

Synthesis of Nanocrystalline Indium Arsenide and Indium Phosphide from Indium(III) Halides and Tris(trimethylsilyl)pnicogens. Synthesis, Characterization, and Decomposition Behavior of $\text{I}_3\text{In}\cdot\text{P}(\text{SiMe}_3)_3$

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Nanocrystalline indium arsenide and indium phosphide were synthesized by heating the products of the independent 1:1 mole ratio reactions of InX_3 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) with $\text{As}(\text{SiMe}_3)_3$ and $\text{P}(\text{SiMe}_3)_3$, respectively, and the 2:1 mole ratio reaction of InCl_3 with $\text{As}(\text{SiMe}_3)_3$. The 1:1 mole ratio reaction of $\text{As}(\text{SiMe}_3)_3$ with InCl_3 produced a black powder, which after annealing at 400 °C afforded InAs crystallites of up to 99.96% purity with an average domain size of 9 nm. InAs obtained from the separate 1:1 mole ratio reactions of InBr_3 and InI_3 with $\text{As}(\text{SiMe}_3)_3$ and the 2:1 mole ratio reaction of InCl_3 with $\text{As}(\text{SiMe}_3)_3$ consisted of crystallites with average domain sizes of 10, 12, and 16 nm, and purities of 99.65%, 85.95%, and 87.90%, respectively. The independent 1:1 mole ratio reactions of InCl_3 and InBr_3 with $\text{P}(\text{SiMe}_3)_3$ both produced colored powders, which after annealing afforded nanocrystalline InP particles with respective purities of 91.53% and 93.08% and average domain size of approximately 4 nm for both samples. The 1:1 mole ratio reaction of InI_3 with $\text{P}(\text{SiMe}_3)_3$ afforded the 1:1 adduct $\text{I}_3\text{In}\cdot\text{P}(\text{SiMe}_3)_3$ (1). Compound 1 crystallizes in the monoclinic system, space group $P2_1/c$, with $a = 16.074(7)$, $b = 9.730(3)$, $c = 16.454(6)$ Å, $V = 2362.1(15)$ Å³, $D_{\text{calc}} = 2.098$ g cm⁻³ for $Z = 4$; the $\text{In}-\text{P}$ bond length is 2.537(3) Å. Decomposition of 1 affords nanocrystalline InP of 84.06% purity with an approximate average domain size of 2.5 nm.

Introduction

Nanoscale materials have recently attracted much attention for their potential applications in optoelectronic devices, as they exhibit unusual properties compared to bulk materials, the most notable being quantum confinement.¹ Thus, synthetic routes to nanocrystalline 13–15 semiconductor compounds have been investigated extensively in the past few years.^{2–6} However, relatively little work has been published regarding the formation of nanocrystalline indium arsenide (InAs) and indium phosphide (InP). These 13–15 compound

semiconductors are promising materials for optoelectronic devices due to their bandgaps, which are narrower than that of gallium arsenide and can be tailored depending on size of the crystallites employed.⁷

Wang and Herron recently prepared nanocrystalline InAs in porous glass from the gas-phase reaction of triethylindium and arsine.⁸ This preparation involved the use of highly toxic arsine gas and high-temperature conditions in order to produce the desired crystallites. These inherent hazards in preparing nanocrystalline InAs can be greatly reduced by using a solution-phase preparation. Uchida et al., obtained nanocrystalline InAs from the reaction of indium(III) acetylacetonate with tris(trimethylsilyl)arsine in refluxing triglyme.⁷ This reaction employs lower temperatures than the gas-phase reaction detailed by Wang and Herron, yet the byproducts of this reaction were not reported; thus a possible source of material contamination was overlooked. Annealing or washing the final product in order to eliminate any remaining impurities is a crucial step in attempts to develop high-purity nanocrystals from solution-phase reactions. In our laboratories, a reaction has been achieved in which both a known and volatile byproduct was formed, and the final product was annealed to remove any lingering impurities. This

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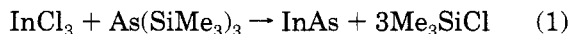
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reaction resulted from the combination of indium(III) chloride and tris(trimethylsilyl)arsine in the solution phase at room temperature, as described in eq 1.



However, the size of the InAs crystallites produced and the effect of using other indium(III) halides on the particle size was not detailed in our previous reports.^{3a,b} Likewise, no data were given on possible 2:1 reactions which may yield compounds similar to that of formula $(\text{Cl}_3\text{Ga}_2\text{As})_n$ ^{3c} or $(\text{Cl}_3\text{GaP})_n$,⁹ which were obtained by the reaction of GaCl_3 and $\text{E}(\text{SiMe}_3)_3$ ($\text{E} = \text{As}, \text{P}$) in 2:1 molar ratio.

In contrast to indium arsenide, significantly more preparations of indium phosphide (InP) have been detailed in the literature.^{10–14} Bradley and co-workers were able to deposit a thin film of InP on a (100) InP substrate using metal–organic molecular beam epitaxy (MOMBE) by subliming and heating the dimeric precursor $[\text{Me}_2\text{InP}(t\text{-Bu})_2]_2$ in the gaseous state.¹⁰ Steigerwald and co-workers obtained polycrystalline InP from the thermal decomposition of $[\text{Me}_2\text{InP}(\text{SiMe}_3)_2]_2$.¹¹ Barron et al. synthesized polycrystalline InP by a method similar to that previously reported from our laboratories to produce GaAs and InAs: the thermal elimination of trimethylsilyl halides from polymeric precursors synthesized by the 1:1 mole ratio reaction of indium(III) halides with tris(trimethylsilyl)phosphine.¹² Theopold and Douglas reported nanocrystalline InP through methanolysis of $[\text{Cp}^*(\text{Cl})\text{InP}(\text{SiMe}_3)_2]_2$,¹³ and Nozik and co-workers synthesized InP of 2.3 nm average particle size from the reaction of chloroindium oxalate with tris(trimethylsilyl)phosphine.¹⁴ The direct synthesis of GaAs by combining GaCl_3 and $\text{As}(\text{SiMe}_3)_3$, originally conducted in our laboratory,^{3a} had been shown by Alivasatos to produce nanocrystals.⁴ Therefore, we decided to investigate Barron's method further in order to determine the size of the particles produced.

In this paper we report our results on the independent reactions of indium(III) halides and tris(trimethylsilyl)arsine and tris(trimethylsilyl)phosphine to afford nanocrystalline samples of both InAs and InP. Additionally, we report the isolation, crystal structure, and decomposition behavior of the 1:1 adduct $\text{I}_3\text{InP}(\text{SiMe}_3)_3$, synthesized from the reaction of indium(III) iodide with tris(trimethylsilyl)phosphine, in contrast to the polymeric compound $[\text{I}_2\text{InP}(\text{SiMe}_3)_2]_x$ previously reported by Barron from the same reaction.¹²

Experimental Section

General Considerations. All manipulations were performed using general Schlenk, dry box, and/or high-vacuum techniques. Solvents were appropriately dried and distilled under nitrogen prior to use. Literature methods were used to prepare $\text{As}(\text{SiMe}_3)_3$,^{15a,b} and $\text{P}(\text{SiMe}_3)_3$.^{15c} InCl_3 , InBr_3 , and InI_3 (99.999% purity) were obtained from Strem Chemicals, Inc. and used as received. X-ray powder diffraction (XRD)

studies were performed on a Phillips XRG 3000 diffractometer using Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$; graphite monochromator). Mass spectra were collected on a JEOL JMS-SX 102A spectrometer operating in the electron ionization mode at 20 eV. X-ray photoelectron spectroscopy (XPS) studies were conducted on a Perkin-Elmer PHI 5400 instrument at the University of North Carolina at Chapel Hill, using a spherical capacitor analyzer (SCA). The X-ray sources for InAs and InP XPS analyses were Al K α (1486.6 eV) and Mg K α (1253.6 eV), respectively, with both samples run under a pressure of $\sim 8 \times 10^{-9}$ Torr. Transmission electron microscopy (TEM) data were collected on a TOPCON EM002B at the North Carolina State University Analytical Instrumentation Facility. UV/vis spectra were collected on a Hewlett-Packard HP8452A spectrophotometer, using 10 mm cuvettes. Suspensions for UV/vis analysis were prepared by sonicating a slurry of InAs or InP in methanol for 15–20 min and then filtering the suspension through Nuclepore Swin-Lok filter holders, using polycarbonate capillary hole membranes with a pore size of 30 nm. Single-crystal X-ray diffraction data were collected on a Rigaku diffractometer using the ω scan mode, and data refined using the NRCVAX System at the University of North Carolina at Chapel Hill Single Crystal X-Ray Facility.¹⁶ Thermogravimetric analysis/differential thermal analysis (TGA/DTA) data were collected on a TA Instruments SDT 2960 simultaneous DTA/TGA instrument. All NMR spectra were obtained in 5 mm tubes using dry, degassed C_6D_6 as the solvent. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were obtained on a Varian XL-300 spectrometer operating at 300 and 75.4 MHz, respectively, and referenced to TMS using the residual protons or carbons of deuterated benzene at δ 7.15 or 128 ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were obtained on a Varian Unity 500 spectrometer operating at 202.3 MHz and referenced externally to H_3PO_4 at δ 0.00 ppm. Elemental analyses were performed by E + R Microanalytical Laboratories, Inc., Corona, NY.

Preparation of InAs from InCl_3 and $\text{As}(\text{SiMe}_3)_3$. InCl_3 (0.500 g, 2.26 mmol) was dissolved in a solution of 30 mL toluene/3 mL diethyl ether in a 200 mL screwtop reaction flask equipped with a Teflon valve and a magnetic stir bar. A solution of $\text{As}(\text{SiMe}_3)_3$ (0.732 g, 2.48 mmol, 10% excess) in 20 mL toluene was then added via pipet to the flask. Upon addition of the InCl_3 , the solution sequentially turned from clear and colorless to cloudy, yellow, orange, red, and then finally brown as addition progressed. The reaction mixture was stirred for 48 h under argon atmosphere at room temperature. The solvents and volatile reaction products were then removed in vacuo to afford a brown-black powder. The powder was collected, washed in pentane, and subsequently loaded into a sublimator for elimination of any remaining Me_3SiCl and annealing under vacuum at 200 °C for 10 min, then ramped by 30 °C increments from 200 to 290 °C, 10 °C increments from 290 to 310 °C, and 30 °C increments from 310 to 400 °C. The sample was heated at 400 °C for 3 h to afford InAs as a black powder (0.362 g, 1.91 mmol, 84.4% yield based on In). Anal. Calcd (found) for InAs: As, 39.49 (40.01); In, 60.51 (59.46) C, 0.00 (0.42); H, 0.00 (0.10); Cl, 0.00 (0.36); In:As ratio 1.00:1.03. Titration of hydrolyzed volatiles required 58.6 mL NaOH (0.098 M), corresponding to elimination of 5.64 mmol (83.2%) Me_3SiCl .

Preparation on InAs from InBr_3 and $\text{As}(\text{SiMe}_3)_3$. InBr_3 (0.250 g, 0.705 mmol) and $\text{As}(\text{SiMe}_3)_3$ (0.240 g, 0.811 mmol, 15.0% excess) were combined in a method similar to that previously described, resulting in a reddish-brown powder. Upon annealing this powder by the method outlined above, a red film was produced on the coldfinger of the sublimator, leaving behind InAs as a shiny black powder, (0.080 g, 0.421 mmol, 59.8% yield based on In). Anal. Calcd (found) for InAs: As, 39.49 (39.38); In, 60.51 (60.27). In:As ratio: 1.00:1.00. Titration of hydrolyzed volatiles required 41.5 mL NaOH

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(0.0379 M), corresponding to elimination of 1.57 mmol (74.3%) Me₃SiBr.

Preparation of InAs from InI₃ and As(SiMe₃)₃. InI₃ (0.506 g, 1.02 mmol) and As(SiMe₃)₃ (0.331 g, 1.12 mmol, 10% excess) were combined in a method similar to that previously described, yielding an orange-red oil, which was extracted with pentane to yield a red-orange powder. Upon annealing this powder by the method detailed above, a red film formed on the coldfinger, leaving behind InAs as a lustrous black powder, (0.028 g, 0.147 mmol, 14.4% yield based on In). Anal. Calcd (found) for InAs: As, 39.49 (32.05); In, 60.51 (53.90). In:As ratio: 1.10:1.00. Titration of hydrolyzed volatiles required 10.3 mL of NaOH (0.1001 M), corresponding to elimination of 1.43 mmol (68.1%) Me₃SiI.

Preparation of InAs from 2:1 Mole Ratio Reaction of InCl₃ and As(SiMe₃)₃. InCl₃ (0.508 g, 2.30 mmol) was dissolved in a mixture of 30 mL toluene/14 mL THF and added via pipet to a solution of As(SiMe₃)₃ (0.304 g, 1.03 mmol) in 25 mL of toluene in a screwtop reaction flask equipped with a Teflon valve and a magnetic stir bar. Upon addition of the InCl₃ solution, the bulk solution turned from clear to orange-red and then dark red-brown upon final addition. The reaction mixture was stirred in an argon atmosphere at room temperature for 72 h. The solvents and volatile reaction products were removed in vacuo to obtain a stick red-brown solid, which was then extracted with pentane and dried under an argon stream to yield a red-brown powder. This sample was sent for elemental analysis as "crude product". Anal. Calcd (found) for Cl₃In₂As, "crude product": As, 18.23 (12.19); In, 55.89 (36.48); Cl, 0.00 (19.98); H, 0.00 (3.75). In:As ratio in "crude product" 1.95:1.00. The remaining sample was annealed under vacuum in a sublimator at 350 °C for 4 h. A yellow powder collected on the coldfinger and a black powder remained in the bottom of the sublimator. The black powder was collected to yield 0.069 g of InAs (0.362 mmol, 31.5% yield based on In). Anal. Calcd (found) for InAs "final product": As, 39.49 (34.71); In, 60.51 (53.19) In:As ratio in "final product" 1.00:1.00. Titration of hydrolyzed volatiles required 20.5 mL NaOH (0.1001 M), corresponding to elimination of 2.05 mmol (66.4%) Me₃SiCl.

Preparation of InP from InCl₃ and P(SiMe₃)₃. InCl₃ (0.245 g, 1.11 mmol) was placed in a screwtop reaction flask equipped with a Teflon valve and a magnetic stir bar, and 50 mL pentane was added. The flask was subjected to ultrasonic irradiation for 90 min to disperse the InCl₃. A solution of P(SiMe₃)₃ in 30 mL of pentane was then added via pipet, after which an additional 20 mL of pentane was added. Upon addition of the tris(trimethylsilyl)phosphine, the suspended powder turned from white to a pale yellow. The flask was returned to the ultrasound bath for 20 min and then allowed to stir in an argon atmosphere at room temperature for 2 days. During this time, the suspended powder turned from pale yellow to bright yellow. The solvents were removed in vacuo to yield an orange powder similar in appearance to that described in ref 12 as [Cl₂InP(SiMe₃)₂]_n. Anal. Calcd (found) for [Cl₂InP(SiMe₃)₂]_n: In, 31.62 (50.15); P, 8.53 (12.25); Cl, 19.85 (13.51); H, 5.00 (3.30); Cl, 19.53 (17.99). In:P ratio in orange powder 1.10:1.00. Titration of hydrolyzed volatiles required 22.9 mL of NaOH (0.098 M), corresponding to elimination of 2.24 mmol (67.4%) Me₃SiCl. Annealing of this powder using the method previously described yielded a red-orange film on the coldfinger of the sublimator. A fine brown-black powder of InP remained in the base (0.093 g, 0.641 mmol, 57.7% yield based on In). Anal. Calcd (found) for InP: In, 78.77 (70.67); P, 21.23 (20.86). In:P ratio in final product: 1.00:1.09.

Preparation of InP from InBr₃ and P(SiMe₃)₃. InBr₃ (0.250 g, 0.705 mmol) and P(SiMe₃)₃ (0.194 g, 0.776 mmol, 10% excess) were combined in a method similar to that described above, to yield a yellow-orange powder similar in appearance to that described in ref 12 as [Br₂InP(SiMe₃)₂]_n. Anal. Calcd (found) for [Br₂InP(SiMe₃)₂]_n: C, 15.94 (13.12); H, 4.01 (3.24); Br, 35.36 (16.56); In, 25.40 (39.92); P, 6.85 (8.74). In:P ratio in yellow-orange powder: 1.23:1.00. Titration of hydrolyzed volatiles required 12.9 mL of NaOH (0.098 M), corresponding to elimination of 1.26 mmol (59.4%) Me₃SiBr. The yellow-orange powder was then annealed in a manner similar to that detailed previously, resulting in InP as a brown-black powder

Table 1. Crystallographic Data and Measurements for I₃In-P(SiMe₃)₃ (1)

molecular formula	C ₉ H ₂₇ I ₃ InPSi ₃
formula weight	746.07
crystal system	monoclinic
space group	P2 ₁ /c
a, Å	16.074(7)
b, Å	9.730(3)
c, Å	16.454(6)
α, deg	90.00
β, deg	113.39(3)
γ, deg	90.00
V, Å ³	2362.1(15)
Z	4
radiation (wavelength, Å)	Mo Kα (0.71703)
μ, mm ⁻¹	5.07
temp, °C	-170
D _{calcd} , g cm ⁻³	2.098
crystal dimensions, mm	0.25 × 0.25 × 0.25
T _{max} ; T _{min}	0.3990; 0.1475
scan type	ω
scan width, deg	1.00
θ _{max} , deg	45.0
no. of reflections recorded	3406
no. of nonequivalent reflns recorded	3077
R _{merge} (on I)	0.013
no. of reflns retained, I > 2.5σ(I)	2123
no. of parameters refined	155
R; R _w ^a	0.040; 0.049
goodness of fit ^b	1.45
max shift/esd in final least-squares cycle	0.000
final max, min ΔQ, e/Å ⁻³	1.540; -1.290

^a R = Σ(|F_o| - |F_c|)/Σ|F_o|; R_w = [Σw(|F_o| - |F_c|)²/Σw|F_o|²]^{1/2}.

^b Goodness-of-fit = [ΣwΔ²/(N_{observations} - N_{parameters})]^{1/2}.

(0.033 g, 0.226 mmol, 32.0% yield based on InBr₃). Anal. Calcd (found) for InP: In, 78.77 (72.80); P, 21.23 (20.28). In:P ratio in final product: 1.00:1.03.

Preparation of I₃In-P(SiMe₃)₃ from InI₃ and P(SiMe₃)₃. InI₃ (0.750 g, 1.51 mmol) was placed in a 200 mL screwtop flask equipped with a Teflon valve, and dissolved in 30 mL of toluene/3 mL of ether. A solution of P(SiMe₃)₃ (0.417 g, 1.66 mmol, 10% excess) in 40 mL of toluene was then added via pipet to the flask. An additional 25 mL of toluene was then added, and the flask was sealed and set to stir for 2 days at room temperature. During this time, the solution turned slightly yellow, but no precipitate was noticed. When the solution was frozen in a liquid nitrogen bath and allowed to thaw, a white pelletlike solid, which redissolved once warmed to room temperature, precipitated out of solution. Removal of the volatiles in vacuo yielded I₃In-P(SiMe₃)₃ as a white-yellow powder (0.962 g, 1.28 mmol, 85.3% yield based on InI₃). ¹H NMR δ 0.29 (d, SiMe₃), ³J_{P-H} = 6.3 Hz. ¹³C NMR δ 2.62 (d, SiMe₃), ²J_{P-C} = 8.3 Hz. ³¹P NMR δ -153.54 (s, P(SiMe₃)₃), -12.98 (s, decomp). Anal. Calcd (found) for C₉H₂₇I₃InPSi₃: In, 15.39 (16.02); P, 4.15 (3.97); C, 14.49 (14.67); H, 3.65 (3.49); I, 51.03 (51.37). MS m/z 743 (C₉H₂₄I₃InPSi₃⁺), 683 (C₇H₁₆I₃InPSi₂⁺), 669 (C₆H₁₅I₃InPSi₂⁺), 595 (C₅H₁₄I₃InPSi⁺), 549 (C₆H₂₀I₂InPSi₂⁺), 496 (InI₃⁺), 429 (C₇H₁₆IInPSi₂⁺), 367 (InI₂⁺), 341 (C₃H₄IInPSi⁺), 242 (InI⁺), 147 (InP⁺). Crystals suitable for X-ray structure determination were grown from toluene at -15 °C in a Dri-Lab refrigerator.

Decomposition of I₃In-P(SiMe₃)₃ To Yield InP. I₃In-P(SiMe₃)₃ (0.180 g, 0.241 mmol) was placed in a sublimator and annealed under vacuum as described above. A red residue collected on the coldfinger, leaving a brown-black powder in the base of the sublimator, yield 0.030 g (0.206 mmol, 85.5% by I₃In-P(SiMe₃)₃), confirmed as InP by XRD, XPS, and EA. Anal. Calcd (found) for InP: In, 78.77 (64.31); P, 21.23 (19.75); C, 0.00 (0.83); H, 0.00 (0.28); I, 0.00 (≤0.50); In:P ratio in final product: 1.00:1.14.

X-ray Structural Solution and Refinement. Crystallographic data are summarized in Table 1. The crystal of 1 used was a colorless block which was mounted on a glass fiber with a viscous oil under a stream of cold dinitrogen. X-ray intensity data were recorded at -170 °C, and the structure was solved by direct methods. Full-matrix least-squares

Table 2. Interatomic Distances (angstroms) and Angles (degrees) for $\text{I}_3\text{InP}(\text{SiMe}_3)_3$ (1), with Estimated Standard Deviations in Parentheses

In(1)–I(1)	2.7252(15)	Si(1)–C(12)	1.838(21)
In(1)–I(2)	2.6975(14)	Si(1)–C(13)	1.892(20)
In(1)–I(3)	2.6914(16)	Si(2)–C(21)	1.89(3)
In(1)–P(1)	2.537(3)	Si(2)–C(22)	1.882(21)
P(1)–Si(1)	2.296(5)	Si(2)–C(23)	1.853(16)
P(1)–Si(2)	2.304(6)	Si(3)–C(31)	1.865(20)
P(1)–Si(3)	2.267(7)	Si(3)–C(32)	1.851(16)
Si(1)–C(11)	1.848(14)	Si(3)–C(33)	1.810(21)
I(1)–In(1)–I(2)	108.29(5)	C(11)–Si(1)–C(12)	109.1(8)
I(1)–In(1)–I(3)	109.53(5)	C(11)–Si(1)–C(13)	110.9(8)
I(1)–In(1)–P(1)	108.60(10)	C(12)–Si(1)–C(13)	113.0(10)
I(1)–In(1)–I(3)	111.18(5)	P(1)–Si(2)–C(21)	104.4(6)
I(2)–In(1)–P(1)	109.31(8)	P(1)–Si(2)–C(22)	107.2(9)
I(3)–In(1)–P(1)	109.87(10)	P(1)–Si(2)–C(23)	108.2(6)
In(1)–P(1)–Si(1)	108.51(17)	C(21)–Si(2)–C(22)	114.2(15)
In(1)–P(1)–Si(2)	108.28(21)	C(21)–Si(2)–C(23)	110.6(9)
In(1)–P(1)–Si(3)	108.58(21)	C(22)–Si(2)–C(23)	111.8(10)
Si(1)–P(1)–Si(2)	110.75(22)	P(1)–Si(3)–C(31)	109.1(12)
Si(1)–P(1)–Si(3)	110.29(24)	P(1)–Si(3)–C(32)	108.5(6)
Si(2)–P(1)–Si(3)	110.4(3)	C(31)–Si(3)–C(32)	109.7(8)
P(1)–Si(1)–C(11)	106.4(4)	C(31)–Si(3)–C(33)	110.8(12)
P(1)–Si(1)–C(13)	108.5(7)	C(32)–Si(3)–C(33)	111.3(10)

refinement with weights based upon counter statistics was performed. Hydrogen atoms were incorporated at their calculated positions using a riding model in the later iterations of refinement which converged at $R = 0.040$ ($R_w = 0.049$). A final difference Fourier synthesis revealed no unusual features (maximum 1.540, minimum $-1.290 \text{ e } \text{\AA}^{-3}$). Crystallographic calculations were performed using the NRCVAX¹⁶ suite of structure determination programs. For all structure-factor calculations, neutral atom scattering factors and their anomalous dispersion corrections were taken from ref 17. Interatomic distances and angles are given for 1 in Table 2. An ORTEP¹⁸ diagram showing the solid-state conformation and atom numbering scheme of 1 is presented in Figure 6. 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 Center.

Results and Discussion

Reaction of toluene solutions of indium(III) chloride and tris(trimethylsilyl)arsine resulted in the formation of a very fine dark brown-black powder which was subsequently annealed to drive the elimination of trimethylsilyl chloride to completion. The resulting product was then analyzed by X-ray powder diffraction (XRD). Reflections in the XRD pattern were evident at d spacings of 3.50, 2.14, and 1.82 \AA , corresponding to the (111), (220), and (311) zinc blende reflections of indium arsenide (Figure 1A).^{19a} Analysis of the XRD pattern using the Scherrer equation²⁰ gave an average domain size of approximately 9 nm, more than twice the average size of the 4 nm InAs particles reported by Uchida.⁷

The quantum confinement threshold for InAs has not, to our knowledge, been calculated. However it can be estimated using a method to calculate the Bohr radius of the exciton for a given semiconductor compound, eq

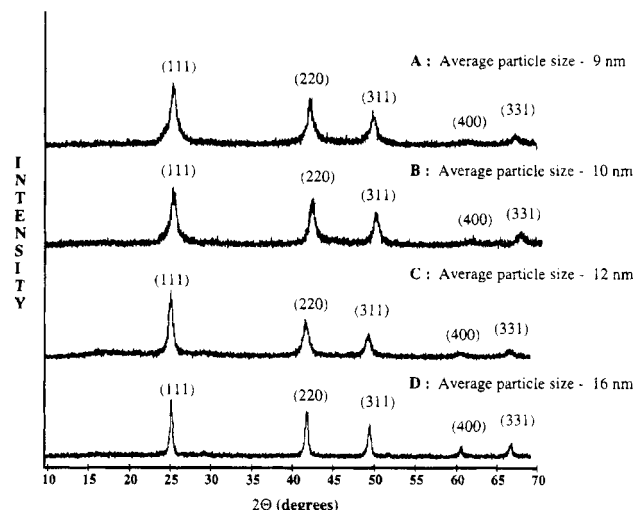


Figure 1. X-ray powder diffraction (XRD) spectra of InAs. (A) XRD of InAs prepared using InCl_3 according to eq 1. (B) XRD of InAs prepared according to eq 1, but using InBr_3 . (C) XRD of InAs prepared according to eq 1, but using InI_3 . (D) XRD of InAs prepared using InCl_3 according to eq 2.

2.^{21a} Using this equation and the constants provided

$$a_B = \left(\frac{h}{2\pi} \right)^2 \epsilon^2 \left[\frac{1}{m_e} + \frac{1}{m_h} \right] \quad (2)$$

in ref 22, the threshold diameter for quantum confinement for InAs was estimated to be 62.5 nm. This calculation places the domain size of InAs obtained from our preparation within the range for quantum confinement for InAs. The TEM image of these particles (Figure 2) clearly shows several overlapping nanocrystalline particles ranging in size from 8.4 to 22.4 nm. XPS spectra of this sample (Figure 3) displayed signals for the binding energies of indium ($\text{In } 3d_{5/2}$ BE = 444.5 eV) and arsenic ($\text{As } 2p_{3/2}$ BE = 1323.4 eV) which are those expected for InAs.²³ Some oxides of indium (In_2O_3) and arsenic (As_2O_3 , BE = 1326.6 eV) were observed to be present due to this sample's exposure to air; however, this layer was shallow and confined to the surface of the sample. A very small amount of chlorine was also detected, which is likely some unreacted InCl_3 . UV/vis analysis of this sample as a suspension in methanol showed an absorption edge at approximately 322 nm (Figure 4). The size of the particles contained in this sample can also be estimated based on this absorption threshold, utilizing an effective mass approximation model proposed by Brus (eq 3).²⁴ Using this equation

$$E = E_g + \left(\frac{h}{2\pi} \right)^2 \frac{\pi^2}{2R^2} \left(\frac{1}{m_e} + \frac{1}{m_h} \right) - \frac{1.8e^2}{\epsilon R} \quad (3)$$

and the constants provided in ref 22, the particle diameter in this InAs sample was estimated to be 4.4 nm. This differs by a factor of 2 from the values estimated by XRD and observed in TEM. It is possible that sonication and filtration of the particles could reduce the average particle size, but it is unlikely that such a large reduction would be seen based on these two factors alone.²⁵ By comparison, the particle diameter obtained by Uchida for InAs from UV/vis was 6.6 nm, slightly larger than but still in agreement with the corresponding TEM and XRD data of the same sample.

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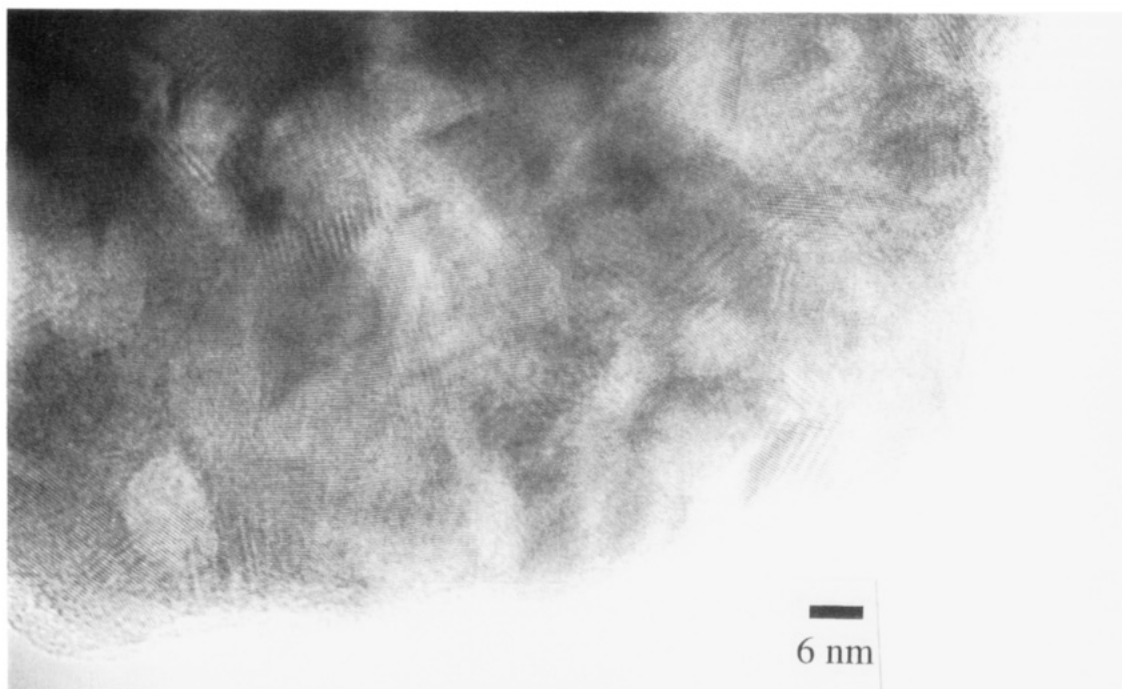
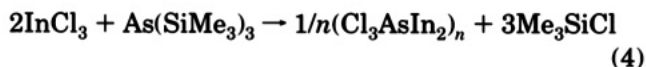


Figure 2. High-resolution TEM image of InAs nanocrystals from the 1:1 mole ratio reaction of InCl_3 with $\text{As}(\text{SiMe}_3)_3$.

Elemental analysis (EA) of the InAs obtained from the preparation described herein showed it to be 99.47% pure, with an In:As ratio of 1.00:1.03. Repeated preparations following the same procedure have yielded InAs in purities up to 99.96% by EA, with domain sizes, remaining at approximately 8–9 nm by XRD.

When indium(III) chloride was replaced with indium(III) bromide in our preparation, a fine reddish-brown powder resulted, which was annealed and analyzed by XRD. The XRD pattern of this material showed reflections corresponding to bona fide indium arsenide (Figure 1B), with an average domain size calculated to be 10 nm. Elemental analysis showed this material to be 99.65% pure indium arsenide, with a mole ratio of 1.00:1.00 for In:As. Similar results were obtained when the analogous reaction was conducted using indium(III) iodide (Figure 1C). The average domain size of these particles was calculated to be 12 nm. Elemental analysis indicated the product was InAs of 85.95% purity, with an In:As ratio of 1.10:1.00. The excess In seen in this sample is likely due to unreacted InI_3 . Differences in the domain size of these samples as compared to those reported by Uchida can be explained by two factors. The temperature of the solvent and the solvent itself could affect domain size by reducing interaction between InAs crystallites. Also, it has been recently observed in our laboratories that annealing of the product increases domain size. The smaller particles reported by Uchida were not annealed.

Interest in generating compounds analogous to those of formula $(\text{Cl}_3\text{EGa}_2)_n$ ($\text{E} = \text{As}, ^{3c}\text{P}^9$) was the motivation behind reactions involving a 2:1 mole ratio of an indium(III) halide with tris(trimethylsilyl)arsine, as described in eq 4. This reaction, when carried out using indium-



(III) chloride, gave a lustrous red-brown powder. Elemental analysis of this powder gave a ratio of 1.95:1.00 for In:As; however, the elemental composition found for this compound differed significantly from that

calculated for $(\text{Cl}_3\text{AsIn}_2)_n$. Upon annealing this powder in a sublimator under vacuum at 350 °C, a yellow solid condensed on the coldfinger. Since GaCl_3 was eliminated when analogous gallium-containing compounds were decomposed, this yellow substance was likely to be indium(III) chloride. Remaining in the base of the sublimator was a fine black powder, which was confirmed by XRD to be InAs of approximately 16 nm domain size (Figure 1D). Elemental analysis of this powder showed it to be 87.90% pure InAs, with an In:As ratio of 1.00:1.00.

Following a method modified from that reported by Barron et al.,¹² InCl_3 and $\text{P}(\text{SiMe}_3)_3$ were combined in a pentane slurry. The solution was sonicated for 20 min and then allowed to stir at room temperature for 2 days. The yellow "crude" powder obtained from this reaction corresponded roughly by EA and physical appearance to that described from Barron's preparation. Annealing this powder by the ramping method described *vide supra* resulted in a lustrous black powder. Reflections in the XRD spectrum of this sample corresponded with the published values for InP (Figure 5A).^{19b} Calculation of the particle size by the Scherrer equation gave the approximate average domain size to be 3.7 nm. This is somewhat larger than the InP particles synthesized by Nozik et al. from chloroindium oxalate and tris(trimethylsilyl)phosphine, which were reported to have an average domain size of 2.3 nm.¹⁴ Estimation of the minimum particle diameter required for quantum confinement effects by eq 2 resulted in a value of 16.4 nm for InP. The InP from our preparation was determined to be 91.53% pure by EA, with an In:P ratio of 1.00:1.09. This sample of InP was comparable with Barron's from a similar preparation in percentage of phosphorous found by EA (20.86% and 20.9%, respectively), as related

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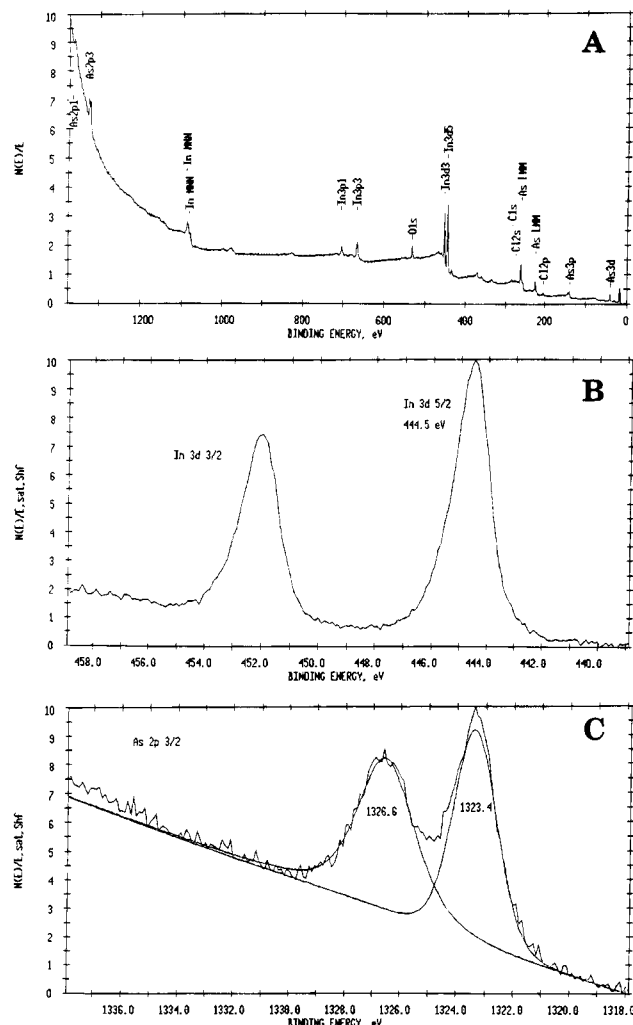


Figure 3. X-ray photoelectron spectra (XPS) of InAs from InCl_3 and $\text{As}(\text{SiMe}_3)_3$. (A) Survey scan of the InAs sample. (B) In region, showing the In 3d_{5/2} peak corresponding to InAs. (C) As region, showing As 2p_{3/2} peaks corresponding to InAs and As_2O_3 .

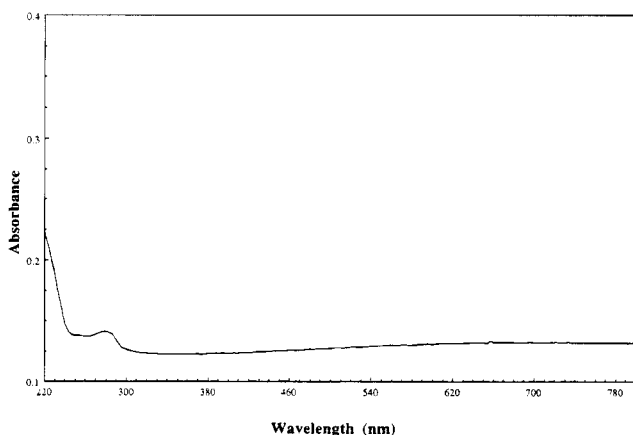


Figure 4. UV/vis spectrum of InAs (suspension in methanol) from InCl_3 and $\text{As}(\text{SiMe}_3)_3$.

to a bona fide sample of InP, which is calculated to have 21.23% P.

Replacement of InCl_3 with InBr_3 in this reaction resulted in a colored powder similar in analysis and appearance to that reported by Barron. Annealing of this sample produced a lustrous black powder. Reflections in the XRD spectrum corresponded with those for InP (Figure 5B).^{19b} Approximate average domain size was calculated to be 4.0 nm. Elemental analysis

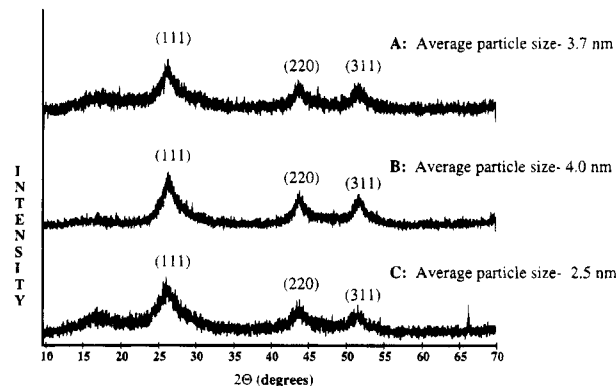


Figure 5. XRD spectra of InP. (A) XRD of InP prepared from the 1:1 mole ratio reaction of InCl_3 with $\text{P}(\text{SiMe}_3)_3$. (B) XRD of InP prepared from the 1:1 mole ratio reaction of InBr_3 with $\text{P}(\text{SiMe}_3)_3$. (C) XRD of InP prepared from the thermal decomposition of $\text{I}_3\text{In} \cdot \text{P}(\text{SiMe}_3)_3$.

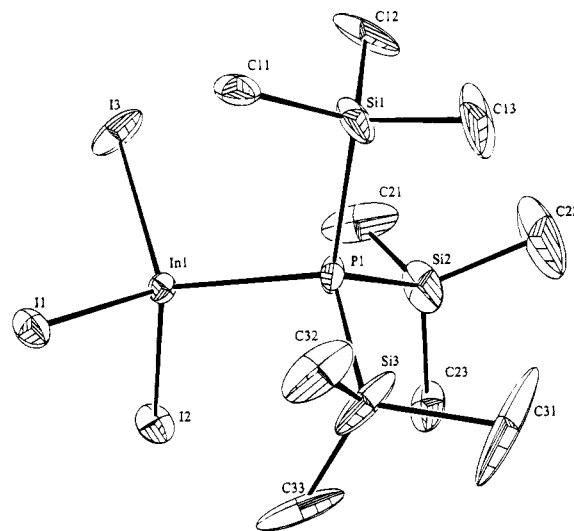


Figure 6. ORTEP diagram showing the solid-state structure of $\text{I}_3\text{In} \cdot \text{P}(\text{SiMe}_3)_3$ (1), with thermal ellipsoids at the 30% probability level. Hydrogen atoms have been omitted for clarity.

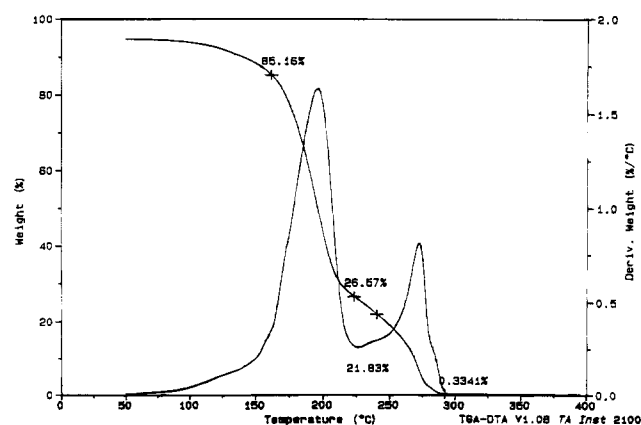


Figure 7. TGA/DTA spectrum of the decomposition of 1. The sample was heated under dynamic vacuum conditions.

reported 93.08% pure InP, with an In:P ratio of 1.00:1.03. Comparison of phosphorus contained in this and Barron's sample of InP synthesized by this method gives percentages of 20.28 and 20.8, respectively.

$\text{P}(\text{SiMe}_3)_3$ was then allowed to react with InI_3 in toluene/ether solution. The solution was stirred at room temperature for 2 days, during which time the solution turned from clear to slightly yellow. Upon freezing and thawing of the solution a white solid precipitated.

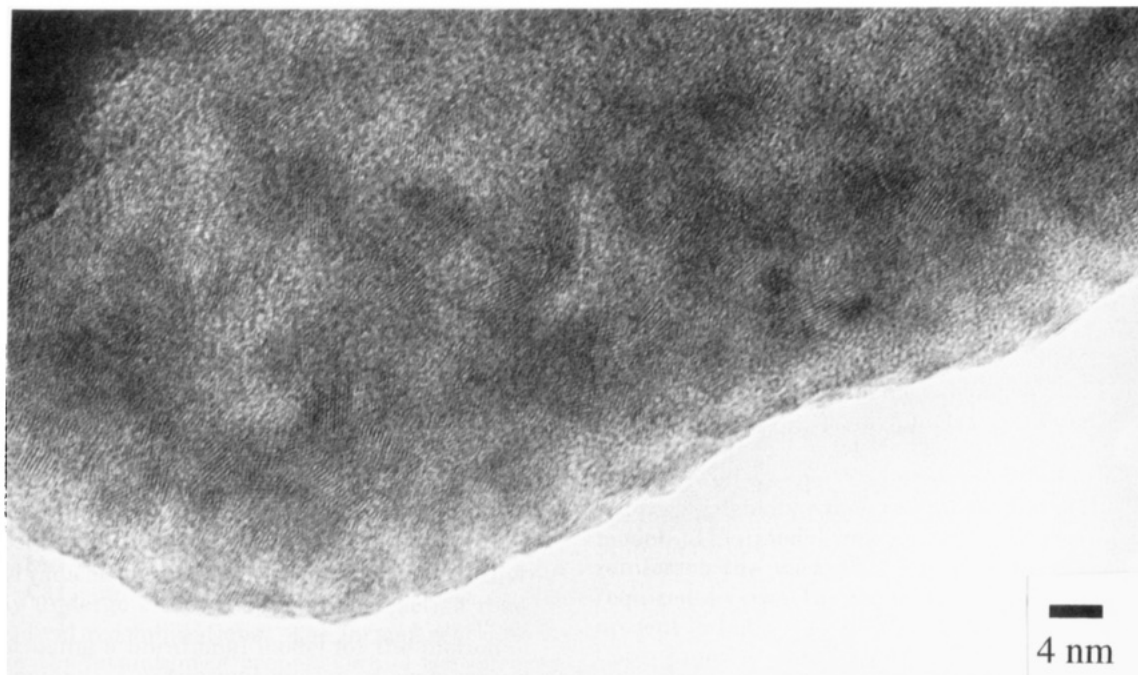


Figure 8. High-resolution TEM image of InP nanocrystals from the thermal decomposition of $\text{I}_3\text{InP}(\text{SiMe}_3)_3$.

Recrystallization from warm toluene afforded X-ray quality crystals. The structure of this sample was determined to be a 1:1 adduct, $\text{I}_3\text{InP}(\text{SiMe}_3)_3$ (**1**), which crystallizes in the monoclinic space group $P2_1/c$ (Figure 6, Table 1). The In–P bond length is 2.54 Å (Table 2), which is considerably shorter than those seen in two other In–P adducts isolated in our laboratory: $(\text{Me}_3\text{CCH}_2)_3\text{InP}(\text{SiMe}_3)_3$ (**2**, average 2.88 Å), and $\text{Me}(\text{Me}_3\text{CCH}_2)_2\text{InP}(\text{SiMe}_3)_3$ (**3**, average 2.80 Å).²⁶ This shorter In–P bond length is likely due to the smaller size of the iodines on the In as compared to the bulky organic substituents on the indium in the other adducts mentioned. When **1** is viewed down the In–P bond, it is clear that it crystallizes in a staggered configuration similar to that seen in one of the forms of both **2** and **3**, and its analogous Ga–As adduct, $\text{I}_3\text{GaAs}(\text{SiMe}_3)_3$.²⁷ Upon exposure to light or ambient atmosphere, **1** was found to rapidly decompose to a yellow powder. ^1H NMR spectra of **1** showed a doublet at δ 0.29 ($^3J_{\text{P-H}} = 6.3$ Hz) which is expected from splitting of the methyl proton resonance on the trimethylsilyl groups by the phosphorus atom. $^{13}\text{C}\{^1\text{H}\}$ NMR of **1** also displayed a doublet, occurring at δ 2.62 ($^2J_{\text{P-C}} = 8.3$ Hz). This signal is also expected as a result of the phosphorus atom splitting the methyl carbon resonance on the trimethylsilyl groups. The $^{31}\text{P}\{^1\text{H}\}$ spectrum of **1** showed a singlet at δ –153.54 and –12.90. The singlet at the lower ppm value is due to the phosphorus atom in **1**. Previous ^{31}P NMRs of the In–P adducts **2** and **3** gave phosphorus resonances at δ –246.60 and –245.16, respectively. It is likely that deshielding of the phosphorus atom by the iodines in **1** is the cause of the downfield shift observed in the ^{31}P signal, as no such effect would be expected from the alkyl groups of **2** and **3**. The singlet observed at δ –12.90 is likely a decomposition product from exposure of **1** to light in solution. The mass spectrum of **1** showed a cluster at 743 m/z

corresponding to $(\text{M} - 3\text{H})^+$. Several fragmentation peaks were also evident, including those expected from the elimination of **1** (549), **2** (341), and **3** (147) mol equiv of trimethylsilyl iodide from **1**.

It is interesting to note that in his previous reports, Barron described the product of this reaction as a polymer of formula $[\text{I}_2\text{InP}(\text{SiMe}_3)_2]_n$.¹² The temperature and reaction time were likely the factors which led to the different products observed. Barron combined InI_3 and $\text{P}(\text{SiMe}_3)_3$ at -78°C and allowed them to warm to room temperature and stir for 2 h before removing the solvents and characterizing the product. In contrast, the preparation presented above was conducted at room temperature and allowed to stir for 2 days. The longer reaction time and higher temperature are plausible explanations for the variance in product composition, as the reagents were allowed time to proceed to their most favored structure in the preparation described *vide supra*, while in Barron's reaction an intermediate was isolated.

Decomposition studies of **1** in a TGA/DTA instrument under vacuum conditions (Figure 7) showed the loss of 58.59 wt % at $150\text{--}225^\circ\text{C}$, and an additional 26.24 wt % loss at $240\text{--}280^\circ\text{C}$. These losses correspond well to a two-step elimination of trimethylsilyliodide (Me_3SiI) from **1**. For each mole of Me_3SiI lost, the weight percentage would be expected to decline by 26.82%. In the first step, 2 mol equiv of Me_3SiI was eliminated, with the loss of the final expected molar equivalent in the second step. The residue remaining after TGA analysis should total 19.54% of the original weight of **1**, corresponding to InP. However, in repeated TGA studies we have noticed that the weight percentage of the remnants of these runs has been close to zero, despite the presence of a small amount of brown-black powder in the crucible. Such an observation could be explained by the volatility of decomposition products of **1**. Upon repeated decomposition studies, an orange powder was seen in the vacuum line after the run was complete. A similar product forms on the coldfinger of the sublimator during bulk decomposition. Such a

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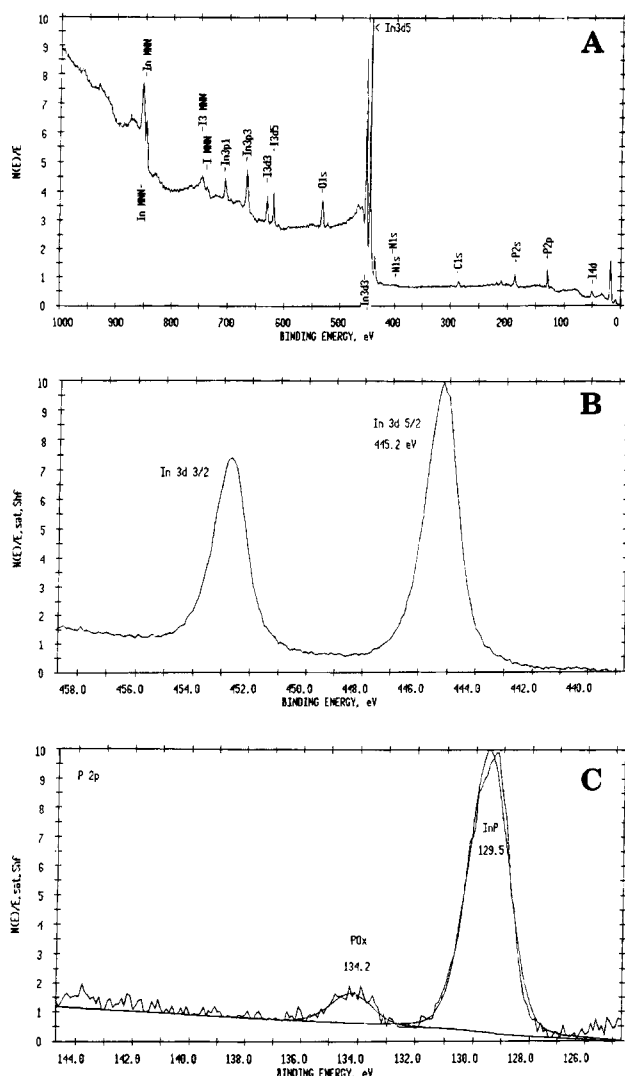


Figure 9. XPS spectra of InP obtained from the thermal decomposition of $\text{I}_3\text{InP}(\text{SiMe}_3)_3$. (A) Survey scan of the InP sample. (B) In region, showing the In $3d_{5/2}$ peak corresponding to InP. (C) P region, showing the P 2p peaks corresponding to InP and PO_x .

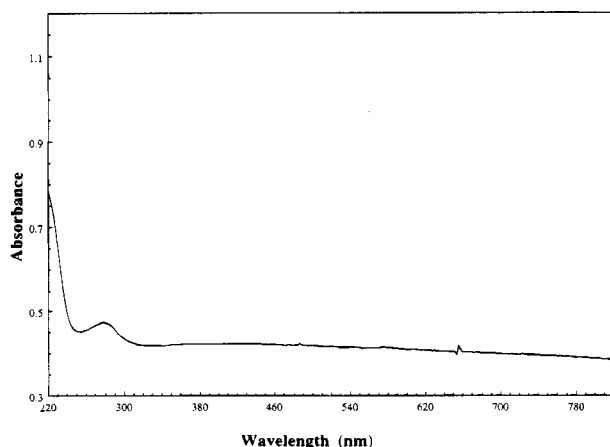


Figure 10. UV/vis spectrum of InP (suspension in methanol) obtained from the thermal decomposition of $\text{I}_3\text{InP}(\text{SiMe}_3)_3$.

volatile intermediate was also evident in the weight lost in the first elimination (58.59%), which is 4.95% high than that calculated for the loss of 2 mol equiv of Me_3SiH (53.64%). These observations, coupled with the small (ca. 20–30 mg) sample size employed in the TGA instrument, can explain the lack of a detectable remnant in the sample cup.

Despite the final weight percentage data from the TGA, compound **1** should still be expected to decompose directly to InP based on the percentage weight loss data and the fragmentation patterns in the mass spectrum. A sample of **1** was therefore annealed by the aforementioned ramping method to give a lustrous black powder. Reflections in the XRD spectrum corresponded with the literature values for InP (Figure 5C). The particle size was calculated to be 2.5 nm, comparable to the 2.3 nm described by Nozik. A TEM image of the sample shows InP nanocrystals (Figure 8) ranging in size from 2.5 to 5.5 nm. Binding energies found by XPS (Figure 9) for the indium (In $3d_{5/2}$ BE = 445.2 eV) and phosphorus (P 2p BE = 129.5 eV) in the sample were consistent with those expected for InP,^{28,29} and also with the values reported by Barron for InP obtained from InI_3 (P 2p 128.5 eV, In $3d_{5/2}$ 444.6 eV). Surface oxidation of this sample to In_2O_3 and PO_x (BE = 134.2 eV) was also observed in this sample as well as some InI_3 contamination. UV/vis analysis of this sample (Figure 10) showed a slow rise in absorption at 342 nm, corresponding by eq 3 to a particle diameter of approximately 3.1 nm. In contrast to the InAs case, these calculated diameters are comparable to those observed by XRD and TEM. This compares well with the 2.7 nm InP particle size estimated by Nozik.¹⁴ Nozik's data from UV/vis for InP also agreed with the corresponding XRD and TEM data. Elemental analysis of this sample indicated InP of 84.06% purity, with an In:P ratio of 1.00:1.14, and phosphorus content of 19.75%. Barron's sample of InP obtained from an oligomeric $[\text{I}_2\text{InP}(\text{SiMe}_3)_2]_x$ intermediate provided InP with a phosphorus content of 20.0%, comparable in purity to the aforementioned sample.

The successful preparation of nanocrystalline InAs and InP from the thermal decomposition and annealing of intermediate powders resulting from silyl cleavage reactions once again demonstrates the utility and versatility of this method to additional combinations of group 13 and group 15 elements. Decomposition of the single-source precursor **1** to nanocrystalline InP further supports this conclusion and demonstrates the feasibility of synthesizing particles of nanometer size domain from precursor compounds. Future work in this area will focus on additional 13–15 systems, including reactions and precursors to form ternary and quaternary compounds.

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Supplementary Material Available: Tables of non-hydrogen atom fractional coordinates and equivalent thermal parameters (3 pages); list of observed and calculated structure amplitudes (9 pages). Ordering information is given on any current masthead page.

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