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Reactions of Neopentylindium(III) Derivatives with Isopropylphosphorus Compounds

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A 1:1 mixture of $\mathrm{In(CH_2CMe_3)_3}$ and $\mathrm{HP(i\text{-}Pr)_2}$ at room temperature undergoes a very slow hydrocarbon elimination reaction to form $\mathrm{[(Me_3CCH_2)_2InP(i\text{-}Pr)_2]_2}$ and neopentane. The indium phosphide $\mathrm{[(Me_3CCH_2)_2InP(i\text{-}Pr)_2]_2}$ has also been prepared by reacting $\mathrm{KIn(CH_2CMe_3)_3H}$ with $\mathrm{ClP(i\text{-}Pr)_2}$ in pentane. When pentane solutions of these reagents were combined at −78 °C and then maintained at ∼20 °C for 2 days, $\mathrm{[(Me_3CCH_2)_2InP(i\text{-}Pr)_2]_2}$, $\mathrm{(Me_3CCH_2)_3In\cdot P(H)(i\text{-}Pr)_2}$, $\mathrm{(Me_3CCH_2)_3In\cdot P_2(i\text{-}Pr)_4}$, $\mathrm{(Me_3CCH_2)_3In\cdot P(CH_2CMe_3)(i\text{-}Pr)_2}$, $\mathrm{H_2}$, indium metal, and KCl were observed. The formation of all products is explained by a set of experimentally verified reactions. An X-ray structural study of $\mathrm{[(Me_3CCH_2)_2InP(i\text{-}Pr)_2]_2}$ shows each molecule to have an unusual puckered four-membered $\mathrm{In_2P_2}$ core.

Introduction

The simplest route to compounds of the type $\mathrm{R_2InPR'_2}$ is the hydrocarbon elimination reaction (eq 1).[1−3] As a

$$\mathrm{InR_3 + HPR'_2 \xrightarrow[\text{reaction}]{\text{hydrocarbon elimination}} R_2LnPR'_2 + RH} \quad (1)$$

phosphine has an unpleasant odor and is typically toxic, we have searched for a preparative route in which the phosphine would be formed and then utilized in situ. Thus, we investigated the reactions of $\mathrm{KIn(CH_2CMe_3)_3H}$ with a variety of chlorophosphines (eq 2). The reagent

$$n\,\mathrm{KIn(CH_2CMe_3)_3H} + n\,\mathrm{ClPR_2} \xrightarrow{\text{pentane}} \mathrm{[(Me_3CCH_2)_2InPR_2]}_n + n\,\mathrm{KCl} + n\,\mathrm{CMe_4} \quad (2)$$

$\mathrm{ClP(t\text{-}Bu)_2}$ produced $\mathrm{[(Me_3CCH_2)_2InP(t\text{-}Bu)_2]_2}$ in high yield, and no side-reactions or -products were observed.[4] However, when $\mathrm{ClPPh_2}$ was used, the products included $\mathrm{[(Me_3CCH_2)_2InPPh_2]}_n$, $\mathrm{(Me_3CCH_2)_3In\cdot P(CH_2CMe_3)Ph_2}$, and $\mathrm{H_2}$.[5] In the following paper the results of our investigations of the reactions that occur in the $\mathrm{ClP(i\text{-}Pr)_2}$ system are described. The detailed chemistry was different from the other two chlorophosphines as $\mathrm{[(Me_3CCH_2)_2InP(i\text{-}Pr)_2]_2}$, $\mathrm{(Me_3CCH_2)_3In\cdot P(H)(i\text{-}Pr)_2}$, $\mathrm{(Me_3CCH_2)_3In\cdot P_2(i\text{-}Pr)_4}$, $\mathrm{(Me_3CCH_2)_3In\cdot P(CH_2CMe_3)(i\text{-}Pr)_2}$, and $\mathrm{H_2}$ were formed.

Results and Discussion

The investigation of the chemistry of the $\mathrm{KIn(CH_2CMe_3)_3H{-}ClP(i\text{-}Pr)_2}$ system was preceded by a study of the reactions that occur between $\mathrm{In(CH_2CMe_3)_3}$ and $\mathrm{HP(i\text{-}Pr)_2}$. The initial product was the adduct $\mathrm{(Me_3CCH_2)_3In\cdot P(H)(i\text{-}Pr)_2}$. Freezing point depression studies and ^{1}H and ^{31}P NMR spectroscopy demonstrated that the adduct is in equilibrium with the Lewis acid and base (eq 3) in benzene solution. The equilibrium constant for

$$\mathrm{(Me_3CCH_2)_3In\cdot P(H)(i\text{-}Pr)_2} \overset{K_\mathrm{d}}{\rightleftharpoons} \mathrm{In(CH_2CMe_3)_3 + HP(i\text{-}Pr)_2} \quad (3)$$

the dissociation of the adduct (K_d) as calculated from the cryoscopic data had a value of $(2.1 \pm 0.2) \times 10^{-3}$ at ∼5 °C. The ^{31}P and ^{1}H NMR spectroscopic data are consistent with this equilibrium also and with the occurrence of rapid exchange between components. Consequently, the chemical shifts of the resonances and the coupling constants depend on the concentrations of the species as well as on the phosphorus-to-indium ratio. Two resonances for the isopropyl methyl groups ($\mathrm{P{-}C{-}CH_3}$) indicate that these methyl groups are not able to rotate freely. In contrast, the methyl protons bonded to the tertiary carbon of the *tert*-butyl group in the closely related adduct $\mathrm{(Me_3CCH_2)_3In\cdot P(H)(t\text{-}Bu)_2}$ rotate freely at ambient temperature.[4] The chemical shifts and coupling constants for the different atoms for a pure adduct $\mathrm{(Me_3CCH_2)_3In\cdot P(H)(i\text{-}Pr)_2}$ were derived by extrapolating the experimental data observed for various mixtures of $\mathrm{HP(i\text{-}Pr)_2}$ and $\mathrm{In(CH_2CMe_3)_3}$ to a hypotheti-

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cal ratio of $HP(i\text{-}Pr)_2$ to $In(CH_2CMe_3)_3$ of zero. The nominal data for the "pure adduct" $(Me_3CCH_2)_3In{\cdot}P(H)(i\text{-}Pr)_2$ are ^{31}P NMR (C_6D_6) δ −15.2 (d, J = 272 Hz); ^1H NMR (C_6D_6) δ 0.89 (dd, $PCCH_3$, J = 13 Hz, 7 Hz), 0.92 (dd, $PCCH_3$, J = 17 Hz, 7 Hz), 1.16 (s, $InCH_2$), 1.31 (s, $InCCCH_3$), 3.05 (d, $In{\cdot}P(H)(i\text{-}Pr)_2$, J = 272.2 Hz). The equilibrium constant for the dissociation of the adduct (eq 3) as calculated from the ^1H and ^{31}P NMR spectral data in the special case when $[HP(i\text{-}Pr)_2] = [In(CH_2CMe_3)_3] = 0.368$ m had a value of 0.008 ± 0.007 at ~20 °C, a number consistent with the constant from the cryoscopic data.

The adduct $(Me_3CCH_2)_3In{\cdot}P(H)(i\text{-}Pr)_2$ undergoes an elimination reaction (eq 1) to form $[(Me_3CCH_2)_2InP(i\text{-}Pr)_2]_2$ and neopentane. When the neat adduct was maintained at ~20 °C, reaction was complete in 6 days. In contrast, a benzene solution eliminated neopentane more slowly, as 45 days was required to convert slightly more than half of the phosphine to the phosphide at ~20 °C. When there was a 5-fold excess of $In(CH_2CMe_3)_3$ over the phosphine in a benzene solution, the elimination reaction was complete in only 4 days at ~20 °C. Similarily, the addition of $Ga(CH_2CMe_3)_3$ to a solution that was equimolal in $In(CH_2CMe_3)_3$ and $HP(i\text{-}Pr)_2$ also accelerated the rate of the elimination reaction, but no $[(Me_3CCH_2)_2GaP(i\text{-}Pr)_2]_2$ was formed. In contrast, a 5-fold excess of $HP(i\text{-}Pr)_2$ slowed the rate of the elimination reaction, as only a trace of the indium phosphide formed after 41 days at ~20 °C. Analogous kinetic observations have been made for the $In(CH_2CMe_3)_3-HP(t\text{-}Bu)_2$ system.[4] All of these experimental observations suggest that this elimination reaction is a reaction of the simple four-coordinate adduct, $(Me_3CCH_2)_3In{\cdot}P(H)R_2$ (eq 1). Excess phosphine might lead to the formation of a five-coordinate adduct that does not undergo elimination.

The new compound $[(Me_3CCH_2)_2InP(i\text{-}Pr)_2]_2$ exists as dimers in benzene solution at all concentrations studied according to the cryoscopic molecular weight and the NMR spectral data. A single line at −1.9 ppm was observed in the ^{31}P NMR spectrum. The ^1H NMR spectrum was also appropriate for a dimer. The resonance for the $P-C-CH_3$ protons was an apparent quartet due to an overlapping doublet of doublets of doublets. This pattern indicates that these methyl protons are coupled to the CH proton of the isopropyl group, the attached phosphorus atom, and the second phosphorus atom of the In_2P_2 ring. Similar coupling has been noted for the ^1H NMR spectra of $[(Me_3CCH_2)_2InP(t\text{-}Bu)_2]_2$[4] and $[Me_2InP(i\text{-}Pr)_2]_2$.[6] The resonance for the $P-CH$ protons was a broad, relatively weak mutiplet due to an overlapping septet of triplets. The presence of only one set of resonances for each type of isopropyl and neopentyl protons suggests that the organic substituents are magnetically equivalent. Thus, the In_2P_2 core might be planar in benzene solution. Alternatively, if the ring is puckered, as identified in the X-ray structural study of a crystal, the ring would have to undergo either a rapid inversion or a rapid dissociation, rotation, and re-formation.

The compound $[(Me_3CCH_2)_2InP(i\text{-}Pr)_2]_2$ crystallizes in the centrosymmetric monoclinic space group $P2/n$ (No. 13)[7] with $Z = 4$. However, each molecule lies on a crystallographic C_2 axis (Wyckoff position e)[7] and has approximate C_{2v} symmetry. The crystallographic asymmetric unit consists of two independent half-molecules. Molecule 1, based upon In(1), P(1), and the symmetry related ($-x$, y, $1/2-z$) In(1A) and P(1A), is depicted in Figure 1. Molecule 2, based upon In(2) and P(2), has a similar geometry. The two independent molecules are separated by approximately one-half a unit cell along the b-axis. Selected interatomic distances and angles are collected in Table 1. The structure of $[(Me_3CCH_2)_2InP(i\text{-}Pr)_2]_2$ is very unusual for a dimeric organoindium phosphide, as the In_2P_2 cores are significantly puckered. The fold angles about the In···In axes are 22.7° for molecule 1 and 21.5° for molecule 2. The fold angles about the P···P axes are 20.5° for molecule 1 and 19.6° for molecule 2. The only other organoindium phosphide with a puckered four-membered ring is $[(Me_3CCH_2)_2In[\mu-P(SiMe_3)_2][\mu\text{-}PH(SiMe_3)]In(CH_2CMe_3)_2$.[8] The folding of the ring allows the isopropyl groups to reduce the crowding around the In_2P_2 four-membered ring. The indium−phosphorus bond lengths average 2.651 Å and are shorter by ~0.05 Å than those observed for other neopentylindium phosphides, i.e., 2.701 Å average for $[(Me_3CCH_2)_2InP(t\text{-}Bu)_2]_2$,[4] 2.632 Å average for $[(Me_3CCH_2)_2InPEt_2]_2$,[1i] 2.637 Å average for $[(Me_3CCH_2)_2InP(H)(C_6H_{11})_2]_3$,[1i] and 2.699 Å for $[(Me_3CCH_2)_2InPPh_2]_3$.[3]

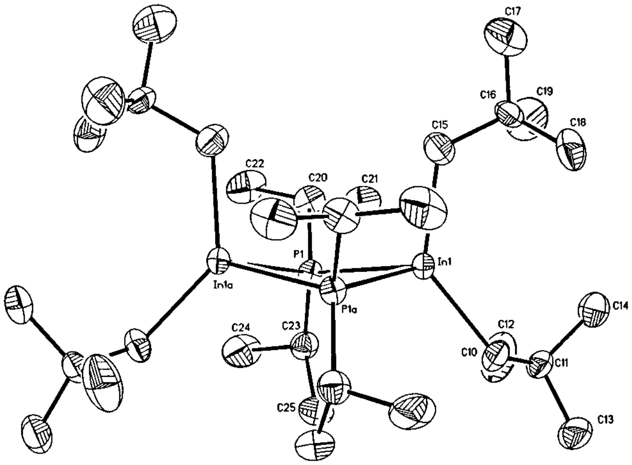

Figure 1. Labeling of atoms for the asymmetric unit and for the core atoms, In(1a) and P(1a), of molecule 1 in crystalline $[(Me_3CCH_2)_2InP(i\text{-}Pr)_2]_2$. The 30% probability envelopes are shown for the anisotropic vibration ellipsoids of all non-hydrogen atoms. All hydrogen atoms have been omitted for the sake of clarity. The crystallographic C_2 axis (along y, at $x = 0$ and $z = 1/4$) is vertical and bisects both the In···In(1a) and P(1)···P(1a) vectors.

Two neopentyl groups are associated with each indium atom with indium−carbon distances averaging 2.220 Å. Inter-ligand angles around indium atoms are $C(10)-In(1)-C(15) = 133.4(4)°$ and $C(30)-In(2)-C(35) = 136.1(6)°$. These angles are much larger than those within $[(Me_3CCH_2)_2InP(t\text{-}Bu)_2]_2$[4] (112.7(2)−117.7(2)°). The increase in the angles between similar substituents might be related to the decrease in the size of the ring (i.e., shorter In−P distances). The C−In−C planes are

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Table 1. Selected Interatomic Distances (Å) and Angles (deg) for[(Me$_3$CCH$_2$)$_2$InP(i-Pr)$_2$]$_2$

(A) Indium–Phosphorus Distances			
In(1)–P(1)	2.638(2)	In(2)–P(2)	2.663(2)
In(1)–P(1A)	2.664(2)	In(2)–P(2A)	2.631(3)
(B) Indium–Carbon Distances			
In(1)–C(10)	2.201(9)	In(2)–C(30)	2.206(9)
In(1)–C(15)	2.248(9)	In(2)–C(35)	2.222(20)
(C) Phosphorus–Carbon Distances			
P(1)–C(20)	1.865(9)	P(2)–C(40)	1.864(13)
P(1)–C(23)	1.853(9)	P(2)–C(43)	1.846(10)
(D) Angles around Indium Atoms			
P(1)–In(1)–P(1A)	83.6(1)	P(2)–In(2)–P(2A)	83.3(1)
P(1)–In(1)–C(10)	117.3(2)	P(2)–In(2)–C(30)	99.7(3)
P(1)–In(1)–C(15)	102.9(2)	P(2)–In(2)–C(35)	104.7(5)
C(10)–In(1)–P(1A)	108.0(2)	C(30)–In(2)–P(2A)	100.9(3)
C(15)–In(1)–P(1A)	98.6(3)	C(35)–In(2)–P(2A)	117.6(6)
C(10)–In(1)–C(15)	133.4(4)	C(30)–In(2)–C(35)	136.1(6)
(E) Angles around Phosphorus Atoms			
In(1)–P(1)–In(1A)	94.6(1)	In(2)–P(2)–In(2A)	94.7(1)
In(1)–P(1)–C(20)	108.4(3)	In(2)–P(2)–C(40)	120.3(4)
In(1)–P(1)–C(23)	115.8(3)	In(2)–P(2)–C(43)	110.1(3)
C(20)–P(1)–In(1A)	112.3(3)	C(40)–P(2)–In(2A)	114.6(5)
C(23)–P(1)–In(1A)	118.5(3)	C(43)–P(2)–In(2A)	108.8(3)
C(20)–P(1)–C(23)	106.7(4)	C(40)–P(2)–C(43)	107.6(6)
(F) Selected Angles around Carbon Atoms			
In(1)–C(10)–C(11)	123.8(6)	In(2)–C(30)–C(31)	122.9(6)
In(1)–C(15)–C(16)	122.6(7)	In(2)–C(35)–C(36)	129.2(17)
P(1)–C(20)–C(21)	113.0(7)	P(2)–C(40)–C(41)	120.0(11)
P(1)–C(20)–C(22)	115.1(7)	P(2)–C(40)–C(42)	111.1(11)
P(1)–C(23)–C(24)	114.5(7)	P(2)–C(43)–C(44)	114.2(7)
P(1)–C(23)–C(25)	110.0(6)	P(2)–C(43)–C(45)	116.4(6)

Table 2. Data for X-ray Crystallographic Studies of [(Me$_3$CCH$_2$)$_2$InP(i-Pr)$_2$]$_2$

molec. formula	$C_{32}H_{72}In_2P_2$
M_r	748.5
cryst syst	monoclinic
space group	$P2/n$ (No. 13)
a, Å	10.969(2)
b, Å	18.581(2)
c, Å	20.814(3)
β, deg	104.920(10)
V, Å^3	4099.2(11)
D_{calcd}, g/cm^3	1.213
Z	4
μ(Mo Ka), mm^{-1}	1.201
T (K)	298
scan mode	$2\theta-\theta$
2θ range, deg	5.0–45.0
h	−11 to 0
k	0 to 20
l	−21 to +22
no. of reflns collected	5927
no. of unique reflns	5392 ($R_{int} = 0.97\%$)
no. of reflns used for refinement	5392 ($F > 0.3\sigma(F)$)
abs corr	semiempirical
T_{min}/T_{max}	0.6364/0.7685
no. of refined params	307
final R indices (all data)^a	$R = 8.18\%$ $R_w = 7.30\%$
largest difference peak, e Å^{-3}	0.69
largest difference hole, e Å^{-3}	−0.57

[a] R indices are defined as follows: $R(\%) = 100\sum||F_o| - |F_c||/\sum|F_o|$; $R_w(\%) = 100[\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

almost perpendicular to the P–In–P planes with angles of 87.7° and 89.8° and are more regular than those in [(Me$_3$CCH$_2$)$_2$InP(t-Bu)$_2$]$_2$ (83.9° and 97.8°).[4]

The neopentyl and isopropyl substituents are arranged in alternating pseudoaxial and pseudoequatorial positions around the four-membered ring. The bond angle P(1)–In(1)–C(10) = 117.3(2)° is closer to an equatorial arrangement (120°), whereas P(1)–In(1)–C(15) = 102.9(2)° is closer to an axial arrangement (90°). The same is observed for In(1)–P(1)–C(23) = 115.8(3)° and In(1)–P(1)–C(20) = 108.4(3)° in molecule 1 and for the analogous angles in molecule 2.

When KIn(CH$_2$CMe$_3$)$_3$H and ClP(i-Pr)$_2$ were allowed to react in pentane, the major products were [(Me$_3$CCH$_2$)$_2$InP(i-Pr)$_2$]$_2$, CMe$_4$, and KCl. Even though the overall reaction appears straightforward, the detailed process is actually very complicated. The complete list of conclusively identified indium–phosphorus products include [(Me$_3$CCH$_2$)$_2$InP(i-Pr)$_2$]$_2$, (Me$_3$CCH$_2$)$_3$In·P(H)(i-Pr)$_2$, (Me$_3$CCH$_2$)$_3$In·P$_2$(i-Pr)$_4$, and (Me$_3$CCH$_2$)$_3$In·P(CH$_2$CMe$_3$)(i-Pr)$_2$ (and/or (Me$_3$CCH$_2$)P(i-Pr)$_2$). Hydrogen gas and indium metal were also observed. These products were observed after KIn(CH$_2$CMe$_3$)$_3$H and ClP(i-Pr)$_2$ were mixed as pentane solutions at −78 °C and the resulting mixture was stirred at ~20 °C for 2 days. All compounds were identified by comparing the resonances in the ^{1}H and ^{31}P NMR spectra of the crude product with the spectra for authentic, fully characterized samples of the pure compounds. It should be noted that the composition of this product mixture changed over time at ~20 °C. The first species to disappear was (Me$_3$CCH$_2$)$_3$In·P(H)(i-Pr)$_2$, and it formed [(Me$_3$CCH$_2$)$_2$InP(i-Pr)$_2$]$_2$. The second species to undergo further reaction was (Me$_3$CCH$_2$)$_3$In·P$_2$(i-Pr)$_4$. It was converted into [(Me$_3$CCH$_2$)$_2$InP(i-Pr)$_2$]$_2$ and (Me$_3$CCH$_2$)P(i-Pr)$_2$.

The new and unexpected compound (Me$_3$CCH$_2$)$_3$In·P$_2$(i-Pr)$_4$ was isolated as low-melting, thermally unstable, long needlelike crystals that grew across the flask as it sat at ~20 °C, a very unusual observation. NMR spectra and a preliminary X-ray structural study[9] confirmed the compound as a diphosphine adduct. The two phosphorus atoms in (Me$_3$CCH$_2$)$_3$In·P$_2$(i-Pr)$_4$ are magnetically equivalent at ambient temperature, as only one line in the ^{31}P NMR spectrum is observed. However, two resonances in the ^{1}H NMR spectrum were observed for the isopropyl methyl groups, but there was only one rersonance for the PCH proton. Thus, the splitting pattern for the PCCH$_3$ protons was apparent triplets that overlapped and for P–CH an apparent septet of triplets. Similar couplings were observed for the carbon atoms of the methyl groups for the isopropyl substituents on the phosphorus atoms as doublets of doublets overlapped to appear as triplets. The heteronuclear correlation spectrum between the ^{13}C and ^{1}H NMR spectra confirmed that the methyl groups of the isopropyl ligands were different. Resonances for two nonequivalent methyl carbon atoms but only one CH carbon atom were observed. One possible process that would exchange phosphorus atoms but would preserve the relative positions of the atoms of the isopropyl groups might involve a type of "rocking motion" during which the bond between indium and one of the phosphorus atoms is broken and then the bond to the other phosphorus atom is formed before the diphosphine can dissociate from the indium.

Equations 4 through 11 explain the formation of all intermediates, the conversion of these species to isolable

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[9] Two attempts were made to carry out a full X-ray diffraction study on this compound. Each time the diffraction data were very poor and the crystal appeared to decompose in the X-ray beam. The data were sufficient to provide a "proof of structure" in the space group $P3_1$.

products and the dependence of the products on the reaction conditions in the $KIn(CH_2CMe_3)_3H-ClP(i\text{-}Pr)_2$ system.

Scheme of Reactions for the $KIn(CH_2CMe_3)_3H-ClP(i\text{-}Pr)_2$ System

$$2\,[KIn(CH_2CMe_3)_3H + ClP(i\text{-}Pr)_2 \rightarrow In(CH_2CMe_3)_3 + P(H)(i\text{-}Pr)_2 + KCl] \quad (4)$$

$$2\,[In(CH_2CMe_3)_3 + HP(i\text{-}Pr)_2 \rightleftharpoons (Me_2CCH_2)_3In{\cdot}P(H)(i\text{-}Pr)_2 \quad (5)$$

$$2\,[(Me_3CCH_2)_3In{\cdot}P(H)(i\text{-}Pr)_2 \rightarrow 1/2\,[(Me_3CH_2)_2InP(i\text{-}Pr)_2]_2 + CMe_4 \quad (6)$$

$$(1-x)\,[1/2\,[(Me_3CCH_2)_2InP(i\text{-}Pr)_2]_2 + ClP(i\text{-}Pr)_2 \xrightarrow{\sim 20\text{ min}} P_2(i\text{-}Pr)_4 + In(CH_2CMe_3)_2Cl] \quad (7)$$

$$(1-x)[In(CH_2CMe_3)_3 + P_2(i\text{-}Pr)_4 \xrightarrow{>30\text{ days}} 1/2\,[(Me_3CCH_2)_2InP(i\text{-}Pr)_2]_2 + (Me_3CCH_2)P(i\text{-}Pr)_2] \quad (8)$$

$$x\,[In(CH_2CMe_3)_3 + ClP(i\text{-}Pr)_2 \xrightarrow{1\text{ day}} In(CH_2CMe_3)_2Cl + (Me_3CCH_2)P(i\text{-}Pr)_2] \quad (9)$$

$$1\,[KIn(CH_2CMe_3)_3H + In(CH_2CMe_3)_2Cl \rightarrow KCl + In(CH_2CMe_3)_3 + In(CH_2CMe_3)_2H] \quad (10)$$

$$1\,[In(CH_2CMe_3)_2H \rightarrow 1/2\,H_2 + 1/3\,In^0 + 2/3\,In(CH_2CMe_3)_3 \quad (11)$$

Overall Reaction as Sum of Above Steps

$$3\,KIn(CH_2CMe_3)_3H + 3\,ClP(i\text{-}Pr)_2 \rightarrow [(Me_3CH_2)_2InP(i\text{-}Pr)_2]_2 + (Me_3CCH_2)P(i\text{-}Pr)_2] + 2/3\,In(CH_2CMe_3)_3 + 2\,CMe_4 + 1/3\,In^0 + 1/2\,H_2 + 3\,KCl \quad (12)$$

Independent synthetic experiments, NMR spectral studies, and experimental observations identified and confirmed all compounds in this sequence. When solutions of $KIn(CH_2CMe_3)_3H$ and $ClP(i\text{-}Pr)_2$ were mixed, a colorless precipitate of KCl was formed. The other products, $In(CH_2CMe_3)_3$ and $HP(i\text{-}Pr)_2$ (eq 4), underwent an elimination reaction (eq 6) to produce $[(Me_3CCH_2)_2InP(i\text{-}Pr)_2]_2$ and CMe_4. The products $P_2(i\text{-}Pr)_4$, $(Me_3CCH_2)P(i\text{-}Pr)_2$, H_2, and indium metal were observed only when the initial reagents were mixed at −78 °C. Cooling decreased the solubility of $KIn(CH_2Me_3)_3H$ and reduced the rate of the initial reaction so that less $KIn(CH_2CMe_3)_3H$ reacted with $ClP(i\text{-}Pr)_2$. Thus, some $ClP(i\text{-}Pr)_2$ was available to react with $[(Me_3CCH_2)_2InP(i\text{-}Pr)_2]_2$ and/or with $In(CH_2CMe_3)_3$ in later steps of the sequence. When $ClP(i\text{-}Pr)_2$ reacted with $[(Me_3CCH_2)_2InP(i\text{-}Pr)_2]_2$, the products were $P_2(i\text{-}Pr)_4$ and $In(CH_2CMe_3)_2Cl$ (eq 7). This reaction was one of the fastest reactions in the sequence, as it was complete in less than 20 min at room temperature according to NMR spectroscopy. However, $P_2(i\text{-}Pr)_4$ was not always an isolable product. It reacted slowly in solution with $In(CH_2CMe_3)_3$ to form $[(Me_3CCH_2)_2InP(i\text{-}Pr)_2]_2$ and $(Me_3CCH_2)P(i\text{-}Pr)_2$ (eq 8); 28 days were necessary to give a yield of 60−70% at room temperature. When no solvent was present, $In(CH_2CMe_3)_3$ and $P_2(i\text{-}Pr)_4$ formed crystals of $(Me_3CCH_2)_3In{\cdot}P_2(i\text{-}Pr)_4$. If any $In(CH_2CMe_3)_3$ and $ClP(i\text{-}Pr)_2$ remained, they reacted to form more tertiary phosphine $(Me_3CCH_2)P(i\text{-}Pr)_2$ and $In(CH_2CMe_3)_2Cl$ (eq 9). This reaction was complete in 1 day at ∼20 °C. The product $In(CH_2CMe_3)_2Cl$ is very important to the overall process because it is a necessary reactant for the formation of H_2. The chloride $In(CH_2CMe_3)_2Cl$ reacted with $KIn(CH_2CMe_3)_3H$ to form $In(CH_2CMe_3)_2H$, $In(CH_2CMe_3)_3$, and KCl (eq 10).[10] The indium hydride $In(CH_2CMe_3)_2H$ was unstable and rapidly decomposed[10,11] to H_2, indium metal, and $In(CH_2CMe_3)_3$ (eq 11). Thus, the source of hydrogen gas and indium metal in the isopropyl phosphine system is the decomposition of $In(CH_2CMe_3)_2H$. To ensure that hydrogen gas was not a product of a reaction between $KIn(CH_2CMe_3)_3H$ with $HP(i\text{-}Pr)_2$ as in the phenylphosphine system,[5] the reagents were combined as a benzene solution. No H_2 was formed in 14 days at room temperature. Hydrogen gas was also not observed when $KIn(CH_2CMe_3)_3H$ and $HP(t\text{-}Bu)_2$ were combined.[4]

Experimental Section

All compounds described in this investigation were exceedingly sensitive to oxygen and moisture and were manipulated either under a purified argon atmosphere in a Vacuum Atmospheres drybox or by using standard vacuum line techniques. All solvents were dried by conventional procedures. The starting compounds $In(CH_2CMe_3)_3$,[12] $KIn(CH_2CMe_3)_3H$,[10] and $Ga(CH_2CMe_3)_3$[13] were prepared by literature methods. The reagent KH was obtained from Aldrich Chemical Co. and was washed with pentane to remove oil prior to use. The chlorophosphine $ClP(i\text{-}Pr)_2$ was purchased from Aldrich Chemical Co. and was purified by vacuum distillation at ambient temperature. The secondary phosphine $HP(i\text{-}Pr)_2$ was prepared from $ClP(i\text{-}Pr)_2$ and $LiAlH_4$. The characterization data agreed with the literature.[14] Elemental analyses were performed by E&R Microanalytical Laboratory, Parsippany, NJ. Melting points were determined with a Mel-Temp by using flame-sealed capillaries filled with argon and are uncorrected. Infrared spectra of samples as Nujol mulls or neat liquids between CsI plates were recorded by using a Perkin-Elmer 683 spectrometer. ^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. ^{13}C NMR spectra were recorded at 125.7 MHz) spectra with a Varian VXR-500 spectrometer. Phosphorus NMR spectra were recorded with a Varian VXR-400 spectrometer operating at 161.9 MHz. All chemical shifts are reported in δ (ppm) units. Proton chemical shifts are referenced to $SiMe_4$ at δ 0.00 ppm and either C_6D_5H at δ 7.15 or the residual proton in the other deuterated solvents, as appropriate. Abbreviations for thre appearance of resonances include dd (doublet of doublets), dt (doublet of triplets), hd (heptet of doublets), and ht (heptet of triplets). Carbon-13 chemical shifts are referenced to $SiMe_4$ at δ 0.00 ppm and to C_6D_6 at δ 128.39 ppm. The ^{31}P NMR spectra are

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[10] Beachley, O. T., Jr.; Chao, S.-H. L.; Churchill, M. R.; See, R. F. *Organometallics* **1992**, *11*, 1486.

[11] Downs, A. J.; Pulham, C. R. *Chem Soc. Rev.* **1994**, 175.

[12] Beachley, O. T., Jr.; Spiegel, E. F.; Kopasz, J. P.; Rogers, R. D. *Organometallics* **1989**, *8*, 1915.

[13] Beachley, O. T., Jr.; Pazik, J. C. *Organometallics* **1988**, *7*, 1516.

[14] (a) Issleib, K.; Krech, F. *J. Organomet. Chem.* **1968**, *13*, 283. (b) Kostyanovsky, R. G.; Plekhanov, V. G.; Elnatanov, Y. I.; Zagurskaya, L. M.; Voznesensky, V. N. *Org. Mass Spectrom.* **1972**, *6*, 1199.

reported relative to 85% H$_3$PO$_4$ in D$_2$O solution at 0.00 ppm via an external standard. Negative chemical shifts are assigned to resonances upfield from the reference. All samples for NMR spectra were contained in flame-sealed NMR tubes. Complete NMR spectral data including data at intermediate times for the various studies are available in the Supporting Information. Freezing points of benzene solutions for calculating molecular weights and equilibrium constants for dissociation of adducts were observed by using an instrument similar to that described by Shriver and Drezdzon.[15]

Synthesis of [(Me$_3$CCH$_2$)$_2$InP(i-Pr)$_2$]$_2$ from In(CH$_2$CMe$_3$)$_3$ and HP(i-Pr)$_2$. The reagents, HP(i-Pr)$_2$ (0.403 g, 3.41 mmol) and In(CH$_2$CMe$_3$)$_3$ (1.121 g, 3.42 mmol), as pentane solutions were combined at −78 °C, and the resulting solution was allowed to stir at ambient temperature for 18 h. Then the pentane was removed by vacuum distillation while holding the solution at approximately −20 °C. The remaining colorless liquid slowly converted at room temperature to a very volatile liquid and a colorless solid. After 6 days the very volatile liquid was removed by vacuum distillation and identified as CMe$_4$, whereas the remaining solid was [(Me$_3$CCH$_2$)$_2$InP(i-Pr)$_2$]$_2$ (1.20 g, 3.21 mmol, 94.1% yield based on HP(i-Pr)$_2$). The indium phosphide may be sublimed under vacuum at 60−65 °C. X-ray quality crystals of [(Me$_3$CCH$_2$)$_2$InP(i-Pr)$_2$]$_2$ were grown by recrystallization from a very small amount of pentane at −30 °C.

[(Me$_3$CCH$_2$)$_2$InP(i-Pr)$_2$]$_2$. Mp: 126.9−127.9 °C. ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ −1.9 (s). ^{31}P NMR (C$_6$D$_6$): δ −1.9 (s). ^{1}H NMR (C$_6$D$_6$): δ 1.25 (dt, [(CH*Me*$_2$)$_2$]$_2$, J = 7 Hz, 7 Hz, 12 H), 1.29 (s, [(*Me*$_3$CCH$_2$)$_2$InP, 18 H), 1.35 (s, [(Me$_3$CC*H*$_2$)$_2$InP, 4 H), 2.44 (ht, PC*H*, J = 7 Hz, 2 H) (see Results and Discussion for description of spectrum). Anal. Calcd for C$_{16}$H$_{36}$InP: C, 51.35; H, 9.70. Found: C, 51.27; H, 9.12. Cryoscopic molecular weight, benzene solution, fw 374 (molality, obsd mol wt, assoc): 0.0477, 771.5, 2.06; 0.0349, 790.9, 2.11; 0.0231, 790.7, 2.11.

Reaction of HP(i-Pr)$_2$ with 1 Equiv of In(CH$_2$CMe$_3$)$_3$ as Followed by NMR Spectroscopy. A benzene-d_6 solution of HP(i-Pr)$_2$ (0.0943 g, 0.798 mmol, 0.368 m) was combined with a benzene-d_6 solution of In(CH$_2$CMe$_3$)$_3$ (0.262 g, 0.798 mmol, 0.368 m) in a glovebox. After a portion of the solution had been added to an NMR tube, the tube was flame-sealed. The progress of the reaction was monitored by NMR spectroscopy. The intensities of the phosphorus signals suggested that slightly more than half of the phosphine had been converted to the phosphide after 45 days. Experimental data are available with the Supporting Information.

Reaction of HP(i-Pr)$_2$ with 5 Equiv of In(CH$_2$CMe$_3$)$_3$ as Followed by NMR Spectroscopy. A benzene-d_6 solution of HP(i-Pr)$_2$ (0.0154 g, 0.130 mmol, 0.140 m) was combined with a benzene-d_6 solution of In(CH$_2$CMe$_3$)$_3$ (0.2141 g, 0.6523 mmol, 0.701 m) as described in the previous experiment, and the progress of the reaction was monitored by NMR spectroscopy. The initial spectrum observed within 30 min of warming the sample to room temperature demonstrated that CMe$_4$ had been formed. The elimination reaction was complete within 4 days. Complete experimental data are available with the Supporting Information.

Reaction of In(CH$_2$CMe$_3$)$_3$ with 5 Equiv of HP(i-Pr)$_2$ as Followed by NMR Spectroscopy. A benzene-d_6 solution of HP(i-Pr)$_2$ (0.0724 g, 0.613 mmol, 0.691 m) was combined with a benzene-d_6 solution of In(CH$_2$CMe$_3$)$_3$ (0.0402 g, 0.123 mmol, 0.138 m) as described in the previous experiment. The progress of the reaction was monitored by NMR spectroscopy, but very little reaction had occurred after 41 days from mixing the reagents. Complete experimental data are available with the Supporting Information.

Determination of the Equilibrium Constant for the Dissociation of (Me$_3$CCH$_2$)$_3$In·P(H)(i-Pr)$_2$ in Benzene Solution by Freezing Point Depression Measurements. Solutions of In(CH$_2$CMe$_3$)$_3$, excess HP(i-Pr)$_2$, and benzene were prepared and then diluted with additional benzene. The freezing point of each solution was measured three times. The presence of excess phosphine in these solutions prevented the formation of [(Me$_3$CCH$_2$)InP(i-Pr)$_2$]$_2$ and the elimination of neopentane during the cryoscopic study. Thus, the observed molalitiy of a solution indicated the total of the concentrations of (Me$_3$CCH$_2$)$_3$In·P(H)(i-Pr)$_2$, In(CH$_2$CMe$_3$)$_3$, and HP(i-Pr)$_2$. (a) Reagents: In(CH$_2$CMe$_3$)$_3$ (0.0601 g, 0.183 mmol), HP(i-Pr)$_2$ (0.0452 g, 0.383 mmol), and benzene (4.7376 g); dilution with additional benzene (1.6060 and 3.3300 g). The following results for each of the three solutions include the calcd molality of HP(i-Pr)$_2$ prior to reaction with In(CH$_2$CMe$_3$)$_3$, obsd molality of solution, calcd dissociation constant of adduct (K_d): 0.0808, 0.0825, 2.1 × 10^{-3}; 0.0603, 0.0620, 2.1 × 10^{-3}; 0.0395, 0.0410, 1.9 × 10^{-3}. (b) Reagents: In(CH$_2$CMe$_3$)$_3$ (0.0365 g, 0.111 mmol), HP(i-Pr)$_2$ (0.0272 g, 0.230 mmol), and benzene (4.6500 g); dilution with additional benzene (1.3970 g). The following results for each of the solutions include the calcd molality of HP(i-Pr)$_2$ prior to reaction with In(CH$_2$CMe$_3$)$_3$, obsd molality of solution, calcd dissociation constant of adduct (K_d): 0.0413, 0.0419, 2.1 × 10^{-3}; 0.0318, 0.0324, 2.3 × 10^{-3}. The average dissociation constant for the adduct (Me$_3$CCH$_2$)$_3$In·P(H)(i-Pr)$_2$ calculated by using all data is (2.1 ± 0.2) × 10^{-3}.

Reaction of KIn(CH$_2$CMe$_3$)$_3$H with ClP(i-Pr)$_2$ at −78 °C. The reagents, ClP(i-Pr)$_2$ (0.906 g, 5.94 mmol) dissolved in 10 mL of pentane and KIn(CH$_2$CMe$_3$)$_3$H (2.19 g, 5.95 mmol) dissolved in 20 mL of pentane, were cooled to −78 °C and combined. The resulting mixture was allowed to slowly warm to room temperature and was stirred for 2 days. The noncondensable gas (H$_2$) that formed during the reaction was measured by using a Toepler pump/gas buret assembly, while the pentane solution was maintained at −196 °C (1.06 mmol H$_2$, 35.5% yield based on KIn(CH$_2$CMe$_3$)$_3$H). The pentane-soluble products were separated from the precipitate by extraction (8 times) through a medium-porosity frit to room temperature. The solvent was removed by vacuum distillation at 0 °C. The pentane-soluble crude products were identified as [(Me$_3$CCH$_2$)$_2$InP(i-Pr)$_2$]$_2$, (Me$_3$CCH$_2$)$_3$In·P(H)(i-Pr)$_2$, and (Me$_3$CCH$_2$)$_3$In·P$_2$(i-Pr)$_4$ with a small amount of (Me$_3$CCH$_2$)P(i-Pr)$_2$ after comparison of the ^{1}H and/or ^{31}P NMR spectrum of the product with the spectra for authentic samples. As the flask sat at room temperature in the drybox, long-needle crystals slowly formed. These crystals were mechanically separated and identified as (Me$_3$CCH$_2$)$_3$In·P$_2$(i-Pr)$_4$ (0.563 g, 1.00 mmol, 33.7% yield based on ClP(i-Pr)$_2$) after comparison of their ^{1}H and ^{31}P NMR spectra and melting point with those for an authentic sample that had been the subject of an X-ray structural study.

Crude Product Mixture. ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ −1.9 (s, [(Me$_3$CCH$_2$)$_2$In·P(i-Pr)$_2$]$_2$), −9.1 (s, (Me$_3$CCH$_2$)$_3$In·P$_2$(i-Pr)$_4$), −15.2 (s, (Me$_3$CCH$_2$)$_3$In·P(H)(i-Pr)$_2$). ^{31}P NMR (C$_6$D$_6$): δ, −1.9 (m, [(Me$_3$CCH$_2$)$_2$InP(i-Pr)$_2$]$_2$), −9.1 (m, (Me$_3$CCH$_2$)$_3$In·P$_2$(i-Pr)$_4$), −15.2 (d, (Me$_3$CCH$_2$)$_3$In·P(H)(i-Pr)$_2$, trace). ^{1}H NMR (C$_6$D$_6$): δ 0.91 (s, (*Me*$_3$CCH$_2$)P(i-Pr)$_2$), 1.07 (s, In(C*H*$_2$CMe$_3$)$_3$), 1.13 (dd, (Me$_3$CCH$_2$)$_3$In·P$_2$(CH*Me*$_2$)$_4$, 14 Hz, 7 Hz), 1.13 (s, InCH$_2$C*Me*$_3$), 1.25 (q, [(Me$_3$CCH$_2$)$_2$InP(CH*Me*$_2$)$_2$]$_2$, 7 Hz), 1.28 (s, [(*Me*$_3$CCH$_2$)$_2$InP(i-Pr)$_2$]$_2$), 1.34 (br, [(Me$_3$CC*H*$_2$)$_2$InP(i-Pr)$_2$]$_2$), 2.04 (st, (Me$_3$CCH$_2$)$_3$In·P$_2$(C*H*Me$_2$)$_4$), 2.43 (st, [(Me$_3$CCH$_2$)$_2$InP(C*H*Me$_2$)$_2$]$_2$).

Long-Needle Crystals: (Me$_3$CCH$_2$)$_3$In·P$_2$(i-Pr)$_4$. Mp: 30−33 °C. ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ −1.9 (br, trace, [(Me$_3$CCH$_2$)$_2$InP(i-Pr)$_2$]$_2$), −6.64 (br, trace, (Me$_3$CCH$_2$)P(i-Pr)$_2$), −9.40 (s, (Me$_3$CCH$_2$)$_3$In·P$_2$(i-Pr)$_4$). ^{31}P NMR (C$_6$D$_6$): δ −9.5 (m, (Me$_3$CCH$_2$)$_3$In·P$_2$(i-Pr)$_4$). ^{1}H NMR (C$_6$D$_6$): δ 1.07 (br, InC*H*$_2$), 1.13 (td, J = 7 Hz, J = 7 Hz, PCH*Me*$_2$), 1.13 (s, InCH$_2$C*Me*$_3$), 1.14 (td, J = 7 Hz, J = 5 Hz, PCH*Me*$_2$), 1.29 (s, [(*Me*$_3$CCH$_2$)$_2$InP(i-Pr)$_2$]$_2$), 2.03 (st, J = 7 Hz, PC*H*Me$_2$) (see Results and Discussion for description of spectrum). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 21.1 (t, PCH*Me*$_2$, J = 10 Hz), 21.1 (t, PCHMe$_2$, J = 6 Hz), 21.8 (t, PCH*Me*$_2$, J = 9 Hz), 33.0 (s, InCH$_2$*C*Me$_3$), 34.7 (s,

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[15] Shriver, D. F.; Drezdzon, M. A. *The Manipulation of Air-Sensitive Compounds*; Wiley: New York, 1986; p 38.

$\mathrm{InCH_2C}\mathit{Me}_3$), 45.1 (s, $\mathrm{InC}\mathit{H}_2\mathrm{CMe_3}$). ^{13}C NMR ($\mathrm{C_6D_6}$): δ 21.1 (qm, $\mathrm{PCH}\mathit{Me}_2$, $J = 126$ Hz), 21.1 (dm, $\mathrm{P}\mathit{C}\mathrm{HMe_2}$, $J = 126$ Hz), 21.8 (qm, $\mathrm{PCH}\mathit{Me}_2$, $J = 126$ Hz), 32.6 (m, $\mathrm{InCH_2}\mathit{C}\mathrm{Me_3}$), 34.8 (qm, $\mathrm{InCH_2C}\mathit{Me}_3$, $J = 124$ Hz), 45.4 (tm, $\mathrm{In}\mathit{C}\mathrm{H_2CMe_3}$, $J = 126$ Hz). Assignments were verified by HETCOR spectroscopy.

Preparation of $\mathbf{P_2(i\text{-}Pr)_4}$. A solution of $\mathrm{ClP(i\text{-}Pr)_2}$ (1.32 g, 8.67 mmol) in 5 mL of toluene was added to an excess of sodium sand (0.241 g, 10.5 mmol) dispersed in 15 mL of toluene. The reaction mixture was refluxed and stirred for 1 day, and a dark blue solution formed. The solvent was removed by vacuum distillation at ambient temperature. The remaining viscous liquid was purified by dynamic vacuum distillation and identified as $\mathrm{P_2(i\text{-}Pr)_4}$ (0.8438 g, 3.60 mmol, 83.0% yield based on $\mathrm{ClP(i\text{-}Pr)_2}$).

$\mathbf{P_2(i\text{-}Pr)_4}$. $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR ($\mathrm{C_6D_6}$): δ −10.3 (s, $\mathrm{P_2(i\text{-}Pr)_4}$) (lit. −11.58,[16] −12.5[17]). ^{31}P NMR ($\mathrm{C_6D_6}$): δ −10.4 (m, $\mathrm{P_2(i\text{-}Pr)_4}$). ^{1}H NMR ($\mathrm{C_6D_6}$): δ 1.14 (dt, $\mathrm{PCH}\mathit{Me}_2$, $J = 7$ Hz, 7 Hz, 3 H), 1.15 (dt, $\mathrm{PCH}\mathit{Me}_2$, $J = 7$ Hz, 7 Hz, 3 H), 2.01 (st, $\mathrm{PC}\mathit{H}\mathrm{Me_2}$, $J = 7$ Hz, 4 Hz, 1 H) (lit. 1.03, 1.98;[16] 1.4−2.2[17]).

Preparation of $\mathbf{(Me_3CCH_2)P(i\text{-}Pr)_2}$. A solution of $\mathrm{ClP(i\text{-}Pr)_2}$ (2.51 g, 16.5 mmol) in 5 mL of methylcyclohexane was added slowly to a solution of $\mathrm{Li(CH_2CMe_3)}$ (1.93 g, 24.8 mmol) in 30 mL of methylcyclohexane that had been cooled under vacuum to −40 to −50 °C with a dry ice/2-propanol bath. The resulting mixture was heated with a 70−75 °C oil bath for 1 day. After the soluble product was separated from the LiCl by extraction through a medium-porosity frit, the methylcyclohexane was removed by vacuum distillation at low temperature (<−30 °C) to leave a viscous yellow liquid. This crude product was purified by vacuum distillation at ambient temperature into a tube cooled to −196 °C. The pure product $\mathrm{(Me_3CCH_2)P(i\text{-}Pr)_2}$ (1.94 g, 10.3 mmol, 62.7% yield based on $\mathrm{ClP(i\text{-}Pr)_2}$) was isolated as a colorless liquid.

$\mathbf{(Me_3CCH_2)P(i\text{-}Pr)_2}$. $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR ($\mathrm{C_6D_6}$): δ −5.0 (s, $\mathrm{(Me_3CCH_2)P(i\text{-}Pr)_2}$). ^{31}P NMR ($\mathrm{C_6D_6}$): δ −5.1 (m, $\mathrm{(Me_3CCH_2)P(i\text{-}Pr)_2}$). ^{1}H NMR ($\mathrm{C_6D_6}$): δ 0.97 (dd, $\mathrm{(Me_3CCH_2)P(CH}\mathit{Me}_2)_2$, $J =$ 11 Hz, 7 Hz, 6 H), 1.02 (dd, $\mathrm{(Me_3CCH_2)P(CH}\mathit{Me}_2)_2$, $J = 13$ Hz, 7 Hz, 6 H), 1.04 (s, $(\mathit{Me}_3\mathrm{CCH_2)P(CHMe_2)_2}$, 9 H), 1.18 (d, $\mathrm{(Me_3CC}\mathit{H}_2\mathrm{)P(CHMe_2)_2}$, $J = 6$ Hz, 2 H), 1.56 (hd, $\mathrm{(Me_3CCH_2)P(C}\mathit{H}\mathrm{Me_2)_2}$, $J = 7$ Hz, 7 Hz, 2 H).). Anal. Calcd for $\mathrm{C_{11}H_{25}P}$: C, 70.17; H, 13.38, P, 16.44. Found: C, 70.17; H, 13.01, P, 16.79.

Synthetic Reaction between $\mathbf{In(CH_2CMe_3)_3}$ and $\mathbf{ClP(i\text{-}Pr)_2}$ to Form $\mathbf{In(CH_2CMe_3)_2Cl}$ and $\mathbf{(Me_3CCH_2)P(i\text{-}Pr)_2}$. The reagents, $\mathrm{ClP(i\text{-}Pr)_2}$ (0.411 g, 2.69 mmol) and $\mathrm{In(CH_2CMe_3)_3}$ (0.883 g, 2.69 mmol), were degassed at −196 °C on the vacuum line and then combined without solvent. The initial mixture was a liquid with only a faint trace of solid. Then after 18 h the mixture became a colorless solid. After 1 more day a gelatinous material was observed. Subsequent recrystallization of the product from pentane at low temperature yielded crystals of $\mathrm{In(CH_2CMe_3)_2Cl}$ (0.606 g, 2.07 mmol, 76.9% yield). Removal of the pentane from the mother liquor by vacuum distillation at ambient temperature provided a liquid that was purified by distillation at 65−75 °C with a short-path still. The distillate was identified as $\mathrm{(Me_3CCH_2)P(i\text{-}Pr)_2}$ (0.0955 g, 0.507 mmol, 18.8% yield).

$\mathbf{In(CH_2CMe_3)_2Cl}$. Mp: 164.2−167.1 °C (lit.[12] 162−165 °C). ^{1}H NMR ($\mathrm{C_6D_6}$): δ 1.09 (s, $\mathrm{In(CH_2C}\mathit{Me}_3)_2\mathrm{Cl}$, 18 H), 1.58 (s, $\mathrm{In(C}\mathit{H}_2\mathrm{CMe_3)_2Cl}$, 4 H) (lit.[12] 1.09, 1.56). No ^{31}P signals.

$\mathbf{(Me_3CCH_2)P(i\text{-}Pr)_2}$. $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR ($\mathrm{C_6D_6}$): δ −5.1 (s, $\mathrm{(Me_3CCH_2)P(i\text{-}Pr)_2}$). ^{31}P NMR ($\mathrm{C_6D_6}$): δ −5.1 (m, $\mathrm{(Me_3CCH_2)P(i\text{-}Pr)_2}$). ^{1}H NMR ($\mathrm{C_6D_6}$): δ 0.97 (dd, $\mathrm{(Me_3CCH_2)P(CH}\mathit{Me}_2)_2$, $J =$ 11 Hz, 7 Hz, 6 H), 1.01 (dd, $\mathrm{(Me_3CCH_2)P(CH}\mathit{Me}_2)_2$, $J = 14$ Hz, 7 Hz, 6 H), 1.03 (s, $(\mathit{Me}_3\mathrm{CCH_2)P(i\text{-}Pr)_2}$, 9 H), 1.18 (d, $\mathrm{(Me_3CC}\mathit{H}_2\mathrm{)P(CHMe_2)_2}$, 2 H), 1.56 (sd, $\mathrm{(Me_3CCH_2)P(C}\mathit{H}\mathrm{Me_2)_2}$, $J =$ 7 Hz, 2 Hz, 2 H). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{C_6D_6}$): δ 18.5 (d, $\mathrm{(Me_3CCH_2)P(CH}\mathit{Me}_2)_2$, $J = 11$ Hz), 19.8 (d, $\mathrm{(Me_3CCH_2)P(}\mathit{C}\mathrm{HMe_2)_2}$, $J = 16$ Hz), 23.6 (d, $\mathrm{(Me_3CCH_2)P(CHMe_2)_2}$, $J = 14$ Hz), 30.8 (d, $(\mathit{Me}_3\mathrm{CCH_2)P(CHMe_2)_2}$, $J = 9$ Hz), 36.4 (d, $\mathrm{(Me_3C}\mathit{C}\mathrm{H_2)P(CHMe_2)_2}$, $J = 23$ Hz).

Reaction between $\mathbf{In(CH_2CMe_3)_3}$ and $\mathbf{ClP(i\text{-}Pr)_2}$ as Followed by NMR Spectroscopy. A $\mathrm{C_6D_6}$ solution of $\mathrm{ClP(i\text{-}Pr)_2}$ (0.0554 g, 0.363 mmol) was added to a $\mathrm{C_6D_6}$ solution of $\mathrm{In(CH_2CMe_3)_3}$ (0.120 g, 0.365 mmol) and transferred to an NMR tube. The total amount of $\mathrm{C_6D_6}$ was 0.770 g. After the tube was evacuated and degassed at −196 °C on a vacuum line, the tube was flame-sealed. NMR spectra were recorded. The formation of $\mathrm{(Me_3CCH_2)P(i\text{-}Pr)_2}$ and $\mathrm{In(CH_2CMe_3)_2Cl}$[10] was complete after 1 day. Complete NMR spectral data are available with the Supporting Information.

Reaction of $\mathbf{In(CH_2CMe_3)_3}$ and $\mathbf{P_2(i\text{-}Pr)_4}$. A reaction tube charged with $\mathrm{P_2(i\text{-}Pr)_4}$ (0.331 g, 1.41 mmol) was connected to a flask that contained $\mathrm{In(CH_2CMe_3)_3}$ (0.464 g, 1.41 mmol) in a glovebox. The mixture was allowed to stand under vacuum for 12 days. A small amount of pentane (10 mL) was then added to the mixture, and the resulting solution was stirred for 18 h. The pentane was subsequently removed by vacuum distillation at a temperature less than −30 °C. A few long-needle crystals, presumably $\mathrm{(Me_3CCH_2)_3In{\cdot}P_2(i\text{-}Pr)_4}$, appeared 1 day after the removal of pentane. The benzene-soluble products were identified by their $^{31}\mathrm{P}\{^1\mathrm{H}\}$, ^{31}P, and ^{1}H NMR spectra as $\mathrm{(Me_3CCH_2)_3In{\cdot}P_2(i\text{-}Pr)_4}$ (43% calcd from integration of ^{1}H NMR spectrum), $\mathrm{[(Me_3CCH_2)_2InP(i\text{-}Pr)_2]_2}$ (29%), and $\mathrm{(Me_3CCH_2)P(i\text{-}Pr)_2}$ (29%).

Products. $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR ($\mathrm{C_6D_6}$): δ −1.9 (s, $\mathrm{[(Me_3CCH_2)_2InP(i\text{-}Pr)_2]_2}$), −5.2 (s, $\mathrm{(Me_3CCH_2)P(i\text{-}Pr)_2}$), −10.3 (s, $\mathrm{(Me_3CCH_2)_3In{\cdot}P_2(i\text{-}Pr)_4}$). ^{31}P NMR ($\mathrm{C_6D_6}$): δ −1.8 (m, $\mathrm{[(Me_3CCH_2)_2InP(i\text{-}Pr)_2]_2}$), −10.3 (m, $\mathrm{(Me_3CCH_2)_3In{\cdot}P_2(i\text{-}Pr)_4}$). ^{1}H NMR ($\mathrm{C_6D_6}$): δ 0.90 (br, ∼1 H), 0.97 (dd, $J =$ 11 Hz, 7 Hz, $\mathrm{(Me_3CCH_2)P(CH}\mathit{Me}_2)_2$, 4 H), 1.01 (dd, $J =$ 13 Hz, 7 Hz, $\mathrm{(Me_3CCH_2)P(CH}\mathit{Me}_2)_2$, 4 H), 1.03 (s, $(\mathit{Me}_3\mathrm{CCH_2)P(CHMe_2)_2}$, ∼3 H), 1.07 (s, $\mathrm{In(C}\mathit{H}_2\mathrm{CMe_3)_3}$, 6 H), 1.13 (dt, $J = 7$ Hz, 7 Hz, $\mathrm{(Me_3CCH_2)_3In{\cdot}P_2(CH}\mathit{Me}_2)_4$, 12 H), 1.14 (dt, $J = 7$ Hz, 7 Hz, $\mathrm{(Me_3CCH_2)_3In{\cdot}P_2(CH}\mathit{Me}_2)_4$, 12 H), 1.14 (s, $\mathrm{In(CH_2C}\mathit{Me}_3)_3$, 27 H), 1.25 (q, $J =$ 7 Hz, $\mathrm{[(Me_3CCH_2)_2InP(CH}\mathit{Me}_2)_2]_2$, 18 H), 1.29 (s, $[(\mathit{Me}_3\mathrm{CCH_2)_2InP(i\text{-}Pr)_2]_2}$, 23 H), 1.36 (br, $\mathrm{[(Me_3CC}\mathit{H}_2\mathrm{)_2InP(i\text{-}Pr)_2]_2}$), 2.02 (ht, $J = 7$ Hz, 4 Hz, $\mathrm{(Me_3CCH_2)_3In{\cdot}P_2(C}\mathit{H}\mathrm{Me_2)_4}$, ∼3 H), 2.44 (ht, J = 7 Hz, 2 Hz, $\mathrm{[(Me_3CCH_2)_2InP(C}\mathit{H}\mathrm{Me_2)_2]_2}$, 2 H).

NMR Spectral Study of Reaction between $\mathbf{In(CH_2CMe_3)_3}$ and $\mathbf{P_2(i\text{-}Pr)_4}$. A reaction tube containing $\mathrm{P_2(i\text{-}Pr)_4}$ (0.0747 g, 0.319 mmol) and $\mathrm{C_6D_6}$ (1.0 mL) was attached to an apparatus charged with $\mathrm{In(CH_2CMe_3)_3}$ (0.1047 g, 0.3189 mmol) in a glovebox. The assembled apparatus was degassed at −196 °C on a vacuum line. The solution of $\mathrm{P_2(i\text{-}Pr)_4}$ was added to the $\mathrm{In(CH_2CMe_3)_3}$, and the resulting solution was then poured into the NMR tube sidearm. The NMR tube was flame-sealed under vacuum. Complete NMR spectral data are available with the Supporting Information.

NMR Spectral Study of Reaction between $\mathbf{[(Me_3CCH_2)_2InP(i\text{-}Pr)_2]_2}$ and $\mathbf{ClP(i\text{-}Pr)_2}$. A reaction tube containing $\mathrm{ClP(i\text{-}Pr)_2}$ (0.312 g, 0.205 mmol) and $\mathrm{C_6D_6}$ (1.0 mL) was attached to an apparatus charged with $\mathrm{[(Me_3CCH_2)_2InP(i\text{-}Pr)_2]_2}$ (0.765 g, 0.204 mmol monomer) in a glovebox. The assembled apparatus was degassed at −196 °C on the vacuum line. The solution of $\mathrm{ClP(i\text{-}Pr)_2}$ was poured onto the $\mathrm{[(Me_3CCH_2)_2InP(i\text{-}Pr)_2]_2}$, and the resulting solution was then poured into the NMR tube sidearm and flame-sealed under vacuum. The initial spectra indicated the presence of only $\mathrm{In(CH_2CMe_3)_2Cl}$ and $\mathrm{P_2(i\text{-}Pr)_4}$. All resonances for the starting materials had disappeared. Thus, reaction was complete within the time required to prepare the sample and record the spectrum, approximately 30 min. Complete NMR spectral data are available with the Supporting Information.

NMR Spectral Study of a Solution Prepared from $\mathbf{KIn(CH_2CMe_3)_3H}$, $\mathbf{In(CH_2CMe_3)_2Cl}$, and $\mathbf{(Me_3CCH_2)P(i\text{-}Pr)_2}$. An NMR tube was charged with $\mathrm{(Me_3CCH_2)P(i\text{-}Pr)_2}$ (0.0374 g, 0.199 mmol), $\mathrm{In(CH_2CMe_3)_2Cl}$ (0.0571 g, 0.195 mmol), and KIn-

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$(CH_2CMe_3)_3H$ (0.0741 g, 0.201 mmol) in the glovebox. The tube was degassed at −196 °C on the vacuum line, C_6D_6 (1.0 mL) was added by vacuum distillation, and finally the tube was flame-sealed under vacuum. Bubbling, most likely due to H_2, was observed upon warming the sample to room temperature, whereas a large amount of a gray solid, probably indium metal, was observed after 1 day. All observations suggest that $KIn(CH_2CMe_3)_3H$ reacted instantly with $In(CH_2CMe_3)_2Cl$, whereas $(Me_3CCH_2)P(CHMe_2)_2$ remained unchanged. Complete NMR spectral data are available with the Supporting Information.

NMR Spectral Study of Reaction Mixture Prepared from $KIn(CH_2CMe_3)_3H$, $In(Me_3CCH_2)_2Cl$, and $ClP(i\text{-}Pr)_2$. The reagents $In(CH_2CMe_3)_3$ (0.161 g, 0.490 mmol) and $ClP(i\text{-}Pr)_2$ (0.0701 g, 0.459 mmol) were combined under vacuum in benzene-d_6 (0.8 mL) and stirred for 18 h. The products $In(CH_2CMe_3)Cl$ and $(Me_3CCH_2)P(i\text{-}Pr)_2$ were then combined with 0.7 mL of a benzene-d_6 solution of $KIn(CH_2CMe_3)_3H$ (0.168 g, 0.457 mmol) at ambient temperature. The resulting solution was stirred for 15 min, and part of the solution (0.9 mL) was poured into the NMR tube sidearm. The products identified by NMR spectroscopy were $(Me_3CCH_2)_3In{\cdot}P_2(i\text{-}Pr)_4$ and $HP(i\text{-}Pr)_2$. In addition a large amount of a gray solid indicative of indium metal was observed after 1 day. Complete NMR spectral data are available with the Supporting Information.

Attempted Reaction between $KIn(CH_2CMe_3)_3H$ with $HP(i\text{-}Pr)_2$. The reagents $KIn(CH_2CMe_3)_3H$ (1.74 g, 4.72 mmol) and $HP(i\text{-}Pr)_2$ (0.557 g, 4.72 mmol) were combined with 25 mL of pentane at room temperature. No reaction occurred. No H_2 formed in 14 days.

Collection of X-ray Diffraction Data and Structure Solution for $[(Me_3CCH_2)_2InP(i\text{-}Pr)_2]_2$. A colorless crystal of approximate orthogonal dimensions 0.3 × 0.3 × 0.4 mm was carefully sealed into a thin-walled glass capillary, then mounted and aligned accurately on a Siemens R3m/V diffractometer. The crystal's Laue symmetry ($2/m$), crystal class (monoclinic), orientation matrix, and cell dimensions were determined as has been described in detail previously.[18]

The intensity data were collected by a coupled θ (crystal)−2θ (counter) scan and were corrected for Lp factors and the effects of absorption (via ψ-scans). The systematic absences, $h0l$ for $l = 2n + 1$ (only), indicate that possible space groups are the noncentrosymmetric Pc (No. 7) and the centrosymmetric $P2/c$ (No. 13). The latter was found to be appropriate by the successful solution of the crystal structure in this higher-symmetry space group.

Crystallographic calculations were carried out by use of the SHELXTL PLUS (Release 4.11(VMS)) program package.[19] The structure was solved by direct methods and refined by a combination of difference Fourier and least-squares refinement techniques. The unit cell contains the expected four molecules, but the crystallographic asymmetric unit consists of two crystallographically independent "half-molecules" lying around 2-fold axes at (0, y, 1/4). Both molecule 1 and molecule 2 possess precise C_2 site symmetry and approximate C_{2v} molecular symmetry. Hydrogen atoms were included in calculated positions, based upon $d(C-H) = 0.96$ Å.[20] Their isotropic thermal parameters were refined in blocks in earlier cycles and then fixed at the end. The final discrepancy index was $R = 8.18\%$ for all 5392 unique reflections (none omitted).

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Supporting Information Available: (1) Complete tables of positional parameters, interatomic distances and angles, anisotropic thermal parameters and calculated positions for hydrogen atoms for the compound studied. (2) Complete ^1H and ^{31}P NMR spectral data for all spectral studies. This material is available free of charge via the Internet at http://pubs.acs.org.

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