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Preliminary Communication

An indium-phosphorus heterocubane as a new type of indium phosphide precursor

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Abstract

The first indium-phosphorus cubane, $[{}^{i}\mathrm{PrIn}(\mu_3\text{-}\mathrm{PSiPh}_3)]_4$ (**1**) has been prepared via the reaction of $\mathrm{Li}_2[\mathrm{PSiPh}_3]$ with $^{i}\mathrm{PrInI}_2$. The structure of **1** has been determined by X-ray analysis: monoclinic, space group $P2_1/c$ with $a = 15.611(3)$, $b = 25.767(2)$, $c = 22.541(6)$ Å, $\beta = 96.19(2)°$, and $Z = 4$. Polycrystalline films of indium phosphide have been grown on Si(100) wafers from **1** in a horizontal hot-wall reactor at 500°C. Compound **1** is unstable with respect to photolysis and electrochemical oxidation; however it is relatively stable toward alcoholysis.

The currently used approach to indium phosphide involves the thermal reaction of indium trialkyls or their adducts with phosphines. In view of the hazards associated with handling *e.g.* PH_3, and the drive toward achieving lower deposition temperatures, considerable interest is emerging in precursors that feature pre-existing bonds between indium and phosphorus. The single-source indium phosphide precursors reported thus far are of the general type $[\mathrm{R}_2\mathrm{In}(\mu\text{-}\mathrm{PR}'_2)]_2$ [1,2]. To our knowledge, there are no examples of more highly condensed species of empirical formula $[\mathrm{RIn}(\mu\text{-}\mathrm{PR}')]_n$. We report the synthesis and X-ray analysis of the first $\mathrm{In}_4\mathrm{P}_4$ cubane along with a preliminary study of its thermal decomposition.

A suspension of $\mathrm{Li}_2[\mathrm{PSiPh}_3]$ was prepared by lithiation of 1.5 g (5.12 mmol) of $\mathrm{Ph}_3\mathrm{SiPH}_2$ [3] with 6.5 ml of 1.6 M ^{n}BuLi in 30 ml of $\mathrm{Et}_2\mathrm{O}$ solution at −78°C. After allowing it to warm to room temperature, the lithium phosphide suspension was added slowly to a cooled (−78°C) suspension of $^{i}\mathrm{PrInI}_2$ [4] (2.1 g, 5.13 mmol) in 30 ml of $\mathrm{Et}_2\mathrm{O}$. The reaction mixture was allowed to reach ambient temperature, and stirring was continued for a further 6 h. After removal of the solvent and volatiles, the resulting yellow residue was extracted with 30 ml of toluene. The filtered solution was concentrated and stored at −20°C, resulting in a 58% yield of a pale yellow crystalline compound (m.p. 310°C, decomp.) of empirical composition $^{i}\mathrm{PrInPSiPh}_3$. The ^{31}P NMR spectrum of the product* displayed a singlet at δ −168.0, thus indicating the equivalence of all phosphorus atoms. The ^{1}H NMR spectrum* demonstrated the presence of ^{i}Pr and $\mathrm{Ph}_3\mathrm{Si}$ substituents. Extensive fragmentation was evident in the electron-impact mass spectrum*; however, the highest m/z peak in the chemical ionization spectrum was detected at 1793, thus suggesting the tetrameric formulation $[{}^{i}\mathrm{PrInPSiPh}_3]_4$. In order to confirm this suggestion, an X-ray diffraction study of $[{}^{i}\mathrm{PrInPSiPh}_3]_4$ was undertaken**; this compound crystallizes with one molecule of toluene in the crystal lattice. The important bond distances and angles are shown in Fig. 1 (caption). The skeletal structure consists of a cube of alternating indium and phosphorus atoms. The cube is slightly distorted in the sense that the average P–In–P and In–P–In angles are 88.8(1)° and 91.2(1)°, respectively. The average In–P bond distance of 2.591(4) Å is very similar to that reported for $\mathrm{In(P\text{-}{}^{t}Bu_2)_3}$ (2.592(14) Å) [5], but somewhat shorter than those in dimers of the type $[\mathrm{R_2InPR'_2}]_2$ (∼2.65 Å) [5–7]. The average indium–indium contact is 3.687(2) Å. Compounds with weak metal–metal interactions have attracted recent theoretical [8] and experimental attention. Short In(I)–

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* ^{1}H NMR ($\mathrm{C_6D_6}$, 300 MHz): δ 0.72 (d, 24H, $J = 7.5$ Hz, $\mathrm{(CH_3)_2CH}$); 1.18 (septet, 4H, $J = 7.5$ Hz, $\mathrm{(CH_3)_2CH}$); 7.12 (m, 36H, *meta* + *para*-H, Si–Ph); 7.69 (m, 24H, *ortho*-H, Si–Ph). ^{31}P NMR ($\mathrm{C_6D_6}$, 121.5 MHz): δ −168.0(s). Mass spectra: (EI, 70 eV), 808 ($\mathrm{M^+/2-2\,{}^{i}Pr}$), 592 ($\mathrm{M^+/2-Ph_3Si-{}^{i}Pr}$), 550 ($\mathrm{M^+/2-Ph_3Si-2\,{}^{i}Pr}$), 259 ($\mathrm{Ph_3Si^+}$), 181 ($\mathrm{Ph_2Si^+}$); (CI, $\mathrm{CH_4}$), 1793 ($\mathrm{M^+}$). Anal. Found: C, 55.98; H, 4.62. Calcd.: C, 56.27, H. 4.95%.

** Crystal data: $\mathrm{C_{91}H_{96}In_4P_4Si_4}$, pale yellow, 0.40 mm × 0.42 mm × 0.42 mm, monoclinic, $P2_1/c$ (no. 14); $a = 15.611(3)$, $b = 25.767(2)$, $c = 22.541(6)$ Å, $\beta = 96.19(2)°$, $Z = 4$; $V = 4014(15)$ Å^3; $T = 20°$C; FW = 1540.80; $D_c = 1.139$ g/cm^3; Mo Kα radiation, $\mu = 4.19$ cm^{-1}; 12,296 data collected $2.0° \leq 2\theta \leq 50°$; 5971 unique reflections with $I \geq 3.0\sigma(I)$, no absorption correction applied; refinement by full-matrix least squares, all non-hydrogen atoms anisotropic; 893 parameters, data-to-parameter ratio = 6.69; final $R = 0.0526$; $R_w = 0.0580$; error of fit = 6.31; largest residual density = 0.57 e Å^{-3} near In(4).

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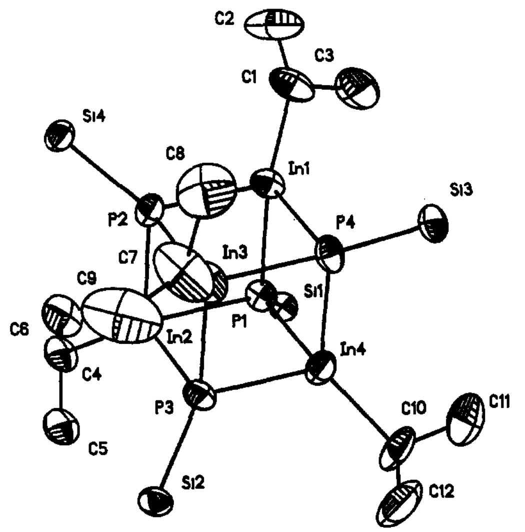

Fig. 1. View (ORTEP) of the structure of 1. Phenyl groups omitted for clarity. Important bond distances (Å) and angles (°): In(1)–P(2) 2.599(4), In(2)–P(2) 2.595(4), In(3)–P(2) 2.603(4), In(3)–P(4) 2.590(4), In(4)–P(1) 2.582(4), In(4)–P(4) 2.583(4) Å, P(1)–In(1)–P(2) 89.7(1), P(1)–In(1)–P(4) 87.3(1), P(2)–In(2)–P(3) 89.4(1), P(2)–In(3)–P(3) 89.3(1), P(3)–In(3)–P(4) 89.4(1), P(1)–In(4)–P(4) 87.6(1), P(3)–In(3)–P(4) 89.4(1), P(1)–In(4)–P(4) 87.6(1), P(2)–In(1)–P(4) 89.4(1), P(1)–In(3)–P(3) 89.3(1), P(3)–In(3)–P(4) 89.4(1), P(1)–In(4)–P(4) 87.6(1), P(2)–In(1)–P(4) 88.3(1), P(1)–In(2)–P(2) 89.2(1), P(1)–In(2)–P(3) 89.1(1), P(2)–In(3)–P(4) 88.1(1), P(1)–In(4)–P(3) 89.4(1) P(3)–In(4)–P(4) 88.9(1), In(1)–P(1)–In(4) 92.5(1), In(1)–P(2)–In(2) 90.7(1), In(2)–P(3)–In(3) 91.2(1), In(3)–P–In(4) 90.8(1), In(1)–P(4)–In(4) 92.6(1), In(1)–P(1)–In(2) 90.4(1), In(2)–P(1)–In(4) 90.4(1), In(1)–P(2)–In(3) 91.5(1), In(2)–P(3)–In(4) 91.1(1), In(1)–P(4)–In(3) 92.0(1), In(3)–P(4)–In(4) 90.8(1).

In(I) contacts have been observed in the dimer $[In\{C_5(CH_2Ph)_5\}]_2$ (3.631(2) Å) [9], the hexamer $[In(C_5Me_5)]_6$ (3.942(1)–3.963(1) Å) [10] and the polymers $[In(C_5H_5)]_\infty$ and $[In(C_5H_4Me)]_\infty$ [11]. To our knowledge the only other short In(III)–In(III) contact is that in the *closo*-indacarborane dimer $1\text{-}[(Me)_2CH]\text{-}1\text{-}In^{III}\text{-}2,3\text{-}(SiMe_3)_2\text{-}2,3,\text{-}C_2B_4H_4$ (3.696(1) Å) [12].

Polycrystalline films of indium phosphide have been grown on Si(100) wafers from the heterocubane precursor in a horizontal hot-wall reactor at 500°C. The films were characterized by X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD). The XPS signals establish an In/P stoichiometry of 1:1. The XRD indicates that (a) the InP film is polycrystalline with a particle size in the range 150–200 Å, and (b) the zinc blende structure is adopted [13].

Compound 1 is unstable with respect to both photolysis and electrochemical oxidation. The electronic absorption spectrum of 1 exhibits maxima at 294, 324, and 354 nm; moreover, the tail of the highest wavelength peak extends into the visible, thus accounting for the pale yellow color of the solid. Irradiation of a toluene solution of 1 at 45°C with 254 nm light results in the appearance of new $^{31}P\{^1H\}$ NMR peaks at δ -117.9(s), -155.3(m), and -156.5(s), together with a complex multiplet in the range -160.7 to -164.5. These photoproducts have not yet been identified. Cyclic voltammetry experiments (10^{-3} M in DMF, 25°C, 0.1 M $[^nBu_4N][BF_4]$ supporting electrolyte, sweep rate 200 mV/s) reveal an irreversible oxidation at +0.96 V *vs.* SCE. Interestingly, 1 is relatively stable toward alcoholysis. Thus, treatment with 16 equiv. of EtOH in C_6D_6 resulted in only trace quantities of Ph_3SiPH_2 after 1 h at 25°C (on the basis of ^{31}P NMR signal intensities). Heating this solution to 70°C for 1 h resulted in ~10% conversion to Ph_3SiPH_2. In the case of ^tBuOH, the alcoholysis reaction is significantly slower, presumably due to the increase in steric bulk of the alkyl group. Efforts are underway to synthesize In_4P_4 and Ga_4As_4 cubanes with smaller substituents with a view to increasing the reactivity toward mild protic reagents.

Acknowledgments

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