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Use of Organoindium Hydrides for the Preparation of Organoindium Phosphides. Synthesis and Molecular Structure of $[(Me_3CCH_2)_2InP(t\text{-}Bu)_2]_2$

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The indium phosphide $[(Me_3CCH_2)_2InP(t\text{-}Bu)_2]_2$ has been prepared from $K[In(CH_2CMe_3)_3H]$ and $ClP(t\text{-}Bu)_2$ in pentane. When $In(CH_2CMe_3)_3$ and $HP(t\text{-}Bu)_2$ were present in a 1:1 mol ratio, heating to 105–115 °C for 5 days was required, whereas when $In(CH_2CMe_3)_3$ and $HP(t\text{-}Bu)_2$ were in a 5:1 mol ratio in pentane solution, the desired indium product formed in 6 days at room temperature. Excess phosphine, $In(CH_2CMe_3)_3$, and $HP(t\text{-}Bu)_2$ in a 1:5 mol ratio in pentane, significantly retarded the rate of formation of $[(Me_3CCH_2)_2InP(t\text{-}Bu)_2]_2$. Thermal decomposition of $[(Me_3CCH_2)_2InP(t\text{-}Bu)_2]_2$ to form InP occurred at 245 °C in 1 h. The compound $[(Me_3CCH_2)_2InP(t\text{-}Bu)_2]_2$ crystallizes in the centrosymmetric orthorhombic space group *Pbcn* (No. 60) with $a = 11.742(3)$ Å, $b = 20.194(6)$ Å, $c = 17.909(4)$ Å, $V = 4246(2)$ Å^3, and $Z = 4$. The structure was solved and refined to $R = 6.68\%$ and $R_w = 6.24\%$ for all 4920 independent reflections and $R = 2.76\%$ and $R_w = 3.47\%$ for those 2525 reflections with $|F_o| > 6.0\sigma(|F_o|)$. The molecule lies on a 2-fold axis which passes through the two indium atoms and requires that the In_2P_2 core be strictly planar.

Compounds of the type $R_2MER'_2$ (M = group 13 element, E = group 15 element) are OMCVD precursors for the preparation of group 13–15 materials such as GaAs[1,3–5] and InP.[2] The original and simplest synthetic route to $R_2InPR'_2$ is probably a hydrocarbon elimination reaction[6–13] between InR_3 and HPR'_2. Metathesis reactions[9,10,14] are also useful for the preparation of $R_2InPR'_2$ but require preparation of InR_2X (X = Cl, Br, I) and $M'ER'_2$ (M = Li, Na, K). Similarly, the Me_3SiCl elimination reaction[15,16] requires the syntheses of InR_2X and $(Me_3Si)PR'_2$. A goal of our research has been to develop a scheme for the synthesis of $R_2InPR'_2$ which would take advantage of the simplicity of the elimination reaction but which would not require the prior synthesis and handling of HPR'_2. Ideally, the secondary phosphine should be formed and then consumed by reaction with the organoindium compound. These concepts have been applied successfully to the synthesis of $[(Me_3CCH_2)_2InP(t\text{-}Bu)_2]_2$ from $K[In(CH_2CMe_3)_3H]$[17] and $ClP(t\text{-}Bu)_2$ in pentane. The new indium phosphide derivative has been prepared in high yield and has been fully characterized, but it was too insoluble in benzene for a cryoscopic molecular weight study.

The reaction of $K[In(CH_2CMe_3)_3H]$ and $ClP(t\text{-}Bu)_2$ leads to the formation of $In(CH_2CMe_3)_3$ and $HP(t\text{-}Bu)_2$ (eq 1) in high, if not quantitative, yield. These reaction

$$K[In(CH_2CMe_3)_3H] + ClP(t\text{-}Bu)_2 \xrightarrow{C_5H_{12}} (Me_3CCH_2)_3InP(H)(t\text{-}Bu)_2 + KCl \quad (1)$$

products subsequently undergo the elimination reaction under appropriate conditions to form $[(Me_3CCH_2)_2InP(t\text{-}Bu)_2]_2$ and neopentane (eq 2). When $In(CH_2CMe_3)_3$ and

$$(Me_3CCH_2)_3InP(H)(t\text{-}Bu)_2 \rightarrow [(Me_3CCH_2)_2InP(t\text{-}Bu)_2]_2 + CMe_4 \quad (2)$$

$HP(t\text{-}Bu)_2$ were present in a 1:1 mol ratio, heating to 105–115 °C for 5 days was necessary to effect the formation of $[(Me_3CCH_2)_2InP(t\text{-}Bu)_2]_2$ in high (~90%) yield. However, when $In(CH_2CMe_3)_3$ and $HP(t\text{-}Bu)_2$ were in a 5:1 mol ratio in pentane solution, large, colorless crystals of the desired indium product formed in 6 days at room temperature. When $In(CH_2CMe_3)_3$ and $HP(t\text{-}Bu)_2$ were present in a 1:5 mol ratio in pentane solution, no $[(Me_3CCH_2)_2InP(t\text{-}Bu)_2]_2$ was formed, even after 1 month. Apparently, excess $In(CH_2CMe_3)_3$ enhances the rate of the elimination reaction. The simple adduct $(Me_3CCH_2)_3InP(H)(t\text{-}Bu)_2$ probably is not involved in the actual

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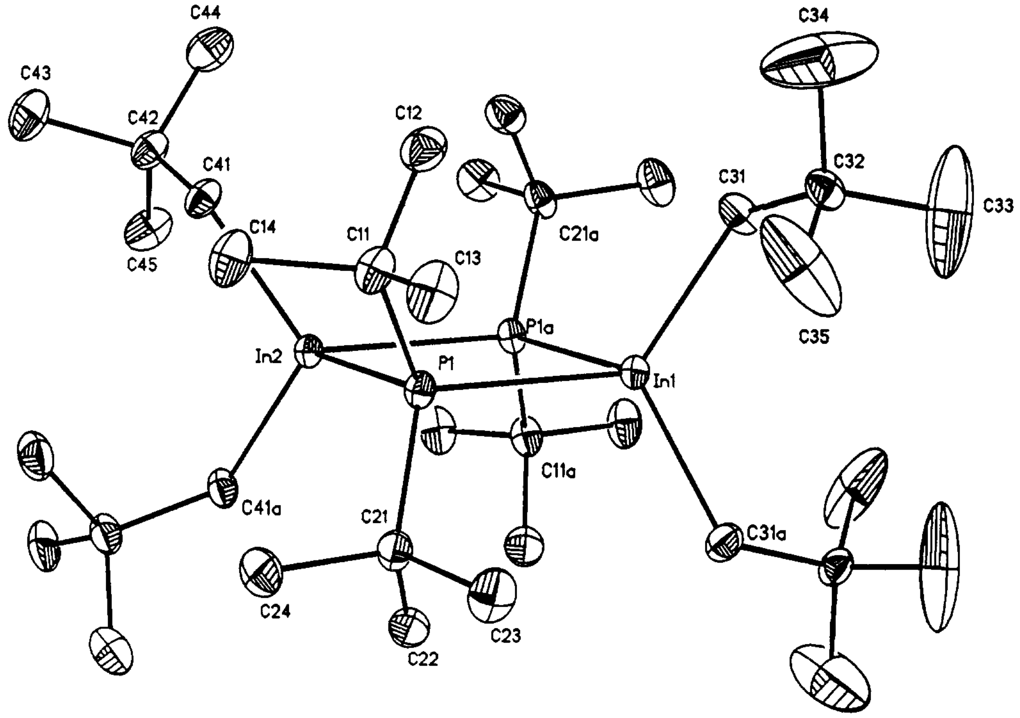

Figure 1. Labeling of atoms in the $[(Me_3CCH_2)_2InP(t\text{-}Bu)_2]_2$ molecule [ORTEP II diagram, with all hydrogen atoms omitted].

elimination reaction at room temperature. If the simple 1:1 adduct had kinetic significance for the elimination reaction, excess $In(CH_2CMe_3)_3$ as well as excess $HP(t\text{-}Bu)_2$ should have increased the rate of elimination similarly. It is also noteworthy that $K[In(CH_2CMe_3)_3H]$ does not deprotonate preformed $HP(t\text{-}Bu)_2$ to form $KP(t\text{-}Bu)_2$, H_2, and $In(CH_2CMe_3)_3$.

The elimination reactions between stoichiometric quantities of $HP(t\text{-}Bu)_2$ and $InMe_3$[11,13] and $InEt_3$[12] have been reported previously. The neat reagents $InMe_3$ and $HP(t\text{-}Bu)_2$ required heating[11] to 170 °C for 6 h to effect formation of $[Me_2InP(t\text{-}Bu)_2]_2$ whereas the preparation of $[Et_2InP(t\text{-}Bu)_2]_2$ utilized a refluxing hexane solution (~70 °C).[12]

The nature of the simple adduct $(Me_3CCH_2)_3In{\cdot}P(H)(t\text{-}Bu)_2$ has been investigated by freezing point depression studies in benzene and by ^1H and ^{31}P NMR spectroscopy.

$$(Me_3CCH_2)_3In{\cdot}P(H)(t\text{-}Bu)_2 \overset{K_d}{\rightleftarrows} In(CH_2CMe_3)_3 + HP(t\text{-}Bu)_2 \quad (3)$$

The equilibrium constant for the dissociation of the adduct in benzene has been calculated from cryoscopic data at ~5 °C to be 0.011 ± 0.002 (K_d), which is comparable to the K_d of 9.1×10^{-3} for the dissociation of $HMe_2Al{\cdot}N(Me)(Ph)(H)$[18] at −63 °C. The K_d of the adduct $HMe_2Al{\cdot}P(Me)(Ph)(H)$[19] is 0.38 at 22 °C. The NMR spectroscopic data for $(Me_3CCH_2)_3In{\cdot}P(H)(t\text{-}Bu)_2$ indicate rapid exchange between the components of the equilibrium. Consequently, the ^1H and ^{31}P NMR chemical shifts and coupling constant data depend upon the phosphorus to indium ratio. Extrapolation of these data to $HP(t\text{-}Bu)_2$:$In(CH_2CMe_3)$ of zero provided nominal data for pure adduct as $^{31}P(\delta)$ 14.70 ppm (dm, ^1J = 269 Hz, ^3J = 12.9 Hz) and $^1H(\delta)$ 3.24 ppm (d, PH, ^1J = 269 Hz). It is also of interest that the adduct $(Me_3CCH_2)_3In{\cdot}P(H)(t\text{-}Bu)_2$ reacts with KH to form $K[In(CH_2CMe_3)_3H]$ and free $HP(t\text{-}Bu)_2$. Thus, $HP(t\text{-}Bu)_2$ can be readily isolated from the reaction of $K[In(CH_2CMe_3)_3H]$ with $ClP(t\text{-}Bu)_2$, if excess KH is present.

A single-crystal X-ray structural study of $[(Me_3CCH_2)_2InP(t\text{-}Bu)_2]_2$ shows that this compound consists of discrete molecular units of $[(Me_3CCH_2)_2InP(t\text{-}Bu)_2]_2$ separated by normal van der Waals distances. The labeling of atoms is provided in Figure 1. Distances and angles are collected in Table I. The molecule has precise C_2 symmetry, with atoms In(1) and In(2) lying on a crystallographic 2-fold axis. This requires that the In_2P_2 core be strictly planar. Indium–phosphorus distances are In(1)–P(1) = In(1)–P(1A) = 2.712(1) Å and In(2)–P(1) = In(2)–P(2A) = 2.690(1) Å (average = 2.701 Å). Internal angles at indium are P(1)–In(1)–P(1A) = 83.0(1)° and P(1)–In(2)–P(1A) = 83.8(1)° (average P–In–P = 83.4°); internal angles at phosphorus are symmetry equivalent, with In(1)–P(1)–In(2) = In(1)–P(1A)–In(2) = 96.6(1)°. Cross-ring distances are clearly nonbonding, with In(1)···In(2) = 4.033 Å and P(1)···P(1A) = 3.515 Å.

Two neopentyl groups are associated with each indium atom, with indium–carbon distances of In(1)–C(31) = In(1)–C(31A) = 2.206(5) Å and In(2)–C(41) = In(2)–C(41A) = 2.219(4) Å (average In–C = 2.213 Å). Interligand angles are C(31)–In(1)–C(31A) = 117.7(2)° and C(41)–In(2)–C(41A) = 112.7(2)°. The P–In–C(neopentyl) angles are not equivalent. Thus P(1)–In(1)–C(31) = 116.6(1)° as compared to P(1A)–In(1)–C(31) = 109.1(1)° and P(1A)–In(2)–C(41) = 119.2(1)° as compared to P(1)–In(2)–C(41) = 109.7(1)°. The C–In–C planes are therefore not precisely perpendicular to the In_2P_2 core. Thus, the C(31)–In(1)–C(31A) plane is oriented at 83.9° to the In_2P_2 core while the C(41)–In(2)–C(41A) plane is oriented at 97.8° to the In_2P_2 core. We note here that the neopentyl groups attached to In(2) are well behaved with normal vibration ellipsoids (see Figure 1) and normal carbon–carbon bond lengths (C(41)–C(42) = 1.552(6) Å and C(42)–CH_3 distances of 1.538(6), 1.529(6), and 1.530(6) Å). In contrast

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Table I. Bond Lengths and Bond Angles for $[(Me_3CCH_2)_2InP(t\text{-}Bu)_2]_2$

In(1)–P(1)	2.712(1)	In(1)–C(31)	2.206(5)
In(1)–P(1A)	2.712(1)	In(1)–C(31A)	2.206(5)
In(2)–P(1)	2.690(1)	In(2)–C(41)	2.219(4)
In(2)–P(1A)	2.690(1)	In(2)–C(41A)	2.219(4)
P(1)–C(11)	1.895(4)	P(1)–C(21)	1.891(4)
C(11)–C(12)	1.529(6)	C(11)–C(13)	1.536(6)
C(11)–C(14)	1.534(6)	C(21)–C(22)	1.540(6)
C(21)–C(23)	1.526(6)	C(21)–C(24)	1.541(6)
C(31)–C(32)	1.539(6)	C(32)–C(33)	1.455(8)
C(32)–C(34)	1.449(8)	C(32)–C(35)	1.457(7)
C(41)–C(42)	1.552(6)	C(42)–C(43)	1.538(6)
C(42)–C(44)	1.529(6)	C(42)–C(45)	1.530(6)
P(1)–In(1)–C(31)	116.6(1)	P(1)–In(1)–P(1A)	83.0(1)
C(31)–In(1)–P(1A)	109.1(1)	P(1)–In(1)–C(31A)	109.1(1)
C(31)–In(1)–C(31A)	117.7(2)	P(1A)–In(1)–C(31A)	116.6(1)
P(1)–In(2)–C(41)	109.7(1)	P(1)–In(2)–P(1A)	83.8(1)
C(41)–In(2)–P(1A)	119.2(1)	P(1)–In(2)–C(41A)	119.2(1)
C(41)–In(2)–C(41A)	112.7(2)	P(1A)–In(2)–C(41A)	109.7(1)
In(1)–P(1)–In(2)	96.6(1)	In(1)–P(1)–C(11)	116.7(1)
In(2)–P(1)–C(11)	110.6(1)	In(1)–P(1)–C(21)	109.6(1)
In(2)–P(1)–C(21)	112.6(1)	C(11)–P(1)–C(21)	110.2(2)
P(1)–C(11)–C(12)	105.9(3)	P(1)–C(11)–C(13)	113.8(3)
C(12)–C(11)–C(13)	109.1(4)	P(1)–C(11)–C(14)	111.9(3)
C(12)–C(11)–C(14)	107.6(3)	C(13)–C(11)–C(14)	108.2(3)
P(1)–C(21)–C(22)	105.8(3)	P(1)–C(21)–C(23)	112.6(3)
C(22)–C(21)–C(23)	108.1(3)	P(1)–C(21)–C(24)	112.4(3)
C(22)–C(21)–C(24)	108.8(3)	C(23)–C(21)–C(24)	109.0(3)
In(1)–C(31)–C(32)	124.9(3)	C(31)–C(32)–C(33)	110.8(5)
C(31)–C(32)–C(34)	109.5(5)	C(33)–C(32)–C(34)	106.8(8)
C(31)–C(32)–C(35)	115.0(4)	C(33)–C(32)–C(35)	106.2(5)
C(34)–C(32)–C(35)	108.2(6)	In(2)–C(41)–C(42)	124.2(3)
C(41)–C(42)–C(43)	109.0(3)	C(41)–C(42)–C(44)	111.0(3)
C(43)–C(42)–C(44)	108.0(4)	C(41)–C(42)–C(45)	112.6(3)
C(43)–C(42)–C(45)	108.1(4)	C(44)–C(42)–C(45)	108.0(4)

to this, the neopentyl groups attached to In(1) are associated with substantial librational motion about the C(31)–C(32) axis, which results in artificial librational shortening of the C(32)–CH_3 bonds (i.e., C(31)–C(32) = 1.539(6) Å but C(32)–C(33) = 1.455(8) Å, C(32)–C(34) = 1.449(8) Å, and C(32)–C(35) = 1.457(7) Å).

The $P(t\text{-}Bu)_2$ ligands with phosphorus–carbon distances of P(1)–C(11) = 1.895(4) Å and P(1)–C(21) = 1.891(4) Å (average P–C = 1.893 Å) also are not strictly perpendicular to the In_2P_2 plane. The C(11)–P(1)–C(21) plane makes an angle of 88.6° with the In_2P_2 plane. The In–P–C angles are inequivalent, with In(1)–P(1)–C(11) = 116.7(1)° as compared to In(1)–P(1)–C(21) = 109.6(1)° and In(2)–P(1)–C(21) = 112.6(1)° as compared to In(2)–P(1)–C(11) = 110.6(1)°.

The structure of $[(Me_3CCH_2)_2InP(t\text{-}Bu)_2]_2$ can be compared with the closely related structures of $[Me_2InP(t\text{-}Bu)_2]_2$[11] and $[Et_2InP(t\text{-}Bu)_2]_2$.[12] Important distances and angles are compared in Table II. The indium–phosphorus and indium–carbon distances in the neopentyl derivative are significantly longer than those in the methyl and ethyl compounds. It is also noteworthy that the indium atoms are further apart in the neopentyl derivative because the P–In–P angles are the smallest of the three compounds. This decreased P–In–P angle might be the result of the larger C–In–C angle needed to keep the more sterically demanding neopentyl ligands apart. The In–P–In angles are also largest for the neopentyl derivative.

The complete characterization of an organoindium phosphide requires the determination of the degree of association of the compound in the solid, solution, and gas phases, if possible. The X-ray structural study demonstrated the existence of the dimer $[(Me_3CCH_2)_2InP(t\text{-}Bu)_2]_2$ as the solid. The low solubility of $[(Me_3CCH_2)_2InP(t\text{-}Bu)_2]_2$ in benzene solution prevented cryoscopic molecular weight studies. Thus, none of the three known *tert*-butyl phosphide derivatives are sufficiently soluble in benzene for molecular weight studies even though all are simple dimers in the solid state.[11,12] The methyl derivative[11] $Me_2InP(t\text{-}Bu)_2$ was even too insoluble in benzene for NMR studies. Even though molecular weight studies were impossible, the ^1H NMR spectrum of $(Me_3CCH_2)_2InP(t\text{-}Bu)_2$ is consistent with the existence of dimers in benzene solution. The resonances for the *tert*-butyl group protons are two overlapping doublets which appear like a triplet. The *tert*-butyl protons are thus coupled to two phosphorus atoms in the four-membered ring. The mass spectrum of $(Me_3CCH_2)_2InP(t\text{-}Bu)_2$ suggests the existence of monomers in the gas phase. In contrast, the mass spectrum of $Me_2InP(t\text{-}Bu)_2$ demonstrated the presence of dimers.[11]

The thermolysis of $[(Me_3CCH_2)_2InP(t\text{-}Bu)_2]_2$ at 245 °C for 1 h in a sealed tube leads to the formation of InP with relatively low contamination by carbon and hydrogen (0.41% C and 0.04% H). The identity of the black solid remaining in the tube as InP was verified by X-ray powder diffraction data and an XPS spectrum. Good quality InP has also been grown from $[Me_2InP(t\text{-}Bu)_2]_2$ at 350–480 °C under OMCVD conditions.[2] Preliminary data indicated that $[Me_2InP(t\text{-}Bu)_2]_2$ decomposed at 240 °C whereas $[(Me_3CCH_2)_2InP(t\text{-}Bu)_2]_2$ decomposed at a lower temperature, 200–202 °C. The lower temperature required for $[(Me_3CCH_2)_2InP(t\text{-}Bu)_2]_2$ might be due to its more facile dissociation to monomers. The more bulky neopentyl groups provide longer and supposedly weaker indium–phosphorus ring bonds which could make the monomer more accessible in the gas phase. The monomer with vacant orbitals should in turn decompose more readily than the dimer. The mass spectra of the two compounds suggest that the monomer of the neopentyl derivative is readily formed in the gas phase. The compound $[Me_2InP(t\text{-}Bu)_2]_2$[11] exhibited masses of species associated with dimers and monomers, whereas no species related to the dimer of the neopentyl derivative were observed.

Experimental Section

All compounds described in this investigation are extremely sensitive to oxygen and moisture and were manipulated in a standard vacuum line or under a purified argon atmosphere in a Vacuum/Atmospheres drybox. The starting compounds $In(CH_2CMe_3)_3$[20] and $K[In(CH_2CMe_3)_3H]$[17] were prepared and purified by literature methods. The chlorophosphine $ClP(t\text{-}Bu)_2$ was purchased from Strem Chemicals, Inc., and distilled twice before use. The reagent KH was obtained from Aldrich Chemical Co. and was washed with pentane to remove oil prior to use. Solvents were dried by conventional procedures. Elemental analyses for $(Me_3CCH_2)_2InP(t\text{-}Bu)_2$ and InP were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY, and by E+R Microanalytical Laboratory, Inc., Corona, NY, respectively. Infrared spectra of Nujol mulls between CsI plates were recorded by means of a Perkin-Elmer 683 spectrometer. The ^1H NMR spectra were recorded at 400 MHz by means of a Varian VXR-400 S spectrometer or at 300 MHz with a Varian Gemini-300 spectrometer. Proton chemical shifts are reported in δ units (ppm) and are referenced to $SiMe_4$ at 0.00 ppm and C_6H_6 at δ 7.15 ppm. The ^{31}P NMR spectra were recorded at 161.9 MHz by means of a Varian VXR-400 S spectrometer. The ^{31}P spectra are referenced to 85% H_3PO_4 at δ 0.00 ppm. All samples for

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Table II. Comparisons of Bond Distances and Angles

	$[Me_2InP(t\text{-Bu})_2]_2$[11]	$[Et_2InP(t\text{-Bu})_2]_2$[12]	$[(Me_3CCH_2)_2InP(t\text{-Bu})_2]_2$
In–C, Å	2.177(6)	2.170(13)	2.206(5)
	2.191(6)	2.176(12)	2.219(4)
	2.184 (av)	2.173 (av)	2.213 (av)
In–P, Å	2.637(4)	2.635(2)	2.712(1)
	2.656(4)		2.690(1)
	2.646 (av)		2.701 (av)
In···In, Å	3.897	3.867	4.033
C–In–C, deg	108.6(3)		117.7(2)
			112.7(2)
P–In–P, deg	85.2(3)	85.6(1)	83.8(1)
			83.0(1)
			83.4 (av)
In–P–In, deg	94.8(2)	94.4(1)	96.6(1)

NMR spectra were contained in sealed NMR tubes. Melting points were observed in sealed capillaries filled with purified argon and are uncorrected. Cryoscopic studies of $(Me_3CCH_2)_3In\cdot P(H)(t\text{-Bu})_2$ in benzene were obtained by using an instrument similar to that described by Shriver and Drezdzon.[21] Mass spectrometry was conducted by using a VG Analytical 70-SE spectrometer. Samples were sealed in microcapillaries filled with purified argon which were broken open just before insertion into the chamber of the spectrometer. Species were ionized by electron impact at 70 eV with the source temperature at 200 °C. Only peaks with m/z greater than 100 and with I_{rel} higher than 10 are reported. Masses of species containing In refer to the ^{115}In isotope. The XPS analysis of InP was performed on a Perkin-Elmer Physical Electronics (PHI) Model 5100 ESCA spectrometer with a Mg $K\alpha_{1,2}$ X-ray source (1253.6 eV) operated at 300 W, 15 kV, and 20 mA and was recorded at a takeoff angle of 45° with a 180° hemispherical detector. The spectrometer was calibrated at a base pressure of 2×10^{-9} Torr and at an operating pressure of 2×10^{-8} Torr with the Ag $3d_{5/2}$ peak set at 367.9 eV with FWHM (full width at half-maximum) of 1.05 and 900 000 counts/s. The binding energy scale was set by Cu $2p_{3/2}$ and Cu $3p_{3/2}$ at 932.5 and 75.0 eV, respectively. The identity of the elements was evaluated by low-resolution (89.45-eV) survey spectra. Binding energies (eV) and peak area for quantitative analysis were recorded by high resolution (35.75 eV) spectra. X-ray powder diffraction analysis of InP was recorded on a Siemens D-500 X-ray diffractometer operated at 40 kV and 30 mA with a graphite-monochromated Cu $K\alpha$ X-ray source at 1.54 Å. The X-ray powder pattern spectrum was generated as 2θ vs intensity and translated into d values.

Synthesis of $[(Me_3CCH_2)_2InP(t\text{-Bu})_2]_2$. A solution of $ClP(t\text{-Bu})_2$ (3.516 g, 19.46 mmol, 15 mL pentane) was slowly added to a solution of $K[In(CH_2CMe_3)_3H]$ (7.181 g, 19.49 mmol, 30 mL pentane) at −40 to ca. −50 °C. The mixture was allowed to warm to room temperature slowly, stirred overnight, and then filtered. The insoluble KCl (0.963 g, 12.92 mmol, 66% yield based on $ClP(t\text{-Bu})_2$) was isolated after eight extractions with pentane. Pentane was then removed from the filtrate at −20 °C by vacuum distillation. The resulting colorless liquid was finally heated at 105–115 °C for 5 days. Neopentane (1.239 g, 17.17 mmol, 88.23% based on $ClP(t\text{-Bu})_2$) was collected by vacuum distillation. The resulting colorless solid was washed three times with a small amount of pentane to leave $[(Me_3CCH_2)_2InP(t\text{-Bu})_2]_2$ (5.702 g, 7.09 mmol, 73% yield based on $ClP(t\text{-Bu})_2$) as a colorless crystalline solid. Mp: 200–202 °C dec. Anal. Calcd for $C_{18}H_{40}InP$: C, 53.74; H, 10.02; P, 7.70. Found: C, 53.75; H, 9.72; P, 7.26. ^1H NMR (C_6D_6): δ 1.39 (s, 18 H, $InCCCH_3$), 1.46 (t, 18 H, $PCCH_3$, J = 6.6 Hz), 1.54 (s, 4 H, $InCH_2$). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 55.0 (s, $PCCH_3$). IR (Nujol mull, cm^{-1}): 1360 (vs, sh), 1226 (m), 1207 (w), 1166 (m), 1113 (m, sh), 1012 (m), 927 (vw), 809 (w), 737 (m), 653 (m), 617 (m), 554 (w), 467 (vw), 450 (w). MS: m/z (I_{rel}), 402 (13, $(Me_3CCH_2)_2InP(t\text{-Bu})_2^+$), 332 (13, $(Me_3CCH_2)(H)InP(t\text{-Bu})_2^+$), 331 (43, $(Me_3CCH_2)InP(t\text{-Bu})_2^+$), 260 (37, $InP(t\text{-Bu})_2^+$), 258 (53, $In(H)(CH_2CMe_3)^+$), 257 (97, $In(CH_2CMe_3)_2^+$), 255 (31, $In(CH_2CMe_3)(C_5H_9)^+$), 201 (16, $In(CH_2CMe_3)(Me)^+$), 186 (30, $In(CH_2CMe_3)^+$), 146 (61, InP or $HP(t\text{-Bu})_2^+$), 145 (14, $P(t\text{-Bu})_2^+$), 115 (100, In^+ or $P(C_3H_7)(C_3H_5)^+$), 113 (34, $P(C_3H_5)_2^+$).

Synthesis of $[(Me_3CCH_2)_2InP(t\text{-Bu})_2]_2$ with Excess $In(CH_2CMe_3)_3$ at Room Temperature. The synthesis of $[(Me_3CCH_2)_2InP(t\text{-Bu})_2]_2$ from $ClP(t\text{-Bu})_2$ (0.964 g, 5.34 mmol), $K[In(CH_2CMe_3)_3H]$ (1.974 g, 5.358 mmol) and excess $In(CH_2CMe_3)_3$ (1.755 g, 5.345 mmol) dissolved in 15 mL of pentane was also accomplished at room temperature. After the solutions of $ClP(t\text{-Bu})_2$ and $K[In(CH_2CMe_3)_3H]$ were combined at −40 to ca. −50 °C and stirred overnight at room temperature, the reaction mixture was filtered to remove KCl. The resulting filtrate was then combined with the additional $In(CH_2CMe_3)_3$. Colorless crystals of $[(Me_3CCH_2)_2InP(t\text{-Bu})_2]_2$ formed after 7 days. The product $[(Me_3CCH_2)_2InP(t\text{-Bu})_2]_2$ (1.374 g, 1.708 mmol, 64% yield based on $ClP(t\text{-Bu})_2$) was finally isolated by filtration 72 days after the addition of $In(CH_2CMe_3)_3$. Characterization data were identical to those previously described.

Synthesis of $[(Me_3CCH_2)_2InP(t\text{-Bu})_2]_2$ by Thermolysis. The reagents, $HP(t\text{-Bu})_2$ (0.302 g, 2.06 mmol) and $In(CH_2CMe_3)_3$ (0.678 g, 2.07 mmol) were combined in a break-seal tube. After the tube was sealed, the mixture was heated at 120–160 °C for 2 days. The condensable gas was removed, measured, and identified as 0.148 g of CMe_4 (2.06 mmol, 99% yield based on $HP(t\text{-Bu})_2$). The remaining crystalline solid was purified by sublimation at 110–125 °C ($\sim 10^{-2}$ mmHg) and identified as $[(Me_3CCH_2)_2InP(t\text{-Bu})_2]_2$ (0.698 g, 0.87 mmol, 84% yield based on $HP(t\text{-Bu})_2$). Characterization data were identical to those previously described.

Preparation of $HP(t\text{-Bu})_2$. A pentane solution of $ClP(t\text{-Bu})_2$ (1.034 g, 5.722 mmol) was added slowly to a mixture of KH (0.329 g, 8.21 mmol) and $K[In(CH_2CMe_3)_3H]$ (2.663 g, 7.229 mmol) in 10 mL of pentane at −40 to ca. −50 °C. After the mixture was warmed to room temperature and stirred for 10 h, pentane was removed by vacuum distillation at low temperature (0 to −20 °C). The crude product was isolated by vacuum distillation into a −196 °C trap. Final purification of $HP(t\text{-Bu})_2$ required removing a trace of pentane by vacuum distillation to yield $HP(t\text{-Bu})_2$ (0.492 g, 3.36 mmol, 59% yield based upon $ClP(t\text{-Bu})_2$). ^1H NMR (δ, C_6D_6): δ 1.16 (d, ^3J = 12 Hz), 3.14 (d, ^1J = 199 Hz). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 19.9 (s). ^{31}P NMR (C_6D_6): δ 19.9 (dm, ^1J = 199 Hz, ^3J = 11 Hz).

Freezing Point Depression Study of $(Me_3CCH_2)_3In\cdot P(H)(t\text{-Bu})_2$ in Benzene. A tube was charged with $In(CH_2CMe_3)_3$ (0.0890 g, 0.271 mmol) and $HP(t\text{-Bu})_2$ (0.0374 g, 0.256 mmol) and then benzene (4.2995 g) was added. The freezing point of the resulting solution was measured three times. The solution was then diluted with 1.6433 g of C_6H_6. The average freezing points were used to calculate an observed molality and K_d: 0.0821 (0.011), 0.0611 (0.010). The experiment was repeated with $In(CH_2CMe_3)_3$ (0.0921 g, 0.281 mmol), $HP(t\text{-Bu})_2$ (0.0326 g, 0.223 mmol), and benzene (4.3892 g and 1.6435 g for dilution). Observed molality (K_d): 0.0798 (0.013), 0.0598 (0.013).

Reactions of $In(CH_2CMe_3)_3$ with $HP(t\text{-Bu})_2$ in Different Ratios. (a) A tube was charged with $HP(t\text{-Bu})_2$ (0.268 g, 1.83

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(21) Shriver, D. F.; Drezdzon, M. A. *The Manipulation of Air Sensitive Compounds*; Wiley: New York, 1986; p 38.

mmol) and pentane solvent (1.968 g). The solution was then added to $In(CH_2CMe_3)_3$ (3.006 g, 9.159 mmol) at room temperature. The resulting solution was permitted to stand at ambient temperature. Colorless crystals were observed after 6 days and isolated after 7 days. The product was isolated by removing the volatile compounds at 60 °C. The nonvolatile solid was identified as $[(Me_3CCH_2)_2InP(t\text{-}Bu)_2]_2$ (0.145 g, 0.181 mmol, 20% yield based on $HP(t\text{-}Bu)_2$). (b) A second experiment which used similar concentrations of reactants $HP(t\text{-}Bu)_2$ (0.306 g, 2.09 mmol) and $In(CH_2CMe_3)_3$ (0.693 g, 2.11 mmol) in pentane (2.137 g) had the same experimental conditions as experiment a. No crystals were observed after 7 days. After all the volatile compounds were removed, only a faint trace of solid (less than 1 mg) remained in the flask. (c) The third experiment had $In(CH_2CMe_3)_3$ (0.702 g, 2.14 mmol), excess $HP(t\text{-}Bu)_2$ (1.557 g, 10.65 mmol), and pentane (2.128 g). Again, no solid was observed after 7 days. After removing all the volatile compounds, no $[(Me_3CCH_2)_2InP(t\text{-}Bu)_2]_2$ remained in the flask.

Thermolysis of $[(Me_3CCH_2)_2InP(t\text{-}Bu)_2]_2$. Crystals of $[(Me_3CCH_2)_2InP(t\text{-}Bu)_2]_2$ (0.618 g, 0.77 mmol) were sealed in a break-seal tube and heated at 245 °C for 1 h. The colorless volatile products (0.233 g) were then removed from the opened tube by vacuum distillation and identified as only hydrocarbons, as no ^{31}P NMR lines were detected. The number and variety of ^1H and ^{13}C NMR lines in the spectrum of the volatile products suggested a mixture of unknown hydrocarbons. The material remaining in the tube was washed with 20 mL of pentane which removed an unknown brown, nonvolatile liquid. The resulting black powder was identified as InP (0.170 g, 1.17 mmol, 76% yield based on $[(Me_3CCH_2)_2InP(t\text{-}Bu)_2]_2$ used). Anal. Found: C, 0.41; H, 0.04. X-ray powder diffraction [obsd (lit.[22])]: 3.56 (3.39), 2.91 (2.93), 2.06 (2.07), 1.76 (1.77), 1.69 (1.69), 1.47 (1.47), 1.35 (1.35), 1.31 (1.31). XPS binding energies (atomic concentration$_{rel}$) (Sample was supported on tape which was also detected with C 1s, 285 (83.09), O 1s, 532 (16.91)): In $d_{5/2}$, 494.5 (21.39); In $d_{3/2}$, 452.1 (21.39); P 2p, 128.5 (11.57); C 1s, 285.0 (51.01); O 1s, 532 (13.18); Cl 2p, 199.4 (2.85).

Collection of X-ray Diffraction Data for $[(Me_3CCH_2)InP(t\text{-}Bu)_2]_2$. A well-formed colorless transparent crystal of dimensions 0.34 × 0.30 × 0.27 mm was selected for the X-ray diffraction study. The crystal was prepared for the study by sealing it into a 0.3-mm thin walled capillary under strict anaerobic conditions. It was then mounted and aligned on a Siemens R3m/V four-circle single-crystal diffractometer. Details of the data collection[23] are presented in Table III.

The crystal belongs to the orthorhombic system. Determination of the space group was rendered difficult due to pseudosymmetry which gave rise to a pseudo-face-centering condition. The structure was finally solved successfully in space group *Pbcn* (No. 60)[24] where the systematic absences are $0kl$ for $k = 2n + 1$, $h0l$ for $l = 2n + 1$, and $hk0$ for $h + k = 2n + 1$. In addition there is a systematic weakness for all reflections with $h + k = 2n + 1$. (Only 460 of 2732 such reflections have $I > 3\sigma(I)$. The mean value for I/σ for reflections with $h + k = 2n + 1$ is 3.0 as compared to a value of 23.0 for all reflections.) The successful solution of the structure in space group *Pbcn* reveals that the systematic weakness of the reflections with $h + k = 2n + 1$ is a result of the two heaviest atoms in the structure (indium atoms with $Z = 49$) lying on a crystallographic 2-fold axis at $x = 0$, $z = {}^3/_4$ (Wyckoff notation c). These two atoms provide contributions only to the intensities of reflections with $h + k = 2n$.[24]

Table III. Experimental Data for the X-ray Diffraction Study of $[(Me_3CCH_2)_2InP(t\text{-}Bu)_2]_2$

Crystal Data	
empirical formula	$C_{36}H_{80}In_2P_2$
cryst size (mm)	0.34 × 0.3 × 0.27
cryst syst	orthorhombic
space group	*Pbcn*
unit cell dimens	
a (Å)	11.742(3)
b (Å)	20.194(6)
c (Å)	17.909(4)
vol ($Å^3$)	4246(2)
Z	4
fw	804.6
dens(calc) (Mg/m^3)	1.259
abs coeff (mm^{-1})	1.163
F(000)	1696
Data Collection	
diffractometer used	Siemens R3m/V
radiation; λ (Å)	Mo Kα; 0.710 73
temp (K)	298
monochromator	highly oriented graphite crystal
2θ range (deg)	4.0–55.0
scan type	2θ–θ
scan speed (deg/min)	constant; 3.00 in ω
scan range (ω) (deg)	0.45 plus Kα separation
bckgd measurement	stationary crystal and stationary counter at beginning and end of scan, each for 25.0% of total scan time
no. of std reflns	3 measd every 97 reflns
index ranges	$0 \le h \le 15, -26 \le k \le 0, 0 \le l \le 23$
no. of reflns collcd	5466
no. of ind reflns	4920
no. of obsd reflns	2525 ($F > 6.0\sigma(F)$)
Solution and Refinement	
system used	Siemens SHELXTL PLUS (VMS)
solution	direct methods
refinement method	full-matrix least squares
quantity minimized	$\sum w(F_o - F_c)^2$
extinction correction	$\chi = 0.00043(5)$, where $F^* = F[1 + 0.002\chi F^2/\sin(2\theta)]^{-1/4}$
hydrogen atoms	riding model, fixed isotropic *U*
weighting scheme	$w^{-1} = \sigma^2(F) + 0.0014F^2$
no. of params refined	183
final *R* indices (all data) (%)	$R = 6.68$, $R_w = 6.24$
R indices (6.0σ data) (%)	$R = 2.76$, $R_w = 3.47$
goodness-of-fit	0.97
largest and mean Δ/σ	0.003, 0.000
data-to-param ratio	26.9:1
largest diff peak (e $Å^{-3}$)	0.61
largest diff hole (e $Å^{-3}$)	–0.51

[It should be noted that we earlier had concluded erroneously that the crystals had a *C*-centered orthorhombic Bravais lattice. Attempts to solve the structure in space groups $Cmc2_1$ (No. 36) and *Cmcm* (No. 63) were unsuccessful, but the structure was apparently solved in space group *Ama*2 (No. 40). Although refinement of data converged with $R = 4.20\%$ and the resulting molecular geometry appeared reasonable, the model had impossibly short intermolecular C(neopentyl)···C(neopentyl) contacts at 2.185 Å. It was this feature that led us back to consider a space group with a primitive orthorhombic lattice.]

Data were collected for one octant of the reciprocal sphere with $2\theta = 4.0$–$55.0°$. Data were corrected for Lorentz and polarization effects but not for absorption. We estimate $\exp(-\mu\Delta t)$ to be 0.966, so that absorption can safely be ignored.

Solution and Refinement of the Structure of $[(Me_3CCH_2)_2InP(t\text{-}Bu)_2]_2$. All crystallographic calculations were carried out with the use of the Siemens SHELXTL PLUS program set.[25] The analytical scattering factors for neutral atoms were corrected for both the real and imaginary components ($\Delta f'$ and $i\Delta f''$) of anomalous dispersion components.[26]

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(22) Joint Committee Powder Diffraction Standards. *Powder Diffraction File Search Manual*; International Centre for Diffraction Data: Swarthmore, PA, 1989; File No. 32-452.

(23) Churchill, M. R.; Lashewycz, R. A.; Rotella, F. J. *Inorg. Chem.* 1977, *16*, 265.

(24) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1965; Vol. 1, pp 149 and 407.

(25) *Siemens SHELXTL Plus Manual*, 2nd ed.; Siemens Analytical Instruments, Madison, WI, 1990.

(26) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. 4, pp 99–101 and 149–150.

Table IV. Final Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for [(Me$_3$CCH$_2$)$_2$InP(*t*-Bu)$_2$]$_2$

	x	*y*	*z*	*U*(eq)[a]
In(1)	0	2741(1)	7500	33(1)
In(2)	0	744(1)	7500	33(1)
P(1)	1526(1)	1735(1)	7580(1)	34(1)
C(11)	2390(3)	1672(2)	8471(2)	47(1)
C(12)	1552(4)	1794(2)	9110(2)	60(2)
C(13)	3365(4)	2178(2)	8521(3)	67(2)
C(14)	2895(4)	978(2)	8577(3)	61(2)
C(21)	2503(3)	1764(2)	6742(2)	46(1)
C(22)	1728(4)	1682(2)	6055(2)	57(2)
C(23)	3123(3)	2426(2)	6670(3)	66(2)
C(24)	3387(3)	1200(2)	6746(3)	62(2)
C(31)	−297(3)	3306(2)	8536(3)	52(1)
C(32)	464(4)	3873(2)	8821(2)	46(1)
C(33)	−26(6)	4513(3)	8633(9)	231(8)
C(34)	535(9)	3843(5)	9628(4)	237(7)
C(35)	1619(5)	3876(3)	8523(5)	175(5)
C(41)	89(3)	135(2)	8530(2)	47(1)
C(42)	−770(4)	−422(2)	8729(2)	50(1)
C(43)	−108(4)	−1027(2)	9020(3)	73(2)
C(44)	−1586(4)	−197(2)	9344(3)	71(2)
C(45)	−1481(4)	−642(2)	8058(3)	69(2)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

The structure was solved by a combination of direct methods and difference-Fourier syntheses. Positional and anisotropic thermal parameters were refined for all non-hydrogen atoms. Hydrogen atoms were included in idealized positions with *d*(C–H) = 0.96 Å and the appropriate staggered tetrahedral geometry.[27] The isotropic thermal parameter of each of these hydrogen atoms was fixed equal to that of the carbon atom to which it was bonded. The final difference-Fourier map contained features ranging from −0.51 to +0.61 e Å^{-3}. Refinement of the ordered model converged with R = 6.68% (R_w = 6.24%) for 183 parameters refined against all 4920 unique reflections (R = 2.76% and R_w = 3.47% for those 2525 reflections with $|F_o| > 6\sigma(|F_o|)$). Final atomic coordinates are collected in Table IV.

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Supplementary Material Available: Tables of anisotropic thermal parameters and calculated positions for all hydrogen atoms (2 pages). Ordering information is given on any current masthead page.

OM9302655

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[27] Churchill, M. R. *Inorg. Chem.* **1973**, *12*, 1213.