in good yield by Me$_3$SiCl elimination (dehalosilylation) from a stoichiometric mixture of P(SiMe$_3$)$_3$[15] and ^{n}Bu$_2$GaCl[16] in diethyl ether. Compound **1** was highly crystalline and, in this state, even moderately air stable. Powdered samples did not show the same atmospheric inertness. Several indications suggest that this compound is a dimeric species. Compound **1** does not react with bases such as Et$_2$O or THF, which indicates that it is coordinatively saturated, and the SiMe$_3$ protons appear as a triplet centered at 0.43 ppm in the ^{1}H NMR due to ^{31}P coupling, a feature which is typical of a P-bridged dimer.[10,14,17]

Due to the highly crystalline nature of **1**, it was possible to establish the connectivity of this material by a single-crystal X-ray analysis. The complex crystallizes in the triclinic space group $P\bar{1}$ with no anomalously short intermolecular contacts and exhibits the anticipated dimeric features (Scheme 1). Only two examples of dimeric gallium phosphido complexes with two alkyl groups on the metal and two SiMe$_3$ groups on the phosphorus center have been characterized, [(Me$_3$CCH$_2$)$_2$GaP(SiMe$_3$)$_2$]$_2$ [17] and [Me$_2$GaP(SiMe$_3$)$_2$]$_2$.[14] Selected bond distances and angles for **1** are presented in Table 1. The molecular core consists of an essentially planar Ga$_2$P$_2$ unit (the sum of the internal angles for the core is 359.8°). The angles within this distorted square are somewhat strained. For example, the P1$-$Ga2$-$P2 angle is 88.5°. Both the bridging P and the Ga centers are in distorted tetrahedral environments.

Table 1. Selected Bond Lengths and Angles of 1

bond	length (Å)	vertices	angle (deg)
Ga1$-$P1	2.463(3)	P1$-$Ga1$-$P2	88.1(1)
Ga1$-$P2	2.451(3)	P1$-$Ga1$-$C21	113.1(3)
Ga1$-$C21	2.00(1)	P1$-$Ga1$-$C22	106.8(3)
Ga1$-$C22	1.99(1)	P2$-$Ga1$-$C21	112.7(3)
Ga2$-$P1	2.445(3)	P2$-$Ga1$-$C22	115.9(3)
Ga2$-$P2	2.454(3)	C21$-$Ga1$-$C22	116.5(4)
Ga2$-$C1	2.010(9)	P1$-$Ga2$-$P2	88.5(1)
Ga2$-$C16	1.99(1)	P1$-$Ga2$-$C1	113.8(3)
P1$-$Si3	2.254(4)	P1$-$Ga2$-$C16	111.6(3)
P1$-$Si4	2.265(4)	P2$-$Ga2$-$C16	112.6(3)
P2$-$Si1	2.258(4)	P2$-$Ga2$-$C16	114.8(3)
P2$-$Si2	2.244(4)	C1$-$Ga2$-$C16	113.3(4)
Si1$-$C3	1.85(1)	Ga1$-$P1$-$Ga2	91.6(1)
Si1$-$C4	1.85(1)	Ga1$-$P1$-$Si3	119.7(1)
Si2$-$C5	1.85(1)	Ga1$-$P1$-$Si4	111.7(1)
Si2$-$C6	1.86(1)	Ga2$-$P1$-$Si3	108.3(1)
Si2$-$C7	1.86(1)	Ga2$-$P1$-$Si4	119.0(1)
Si2$-$C26	1.86(1)	613$-$P1$-$Si4	106.7(2)
Si3$-$C14	1.84(1)	Ga1$-$P2$-$Ga2	91.7(1)
Si3$-$C15	1.85(1)	Ga1$-$P2$-$Si1	111.0(1)
Si3$-$C27	1.87(1)	Ga1$-$P2$-$Si2	118.8(1)
Si4$-$C11	1.85(1)	Ga2$-$P2$-$Si1	119.6(1)
Si4$-$C12	1.85(1)	Ga2$-$P2$-$Si2	109.9(1)
Si4$-$C13	1.85(1)	Si1$-$P2$-$Si2	106.1(2)
		Ga2$-$C1$-$C2	105.9(6)
		Ga2$-$C16$-$C17	109.0(6)
		Ga1$-$C22$-$C23	108.5(7)

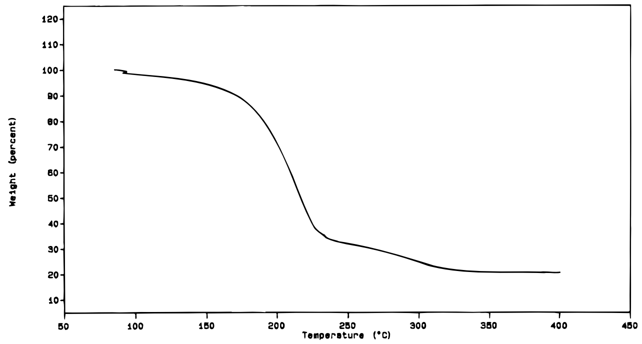


Figure 1. Thermogravimetric analysis trace for the thermolysis of [^{n}Bu$_2$GaP(SiMe$_3$)$_2$]$_2$ (**1**) showing a 77% weight loss attributed to GaP formation (theoretical ceramic yield = 28%).

These results contrast with the reported reaction between P(SiMe$_3$)$_3$ and (Me$_3$SiCH$_2$)$_2$GaBr or (Me$_3$CCH$_2$)$_2$GaCl which produced [(Me$_3$SiCH$_2$)BrGaP(SiMe$_3$)$_2$]$_2$ and [(Me$_3$CCH$_2$)ClGaP(SiMe$_3$)$_2$]$_2$, respectively.[17] These researchers employed the reaction of LiP(SiMe$_3$)$_2$ and (Me$_3$CCH$_2$)$_2$GaCl to prepare [(Me$_3$CCH$_2$)$_2$GaP(SiMe$_3$)$_2$]$_2$.

Since **1** exhibited some air stability in the crystalline state, it was possible to perform a thermogravimetric analysis (TGA) on this compound. As shown in Figure 1, complex **1** exhibited two main weight losses (200 and 275 °C) which result in a total mass loss of 77%. This value is consistent with the ceramic yield of GaP from **1** of 28% (72% expected weight-loss). The small deviation of the experimental values from the theoretical ones is likely due to the fact that **1** is air sensitive and may have begun to react with O$_2$ and water in the atmosphere. The two weight losses that were seen in the TGA might be due to there being two steps in the thermolysis reaction or the result of the low volatility of one of the products. In other words, the first weight

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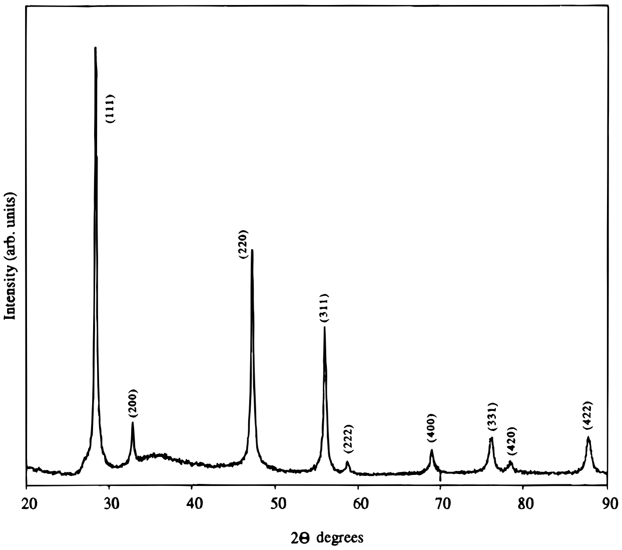
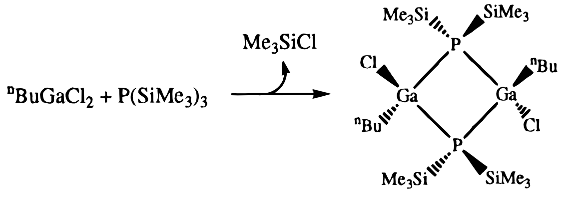


Figure 2. Powder X-ray diffraction pattern of the gray solid obtained directly from the thermolysis of $[^nBu_2GaP(SiMe_3)_2]_2$ (**1**) at 400 °C without annealing. Indexing is for GaP.

loss may be due to reaction while the second small weight loss is the vaporization of a volatile side product (e.g., butyltrimethylsilane) of the reaction. Interestingly, two weight losses were also observed in the thermal analysis of the adduct $(Me_3SiCH_2)_3Ga \cdot P(SiMe_3)_3$.[18] However, since no analysis of the product solid was carried out in that study, further comparison is not possible.

A bulk thermolysis of compound **1** in the solid state at 400 °C (N_2 atmosphere) produced a gray-black material within a matter of minutes. During heating, a clear liquid was observed to reflux above the hot zone of the furnace. This liquid appeared viscous at room temperature and was soluble in benzene. A ^1H NMR spectrum and MS confirmed this compound to be butyltrimethylsilane.[19] The powder X-ray diffraction (PXRD) pattern of the gray-black material identified it as GaP, which was produced in a 96% yield (Figure 2).[20] This material showed crystallinity, without annealing, at a thermolysis temperature substantially below the melting point (1467 °C) of GaP.[21] There was no evidence of any other crystalline material by PXRD. An X-ray fluorescence (XRF) analysis confirmed the ratio of Ga:P to be 1:1 and revealed a small impurity of silicon, which may arise from incomplete removal of the viscous side product $BuSiMe_3$. Regardless of the source, incorporation of even a small amount of Si in group 13/15 materials is cause for concern in any practical application of the material.

The rapid, room temperature dehalosilylation reaction that lead to the formation of **1** compared with the requirement of more forcing conditions to promote the dealkylsilylation reaction that produced GaP suggested that the trimethylsilyl chloride elimination may occur easier than alkyl group elimination and prompted our investigation of the reaction of $^nBuGaCl_2$[15] with $P(SiMe_3)_3$. Rather than elimination of both chloride groups as Me_3SiCl and formation of a phosphinido moiety at the gallium center, the room temperature reaction produced $(^nBu)(Cl)GaP(SiMe_3)_2$ (**2**) in a fair yield with no other isolated product (eq 1). The NMR



(1)

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spectra of **2** are understandably similar to those of **1** with regard to chemical shift and splitting pattern, thus indicating that this compound is a stable phosphorus-bridged dimer in solution. In particular, the triplet for the $SiMe_3$ groups at 0.48 ppm supports this assumption. Compound **2** provides a rather unique example of a Ga center which has three different substituents.[17]

Subsequent thermolysis of **2** in an NMR tube at a mere 90 °C showed the desired elimination of trimethylsilyl chloride, as indicated by the appearance of a singlet at 0.09 ppm. Unfortunately, the emergence of at least five other trimethylsilyl signals implied that several other reactive pathways are open to this compound at such a temperature. All of these signals fall between 1.50 and 0.50 ppm and are split by phosphorus. Due to the complexity of this transformation, the isolation of these products was not attempted at this time and will be the focus of future investigations.

In an attempt to prepare the indium analogue of **1**, $(^nBu)_2InCl$ was stirred in diethyl ether with $P(SiMe_3)_3$. Reaction occurred immediately, as indicated by a slight yellowing of the solution. The reaction mixture was allowed to stir overnight, the volatile materials were removed under vacuum, and the resulting white solid was recrystallized in toluene, generating $[(^nBu)_2InP(SiMe_3)_2]_2$ (**3**) in good yield. The formulation of **3** as the analogue to **1** is based on the similarities of the spectral features of these two compounds. The lack of evidence for coordinated diethyl ether in the ^1H NMR of **3** and the fact that, as with **1**, the signal for the trimethylsilyl protons (0.41 ppm) is split into a triplet by coupling to phosphorus is evidence that this complex has a dimeric structure similar to **1**. Furthermore, the ^1H NMR of **3** for the ^nBu groups is similar to that of **1**, with only the multiplet for the α-CH_2 appearing at a lower field than the signal for the CH_3 triplet, due to the increased deshielding effect of the indium nucleus.

The thermolysis of **3** at 400 °C under nitrogen in a Schlenk tube produced a liquid side product and a dark gray solid. When the solid was washed with acetone and air dried, it appeared to have a high degree of crystallinity. A PXRD pattern of this solid revealed two distinct products: InP and metallic indium (Figure 3).[22,23] An XRF analysis of this material was consistent with this observation and gave a ratio of In:P of 2:1.

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(20) GaP: Joint Committee for Powder Diffraction Data, Center for Diffraction Data: PA; Card No. 32-397.

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(22) InP: Joint Committee for Powder Diffraction Data, Center for Diffraction Data: PA; Card No. 32-452.

(23) In^0: Joint Committee for Powder Diffraction Data, Center for Diffraction Data: PA; Card No. 5-642.

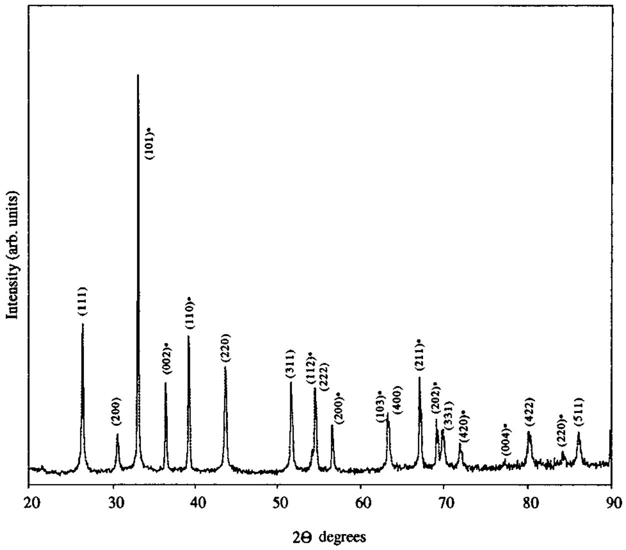
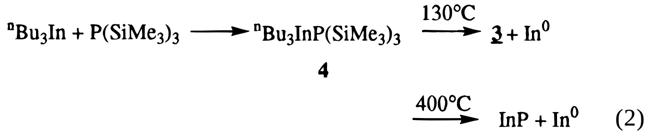


Figure 3. Powder X-ray diffraction pattern of the solid obtained directly from the thermolysis of $[^{n}Bu_2InP(SiMe_3)_2]_2$ (**1**) at 400 °C without annealing. The pattern is indexed as a mixture of InP [(*hkl*)] and In^0 [(*hkl*)•].

Metallic indium presumably resulted from β-hydrogen and reductive elimination reactions of the butyl groups, which was confirmed by the presence of butene and butane in the ^1H NMR and MS analysis of the side products. Butyltrimethylsilane was also observed, which indicated that the dealklysilylation occured to produce InP.

The alkyl−silyl elimination from **3** motivated the exploration of such a reaction from a mixture of $P(SiMe_3)_3$ and $In(^{n}Bu)_3$. When $In(^{n}Bu)_3$[24] was stirred in hexane with $P(SiMe_3)_3$ followed by evaporation of the solvent, a viscous liquid product was isolated (eq 2). The ^1H



$$^{n}Bu_3In + P(SiMe_3)_3 \longrightarrow \underset{\mathbf{4}}{^{n}Bu_3InP(SiMe_3)_3} \xrightarrow{130°C} \mathbf{3} + In^0 \xrightarrow{400°C} InP + In^0 \qquad (2)$$

NMR for this compound confirms the presence of the phosphido moiety, and the integration gave a 1:1 ratio of butyl and trimethylsilyl groups. The trimethylsilyl signal for the monomeric adduct $(^{n}Bu)_3In{\cdot}P(SiMe_3)_3$ (**4**) is split into a doublet by coupling to ^{31}P ($J_{PH} = 6$ Hz), as expected for such species.[6,10,18]

The thermal reactivity of complex **4** was investigated at various temperatures. At 110 °C and over a 24 h period, no reactivity was observed. Upon heating to 130 °C in a sealed tube, a gray insoluble solid was formed. The PXRD pattern of this solid showed indium metal as the only obvious phase. The soluble material from this reaction was examined by ^1H NMR and was shown to be $[(^{n}Bu)_2InP(SiMe_3)_2]_2$ (**3**), which is obviously the result of elimination of an alkylsilane ($^{n}BuSiMe_3$) from **4**.

When the thermolysis of **4** was performed under the same conditions as used for **3** (400 °C, N_2) and after removal of liquid side products, a gray solid remained, which produced a PXRD pattern that again showed the presence of both In metal and InP. An XRF analysis of the gray solid gave an In:P ratio of 3:1.

Comparison of these thermolyses can be made with related adducts that have been recently reported. $(Me_3SiCH_2)_3In{\cdot}P(SiMe_3)_3$ displayed a single-step decomposition during a TGA measurement, however, no further analysis of the solid was provided.[18] Thermolysis of $I_3In{\cdot}PTMS_3$ was carried out under similar conditions to the thermolysis of **4** to yield InP of 84% purity, which contained a slight excess of phosphorus.[6] The stepwise transformation of $Me_3In{\cdot}PTMS_3$ produced a dimer, $[Me_2InP(SiMe_3)_2]_2$, which ultimately yielded a mixture of InP and In metal under conditions similar to those employed in this study.[10] The fact that our experiments with **3** and **4** produced a significant amount of metallic In is consistent with the ability of the butyl moiety to undergo a combination of β-hydrogen and reductive eliminations.

Conclusion

Although $[(^{n}Bu)_2GaP(SiMe_3)_2]_2$ (**1**) produces GaP by dealkylsilylation, it appears that production of indium metal from both **3** and **4** can occur at fairly low temperatures, and therefore, these two compounds are not suitable for the production of pure InP. The contrast in the reactivity between the indium and gallium complexes of the general formula $[^{n}Bu_2MP(SiMe_3)_2]_2$ is striking and appears to be partially attributable to a difference in ease with which the metal can undergo β-hydrogen elimination. The fact that $[Me_2InP(SiMe_3)_2]_2$ also yields In^0 points to a general feature of such species to follow more than one thermolysis pathway, while the thermolysis of the gallium analogue proceeds to one product.

The suitability of bis(alkyl)gallium bis(trimethylsilyl)phosphido species as precursors to GaP has been demonstrated by the clean transformation of the dimeric species, $[(^{n}Bu)_2GaP(SiMe_3)_2]_2$ (**1**), to GaP. In the case of $[(^{n}Bu)(Cl)GaP(SiMe_3)_2]_2$ (**2**), the presence of a chloro ligand on the gallium center appears to complicate the course of the reaction. In contrast, analogous indium complexes that possess β-hydrogens simultaneously follow two thermally-activated pathways: the productive dealkylsilylation route and a β-hydrogen/reductive elimination pathway which leads to In^0. Our continuing investigations are oriented at describing these and other features which influence the capability of molecular species to function as precursors to extended solid materials.

Experimental Section

General Considerations. All manipulations were carried out in a Vacuum Atmospheres Co. drybox or on a vacuum line using standard Schlenk techniques. Diethyl ether was dried with Na/K alloy and distilled using benzophenone as an indicator. Pyridine was distilled from CaH_2 under N_2. $GaCl_3$ and $InCl_3$ were sublimed under vacuum at 30 and 300 °C, respectively. $^{n}BuLi$ was used as received from Aldrich Chemical Co. $^{n}Bu_2InCl$ was prepared by a modification of the literature preparation of Me_2InCl substituting $^{n}BuLi$ for MeLi.[25] $P(SiMe_3)_3$,[15] $^{n}BuGaCl_2$,[16] $^{n}Bu_2GaCl$,[16] and Bu_3In[23] were prepared according to literature procedures. Butyltrimethylsilane was identified by comparison with literature data.[19] ^1H NMR spectra were run on a Gemini 200 MHz spectrometer with deuterated benzene as a solvent and internal standard. Infrared spectra were run on a Mattson 3000 FTIR spectrom-

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eter in a Nujol mull between NaCl plates. All elemental analyses were run on a Perkin Elmer PE CHN 4000 elemental analysis system. A Philips PW2400 spectrometer was used for X-ray fluorescence (XRF) measurements. Powder X-ray diffraction (PXRD) patterns were collected with a Philips PW 3710 based Xpert system using Cu Kα radiation and with the samples mounted on a no-background Si holder. Thermal gravimetric analyses were performed with a Polymer Laboratories STA1500HF. All measurements were carried out with an alumina sample pan.

Synthesis of [(^{n}Bu)$_2$GaP(SiMe$_3$)$_2$]$_2$ (1). To a stirring solution of ^{n}Bu$_2$GaCl (0.5 g, 2.3 mmol) dissolved in diethyl ether, P(SiMe$_3$)$_3$ (0.56 g, 2.2 mmol) was added dropwise. The yellow solution was stirred overnight and then evaporated to dryness. The resulting yellow solid was dissolved in approximately 5 mL of hexane and cooled to −30 °C to recrystallize. Clear cubic crystals of **1** were collected (0.59 g, 72%). IR (Nujol, cm^{-1}): 2948 (s), 1456 (w), 1402 (w), 1373 (w), 1241 (s), 1043 (m), 836 (s), 748 (m), 688 (m), 626 (s), 464 (m), 420 (s). ^{1}H NMR (C$_6$D$_6$): δ 1.67 (m, 4H, butyl β-CH$_2$), 1.58 (m, 4H, butyl γ-CH$_2$), 1.06 (t, 6H, butyl CH$_3$), 0.99 (m, 4H, butyl α-CH$_2$), 0.43 (t, 18H, SiCH$_3$). ^{31}P NMR (C$_6$D$_6$): δ −227. Anal. Calcd for $C_{28}H_{72}Si_4Ga_2P_2$: C, 46.54; H, 10.04. Found: C, 46.22; H, 9.77.

Synthesis of [(^{n}Bu)(Cl)GaP(SiMe$_3$)$_2$)]$_2$ (2). To a stirring solution of ^{n}BuGaCl$_2$ (1.00 g, 5.1 mmol) dissolved in diethyl ether, P(SiMe$_3$)$_3$ (1.3 g, 5.2 mmol) was added dropwise. This homogeneous, colorless solution was stirred and heated in a sealed vessel to 110 °C overnight. It was then evaporated to dryness, and the resulting white solid was dissolved in approximately 5 mL of pyridine and cooled to −30 °C to recrystallize. White crystal filaments of **2** were collected (0.73 g, 43%). IR (Nujol, cm^{-1}): 1454 (s), 1377 (m), 1244 (m), 845 (s), 827 (m), 750 (w), 723 (w), 698 (w), 657 (w), 629 (m). ^{1}H NMR (C$_6$D$_6$): δ 1.84 (m, 2H, butyl β-CH$_2$), 1.52 (m, 2H, butyl γ-CH$_2$), 1.14 (m, 2H, butyl α-CH$_2$), 0.98 (t, 3H, butyl CH$_3$), 0.48 (t, 18H, SiCH$_3$). ^{31}P NMR (C$_6$D$_6$): δ −227. Anal. Calcd for $C_{20}H_{54}Cl_2Si_4Ga_2P_2$: C, 35.36; H, 8.01. Found: C, 35.66; H, 7.74.

Synthesis of [(^{n}Bu)$_2$InP(SiMe$_3$)$_2$]$_2$ (3). To a stirring solution of ^{n}Bu$_2$InCl (0.50 g, 1.9 mmol) dissolved in diethyl ether, P(SiMe$_3$)$_3$ (0.47 g, 1.9 mmol) was added dropwise, and this homogeneous, colorless solution was stirred overnight. After evaporation to dryness, the resulting white solid was dissolved in approximately 5 mL of toluene and cooled to −30 °C to recrystallize. White microcrystalline **3** was collected (0.45 g, 59%). IR (Nujol, cm^{-1}): 1462 (w), 1402 (w), 1373 (w), 1259 (m), 1242 (s), 1043 (m), 837 (s), 748 (m), 688 (w), 627 (m), 465 (w), 420 (m). ^{1}H NMR (C$_6$D$_6$): δ 1.88 (m, 4H, butyl β-CH$_2$), 1.56 (m, 4H, butyl γ-CH$_2$), 1.20 (m, 4H, butyl α-CH$_2$), 1.05 (t, 6H, butyl CH$_3$), 0.41 (t, 18H, SiCH$_3$). ^{31}P NMR (C$_6$D$_6$): δ −242. Anal. Calcd for $C_{28}H_{72}Si_4In_2P_2$: C, 41.48; H, 8.93. Found: C, 41.85; H, 9.28.

Synthesis of (^{n}Bu)$_3$InP(SiMe$_3$)$_3$ (4). Addition of P(SiMe$_3$)$_3$ (0.5 g, 2 mmol) to a hexane solution of ^{n}Bu$_3$In (2 mmol) gave an immediate yellowing of the solution. The solution was allowed to stir overnight, followed by removal of the solvent, under vacuum, to yield a clear oil (0.67 g, 72%). ^{1}H NMR (C$_6$D$_6$): δ 1.96 (m, 6H, butyl β-CH$_2$), 1.61 (sextet, 6H, butyl γ-CH$_2$), 1.50 (t, 9H, butyl CH$_3$), 0.91 (m, 6H, butyl α-CH$_2$), 0.26 (d, 27H, SiCH$_3$). ^{31}P NMR (C$_6$D$_6$): δ −251. Anal. Calcd for $C_{21}H_{54}InPSi_3$: C, 47.00; H, 10.14. Found: C, 46.64; H, 9.77.

Thermolysis of (1). In a typical experiment, 0.5 g of starting material [(^{n}Bu)$_2$GaP(SiMe$_3$)$_2$]$_2$ (**1**) (0.69 mmol) was heated at 400 °C under nitrogen for 10 min, forming a clear liquid and gray solid. The mixture was placed under vacuum at 400 °C for 50 min. The gray solid was then washed with acetone in air and left to air dry. A gray powder (0.13 g) was collected Yield: 96% based on GaP. XRF gave a Ga:P ratio of 1.0:1.0 and a Si content of <2%. The solid was confirmed to be GaP by PXRD. Anal. Found: C, 2.18; H, 0.78.

Thermolysis of (3). Carried out using 0.5 g of **3** (0.62 mmol) at 400 °C under nitrogen in a Schlenk tube to produce a liquid side product and a dark gray solid. The solid was washed with acetone and air dried to yield 0.10 g of InP and In, as confirmed by PXRD. An XRF analysis of the solid gave a ratio of In:P of 2:1 and a Si content of 7%. Anal. Found: C, 3.63; H, 1.07.

Thermolysis of (4). A sample of 0.5 g (0.93 mmol) of **4** was thermolyzed under the same conditions as used for **3**. After removal of liquid side-products, a gray solid possessing a PXRD pattern showing the presence of both In metal and InP was produced (0.11 g). An XRF analysis of the solid gave an In:P ratio of 3:1 and a Si content of 10%. Anal. Found: C, 3.89; H, 0.93.

X-ray Crystallography. Data were collected on a Rigaku AFC6S diffractometer with graphite-monochromated Mo Kα radiation at −148 °C using the $\omega-2\theta$ scan technique to a maximum 2θ value of 40° for crystals mounted on glass fibers. Cell constants and orientation matrices were obtained from the least-squares refinement of 25 carefully centered high-angle reflections. Redundant reflections were removed from the data set. The intensities of three representative reflections were measured after every 150 reflections to monitor the crystal and instrument stability. Data were corrected for Lorentz and polarization effects but not for absorption. The structure was solved by direct methods. The non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were located in the difference Fourier maps and refined isotropically in the case of favorable observation/parameter ratio. The final cycle of full-matrix least-squares refinement was based on the number of observed reflections with $I > 2.5\sigma(I)$. Anomalous dispersion effects were included in F_{calcd}. All calculations were performed using the NRCVAX package. Details of the data collection, refinement, and final atomic coordinates are reported in the Supporting Information.

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Supporting Information Available: Text providing a description of the structural solutions, tables of atomic positions, thermal parameters, crystallographic data, and bond distances and angles, and an ORTEP drawing of **1** (22 pages). Ordering information is given on any current masthead page.

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