Reaction of KIn(CH₂CMe₃)₃H with Chlorodiphenylphosphine

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Summary: The reaction between $KIn(CH_2CMe_3)_3H$ and $ClPPh_2$ in pentane or benzene produces significant yields of two indium—phosphorus compounds, $(Me_3CCH_2)_2$ -InPPh₂ and $(Me_3CCH_2)_3In P(CH_2CMe_3)Ph_2$. This unexpected adduct incorporates a neopentyl group that was originally a substituent on the indium reagent. The other products of the reaction are CMe_4 , H_2 , and KCl. The formation of all products is explained by a set of experimentally verified reactions.

Introduction

The original and simplest route to compounds of the type $R_2InPR'_2$ involves the use of the hydrocarbon elimination reaction^{1–3} between InR_3 and HPR'_2 . Even

$$InR_3 + HPR'_2 \xrightarrow{hydrocarbon elimination} R_2InPR'_2 + RH$$
 (1)

though the metathetical reaction⁴ between InR₂Cl and LiPR'₂ and the Me₃SiCl elimination reaction⁵ between InR₂Cl and (Me₃Si)PR'₂ have also been exceedingly useful and productive reactions to prepare R₂InPR'₂, the latter reactions require the synthesis of more starting materials than are needed for the simple hydrocarbon elimination reaction. Therefore, a goal of our research has been to develop a procedure for the preparation of R₂InPR'₂ that would take advantage of the simplicity of the hydrocarbon elimination reaction but that would

J. D.; Banks, M. A. Rogers, R. D. Organometallics **1995**, 14, 3448. (2) Beachley, O. T., Jr.; Kopasz, J. P.; Zhang, H.; Hunter, W. E.; Atwood, J. L. J. Organomet. Chem. **1987**, 325, 69. not require the prior synthesis and handling of HPR'₂. Ideally, the secondary phosphine should be formed insitu and then be consumed by reaction with the organoindium compound. This goal was realized with the synthesis of $[(Me_3CCH_2)_2InP(t-Bu)_2]_2$ in high, if not quantitative, yield by reacting KIn(CH₂CMe₃)₃H⁶ with ClP(t-Bu)₂ in pentane (eq 2).⁷ In contrast, we have found

$$KIn(CH_{2}CMe_{3})_{3}H + ClP(t-Bu)_{2} \xrightarrow{\text{pentane}} (Me_{3}CCH_{2})_{2}InP(t-Bu)_{2} + KCl + CMe_{4} (2)$$

that the reaction between $KIn(CH_2CMe_3)_3H$ and $ClPPh_2$ forms a different set of products and thus involves some reactions that were not observed for the *tert*-butyl phosphine system.⁷

Results and Discussion

The reaction between KIn(CH₂CMe₃)₃H and ClPPh₂ in either pentane or benzene produces two indiumphosphorus compounds (Me₃CCH₂)₂InPPh₂^{2,3} and (Me₃-CCH₂)₃In·P(CH₂CMe₃)Ph₂, which account for approximately 85-90% of the initial indium and phosphorus. The other products that were isolated from the reaction included CMe₄, H₂, and KCl. The identity of the principal product (Me₃CCH₂)₂InPPh₂ was confirmed by observing that its physical properties as well as its ¹H and ³¹P NMR spectra were identical with those for samples prepared by the elimination reaction between In(CH₂CMe₃)₃ with HPPh₂ in pentane or benzene solution.^{2,3} Thus, (Me₃CCH₂)₂InPPh₂ has been synthesized directly from the chlorophosphine without the intermediate preparation and isolation of HPPh₂. The second indium-phosphorus product is (Me₃CCH₂)₃In·P(CH₂-CMe₃)Ph₂, an adduct of a tertiary phosphine that contains a neopentyl group that was a substituent on the initial indium reagent. The ¹H and ³¹P NMR spectra of this adduct were identical with those of a sample prepared from a 1:1 mixture of In(CH₂CMe₃)₃ and

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 $P(CH_2CMe_3)Ph_2$ that had been prepared independently by using the literature method.⁸

The occurrence of the reactions shown by eq 3-9 readily explains the formation of all products, is in

Pathway for Reaction between KIn(CH2CMe3)3H and CIPPh2

2 {KIn(CH ₂ CMe ₃) ₃ H + CIPPh ₂ \longrightarrow In(CH ₂ CMe ₃) ₃ + HPPh ₂ + KCI}	(3)
$ln(CH_2CMe_3)_3 + HPPh_2 \longrightarrow (Me_3CCH_2)_2 lnPPh_2 + CMe_4$	(4)
$KIn(CH_2CMe_3)_3H + HPPh_2 \longrightarrow H_2 + K[(Me_3CCH_2)_3InPPh_2]$	(5)
$ \begin{array}{c} K[(Me_3CCH_2)_3InPPh_2] + CIPPh_2 & \longrightarrow & (Me_3CCH_2)_2InPPh_2 + \\ & (Me_3CCH_2)PPh_2 + KCI \end{array} $	(6)
$ln(CH_2CMe_3)_3 + ClPPh_2 \longrightarrow ln(CH_2CMe_3)_2Cl + (Me_3CCH_2)PPh_2$	(7)
$\label{eq:charged_constraint} \begin{array}{c} K[(Me_3CCH_2)_3lnPPh_2] + In(CH_2CMe_3)_2CI & \longrightarrow In(CH_2CMe_3)_3 + \\ & (Me_3CCH_2)_2lnPPh_2 + KCI \end{array}$	(8)
$ln(CH_2CMe_3)_3 + (Me_3CCH_2)PPh_2 \longrightarrow (Me_3CCH_2)_3ln \bullet P(CH_2CMe_3)Ph_2$	(9)
<u>Overall Reaction as Sum of Above Steps</u> (Equations 6 and 7 with 8 are alternative routes to $(Me_3CCH_2)_2InPPh_2$)	
$3 \text{ Kin}(\text{CH}_2\text{CMe}_3)_3\text{H} + 3 \text{ CIPPh}_2 \xrightarrow{C_5\text{H}_{12} \text{ or}} C_{\text{e}\text{H}_6} 2 \text{ (Me}_3\text{CCH}_2)_2\text{InPPh}_2 +$	
$(Me_3CCH_2)_3 In \cdot P(CH_2CMe_3)Ph_2 + 3 KCI + CMe_4 + H_2$	(10)

agreement with their observed percentage yields, and is consistent with indium and phosphorus chemistry. All reactions in this sequence have been verified by independent experiments. These reactions account for the formation of $(Me_3CCH_2)_3In \cdot P(CH_2CMe_3)Ph_2$ and H_2 , the two products that were unexpected on the basis of the reaction between $KIn(CH_2CMe_3)_3H$ with $CIP(t-Bu)_2$.⁷ These two products also explain why $(Me_3CCH_2)_2InPPh_2$ and CMe_4 were not formed in equimolar amounts as required by the balanced equation for the hydrocarbon elimination reaction (eq 4). The percentage yield of $(Me_3 CCH_2)_2InPPh_2$ (40.2%) was significantly higher than the yield of CMe_4 (27.0%). Thus, $(Me_3CCH_2)_2InPPh_2$ must be formed by more reactions than only the hydrocarbon elimination reaction.

When the original reagents KIn(CH₂CMe₃)₃H and ClPPh₂ were combined, an insoluble solid formed. This observation suggests the presence of KCl, whereas In-(CH₂CMe₃)₃ and HPPh₂ (eq 3) would be soluble in pentane and benzene and undergo the hydrocarbon elimination reaction to form (Me₃CCH₂)₂InPPh₂ and CMe_4 (eq 4).² However, since both the initial reaction (eq 3) and the elimination reaction (eq 4) are relatively slow,² additional reactions occur to produce (Me₃CCH₂)₂-InPPh₂. The second route to (Me₃CCH₂)₂InPPh₂ must begin with the reaction between HPPh₂ and KIn(CH₂-CMe₃)₃H to form H₂, an observed but unexpected product, and K[(Me₃CCH₂)₃InPPh₂] (eq 5). These observations suggest that KIn(CH₂CMe₃)₃H reacts faster with HPPh₂ than with ClPPh₂. An independent experiment verified that a solution of KIn(CH₂CMe₃)₃H reacted with HPPh₂ within minutes of mixing to form H₂ and an insoluble solid, presumably K[(Me₃CCH₂)₃- $InPPh_2$ (eq 5). An additional datum in support of the occurrence of these reactions is the observation that 96.8% of the hydridic hydrogen initially available in KIn(CH₂CMe₃)₃H is accounted for by the formation of H₂ (both hydrogen atoms originate with this hydride) and CMe₄. After K[(Me₃CCH₂)₃InPPh₂] has been formed,

it can react with ClPPh₂ to form (Me₃CCH₂)₂InPPh₂, $P(CH_2CMe_3)Ph_2$, and KCl (eq 6), as verified by an independent experiment. Thus, K[(Me₃CCH₂)₃InPPh₂] transferred a neopentyl group to ClPPh₂ to form P(CH₂-CMe₃)Ph₂ rather than a PPh₂ group to form P₂Ph₄. A second route to P(CH₂CMe₃)Ph₂ involves the reaction between In(CH₂CMe₃)₃ and ClPPh₂ (eq 7), two species likely to be present in the reaction mixture. However, the indium product from this reaction (eq 7), In(CH₂- $CMe_3)_2Cl_{,8}$ was not an observed product from the reaction between KIn(CH₂CMe₃)₃H and ClPPh₂. Thus, In(CH₂CMe₃)₂Cl⁸ must have reacted with another species such as K[(Me₃CCH₂)₃InPPh₂] if it was formed at all. Independent experimental observations demonstrated that In(CH₂CMe₃)₂Cl reacts readily with K[(Me₃-CCH₂)₃InPPh₂] to form In(CH₂CMe₃)₃, (Me₃CCH₂)₂-InPPh₂, and KCl (eq 8). Trisneopentylindium reacts, in turn, with P(CH₂CMe₃)Ph₂ to form the observed adduct (eq 9). The availability of two different paths to P(CH₂-CMe₃)Ph₂ (eqs 6 and 7) permits all intermediates to be consumed but only two indium phosphorus products to be isolated at the end of the reaction. The overall reaction is summarized by eq 10.

The series of equations shown by eq 3-9 accounts for all products from the reaction between KIn(CH₂-CMe₃)₃H and ClPPh₂. The initial reaction between KIn-(CH₂CMe₃)₃H and ClPPh₂ (eq 3) and the hydrocarbon elimination reaction (eq 4) are slower than the reactions depicted by eqs 5, 6, 7, 8, and 9. The apparent slowness of the replacement of the chlorine on phosphorus by the hydridic hydrogen on indium and the even slower elimination reaction between In(CH₂CMe₃)₃ and HPPh₂ provide the opportunity for the occurrence of reactions not observed for the KIn(CH₂CMe₃)₃H and ClP(t-Bu)₂ system.⁷

Experimental Section

All compounds were manipulated in a standard vacuum line or in a purified argon atmosphere. The starting materials KH and ClPPh₂ were purchased from Aldrich Chemical Co., HPPh₂ was purchased from Strem Chemicals, Inc., and In(CH₂CMe₃)₃⁹ and KIn(CH₂CMe₃)₃H⁶ were prepared by using literature methods. All solvents were dried by conventional procedures. The ¹H NMR spectra were recorded at 400 MHz by using a Varian Unity-Inova 400 spectrometer. Proton chemical shifts are reported in δ (ppm) units and are referenced to SiMe₄ at δ 0.00 ppm and benzene at δ 7.15 ppm. The ³¹P NMR spectra are referenced to 85% H_3PO_4 at δ 0.00 ppm. All samples for NMR spectra were contained in sealed NMR tubes. Infrared spectra of solids were observed as Nujol mulls between KBr plates and were recorded with a Perkin-Elmer 683 spectrometer. Melting points were determined with a Mel-Temp by using flame-sealed capillaries filled with purified argon and are uncorrected.

Synthesis of (Me₃CCH₂)₂InPPh₂ from KIn(CH₂CMe₃)₃H and CIPPh₂. (a) Mixing Reagents at -45 °C in Pentane. A tube, charged with 0.881 g (2.39 mmol) of KIn(CH₂CMe₃)₃H and 10 mL of pentane, was connected to a two-necked flask that contained 0.529 g (2.40 mmol) of ClPPh₂ and 20 mL of pentane. The solution of ClPPh₂ was cooled to -45 °C with a 2-propanol/dry ice bath, and then the reagents were combined. The resulting mixture was slowly warmed to room temperature and stirred for 2 days. The noncondensable gas H₂ (0.667 mmol, 55.8% based on KIn(CH₂CMe₃)₃H, see Results and

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Discussion) was measured with a Toepler pump-gas buret assembly while the solution was maintained at -196 °C. Then the product mixture was warmed to room temperature and filtered with a medium glass frit, and the pentane was removed by vacuum distillation. The insoluble solid (KCl) was isolated and weighed in the drybox (0.168 g, 2.25 mmol, 94.1% yield based on KIn(CH₂CMe₃)₃H). The pentane-soluble solid was transferred to a sublimator, whereupon the adduct (Me₃-CCH₂)₃In·P(CH₂CMe₃)Ph₂ (0.476 g, 0.815 mmol, 34.1% yield based on KIn(CH₂CMe₃)₃H) sublimed at 90-115 °C. The residue was impure (Me₃CCH₂)₂InPPh₂ (0.566 g, 1.29 mmol, 54.0% yield based on KIn(CH₂CMe₃)₃H). The organoindium phosphide was purified by recrystallization from 20 mL of pentane at -30 °C to yield 0.301 g (0.681 mmol) in the first crop of cystals and then 0.265 g (0.598 mmol) in the second. Thus, the total yield of (Me₃CCH₂)₂InPPh₂ was 0.566 g (1.28 mmol, 53.5% yield based on KIn(CH₂CMe₃)₃H).

(**Me₃CCH₂)₂InPPh₂:** mp 143–150 °C dec (lit.^{2,3} 143–150 °C dec); ³¹P{¹H} NMR (C₆D₆) δ –49.7 (s, [(Me₃CCH₂)₂InPPh₂]₂), –30.2 (s, (Me₃CCH₂)₂InPPh₂) (lit.^{2,3} –49.40, –29.95); ¹H NMR (C₆D₆) δ 1.00 (s, CMe₃, 1 H), 1.06 (s, CMe₃, 18 H), 1.46 (br, PInCH₂, 4 H) (lit.^{2,3} 1.03, 1.10, 1.47 (t)).

(Me₃CCH₂)₃In·P(CH₂CMe₃)Ph₂: mp 82-84 °C; ³¹P{¹H} NMR (C₆D₆) δ -23.1 (s, (Me₃CCH₂)₃In·P(CH₂CMe₃)Ph₂); ¹H NMR (C₆D₆) δ 0.96 (s, PCCMe₃, 9 H), 1.09 (s, InCH₂, 6 H), 1.14 (s, InCCMe₃, 27 H), 2.07 (d, PCH₂, J = 4 Hz, 2 H).

(b) Mixing Reagents at 0 °C in Benzene. The reagents $KIn(CH_2CMe_3)_3H$ (1.39 g, 3.78 mmol) and $ClPPh_2$ (0.835 g, 3.78 mmol) were combined as described previously for pentane but by using benzene at an initial reaction temperature of 0 °C. The isolated products included H_2 (1.32 mmol, 69.8% yield based on KIn(CH₂CMe₃)₃H), CMe₄ (separated by vacuum fractional distillation through two -78 °C traps into a -196 °C trap, 0.0735 g, 1.02 mmol, 27.0% yield based on KIn(CH₂CMe₃)₃H), KCl (0.252 g, 3.39 mmol, 89.7% yield based on KIn(CH₂CMe₃)₃H), (Me₃CCH₂)₃In·P(CH₂CMe₃)₃H), and (Me₃-CCH₂)₂InPPh₂ (0.674 g, 1.52 mmol, 40.2% yield based on KIn(CH₂CMe₃)₃H). The characterization data (mp, ³¹P and ¹H NMR spectra) for the two indium–phosphorus products were identical to data given previously.

Synthesis of P(CH₂CMe₃)Ph₂. The Lewis base P(CH₂-CMe₃)Ph₂ was synthesized from ClPPh₂ (10.2 g, 46.1 mmol) and (Me₃CCH₂)MgCl (61.6 mmol) at 0 °C as described in the literature.⁸ The phosphine (7.91 g, 30.9 mmol, 67.0% yield based on ClPPh₂) was isolated as a colorless liquid by vacuum distillation (10⁻³ mm) at an oil bath temperature of 100–110 °C and a head temperature of 70–74 °C. Additional drying of the phosphine with MgSO₄ followed by short-path vacuum distillation at a head temperature of 84–94 °C and 10⁻³ mm pressure (bp lit.⁸ 110–111 °C, 0.2 mm) gave the pure phosphine: ³¹P{¹H} NMR (C₆D₆) δ –23.1 (lit.⁸ –23.3); ¹H NMR (C₆D₆) δ 0.99 (s, PCCMe₃, 9 H), 2.07 (d, PCH₂, *J* = 5 Hz, 2 H), 7.04 (td, Ph, *J* = 11 Hz, 10 H), 7.45 (dd, Ph, *J* = 10 Hz, 10 H) (lit.⁸ CDCl₃: 1.00, 2.15, 7.13–7.62).

Synthesis and NMR Spectra of $(Me_3CCH_2)_3In \cdot P(CH_2-CMe_3)Ph_2$. An NMR tube was charged with $P(CH_2CMe_3)Ph_2$ (0.124 g, 0.482 mmol), $In(CH_2CMe_3)_3$ (0.159 g, 0.483 mmol), and C_6D_6 . The walls of the tube were carefully rinsed with the benzene to ensure complete mixing of the reagents. Then after the tube was flame sealed under vacuum, the NMR spectrum was recorded immediately. ³¹P{¹H} NMR (C_6D_6) δ : -22.8. ¹H NMR (C_6D_6) δ : 0.90 (s, PCCMe₃, 9 H), 1.16 (s, InCH₂, 6 H), 1.19 (s, InCCMe₃, 27 H), 2.08 (d, PCH₂, J = 5 Hz, 2 H).

Reaction of KIn(CH₂CMe₃)₃H with HPPh₂. A pentane solution of HPPh₂ (0.403 g, 2.16 mmol) was added to a pentane solution of KIn(CH₂CMe₃)₃H (0.802 g, 2.18 mmol) that had been cooled to -50 to -60 °C. Bubbling, formation of a precipitate, and a color change from colorless to light yellow were observed upon mixing the reagents. After the solution had been warmed to room temperature and stirred for 18 h, the noncondensable gas (H₂) was measured at -196 °C with a Toepler pump-gas buret assembly (1.40 mmol H₂, 64.8% H₂ based on HPPh₂).

NMR Spectral Study of Reaction Products after Mixing In(CH₂CMe₃)₃ with ClPPh₂. A small tube was charged with ClPPh2 (0.182 g, 0.826 mmol), In(CH2CMe3)3 (0.271 g, 0.827 mmol), and C_6D_6 (1 mL). Then, a portion of the contents was transferred to an NMR tube under vacuum and the NMR tube was flame-sealed. The NMR spectrum was recorded 30 min after mixing of reagents. The products identified by the NMR spectrum included In(CH₂CMe₃)₂Cl and P(CH₂CMe₃)-Ph₂. ³¹P{¹H} NMR (C₆D₆) δ : -41.0 (d, J = 310 Hz, trace HPPh₂), -21.1 (s, P(CH₂CMe₃)Ph₂), -21.2 (d, J = 310 Hz, trace). ³¹P NMR (C₆D₆) δ : -41.2 (d, J = 314 Hz, trace), -21.1 (s, P(CH₂CMe₃)Ph₂), -21.2 (d, J = 310 Hz, trace). ¹H NMR (C₆D₆) δ : 0.86 (br, 0.8 H), 0.90 (s, 0.4 H), 0.94 (br, PCCMe₃, 7.4 H), 1.17 (s, InCCMe₃, 18 H), 1.27 (br, 1.3. H), 1.30 (s, 4.3 H), 1.56 (s, InCH₂, 4 H), 7.09 (d, PPh, J = 6 Hz, 5.3 H), 7.38 (br, 0.4 H), 7.43 (td, PPh, J = 8 Hz, 3.2 H).

Synthetic Scale Reaction between In(CH₂CMe₃)₃ and CIPPh₂. A pentane (5 mL) solution of CIPPh₂ (0.980 g, 4.44 mmol) was added to a pentane (15 mL) solution of In(CH2- CMe_3)₃ (1.46 g, 4.44 mmol) at -78 °C. The reaction mixture was allowed to warm slowly to room temperature and was stirred overnight. Pentane was removed by vacuum distillation while holding the product mixture at -30 °C. Then In(CH₂- $CMe_3)_2Cl$ was crystallized from fresh pentane at -20 to -30°C and isolated by filtration. After the pentane was removed by vacuum distillation with the flask held in an ice bath, 0.966 g of In(CH2CMe3)2Cl (3.30 mmol, 74.3% yield based on ClPPh2) and a cloudy viscous liquid were obtained. The cloudy liquid was purified by vacuum distillation with a short-path still by using an oil bath at 105 °C. The phosphine P(CH₂CMe₃)Ph₂ (0.827 g, 3.23 mmol, 72.7% based on ClPPh₂) distilled at a head temperature of 78 °C.

In(CH₂CMe₃)₂Cl: ¹H NMR (C_6D_6) δ 1.09 (s, InCCMe₃, 9 H), 1.58 (s,InCH₂, 2 H) (lit.⁶ 1.09, 1.58).

P(CH₂CMe₃)Ph₂: ¹H NMR (C₆D₆) δ 1.01 (s, PCH₂, 9 H), 1.13 (s, InCCMe₃, ~1 H), 1.51 (s, InCH₂, ~0.2 H), 2.09 (d, PCH₂C, *J* = 4 Hz, 2 H), 7.08 (m, p, m-H of PPh, 6 H), 7.47 (t, o-H of PPh, 4H); ³¹P{¹H} NMR (C₆D₆) δ -21.4 (s, P(CH₂CMe₃)-Ph₂); ³¹P NMR (C₆D₆) δ -21.4 (br, P(CH₂CMe₃)Ph₂).

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