Organometallics 1990, 9, 2488–2492

Phenyl rings were refined as isotropic rigid groups (C–C = 1.395 Å). All hydrogens, except that bonded to C(9), were introduced into calculations in constrained geometry (C–H = 0.97 Å). H(C9) was allowed to vary with a fixed U value of 0.06 Å^2. All H isotropic thermal parameters were first refined; then, from the found values, they were kept fixed to 0.07 Å^2 for methyls, 0.06 Å^2 for ethyls, and 0.065 Å^2 for other groups. All other atoms were refined anisotropically. The atomic scattering factors used were those proposed by Cromer and Waber[14] with anomalous dispersion effects[15] and those by Stewart et al.[16] for H atoms.

The final full-matrix least-squares refinement converged to $R = \sum||F_o| - |F_c||\sum|F_o| = 0.031$ and $R_w = [(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.032$ with $w = [\sigma^2(F_o) + 0.01F_o^2]^{-1}$. The error in an observation of unit weight was $S = [\sum w(|F_o| - |F_c|)^2/(n - m)]^{1/2} = 1.13$ with $n = 3226$ observations and $m = 292$ variables. An analysis of variance showed no unusual trends. In the last cycle of refinement the maximum parameter shift/esd was 0.4 (a H parameter). A final difference Fourier map showed a residual electron density of 0.3 e/Å^3 near F atoms. The final fractional atomic coordinates are listed in Table III.

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Supplementary Material Available: Tables of hydrogen atom coordinates, thermal parameters, and bond lengths and angles (4 pages); a listing of structure factors (16 pages). Ordering information is given on any current masthead page.

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Reagents Based on Cyclopentadienyl Derivatives of the Group 14 Elements for the Synthesis of Indium(I) Derivatives. Crystal and Molecular Structure of In($C_5H_4SiMe_3$)

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Cyclopentadienyl trimethyl derivatives of the group 14 elements ($C_5H_4MMe_3$, M = Si, Ge, Sn) have been investigated for their effects on indium(I) chemistry. The compounds In($C_5H_4SiMe_3$) and In($C_5H_4GeMe_3$) have been prepared from the corresponding lithium cyclopentadienyl reagent $LiC_5H_4MMe_3$ and InCl. Characterization data have included partial elemental analyses (C, H), physical properties, IR and ^{1}H NMR spectroscopic data, oxidation reactions with dilute aqueous HCl, and a single-crystal X-ray structural study in the case of In($C_5H_4SiMe_3$). When cyclopentadienyltrimethyltin, $C_5H_5SnMe_3$, was combined with InCl in diethyl ether, In(C_5H_5) and Me_3SnCl were formed in good yields. In($C_5H_4SiMe_3$) crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ (C_{2h}^5; No. 14) with a = 9.171 (5) Å, b = 9.910 (6) Å, c = 11.677 (7) Å, β = 97.30 (5)°, V = 1052.6 (11) Å^3, and Z = 4. Diffraction data (Mo Kα radiation, 2θ = 4.5–50.0°) were collected on a Syntex P2$_1$ automated four-circle diffractometer, and the structure was solved and refined to R_F = 5.0% and R_{wF} = 4.0% for all 1851 independent reflections (R_F = 3.1% and R_{wF} = 3.5% for those 1336 data with $|F_o| > 6\sigma|F_o|$)). The solid-state structure consists of infinite zigzag chains of $[In(C_5H_4SiMe_3)]_\infty$. Each indium atom interacts with two η^5-$C_5H_4SiMe_3$ ligands with a centroid···In···centroid angle of 131.78°, and each η^5-$C_5H_4SiMe_3$ ligand is linked to two indium atoms with In···centroid···In angles of 175.94°. There are no short interstrand In···In interactions, the shortest such distance being 5.428 Å. Thus, In($C_5H_4SiMe_3$) is the first cyclopentadienylindium(I) derivative with no apparent indium–indium interactions.

Introduction

The low-oxidation-state compounds of the group 13 elements provide the focus for an interesting area of research. The cyclopentadienylindium(I) derivatives In(C_5H_5)[1] and In(C_5H_4Me)[1] exist in the solid state as zigzag chains but with slightly different structures. The packing of the In(C_5H_5) units leads to a structure in which each indium atom is 3.986 (1) Å away from two other indium atoms. The structure of In(C_5H_4Me) has one indium atom at 3.986 (1) Å from only one other indium atom. The compound In[$C_5(CH_2Ph)_5$][3] forms quasi-dimeric units with indium–indium distances of 3.631 (2) Å, the shortest observed to date. It is noteworthy that the pentamethylcyclopentadienyl moiety in In(C_5Me_5)[4] leads to apparent hexameric clusters in the solid state with indium–indium distances of 3.963 (1) and 3.943 (1) Å. These observations suggest that the nature of the cyclopentadienyl moiety influences the number of indium–indium interactions per indium atom. There are no two cyclopentadienylindium(I) derivatives that have identical structures. It is of significance to realize that the interactions between the indium atoms are apparently weak. Only monomeric species have been observed by electron diffraction techniques for the gas phase of In(C_5H_5),[1] In(C_5H_4Me),[1] and In(C_5Me_5).[4a] The gas-phase structure of In[$C_5(CH_2Ph)_5$] has not been reported. Thus, in order to learn more about the factors that

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affect the structures of cyclopentadienylindium(I) derivatives, we considered it important to investigate the effects of a series of related substituents such as $SiMe_3$, $GeMe_3$, and $SnMe_3$. During the course of this study, the synthesis of $In(C_5H_4SiMe_3)$ was reported.[5]

This paper serves to report on the preparation and properties of $In(C_5H_4SiMe_3)$ and $In(C_5H_4GeMe_3)$ as well as on the crystal and molecular structure of $In(C_5H_4SiMe_3)$. It is regrettable that crystals of $In(C_5H_4GeMe_3)$ were unsuitable for an X-ray structural study. When an attempt was made to prepare the tin analogue $In(C_5H_4SnMe_3)$, transfer of the cyclopentadienyl group from tin to indium was observed. Thus, a new synthetic route to cyclopentadienylindium(I) from $Me_3SnC_5H_5$ and InCl was discovered. The synthesis of $In(C_5H_4SnMe_3)$ has not been realized to date.

Experimental Section

All compounds described in this investigation were extremely sensitive to oxygen and water and were manipulated in a standard vacuum line or under a purified argon atmosphere by using a Vacuum Atmospheres Dri-Lab. The cyclopentadienylindium(I) derivatives were so exceedingly sensitive to trace quantities of moisture that all glassware used for their preparation, characterization, and handling was flame-heated under dynamic vacuum and then permitted to stand in the drybox for approximately 2 h prior to use. All solvents were purified before use. Indium(I) chloride was purchased from Strem Chemicals, Inc., and was used without further purification. The reagents LiC_5H_5[1] and $Me_3Sn(C_5H_5)$[6] were prepared as previously described. Since the purity of the cyclopentadienyl reagents $Li(C_5H_4SiMe_3)$ and $Li(C_5H_4GeMe_3)$ is critical for the synthesis of the indium(I) compound, their preparation is described in this section. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY. Infrared spectra of Nujol mulls were recorded with a Perkin-Elmer 683 spectrometer. Absorption intensities are reported with the abbreviations w (weak), m (medium), s (strong), sh (shoulder), br (broad), and v (very). The ^1H NMR spectra were recorded immediately after sample preparation at 300 MHz with a Varian Gemini-300 NMR spectrometer. Chemical shifts are reported in δ units (ppm) and are referenced to $SiMe_4$ at δ 0.00 and benzene at δ 7.13. All NMR tubes were sealed under vacuum.

Synthesis of $Li(C_5H_4SiMe_3)$.[6] A small reaction tube was charged with 2.7 mL of previously dried and degassed Me_3SiCl (29 mmol) and was attached to a two-neck round-bottom flask that contained 1.46 g of $Li(C_5H_5)$ (20.2 mmol) and 40 mL of THF. Me_3SiCl was slowly added to $Li(C_5H_5)$/THF at room temperature over a 20-min period. After 16 h of vigorous stirring, the solution became orange. THF and the product, $Me_3SiC_5H_5$, were removed from the LiCl and transferred to a clean flask by vacuum distillation. Another reaction tube that contained 8.4 mL of 2.5 M $LiBu^n$ (21 mmol) was connected to the new flask, which contained the $Me_3SiC_5H_5$ and THF. The lithiating reagent was then added very slowly at −78 °C to $Me_3SiC_5H_5$. The solution was slowly (2 h) warmed to room temperature and stirred for 12 h. The excess $LiBu^n$ was separated from the white solid product with pentane by using normal washing procedures to leave 2.64 g of $Li(C_5H_5SiMe_3)$ (18.3 mmol, 90.7% yield based on $Li(C_5H_5)$).

Synthesis of $In(C_5H_4SiMe_3)$. A dumper was charged with 0.879 g of InCl (5.85 mmol) and was attached to a two-neck round-bottom flask that contained 0.906 g of $Li(C_5H_4SiMe_3)$ (7.93 mmol). After the distillation of 25 mL of diethyl ether, InCl was slowly added at room temperature. Twelve hours later, the solution was light gray. The solvent was removed, and the reaction flask was fitted with a glass elbow, which was connected to a 100-mL round-bottom flask. The product, $In(C_5H_4SiMe_3)$, was separated from LiCl by sublimation at 25 °C under dynamic vacuum into a receiving flask at −196 °C. The product was transferred to a straight-tube sublimator, where the compound was sublimed at 27 °C up the walls of the tube. The product, $In(C_5H_4SiMe_3)$, was isolated in 91.3% yield (1.34 g, 5.34 mmol) based on InCl. Crystallographic-quality crystals were obtained by very slow sublimation in a narrow (8-mm) glass tube at 27 °C: colorless crystalline solid; mp 51.4–51.8 °C; sublimed at 27 °C (0.001 mmHg). ^1H NMR (benzene-d_6): δ 6.13 (s, 4 H, C_5H_4), 0.27 (s, 9 H, Me_3). FTIR (Nujol mull, cm^{-1}): 1300 (w), 1246 (s), 1182 (sh), 1172 (s), 1035 (s), 901 (s), 834 (s), 771 (s), 752 (sh), 690 (w), 629 (m), 412 (m), 317 (m), 300 (sh). Anal. Calcd: C, 38.12; H, 5.20. Found: C, 38.01; H, 5.31. $In(C_5H_4SiMe_3)$ is not pyrophoric, but the compound is extremely sensitive to oxygen and water.

Hydrolysis of $In(C_5H_4SiMe_3)$. A known quantity of $In(C_5H_4SiMe_3)$ (0.213 g, 0.845 mmol) was placed in a 100-mL round-bottom flask. This flask was evacuated while at −196 °C, and then ~20 mL of 3 M HCl was added. The compound immediately decomposed to indium metal upon exposure to aqueous acid. Then, the metal apparently reacted with the acid. The hydrolysis was allowed to proceed for 3 days at ~100 °C. The noncondensable gas was isolated and measured by means of a Töpler pump–gas buret assembly. The volume of H_2 collected, 15.35 cm^3 of H_2 at STP, (0.733 mmol) corresponds to a 86.72% yield based on the oxidation of indium(I) to indium(III) with formation of 1 mol of H_2/mol of indium(I).

Synthesis of $Me_3GeC_5H_5$. The procedure by Davison and Rakita[6] for the preparation of (trimethylgermyl)cyclopentadiene was modified slightly. A two-neck Solv-Seal flask that was charged with 0.295 g of $Li(C_5H_5)$ (4.10 mmol) was equipped with a small dumper tube charged with 0.590 g of Me_3GeBr (2.98 mmol). The reactants were mixed together after 25 mL of Et_2O was distilled into the flask. The mixture was refluxed for 6 h. The resulting solution containing (trimethylgermyl)cyclopentadiene was used without purification for the preparation of $Li(C_5H_4GeMe_3)$.

Synthesis of $Li(C_5H_4GeMe_3)$. A flask that was equipped with a small tube containing 1.2 mL of 2.5 M $LiBu^n$ was charged with the diethyl ether solution of $Me_3GeC_5H_5$ from the above reaction. After the solution was cooled to −78 °C, the $LiBu^n$ solution was added. The mixture was warmed to room temperature and was stirred for 12 h. Diethyl ether was removed then by vacuum distillation. The resulting product was washed with pentane to leave 0.510 g of $Li(C_5H_4GeMe_3)$ as a colorless solid (2.70 mmol, 90.6% yield based on Me_3GeBr). ^1H NMR (THF-d_8): δ 0.21 (s, Me_3), 5.85 (s, ring H). ^{13}C NMR (THF-d_8): δ 0.02 (s, Me_3), 107 (d, ring H). FTIR (Nujol mull, cm^{-1}): 3078 (w), 1231 (w), 1159 (w), 1053 (vw), 1033 (m), 862 (vw), 829 (m), 766 (vs), 755 (sh), 655 (w), 594 (m), 570 (w), 506 (m, br).

Synthesis of $In(C_5H_4GeMe_3)$. A small dumper that was charged with 1.23 g of InCl (8.19 mmol) was connected to a two-neck flask containing 1.55 g of $Li(C_5H_4GeMe_3)$ (8.22 mmol). The assembly was evacuated, and 25 mL of dry diethyl ether was distilled into the flask. After the mixture of Et_2O and $Li(C_5H_4GeMe_3)$ reached room temperature, InCl was added, all at once. The mixture immediately turned gray (possibly due to the formation of indium metal). This mixture was stirred in the dark for 19 h, after which time the mixture was dark gray. Ether was quickly removed at 0 °C. In an inert-atmosphere glovebox, an 80° glass elbow connected to a clean Schlenk flask was attached to the two-neck reaction flask. The clean Schlenk flask was placed in a −196 °C bath and then was evacuated. Then, the impure product was dynamically sublimed from the reaction flask into the clean Schlenk flask. The product was transferred to a straight tube and sublimed at 38 °C. This slow sublimation provided colorless, needlelike crystals. ((Trimethylgermyl)cyclopentadienyl)indium(I) (2.18 g, 7.35 mmol) was isolated in 89.4% yield based on InCl: colorless crystalline solid; mp 50.0–52.0 °C, ~120 °C yellow color formed, ~220 °C opaque yellow liquid observed. Attempts to grow crystals of $In(C_5H_4GeMe_3)$ of appropriate quality for an X-ray diffraction study were unsuccessful. Hydrolysis: 0.927 mol of H_2/mol of $In(C_5H_4GeMe_3)$. ^1H NMR (benzene-d_6): δ 0.30 (s, Me_3), 6.05 (t, ring H), 6.13 (t, ring H). FTIR (Nujol mull, cm^{-1}): 1304 (w), 1233 (m), 1159 (m), 1029 (m), 823 (vs), 768 (s), 599 (m), 570 (m). Anal. Calcd: C, 32.40; H, 4.42. Found: C, 32.03; H, 4.66. MS (EI, 70 eV; m/z relative intensities): 115, 100, In^+; 283, 60 $M^+ - Me$; 298, 45, M^+.

Collection of X-ray Diffraction Data for $In(C_5H_4SiMe_3)$. The crystal chosen for the X-ray diffraction study (dimensions ~0.07 × 0.3 × 0.7 mm) was cut from a larger transparent colorless

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Table I. Experimental Data for the X-ray Diffraction Study of $In(C_5H_4SiMe_3)$

(A) Crystal Parameters at 21 °C (294 K)

cryst syst: monoclinic
space group: $P2_1/c$ (No. 14)
$a = 9.171$ (5) Å
$Z = 4$
$b = 9.910$ (6) Å
formula: $C_8H_{13}InSi$
$c = 11.677$ (7) Å
mol wt: 252.1
$\beta = 97.30$ (5)°
D(calcd) = 1.59 g/cm^3
$V = 1052.6$ (11) Å^3

(B) Measurement of Intensity Data

diffractometer: Syntex $P2_1$
radiation: Mo $K\bar{\alpha}$ ($\bar{\lambda}$ = 0.710 730 Å)
monochromator: pyrolytic graphite (2θ = 12.2°), equatorial mode; assumed 50% perfect/50% ideally mosaic for polarizn cor
rflns measd: $+h,+k,\pm l$ for 2θ = 4.5–50.0° at 6.0 deg/min in 2θ; 1972 rflns measd, yielding 1851 unique data ($R(I)$ = 2.19%, $R(wI)$ = 2.68% for 121 pairs of equiv rflns ($0kl$ and $0k\bar{l}$))
bkgds: stationary cryst and counter at each end of 2θ scan, each for $^1/_4$ of total scan time
std rflns: three approx mutually orthogonal rflns collected before each batch of 97 data points; neither decay nor signif fluctuations obsd
abs cor: μ(Mo $K\bar{\alpha}$) = 22.8 cm^{-1}, corrected empirically by interpolation (both in 2θ and ϕ) between five normalized close-to-axial ψ scans: 140 (2θ = 17.06°, T_{min}/T_{max} = 0.644); 051 (20.92°, 0.633); 06$\bar{1}$ (25.05°, 0.605); 171 (29.66°, 0.627), 081 (33.47, 0.624)

Table II. Final Positional Parameters for $In(C_5H_4SiMe_3)$

atom	x	y	z	B, Å^2
In	0.94501 (4)	0.71987 (4)	0.65988 (3)	
Si	0.68835 (15)	0.46133 (13)	0.80110 (11)	
C(1)	0.88131 (48)	0.47293 (38)	0.76904 (31)	
C(2)	1.00158 (51)	0.53503 (42)	0.83774 (32)	
C(3)	1.12870 (51)	0.52320 (46)	0.78152 (38)	
C(4)	1.09044 (55)	0.45424 (47)	0.67808 (39)	
C(5)	0.93896 (52)	0.42215 (42)	0.66932 (33)	
C(6)	0.65883 (80)	0.30812 (62)	0.88825 (71)	
C(7)	0.64672 (75)	0.60960 (61)	0.88768 (66)	
C(8)	0.56354 (77)	0.45594 (83)	0.66212 (60)	
H(2)	0.9977	0.5769	0.9117	4.8 (10)
H(3)	1.2263	0.5579	0.8093	4.8 (10)
H(4)	1.1553	0.4315	0.6230	4.8 (10)
H(5)	0.8836	0.3758	0.6055	4.4 (10)
H(6A)	0.5604	0.3034	0.9065	8.8 (17)
H(6B)	0.6823	0.2278	0.8515	11.0 (23)
H(6C)	0.7227	0.3122	0.9629	12.3 (28)
H(7A)	0.5486	0.6062	0.9070	9.2 (18)
H(7B)	0.7122	0.6112	0.9608	12.4 (27)
H(7C)	0.6605	0.6917	0.8490	6.6 (15)
H(8A)	0.4653	0.4520	0.6761	16.9 (37)
H(8B)	0.5779	0.5381	0.6194	11.5 (25)
H(8C)	0.5876	0.3818	0.6175	10.5 (22)

plate. It was sealed into a thin-walled glass capillary. The crystal was mounted and accurately aligned on a Syntex $P2_1$ automated four-circle diffractometer with its extended direction close to coincident with the ϕ axis. Subsequent setup operations and collection of the X-ray diffraction data were carried out as previously described;[7] details are collected in Table I.

Since the crystal was purported to be somewhat sensitive to UV/visible light, data were collected at a fairly high scan speed (6.0 deg/min in 2θ). The $2/m$ Laue symmetry and the systematic absences ($h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$) are compatible only with the centrosymmetric monoclinic space group $P2_1/c$ (C_{2h}^5; No. 14). All data were corrected for absorption, symmetry-equivalent reflections were averaged, and Lorentz and polarization factors were applied. Interestingly, no correction for crystal decay was necessary. A Wilson plot was used to place the data on an approximately absolute scale; it also provided the overall isotropic thermal parameter, $\bar{B}$ = 4.58 Å^2.

Solution and Refinement of the Structure of $In(C_5H_4SiMe_3)$. All calculations were performed by use of our locally modified version of the Syntex XTL interactive crystallographic program package. Throughout the analysis, calculated structure factors were based upon the analytical expressions for the scattering factors of the neutral atoms;[8a] corrections for both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion were included for all non-hydrogen atoms.[8b]

The function minimized in least-squares refinement processes was $\sum w(|F_o| - |F_c|)^2$, where $w = [\sigma(|F_o|)^2 + (0.015|F_o|)^2]^{-1}$. Discrepancy indices referred to below are defined in eq 1–3. In eq 3, NO = number of observations and NV = number of variables.

$$R_F\,(\%) = 100\sum||F_o| - |F_c||/\sum|F_o| \tag{1}$$

$$R_{wF}\,(\%) = 100[\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} \tag{2}$$

$$\mathrm{GOF} = [\sum w(|F_o| - |F_c|)^2/(\mathrm{NO} - \mathrm{NV})]^{1/2} \tag{3}$$

The coordinates of the indium atom were easily determined from a Patterson synthesis. The remaining non-hydrogen atoms were located from a difference-Fourier synthesis. Full-matrix least-squares refinement (anisotropic for all non-hydrogen atoms) led to convergence with R_F = 5.0%, R_{wF} = 4.0%, and GOF = 1.40 for all data (104 parameters refined against 1851 data). Discrepancy indices for those 1336 reflections with $|F_o| > 6\sigma(|F_o|)$ were R_F = 3.1% and R_{wF} = 3.5%.

Hydrogen atoms were not located directly but were input in calculated positions with d(C–H) = 0.95 Å[9] and the appropriate trigonal-planar or staggered-tetrahedral geometry. The isotropic parameters of these atoms were refined. An isotropic secondary extinction parameter was calculated from those data with $I_o > 2 \times 10^5$ counts, based upon the approximation to the Zachariasen correction shown in eq 4; the value determined for g was 3.2×10^{-8}.

$$|F_{o,cor}| = |F_{o,uncor}|(1.0 + gI_o) \tag{4}$$

The correctness of the structure was confirmed from a final difference-Fourier map, in which the strongest feature was a peak of height 0.75 e/Å^3 close to the position of the indium atom. An analysis of $\sum w\Delta^2$ as a function of parity or identity of Miller indices, $(\sin\theta)/\lambda$, $|F_o|$, or sequence number showed no anomalous features; the weighing scheme is thus appropriate.

Final atomic coordinates are collected in Table II.

Reaction of $Me_3SnC_5H_5$ with InCl. A side-arm dumper containing 0.254 g of InCl (1.69 mmol) was connected to a two-neck flask that contained 0.279 g of $Me_3SnC_5H_5$ (1.21 mmol). Approximately 25 mL of diethyl ether was distilled into the reaction flask. After the solution reached room temperature, InCl was added all at once. Interestingly, no indium metal formed. The reaction mixture was protected from light while being stirred vigorously for 12 h. The solvent was removed by vacuum distillation while at −20 °C. Cyclopentadienylindium(I) formed very fine, hairlike, yellow crystals, and chlorotrimethylstannane formed very thick, triangular-shaped, colorless crystals after all the solvent had been removed. Since Me_3SnCl was more volatile than $In(C_5H_5)$, Me_3SnCl was removed by sublimation to leave pure $In(C_5H_5)$. The indium(I) product was finally sublimed at 80 °C to a clean portion of the reaction flask. The pale yellow crystals of $In(C_5H_5)$ (0.131 g, 0.731 mmol) were obtained in 60.4% yield based on $Me_3SnC_5H_5$. $In(C_5H_5)$: pale yellow crystalline solid; mp 168.0–170.0 °C (lit.[1] mp 169.3–171.0 °C); sublimed at 80 °C, 0.001 mmHg; ^{1}H NMR (benzene-d_6) δ 5.95 (s) (lit.[1] 5.93 (s)). Me_3SnCl: colorless crystalline solid; mp 36.2–38.2 °C (lit.[10] 37 °C); sublimed at 25° C, 0.001 mmHg; ^{1}H NMR (benzene-d_6) δ 0.21 (s).

Results and Discussion

The indium(I) derivatives $In(C_5H_4SiMe_3)$ and $In(C_5H_4GeMe_3)$ have been prepared from InCl and the appropriate lithium cyclopentadienyl reagent ($LiC_5H_4SiMe_3$,

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Table III. Interatomic Distances (Å) and Angles (deg) for In(C$_5$H$_4$SiMe$_3$)^a

(A) In–C Distances			
In–C(1)	2.854 (4)	In–C(1)*	3.029 (4)
In–C(2)	2.769 (4)	In–C(2)*	3.161 (4)
In–C(3)	2.837 (5)	In–C(3)*	3.175 (5)
In–C(4)	2.947 (5)	In–C(4)*	3.039 (5)
In–C(5)	2.953 (4)	In–C(5)*	2.930 (4)
av	2.872	av	3.067
In···centroid	2.609	In···centroid*	2.822
(B) C–C Distances			
C(1)–C(2)	1.419 (6)	C(4)–C(5)	1.416 (7)
C(2)–C(3)	1.414 (6)	C(5)–C(1)	1.430 (6)
C(3)–C(4)	1.393 (6)		
		av	1.414
(C) Si–C Distances			
Si–C(1)	1.858 (5)	Si–C(7)	1.851 (7)
Si–C(6)	1.867 (7)	Si–C(8)	1.864 (7)
(D) C–In–C and C–C–C Angles			
C(1)–In–C(2)	29.19 (12)	C(5)–C(1)–C(2)	105.76 (35)
C(2)–In–C(3)	29.18 (13)	C(1)–C(2)–C(3)	109.21 (37)
C(3)–In–C(4)	27.80 (13)	C(2)–C(3)–C(4)	108.16 (40)
C(4)–In–C(5)	27.77 (12)	C(3)–C(4)–C(5)	108.01 (40)
C(5)–In–C(1)	28.45 (12)	C(4)–C(5)–C(1)	108.85 (38)
centroid-In-centroid*	131.78	In-centroid-In**	175.94
(E) C–Si–C and C–C–Si Angles			
C(1)–Si–C(6)	111.58 (26)	C(6)–Si–C(7)	107.08 (32)
C(1)–Si–C(7)	109.21 (26)	C(6)–Si–C(8)	109.63 (33)
C(1)–Si–C(8)	108.75 (27)	C(7)–Si–C(8)	110.59 (32)
C(2)–C(1)–Si	127.20 (31)	C(5)–C(1)–Si	127.04 (31)
(F) In···In Distances <6 Å			
In···In ($2 - x, -^1/_2 + y, 1^1/_2 - z$)	5.428		
In···In ($2 - x, ^1/_2 + y, 1^1/_2 - z$)	5.428		
In···In ($x, 1^1/_2 - y, -^1/_2 + z$)	5.869		
In···In ($x, 1^1/_2 - y, ^1/_2 + z$)	5.869		
In···In ($2 - x, 1 - y, 1 - z$)	5.908		

^{a} Symmetry transformations: single asterisk, $2 - x, ^1/_2 + y, ^1/_2 - z$; double asterisks, $2 - x, -^1/_2 + y, 1^1/_2 - z$.

LiC$_5$H$_4$GeMe$_3$) in diethyl ether by using a modification of the general procedure developed by Peppe, Tuck, and Victoriano.[11] In contrast, the cyclopentadienyltin reagent Me$_3$SnC$_5$H$_5$ reacts with InCl in diethyl ether to form In(C$_5$H$_5$) and Me$_3$SnCl. The two compounds In(C$_5$H$_4$SiMe$_3$) and In(C$_5$H$_4$GeMe$_3$) have been characterized by partial elemental analyses (C and H), physical properties, IR and ^{1}H NMR spectroscopic data, and oxidation reactions with dilute aqueous HCl. In addition, In(C$_5$H$_4$SiMe$_3$) has been studied by single-crystal X-ray diffraction techniques. The use of high-purity reagents and very clean, dry glassware lead to better than 90% yields of In(C$_5$H$_4$SiMe$_3$) and In(C$_5$H$_4$GeMe$_3$). Thus, the syntheses of In(C$_5$H$_4$SiMe$_3$) and In(C$_5$H$_4$GeMe$_3$) from the corresponding lithium cyclopentadienyl reagents provide the highest percent yield of any cyclopentadienylindium(I) derivative that has been prepared to date, including In(C$_5$H$_5$),[1] In(C$_5$H$_4$Me),[1] In(C$_5$Me$_5$),[4] and In[C$_5$(CH$_2$Ph)$_5$].[3] It is of significance to note that In(C$_5$H$_4$SiMe$_3$) has proven to be the compound which can be prepared and manipulated either as the pure compound or in solution with the least apparent decomposition.

The structure of In(C$_5$H$_4$SiMe$_3$) consists of (theoretically) infinite zigzag chains based on [In(C$_5$H$_4$SiMe$_3$)]$_\infty$. The labeling of atoms in the basic In(C$_5$H$_4$SiMe$_3$) unit is illustrated in Figure 1. In the solid state each indium atom interacts with two (trimethylsilyl)cyclopentadienyl ligands (∠centroid···In···centroid ($2 - x, ^1/_2 + y, ^1/_2 - z$) = 131.78°) and each cyclopentadienyl ligand is "inversely sandwiched" between two indium atoms (∠In···centroid···In ($2 - x, -^1/_2 + y, 1^1/_2 - z$) = 175.94°) (see Figure 2).

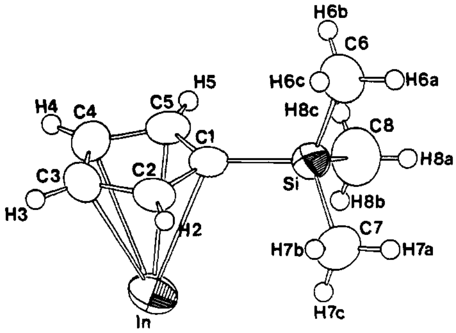

Figure 1. Labeling of atoms in the basic asymmetric unit of In(C$_5$H$_4$SiMe$_3$) (ORTEP diagram; 30% ellipsoids, with hydrogen atoms artificially reduced).

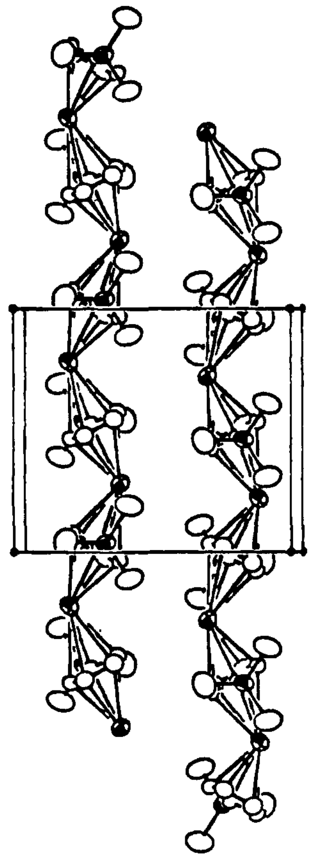

Figure 2. Packing diagram for In(C$_5$H$_4$SiMe$_3$) showing the infinite zigzag chains (*b* is vertical and *c* is horizontal). Only indium and silicon atoms are shaded. Hydrogen atoms are omitted for clarity.

The basic carbocyclic ring, defined by atoms C(1) through C(5), is associated with In–C distances of 2.837 (5)–2.953 (4) Å (average 2.872 Å) and an In···centroid distance of 2.609 Å. The second carbocyclic ring (atoms C(1)*–C(5)*; related to the basic asymmetric unit by the transformation $2 - x, ^1/_2 + y, 1^1/_2 - z$ (i.e., a 2_1 axis)) is associated with In–C* distances of 2.930 (4)–3.175 (5) Å (average 3.067 Å) and an In···centroid* distance of 2.822 Å. These distances may be compared to those in the related zigzag polymers (InC$_5$H$_5$)$_\infty$ (In–C = 2.853 (22)–3.091 (21) Å, In–C* = 2.863 (20)–2.983 (17) Å, In···centroid = 2.726 Å, In···centroid* = 2.687 Å)[1] and (InC$_5$H$_4$Me)$_\infty$ (In–C = 2.800 (5)–2.924 (5) Å, In–C* = 2.952 (5)–3.083 (5) Å, In···centroid = 2.609 Å, In···centroid* = 2.771 Å). Thus, differences between In–C and In–C* (or In···centroid and In···centroid*) distances increase in the order InC$_5$H$_5$ <

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[11] Peppe, C.; Tuck, D. G.; Victoriano, L. *J. Chem. Soc., Dalton Trans.* 1981, 2592.

$InC_5H_4Me < InC_5H_4SiMe_3$, i.e., the order of bulkiness of the substituent.

Unlike both $[InC_5H_5]_\infty$ (in which In···In (min) = 3.986 (1) Å) and $[InC_5H_4Me]_\infty$[1] (In···In (min) = 3.986 (1) Å), there are no close indium···indium contacts in $[InC_5H_4SiMe_3]_\infty$. The shortest such distances are In···In ($2 - x, -1/2 + y, 1^1/_2 - z$) and In···In ($2 - x, 1/2 + y, 1^1/_2 - z$) at equivalent distances of 5.428 Å. Thus, $In(C_5H_4SiMe_3)$ is the first cyclopentadienylindium(I) derivative with no apparent indium–indium interactions.

The $C_5H_4SiMe_3$ ligands show no unusual librational modes and are locked into the crystal lattice. Individual C–C bond lengths range from C(3)–C(4) = 1.393 (6) Å through C(5)–C(1) = 1.430 (6) Å, averaging 1.414 Å. The C(cyclopentadienyl)–Si distance is C(1)–Si = 1.858 (5) Å, and Si–C(Me) distances are Si–C(6) = 1.867 (7) Å, Si–C(7) = 1.851 (7) Å, and Si–C(8) = 1.864 (7) Å (average 1.858 Å). Angles at Si show no chemically significant deviations from the true tetrahedral value of 109.47°; thus, C(1)–Si–C(Me) = 108.75 (27)–111.58 (26)° and C(Me)–Si–C(Me) = 107.08 (32)–110.59 (32)°.

The existence of indium in the +1 oxidation state for $In(C_5H_4SiMe_3)$ and $In(C_5H_4GeMe_3)$ has been confirmed by their reactions with dilute, aqueous HCl. The ratio of mol of H_2/mol of indium(I) compound was 0.867 and 0.927 for $In(C_5H_4SiMe_3)$ and $In(C_5H_4GeMe_3)$, respectively. These experimental results are consistent with the balanced chemical equation

$$In(C_5H_4R) + 3H^+(aq) \rightarrow In^{3+}(aq) + H_2 + C_5H_5R$$

It is noteworthy that indium metal was formed as the initially observable product when the reagents were combined. Then, hydrogen formation was observed. Identical observations have been reported for the hydrolysis of $In(C_5H_5)$,[1] $In(C_5H_4Me)$,[1] and $In(C_5Me_5)$.[4]

The reaction of $Me_3SnC_5H_5$ with InCl in diethyl ether provides a new preparative route to $In(C_5H_5)$:

$$InCl(s) + Me_3SnC_5H_5 \xrightarrow{Et_2O} In(C_5H_5) + Me_3SnCl$$

This reaction is noteworthy because elemental indium is not observed. In contrast, gray indium metal was observed in all previous reactions, which used lithium cyclopentadienyl derivatives[1,3,4] as alkylating reagents for InCl. These observations suggest that $In(C_5H_5)$ is stable to decomposition to elemental indium in dry diethyl ether. The cyclopentadienyl anion might be the apparent reducing agent of $In(C_5H_5)$ or InCl. The cyclopentadienyl anion has been proposed as a reducing agent[12] during the synthesis of $In(C_5H_5)$ from $InCl_3$ and NaC_5H_5. The two products from the new reaction, $In(C_5H_5)$ and Me_3SnCl, were readily separated and characterized according to their physical properties and by ^1H NMR and IR spectroscopy. All experimental data agreed with literature values. The melting point of $In(C_5H_5)$ prepared by the new reaction was 168.0–170.0 °C (lit.[1] mp 169.3–171.0 °C). Similarly, the melting point of Me_3SnCl, 36.2–38.2 °C, was in good agreement with the literature[10] (37 °C). Thus, the Me_3SnCl elimination reaction is apparently analogous to the Me_3SiCl elimination reaction that has been used so successfully to prepare group 13–15 compounds such as $[Cl_2GaAs(CH_2SiMe_3)_2]_3$.[13]

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Supplementary Material Available: A table of anisotropic thermal parameters (1 page); a table of observed and calculated structure factor amplitudes (9 pages). Ordering information is given on any current masthead page.

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