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# *Communications*

## Formation of Indium Phosphide from $In(CH_3)_3$ and $P(Si(CH_3)_3)_3$

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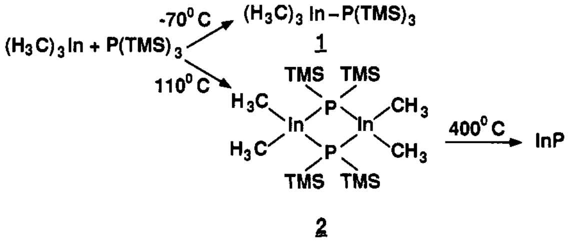
The preparation of indium phosphide is an important technological challenge to synthesis chemistry.[1] It is of particular importance to devise reactions that employ reagents that are volatile such that InP films can be deposited from the vapor. The prototypical such reaction is the formation of InP from trimethylindium, $In(CH_3)_3$, and phosphine, $PH_3$.[2] The danger associated with $PH_3$ is notorious[3] and has spurred the search for its replacement. In this communication we report that the reaction of trimethylindium, $In(CH_3)_3$, with tris(trimethylsilyl)phosphine, $P(TMS)_3$, gives InP. In this way $P(TMS)_3$ can be viewed as a direct replacement for $PH_3$. Since $P(TMS)_3$ is a liquid, it is intrinsically safer than the gas, $PH_3$. We were led to the reaction of $In(CH_3)_3$ with $P(TMS)_3$ by our observation[4] that the reaction of dimethylcadmium, $Cd(CH_3)_2$, with bis(trimethylsilyl)selenium, $Se(TMS)_2$, gives the II–VI compound CdSe and $Si(CH_3)_4$.

The reaction of $In(CH_3)_3$ with $P(TMS)_3$ does give InP, but at temperatures higher than those required in the CdSe analogue. When $In(CH_3)_3$ and $P(TMS)_3$ are combined at low temperature in pentane or toluene a one-to-one adduct, $(CH_3)_3InP(TMS)_3$, 1, is formed.[5] When we heat the same reagents to reflux in toluene $[(CH_3)_2InP(TMS)_2]_2$, 2 is formed in good yield.[6] It is the latter solid that gives polycrystalline InP when heated.[7] These results are summarized in the eq 1.



(1)

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(3) Reference 1, pp 29–31.

(4) Stuczynski, S. M.; Brennan, J. B.; Steigerwald, M. L. *Inorg. Chem.* **1989**, *28*, 4431.

(5) Preparation of 1 (conducted under inert atmosphere). $P(TMS)_3$ (Strem Chemicals, 0.39 g, 1.55 mmol) in 3 mL of pentane was added dropwise to a suspension of $In(CH_3)_3$ (Alfa, 0.25 g, 1.55 mmol) in 3 mL of pentane at −70 °C. The $In(CH_3)_3$ dissolved, and over the space of several hours 1 formed as a colorless crystalline solid (0.50 g, 78%). $^1H$ NMR (GE QE-300 spectrometer; $\delta$ in ppm relative to $Si(CH_3)_4$; $C_6D_6$ solvent) $\delta$ 0.25 (d, $J_{PH} = 4.7$ Hz, 27 H, $SiCH_3$), 0.01 (br s, 9 H, $InCH_3$). $^{13}C\{^1H\}$ NMR ($\delta$ in ppm relative to $Si(CH_3)_4$, $C_6D_6$ solvent) $\delta$ 2.98 (SiC), −6.37 (InC). Mp 210 °C (dec). The mass spectrum of this compound (included in the supplementary material) is consistent with $(CH_3)_3InP(TMS)_3$, showing the separate fragmentation of $In(CH_3)_3$ and $P(TMS)_3$ (see ref 8b).

(6) Preparation of 2 (conducted under inert atmosphere): $P(TMS)_3$ (1.55 g, 6.2 mmole) was added at room temperature to a solution of $In(CH_3)_3$ (0.99 g, 6.2 mmole) in 6 mL of toluene. The resulting solution was heated to reflux 18 h. At that point the mixture was cooled to room temperature, and 2 crystallized (1.70 g, 2.1 mmol, 85%). $^1H$ NMR ($\delta$ in ppm relative to $Si(CH_3)_4$, $C_7D_8$ solvent) $\delta$ 0.34 (t, $J_{PH} = 2.7$ Hz, 36 H, $SiCH_3$), 0.22 (t, $J_{PH} = 2.7$ Hz, 12 H, $InCH_3$). $^{31}P\{^1H\}$ NMR ($\delta$ in ppm relative to 85% $H_3PO_4$ (external), $C_7D_8$ solvent) $\delta$ −239.8. $^{13}C\{^1H\}$ NMR ($\delta$ in ppm relative to $Si(CH_3)_4$, $C_7D_8$ solvent) $\delta$ 4.34 (SiC), −3.63$\delta$ (InC). Mp 240–245 °C (dec). The mass spectrum of this compound shows (M + 1) peak at 645. Analysis (Analytische Laboratorien) for $C_136H_{48}In_2P_2Si_4$: C, H, In, P, Si.

(7) Pyrolysis of 2 to give InP. Compound 2 (125 mg, $1.9 \times 10^{-4}$ mol) was sealed under vacuum ($10^{-2}$ Torr) and heated at 400 °C for 22 h. This gave a black solid (53 mg) whose X-ray powder diffraction pattern shows InP with small interferences due to elemental In. EDS analysis shows InP (In/P molar ratio 1.07) with a small amount of Si contamination (≤2%).

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The acid–base adduct 1 forms readily at low temperature. It is an air-sensitive crystalline solid that is soluble in both aliphatic and aromatic hydrocarbons. The proton NMR spectrum of 1 shows the expected doublet for the TMS protons and a broad singlet for the methyl protons on indium. The mass spectrum is consistent with the assigned structure. A number of similar adducts between $In(CH_3)_3$ and Lewis bases have been reported.[1c,e,2,8]

Compound 2 is a colorless, crystalline solid that is soluble in typical organic solvents and reacts slowly with air. The mass spectrum of 2 shows the parent ion and a fragmentation pattern consistent with $[(CH_3)_2InP(TMS)_2]_2$. The proton NMR spectrum of 2 shows two triplets, as has been observed in the related compound $[(CH_3)_2GaP(t\text{-}Bu)_2]_2$.[9] The $^{31}P$ NMR and $^{13}C$ NMR spectra are both consistent with the assigned structure. To verify the assignment, we examined 2 crystallographically. The structure of 2 is similar to those of analogous, known compounds prepared by different routes;[1h,9,10] therefore details of the structure and its determination are included as supplementary material (see the paragraph at the end of the paper).

Tetramethylsilane is formed concomitantly with 2. Gentle heating of $In(CH_3)_3$ and $P(TMS)_3$ in the absence of solvent gives tetramethylsilane as the only observed low-boiling product.[11] This is analogous to the CdSe case[4] in which $Si(CH_3)_4$ was the only observed organic byproduct.

Powder X-ray diffraction shows that polycrystalline InP is formed in the vacuum thermolysis of 2 at 400 °C. There are also small reflections due to contamination from elemental In. Energy-dispersive X-ray analysis (EDS), Figure 1, is consistent with this. It shows the In/P molar ratio to be 1.07.

EDS shows that there is a small amount of Si contaminating this InP. The incorporation of silicon from silylated precursors is a cause for concern since silicon is an electronically active element. The data in Figure 1 show that the level of Si incorporation, although not zero, is not high. Even though contamination by silicon is unacceptable practically, the present results are encouraging since the crude thermolysis procedure we used gave almost complete removal of the silicon from the precursor solid. The potential for practical utility of the present reaction lies in vapor phase processing. In typical vapor-phase epitaxy (VPE)[1a] there is a constant and substantial carrier gas flow that allows for the continuous removal of contaminants. Were the present process adapted to film preparation, the likely contaminants (such as $Si(CH_3)_4$) would be removed as formed. To whatever extent the Si incorporation is due to long-term, high-temperature contact between the finely divided InP and $Si(CH_3)_4$ in our thermolysis, VPE processing would yield silicon-free InP. It is also possible that the silicon contamination is due to the inefficient diffusion of potential contaminants in the solid state. Since 2 was thermolyzed as a solid, species such as $Si(CH_3)_3$, $CH_3$, and/or $Si(CH_3)_4$ could have been trapped in the growing InP lattice. This will be a much less significant problem in vapor-phase processing.

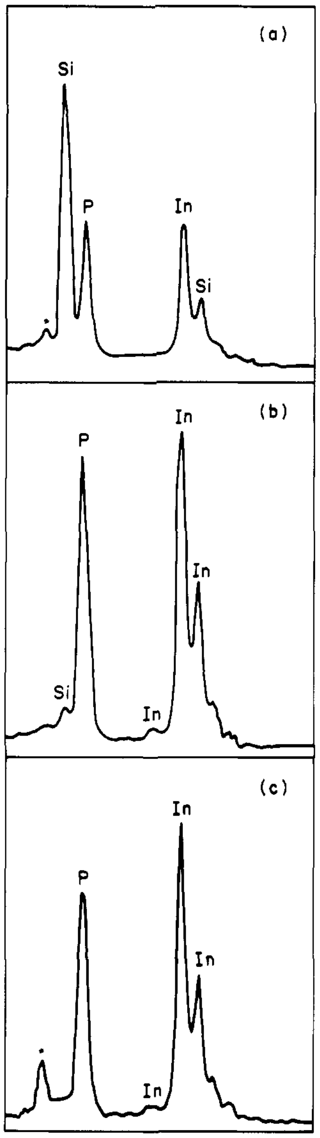

Figure 1. Energy-dispersive X-ray spectra. The peaks are labeled with the elements responsible for the fluorescence: (a) compound 2 (the asterisk indicates Al fluorescence due to the sample holder); (b) product of the pyrolysis of 2 (InP); (c) commercial InP.

Although $P(TMS)_3$ is a distillable liquid, its vapor pressure at room temperature is not high (bp 243 °C at 760 Torr). The benefit of the low vapor pressure is increased safety, but the drawback is that $P(TMS)_3$ is not volatile enough for atmospheric pressure VPE. The most important conclusion we draw from this work is that the trimethylsilyl groups in $P(TMS)_3$ are functional equivalents to the hydrogen atoms in $PH_3$. This suggests that the set of compounds $H_nP(TMS)_{3-n}$ will react essentially identically with $InMe_3$ (and similar metal alkyls). $HP(TMS)_2$ boils at 170 °C and $H_2P(TMS)$ boils at 78 °C;[12]

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(8) (a) Coates, G. E.; Whitcombe, R. A. *J. Chem. Soc.* **1956**, 3351. (b) Bradley, D. C.; Dawes, H.; Frigo, D. M.; Hursthouse, M. B.; Hussain, B. *J. Organomet. Chem.* **1987**, *325*, 55. (c) Foster, D. F.; Rushworth, S. A.; Cole-Hamilton, D. J.; Cafferty, R.; Harrison, J.; Parkes, P. *J. Chem. Soc., Dalton Trans.* **1988**, 7.

(9) Arif, A. M.; Benac, B. L.; Cowley, A. H.; Geerts, R.; Jones, R. A.; Kidd, K. B.; Power, J. M.; Schwab, S. T. *J. Chem. Soc., Chem. Commun.* **1986**, 1543.

(10) (a) Beachley, O. T.; Kopasz, J. P.; Zhang, H.; Hunter, W. E.; Atwood, J. L. *J. Organomet. Chem.* **1987**, *325*, 69. (b) Wells, R. L.; Purdy, A. P.; McPhail, A. T.; Pitt, C. G. *J. Organomet. Chem.* **1986**, *308*, 281. (c) Byrne, F. K.; Douglas, T.; Theopold, K. H. *Mater. Res. Soc. Symp. Proc.* **1989**, *131*, 59. (d) Alcock, N. W.; Degnan, I. A.; Wallbridge, M. G. H.; Powell, H. R.; McPartlin, M.; Sheldrick, G. M. *J. Organomet. Chem.* **1989**, *361*, C33.

(11) $In(CH_3)_3$ (319 mg, 2.0 mmol) and $P(TMS)_3$ (500 mg, 2.0 mmol) were combined without additional solvent in an argon-filled Schlenk tube equipped with a coldfinger condenser. The vessel was closed and the reagents were heated to 100 °C. Colorless liquid began to condense on the coldfinger. After 5 h the vessel was cooled, and this volatile liquid was vacuum transferred to a second Schlenk tube. The liquid was shown by $^1H$ NMR and mass spectroscopies to be pure $Si(CH_3)_4$. The solid was shown (by $^1H$ and $^{13}C$ NMR spectroscopies) to be a mixture of 1 and 2 (approximately 1:1) contaminated with very small amounts of unidentified side products.

(12) Maier, L. In *Organic Phosphorus Compounds*; Kosolapoff, G. M., Maier, L., Eds. Wiley-Interscience: New York, 1972; Vol. 1, Chapter 2.

therefore the vapor pressure of the $PH_3$ equivalent can be chosen to fit the particular experimental need.

While we have concentrated on phosphorus and phosphines in this work, we believe that the reaction technology is directly transferable to arsenic and arsines. For example, we expect that the reaction of $Ga(CH_3)_3$ with $As(TMS)_3$ will give GaAs under conditions that are similar to those we report for the preparation of InP. The relationship between structure, reactivity, and thermochemistry in the silylated arsines is expected to be the same as that in the phosphines, so we believe this prediction is warranted.

**Acknowledgment**. We gratefully acknowledge A. M. Mujsce for the determination of mass spectral data.

**Note added in proof**: After this paper was submitted it was reported that $Ga(CH_3)_3$ and $As(Si(CH_3)_3)_3$ react to give GaAs (Berry, A. D.; et al. Symposium E. MRS Fall Meeting, Boston, MA, 1990, paper E2.8).

**Supplementary Material Available:** Tables listing positional and thermal parameters for **2**, summarizing crystallographic data; table of distances and angles, and the mass spectrum of **1** (6 pages); table of calculated and observed structure factors (4 pages). Ordering information is given on any current masthead page.

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# Preparation of a Novel Gallium Arsenide Single-Source Precursor Having the Empirical Formula $AsCl_3Ga_2$

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Properly sized clusters/crystallites of the semiconductor gallium arsenide (GaAs) are expected to exhibit a range of interesting and useful properties, among them being superior nonlinear optical qualities.[1] Notwithstanding this potential, schemes for the facile synthesis and isolation of such particulates had not been forthcoming until recently. In 1990, Alivisatos et al.[2] reported that GaAs nanocrystals are produced by a specific dehalosilylation reaction (eq 1)

$$\underset{\mathbf{1}}{GaCl_3} + \underset{\mathbf{2}}{(Me_3Si)_3As} \rightarrow GaAs + 3Me_3SiCl \tag{1}$$

as initially carried out in our laboratories.[3] Furthermore, in some important experiments, they demonstrated that the same reaction carried out in quinoline afforded somewhat smaller crystallites that are soluble in pyridine as well as quinoline.[2]

Although the transformation described by eq 1 affords a relatively straightforward route to GaAs, both reactants must be manipulated in an inert atmosphere [*$(Me_3Si)_3As$ is pyrophoric*] by using appropriate equipment and laboratory technique. Thus, safer, less moisture- and air-sensitive precursors could well prove more useful and facilitate investigation of microcrystalline GaAs by those who may otherwise have to forego such studies due to the hazards and handling difficulties intrinsic to many gallium and arsenic compounds. Here we report that compounds **1** and **2** mixed in either a 2:1 or a 3:1 mole ratio react at room temperature to yield in each case the same relatively stable yellow solid product having the empirical formula $AsCl_3Ga_2$ (**3**, eq 2).[4]

$$\underset{\mathbf{1}}{2GaCl_3} + \underset{\mathbf{2}}{(Me_3Si)_3As} \rightarrow 1/n\underset{\mathbf{3}}{(AsCl_3Ga_2)_n} + 3Me_3SiCl \tag{2}$$

Upon heating, new single-source precursor **3** eliminates **1** via a novel reaction pathway to give microcrystalline GaAs (eq 3).[5]

$$1/n\underset{\mathbf{3}}{(AsCl_3Ga_2)_n} \rightarrow GaAs + \underset{\mathbf{1}}{GaCl_3} \tag{3}$$

Substance **3** possesses a number of properties that make it a potentially useful material, and for those accustomed to handling moisture- and air-sensitive compounds, its synthesis is not difficult. Although there was a variation in the percentages of impurities in the yellow material obtained from seven separate preparations, three complete and four partial elemental analyses are consistent with an As:Cl:Ga ratio of 1:3:2 (within experimental error). The X-ray powder pattern for **3** contained only broad, diffuse lines approximately centered on the corresponding major lines in the pattern obtained from a bona fide sample of GaAs. It should be noted that we have made no effort to date to optimize the reaction conditions or make special intensive efforts to purify the yellow powder; however, the apparently exclusive As, Cl, Ga empirical composition of **3** may prove invaluable for obtaining GaAs free of any

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[1] For example, see the following and references therein: (a) Steigerwald, M. L.; Brus, L. E. *Acc. Chem. Res.* **1990**, *23*, 183–188. (b) Dagani, R. *Chem. Eng. News* **1990**, *June 11*, 21–25. (c) Sandroff, C. J.; Harbison, J. P.; Ramesh, R.; Andrejco, M. J.; Hegde, M. S.; Hwang, D. M.; Chang, C. C.; Vogel, E. M. *Science* **1989**, *245*, 391–393.

[2] Olshavsky, M. A.; Goldstein, A. N.; Alivisatos, A. P. *J. Am. Chem. Soc.* **1990**, *112*, 9438.

[3] (a) Wells, R. L.; Pitt, C. G.; McPhail, A. T.; Purdy, A. P.; Shafieezad, S.; Hallock, R. B. *Chem. Mater.* **1989**, *1*, 4–6. (b) Wells, R. L.; Pitt, C. G.; McPhail, A. T.; Purdy, A. P.; Shafieezad, S.; Hallock, R. B. *Mater. Res. Soc. Symp. Proc.* **1989**, *131*, 45–50.

[4] Typical procedure for the preparation of $AsCl_3Ga_2$ (**3**); reactants mixed in a 2:1 mole ratio: In an argon filled Vacuum Atmospheres HE-43 Dri-Lab, $GaCl_3$ (**1**, 2.237 g, 12.91 mmol) was transferred to a 500-mL bulb (equipped with a Teflon valve and a magnetic stir bar) by using a small amount of dry pentane to facilitate transfer. Following degassing on a vacuum line and addition of dry pentane (175 mL) by distillation under high vacuum, the flask was returned to the Dri-Lab. Upon addition, by pipet, of $(Me_3Si)_3As$[6] (**2**, 1.900 g, 6.452 mmol, slightly diluted with dry pentane) to the solution of **1**, the precipitate that formed quickly changed from white to yellow. After stirring for 16 days at room temperature, removal of the volatiles in vacuo afforded **3** as a yellow solid (2.09 g, 101% yield; 102% yield based on $Me_3SiCl$, see below). Mp measurement behavior: >100 °C, sample began to darken; 280 °C, orange; 290 °C, red–orange, and colorless crystals (presumably $GaCl_3$) formed in the cooler portions of the capillary. Anal. Calcd (found) for $AsCl_3Ga_2$: C, 0.00 (6.17); H, 0.00 (0.89); As, 23.36 (21.11); Cl, 33.16 (29.70); Ga, 43.48 (38.80); Si, 0.00 (0.22) (As:Cl:Ga mol ratio = 1.00:3.06:1.98). The volatiles were shown to contain 19.8 mmol of $Me_3SiCl$ (102% of theoretical, based on **2**); determined as HCl after hydrolysis of volatiles and titration with standard NaOH.

[5] Typical procedure for the preparation of GaAs from $AsCl_3Ga_2$ (**3**): In an argon-filled Vacuum/Atmospheres HE-43 Dri-Lab, **3** (0.080 g, 0.25 mmol) was briefly washed once in boiling toluene, once in boiling benzene, and twice with hot pentane, and the resulting fine dry powder was carefully loaded into a sublimator equipped with a cold-finger condenser. Upon evacuation to 0.01 mTorr and slight warming with a heat gun to drive off any residual hydrocarbons, followed by the apparatus being sealed under static vacuum by a Teflon valve and heating from 40 to 260 °C over 1 h in an oil bath while cooling the condenser with tap water, small amounts of both yellow and white sublimates as well as an unsublimed orange powder were observed. Further heating for 22 h with a sand bath maintained between 380 and 410 °C gave additional yellow and white as well as orange sublimates and a black powder that on removal from the bottom of the sublimator and subsequent washing in the manner used for the precursor (vide supra), was shown to be microcrystalline GaAs (0.032 g, 90% yield). Anal. Calcd (found) for AsGa: C, 0.00 (5.17); H, 0.00 (0.35); As, 51.80 (47.94); Cl, 0.00 (2.41); Ga, 48.21 (44.95); Si, 0.00 (≤0.22) (As:Ga mol ratio = 1.00:1.01). X-ray powder diffraction pattern identical with that of a bona fide sample of GaAs. White sublimate, $GaCl_3$ (mp comparable to that of a bona fide sample, 74–76 °C).

[6] Becker, V. G.; Gutekunst, G.; Wessely, H. J. *Z. Anorg. Allg. Chem.* **1980**, *462*, 113–129.

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