Chemistry of Indium(III) Tris(cyclopentadienide). Reactions with Diphenylphosphine, *tert*-Butyl Alcohol, and Acetylacetone. Cyclopentadiene and Reductive Elimination Reactions

O. T. Beachley, Jr.,* David J. MacRae, and Andrey Yu. Kovalevsky

Department of Chemistry, University at Buffalo, The State University of New York, Buffalo, New York 14260

Received December 30, 2002

Indium(III) tris(cyclopentadienide) $In(C_5H_5)_3$ reacts with diphenylphosphine at room temperature to form the indium(I) derivative $In(C_5H_5)$, P_2Ph_4, and C_5H_6. These products are consistent with the occurrence of an initial cyclopentadiene elimination reaction between $In(C_5H_5)_3$ and $HPPh_2$ and then reduction at indium. In contrast, *tert*-butyl alcohol undergoes a typical stoichiometric cyclopentadiene elimination reaction with $In(C_5H_5)_3$ to form $[(C_5H_5)_2InO(t\text{-}Bu)]_2$. Acetylacetone (Hacac) also reacts with $In(C_5H_5)_3$, but the expected product(s) of the cyclopentadiene elimination reactions $(C_5H_5)_2In(acac)$ and $(C_5H_5)In(acac)_2$ are unstable and redistribute their ligands to form $In(C_5H_5)_3$ and $In(acac)_3$, as appropriate. The reagent *tert*-butylamine does not eliminate cyclopentadiene when combined with $In(C_5H_5)_3$ at room temperature.

Introduction

Even though cyclopentadiene elimination reactions between $R_2Ga(C_5H_5)$ (R = Me,[1] Et,[2] CH_2CMe_3[3]) and HER′ (E = O, S; R′ = organic groups) and HER′$_2$ (E = N, P; R′ = organic groups, H) have proven to be especially useful for the preparation of organogallium derivatives with the simplest formulas R_2GaXR' (X = O, S) and $R_2GaYR'_2$ (Y = N, P), no elimination reactions of $Ga(C_5H_5)_3$ have been described to date. The elimination reactions of $R_2Ga(C_5H_5)$ typically occur at or below room temperature and produce gallium-containing products in nearly quantitative yields. The recent availability of pure $In(C_5H_5)_3$ in useful quantities[4] provided us the opportunity to investigate its propensity to undergo cyclopentadiene elimination reactions and form new compounds. In this paper, the nature of the reaction chemistry of $In(C_5H_5)_3$ with diphenylphosphine, *tert*-butylamine, *tert*-butyl alcohol, and acetylacetone (2,4-pentanedione) are described. Each of these reagents produced different experimental observations and reaction products.

Results and Discussion

The reaction between $In(C_5H_5)_3$ and $HPPh_2$ at room temperature is very significant to group 13 chemistry. The products, indium(I) cyclopentadienide $In(C_5H_5)$,[5] diphosphine P_2Ph_4,[6] and cyclopentadiene (eq 1) are

$$In(C_5H_5)_3 + 2HPPh_2 \xrightarrow[\sim 20\ ^\circ C]{\text{benzene}} In(C_5H_5) + P_2Ph_4 + 2C_5H_6 \quad (1)$$

consistent with the occurrence of an oxidation−reduction reaction. Both the indium(I) product $In(C_5H_5)$ and the diphosphine P_2Ph_4 were isolated in high yields (∼80% and ∼90%, respectively, as based on the limiting reagent and eq 1). The products were independent of the ratio of $In(C_5H_5)_3$ to $HPPh_2$ and of the nature of the solvent. Reactions of $In(C_5H_5)_3$ with $HPPh_2$ in mole ratios of 1:2 and 1:1 and in the solvents diethyl ether, THF, toluene, and benzene were investigated. When the ratio of $In(C_5H_5)_3$ to $HPPh_2$ was 1:1 and the solvent was toluene, experimental observations of the solubilities and decomposition points of products were consistent with the presence of unreacted and insoluble $In(C_5H_5)_3$, as required by eq 1. When the solvent was THF, the indium(I) product $In(C_5H_5)$ was stabilized to decomposition to indium metal by $In(C_5H_5)_3$.[4] However, when THF was present and $In(C_5H_5)_3$ was absent, a film of indium metal formed on the walls of the glassware.[4]

^{31}P NMR spectral studies of a mixture of $In(C_5H_5)_3$ and $HPPh_2$ in a 1:2.3 mole ratio in d_6-benzene are consistent with the elimination of cyclopentadiene followed by a reductive elimination reaction of a new compound such as $(C_5H_5)In(PPh_2)_2$ to form $In(C_5H_5)$ and P_2Ph_4. The ^{31}P NMR spectrum of a reaction mixture recorded approximately 15 min after warming the

* Corresponding author.

(1) Beachley, O. T., Jr.; Royster, T. L.; Arhar, J. R.; Rheingold, A. L. *Organometallics* **1993**, *12*, 1976.
(2) Beachley, O. T., Jr.; Rosenblum, D. B.; Churchill, M. R.; Lake, C. H.; Toomey, L. M. *Organometallics* **1996**, *15*, 3653.
(3) Beachley, O. T., Jr.; Maloney, J. D.; Rogers, R. D. *Organometallics* **1997**, *16*, 3267.
(4) Beachley, O. T., Jr.; MacRae, D. J.; Kovalevsky, A. Yu.; Zhang, Y.; Li, X. *Organometallics* **2002**, *21*, 4632.
(5) (a) Beachley, O. T., Jr.; Pazik, J. P.; Glassman, T. E.; Churchill, M. R.; Fettinger, J. C.; Blom, R. *Organometallics* **1988**, *7*, 1051. (b) Fischer, E. O.; Hofmann, H. P. *Angew. Chem.* **1957**, *69*, 639.
(6) (a) Horn, H. G.; Sommer, K. *Spectrochim. Acta* **1971**, *27A*, 1049. (b) Chao, S.-H., L. Ph.D. Dissertation, University at Buffalo, The State University of New York, 1995.

10.1021/om021054f CCC: $25.00
Publication on Web 03/15/2003

sample to room temperature from −196 °C exhibited resonances at −13.7, −26.8, and −39.5 ppm with relative intensities of 2.2, 8.8, and 89.0, respectively. The resonances at −13.7 and −39.5 ppm can be assigned to P_2Ph_4[6] and $HPPh_2$,[7] respectively. The resonance at −26.8 ppm is due to an intermediate. The unknown compounds $(C_5H_5)In(PPh_2)_2$, $(C_5H_5)_2InPPh_2$, and $(C_5H_5)_3In{\cdot}HPPh_2$ or a mixture of these compounds that are undergoing rapid chemical exchange are possible candidates. After 1 h the resonance at −13.5 ppm due to P_2Ph_4 had increased in intensity, whereas the other two resonances had decreased in intensity. After 24 h at room temperature the resonance at −26.8 ppm due to the intermediate had disappeared, whereas the intensity of the resonance for P_2Ph_4 at −13.7 ppm had increased further. The resonance for $HPPh_2$ decreased, as expected from the stoichiometric ratio of reactants. After an additional 4 days the ^{31}P NMR spectrum remained essentially unchanged.

The isolated products of $In(C_5H_5)$ and P_2Ph_4, the reaction stoichiometry, the observation of an reaction intermediate, and the relatively slow rate of the reaction between $In(C_5H_5)_3$ with $HPPh_2$ suggest that a reductive elimination reaction of $(C_5H_5)In(PPh_2)_2$ produces the observed products. Two closely related reaction pathways can be envisioned for the formation of $(C_5H_5)In(PPh_2)_2$. One reaction pathway utilizes the elimination of one molecule of cyclopentadiene to form $(C_5H_5)_2InPPh_2$ and a subsequent ligand redistribution reaction to form $(C_5H_5)In(PPh_2)_2$ and $In(C_5H_5)_3$. The second possible reaction pathway involves the formation of $(C_5H_5)In(PPh_2)_2$ by the elimination of two molecules of cyclopentadiene from each molecule of $In(C_5H_5)_3$. However, as the elimination of the first molecule of cyclopentadiene from $In(C_5H_5)_3$ and $HPPh_2$ was observed to be slow, especially slow when compared to the cyclopentadiene elimination reaction between $Me_2In(C_5H_5)$ and $HPPh_2$,[8] a second elimination of C_5H_6 would be most unlikely. The formation of Me_2InPPh_2[9] from $Me_2In(C_5H_5)$ and $HPPh_2$ was complete within 15 min of warming the solution from −196 °C to room temperature, according to NMR spectral studies,[8] whereas a mixture of $In(C_5H_5)_3$ and $HPPh_2$ required a significantly longer time for complete reaction. As the elimination of the first molecule of C_5H_6 is slow, the elimination of the second molecule of cyclopentadiene is expected to be even slower, according to previous observations of elimination reactions in group 13 chemistry.[10] Thus, the intermediate $(C_5H_5)In(PPh_2)_2$ is most likely formed by a ligand redistribution reaction of $(C_5H_5)_2InPPh_2$. The presence of three bulky substituents on indium hinders dimerization, maintains the availability of both Lewis acid and base sites, and enables ligand redistribution to occur. A ligand redistribution reaction of $(C_5H_5)_2InPPh_2$ would be consistent with the observed chemistry of other newly observed indium(III) cyclopentadienide compounds (see below).

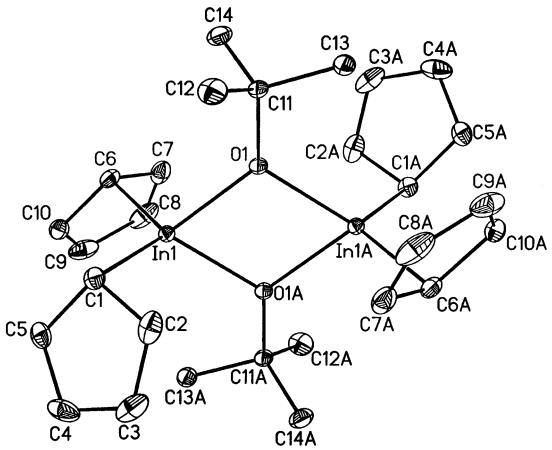

Figure 1. Molecular geometry and labeling of atoms for $[(C_5H_5)_2InO(t\text{-}Bu)]_2$ (50% probability ellipsoids for nonhydrogen atoms, hydrogen atoms omitted for clarity).

The reaction of $In(C_5H_5)_3$ with *t*-BuOH in a 1:1 mole ratio in THF solution led to the isolation of $[(C_5H_5)_2InO(t\text{-}Bu)]_2$ as pale yellow crystals in ∼87% yield (eq 2). The compound is soluble in THF and Et_2O and very

$$In(C_5H_5)_3 + HO(t\text{-}Bu) \xrightarrow[20\ °C]{THF} {}^1/_2[(C_5H_5)_2InO(t\text{-}Bu)]_2 + C_5H_6 \quad (2)$$

slightly soluble in benzene but exhibits only trace solubility in pentane. Thus, cryoscopic molecular weight studies in benzene were not possible, due to the very low solubility of the compound. Furthermore, the compound did not melt but decomposed at ∼125 °C. Thus, the physical properties of $[(C_5H_5)_2InO(t\text{-}Bu)]_2$ are unusual when compared with those of other compounds of the types $[R_2MXR']_n$ and $[R_2MYR'_2]_m$ (M = Ga, In; X = O, S; Y = N, P).[10]

The results of an X-ray structural study of $(C_5H_5)_2InO(t\text{-}Bu)$ help to explain the origin of its unusual physical properties. The compound is dimeric in the solid state with two terminal cyclopentadienide ligands and one bridging *tert*-butoxide ligand for each indium atom. The molecular structure and the labeling of the atoms in the dimer are shown in Figure 1. Selected bond distances and angles are collected in Table 1. The In···In distance of 3.378(1) Å is longer than those observed in comparable indium *tert*-butoxide complexes (3.312(9) Å for $[(Me)(Cl)InO(t\text{-}Bu)]_2$[11] and 3.346(1) Å for $[(t\text{-}BuO)_2InO(t\text{-}Bu)]_2$[12]). Interligand angles in $[(C_5H_5)_2InO(t\text{-}Bu)]_2$ exhibit significant distortion from regular tetrahedral values, ranging from O(1)−In(1)−O(1A) = 75.03(6)° to O(1A)−In(1)−C(6) = 118.26(7)°. The In−O bond distances are In(1)−O(1) = 2.141(2) Å and In(1)−O(1A) = 2.118(2) Å. The oxygen has trigonal-planar geometry and can be considered sp^2 hybridized. The C(13) methyl group is in an *eclipsed* conformation with respect to O(1)−In(1A), the torsion angle for In(1A)−O(1)−C(11)−C(13) being −1.8(2)° (Figure 2). The observed conformation permits the hydrogen atoms on

(7) Banks, M. A.; Beachley, O. T., Jr.; Maloney, J. D.; Rogers, R. D. *Polyhedron* **1990**, *9*, 335.
(8) MacRae, D. J. Ph.D. Dissertation, University at Buffalo, The State University of New York, 2002.
(9) (a) Arif, A. M.; Barron, A. R. *Polyhedron* **1988**, *7*, 2091. (b) Burns, J. A.; Dillingham, M. D. B.; Hill, J. B.; Gripper, K. D.; Pennington, W. T.; Robinson, G. H. *Organometallics* **1994**, *13*, 1514. (c) Aitchison, K. A.; Backer-Dirks, J. D.; Bradley, D. C.; Faktor, M. M.; Frigo, D. M.; Hursthouse, M. B.; Hussain, B.; Short, R. L. *J. Organomet. Chem.* **1989**, *366*, 11.
(10) (a) Coates, G. E.; Green, M. L. H.; Wade, K. *Organometallic Compounds*; Methuen: London, 1967; Vol. 1. (b) Cowley, A. H.; Jones, R. A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1208.
(11) Veith, M.; Hill, S.; Huch, V. *Eur. J. Inorg. Chem.* **1999**, 1343.
(12) Suh, S.; Hoffman, D. M. *J. Am. Chem. Soc.* **2000**, *122*, 9396.

Table 1. Selected Bond Distances (Å) and Angles (deg) for $[(C_5H_5)_2InO(t\text{-}Bu)]_2$[a]

(A) Selected Bond Distances			
In(1)−O(1A)	2.118(2)	In(1)−O(1)	2.141(2)
In(1)−C(6)	2.223(2)	In(1)−C(1)	2.226(2)
In(1)−In(1A)	3.3782(3)	O(1)−C(11)	1.451(2)
(B) Carbon−Carbon Distances for Cyclopentadienide Ring			
C(1)−C(2)	1.459(3)	C(1)−C(5)	1.463(3)
C(2)−C(3)	1.358(4)	C(3)−C(4)	1.430(4)
C(4)−C(5)	1.361(4)	C(6)−C(7)	1.456(3)
C(6)−C(10)	1.468(3)	C(7)−C(8)	1.356(4)
C(8)−C(9)	1.427(4)	C(9)−C(10)	1.356(4)
C(11)−C(13)	1.514(3)	C(11)−C(14)	1.519(3)
C(11)−C(12)	1.519(3)		
(C) Selected Bond Angles			
O(1A)−In(1)−O(1)	75.03(6)	O(1A)−In(1)−C(6)	118.26(7)
O(1)−In(1)−C(6)	111.96(7)	O(1A)−In(1)−C(1)	117.35(7)
O(1)−In(1)−C(1)	107.40(7)	C(6)−In(1)−C(1)	117.68(8)
C(11)−O(1)−In(1A)	125.02(1)	C(11)−O(1)−In(1)	130.0(1)
In(1A)−O(1)−In(1)	104.97(6)	C(2)−C(1)−In(1)	104.6(1)
C(5)−C(1)−In(1)	106.3(2)	C(7)−C(6)−In(1)	106.5(2)
C(10)−C(6)−In(1)	105.7(2)		

[a] Symmetry transformation used to generate equivalent atoms: (1A) $1 - x, 2 - y, -z$.

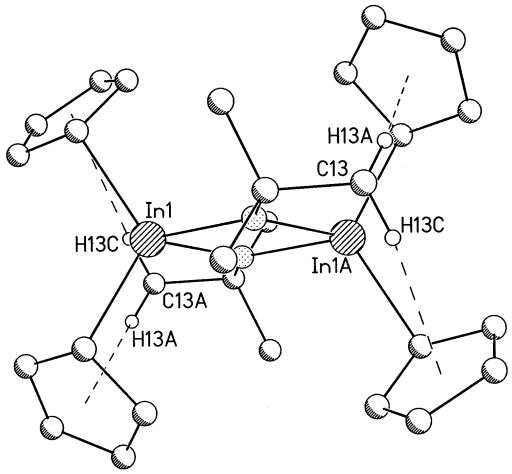

Figure 2. Molecular structure of $[(C_5H_5)_2InO(t\text{-}Bu)]_2$ showing intramolecular hydrogen−cyclopentadienide interactions.

C(13) to form nonconventional intramolecular hydrogen bonds between the C−H and the cyclopentadienide rings. The distance between H(13A) and the nearest cyclopentadienide ring is 2.85 Å, and the angle between C(13)−H(13A) and the center of the nearest cyclopentadienide ring is 157°. The distance between H(13C) and the nearest cyclopentadienide ring is 2.83 Å, and the angle between C(13)−H(13C) and the center of the nearest cyclopentadienide ring is 155°. Thus, this hydrogen bond interaction might be a contributing factor to the slightly shortened In(1)−O(1A) distance.

Each cyclopentadienide ligand is coordinated η^1 to the indium center In(1), with atoms C(1) and C(6) having essentially sp^3 hybridization. The hydrogen atoms bonded to C(1) and C(6) are displaced from the plane of the cyclopentadienide ligand by 0.55 and −0.45 Å, respectively. The In(1)−C(1) distance of 2.226(2) Å and In(1)−C(6) distance of 2.223(2) Å are similar to the In−C distances for the terminal cyclopentadienide ligands in $In(C_5H_5)_3$ (average 2.229(2) Å) but slightly shorter than the In−C distances for the cyclopentadienide ligands in $In(C_5H_5)_3{\cdot}PPh_3$[4] (average 2.263(2) Å). The cyclopentadienide ligands have largely nonconjugated π systems with C(2)−C(3), C(4)−C(5) and C(7)−C(8), C(9)−C(10) being essentially double bonds and C(1)−C(2), C(1)−C(5), C(4)−C(3) and C(6)−C(7), C(6)−C(10), C(9)−C(8) being essentially single bonds.

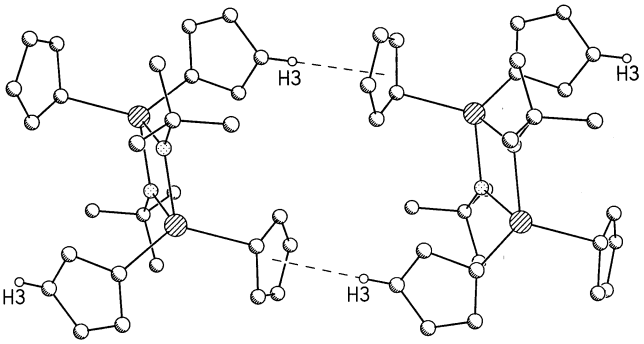

Figure 3. Molecular structure of $[(C_5H_5)_2InO(t\text{-}Bu)]_2$ showing intermolecular hydrogen−cyclopentadienide interactions.

Molecules of $[(C_5H_5)_2InO(t\text{-}Bu)]_2$ form layers in the *ab* crystallographic plane. Each layer consists of chains along the crystallographic axis *b*, where molecules are connected by intermolecular H···π hydrogen bonds between the hydrogen atoms of a cyclopentadienide ligand and the π bonds of the cyclopentadienide ligand of the adjacent molecule (Figure 3).[13] The H(3) distance to the nearest cyclopentadienide ring is 2.75 Å, and the angle between C(3)−H(3) and the nearest cyclopentadienide ring is 178°.

The elimination of cyclopentadiene from $In(C_5H_5)_3$ and H(acac) (acac = 2,4-pentanedionate) is significantly faster than the elimination of methane from $InMe_3$ and H(acac). Reaction of a THF solution of $In(C_5H_5)_3$ with excess H(acac) at room temperature to form $In(acac)_3$[14] was complete in 15 min, whereas the corresponding reaction of $InMe_3$ in the absence of solvent required 26 days at the same temperature. These experiments demonstrated the facile nature of the cyclopentadiene elimination reaction in indium chemistry, especially in comparison with the methane elimination reaction.

The attempted synthesis of compounds that incorporate both cyclopentadienide and β-diketonate ligands was pursued by metathetical and ligand redistribution reactions, but no pure products of the desired type could be isolated and characterized. The desired compounds were unstable due to the occurrence of ligand redistribution reactions (eq 3 and 4). The preparation of $(C_5H_5)_2$-

$$2(C_5H_5)_2In(acac) \rightarrow (C_5H_5)In(acac)_2 + In(C_5H_5)_3 \quad (3)$$

$$2(C_5H_5)In(acac)_2 \rightarrow (C_5H_5)_2In(acac) + In(acac)_3 \quad (4)$$

In(acac) was investigated by using a sequence of metathetical reactions. The initial reaction between $InCl_3$ and $Li(C_5H_5)$ in a 1:2 mole ratio in THF solution led to the formation of $(C_5H_5)_2InCl{\cdot}n$THF, in situ.[15] Then, Na(acac) was added and a yellow crystalline product, believed to be $(C_5H_5)_2In(acac)$, was isolated. The initial

(13) (a) Abernathy, C. D.; Macdonald, C. L. B.; Clyburne, J. A. C.; Cowley, A. H. *Chem. Commun.* **2001**, 61. (b) Harder, S. *Chem. Eur. J.* **1999**, *5*, 1852. (c) Alkorta, I.; Rozas, I.; Elguero, J. *Chem. Soc. Rev.* **1998**, *27*, 163.

(14) McClelland, B. W. J. *Appl. Crystallogr.* **1974**, *7*, 90.

^{1}H NMR spectrum in d_6-benzene solution exhibited three broad resonances at 6.20, 5.01, and 1.72 ppm for the protons of C_5H_5 and for the unique proton and methyl group protons on the acetylacetonate ligand, respectively. However, after only 1 day, the resonance at 1.72 ppm for the methyl groups on the acetylacetonate ligand and the resonance at 5.01 ppm for the unique proton on the acetylacetonate ligand broadened and began to split into two resonances each. After 3 days, the lines were sharper and the resonances for the acetylacetonate protons had clearly split into two lines for each type of proton. In addition, a yellow insoluble solid, $In(C_5H_5)_3$,[4] coated the walls of the NMR tube. These observations support the occurrence of a ligand redistribution reaction of $(C_5H_5)_2In(acac)$ to form (C_5H_5)-$In(acac)_2$ and $In(C_5H_5)_3$ (eq 3). As $(C_5H_5)_2In(acac)$ underwent a ligand redistribution reaction, the synthesis of $(C_5H_5)In(acac)_2$ with two β-diketonate ligands was investigated. The synthetic scheme involved the reaction of $(C_5H_5)InCl_2 \cdot n$THF,[15] prepared in situ, with Na(acac). However, experimental observations suggest that (C_5H_5)-$In(acac)_2$ is also unstable and forms $In(acac)_3$ (eq 4). Even though the ^{1}H NMR spectrum of the initial product in d_8-THF had sharp lines for the acetylacetonate protons, the chemical shifts and the relative intensities of the observed lines suggested that the product was impure. The ratio of the integration values for the resonances for the cyclopentadienide ligand, the unique proton, and the methyl protons of the acetylacetonate ligand was 4.56:2.25:12.20, whereas 5:2:12 would be expected for pure $(C_5H_5)In(acac)_2$. In addition, lines of low intensity for $In(acac)_3$ were also present. Confirmation of these reactions was achieved by investigating ligand redistribution reactions between $In(C_5H_5)_3$ and $In(acac)_3$ in THF solutions. No pure products could be isolated. Last, it should be noted that $In(C_5H_5)_3$ does not undergo a cyclopentadiene elimination reaction when combined with $NH_2(t\text{-Bu})$, a primary amine.

Experimental Section

All compounds described in this investigation were 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. The indium(III) derivative $In(C_5H_5)_3$ was prepared in THF solution[4] and used within 2 weeks of preparation. The other starting materials $InMe_3$[16] and Na(acac)[17] were prepared by literature methods, whereas $InCl_3$ and $HPPh_2$ were purchased from Strem Chemicals, Inc. Indium(III) chloride was used as received, but the phosphine was distilled under dynamic vacuum at ~100 °C prior to use. *tert*-Butyl alcohol was dried by stirring with CaH_2 for 8 h, whereas acetylacetone was dried by stirring with K_2CO_3 for 4 h. Each reagent was vacuum-distilled into a storage tube after drying. All solvents were carefully dried by using conventional procedures. Elemental analyses were performed by Oneida Research Services, Whitesboro, NY. Melting points were determined with a Mel-Temp by using flame-sealed capillaries filled with argon and are uncorrected. ^{1}H NMR spectra were recorded with either a Varian Unity-Nova 400 or a 500 spectrometer (400 and 500 MHz, respectively), whereas ^{31}P NMR (161.9 MHz) spectra were recorded with the Varian Unity-Nova 500 spectrometer. Proton chemical shifts are reported in δ (ppm) units and are referenced to $SiMe_4$ at δ 0.00 ppm with C_6D_5H at δ 7.15 ppm or the proton impurities in d_8-THF at 1.73. Phosphorus chemical shifts are referenced to 85% H_3PO_4 at δ 0.00 ppm. All samples for NMR spectra were contained in flame-sealed NMR tubes. The deuterated solvents benzene-d_6 and THF-d_8 were purchased from either Aldrich Chemical Co. or Cambridge Isotopes, Inc. and were dried with P_4O_{10} and then vacuum-distilled into tubes coated with sodium mirrors. Infrared spectra of samples as Nujol mulls between CsI plates were recorded by using a Perkin-Elmer 683 spectrometer.

Reaction of $In(C_5H_5)_3$ with $HPPh_2$ in Et_2O in a 1:2 Mole Ratio. A tube that contained 0.929 g (4.99 mmol) of $HPPh_2$ and ~5 mL of Et_2O was connected to a flask that held 0.774 g (2.50 mmol) of $In(C_5H_5)_3$ and a magnetic stir bar. The solvent, 25 mL of Et_2O, was added by vacuum distillation to the flask, and then the contents were warmed to room temperature. $HPPh_2/Et_2O$ was then added rapidly. After 15 min the solution was bright yellow with only a trace of precipitate. The solution became less yellow over a period of 2 h, and a colorless precipitate was clearly visible. After 3 h, the solution was more turbid with a creamy-colored precipitate and pale yellow needlelike crystals on the walls of the flask. The Et_2O was removed first by vacuum distillation at 0 °C, and then the pale yellow crystals of $In(C_5H_5)$ (0.380 g, 2.11 mmol, 84.7% yield based on $In(C_5H_5)_3$) were isolated by flask to flask vacuum sublimation at 50 °C through a 90° elbow. The residue was extracted through a medium-porosity frit with 2 × 20 mL of benzene and then washed with cold pentane to yield colorless crystals of P_2Ph_4 (0.892 g, 2.41 mmol, 96.5% based on $In(C_5H_5)_3$). $In(C_5H_5)$: mp 169.2−170.1 °C dec (lit.[5] mp 169.3−171 °C dec). P_2Ph_4: mp 121.5−122.9 °C (lit.[6] mp 120.5 °C); ^{1}H NMR (d_6-benzene) δ 7.54 (m, P−C_6H_5, 10.0 H), 6.94 (m, P−C_6H_5, 15.0 H); ^{31}P{^{1}H} (d_6-benzene) δ −13.6 (s).

Reaction between $In(C_5H_5)_3$ and an Equimolar Quantity of $HPPh_2$ in THF. The reagents, 0.602 g (3.23 mmol) of $HPPh_2$ and 1.00 g (3.23 mmol) of $In(C_5H_5)_3$, were reacted in THF as described previously. Over 1 h the solution became increasingly more orange, but a trace of a gray precipitate was visible. The THF was removed by vacuum distillation to leave yellow needles and a pale yellow powder. The crude product was extracted one time with ~20 mL of benzene. When most of the benzene had been removed from the collection flask by vacuum distillation, a gold/silver metallic mirror due to the decomposition on $In(C_5H_5)$ to indium metal was present on the walls of the collection flask. Benzene-soluble crude product (P_2Ph_4 and $In(C_5H_5)$): ^{1}H NMR (d_6-benzene) δ 7.54 (m, P−C_6H_5, 8.2 H), 6.94 (m, P−C_6H_5, 13.3 H), 6.07 (br, In−C_5H_5, 5.0 H); ^{31}P{^{1}H} δ −13.92 (s). Residue (P_2Ph_4): ^{1}H NMR (d_6-benzene) δ 7.53 (m, P−C_6H_5, 3.0 H), 6.95 (m, P−C_6H_5, 5.7 H), 6.08 (br, In−C_5H_5, 5.0 H); ^{31}P{^{1}H} NMR (d_6-benzene) δ −13.62 (s, 55.4), −24.9 (s, 32.1). A single crystal of $In(C_5H_5)$ isolated from the residue had a melting point of 167.2−169.9 °C dec (lit.[5] mp 169.3−171 °C dec).

Reaction between $In(C_5H_5)_3$ and an Equimolar Quantity of $HPPh_2$ in Toluene. The reagents, 0.737 g (9.96 mmol) of $HPPh_2$, 1.265 g (4.079 mmol) of $In(C_5H_5)_3$, and ~35 mL of freshly dried toluene, were combined as described previously. The reaction mixture changed in appearance from a suspension of a bright yellow solution with a yellow precipitate to a yellow solution after 1 h. Then, the product mixture was cooled to 0 °C in an ice bath and the toluene was removed by vacuum distillation to leave a pale yellow crystalline product and a fine yellow powder. Flask-to-flask vacuum sublimation at 50 °C through a 90° elbow produced 0.285 g (1.584 mmol, 80.0% yield based on $HPPh_2$) of $In(C_5H_5)$ as pale yellow crystals. The residue, 1.632 g, was isolated, and both ^{1}H and ^{31}P NMR spectra were recorded. Sublimate $In(C_5H_5)$: mp 169.4−170.0

(15) Visona, P.; Benetollo, F.; Rossetto, G.; Zanella, P. *Polyhedron* **1996**, *15*, 1743.
(16) Bradley, D. C.; Chudzynska, H. C.; Harding, I. S. In *Inorganic Syntheses*; Cowley, A. H., Ed.; Wiley: New York, 1997; Vol. 31, p 67.
(17) Shin, H.-K.; Chi, K. M.; Farkas, J.; Hampden-Smith, M. J.; Kodas, T. T.; Duesler, E. N. *Inorg. Chem.* **1992**, *31*, 424.

°C dec (lit.[5] mp 169.3−171 °C dec). Residue (mixture of P_2Ph_4, C_5H_6, and $In(C_5H_5)_x$): ^{1}H NMR (THF-d_8) δ 7.35 (m, P−C$_6H_5$, 5.7 H), 7.20 (m, P−C$_6H_5$, 9.4 H), 6.51 (m, C_5H_6, trace H), 6.40 (m, C_5H_6, trace), 6.61 (m, C_5H_6, trace), 6.19 (s, In−C_5H_5, trace), 5.79 (s, In−C_5H_5, 5.0 H), 5.42 (s, In−C_5H_5, trace), 2.98 (m, C_5H_6, trace), 2.93 (m, C_5H_6, trace); ^{31}P{^{1}H} NMR (d_6-benzene) δ −13.29 (s).

^{1}H NMR Spectral Study of Reaction between $In(C_5H_5)_3$ and $HPPh_2$ in a 1:2.3 Mole Ratio in d_6-Benzene. A sample of $In(C_5H_5)_3$ (0.100 g, 0.323 mmol) was placed in a small reaction vessel attached to an NMR tube, whereas $HPPh_2$ (0.139 g, 0.747 mmol) dissolved in carefully dried d_6-benzene was contained in a side-tube dumper attached to the apparatus. $HPPh_2$ was then added, and a bright yellow solution formed. The sample was then carefully poured into the NMR tube and cooled to −196 °C. The NMR tube was flame-sealed and maintained at −196 °C until ^{1}H and ^{31}P NMR spectra were recorded. The mixture of P_2Ph_4, $HPPh_2$, C_5H_6, and $In(C_5H_5)_x$ gave the following NMR data. 15 min after warming: ^{1}H NMR δ 7.36 (m, P−C$_6H_5$, 8.5 H), 7.00 (m, P−C$_6H_5$, 14.3 H), 6.47 (m, C_5H_6, 0.9 H), 6.28 (m, C_5H_6, 0.9 H), 5.97 (br, In−C_5H_5, 5.0 H), 5.2 (d, J_{P-H}215.6 Hz, H−PPh$_2$, 1.7 H), 2.69 (m, C_5H_6, 1.1 H); ^{31}P{^{1}H} NMR δ −13.7 (s, $P_2(C_6H_5)_4$, 2.2 P), −26.8 (s, 8.8 P), −39.5 (s, H$P(C_6H_5)_2$, 89.0). 1 h after warming: ^{1}H NMR δ 7.53 (m, P−C$_6H_5$, 4.7 H), 7.36 (m, P−C$_6H_5$, 9.9 H), 7.02 (m, P−C$_6H_5$, 11.6 H), 6.95 (m, P−C$_6H_5$, 10.4 H), 6.48 (m, C_5H_6, 1.8 H), 6.29 (m, C_5H_6, 1.8 H), 6.00 (s, In−C_5H_5, 5.0 H), 2.69 (m, C_5H_6, 2.3 H); ^{31}P{^{1}H} NMR −13.7 (s, $P_2(C_6H_5)_4$, 20.5 P), −26.8 (s, 1.5 P), −39.4 (s, H$P(C_6H_5)_2$, 78.0 P). 24 h after warming: ^{1}H NMR 7.54 (m, P−C$_6H_5$, 11.6 H), 7.36 (m, P−C$_6H_5$, 14.5 H), 7.01 (m, P−C$_6H_5$, 22.8 H), 6.95 (m, P−C$_6H_5$, 14.8 H), 6.48 (m, C_5H_6, 3.0 H), 6.29 (m, C_5H_6, 3.0 H), 5.96 (s, In−C_5H_5, 5.0 H), 2.69 (m, C_5H_6, 4.9 H); ^{31}P{^{1}H} NMR −13.7 (s, $P_2(C_6H_5)_4$, 30.3 P), −39.4 (s, H$P(C_6H_5)_2$, 69.7 P). 5 days after warming: ^{1}H NMR 7.54 (m, P−C$_6H_5$, 12.8 H), 7.37 (m, P−C$_6H_5$, 11.4 H), 7.01 (m, P−C$_6H_5$, 18.8 H), 6.95 (m, P−C$_6H_5$, 16.2 H), 6.49 (m, C_5H_6, 2.5 H), 6.29 (m, C_5H_6, 2.5 H), 5.96 (s, In−C_5H_5, 5.0 H), 5.58 (s, 1.6 H), 2.69 (m, C_5H_6, 3.4 H); ^{31}P{^{1}H} NMR −13.7 (s, $P_2(C_6H_5)_4$, 30.0 P), −39.4 (s, H$P(C_6H_5)_2$, 55.8 P).

Synthesis of $(C_5H_5)_2InO(t\text{-}Bu)$. A reaction flask charged with 0.889 g (2.87 mmol) of $In(C_5H_5)_3$ dissolved in approximately 15 mL of THF was connected to a tube fitted with a Teflon valve that contained 0.201 g (2.72 mmol) of *t*-BuOH and 3 mL of C_5H_{12}. After the apparatus had been evacuated at −196 °C, *tert*-butyl alcohol was added by vacuum distillation and the reaction mixture was stirred for 30 h at room temperature. Then, all material volatile at room temperature was removed by vacuum distillation. The product was isolated by extraction with 4 × 20 mL of benzene through a medium-porosity frit to give 0.864 g (2.37 mmol, 87.4% based on t-BuOH) of $(C_5H_5)_2InO(t\text{-}Bu)$ as pale yellow crystals. $(C_5H_5)_2InO(t\text{-}Bu)$: pale yellow crystals turned tan at 126.8 °C and gradually became reddish brown as it became a liquid at 162.7 °C (dec); ^{1}H NMR (d_6-benzene) δ 6.22 (s, C_5H_5, 10 H), 0.97 (s, O−C$(CH_3)_3$, 9.2 H). Anal. Calcd: C, 52.86; H, 6.02. Found: C, 52.74; H, 6.05. Solubility: very soluble in THF; slight solubility in Et_2O and C_6H_6; trace solubility in C_5H_{12}; insufficient solubility in benzene for a cryoscopic molecular weight study.

Collection of X-ray Diffraction Data and Structural Solution for $[(C_5H_5)_2InO(t\text{-}Bu)]_2$. A well-defined crystal was covered with Infineum V8512 oil (Infineum USA L. P., 1900 East Linden Avenue, Linden, NJ 07036) and mounted on a Bruker SMART1000 CCD diffractometer equipped with a rotating anode (Mo Kα radiation, λ = 0.710 73 Å). X-ray diffraction data were collected at 90 K. Details are provided in Table 2. Data collection involved four sets of frames (600 frames in each set) and covered half-reciprocal space using the ω-scan technique (0.3° frame width) with different φ angles. Reflection intensities were integrated by using the SAINTPLUS program.[18] The solution and refinement of the structure were performed by use of the SHELXTL program package.[19] The structure was refined by full-matrix least squares against F^2. Non-hydrogen atoms were refined in an anisotropic approximation. The hydrogen atoms were located from difference electron density Fourier syntheses. Subsequently, the positions of the hydrogen atoms were refined with $U_{iso} = 1.5U_{eq}$ of the connected non-hydrogen atoms for CH_3 groups and with $U_{iso} = 1.2U_{eq}$ for the remaining hydrogen atoms. Data were corrected for absorption by using the Bruker AXS SADABS program that is a part of the SAINTPLUS package.[18]

Table 2. Data for X-ray Crystallographic Studies of $[(C_5H_5)_2InO(t\text{-}Bu)]_2$.

mol formula	$C_{28}H_{38}O_2In_2$
M_r	636.22
cryst shape	yellow plate
cryst syst	monoclinic
space group	$P2_1/n$
a, Å	9.5616(1)
b, Å	9.2108(1)
c, Å	15.1986(2)
α, deg	90
β, deg	99.578(1)
γ, deg	90
V, Å^3	1319.88(3)
D_{calcd}, g/cm^3	1.601
Z	2
μ(Mo Kα), mm^{-1}	1.768
T (K)	90(1)
max 2θ, deg	60.0
abs cor method	SADABS[18]
no. of rflns measd	23182
no. of unique rflns (R_{int})	3847 (0.064)
no. of rflns, $I > 4\sigma(I)$	3121
no. of refined params	202
R1 ($I > 2\sigma(I)$)	0.026
wR2	0.055
goodness of fit	1.063
extinction coeff	none

Synthesis of $In(acac)_3$ by a Cyclopentadiene Elimination Reaction between $In(C_5H_5)_3$ and H(acac). A Schlenk flask was charged with 0.230 g (0.743 mmol) of $In(C_5H_5)_3$ and a magnetic stir bar. The apparatus was evacuated at −196 °C, and approximately 5 mL of THF was added by vacuum distillation. Next, ∼2 mL (∼19 mmol) of H(acac) was added by vacuum distillation. The reaction mixture was then stirred vigorously for 15 min at room temperature. THF, unreacted H(acac), and C_5H_6 were removed by vacuum distillation to leave 0.302 g (0.733 mmol, 98.7% yield based on $In(C_5H_5)_3$) of $In(acac)_3$ as a colorless powder. $In(acac)_3$: mp 185.9−186.4 °C (lit.[14] mp 186 °C); ^{1}H NMR (d_6-benzene) δ 5.12 (s, acac H, 0.99 H), 1.70 (s, acac CH_3, 6.01 H).

Synthesis of $In(acac)_3$ by Methane Elimination Reaction between $InMe_3$ and H(acac). In the drybox, a 200 mL Solv-seal Schlenk flask was charged with 0.355 g (2.22 mmol) of $InMe_3$. The reaction flask was cooled to −196 °C and evacuated. Next, ∼2 mL (∼19 mmol) of H(acac) was added by vacuum distillation. The reactants were slowly warmed to room temperature, and bubbles were observed. After 1 day at 20 °C, colorless crystals were present in the flask. Methane gas was removed at −196 °C by vacuum distillation. The progress of the reaction was monitored for 26 days by using a manometer to measure the pressure at −196 °C. When pressure was observed at −196 °C, the noncondensable gas was removed by vacuum distillation. After 26 days, no pressure was observed. The suspension was maintained for 2 more days

(18) SMART and SAINTPLUS, Area Detector Control and Integration Software, Version 6.01; Bruker Analytical X-ray Systems, Madison, WI, 1999.

(19) SHELXTL, An Integration System for Solving, Refining, and Displaying Crystal Structures from Diffraction Data, Version 5.10; Bruker Analytical X-ray Systems, Madison, WI, 1997.

to ensure complete reaction. Removal of the residual H(acac) by vacuum distillation afforded 0.900 g (2.18 mmol, 98.3% yield based on $InMe_3$) of $In(acac)_3$ as pale yellow crystals. $In(acac)_3$: mp 185.2−186.3 °C (lit.[14] mp 186 °C); ^{1}H NMR (d_6-benzene) δ 5.12 (s, acac H, 1.01 H), 1.71 (s, acac CH_3, 5.99 H).

Ligand Redistribution Reaction between $In(acac)_3$ and $In(C_5H_5)_3$ in a 2:1 Mole Ratio. A sidearm dumper charged with 0.129 g of $In(C_5H_5)_3$ (0.364 mmol) dissolved in ∼10 mL of THF was connected to a Schlenk flask charged with 0.300 g of $In(acac)_3$ (0.728 mmol). The solution of $In(C_5H_5)_3$ was added to the $In(acac)_3$, and the mixture was stirred by means of a magnetic stir bar for 14 h at room temperature. The THF was then removed, and ∼15 mL of toluene was added by vacuum distillation. Extraction of the product(s) through a glass frit produced a mixture of yellow and colorless crystals after the solution was cooled to −35 °C. The toluene was decanted back into the original reaction flask through the frit and then removed by vacuum distillation. The isolated product was a mixture of yellow and colorless crystals that weighed 0.076 g (0.20 mmol, if pure $(C_5H_5)In(acac)_2$, 55% based on $In(C_5H_5)_3$). Product: yellow crystals melted with decomposition at ∼134 °C and then colorless crystals in the same melting point tube melted at 186.3−187.6 °C (lit.[14] mp for $In(acac)_3$ 186 °C); ^{1}H NMR (THF-d_8) δ 5.94 (s, (C_5H_5), 4.6 H), 5.37 (s, acac H, 2.3 H), 1.91 (s, acac CH_3, 12.2 H). See Results and Discussion.

Attempted Synthesis of $(C_5H_5)In(acac)_2$ by a Metathetical Reaction. The reagents, 0.070 g (0.975 mmol) of $Li(C_5H_5)$ and then 0.212 g (2.00 mmol) of Na(acac) as contained in separate sidearm dumpers, were added in succession at room temperature to 0.220 g (0.995 mmol) of $InCl_3$ dissolved in ∼15 mL of THF in order to initially form $(C_5H_5)InCl_2$[15] in situ and then form $(C_5H_5)In(acac)_2$. After the first two reagents had been combined and stirred for 4 h, Na(acac) was added. A light yellow solution formed. The final reaction mixture was stirred for 12 h at room temperature, and the THF was removed by vacuum distillation from the resulting yellow solution. The crude product was extracted through a medium-porosity frit by using ∼30 mL of benzene. Removal of the benzene left 0.307 g of a yellow powder (0.813 mmol if pure $(C_5H_5)In(acac)_2$, 72% based on $InCl_3$). Product: mp 133.6−138.3 °C dec; ^{1}H NMR (THF-d_8) δ 5.94 (s, (C_5H_5), 4.8 H), 5.37 (s, acac H, 2.1 H), 1.91 (s, acac CH_3, 10.1 H). See Results and Discussion.

Attempted Synthesis of $(C_5H_5)_2In(acac)$ by a Metathetical Reaction. Three reagents, 0.221 g (1.00 mmol) of $InCl_3$, 0.145 g (2.02 mmol) of $Li(C_5H_5)$, and 0.106 g (1.00 mmol) of Li(acac), were combined in ∼15 mL of THF and permitted to react as described previously. The THF was then removed by vacuum distillation, and the crude product was extracted with ∼30 mL of benzene. A yellow powder (0.262 g, 0.762 mmol if pure $(C_5H_5)_2In(acac)$, 79.8% based on $InCl_3$) of $(C_5H_5)_2In(acac)$ was isolated. Product: mp 79.2−82.4 °C dec; ^{1}H NMR (d_6-benzene) δ 6.20 (br, (C_5H_5), 10.0 H), 5.01 (br, acac H, 1.0 H), 1.72 (br, acac CH_3, 7.2 H). See Results and Discussion.

^{1}H NMR Spectral Study of a Mixture of $In(C_5H_5)_3$ and $H_2N(t\text{-Bu})$ in THF-d_8. An NMR tube was charged with 0.008 g (3×10^{-2} mmol) of $In(C_5H_5)_3$ and evacuated. Next, ∼1 mL of $H_2N(t\text{-Bu})$ was added by vacuum distillation at −196 °C, and then the contents were warmed to room temperature. The excess $H_2N(t\text{-Bu})$ was removed by vacuum distillation for 15 min. The product was recooled to −196 °C, and 0.7 mL of THF-d_8 was added by vacuum distillation. The NMR tube was flame-sealed and was maintained at −196 °C until the sample was inserted into the NMR spectrometer. ^{1}H NMR spectra of the sample over 15 days provided no evidence of cyclopentadiene elimination. ^{1}H NMR: 15 min after warming the solution to room temperature, δ 5.88 (br, C_5H_5, 15 H), 1.18 (br, $H_2N(t\text{-Bu})$, 2.1 H), 1.07 (br, $H_2N(t\text{-}Bu)$, 9.1 H); after 15 days at room temperature, δ 5.88 (br, C_5H_5, 15 H), 1.18 (br, $H_2N(t\text{-Bu})$, 2.2 H), 1.07 (br, $H_2N(t\text{-}Bu)$, 9.0 H).

Supporting Information Available: Complete tables of positional parameters, interatomic distances and angles, anisotropic thermal parameters, and positions for hydrogen atoms and packing diagrams for the compound studied. This material is available free of charge via the Internet at http://pubs.acs.org.

OM021054F