Chemistry of $In(C_5H_5)_3$ and Some Heteroleptic Organoindium(III) Derivatives. Crystal and Molecular Structures of $In(C_5H_5)_3$, $(C_5H_5)_3In\cdot PPh_3$, and $(Me_3CCH_2)_2In(C_5H_5)$

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Pure $In(C_5H_5)_3$ has been prepared in high yields from $InCl_3$ and $Li(C_5H_5)$ in THF solution with the absence of external heating. Neat $In(C_5H_5)_3$ readily decomposes at 150 °C to form $In(C_5H_5)_{(s)}$ and cyclopentadiene as the primary products whereas a benzene suspension decomposes under refluxing conditions. $In(C_5H_5)_3$ forms an isolable 1:1 adduct with PPh_3 but NMe_3, THF, and Et_2O do not form stable adducts. Ligand redistribution reactions with InR_3 (R = Me and CH_2CMe_3) in THF solution provided $R_2In(C_5H_5)$ and $RIn(C_5H_5)_2$. These heteroleptic organoindium(III) compounds have been isolated as analytically pure crystalline solids, but in THF solution they form equilibrium mixtures of the adducts of InR_3, $R_2In(C_5H_5)$, $RIn(C_5H_5)_2$, and $In(C_5H_5)_3$, as appropriate. Crystals of $[In(C_5H_5)_3]_n$, $(C_5H_5)_3In\cdot PPh_3$, and $[(Me_3CCH_2)_2In(C_5H_5)]_n$ were characterized by single-crystal X-ray structural studies.

Introduction

Our recent research has been designed to gain a fundamental understanding of the detailed nature of heteroleptic organometallic compounds of the heavier group 13 elements. The gallium compounds R_2GaCp and $RGaCp_2$ (R = Me,[1,2] Et,[3] CH_2CMe_3;[4] Cp = C_5H_5,[1,2,4] C_5H_4Me[2,3]) were prepared in nearly quantitative yields by ligand redistribution reaction between GaR_3 and $GaCp_3$ (eqs 1 and 2). Many of these heteroleptic compounds were isolated as analytically pure solids that were chemically stable at room temperature,[1−3] whereas in other cases pure single compounds could not be obtained.[4] The analytically pure derivatives were crystalline solids. In contrast, liquids were typically unstable at room temperature because their ligands redistributed to form more symmetrical derivatives. X-ray structural studies of the crystalline solids revealed linear polymers with four-coordinate gallium atoms that were bridged by cyclopentadienide groups through their 1- and 3-positions. Even though many compounds were isolated as analytically pure crystalline solids, dissolution always produced equilibrium mixtures of multiple species (eqs 3 and 4). Cryoscopic molecular weight studies of benzene solutions were consistent with the presence of monomers.

$$2GaR_3 + GaCp_3 \rightarrow 3R_2GaCp \qquad (1)$$

$$GaR_3 + 2GaCp_3 \rightarrow 3RGaCp_2 \qquad (2)$$

$$2R_2GaCp \rightleftharpoons RGaCp_2 + GaR_3 \qquad (3)$$

$$2RGaCp_2 \rightleftharpoons R_2GaCp + GaCp_3 \qquad (4)$$

To prepare heteroleptic organoindium compounds and gain an understanding of their chemistry, we needed pure $In(C_5H_5)_3$, a necessary starting material for the preparation of these types of compounds by ligand redistribution reactions. In this paper, we describe a reliable procedure for the synthesis of $In(C_5H_5)_3$ as well as a description of its physical and chemical properties. This compound was used, in turn, for the preparation of the heteroleptic derivatives $R_2In(C_5H_5)$ and $RIn(C_5H_5)_2$ (R = Me, CH_2CMe_3).

Results and Discussion

The synthesis of analytically pure $In(C_5H_5)_3$ in high yields has been achieved by reacting $InCl_3$ with $Li(C_5H_5)$ in a 1:3.09 mol ratio in THF solution at room temperature. Since all reactants and products were soluble in THF, reaction times were kept short. Furthermore, no external heating was employed during the preparative reaction or during the isolation and purification of the product. The initial indium-containing product $(C_5H_5)_3In\cdot THF$ was readily separated from LiCl and excess $Li(C_5H_5)$ by extraction with benzene at room temperature. The THF was then removed quantitatively from the unstable adduct by vacuum distillation at room temperature. A final washing of the product with pentane produced $In(C_5H_5)_3$ as a bright yellow powder that did not melt but appeared to decompose at ~160−164 °C as shown by a color change from bright yellow to orange

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[2] Beachley, O. T., Jr.; Mosscrop, M. T. *Organometallics* **2000**, *19*, 4550.

[3] Beachley, O. T., Jr.; Rosenblum, D. B.; Churchill, M. R.; Lake, C. H.; Krajkowski, L. M. *Organometallics* **1995**, *14*, 4402.

[4] Beachley, O. T., Jr.; Maloney, J. P.; Rogers, R. D. *Organometallics* **1997**, *16*, 3267.

10.1021/om0202322 CCC: $22.00

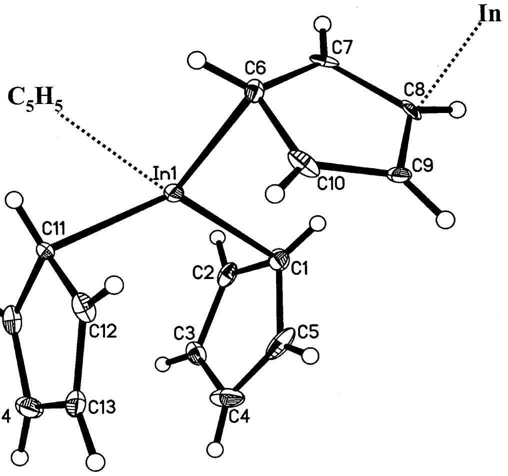

Figure 1. Molecular geometry and labeling of atoms for $[In(C_5H_5)_3]_n$ (50% probability ellipsoids for non-hydrogen atoms).

Table 1. Selected Bond Distances (Å) and Angles (deg) for $In(C_5H_5)_3$[a]

(A) Indium−Carbon Distances			
In(1)−C(1)	2.229(4)	In(1)−C(11)	2.229(4)
In(1)−C(6)	2.389(4)	In(1)−C(8)#1	2.482(4)
In(1)#2−C(8)	2.482(4)		
(B) Carbon−Carbon Distances for Cyclopentadienide Rings			
C(1)−C(2)	1.453(6)	C(8)−C(9)	1.441(5)
C(1)−C(5)	1.461(6)	C(9)−C(10)	1.360(5)
C(2)−C(3)	1.366(6)	C(11)−C(15)	1.458(5)
C(3)−C(4)	1.423(6)	C(11)−C(12)	1.476(5)
C(4)−C(5)	1.358(6)	C(12)−C(13)	1.352(6)
C(6)−C(7)	1.419(6)	C(13)−C(14)	1.438(5)
C(6)−C(10)	1.442(5)	C(14)−C(15)	1.363(6)
C(7)−C(8)	1.408(5)		
(C) Angles around Indium			
C(11)−In(1)−C(1)	129.9(2)	C(11)−In(1)−C(6)	104.2(1)
C(11)−In(1)−C(8)#1	108.8(1)	C(6)−In(1)−C(8)#1	99.4(1)
C(1)−In(1)−C(8)#1	102.0(1)		

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x + 3/2, y + 1/2, z$; #2 $-x + 3/2, y - 1/2, z$.

to brown that occurred slowly. Even though the pure solid appeared to decompose at ~160−164 °C, heating of a suspension of $In(C_5H_5)_3$ in benzene to reflux was sufficient to induce decomposition as observed by a change in its color from bright yellow to brownish orange and a shift of the single resonance in its ^1H NMR spectrum to higher field (see later paragraph). As $In(C_5H_5)_3$ does not melt and ^1H NMR spectra of solutions containing the compound do not identify the presence of multiple In-C_5H_5 species due to rapid exchange of C_5H_5 substituents, the only tool for evaluating the purity of $In(C_5H_5)_3$ is its elemental analysis. The isolation of pure $In(C_5H_5)_3$ requires the use of pure reagents and paying careful attention to the details of the preparative procedure.

The structure of $In(C_5H_5)_3$ (Figure 1) consists of infinite polymeric chains that are located along the crystallographic *b* axis. Each indium is bonded to four cyclopentadienide groups. Two cyclopentadienide groups are monohapto or terminal whereas the other two form bridges between two indium atoms by using the carbon atoms at the 1- and 3-positions of the rings. Selected interatomic distances and angles are collected in Table 1. The structure of another polymorphic modification of $In(C_5H_5)_3$ was reported previously.[5] The space group for the earlier structure was $P2_12_12_1$ whereas the current structural study has identified the *Pbca* space group with a unit cell that is almost twice as large as the original. The indium atom has a distorted tetrahedral configuration. The largest C−In−C angle occurs between the two terminal cyclopentadienide groups and is 129.9(2)° for C(11)−In(1)−C(1) whereas the second largest angle occurs between the two bridging cyclopentadienide groups, C(6)−In(1)−C(8′) ($1.5 - x, y + 0.5, z$) at 99.4(1)°. The terminally coordinated cyclopentadienide rings have largely nonconjugated π-systems with C(1)−C(3), C(4)−C(5), C(12)−C(13), and C(14)−C(15) being essentially double bonds. The ipso-carbon atoms C(1) and C(11) are bonded to In(1) by using almost sp^3-hybridized orbitals as shown by the positions of the hydrogen atom. These hydrogen atoms are displaced from the corresponding plane of the cyclopentadienide ring by 0.23 Å for H(1) and −0.43 Å for H(11). The bridging cyclopentadienide groups have an allyl-like conjugated π-system containing C(6)−C(7)−C(8) atoms and a double bond between C(9) and C(10). Thus, atoms C(6) and C(8) have close to sp^2-hybridization. The cyclopentadienide ring with atoms C(1) through C(5) is positioned almost on top of the ring with C(11) through C(15). The angle between their planes is 17.7°. The positioning of these two rings results in a short van der Waals contact between C(4) and C(14) of 3.38 Å. The sum of the van der Waals radii is 3.42 Å.[6] Thus, there might be some degree of $\pi-\pi$ interaction. There are no short distances that might be indicative of interactions between the chains.

The preparation of $In(C_5H_5)_3$ has been described in two articles. The initial preparation[7] utilized the reaction between $InCl_3$ and excess $Na(C_5H_5)$ in diethyl ether but the yield was minimal and the elemental analysis suggested that the sample was impure as the percent carbon was low (calcd 58.11, found 56.49). The major indium-containing product, indium(I) cyclopentadienide, was isolated by sublimation when the crude reaction product was heated at 150 °C. The second synthesis[8] of $In(C_5H_5)_3$ had two major modifications to the original procedure. The reagent $Na(C_5H_5)$ was replaced with $Li(C_5H_5)$ and the product was isolated with refluxing benzene. The percent carbon observed for this product was low also (calcd 58.11, found 57.6). It is noteworthy that neither of these papers reported a melting point, a decomposition temperature, or a solubility study of the compound in any solvent. When we attempted to prepare $In(C_5H_5)_3$ using the method described by Poland and Tuck,[8] impure $In(C_5H_5)_3$ was obtained. Details of these experiments and the resulting products are provided with the Supporting Information.

The solubility of $In(C_5H_5)_3$ in benzene and its properties after heating in benzene were investigated in order to learn possible reasons for the poor elemental analyses for the products isolated by us after using the method of Poland and Tuck.[8] Pure $In(C_5H_5)_3$ has minimal solubility in benzene at room temperature. Heating to 60 °C increased the solubility but decomposition also

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(5) Einstein, F. W. B.; Gilbert, M. M.; Tuck, D. G. *Inorg. Chem.* **1972**, *11*, 2832.

(6) Zefirov, Y. V.; Zorkii, P. M. *Russ. Chem. Rev.* **1989**, *58*, 713.

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occurred. All of the originally soluble $In(C_5H_5)_3$ did not redissolve upon reheating. The chemical shift of the resonance for the C_5H_5 protons moved to higher field with heating and new resonances for C_5H_6 and dicyclopentadiene appeared in the spectrum and increased in intensity as the sample was heated for longer times. Thus, C_5H_6 was formed by thermal decomposition, not hydrolysis.

Pure $In(C_5H_5)_3$ decomposes readily at 150 °C to form $In(C_5H_5)$[7,9] and C_5H_6 as the isolated products. Heating for only 15 min was sufficient to completely decompose a 2.6-mmol sample as ~81% of the indium was converted to $In(C_5H_5)$. These observations of the thermal decomposition of $In(C_5H_5)_3$ are consistent with our observations of heating the compound with benzene and with the observed instability of $In(C_5Me_5)_3$.[9] Thus, the formation of $In(C_5H_5)$ from the decomposition of $In(C_5H_5)_3$ does not require $Na(C_5H_5)$.[8]

When $In(C_5H_5)_3$ and $In(C_5H_5)$ were present in a THF solution, the indium(III) species stabilized $In(C_5H_5)$. The solution remained pale yellow for more than 4 months while being held at ~20 °C. In contrast, a THF solution of only $In(C_5H_5)$ that was initially light yellow after warming from −196 to ~20 °C became brown after 20 min and very dark brown, almost black, with a metallic mirror on the NMR tube after 45 min. The ^1H NMR spectrum of the THF solution of $In(C_5H_5)_3$ and $In(C_5H_5)$ exhibited only a single line for the C_5H_5 protons. Exchange of C_5H_5 moieties through the formation of an indium(II) species $THF\cdot(C_5H_5)_2In-In(C_5H_5)_2\cdot THF$ with σ-bonded C_5H_5 moieties is consistent with indium chemistry[11] and with the hypothesis that decomposition of $In(C_5H_5)$ in THF involves a transformation from a π- to a σ-bonded species prior to cleavage of the indium−carbon bond.[9] Thus, the change in chemical shift of the single resonance for the cyclopentadienide protons to higher field as samples of $In(C_5H_5)_3$ are heated in benzene could be due to the presence of $In(C_5H_5)$ which, in turn, is exchanging C_5H_5 ligands with $In(C_5H_5)_3$ through the formation of an indium(II) species.

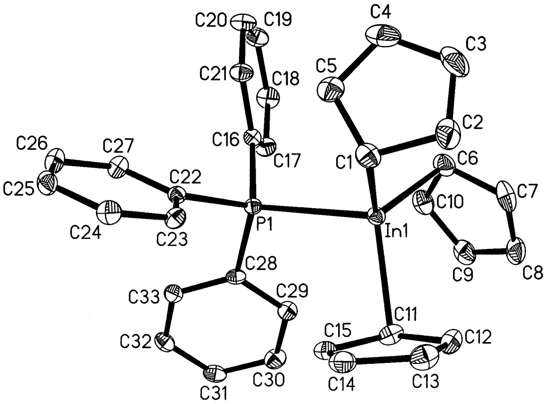

Figure 2. Molecular geometry and labeling of atoms for $(C_5H_5)_3In\cdot PPh_3$ (50% probability ellipsoids for non-hydrogen atoms, hydrogen atoms are omitted for clarity).

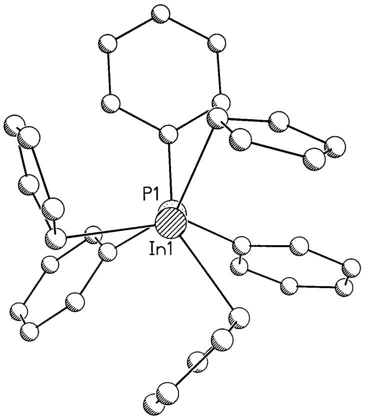

Figure 3. Arrangement of atoms about the indium−phosphorus vector in $(C_5H_5)_3In\cdot PPh_3$.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $(C_5H_5)_3In\cdot PPh_3$

(A) Indium−Phosphorus and Indium−Carbon Distances			
In(1)−P(1)	2.6992(4)	In(1)−C(1)	2.256(2)
In(1)−C(6)	2.270(2)	In(1)−C(11)	2.263(2)
(B) Phosphorus−Carbon Distances			
P(1)−C(16)	1.816(2)	P(1)−C(28)	1.821(2)
P(1)−C(22)	1.814(2)		
(C) Angles around Indium			
C(1)−In(1)−C(11)	113.68(6)	C(1)−In(1)−P(1)	106.22(5)
C(1)−In(1)−C(6)	114.09(7)	C(11)−In(1)−P(1)	102.53(5)
C(11)−In(1)−C(6)	115.02(7)	C(6)−In(1)−P(1)	103.57(5)
(D) Angles around Phosphorus			
C(22)−P(1)−C(16)	105.10(7)	C(16)−P(1)−C(28)	105.46(7)
C(22)−P(1)−C(28)	105.93(7)	C(22)−P(1)−In(1)	114.63(5)
C(16)−P(1)−In(1)	111.46(5)	C(28)−P(1)−In(1)	113.48(5)

Indium(III) cyclopentadienide is a good Lewis acid to phosphines but not to amines and ethers. The pale yellow adduct $In(C_5H_5)_3\cdot PPh_3$ exists as simple monomeric species in the crystalline state and in benzene solution. No dissociation of the adduct in the concentration range of 0.07 to 0.03 *m* was observed during cryoscopic molecular weight studies. The molecular geometry of the adduct as determined by an X-ray structural study and the labeling of the atoms is shown in Figure 2. The arrangement of the substituents on indium relative to those on phosphorus is shown in Figure 3. Selected interatomic distances and angles are collected in Table 2. The substituents around indium and phosphorus atoms are arranged in distorted tetrahedral environments. The indium−carbon distances of 2.256(2), 2.270(2), and 2.263(2) Å are very similar to the terminal $In-C(C_5H_5)$ distances in $In(C_5H_5)_3$ of 2.229(4) Å but shorter than the bridging $In-C(C_5H_5)$ distances of 2.389(4) and 2.482(4) Å determined in the present study. The $In-C(C_5H_5)$ distance in the five-coordinate adduct $Cl_2(C_5H_5)In\cdot(THF)_2$[12] is longer at 2.377(2) Å. The cyclopentadienide ligands are arranged around the indium with a propeller-like orientation in an *-sc*-conformation with respect to the phenyl substituents as seen in Figure 3. The phenyl groups are rotated with respect to each other so that the dihedral angles between their planes are −81.2°, −52.5°, and 53.1°. The torsion angles along the indium−phosphorus bond of C(1)−In(1)−P(1)−C(22), C(6)−In(1)−P(1)−C(16), and C(11)−In(1)−P(1)−C(28) are −25.29(7)°, −26.56(7)°, and −27.64(7)°, respectively. The indium−phosphorus bond

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[12] Visona, P.; Benetollo, F.; Rossetto, G.; Zanella, P. *Polyhedron* **1996**, *15*, 1743.

distance of 2.699(2) Å is shorter than the corresponding distances in both $(Me_3In)_2$·diphos of 2.755(4) Å[13] and H_3In·$[P(C_6H_{11})_3]_2$ of 2.9869(5) Å.[14] The cyclopentadienide groups have the characteristic features of simple σ-bonded monohapto rings.

The possibility of weak intermolecular interactions between some *p*-hydrogen atoms on the phenyl rings in one adduct molecule and a carbon−carbon π-bond of a cyclopentadienide ring in a neighboring molecule exists. The distance between the appropriate atoms for this possible interaction between H(27A)···π C(14′)−C(15′) $(2.5 - x, 0.5 + y, 0.5 - z)$ is 2.62 Å, and the angle between C(27)−H(27A)···π(C(14′)−C(15′) is 162°. The distance between H(32A)···C(7) $(1 + x, y, z)$ is 2.836 Å. The sum of van der Waals radii for carbon and hydrogen is 2.870 Å.[6] These intermolecular contacts might help the adduct crystallize by making 3-dimensional networks of the molecules.

The heteroleptic organoindium compounds $Me_2In(C_5H_5)$ and $(Me_3CCH_2)_2In(C_5H_5)$ were prepared as colorless solids in nearly quantitative yields by facile stoichiometric ligand redistribution reactions between $In(C_5H_5)_3$ and InR_3 (R = Me and CH_2CMe_3) in THF solution (eq 1) at room temperature. The THF was readily removed from these compounds by vacuum distillation at ∼20 °C. Each product was purified by sublimation at 100−110 °C. The physical properties of $Me_2In(C_5H_5)$ as prepared by the ligand-redistribution reaction were identical with those previously reported.[15] Samples of pure $Me_2In(C_5H_5)$ decompose at ∼200 °C to an unknown dark brown material. No $In(C_5H_5)$ was observed. An analytically pure sample of $(Me_3CCH_2)_2In(C_5H_5)$ also decomposed at 188−190 °C to an unknown dark brown material. No $In(C_5H_5)$ was observed.

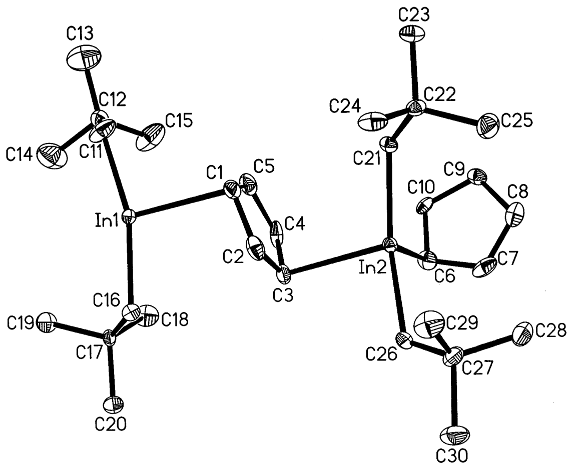

Figure 4. Molecular geometry and labeling of atoms for $[(Me_3CCH_2)_2In(C_5H_5)]_n$ (50% probability ellipsoids for nonhydrogen atoms, hydrogen atoms are omitted for clarity).

Table 3. Selected Bond Distances (Å) and Angles (deg) for $(Me_3CCH_2)_2In(C_5H_5)$[a]

(A) Indium-Carbon Distances			
In(1)−C(1)	2.517(5)	In(1)−C(11)	2.180(5)
In(1)−C(16)	2.148(5)	In(1)−C(9)#1	2.543(5)
In(1)#2−C(9)	2.543(5)	In(2)−C(3)	2.550(5)
In(2)−C(6)	2.539(5)	In(2)−C(21)	2.160(5)
In(2)−C(26)	2.190(4)	In(3)−C(31)	2.534(4)
In(3)−C(41)	2.183(4)	In(3)−C(39)#2	2.530(5)
In(3)−C(46)	2.135(5)	In(3)#2−C(39)	2.530(5)
In(4)−C(33)	2.539(5)	In(4)−C(36)	2.519(4)
In(4)−C(51)	2.162(5)	In(4)−C(56)	2.179(4)
(B) Carbon−Carbon Distances for Cyclopentadienide Ring			
C(1)−C(2)	1.418(7)	C(1)−C(5)	1.417(7)
C(2)−C(3)	1.404(7)	C(3)−C(4)	1.419(7)
C(4)−C(5)	1.380(7)	C(6)−C(10)	1.401(6)
C(6)−C(7)	1.436(7)	C(7)−C(8)	1.388(7)
C(8)−C(9)	1.429(6)	C(9)−C(10)	1.408(6)
C(31)−C(32)	1.403(6)	C(31)−C(35)	1.426(6)
C(32)−C(33)	1.397(6)	C(33)−C(34)	1.443(6)
C(34)−C(35)	1.386(6)	C(36)−C(37)	1.442(6)
C(37)−C(38)	1.380(6)	C(38)−C(39)	1.438(7)
C(39)−C(40)	1.418(7)	C(36)−C(40)	1.411(7)
(C) Angles around Indium			
C(16)−In(1)−C(11)	150.9(2)	C(16)−In(1)−C(1)	103.8(2)
C(11)−In(1)−C(1)	100.3(2)	C(16)−In(1)−C(9)#1	106.1(2)
C(11)−In(1)−C(9)#1	89.0(2)	C(1)−In(1)−C(9)#1	91.9(5)
C(21)−In(2)−C(26)	152.3(2)	C(21)−In(2)−C(6)	102.4(2)
C(26)−In(2)−C(6)	100.1(2)	C(21)−In(2)−C(3)	105.4(2)
C(26)−In(2)−C(3)	89.9(2)	C(6)−In(2)−C(3)	91.5(2)
C(46)−In(3)−C(41)	145.8(2)	C(46)−In(3)−C(39)#2	103.1(2)
C(41)−In(3)−C(39)#2	91.8(2)	C(46)−In(3)−C(31)	107.98(16)
C(41)−In(3)−C(31)	98.9(2)	C(39)#2−In(3)−C(31)	100.8(2)
C(51)−In(4)−C(56)	145.6(2)	C(51)−In(4)−C(36)	109.0(2)
C(56)−In(4)−C(36)	98.7(2)	C(51)−In(4)−C(33)	102.1(2)
C(56)−In(4)−C(33)	91.2(2)	C(36)−In(4)−C(33)	102.1(2)

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x+1, y, z$; #2 $-x-1, y, z$.

An X-ray structural study of $(Me_3CCH_2)_2In(C_5H_5)$ revealed that the compound exists as a polymer with cyclopentadienide units bridging $In(CH_2CMe_3)_2$ moieties. The structure is fully ordered in the monoclinic cell and the $P2_1$ space group. However, as the angle β in the unit cell is essentially 90°, twinning exists in the structure. Thus, the absolute configuration of the molecule could not be determined. The unit cell contains two asymmetric units, each of which consists of two $(Me_3CCH_2)_2In(C_5H_5)$ monomers as depicted in Figure 4. Selected interatomic distances and angles are collected in Table 3. Each asymmetric unit contains two monomeric segments of the polymeric chain which have slightly different geometries with respect to the $In-C_5H_5-In$ connections. Every indium atom is in contact with four carbon atoms, two from terminal CH_2CMe_3 groups and two from bridging C_5H_5 moieties, in a highly distorted tetrahedral environment. The $C(CH_2Me_3)-In-C(CH_2Me_3)$ angles are significantly larger than the angle for an ideal trigonal-planar arrangement of atoms with values of 150.9(2)° [In(1)], 152.3(2)° [In(2)], 145.8(2)° [In(3)], and 145.6(2)° [In(1)], while the $C(C_5H_5)-In-C(C_5H_5)$ angle is less than the ideal tetrahedral angle with values of 91.9(2)° [In(1)], 91.5(2)° [In(2)], 100.8(2)° [In(3)], and 102.1(2)° [In(4)]. The bridging indium−carbon(C_5H_5) bond distances (Å) of 2.517(5) for In(1)−C(1), 2.543(5) for In(1)−C(9, #1), 2.550(5) for In(2)−C(3), 2.530(5) for In(3)−C(39, #2), 2.534(4) for In(3)−C(31), 2.539(5) for In(4)−C(33), and 2.519(4) for In(4)−C(36) are slightly longer than those in $In(C_5H_5)_3$ at 2.389(4) and 2.482(4) Å and in $Me_2In(C_5H_5)$ at 2.457(12) and 2.484(12) Å.[15] The $In-C(CH_2CMe_3)$ bond distances are similar to the In−Me distances of 2.118(14) and 2.129(13) Å in $Me_2In(C_5H_5)$[15] and the $In-C(CH_2CMe_3)$ distance of 2.12(2) Å in $[In(CH_2CMe_3)Cl_2]_x$.[16] The In−C bond vectors are almost parallel in the asymmetric unit for indium-

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[13] Bradley, D. C.; Chudzynska, H.; Faktor, M. M.; Frigo, D. M.; Hursthouse, M. B.; Hussain, B.; Smith, L. M. *Polyhedron* **1988**, *7*, 1289.

[14] Cole, M. L.; Hibbs, D. E.; Jones, C.; Smithies, N. A. *J. Chem. Soc., Dalton Trans.* **2000**, 545.

[15] Beachley, O. T., Jr.; Robirds, E. S.; Atwood, D. A.; Wei, P. *Organometallics* **1999**, *18*, 2561.

(1) and -(2) with the angles between these vectors being 177.5° and 176.6°. These vectors are slightly bent in the asymmetric unit for indium(3) and -(4) where the angles are 169.7° and 169.3°. The planes of the C_5H_5 rings are slightly tilted with respect to the C−In bonds by 12.2° and 11.3° for C1···C5, 13.6° and 11.2° for C6···C10, 6.2° and 13.5° for C31···C35, and 15.9° and 13.5° for C36···C40. The carbon−carbon distances within each C_5H_5 ring are appropriate for a delocalized allyl-type bonding between the carbon atoms at the 1, 2, and 3 positions of the ring whereas the carbon−carbon distance between the atoms at the 4 and 5 positions is shorter and representative of a double bond. Thus, each indium(III) atom can be considered to have two normal σ-bonds to the neopentyl carbon atoms and a three-centered two-electron bond across the $C(C_5H_5)-In-C(C_5H_5)$ system.

The first examples of heteroleptic organoindium compounds that incorporate two cyclopentadienide groups $MeIn(C_5H_5)_2$ and $(Me_3CCH_2)In(C_5H_5)_2$ have been prepared as analytically pure yellow solids by ligand redistribution reactions (eq 2) in THF solutions. The preparative reactions utilized excess $In(C_5H_5)_3$. The equilibrium in which the ligands of $RIn(C_5H_5)_2$ redistribute to form $R_2In(C_5H_5)$ and $In(C_5H_5)_3$ in THF solution (eq 4) must be shifted to minimize the amount of $R_2In(C_5H_5)$, a potential impurity that has a sublimation temperature that is similar to or slightly less than that of $RIn(C_5H_5)_2$. Analytically pure $MeIn(C_5H_5)_2$ was isolated easily by sublimation at 110−120 °C. Decomposition, rather than melting, occurred at 150−160 °C but only very small amounts of $In(C_5H_5)$ were formed. Analytically pure, yellow $(Me_3CCH_2)In(C_5H_5)_2$ was also isolated by sublimation at 90−95 °C but it was necessary to remove a small amount of $(Me_3CCH_2)_2In(C_5H_5)$ that sublimed as a colorless solid prior to the sublimation of $(Me_3CCH_2)In(C_5H_5)_2$. The two compounds $(Me_3CCH_2)_2In(C_5H_5)$ and $(Me_3CCH_2)In(C_5H_5)_2$ are readily distinguished by their color. Careful control of the temperature during sublimation is necessary for the isolation of analytically pure $(Me_3CCH_2)In(C_5H_5)_2$. It is of interest that $(Me_3CCH_2)In(C_5H_5)_2$ sublimed at a lower temperature than $MeIn(C_5H_5)_2$. This observation suggests that the cyclopentadienide bridge bonds that stabilize the compounds as solids appear to be weaker in $(Me_3CCH_2)In(C_5H_5)_2$ than in $MeIn(C_5H_5)_2$. X-ray structural studies of $(Me_3CCH_2)In(C_5H_5)_2$ and $MeIn(C_5H_5)_2$ were prevented by severe twining of the crystals.

The neopentyl derivative $(Me_3CCH_2)In(C_5H_5)_2$ melts at 126.4−126.9 °C. If heating is immediately quenched after the compound melts, the observed melting point is reproducible. However, the melt does decompose. When a sample of pure $(Me_3CCH_2)In(C_5H_5)_2$ was heated at 150 °C in a sealed, evacuated tube, pale yellow crystals of $In(C_5H_5)$ collected in the coolest part of the tube whereas colorless needles of $(Me_3CCH_2)_2In(C_5H_5)$ formed on the warmer walls. A condensable gaseous product was identified as C_5H_6 with a trace of CMe_4. These data suggest that $(Me_3CCH_2)In(C_5H_5)_2$ melted and then redistributed its ligands to form initially a mixture of $(Me_3CCH_2)_2In(C_5H_5)$ and $In(C_5H_5)_3$ (eq 5).

$$2(Me_3CCH_2)In(C_5H_5)_{2(melt)} \xrightarrow{150\ °C} In(C_5H_5)_3 + (Me_3CCH_2)_2In(C_5H_5)_{(s)} \quad (5)$$

The homoleptic derivative $In(C_5H_5)_3$ then decomposed to $In(C_5H_5)$ and C_5H_6 (eq 6) whereas the $(Me_3CCH_2)_2In(C_5H_5)$ sublimed without decomposition to the cooler walls of the apparatus.

$$In(C_5H_5)_3 \xrightarrow{150\ °C} In(C_5H_5)_{(s)} + C_5H_6 + \text{organic produce(s)} \quad (6)$$

Even though all of the heteroleptic organoindium derivatives of the types $R_2In(C_5H_5)$ and $RIn(C_5H_5)_2$ (R = Me, CH_2CMe_3) can be isolated as pure compounds in the solid state, they dissolve in THF to form adducts that redistribute their ligands to form equilibrium mixtures of InR_3·THF, $R_2In(C_5H_5)$·THF, $RIn(C_5H_5)_2$·THF, and $In(C_5H_5)_3$·THF, as appropriate (eqs 3 and 4). Dissolution of all known organoindium(III) cyclopentadienide derivatives at room temperature requires the use of a Lewis base with significant donor ability. The cyclopentadienide bridges in the polymer must be broken for dissolution to occur. Thus, these compounds are exceedingly soluble in THF, a strong base, but are essentially insoluble in nonbasic solvents and in weakly basic solvents such as C_5H_{12}, C_6H_6, Et_2O, $HCCl_3$, and CCl_4. In contrast, the cyclopentadienide bridges in the related gallium derivatives are weaker as $Me_2Ga(C_5H_4Me)$,[2] $Et_2Ga(C_5H_4Me)$,[2] $Et_2Ga(C_5H_5)$,[3] and $EtGa(C_5H_5)_2$[3] dissolve in benzene and form monomers in solution. The ^1H NMR spectrum of $(Me_3CCH_2)_2In(C_5H_5)$ in THF solution at ~20 °C clearly demonstrates the occurrence of the ligand redistribution equilibria and the presence of $(Me_3CCH_2)_2In(C_5H_5)$·THF, $(Me_3CCH_2)In(C_5H_5)_2$·THF, $In(CH_2CMe_3)_3$·THF, and $In(C_5H_5)_3$·THF (eqs 3 and 4). Six resonances are observed for the methyl and methylene protons for the neopentyl groups. However, only one resonance for the cyclopentadienide protons can be seen. Cooling of the solution to −60 °C, the lowest temperature studied, did not change the spectrum. The cyclopentadienide protons for the three different species were not resolved. The resonances for the neopentyl substituents associated with each of the three compounds in the solution were identified by comparing the chemical shifts of each line with the resonances for the independent species.

Although $Me_2In(C_5H_5)$ is isolable as an analytically pure solid, it exists in THF solution as a mixture of $Me_2In(C_5H_5)$·THF, $MeIn(C_5H_5)_2$·THF, $InMe_3$·THF, and $In(C_5H_5)_3$·THF according to NMR spectroscopy. Even though four compounds are present in THF solution, only three resonances, two for In−Me protons and one for C_5H_5 protons, are observed at ~20 °C. As the solution was cooled to −40 °C, one of the original In−Me resonances moved from −0.52 ppm to slightly higher field and split into two lines at −0.53 and −0.56 ppm. The second In−Me resonance at −1.10 ppm shifted to higher field also. The new line at −0.53 ppm is assigned to $Me_2In(C_5H_5)$·THF whereas the one at −0.56 ppm is for $InMe_3$·THF on the basis of their relative intensities. Pure $InMe_3$·THF dissolved in THF has a single resonance at −0.55 ppm. The second In−Me resonance that

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(16) Beachley, O. T., Jr.; Spiegel, E. F.; Kopasz, J. P.; Rogers, R. D. *Organometallics* **1989**, *8*, 1915.

shifted from −1.10 to −1.64 ppm over the temperature range of 20 to −90 °C may be assigned to the In−Me group in $MeIn(C_5H_5)_2$·THF. The resonance corresponding to the C_5H_5 protons shifted from 6.04 to 5.97 ppm over the temperature range of 20 to −90 °C. Conformation of these assignments for the various In−Me resonances was obtained by preparing a THF solution of $Me_2In(C_5H_5)$ with one small crystal of $InMe_3$. The resonances for the In−Me groups occurred at −0.55 and −0.56 ppm at −90 °C whereas the resonance at higher field disappeared because the equilibrium had been shifted. These temperature-dependent NMR spectroscopic data are consistent with the occurrence of ligand redistribution equilibria (eqs 3 and 4) and with the exchange of methyl groups and cyclopentadienide groups between the different species. The resonances of the cyclopentadienide ligands for the different species could not be resolved at any temperature studied.

The monomethyl derivative $MeIn(C_5H_5)_2$ exists as a mixture of $MeIn(C_5H_5)_2$·THF, $Me_2In(C_5H_5)$·THF, $In(C_5H_5)_3$·THF, and possibly $InMe_3$·THF in THF solution. Two In−Me lines and one C_5H_5 line are observed at ~20 °C. Thus, the methyl groups are exchanging between the different species as are the cyclopentadienide groups. When the temperature was lowered from 20 to −80 °C, the most intense In−Me resonance shifted from −1.09 to −1.49 ppm whereas the smaller line moved from −0.37 to −0.03 ppm. The resonance corresponding to the C_5H_5 protons broadened and shifted from 5.98 to 5.85 ppm between 20 and −40 °C. At −60 °C the C_5H_5 protons exhibited lines at 6.06 and 5.72 ppm. Additional lowering of the temperature to −80 °C caused the cyclopentadienide resonances to shift to 6.02 and 5.71 ppm. The presence of an In−Me resonance associated with $Me_2In(C_5H_5)$·THF at a chemical shift other than at 0.53 ppm suggests that $InMe_3$·THF is present in solution. Even though no resonance for $InMe_3$·THF was observed, its presence is required by the balanced chemical equation for the ligand redistribution reaction of $Me_2In(C_5H_5)$·THF (eq 3).

^{1}H NMR spectroscopy suggests that $(Me_3CCH_2)In(C_5H_5)_2$ exists in THF solution as an equilibrium mixture of $(Me_3CCH_2)In(C_5H_5)_2$·THF, $(Me_3CCH_2)_2In(C_5H_5)$·THF, $(Me_3CCH_2)_3In$·THF, and $In(C_5H_5)_3$·THF (eqs 3 and 4). The resonances for the methyl protons associated with the neopentyl groups for all three species were observed at 20 °C. However, only two of the three resonances for the methylene protons for the neopentyl groups could be observed. The line for the methylene protons for $(Me_3CCH_2)_3In$·THF was not observed, possibly because its intensity is expected to be extremely low and/or the resonance is masked by other resonances. The compound $(Me_3CCH_2)_3In$·THF will be formed by the redistribution of $(Me_3CCH_2)_2In(C_5H_5)$·THF, a product of the initial redistribution reaction (eq 3). Only minor changes for the chemical shifts for the resonances of the neopentyl methyl protons were observed as the temperature was lowered. Thus, the resonances at 0.99, 0.83, and 1.10 ppm for $(Me_3CCH_2)_2In(C_5H_5)$·THF, $(Me_3CCH_2)In(C_5H_5)_2$·THF, and $(Me_3CCH_2)_3In$·THF, respectively, at 20 °C were observed at 1.00, 0.84, and 1.10 ppm, respectively, at −50 °C. In contrast, the methylene protons on the neopentyl substituents shifted more significantly as the lines for $(Me_3CCH_2)_2In(C_5H_5)$·THF and $(Me_3CCH_2)In(C_5H_5)$·THF at 0.61 and 0.37 ppm, respectively, moved to 0.54 and 0.25 ppm at −50 °C. The single resonance associated with the C_5H_5 protons appeared at 6.03 ppm at 20 °C but was broader and slightly shifted to 6.04 ppm at −30 °C. At −40 °C the resonance split into two lines at 5.95 and 6.05 ppm. The resonance at 6.05 ppm may be assigned to the C_5H_5 protons for the cyclopentadienide groups for both $(Me_3CCH_2)In(C_5H_5)_2$·THF and $(Me_3CCH_2)_2In(C_5H_5)$·THF whereas the resonance at 5.95 ppm may be assigned to $In(C_5H_5)_3$·THF. The chemical shift of the resonance at 6.05 ppm remained constant to −60 °C, whereas the resonance at 5.95 assigned to $In(C_5H_5)_3$·THF shifted to 5.93 ppm at −60 °C, the lowest temperature studied.

The equilibrium constants for the ligand redistribution reactions for THF solutions of $Me_2In(C_5H_5)$ (eq 3), $(Me_3CCH_2)_2In(C_5H_5)$ (eq 3), $MeIn(C_5H_5)_2$ (eq 4), and $(Me_3CCH_2)In(C_5H_5)_2$ (eq 4) have calculated values of 3.9×10^{-3}, 3.2×10^{-3}, 0.15, and 2.0×10^{-2}, respectively, at the normal operating temperature of the instrument. The equilibrium constants for the methyl derivatives were calculated on the basis of the integrations of the methyl resonances whereas the equilibrium constants for the neopentyl derivatives were based on the integrations for the methyl protons for the *tert*-butyl groups on the neopentyl substituents. More accurate, detailed, and complete thermodynamic data results could not be obtained for these systems as the resonances were not resolved fully.

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 starting materials $Li(C_5H_5)$,[9] $InMe_3$,[17] and $In(CH_2CMe_3)_3$[16] were prepared by literature methods whereas $InCl_3$ was purchased from Strem Chemicals, Inc. and was used as received. Special care was taken during the preparation of $Li(C_5H_5)$ to ensure its purity.[9] All solvents were carefully dried by using conventional procedures. Elemental analyses were performed by either E&R Microanalytical Laboratory, Parsippany, NJ, or 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 (400 MHz) spectra were recorded with a Varian Unity-Nova 400 spectrometer whereas ^{13}C NMR (125.7 MHz) spectra were recorded with a 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 and C_6D_5H at δ 7.15 ppm or the proton impurities in d_8-THF at 1.73 and 3.58 ppm. Carbon chemical shifts are referenced to $SiMe_4$ at δ 0.00 and to d_8-THF at δ 67.40 and 25.27 ppm. All samples for NMR spectra were contained in flame-sealed NMR tubes. Deuterated solvents, benzene-d_6 and THF-d_8, were purchased from Aldrich Chemical Co. and Cambridge Isotopes, Inc., respectively, dried with P_4O_{10}, and vacuum distilled into tubes coated with sodium mirrors. The benzene-d_6 was purchased as 99.6% atom percent deuterated. Molecular weights were measured cryoscopically in benzene solution by using an instrument similar to that described by Shriver and Drezdon.[18]

Synthesis of $In(C_5H_5)_3$ in THF Solution. A three-necked Solv-Seal flask that contained 2.19 g (30.4 mmol) of $Li(C_5H_5)$

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(17) Bradley, D. C.; Chudzynska, H. C.; Harding, I. S. *Inorganic Syntheses*; Cowley, A. H., Ed.; John Wiley and Sons Inc.: New York, 1997; Vol. 31, p 67.

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

and 75 mL of THF was connected to a sidearm dumper charged with 2.17 g (9.81 mmol) of $InCl_3$ and to a medium porosity frit. A THF solution of $InCl_3$ was added to the $Li(C_5H_5)$/THF solution over a period of 1 h and then the resulting solution was stirred for 3 h at room temperature. Flask-to-flask vacuum distillation at room temperature was used to remove most of the THF. The color changed from colorless to orange/yellow. When a thick, viscous material was present, it was dynamically evacuated for an additional 2 h until a thick paste remained. Then approximately 75 mL of benzene was added by vacuum distillation to the resulting mixture of $In(C_5H_5)_3$·THF, LiCl, and excess $Li(C_5H_5)$. The resulting solution of $In(C_5H_5)_3$·THF was separated from the insoluble material by filtration. The benzene and the remaining THF were removed by flask-to-flask vacuum distillation and then by dynamic evacuation for ~4 h. Finally, approximately 75 mL of pentane was added to the product and the resulting suspension was stirred for 2 h. The pentane was removed rapidly by vacuum distillation to produce a dry powder that was dynamically evacuated for an additional 4 h. The final product $In(C_5H_5)_3$ was a bright yellow powder that weighed 2.36 g (7.61 mmol, 77.6% yield based on $InCl_3$). **$In(C_5H_5)_3$:** Mp: color change from bright yellow to orange at ~160−164 °C dec. ^1H NMR (THF-d_8): δ 5.90 (s, C_5H_5). ^{13}C NMR (THF-d_8) δ 111.09 (s, C_5H_5). Anal. Calcd for $C_{15}H_{15}In$: C, 58.10; H, 4.88; In, 37.03. Found: C, 58.06; H, 4.87; In, 36.96. Solubility: soluble in THF; no appreciable solubility in Et_2O, C_6H_6, C_5H_{12}, or $CHCl_3$.

Thermal Decomposition of $In(C_5H_5)_3$. An evacuated break-seal tube that contained 0.803 g (2.59 mmol) of $In(C_5H_5)_3$ was placed halfway into a 150 °C oven. After ~1 min of heating pale yellow crystals began to collect at the cool end of the tube and a brown solid was observed in the bottom of the tube. A total of 15 min of heating was used to completely decompose the sample. The tube was opened and the volatile, condensable material was transferred to an NMR tube and identified as C_5H_6. The pale, yellow crystalline solid was identified as $In(C_5H_5)$ (0.379 g, 2.11 mmol, 81.3% yield based on $In(C_5H_5)_3$). The unidentified brown residue that was insoluble in common organic solvents weighed 0.392 g. **Pale yellow crystals:** $In(C_5H_5)$. Mp 168.6−169.7 °C dec (lit.[9] mp 169.3−171 °C dec). ^1H NMR (THF-d_8): δ 5.99 (s, C_5H_5). **Volatile liquid (C_5H_6 and $C_{10}H_{12}$):** ^1H NMR (C_6D_6): δ 6.49 (m, 27.99 H, C_5H_6), 6.29 (m, 29.37 H, C_5H_6), 5.93 (m, 1.01 H, C_5H_6), 5.48 (m, 0.97 H, C_5H_6), 3.57 (m, 0.73 H, $C_{10}H_{12}$), 3.12 (m, 0.82 H, $C_{10}H_{12}$), 2.70 (m, 34.27 H, $C_{10}H_{12}$), 2.59 (m, 1.02 H, $C_{10}H_{12}$), 2.11 (m, 1.06 H, $C_{10}H_{12}$), 1.58 (m, 1.76 H, $C_{10}H_{12}$), 1.18 (s, 0.57 H, $C_{10}H_{12}$), 1.16 (s, 0.43 H, $C_{10}H_{12}$).

Reaction of $In(C_5H_5)_3$ with $In(C_5H_5)$. A sidearm dumper was charged with 0.15 g (0.48 mmol) of $In(C_5H_5)_3$ and connected to a reaction vessel charged with 0.086 g (0.48 mmol) of $In(C_5H_5)$ and a magnetic stir bar. Solvent (1 mL of THF-d_8) was added by vacuum distillation, the reactants were mixed, and the resulting solution was poured into the NMR tube. The NMR tube was flame-sealed and maintained at −196 °C until the ^1H NMR spectrum was recorded. Solvent (THF-d_8) was vacuum distilled into a second NMR tube that contained 0.126 g (0.700 mmol) of $In(C_5H_5)$. This NMR tube was flame-sealed and maintained at −196 °C until the ^1H NMR spectrum was recorded. **$In(C_5H_5)_3$ and $In(C_5H_5)$:** ^1H NMR (THF-d_8): initial spectrum, 20 min after warming, pale yellow solution, δ 5.940 (s, C_5H_5), 4 months after solution preparation, pale yellow solution, δ 5.934 (s, C_5H_5). ^{13}C NMR (THF-d_8): 4 months after solution preparation, δ 108.07 (s, C_5H_5). **$In(C_5H_5)$:** ^1H NMR (THF-d_8): initial spectrum, 10 min after warming, brown solution, δ 5.985 (s, C_5H_5), C_5H_6 negligible; 20 h after warming, black precipitate, δ 6.500 (m, C_5H_6, 0.21 H), 6.407 (m, C_5H_6, 0.23 H), 5.986 (s, C_5H_5, 5.00 H), 2.935 (s, C_5H_6, 0.35 H); 72 h after warming, black precipitate, δ 6.503 (m, C_5H_6, 0.20 H), 6.403 (m, C_5H_6, 0.23 H), 5.986 (s, C_5H_6, 5.00 H), 2.934 (s, C_5H_6, 0.37 H); 4 months after solution preparation, black precipitate, δ 6.503 (m, C_5H_6, 0.20 H), 6.404 (m, C_5H_6, 0.23 H), 5.985 (s, C_5H_5, 5.00 H), 2.932 (s, C_5H_6, 0.41 H). ^{13}C NMR (THF-d_8) 4 months after solution preparation, δ 106.82 (s, C_5H_5).

Studies of Lewis Acidity of $In(C_5H_5)_3$. (a) NMe_3. A flask was charged with 0.052 g (0.017 mmol) of $In(C_5H_5)_3$, 0.020 g (0.085 mmol) of NMe_3, and 5 mL of C_6H_6. The resulting cloudy yellow suspension was maintained at room temperature for 2 h. The material, volatile at room temperature, was removed by trap-to-trap vacuum distillation to leave a cream-colored product. Finally, the flask was dynamically evacuated for an additional 24 h and the product turned yellow. The final product weighed 0.050 g. Thus, the $In(C_5H_5)_3$ retained only a very small amount of NMe_3. Mp: 121 °C (sample began to turn tan), 136 °C (sample turned brown), 141 °C (apparent melting). Crystals of $In(C_5H_5)$ were observed in the cooler part of the melting point capillary at the conclusion of the melting point experiment. ^1H NMR (THF-d_8): δ 5.85 (s, C_5H_5, 15.0 H), 1.12 (s, NCH_3, 1.8 H). **(b) PPh_3.** A flask was charged with 0.805 g (2.59 mmol) of $In(C_5H_5)_3$ and 0.525 g (2.00 mmol) of PPh_3 and approximately 10 mL of C_6H_6. The resulting bright-yellow suspension in C_6H_6 was stirred for 1 h and filtered through a medium porosity frit. The benzene was removed by vacuum distillation and replaced with 10 mL of C_5H_{12}. Washing of the product with cold pentane provided 1.02 g (1.79 mmol, 89.5% yield based on PPh_3) of $In(C_5H_5)_3$·PPh_3 as pale yellow crystals. **$In(C_5H_5)_3$·PPh_3:** Mp 159 °C (sample began to turn orange), 169 °C (sample suddenly melted and became orange red), 180 °C (sample turned brown). Crystals of $In(C_5H_5)$ were observed in the cooler part of the melting point capillary at the conclusion of the melting point experiment. Anal. Calcd for $C_{33}H_{30}InP$: C, 69.25; H, 5.28. Found: C, 68.83; H, 5.24. Solubility: soluble in THF and C_6H_6; no appreciable solubility in pentane. ^1H NMR (THF-d_8): δ 5.95 (s, C_5H_5, 15H), 7.30 (br m, PPh, 15H). ^1H NMR (C_6D_6): δ 6.20 (s, C_5H_5, 15H), 7.00 (m, PPh), 7.43 (m, PPh). $^{31}P\{^1H\}$ NMR (THF-d_8): δ −3.08 (s). $^{31}P\{^1H\}$ NMR (C_6D_6) δ 5.95 (s). Cryoscopic molecular weight, benzene solution, formula weight 572 (observed molality, observed molecular weight, association): 0.0688, 582, 1.02; 0.0406, 588, 1.03; 0.0274, 584, 1.02.

Synthesis of $Me_2In(C_5H_5)$ by a Ligand Redistribution Reaction. A THF solution of 0.655 g (4.10 mmol) of $InMe_3$ was allowed to react with 0.636 g (2.05 mmol) of $In(C_5H_5)_3$ at room temperature for 1 h. After the THF was removed by vacuum distillation, the flask was dynamically evacuated for an additional 3 h. The resulting colorless solid was sublimed at 100−110 °C to produce 1.19 g (5.67 mmol, 92.2% yield) of $Me_2In(C_5H_5)$. **$Me_2In(C_5H_5)$:** Colorless solid. Mp 190−196 °C dec (color change to dark brown) (lit.[15] mp 195−200 °C dec). Solubility: soluble in THF; no appreciable solubility in Et_2O, C_6H_6, or C_5H_{12}. ^1H NMR (THF-d_8): δ 6.04 (s, C_5H_5, 5.00H), −0.52 (s, $Me_2In(C_5H_5)$·THF and $InMe_3)$·THF, 5.78H), −1.10 (s, $MeIn(C_5H_5)_2$·THF, 0.22 H) (lit. ^1H NMR (d_8-THF): δ 6.05 (s, C_5H_5, 2.19H), 0.11 (s, $InMe_3)$·THF, 0.48H), −0.52 (s, $Me_2In(C_5H_5)$·THF, 6.0H), −1.11 (s, $MeIn(C_5H_5)_2)$·THF, 0.11H).

Synthesis of $(Me_3CCH_2)_2In(C_5H_5)$ by a Ligand Redistribution Reaction. A THF solution of 1.42 g (4.33 mmol) of freshly sublimed $In(CH_2CMe_3)_3$ was allowed to react with 0.672 g (2.17 mmol) of $In(C_5H_5)_3$ dissolved in THF. After the THF was removed by vacuum distillation, the product was sublimed at 100−110 °C to produce 1.923 g (5.97 mmol, 91.7% yield) of $(Me_3CCH_2)_2In(C_5H_5)$. **$(Me_3CCH_2)_2In(C_5H_5)$:** Colorless solid. Mp 188−190 °C dec (color change to brown). Anal. Calcd for $C_{15}H_{27}In$: C, 55.92; H, 8.45. Found: C, 55.91; H, 8.33. Solubility: soluble in THF; no appreciable solubility in Et_2O, C_6H_6, or C_5H_{12}. ^1H NMR (THF-d_8): δ 6.07 (s, C_5H_5, 4.78H), 0.99 (s, $(Me_3CCH_2)_2In(C_5H_5)$, 15.81H), 0.61 (s, $(Me_3CCH_2)_2In(C_5H_5)$, 3.76H), 0.82 (s, $(Me_3CCH_2)In(C_5H_5)_2$, 0.47H), 0.49 (s, $(Me_3CCH_2)In(C_5H_5)_2$, 0.01H), 1.11 (s, $(Me_3CCH_2)_3In$, 1.83H), 0.81 (s, $(Me_3CCH_2)_3In$, 0.35H).

Table 4. Data for X-ray Crystallographic Studies of $[In(C_5H_5)_3]_n$, $(C_5H_5)_3In{\cdot}PPh_3$, and $[(Me_3CCH_2)_2In(C_5H_5)]_n$

	$[In(C_5H_5)_3]_n$	$(C_5H_5)_3In{\cdot}PPh_3$	$[(Me_3CCH_2)_2In(C_5H_5)]_n$
molec. formula	$C_{15}H_{15}In$	$C_{33}H_{30}InP$	$C_{15}H_{27}In$
M_r	310.09	572.36	322.19
cryst shape	yellow plate	yellow brick	colorless brick
cryst syst	orthorhombic	monoclinic	monoclinic
space group	*Pbca*	$P2_1/n$	$P2_1$
a, Å	9.8029(3)	11.0573(2)	9.7386(1)
b, Å	9.5808(3)	15.3171(3)	14.9887(2)
c, Å	24.6957(7)	16.8052(3)	20.7791(3)
α, deg	90	90	90
β, deg	90	108.559(1)	90.0068(4)
γ, deg	90	90	90
V, Å^3	2319.4(1)	2698.21(9)	3033.10(7)
D_{calcd}, g/cm^3	1.776	1.409	1.411
Z	8	4	4
μ(Mo Kα), mm^{-1}	2.005	0.954	1.535
T (K)	90(1)	90.0(1)	90.0(1)
max. 2θ, deg	50.0	60.0	58.5
absorp. corr. meth.	SADABS[19]	SADABS[19]	SADABS[19]
reflns measd	21659	48046	32340
unique reflns (R_{int})	2039(0.067)	7876 (0.059)	14405 (0.047)
reflns $I > 4\sigma(I)$	1526	6571	13854
refined parameters	190	406	629
R [$I > 2\sigma(I)$]	0.028	0.028	0.026
wR_2	0.065	0.065	0.061
goodness-of-fit	1.028	1.204	1.013
extinction coeff.	None	None	0.0068(1)

Synthesis of $MeIn(C_5H_5)_2$ by a Ligand Redistribution Reaction with Excess $In(C_5H_5)_3$. The same procedure as described for the preparation of $Me_2In(C_5H_5)$ was used to prepare $MeIn(C_5H_5)_2$. Reagents: 0.164 g (1.02 mmol) of freshly sublimed $InMe_3$, 0.953 g (3.07 mmol) of $In(C_5H_5)_3$, and 10 mL of THF. The resulting yellow solid was sublimed at 110−120 °C to produce 0.649 g (2.497 mmol, 81.6% yield based on $InMe_3$) of $MeIn(C_5H_5)_2$. **$MeIn(C_5H_5)_2$:** Yellow solid. Mp 150.7−160.2 °C dec (gradual change from yellow to viscous brown liquid). Anal. Calcd for $C_{11}H_{13}In$: C, 50.81; H, 5.04; In, 44.15. Found: C, 50.57; H, 5.32; In, 44.03. Solubility: soluble in THF; no appreciable solubility in Et_2O, C_6H_6, or C_5H_{12}. Attempts to grow crystallographic quality crystals by slow sublimation at 130−140 °C produced severely twinned crystals that were not useful. ^1H NMR (THF-d_8): δ 5.98 (s, C_5H_5, 10.7H), −0.37 (s, $Me_2In(C_5H_5)$, 0.23H), −1.09 (s, $MeIn(C_5H_5)_2$, 2.06H).

Synthesis of $(Me_3CCH_2)In(C_5H_5)_2$ by a Ligand Redistribution Reaction with Excess $In(C_5H_5)_3$. The same procedure as described for the preparation of $Me_2In(C_5H_5)$ was used to prepare $(Me_3CCH_2)In(C_5H_5)_2$. Reagents: 0.282 g (0.859 mmol) of freshly sublimed $In(CH_2CMe_3)_3$, 0.799 g (2.58 mmol) of $In(C_5H_5)_3$, and 10 mL of THF. The resulting yellow solid was heated at 90−95 °C to isolate the product by sublimation. A small amount of a colorless solid identified as $(Me_3CCH_2)_2In(C_5H_5)$ that sublimed initially was removed. Then the sample was reheated and 0.766 g (2.42 mmol, 94% yield based on $In(CH_2CMe_3)_3$) of $(Me_3CCH_2)In(C_5H_5)_2$ as a yellow solid was isolated from the coldfinger of the sublimator. **$(Me_3CCH_2)In(C_5H_5)_2$:** Yellow solid. Mp 126.4−126.9 °C dec (gradual change from yellow to viscous brown liquid). Anal. Calcd for $C_{15}H_{21}In$: C, 56.99; H, 6.70. Found: C, 56.86; H, 6.69. Solubility: soluble in THF; no appreciable solubility in Et_2O, C_6H_6, or C_5H_{12}. ^1H NMR (THF-d_8): δ 6.03 (s, C_5H_5, 10.14H), 0.99 (s, $(Me_3CCH_2)_2In(C_5H_5)$, 0.91H), 0.61 (s, $(Me_3CCH_2)_2In(C_5H_5)$, 0.19H), 0.83 (s, $(Me_3CCH_2)In(C_5H_5)_2$, 7.87H), 0.37 (s, $(Me_3CCH_2)In(C_5H_5)_2$, 1.77H), 1.10 (s, $(Me_3CCH_2)_3In$, 0.11H).

Thermal Decomposition of $(Me_3CCH_2)In(C_5H_5)_2$. A break-seal tube that contained 0.972 g (3.07 mmol) of $(Me_3CCH_2)In(C_5H_5)_2$ was evacuated and flame sealed. The tube was placed halfway into a 150 °C oven. Immediately, the $(Me_3CCH_2)In(C_5H_5)_2$ began to melt and pale yellow crystals collected at the coolest end of the tube while colorless needles formed on the walls of the tube immediately above the oven. After the tube was heated for 15 min, a trace of a brown residue was observed at the bottom of the tube. The tube was opened and the condensable gases transferred to an NMR tube. The yellow crystalline solid was collected in the drybox and identified as $In(C_5H_5)$ (0.211 g, 1.17 mmol, 76% yield based on eqs 5 and 6) by its physical properties and ^1H NMR spectrum. The colorless needles were identified as $(Me_3CCH_2)_2In(C_5H_5)$ (0.452 g, 1.40 mmol, 91% based on eqs 5 and 6). **Pale yellow crystals:** $In(C_5H_5)$. Mp 169.8−170.4 °C dec. ^1H NMR (THF-d_8): δ 5.99 (s, C_5H_5). **Colorless needles:** $(Me_3CCH_2)_2In(C_5H_5)$. Mp 188.2−191.4 °C dec. ^1H NMR (THF-d_8): δ 6.08 (s, C_5H_5, 4.89H), 0.99 (s, $(Me_3CCH_2)_2In(C_5H_5)$, 15.75H), 0.61 (s, $(Me_3CCH_2)_2In(C_5H_5)$, 3.74H), 0.82 (s, $(Me_3CCH_2)In(C_5H_5)_2$, 0.51H), 0.49 (s, $(Me_3CCH_2)In(C_5H_5)_2$, 0.01H), 1.11 (s, $(Me_3CCH_2)_3In$, 1.79H), 0.82 (s, $(Me_3CCH_2)_3In$, 0.31H). **Volatile liquid:** C_5H_6 and CMe_4. ^1H NMR (C_6D_6): δ 6.48 (m, C_5H_6, 15.13 H), 6.29 (m, C_5H_6, 16.25 H), 3.58 (m, C_5H_6, 1.22 H), 2.68 (m, $C_{10}H_{12}$, 27.78 H), 1.41 (m, $C_{10}H_{12}$, 1.28 H), 1.24 (m, $C_{10}H_{12}$, 1.20 H), 0.91 (s, CMe_4, 12 H), 0.86 (m, $C_{10}H_{12}$, 1.35 H), 0.39 (s, 0.38 H).

Collection of X-ray Diffraction Data and Structural Solutions for $[In(C_5H_5)_3]_n$, $In(C_5H_5)_3{\cdot}PPh_3$, and $[(Me_3CCH_2)_2In(C_5H_5)]_n$: General Features. Well-defined crystals of the title compounds were 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 the rotating anode (Mo Kα radiation, λ = 0.71073 Å). X-ray diffraction data were collected at 90 K. Details for all compounds are provided in Table 4. Data collection for each compound involved four sets of frames (600 frames in each set) and covered half-reciprocal space using the ω-scans technique (0.3° frame width) with different φ angles. Reflection intensities were integrated by using the SAINTPLUS program.[19] The solution and refinement of the structures were performed by use of the SHELXTL program package.[20] The structures were refined by full-matrix least squares against F^2. Non-hydrogen atoms were refined in anisotropic approximation. The hydrogen atoms were located

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(19) *SMART* and *SAINTPLUS*, Area detector control and integration software, Ver. 6.0 1; Bruker Analytical X-ray Systems: Madison, WI, 1999.

(20) *SHELXTL*, Ver. 5.10; An integration system for solving, refining, and displaying crystal structures from diffraction data; Bruker Analytical X-ray Systems: Madison, WI, 1997.

from difference electron density Fourier syntheses and refined in isotropic approximation for $[In(C_5H_5)_3]_n$, with $U_{iso} = 1.2U_{eq}$ of the preceding carbon atom for $In(C_5H_5)_3{\cdot}PPh_3$, or as idealized CH_3 groups with $U_{iso} = 1.5U_{eq}$ and by using the riding model with $U_{iso} = 1.2U_{eq}$ of the preceding carbon atom for $[(Me_3CCH_2)_2In(C_5H_5)]_n$. Data were corrected for absorption by using the Bruker AXS SADABS program that is a part of the SAINTPLUS package.[19]

The structure of $(Me_3CCH_2)_2In(C_5H_5)$ provides an example of twinning by *pseudo*-merohedry,[21,22] which occurs when the metric symmetry is higher than the symmetry of the structure. The structure appeared to be orthorhombic with all angles in the unit cell of exactly 90°. Although the $|E^2 - 1|$ value of 0.867 was close to that for the centrosymmetric space group, the systematic absences only for three mutually orthogonal 2_1 screw axes were found giving only one acceptable space group $P2_12_12_1$ and indicating the presence of both racemic twinning and general twinning in the structure. The structure could then be solved in the monoclinic space group $P2_1$, which requires the transformation of the unit cell. The R_{int} value for the orthorhombic space group was 0.083, significant but just slightly higher than that for the monoclinic space group (0.047). The structure was solved by the Patterson method, which gave the positions of the indium atoms. Structural refinement was completed by using the twining law (1 0 0; 0 −1 0; 0 0 −1) for the generation of the unequal components, which were doubled to satisfy the racemic twining. The three scale factors for twin components were refined to values 0.20385, 0.35935, and 0.16834.

Supporting Information Available: Experimental details for the attempted synthesis of $In(C_5H_5)_3$ by the literature[8] method; variable-temperature NMR spectral data for heteroleptic organoindium cyclopentadienide compounds; solubility and stability of $In(C_5H_5)_3$ in benzene; and complete tables of positional parameters, interatomic distances and angles, anisotropic thermal parameters, and positions for hydrogen atoms and packing diagrams for the three compounds studied. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0202322

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(22) Herbst-Irmer, R.; Sheldrick, G. M. *Acta Crystallogr.* **1998**, *B54*, 443.