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Cyclopentadiene Elimination Reactions for the Preparation of Organoindium(III) Derivatives. Crystal and Molecular Structures of $Me_2In(acac)$, $(Me_3CCH_2)_2In(acac)$, $(Me)(Me_3CCH_2)In(acac)$, and $[Me_2InNH(t\text{-}Bu)]_2$

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The compounds $R_2InO(t\text{-}Bu)$, $R_2In(acac)$, $R_2InSSiPh_3$, and R_2InPPh_2 ($R = Me$, CH_2CMe_3) and $Me_2InNH(t\text{-}Bu)$ have been prepared in nearly quantitative yields by the cyclopentadiene elimination reaction between $R_2In(C_5H_5)$ and the appropriate alcohol, thiol, phosphine or amine. All reactions except those of $H_2N(t\text{-}Bu)$ occur readily at room temperature. Even though solutions of $R_2In(C_5H_5)$ exist as equilibrium mixtures of $R_2In(C_5H_5)$, $RIn(C_5H_5)_2$, $In(C_5H_5)_3$, and InR_3, neither methane nor neopentane was observed as a product from the above reaction mixtures. A ligand redistribution reaction between $Me_2In(C_5H_5)$ and $(Me_3CCH_2)_2In(C_5H_5)$ was used to prepare $(Me)(Me_3CCH_2)In(C_5H_5)$ that, in turn, was reacted with H(acac) to form $(Me)(Me_3CCH_2)In(acac)$, an indium compound with three different substituents. The compounds $Me_2In(acac)$, $(Me_3CCH_2)_2In(acac)$, and $(Me)(Me_3CCH_2)In(acac)$ exist as centrosymmetric dimers in the solid state, but in benzene solution $Me_2In(acac)$ is a monomer−dimer equilibrium mixture, whereas $(Me_3CCH_2)_2In(acac)$ is a monomer. The thiolate $Me_2InSSiPh_3$ is an equilibrium mixture of dimers and trimers in benzene solution, but $(Me_3CCH_2)_2InSSiPh_3$ is a dimer. The phosphide Me_2InPPh_2 is an equilibrium mixture of monomers and dimers when dissolved in benzene. The *tert*-butylamide $Me_2InNH(t\text{-}Bu)$, when dissolved in benzene, is a mixture of monomers and dimers with both cis and trans configurations, but only a dimer with the trans configuration exists in the solid state.

Introduction

Even though solutions of R_2GaCp ($R = Me$,[1,2] Et,[3] CH_2CMe_3;[4] $Cp = C_5H_5$, C_5H_4Me, $C_5H_4SiMe_3$) exist as equilibrium mixtures of R_2GaCp, $RGaCp_2$, GaR_3, and $GaCp_3$, reactions with HXR′ (X = O, S; R′ = organic groups)[5−7] and HYR'_2 (Y = N, P; R′ = organic groups, H)[5−7] produce organogallium derivatives with the simplest formulas R_2GaXR' and $R_2GaYR'_2$ and the cyclopentadiene exclusively (eq 1). No methane, ethane, or

$$R_2Ga(C_5H_5) + HYR'_2 \xrightarrow{\text{solvent}} {}^1/_2[R_2GaYR'_2]_2 + C_5H_6 \quad (1)$$

neopentane is formed. These cyclopentadiene elimination reactions typically occur at or below room temperature and produce gallium-containing products in nearly quantitative yields and in excellent purity. Since organoindium cyclopentadienide derivatives exist as equilibrium mixtures of compounds such as the gallium derivatives but InR_3 is more reactive than GaR_3 ($R = Me$, CH_2CMe_3) to protonic reagents,[8] we wanted to learn more about the corresponding cyclopentadiene elimination reaction in organoindium chemistry. Thus, the reactions of $Me_2In(C_5H_5)$[9] and $(Me_3CCH_2)_2In(C_5H_5)$[9a] with *tert*-butyl alcohol, acetylacetone (2,4-pentanedione), triphenylsilanethiol, diphenylphosphine, and *tert*-butylamine, a series of bases with protons of varying acidities, were investigated.

Results and Discussion

The cyclopentadiene elimination reaction is exceedingly useful for the preparation of organoindium(III) derivatives of oxygen-, sulfur-, nitrogen-, and phosphorus-containing substituents. Products of the types R_2InXR' and $R_2InYR'_2$ ($R = Me$, CH_2CMe_3; X = O, S; Y = N, P) were formed in nearly quantitative yields and in excellent purity. All reactions except those of the amine occurred at room temperature or below. No reaction between $Me_2In(C_5H_5)$ and $H_2N(t\text{-}Bu)$ was observed at

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room temperature. Even though $R_2In(C_5H_5)$ incorporates two different organic ligands, only cyclopentadiene (C_5H_6) is formed. The thermodynamically more stable compound, CH_4 or CMe_4, is not a product of the reaction. Thus, the course of the cyclopentadiene elimination reaction must be controlled by kinetic rather than thermodynamic factors.

The cyclopentadiene elimination reaction between $Me_2In(C_5H_5)$ and t-BuOH in a 1:1 mole ratio at room temperature provided $[Me_2InO(t\text{-}Bu)]_2$ in nearly quantitative yield. No methane was evolved during this reaction, even though an ether solution of $InMe_3{\cdot}Et_2O$ reacts readily with t-BuOH at 25−35 °C.[10] The indium-containing product was initially isolated as a colorless waxy solid after sublimation at 35 °C. However, when $Me_2InO(t\text{-}Bu)$ was allowed to stand under vacuum at room temperature for 4−5 days, the compound changed from an opaque colorless film to individual crystals that rotated the plane of polarized light. However, a single crystal suitable for an X-ray structural study could not be isolated. The crystals deformed during contact and became waxy again. Cryoscopic molecular studies in benzene solution indicated that $Me_2InO(t\text{-}Bu)$ is dimeric over the concentration range of 0.03−0.09 *m*. The ^1H NMR spectrum in d_6-benzene exhibited two sharp resonances.

The new compound $[(Me_3CCH_2)_2InO(t\text{-}Bu)]_2$ was synthesized from $(Me_3CCH_2)_2In(C_5H_5)$ and t-BuOH at room temperature in high yield. Neopentane was not observed. The compound was dimeric in benzene solution according to cryoscopic molecular studies in the concentration range of 0.02−0.05 *m*. A molecular weight determination was also attempted at the higher concentration of 0.078 *m*, but crystals formed as the solution was cooled. Thus, $[(Me_3CCH_2)_2InO(t\text{-}Bu)]_2$ has limited solubility in benzene and trace solubility in pentane but is readily soluble in Et_2O and THF. The ^1H NMR spectrum in d_6-benzene exhibited three sharp singlets.

The derivative $Me_2In(acac)$ was prepared by methane elimination between $InMe_3$ and Hacac in the absence of solvent, as had been done previously.[11] The analytically pure compound was isolated as colorless crystals, but its melting point (136.9−137.8 °C with decomposition at ~200 °C) was different from that reported in the literature[11] (118 °C dec). Cryoscopic molecular weight studies in benzene solution suggest that the compound exists as an equilibrium mixture of species, because the degree of association decreased from 1.23 to 1.09 as the solution was diluted from 0.068 to 0.010 *m*. Thus, dimethylindium acaetylacetonate is very different from $Me_2Ga(acac)$,[12a] $Et_2Ga(acac)$,[12a] $(mesityl)_2Ga(acac)$,[12a] $R_2Ga(bdk)$[12a] (R = Me, Et, mesityl; bdk = tfac, hfac, tmhd), and other gallium(III) β-diketonate derivatives.[12b] All of these gallium compounds are monomeric in the solid state and in benzene solution. ^1H NMR spectra of $Me_2In(acac)$ in both d_6-benzene and d_8-THF solutions exhibited only sharp single resonances whose chemical shifts were independent of concentration in the range studied.

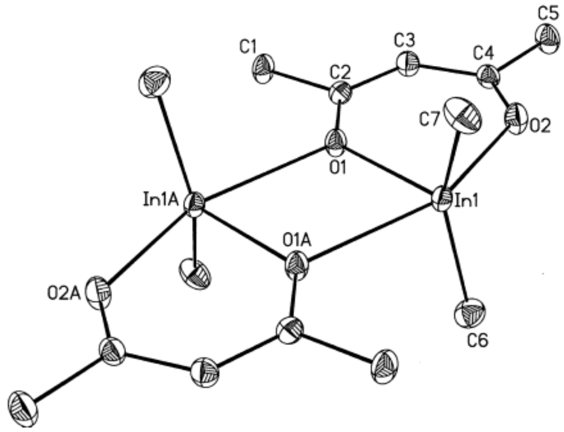

Figure 1. Molecular geometry and labeling of atoms for $Me_2In(acac)$ (50% probability ellipsoids for non-hydrogen atoms; hydrogen atoms are omitted for clarity).

Table 1. Selected Bond Distances (Å) and Angles (deg) for $Me_2In(acac)$[a]

Bond Distances

In(1)−C(6)	2.129(2)	In(1)−C(7)	2.131(2)
In(1)−O(1)	2.198(1)	In(1)−O(1)	2.198(1)
In(1)−O(2)	2.256(1)	In(1)−O(1A)	2.551(1)
O(1)−C(2)	1.298(2)	O(1)−In(1A)	2.551(1)
O(2)−C(4)	1.258(2)	C(1)−C(2)	1.505(2)
C(2)−C(3)	1.381(2)	C(3)−C(4)	1.416(2)
C(4)−C(5)	1.505(2)		

Bond Angles

C(6)−In(1)−C(7)	145.81(9)	C(6)−In(1)−O(1)	107.22(6)
C(7)−In(1)−O(1)	105.67(7)	C(6)−In(1)−O(2)	95.64(6)
C(7)−In(1)−O(2)	97.41(6)	O(1)−In(1)−O(2)	82.87(5)
C(6)−In(1)−O(1A)	90.62(6)	C(7)−In(1)−O(1A)	90.97(6)
O(1)−In(1)−O(1A)	71.70(4)	O(2)−In(1)−O(1A)	154.52(4)
C(2)−O(1)−In(1)	128.7(1)	C(2)−O(1)−In(1A)	123.0(1)
In(1)−O(1)−In(1A)	108.30(4)	C(4)−O(2)−In(1)	128.7(1)
O(1)−C(2)−C(3)	126.5(2)	O(1)−C(2)−C(1)	115.2(1)
C(3)−C(2)−C(1)	118.3(2)	C(2)−C(3)−C(4)	127.6(2)
O(2)−C(4)−C(3)	125.6(2)	O(2)−C(4)−C(5)	116.8(2)
C(3)−C(4)−C(5)	117.6(2)		

[a] Symmetry transformations used to generate equivalent atoms: −*x*, 1 − *y*, 1 − *z*.

An X-ray structural study of $Me_2In(acac)$ revealed the compound to be a centrosymmetric dimer in the solid state (Figure 1) with an inversion center interrelating In(1) and In(1A). Bond distances and angles are collected in Table 1. Each indium center is five-coordinate with a distorted pseudo-trigonal-bipyramidal geometry. The equatorial plane is defined by C(6), C(7), and O(1), while O(2) and O(1A) occupy axial positions. The corresponding bond angles O(2)−In(1)−O(1A), C(6)−In(1)−C(7), and O(1)−In(1)−C(6) are 154.52(4), 145.81(9), and 107.22(6)°, respectively.

One of the acetylacetonate oxygen atoms bridges two indium atoms in an asymmetric manner. The In(1)−O(1) bond length of 2.198(1) Å is considerably shorter than the In(1)−O(1A) length of 2.551(1) Å. The In(1)−O(2) bond is 2.256(1) Å, a distance which is in agreement with it being in a pseudo-axial position. The In−O distances in $In(acac)_3$ that involve six-coordinate indium range from 2.118(5) to 2.138(4) Å.[13] The bridging oxygen O(1) in $Me_2In(acac)$ has a trigonal-planar configuration in which the sum of the bond angles around it is 360.0-

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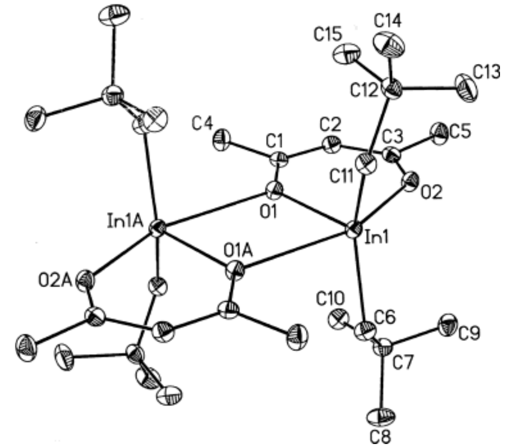

Figure 2. Molecular geometry and labeling of atoms for $(Me_3CCH_2)_2In(acac)$ (50% probability ellipsoids for nonhydrogen atoms; hydrogen atoms are omitted for clarity).

Table 2. Selected Bond Distances (Å) and Angles (deg) for $(Me_3CCH_2)_2In(acac)$[a]

Bond Distances			
In(1)−C(6)	2.169(2)	In(1)−C(11)	2.169(2)
In(1)−O(1)	2.195(1)	In(1)−O(2)	2.203(1)
O(1)−C(1)	1.288(2)	O(2)−C(3)	1.263(2)
C(1)−C(2)	1.395(3)	C(1)−C(4)	1.498(3)
C(2)−C(3)	1.403(3)	C(3)−C(5)	1.506(3)
C(6)−C(7)	1.539(3)	C(7)−C(10)	1.520(3)
C(7)−C(9)	1.531(3)	C(7)−C(8)	1.532(3)
C(11)−C(12)	1.535(3)	C(12)−C(15)	1.522(3)
C(12)−C(13)	1.529(3)	C(12)−C(14)	1.536(3)

Bond Angles			
C(6)−In(1)−C(11)	137.12(8)	C(6)−In(1)−O(1)	109.23(7)
C(11)−In(1)−O(1)	106.42(7)	C(6)−In(1)−O(2)	103.36(7)
C(11)−In(1)−O(2)	103.53(7)	O(1)−In(1)−O(2)	83.63(5)
C(1)−O(1)−In(1)	127.9(1)	C(3)−O(2)−In(1)	129.1(1)
O(1)−C(1)−C(2)	126.4(2)	O(1)−C(1)−C(4)	115.8(2)
C(2)−C(1)−C(4)	117.8(2)	C(1)−C(2)−C(3)	127.1(2)
O(2)−C(3)−C(2)	125.6(2)	O(2)−C(3)−C(5)	115.5(2)
C(2)−C(3)−C(5)	118.9(2)	C(7)−C(6)−In(1)	121.4(1)
C(10)−C(7)−C(9)	109.7(2)	C(10)−C(7)−C(8)	108.5(2)
C(9)−C(7)−C(8)	108.5(2)	C(10)−C(7)−C(6)	111.0(2)
C(9)−C(7)−C(6)	110.7(2)	C(8)−C(7)−C(6)	108.4(2)
C(12)−C(11)−In(1)	121.2(1)	C(15)−C(12)−C(13)	110.1(2)
C(15)−C(12)−C(11)	111.1(2)	C(13)−C(12)−C(11)	110.3(2)
C(15)−C(12)−C(14)	108.4(2)	C(13)−C(12)−C(14)	108.4(2)
C(11)−C(12)−C(14)	108.5(2)		

[a] Symmetry transformations used to generate equivalent atoms: 1 − *x*, 1 − *y*, 1 − *z*.

(2)°; thus, it can be considered sp^2-hybridized. The acetylacetonate ligand is planar, but the π-system is not completely delocalized. The bond distance O(1)−C(2) (1.298(2) Å) is significantly longer than the bond distance for O(2)−C(4) (1.258(2) Å). Thus, the C−O bond (1.298(2) Å) between the bridging oxygen atom and the indium atom has a lower bond order than the C−O bond (1.258(2) Å) between the indium and the nonbridging oxygen.

Cyclopentadiene elimination reactions were used to prepare $(Me_3CCH_2)_2In(acac)$ and $Me_2In(acac)$. Neither neopentane nor methane was formed, even though $InMe_3$ and $In(CH_2CMe_3)_3$ have been observed to react readily with H(acac) at room temperature. Experimental observations indicate that the cyclopentadiene elimination reaction between $Me_2In(C_5H_5)$ and Hacac is faster than the methane elimination reaction between $InMe_3$ and Hacac. Several properties of $(Me_3CCH_2)_2In(acac)$ are very different from those of $Me_2In(acac)$. The neopentyl derivative melted at a lower temperature and was monomeric in benzene solution in the concentration range of 0.04−0.08 *m* according to cryoscopic molecular studies. However, an X-ray structural study of $(Me_3CCH_2)_2In(acac)$ indicated that the compound was a centrosymmetric dimer with an inversion center between In(1) and In(1A) and short van der Waals contacts between O(1) and In(1A) (2.759 Å) (Figure 2 and Table 2). The configuration about indium is irregular, due to the acetylacetonate ligand, with the angle O(1)−In(1)−O(2) being 83.63(5)°. The other bond angles about indium are C(6)−In(1)−C(11) at 137.12(8)°, C(6)−In(1)−O(1) at 109.23(7)°, and C(11)−In(1)−O(2) at 103.53(7)°. The short van der Waals contacts result in the inequality of the O(1)−C(1) and O(2)−C(3) bond lengths. The acetylacetonate ligand is planar.

A ligand redistribution reaction between $Me_2In(C_5H_5)$ and $(Me_3CCH_2)_2In(C_5H_5)$ in a 1:1 mole ratio in THF solution was investigated in order to determine whether a compound with three different organic ligands, $(Me)(Me_3CCH_2)In(C_5H_5)$, could be prepared, isolated, and characterized as a pure compound in a specific phase. The product of the redistribution reaction was purified by heating to 90 °C, during which a colorless glass "sublimed" to the coldfinger. Scrapping of the coldfinger produced a hard, dry powder that "melted" sharply at 92.4−94.2 °C. Even though the powder "melted" sharply, many observations suggest that the product is a mixture of possibly $(Me)(Me_3CCH_2)In(C_5H_5)$, $Me_2In(C_5H_5)$, $(Me_3CCH_2)_2In(C_5H_5)$, $InMe_3$, and/or $In(CH_2CMe_3)_3$. First, the isolated product was exceedingly soluble in benzene, pentane, THF, and diethyl ether. All other organoindium(III) cyclopentadienide derivatives are insoluble in diethyl ether, benzene, and pentane but soluble only in a strongly coordinating solvent such as THF.[9] Attempts to recrystallize the product by slow cooling of a pentane solution resulted in the formation of a gelatinous material that became a rigid foam after solvent removal. Likewise, attempted crystal growth by slow sublimation resulted in the formation of an amorphous material that resembled liquid droplets with no evidence of crystallinity, according to observations with a polarizing microscope. ^1H NMR spectra in both d_8-THF and d_6-benzene exhibited more resonances than would be expected for $(Me)(Me_3CCH_2)In(C_5H_5)$, but these observations are consistent with organoindium(III) cyclopentadienide chemistry. Many of the resonances in the d_8-THF solution could be identified with species formed by multiple ligand redistribution reactions.[9] When d_6-benzene was the solvent, the resonances were extremely broad. No specific assignments could be made for these resonances, as no other indium cyclopentadienide derivative has been sufficiently soluble in benzene for characterization by ^1H NMR spectroscopy.[9]

As there was no readily available method to determine the purity or existence of $(Me)(Me_3CCH_2)In(C_5H_5)$ as a single compound in the condensed state, a sample that might be the proposed compound was reacted with acetylacetone in pentane in an attempt to prepare $(Me)(Me_3CCH_2)In(acac)$ by a cyclopentadiene elimination reaction. The chelated acetylacetonate ligand might be expected to hinder ligand redistribution reactions[12] and enable the isolation of $(Me)(Me_3CCH_2)In(acac)$ as a pure

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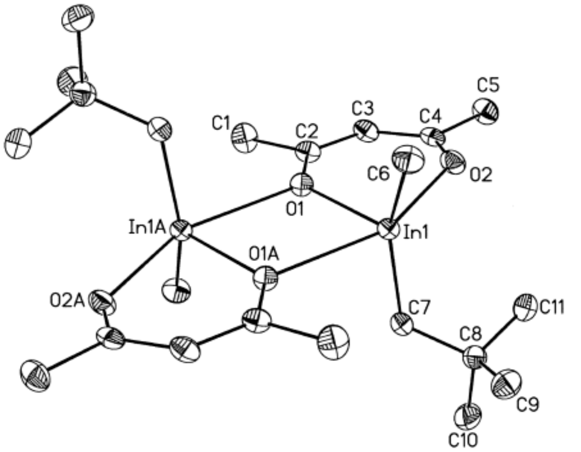

Figure 3. Molecular geometry and labeling of atoms for $(Me)(Me_3CCH_2)In(acac)$ (50% probability ellipsoids for non-hydrogen atoms; hydrogen atoms are omitted for clarity).

Table 3. Selected Bond Distances (Å) and Angles (deg) for $(Me)(Me_3CCH_2)In(acac)^a$

Bond Distances			
In(1)−C(6)	2.141(2)	In(1)−C(7)	2.155(2)
In(1)−O(1)	2.206(2)	In(1)−O(2)	2.262(2)
In(1)−O(1A)	2.569(2)	O(1)−C(2)	1.300(3)
O(1)−In(1A)	2.569(2)	O(2)−C(4)	1.257(3)
C(1)−C(2)	1.509(3)	C(2)−C(3)	1.387(3)
C(3)−C(4)	1.413(3)	C(4)−C(5)	1.511(3)
C(7)−C(8)	1.535(3)	C(8)−C(9)	1.528(3)
C(8)−C(11)	1.535(3)	C(8)−C(10)	1.535(4)
Bond Angles			
C(6)−In(1)−C(7)	150.1(1)	C(6)−In(1)−O(1)	107.38(8)
C(7)−In(1)−O(1)	101.15(8)	C(6)−In(1)−O(2)	93.12(8)
C(7)−In(1)−O(2)	99.36(8)	O(1)−In(1)−O(2)	82.36(6)
C(6)−In(1)−O(1A)	91.57(8)	C(7)−In(1)−O(1A)	88.70(7)
O(1)−In(1)−O(1A)	72.32(6)	O(2)−In(1)−O(1A)	154.49(6)
C(2)−O(1)−In(1)	127.9(1)	C(2)−O(1)−In(1A)	123.8(1)
In(1)−O(1)−In(1A)	107.68(6)	C(4)−O(2)−In(1)	128.4(2)
O(1)−C(2)−C(3)	126.7(2)	O(1)−C(2)−C(1)	115.3(2)
C(3)−C(2)−C(1)	118.0(2)	C(2)−C(3)−C(4)	127.6(2)
O(2)−C(4)−C(3)	125.0(2)	O(2)−C(4)−C(5)	116.9(2)
C(3)−C(4)−C(5)	118.1(2)	C(8)−C(7)−In(1)	120.3(2)
C(9)−C(8)−C(7)	110.2(2)	C(9)−C(8)−C(11)	109.4(2)
C(7)−C(8)−C(11)	110.5(2)	C(9)−C(8)−C(10)	108.8(2)
C(7)−C(8)−C(10)	109.6(2)	C(11)−C(8)−C(10)	108.2(2)

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

solid. An X-ray structural study of a single crystal isolated from the recrystallized bulk product obtained from the cyclopentadiene elimination reaction identified the presence of $(Me)(Me_3CCH_2)In(acac)$ (see the following paragraph). The melting point of the solid was sharp (52.7−53.5 °C), but an elemental analysis suggested the bulk sample was impure, as the percentages of carbon and hydrogen were low. The ^1H NMR spectra of d_6-benzene and d_8-THF solutions of the bulk material indicated the product changed with time. Thus, these data suggest that $(Me)(Me_3CCH_2)In(acac)$, when in solution, undergoes ligand redistribution reactions. It is noteworthy that d_6-benzene solutions of $Me_2In(acac)$ and of $(Me_3CCH_2)_2In(acac)$ alone do not appear to undergo ligand redistribution reactions. However, when $Me_2In(acac)$ and $(Me_3CCH_2)_2In(acac)$ were mixed in a 1:1 mole ratio in d_6-benzene in an NMR tube, resonances for $In(acac)_3$[14] were observed after a few days. In contrast, a mixture of $In(acac)_3$ and $Me_2In(acac)$ did not undergo ligand redistribution at room temperature or after heating at 75 °C for 6 days. Even though no example of a gallium β-diketonate derivative bearing two different organic ligands has been characterized as a pure compound, other derivatives with multiple substituents such as $(Me)(Cl)Ga(acac)$,[12b] $(Et)(Cl)Ga(acac)$,[12b] $(Mes)(Cl)Ga(acac)$,[12b] and $[N(SiMe_3)_2](Cl)Ga(acac)$[12b] exist as single compounds.

The X-ray structural study of the single crystal isolated from the product of the reaction of $(Me)(Me_3CCH_2)In(C_5H_5)$ with acetylacetone revealed $(Me)(Me_3CCH_2)In(acac)$ to be a centrosymmetric dimer with the inversion center located between In(1) and In(1A) (Figure 3 and Table 3). Each indium center is five-coordinate with highly distorted pseudo-trigonal-bipyramidal geometry. The equatorial plane is formed by C(6), C(7), and O(1), while O(2) and O(1A) occupy the axial positions. The corresponding bond angles O(2)−In(1)−O(1A), C(6)−In(1)−C(7), and O(1)−In(1)−C(6) are 154.49(6), 150.1(1), and 107.38(8)°, respectively (Table 3). One of the acetylacetonate oxygen atoms (O(1)) bridges two indium atoms, but the associated indium−oxygen bonds are different, with In(1)−O(1) (2.206(2) Å) being considerably shorter than In(1)−O(1A) (2.569(2) Å). The In(1)−O(2) bond has a length of 2.262(2) Å, which is in agreement with the fact that it is a pseudo-axial bond. The bridging oxygen (O(1)) is in a trigonal-planar configuration, with the sum of the bond angles around it being 359.5(3)°; thus, it can be considered to be sp^2-hybridized.

Although the acetylacetonate ligand is planar, the indium center (In(1)) is displaced from the acetylacetonate plane by −0.306 Å in the direction of the neopentyl ligand and the fused-ring system in the dimer has a *zigzag* conformation. The acetylacetonate ligand shows a high degree of π-delocalization, but the carbon−oxygen bonds are not equal. The O(1)−C(2) bond (1.300(3) Å) is longer than O(2)−C(4) (1.257(3) Å), indicating more single-bond character than for the latter.

The availability of X-ray structural data for $Me_2In(acac)$, $Me_2In(hfac)$,[15] $(Me_3CCH_2)_2In(acac)$, and $(Me)(Me_3CCH_2)In(acac)$ permits a comparison of their many features and with those of other oxygen-bridged indium-containing dimers. All of these acetylacetonate derivatives exist as centrosymmetric dimers with an inversion center located between the five-coordinate indium atoms. The In(1)···O(1A) distances are 2.551(1) and 2.569(2) Å for $Me_2In(acac)$ and $(Me)(Me_3CCH_2)In(acac)$, respectively, whereas the corresponding distances for $Me_2In(hfac)$[15] and $(Me_3CCH_2)_2In(acac)$ at 2.869(2) and 2.759(3) Å, respectively, are significantly longer. These distances are much longer than the bridging distances in other simple four-coordinate indium oxygen dimers such as $[(C_5H_5)_2InO(t\text{-}Bu)]_2$ at 2.129 Å (average),[14] $\{[(t\text{-}Bu)O]_2InO(t\text{-}Bu)\}_2$ at 2.111 Å[16] (average), and $[MeClInO(t\text{-}Bu)]_2$ at 2.116 Å (average).[17] This difference in bond lengths in the β-diketonate derivatives may indicate a considerably higher degree of bonding interactions between the indium and bridging oxygen atoms in $Me_2In(acac)$ and $(Me)(Me_3CCH_2)In(acac)$ than in $Me_2In(hfac)$[15] and $(Me_3CCH_2)_2In(acac)$, but steric and/or

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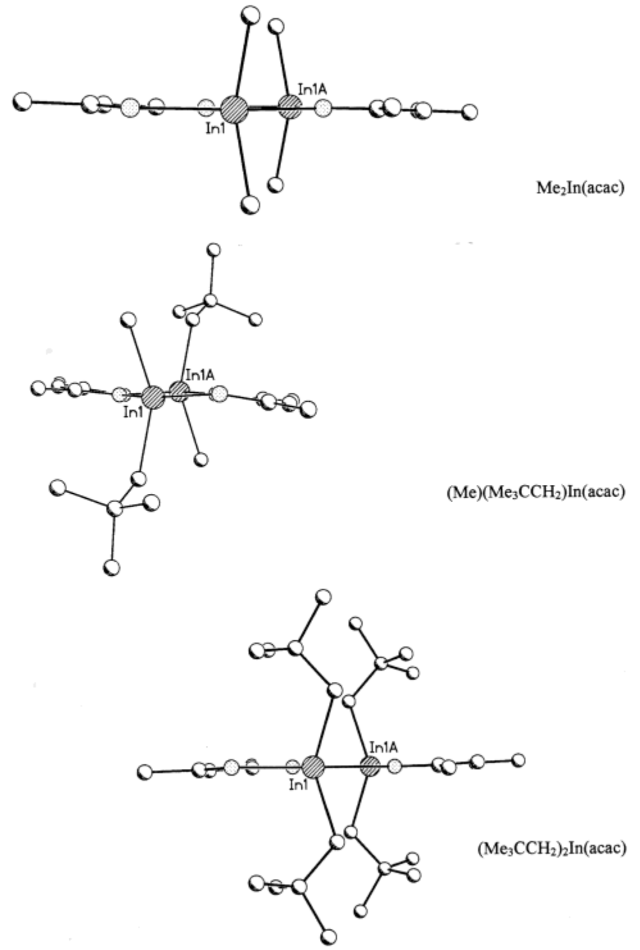

Figure 4. Views of indium acetylacetonate derivatives that show conformations of the chelate rings.

electronic effects associated with the substituents on the metal center or the β-diketonate ligand may be significant also. The steric bulkiness of the neopentyl ligand in (Me$_3$CCH$_2$)$_2$In(acac) or the strong electron-withdrawing nature of the trifluoromethyl groups on the hexafluoroacetylacetonate ligand in Me$_2$In(hfac)[15] may be responsible for the deviation in the bonding interactions between the individual R$_2$In(β-diketonate) units. The six-membered InO$_2$C$_3$ rings in Me$_2$In(acac), Me$_2$In(hfac),[15] and (Me$_3$CCH$_2$)$_2$In(acac) are planar, whereas the corresponding ring in (Me)(Me$_3$CCH$_2$)In(acac) is nonplanar, with the indium being displaced from the plane of the O$_2$C$_3$ ring by −0.306 Å in the direction of the neopentyl ligand (Figure 4). This distortion of the metallacyclic ring from planarity may be due to the inequality in steric bulkiness of the methyl and neopentyl ligands.

The compound (t-Bu)$_2$In(acac) was prepared by a metathetical reaction between (t-Bu)$_2$InCl[18] and Na(acac), rather than by a cyclopentadiene elimination reaction. It is of interest that the chelating acetylacetonate ligand was not able to stabilize (t-Bu)$_2$In(acac) sufficiently for complete characterization at room temperature. A gray material believed to be indium metal became apparent after approximately 1 week of storage in the drybox. Even though the compound decomposed, most likely by a β-hydride elimination reaction, the compound did not form an isolable adduct with Et$_2$O, THF, PPh$_3$, or pyridine. The ^{1}H NMR spectrum of a d_6-benzene solution of (t-Bu)$_2$In(acac) exhibited three sharp resonances.

The cyclopentadiene elimination reaction is an efficient method for the preparation of Me$_2$InSSiPh$_3$[19] and (Me$_3$CCH$_2$)$_2$InSSiPh$_3$. The compound Me$_2$InSSiPh$_3$ was previously prepared by the methane elimination reaction between InMe$_3$ and HSSiPh$_3$ in toluene solution at room temperature.[19] The sample of the compound prepared in the present study did not melt but decomposed at 159.2−162.3 °C. The earlier work described a melting point of 160 °C with no mention of decomposition.[19] A benzene solution of Me$_2$InSSiPh$_3$ exists as an equilibrium mixture of species, probably dimers and trimers, in the concentration range of 0.01−0.03 m. The degree of association decreased from 2.46 to 2.37 as the solution was diluted from 0.0304 to 0.0175 m. Limited solubility prevented molecular weight measurements at higher concentrations. Although Me$_2$InSSiPh$_3$ is a mixture of dimers and trimers in benzene solution according to the molecular weight study, only three ^{1}H NMR resonances were observed for a d_6-benzene solution. The derivative Me$_2$InSSiPh$_3$ is trimeric in the solid state.[19] The closely related compound (Me$_3$CCH$_2$)$_2$InSSiPh$_3$ is similar to Me$_2$InSSiPh$_3$, as it decomposed rather than melted upon heating. The compound is dimeric in benzene solution in the concentration range of 0.02 to 0.10 m.

The cyclopentadiene elimination reaction is also an excellent synthetic method for the preparation of Me$_2$InPPh$_2$[20] and (Me$_3$CCH$_2$)$_2$InPPh$_2$.[21] In contrast, HPPh$_2$ reacted with In(C$_5$H$_5$)$_3$ to reduce indium(III) to indium(I) to form indium(I) cyclopentadienide (In(C$_5$H$_5$)) and P$_2$Ph$_4$ as final products.[14] The reaction between Me$_2$In(C$_5$H$_5$) and HPPh$_2$ in a benzene solution at room temperature produced a colorless powder that did not melt but decomposed at 188.9−192.4 °C. Even though Me$_2$InPPh$_2$ has been described in three previous papers,[20] characterization data were inconsistent. The compound has been described as melting at either 243 °C[20a] or 245 °C[20c] but with decomposition beginning at either 140 °C[20c] or 185 °C.[20c] It should be noted that (Me$_3$CCH$_2$)$_2$InPPh$_2$ undergoes thermal decomposition rather than melting.[21] ^{1}H and ^{31}P NMR spectra of Me$_2$InPPh$_2$ are also different from those reported in the previous studies, but the current spectra are consistent with the spectral data for (Me$_3$CCH$_2$)$_2$InPPh$_2$.[21] The ^{1}H NMR spectrum of Me$_2$InPPh$_2$ in d_6-benzene exhibited two singlets for the protons of the methyl groups bonded to indium and two broad resonances for the protons associated with the phenyl groups. Previous workers[20] described only one resonance each for the protons of the methyl groups and of the phenyl groups. Similarly, the ^{31}P NMR spectrum in d_6-benzene solution had two

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resonances, one at −24.8 ppm and the other at −52.8 ppm, whereas only one had been reported previously.[20] The current NMR spectral data suggest the existence of an equilibrium between two species, possibly monomers and dimers, because the chemical shifts of the ^{31}P NMR resonances for Me_2InPPh_2 are similar to those observed for the monomer/dimer equilibrium reported for $(Me_3CCH_2)_2InPPh_2$[21] (−30.8 ppm, monomer; −49.4 ppm, dimer). Thus, the physical properties, NMR spectra, and structures of Me_2InPPh_2 and $(Me_3CCH_2)_2InPPh_2$ are now comparable and are in complete agreement. Both compounds are trimers in the solid state and equilibrium mixtures of monomers and dimers in solution. The closely related compounds $(i\text{-}Pr)_2InPPh_2$ and $(PhCH_2)_2InPPh_2$ also exist as trimers in the solid state and as equilibrium mixtures of monomers and dimers in benzene solution, according to cryoscopic molecular weight studies.[22]

The reaction of $Me_2In(C_5H_5)$ with $H_2N(t\text{-}Bu)$ is significantly slower than the corresponding reactions of any of the other reagents described in this paper and with the corresponding reactions of $R_2Ga(C_5H_5)$ (R = Me, Et)[5−7] with amines, but the elimination of C_5H_6 is faster than the elimination of methane from $InMe_3$ with the primary amines $H_2N(i\text{-}Pr)$ (∼120 °C)[23] and $H_2N(C_6F_5)$ (∼110 °C).[24] Heating of a benzene solution of $Me_2In(C_5H_5)$ and $H_2N(t\text{-}Bu)$ in a 75 °C oil bath for at least 2 days was required to achieve complete reaction for the isolation of $Me_2InNH(t\text{-}Bu)$ in ∼92% yield. Even though the trans isomer of the dimer $[Me_2InNH(t\text{-}Bu)]_2$ was observed in the solid state by an X-ray structural study (see below), cryoscopic molecular weight studies in benzene solutions as well as ^1H NMR spectra of d_8-THF and d_6-benzene solutions suggest that the compound exists as a mixture of monomers and dimers with both cis and trans configurations. The resonances assigned to the monomeric species disappeared as the concentration of $Me_2InNH(t\text{-}Bu)$ in each solvent was increased. The observed percentage of monomer for the most dilute solutions in both solvents was approximately 7%, whereas the ratio of cis and trans isomers was 45/55 for d_6-benzene and 41/59 for d_8-THF.

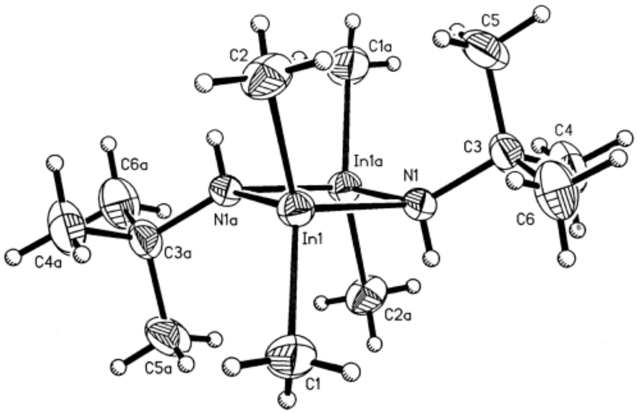

Figure 5. Molecular geometry and labeling of atoms for $[Me_2InNH(t\text{-}Bu)]_2$ (30% probability ellipsoids for nonhydrogen atoms; hydrogen atoms are artificially reduced).

Table 4. Selected Bond Distances (Å) and Angles (deg) for $[Me_2InNH(t\text{-}Bu)]_2$

	Bond Distances		
In(1)−N(1)	2.230(3)	In(1)−N(1A)	2.220(3)
In(1A)-N(1)	2.220(3)	In(1)−C(1)	2.160(4)
In(1)−C(2)	2.157(4)	In(1)···In(1A)	3.335(2)
N(1)−C(3)	1.495(4)	N(1)−H(1)	0.81(3)
	Bond Angles		
N(1)−In(1)-C(1)	106.6(1)	N(1)−In(1)-C(2)	116.1(1)
C(1)−In(1)-C(2)	121.5(2)	N(1)−In(1)···In(1A)	41.3(1)
C(1)−In(1)-In(1A)	119.2(1)	C(2)−In(1)-In(1A)	119.3(1)
N(1)−In(1)-N(1A)	82.9(1)	C(1)−In(1)-N(1A)	116.5(1)
C(2)−In(1)-N(1A)	107.0(1)	In(1A)···In(1)−N(1A)	41.6(1)
In(1)−N(1)-H(1A)	97(2)	In(1)−N(1)-C(3)	122.6(2)
H(1A)-N(1)−C(3)	108(2)	In(1)−N(1)-In(1A)	97.1(1)
H(1A)-N(1)−In(1A)	104(2)	C(3)−N(1)-In(1A)	123.9(2)

The compound $[Me_2InNH(t\text{-}Bu)]_2$ crystallizes in the centrosymmetric space group $P2_1/n$ with $Z = 2$ (Figure 5 and Table 4). The molecule lies on a crystallographic inversion center and has precise C_i symmetry. This symmetry requires the two NH(t-Bu) ligands associated with sp^3-hybridized nitrogen atoms to be in a mutually trans configuration, with one t-Bu group above the plane of the In_2N_2 ring and the other below it. The In_2N_2 ring is precisely planar, with In(1)−N(1) = In(1A)−N(1A) = 2.230(3) Å and In(1)−N(1A) = In(1A)−N(1) = 2.220(3) Å. The internal angle at the indium atom is acute (N(1)−In(1)−N(1A) = 82.9(1)°, while that at nitrogen is obtuse (In(1)−N(1)−In(1A) = 97.1(1)°). The In(1)···In(1A) distance is 3.335(2) Å. The two independent indium−methyl bond lengths are In(1)−C(1) = 2.160(4) Å and In(1)−C(2) = 2.157(4) Å with an interligand angle of C(1)−In(1)−C(2) = 121.5(2)°. It is of interest that an X-ray structural study of the closely related compound $[Me_2InNH(i\text{-}Pr)]_2$[23] revealed the crystal to contain both cis and trans isomers, a most unusual observation. A review of the chemistry of amido derivatives of gallium and indium[25] suggests that many compounds of this type exist as the two geometrical isomers in solution but only $[Me_2InNH(i\text{-}Pr)]_2$[23] exists as both isomers in the solid state, whereas $Me_2InNH(t\text{-}Bu)$ is the only indium amido derivative to our knowledge that has been observed by NMR spectroscopy to exist as an equilibrium mixture of monomers and dimers in benzene solution and to be a dimer in the solid state.

Both synthetic scale reactions and ^1H NMR spectral studies (see the Supporting Information) have been used to elucidate the reasons for the cyclopentadiene elimination reaction between $Me_2In(C_5H_5)$ and $H_2N(t\text{-}Bu)$ being slow in comparison with others in this study. Three of the four equations that describe the overall process (eqs 2−5) are specifically shown as equilibria,

$$Me_2In(C_5H_5) + H_2N(t\text{-}Bu) \rightleftharpoons Me_2(C_5H_5)In\text{-}NH_2(t\text{-}Bu) \quad (2)$$

$$Me_2(C_5H_5)In\text{-}NH_2(t\text{-}Bu) \rightleftharpoons Me_2InNH(t\text{-}Bu) + C_5H_6 \quad (3)$$

$$Me_2InNH(t\text{-}Bu) \rightleftharpoons {}^1/_2[Me_2InNH(t\text{-}Bu)]_2 \quad (4)$$

$$C_5H_6 \rightarrow C_{10}H_{12} \quad (5)$$

because both the forward and reverse reactions have been observed experimentally. The experimental data support the following conclusions. (1) The cyclopenta-

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diene elimination reaction (eq 3) is faster in benzene than in THF solution, but both solutions must be heated to achieve complete reaction. There was no apparent reaction when a solution of $Me_2In(C_5H_5)$ and H_2N(t-Bu) in benzene was maintained at room temperature for 30 days. (2) Removal of the volatile products from the reaction mixture enhanced the rate of formation of Me_2InNH(t-Bu). (3) The absence of solvent did not accelerate significantly the rate of formation of Me_2InNH(t-Bu). (4) The reaction between Me_2InNH(t-Bu) and C_5H_6 (the reverse of eq 3) is faster in THF than in d_6-benzene. These data suggest that the occurrence of a significant reaction between $Me_2In(C_5H_5)$ and H_2N(t-Bu) to form Me_2InNH(t-Bu) requires dimerization of the indium amide monomer (eq 4) and/or the removal or dimerization of cyclopentadiene (eq 5). As the relative rates of the reactions depend on the characteristics of the solvent, reaction may proceed by the initial formation of a Lewis acid/base adduct (eq 2), which is then followed by proton transfer from the coordinated Lewis base to the cyclopentadienide ligand (eq 3). The monomeric amide can either dimerize to form the observed product (eq 4) or be protonated by cyclopentadiene to reform the Lewis acid/base adduct. A strongly coordinating solvent such as THF can displace the amine from $Me_2In(C_5H_5)\cdot NH_2$(t-Bu), thereby reducing the concentration of adduct and slowing the overall rate of the cyclopentadiene elimination reaction. However, THF can also stabilize Me_2InNH(t-Bu) as the monomer by forming an adduct and, in turn, facilitate its protonation by cyclopentadiene. Removal of C_5H_6 either physically by vacuum distillation or chemically by a Diels−Alder dimerization provides an alternative way to shift the equilibria and enhance the formation of product.

The characterization data for compounds of the types R_2InXR' and $R_2InYR'_2$ (R = Me, CH_2CMe_3; X = O, S; Y = N, P; R′ = organic groups) have established that the degree of association depends on the physical state of the compound. Molecules as solids frequently exhibit degrees of association different from those of species in solution. Thus, thermodynamic parameters contribute significantly to the detailed nature of these types of compounds. An X-ray structural study of a specific organoindium(III) compound cannot be used to define the nature of the compound in solution. Dissociative reactions as well as ligand redistribution reactions play significant roles in group 13 chemistry.

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[8a] and used within 2 weeks of its preparation. The starting materials $Me_2In(C_5H_5)$,[9] $(Me_3CCH_2)_2In(C_5H_5)$,[9a] (t-Bu)$_2$InCl,[18] and In(acac)$_3$[14] were prepared by literature methods, whereas t-BuOH, Hacac, $HPPh_2$, H_2N(t-Bu), and $InCl_3$ were purchased from either Strem Chemicals, Inc. or Aldrich Chemical Co. *tert*-Butyl alcohol was dried by stirring with CaH_2 for 8 h and then vacuum-distilled, whereas acetylacetone was dried over K_2CO_3 and distilled prior to use. The phosphine was distilled under dynamic vacuum at ~100 °C, whereas *tert*-butylamine was dried with KOH. Indium(III) chloride was used as received. All volatile reagents were vacuum-distilled into storage tubes 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 δ 1.73 ppm. 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 d_6-benzene and d_8-THF were purchased from either Aldrich Chemical Co. or Cambridge Isotopes, Inc., were dried with P_4O_{10}, and then were 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. Molecular weights were measured cryoscopically in benzene solution by using an instrument similar to that described by Shriver and Drezdon.[26]

Synthesis of Me_2InO(t-Bu).[10] A tube that contained 0.522 g (7.04 mmol) of t-BuOH dissolved in 4 mL of Et_2O was connected to a flask charged with 1.48 g (7.04 mmol) of $Me_2In(C_5H_5)$ dissolved in approximately 10 mL of Et_2O and equipped with a magnetic stir bar. The t-BuOH/Et_2O solution was added to the $Me_2In(C_5H_5)$ at room temperature. The initially insoluble $Me_2In(C_5H_5)$ dissolved after 5 min of stirring. The reaction mixture was stirred for 1 h, and all material volatile at room temperature was removed by vacuum distillation. Flask-to-flask sublimation at 35 °C produced 1.51 g (6.92 mmol, 98.3% based on $Me_2In(C_5H_5)$) of Me_2InO(t-Bu)[10] as a colorless waxy solid.

Me_2InO(t-Bu): mp 84.3−87.6 °C (appeared to shrink in tube, possible glass transition), 90.2−91.5 °C (melted) (lit.[10] mp 90 °C); ^{1}H NMR (d_6-benzene, δ) 0.89 (s, InCH_3, 6.0 H), 1.09 (s, OC$(CH_3)_3$, 9.0 H). Cryoscopic molecular weight, benzene solution, formula weight 218.00 (observed molality, observed mol wt, association): 0.0936, 435, 2.00; 0.0516, 433, 1.99; 0.0301, 443, 2.03. Soluble in THF, Et_2O, C_6H_6, and C_5H_{12}.

Synthesis of $(Me_3CCH_2)_2InO$(t-Bu). The reagents, 1.478 g (7.040 mmol) of $(Me_3CCH_2)_2In(C_5H_5)$ dispersed in 10 mL of Et_2O and 0.522 g (7.04 mmol) of t-BuOH dissolved in 4 mL of Et_2O, were combined as described for the previous reaction. The initially insoluble $(Me_3CCH_2)_2In(C_5H_5)$ dissolved after 5 min of stirring at room temperature. After the reaction mixture was stirred for 1 h, all material volatile at room temperature was removed by vacuum distillation. A fine-porosity frit attached to a round-bottom flask was fitted to the Schlenk flask, and the product was isolated by recrystallization from 2 × 20 mL of Et_2O at −40 °C. After the resulting crystals were washed with pentane at 0 °C, 1.51 g (6.92 mmol, 98.3% based on $(Me_3CCH_2)_2In(C_5H_5)$) of $(Me_3CCH_2)_2InO$(t-Bu) was isolated as a colorless solid.

$(Me_3CCH_2)_2InO$(t-Bu): mp 120.5−130.2 °C dec; ^{1}H NMR (d_6-benzene, δ) 1.25 (s, CH_2CCH_3, 18.00 H), 1.35 (s, OC$(CH_3)_3$, 9.0 H), 1.37 (s, InCH_2, 4.0 H). Anal. Calcd for $C_{14}H_{31}InO$: C, 50.92; H, 9.46. Found: C, 50.48; H, 9.29. Cryoscopic molecular weight, benzene solution, formula weight 330.21 (observed molality, observed mol wt, association): 0.0449 *m*, precipitate formed as solution cooled; 0.0495, 683, 2.07; 0.0220, 672, 2.04. Soluble in THF and Et_2O, slightly soluble in C_6H_6, and trace solubility in C_5H_{12}.

Synthesis of Me_2In(acac)[11] from $InMe_3$ and Hacac. After a Schlenk flask was charged with 0.251 g (1.57 mmol) of $InMe_3$, 0.165 g (1.65 mmol) of Hacac was vacuum-distilled

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

onto the $\mathrm{InMe_3}$. The reactants were slowly warmed to room temperature, and bubbling occurred. After 4 h at 20 °C, bubbling ceased and $\mathrm{CH_4}$ and excess Hacac were removed by vacuum distillation. Sublimation of the resulting product at 40 °C produced 0.334 g (1.37 mmol, 87.5% based on $\mathrm{InMe_3}$) of $\mathrm{Me_2In(acac)}$ as a colorless solid. Crystals suitable for an X-ray structural study were grown by slow sublimation in a sealed tube placed above a 150 °C drying oven.

$\mathrm{Me_2In(acac)}$: mp 136.9−137.8 °C; dec pt ∼200 °C (lit.[11a] mp 118 °C dec); $^1\mathrm{H}$ NMR (d_8-THF, δ) −0.28 (s, $\mathrm{InC}H_3$, 6.01 H), 5.94), 1.83 (s, acac $\mathrm{C}H_3$, 6.01 H), 5.20 (s, acac H, 0.98 H); $^1\mathrm{H}$ NMR ($\mathrm{C_6D_6}$, δ) 0.11 (s, $\mathrm{InC}H_3$, 5.94 H), 1.71 (s, acac $\mathrm{C}H_3$, 6.07 H), 4.98 (s, acac H, 0.99 H); $^{13}\mathrm{C}$ NMR (d_6-benzene, δ) −4.67 (s, $\mathrm{In}C\mathrm{H_3}$), 28.08 (s, acac $C\mathrm{H_3}$), 100.27 (s, acac $-C-C-$), 192.28 (s, acac $C-\mathrm{O}$); IR 1597 $\mathrm{cm^{-1}}$ (m, C−O). Anal. Calcd for $\mathrm{C_7H_{13}InO_2}$: C, 34.46; H, 5.37. Found: C, 34.39; H, 5.27. Cryoscopic molecular weight, benzene solution, formula weight 243.99 (observed molality, observed mol wt, association): 0.0678, 299, 1.23; 0.0549, 283, 1.16; 0.0480, 278, 1.138; 0.0420, 275, 1.13; 0.0244, 270, 1.11; 0.0099, 266, 1.09 (lit.[10b] 302). Soluble in THF, $\mathrm{Et_2O}$, $\mathrm{C_6H_6}$, and $\mathrm{C_5H_{12}}$.

Synthesis of $\mathrm{Me_2In(acac)}$. A Schlenk flask was charged with 0.344 g (1.64 mmol) of $\mathrm{Me_2In(C_5H_5)}$, approximately 25 mL of $\mathrm{C_5H_{12}}$, and a magnetic stir bar. After the mixture was cooled to −196 °C, 0.160 g (1.60 mmol) of Hacac was added by vacuum distillation. The reaction mixture was slowly warmed to room temperature and stirred vigorously. After 10 min the mixture was clear and colorless, but after 30 min the solution was yellow. Then, all material volatile at 20 °C was removed by vacuum distillation. Sublimation at 40 °C produced 0.200 g (0.820 mmol, 87.5% based on $\mathrm{Me_2In(C_5H_5)}$) of $\mathrm{Me_2In(acac)}$ as a colorless solid.

$\mathrm{Me_2In(acac)}$: mp 137.9−138.4 °C; $^1\mathrm{H}$ NMR spectrum was identical with that observed for a sample of $\mathrm{Me_2In(acac)}$ prepared by the methane elimination reaction.

Synthesis of $\mathrm{(Me_3CCH_2)_2In(acac)}$. A Schlenk flask was charged with 0.554 g (1.72 mmol) of $\mathrm{(Me_3CCH_2)_2In(C_5H_5)}$, 0.173 g (1.72 mmol) of Hacac, and 30 mL of $\mathrm{C_6H_6}$ and stirred at room temperature with a magnetic stir bar. Then, $\mathrm{C_6H_6}$, $\mathrm{C_5H_6}$, and unreacted Hacac were removed by vacuum distillation. Recrystallization of the product from pentane at −30 °C produced 0.559 g (1.57 mmol, 91.3% based on $\mathrm{(Me_3CCH_2)_2In(C_5H_5)}$) of $\mathrm{(Me_3CCH_2)_2In(acac)}$ as a colorless crystalline solid. Sublimation at 40 °C in a sealed tube produced crystallographic quality crystals.

$\mathrm{(Me_3CCH_2)_2In(acac)}$: mp 44.6−45.8 °C; $^1\mathrm{H}$ NMR (d_6-benzene, δ) 1.13 (s, $Me_3\mathrm{CCH_2}$, 18 H), 1.16 (s, $\mathrm{Me_3CC}H_2$, 4 H), 1.73 (s, acac CH_3, 6 H), 5.06 (s, acac H, 1 H). Anal. Calcd for $\mathrm{C_{15}H_{29}InO_2}$: C, 50.58; H, 8.21. Found: C, 50.75; H, 8.18. Cryoscopic molecular weight, benzene solution, formula weight 356.21 (observed molality, observed mol wt, association): 0.0787, 353, 0.99; 0.0594, 364, 1.02; 0.0458, 352, 0.99. Soluble in THF, $\mathrm{Et_2O}$, $\mathrm{C_6H_6}$, and $\mathrm{C_5H_{12}}$.

Synthesis of $\mathrm{(Me_3CCH_2)_2In(acac)}$ from $\mathrm{In(CH_2CMe_3)_3}$ and Hacac. The reagents, 0.3021 g (0.9203 mmol) of $\mathrm{In(CH_2CMe_3)_3}$, 0.101 g (1.01 mmol) of Hacac, and benzene, were combined as described in the previous experiment. The product, 0.301 g (0.846 mmol, 91.9% based on $\mathrm{In(CH_2CMe_3)_3}$) of $\mathrm{(Me_3CCH_2)_2In(acac)}$, was isolated as colorless blocks after recrystallization from 2 × 20 mL of pentane at −30 °C.

$\mathrm{(Me_3CCH_2)_2In(acac)}$: characterization data were identical with those obtained for a sample of $\mathrm{(Me_3CCH_2)_2In(acac)}$ prepared by the cyclopentadiene elimination reaction.

Attempted Synthesis of $\mathrm{(Me)(Me_3CCH_2)In(C_5H_5)}$ from $\mathrm{Me_2In(C_5H_5)}$ and $\mathrm{(Me_3CCH_2)_2In(C_5H_5)}$. A reaction mixture was prepared by dissolving 0.590 g (1.83 mmol) of $\mathrm{(Me_3CCH_2)_2In(C_5H_5)}$ and 0.385 g (1.83 mmol) of $\mathrm{Me_2In(C_5H_5)}$ in ∼10 mL of THF. After the resulting light yellow solution was stirred with a magnetic stir bar at room temperature for 1.5 h, the THF was removed by vacuum distillation to leave a colorless, rigid foam. The flask was dynamically evacuated for an additional 3 h. The resulting colorless material was sublimed at 90 °C to produce 0.891 g of $\mathrm{(Me)(Me_3CCH_2)In(C_5H_5)}$ (3.35 mmol, 91.4% yield, if pure).

$\mathrm{(Me)(Me_3CCH_2)In(C_5H_5)}$: mp 92.4−94.2 °C; $^1\mathrm{H}$ NMR (d_8-THF, δ): −1.10 (s, $Me\mathrm{In(C_5H_5)_2}$, 0.22 H), −0.52 (s, $Me_2\mathrm{In(C_5H_5)}$, 5.78 H), 0.37 (s, $\mathrm{(Me_3CC}H_2\mathrm{)In(C_5H_5)_2}$, 1.77 H), 0.61 (s, $\mathrm{(Me_3CC}H_2\mathrm{)_2In(C_5H_5)}$, 0.19 H), 0.83 (s, $Me_3\mathrm{CCH_2)In(C_5H_5)_2}$, 7.87 H), 0.99 (s, $\mathrm{(}Me_3\mathrm{CCH_2)_2In(C_5H_5)}$, 0.91 H), 1.10 (s, $\mathrm{(}Me_3\mathrm{CCH_2)_3In}$, 0.11 H), 6.04 (s, $\mathrm{C_5}H_5$, 5.00H). Soluble in THF, $\mathrm{Et_2O}$, $\mathrm{C_6H_6}$, and $\mathrm{C_5H_{12}}$.

Attempted Synthesis of $\mathrm{(Me)(Me_3CCH_2)In(acac)}$ from $\mathrm{(Me)(Me_3CCH_2)\text{-}In(C_5H_5)}$ and Hacac. A Schlenk flask was charged with 0.520 g (1.96 mmol) of $\mathrm{(Me)(Me_3CCH_2)In(C_5H_5)}$, approximately 15 mL of $\mathrm{C_5H_{12}}$, and a magnetic stir bar. After the mixture was stirred for 10 min, 0.200 g (2.00 mmol) of Hacac was added by vacuum distillation. The reaction mixture was warmed to room temperature, and the clear, colorless solution was stirred for 15 min. Then, the volatile components were removed by vacuum distillation. Recrystallization of the product from pentane at −30 °C produced 0.547 g of colorless crystals (1.90 mmol of $\mathrm{(Me)(Me_3CCH_2)In(acac)}$, if pure, 96.9% yield based on $\mathrm{(Me)(Me_3CCH_2)In(C_5H_5)}$).

$\mathrm{(Me)(Me_3CCH_2)In(acac)}$: mp 52.7−53.5 °C; $^1\mathrm{H}$ NMR (d_6-benzene, δ) initial spectrum 0.02 (s, $\mathrm{In}CH_3$, 4.9 H), 0.13 (s, $\mathrm{In}CH_3$, 11.7 H), 1.07 (s, $\mathrm{CH_2C}CH_3$, 39.2 H), 1.11 (s, $CH_2\mathrm{CMe_3}$, 8.6 H), 1.72 (s, acac CH_3, 30.7 H), 5.04 (s, acac H, 4.2 H), spectrum after 24 h at room temperature 0.02 (s, $\mathrm{In}CH_3$, 7.0 H), 0.13 (s, $\mathrm{In}CH_3$, 10.4), 1.06 (s, $\mathrm{CH_2C}CH_3$, 31.6 H), 1.11 (s, $CH_2\mathrm{CMe_3}$, 6.9 H), 1.13 (s, $\mathrm{CH_2C}CMe_3$, 6.5 H), 1.16 (s, $CH_2\mathrm{CMe_3}$, 1.5 H), 1.72 (s, acac CH_3, 6.0 H), 5.04 (s, acac H, 1.0 H), spectrum after 6 months at room temperature 0.03 (s, $\mathrm{In}CH_3$, 2.5 H), 0.14 (s, $\mathrm{In}CH_3$, 3.2 H), 0.91 (s, $\mathrm{CH_2CMe_3}$, 1.8 H), 1.07 (s, $\mathrm{CH_2C}Me_3$, 5.5 H), 1.12 (s, $\mathrm{C}H_2\mathrm{CMe_3}$, 3.1 H), 1.14 (s, $\mathrm{CH_2C}Me_3$, 5.0 H), 1.17 (s, $\mathrm{C}H_2\mathrm{CMe_3}$, 2.6 H), 1.21 (s, $\mathrm{CH_2C}Me_3$, 3.0 H), 1.73 (s, acac CH_3, 6.5 H), 1.74 (s, acac CH_3, 5.0 H), 5.03 (s, acac H, 0.2 H), 5.05 (s, acac H, 0.9 H), 5.07 (s, acac H, 0.6 H), 5.12 (s, acac H, 0.2 H). Anal. Calcd for $\mathrm{C_{11}H_{21}InO_2}$: C, 44.02; H, 7.05. Found: C, 42.83; H, 6.81. Soluble in THF, $\mathrm{Et_2O}$, $\mathrm{C_6H_6}$, and $\mathrm{C_5H_{12}}$.

Synthesis of $\mathrm{(t\text{-}Bu)_2In(acac)}$. A Schlenk flask charged with 0.993 g (3.75 mmol) of $\mathrm{(t\text{-}Bu)_2InCl}$[18] was fitted with a sidearm dumper that contained 0.468 g (3.84 mmol) of Na(acac) and a 90° elbow fitted to a another Schlenk flask. The apparatus was evacuated, and 50 mL of diethyl ether was distilled onto the $\mathrm{(t\text{-}Bu)_2InCl}$. Na(acac) was added to the $\mathrm{(t\text{-}Bu)_2InCl}$ over 1 h. After the solution was stirred for an additional 4 h, the ether was removed by vacuum distillation. The $\mathrm{(t\text{-}Bu)_2In(acac)}$ was then vacuum-distilled at 40 °C through the elbow to give 1.02 g (3.10 mmol, 82.7% based on $\mathrm{(t\text{-}Bu)_2InCl}$) of $\mathrm{(t\text{-}Bu)_2In(acac)}$ as a colorless liquid that decomposed to a black solid in the drybox.

$\mathrm{(t\text{-}Bu)_2In(acac)}$: mp ∼−8 °C; $^1\mathrm{H}$ NMR (d_6-benzene, δ) 1.36 (s, $\mathrm{C(C}H_3\mathrm{)_3}$, 18.1 H), 1.75 (s, acac-$\mathrm{C}H_3$, 6.0 H), 5.04 (s, acac H, 0.92 H); $^{13}\mathrm{C}$ NMR (d_6-benzene) δ 31.68 (s, t-Bu $C\mathrm{H_3}$), 35.75 (s, t-Bu C), 28.03 (s, acac $C\mathrm{H_3}$), 100.27 (s, acac $-C-C-$), 193.06 (s, acac $C-\mathrm{O}$); IR 1583 $\mathrm{cm^{-1}}$ (m, C−O). Soluble in THF, $\mathrm{Et_2O}$, $\mathrm{C_6H_6}$, and $\mathrm{C_5H_{12}}$. The compound did not form an isolable adduct with $\mathrm{OEt_2}$, THF, pyridine, or $\mathrm{PPh_3}$ and was insufficiently stable to obtain an elemental analysis from an external laboratory.

Synthesis of $\mathrm{Me_2InSSiPh_3}$.[19] A flask was charged with 0.977 g (4.65 mmol) of $\mathrm{Me_2In(C_5H_5)}$, ∼20 mL of $\mathrm{C_6H_6}$, and a magnetic stir bar while a sidearm dumper contained 1.24 g (4.25 mmol) of $\mathrm{HSSiPh_3}$. After ∼15 min after the addition of the thiol, most of the $\mathrm{Me_2In(C_5H_5)}$ had dissolved but a cloudy colorless suspension remained. The suspension was stirred for a total of 4 h, and then the $\mathrm{C_6H_6}$ was removed by vacuum distillation. The product was isolated by extraction with 3 × 30 mL of $\mathrm{C_5H_{12}}$ through a medium-porosity frit followed by cooling to −30 °C to give 1.56 g (3.58 mmol, 84.3% based on $\mathrm{HSSiPh_3}$) of $\mathrm{Me_2InSSiPh_3}$ as colorless crystals.

$Me_2InSSiPh_3$: mp 159.2−162.3 °C (dec as indicated by a color change to a yellow solid and then to a tan liquid (lit.[19] mp 160 °C); ^1H NMR (d_6-benzene, δ) −0.01 (s, CH_3, 6 H), 7.09 (m, C_6H_5, 9 H), 7.78 (m, C_6H_5, 6 H), (lit.[18] ^1H NMR (d_6-benzene) δ 0.00 (s, CH_3, 6 H)), 7.10 (m, C_6H_5, 9 H), 7.79 (m, C_6H_5, 6 H). Cryoscopic molecular weight, benzene solution, formula weight 436.35 (observed molality, observed mol wt, association): 0.0304, 1072, 2.46; 0.0175, 1034, 2.37.

Synthesis of $(Me_3CCH_2)_2InSSiPh_3$. The reagents, 1.033 g (3.206 mmol) of $(Me_3CCH_2)_2In(C_5H_5)$ and 0.849 g (2.903 mmol) of $HSSiPh_3$, were reacted in ∼20 mL of C_6H_6 as described for the synthesis of $Me_2InSSiPh_3$. After ∼20 min most of the $(Me_3CCH_2)_2In(C_5H_5)$ had dissolved but a cloudy colorless suspension remained. The suspension was stirred for 4 h, and then the C_6H_6 was removed by vacuum distillation. The crude product was isolated by extraction with 3 × 20 mL of benzene through a medium-porosity frit as a colorless goo with a suspended solid. The crude product was recrystallized from 3 × 30 mL of pentane followed by cooling to −30 °C to give 1.39 g (2.53 mmol, 87.1% based on $HSSiPh_3$) of $(Me_3CCH_2)_2InSSiPh_3$ as colorless crystals.

$(Me_3CCH_2)_2InSSiPh_3$: mp 135.9 °C began to turn tan, 142.7−150.2 °C glass transition, continually became darker brown until 198.2−200.7 °C, when all material appeared to melt; ^1H NMR: (d_6-benzene, δ) 1.04 (s, Me_3CCH_2, 18 H), 1.23 (s, Me_3CCH_2, 4 H), 7.19 (m, C_6H_5, 9 H), 7.78 (m, C_6H_5, 6 H). Anal. Calcd for $C_{28}H_{37}InSSi$: C, 61.31; H, 6.80. Found: C, 61.24; H, 6.65. Cryoscopic molecular weight, benzene solution, formula weight 548.56 (observed molality, observed mol wt, association): 0.0968, 1079, 1.97; 0.0547, 1080, 1.97; 0.0236, 1109, 2.02.

Synthesis of Me_2InPPh_2.[20] The reagents, 0.502 g (2.39 mmol) of $Me_2In(C_5H_5)$ and 0.423 g (2.27 mmol) of $HPPh_2$ dissolved in ∼2 mL of C_6H_6, were combined in ∼20 mL of C_6H_6. After ∼5 min most of the $Me_2In(C_5H_5)$ had dissolved but a cloudy, colorless suspension remained. The suspension was stirred for 4 h, and then the C_6H_6 was removed by vacuum distillation. The product was isolated by extraction with 2 × 30 mL of C_5H_{12} through a medium-porosity frit and then recrystallized by cooling to −30 °C to give 0.708 g (2.14 mmol, 94.3% based on $HPPh_2$) of Me_2InPPh_2 as colorless crystals.

Me_2InPPh_2: mp 188.9−192.4 °C dec (lit. 243 °C melting,[20a] 140 °C began to decompose,[20c] 185 °C darkened slightly,[20c] 245 °C melting[20c]); ^1H NMR (d_6-benzene, δ) 0.19 (s, Me_2InPPh_2 dimer, 6.0 H), 0.30 (s, Me_2InPPh_2 monomer, 0.60 H), 7.39 (br, PC_6H_5, 4.2 H); $^{31}P\{^1H\}$ NMR (d_6-benzene, δ) −24.8 (s, monomer, 5.3 P), −52.8 (s, dimer, 94.7 P). (lit.[20a] ^1H NMR (d_6-benzene, δ) 0.182 (d of t, 18 H, In*Me*), 6.93−7.39 (mult, 30 H, PC_6H_5); lit.[20a] $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ) −54.23 (s); lit.[20b] ^1H NMR (d_6-benzene, δ) 0.17 (s, 6 H, In*Me*), 7.39 (m, 4 H, PC_6H_5), 6.95 (m, 6 H, PC_6H_5); lit.[20b] $^{31}P\{^1H\}$ NMR (d_6-benzene, δ) −56.6 (s); lit.[20c] ^1H NMR (d_6-benzene, δ) 0.18, s, In*Me*, 6.8−7.7, m, PC_6H_5); lit.[20c] $^{31}P\{^1H\}$ NMR (d_6-benzene) −53.1 (s)).

Synthesis of $(Me_3CCH_2)_2InPPh_2$.[21] A flask was charged with 0.723 g (2.24 mmol) of $(Me_3CCH_2)_2In(C_5H_5)$ and ∼20 mL of C_6H_6, whereas an addition tube contained 0.400 g (2.15 mmol) of $HPPh_2$ and ∼2 mL of C_6H_6. The reagents were combined, and ∼5 min after mixing most of the $(Me_3CCH_2)_2In(C_5H_5)$ had dissolved, but a cloudy colorless suspension remained. The suspension was stirred for 4 h, and then the volatile material was removed by vacuum distillation. The product was isolated by extraction with 2 × 20 mL of C_5H_{12} through a medium-porosity frit and recrystallized by cooling to −30 °C to give 0.867 g (1.96 mmol, 91.2% based on $HPPh_2$) of $(Me_3CCH_2)_2InPPh_2$ as colorless crystals.

$(Me_3CCH_2)_2InPPh_2$: mp 138.3−139.1 °C phase transition, 142.7−148.9 °C dec (lit.[22a] mp 143.5−150 °C dec); ^1H NMR (d_6-benzene, δ) 1.03 (s, $(CH_3)_3CCH_2$, 3.1 H), 1.08 (s, $(CH_3)_3CCH_2$, 18.0 H), 1.48 (s, Me_3CCH_2, 4.8 H), 7.01 (m, PC_6H_5, 3.2 H), 7.06 (m, PC_6H_5, 5.0 H), 7.60 (m, PC_6H_5, 5.2 H); $^{31}P\{^1H\}$ NMR (d_6-benzene, δ) −29.14 (s, monomer, 85.5 P), −48.64 (s, dimer, 14.5 P).

Table 5. Data for X-ray Crystallographic Studies of $Me_2In(acac)$, $(Me_3CCH_2)_2In(acac)$, and $(Me)(Me_3CCH_2)In(acac)$

	$Me_2In(acac)$	$(Me_3CCH_2)_2$-In(acac)	(Me)(Me_3CCH_2)-In(acac)
mol formula	$C_{14}H_{26}In_2O_4$	$C_{30}H_{58}In_2O_4$	$C_{22}H_{42}In_2O_4$
M_r	487.99	712.52	600.20
cryst shape	colorless parallelepiped	colorless parallelepiped	colorless parallelepiped
cryst syst	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a, Å	7.7868(3)	9.5246(8)	11.112(2)
b, Å	8.3327(4)	9.5363(8)	7.265(2)
c, Å	8.5418(4)	9.8629(8)	16.555(3)
α, deg	101.719(1)	102.705(2)	90
β, deg	112.587(1)	91.902(2)	102.43(3)
γ, deg	107.314(1)	104.773(2)	90
V, Å^3	455.76(4)	841.2(1)	1305.1(5)
D_{calcd}, g/cm^3	1.778	1.406	1.527
Z	1	1	2
μ(Mo Kα), mm^{-1}	2.538	1.399	1.788
T (K)	90(1)	90.0(1)	90.0(1)
max 2θ, deg	60.0	59.2	75.5
abs cor method	SADABS[27]	SADABS[27]	SADABS[27]
no. of rflns measd	7993	7724	19 386
no. of unique rflns (R_{int})	2651(0.027)	3826 (0.017)	5618 (0.045)
no. of rflns with $I > 4\sigma(I)$	2537	3447	4106
no. of refined params	131	279	134
R1 ($I > 2\sigma(I)$)	0.019	0.021	0.033
wR2	0.045	0.050	0.077
goodness of fit	1.097	1.07	0.991
extinction coeff	0.033(2)	none	0.0059(4)

Synthesis of $Me_2InNH(t\text{-}Bu)$. A tube equipped with a Teflon valve was charged with 0.579 g (2.76 mmol) of $Me_2In(C_5H_5)$, 0.200 g (2.70 mmol) of $H_2N(t\text{-}Bu)$, and ∼5 mL of benzene and heated to 75 °C with an oil bath for 3 days. The material volatile at room temperature was removed by vacuum distillation. The solid remaining in the tube was sublimed at 45 °C to a coldfinger, and 0.543 g (2.50 mmol, 91.6% yield based on $H_2N(t\text{-}Bu)$) of $Me_2InNH(t\text{-}Bu)$ as a colorless powder was obtained.

$Me_2InNH(t\text{-}Bu)$: mp 48−50 °C phase transition, 60.7−62.9 °C melting; ^1H NMR (d_6-benzene, δ) −0.11 (s, $InCH_3$ cis, 7.6 H), −0.05 (s, $InCH_3$ monomer, 0.9 H), 0.03 (s, $InCH_3$ trans, 19.9 H), 0.17 (s, $InCH_3$ cis, 7.7 H), 0.77 (s, N*H*, 5.7 H), 0.87 (s, t-*Bu* monomer, 3.5 H), 0.96 (s, t-*Bu* trans, 30.4 H), 0.99 (s, t-*Bu* cis, 24.4 H); ^1H NMR (d_8-THF, δ) −0.52 (s, $InCH_3$ monomer, 0.88 H), −0.40 (s, In−CH_3 cis, 6.8 H), −0.23 (s, In−CH_3 trans, 21.7 H), −0.05 (s, In−CH_3 cis, 6.8 H), 1.09 (s, t-*Bu* monomer, 4.4 H), 1.14 (s, t-*Bu* trans, 32.3 H), 1.15 (s, t-*Bu* cis, 22.1 H), 1.38 (br, N−*H*, 2.1 H), 1.43 (br, N−*H*, 3.0 H). Anal. Calcd for $C_6H_{16}InN$: C, 33.21; H, 7.43; N, 6.45. Found: C, 33.27; H, 7.58; N, 6.34. Cryoscopic molecular weight, benzene solution, formula weight 217.02 (observed molality, observed mol wt, association): 0.0689, 456, 2.10; 0.0545, 443, 2.04; 0.0342, 415, 1.91.

Collection of X-ray Diffraction Data and Structural Solutions for $Me_2In(acac)$, $(Me_3CCH_2)_2In(acac)$, (Me)$(Me_3CCH_2)In(acac)$ and $[Me_2InNH(t\text{-}Bu)]_2$: General Features. (a) A well-defined crystal of each of the acetylacetonate derivatives were covered with Infineum V8512 oil (Infineum USA LP, 1900 East Linden Ave., Linden, NJ 07036) and mounted on a Bruker SMART1000 CCD diffractometer equipped with the rotating anode (Mo Kα radiation, λ = 0.710 73 Å). X-ray diffraction data were collected at 90 K. Details for these compounds are provided in Table 5. Data collection for each compound involved 4 sets of frames (600

Table 6. Data for X-ray Crystallographic Studies of $[Me_2InNH(t\text{-}Bu)]_2$

mol formula	$C_{12}H_{32}In_2N_2$
M_r	434.0
cryst syst	monoclinic
space group	$P2_1/n$ (No. 14)
a, Å	7.005(3)
b, Å	12.109(4)
c, Å	11.114(5)
α, deg	90
β, deg	94.16(3)
γ, deg	90
V, Å^3	940.3(7)
D_{calcd}, g/cm^3	1.533
Z	2
μ(Mo Kα), mm^{-1}	2.402
T (K)	295
F(000)	432
2θ range, deg	6.0−50.0
h	−8 to +8
k	−14 to +14
l	−13 to +13
no. of rflns collected	6624
no. of indep rflns	1660 (R_{int} = 1.73%)
no. of rflns for refinement	1381 ($>6\sigma$)
weighting scheme, w^{-1}	$\sigma^2(F) + 0.0014F^2$
χ (secondary extinction)	0.0045(4)
T_{max}/T_{min}	0.5501/0.3532
no. of refined params	80
final R indices[a] (obsd data), %	
R	2.27
R_w	3.57
final R indices[a] (all data), %	
R	2.83
R_w	4.53
goodness of fit	0.88
largest, mean Δ/σ	0.002, 0.000
data to param ratio	17.3:1
largest diff peak, e Å^{-3}	0.91
largest diff hole, e Å^{-3}	−0.56

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

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.[27] The solution and refinement of the structures were performed by use of the SHELXTL program package.[28] The structures were refined by full-matrix least squares against F^2. Non-hydrogen atoms were refined in the anisotropic approximation. The hydrogen atoms were located from difference electron density Fourier syntheses. Hydrogen atoms were subsequently refined 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 $(Me_3CCH_2)_2In(acac)$ and $Me(Me_3CCH_2)In(acac)$. The positions of the hydrogen atom in the case of $Me_2In(acac)$ were refined with $U_{iso} = 1.5U_{eq}$ for CH_3 and with $U_{iso} = 1.2U_{eq}$ for the other hydrogen atoms. Data were corrected for absorption by using the Bruker AXS SADABS program that is a part of the SAINTPLUS package.[27]

(b) A crystal of size 0.9 × 0.3 × 0.13 mm of $[Me_2InNH(t\text{-}Bu)]_2$ was sealed in a thin-walled glass capillary and mounted on a Siemens R3m/V diffractometer. Unit cell parameters were obtained from a least-squares analysis of 50 automatically centered reflections.[29] The Laue symmetry (C_{2h}) indicated the monoclinic system, and the systematic absences established the space group as $P2_1/n$ (No. 14). A complete sphere of data was collected for $2\theta = 6.0-50.0°$. Data were corrected for the effects of absorption ($T = 0.3532-0.5501$) and for Lp factors. The 6624 reflections thus collected were reduced to a unique set of 1660 independent reflections with $R_{int} = 1.73\%$ for the four equivalent forms. Details are given in Table 6. All crystallographic calculations were carried out by use of the SHELXPLUS (release 4.11 (VMS)) program package.[30] The analytical scattering factors for neutral atoms were corrected for $\Delta f'$ and $\Delta f''$ components of anomalous dispersion.[31] The structure was solved with a Patterson map and a difference Fourier synthesis and was refined to $R = 2.27\%$ for those 1381 reflections with $F_o > 6\sigma(F_o)$ and $R = 2.83\%$ for all 1660 independent reflections.

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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 four compounds studied (these data are also available as CIF files) and text giving ^1H NMR spectral data for reactions between $Me_2In(C_5H_5)$ and $HPPh_2$, $Me_2In(C_5H_5)$ and $H_2N(t\text{-}Bu)$, $Me_2InNH(t\text{-}Bu)$ and C_5H_6, $Me_2In(C_5H_5)$ and H(acac), $Me_2In(acac)$ and $(Me_3CCH_2)_2In(acac)$ as well as for $In(acac)_3$ and $InMe_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(31) (a) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. 4, pp 99−101. (b) *Ibid.*, pp 149−150.