

AD-A221 260

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE			Form Approved OMB No 0704-0188	
1a REPORT SECURITY CLASSIFICATION Unclassified		1b RESTRICTIVE MARKINGS		
2a SECURITY CLASSIFICATION AUTHORITY DTIC ELECTED		3 DISTRIBUTION/AVAILABILITY OF REPORT Distribution list enclosed		
2b DECLASSIFICATION/DOWNGRADING SCHEDULE MAY 08 1990		5 MONITORING ORGANIZATION REPORT NUMBER(S)		
4 PERFORMING ORGANIZATION REPORT NUMBER(S) 25		7a NAME OF MONITORING ORGANIZATION Office of Naval Research		
6a NAME OF PERFORMING ORGANIZATION State University of New York at Buffalo		7b ADDRESS (City, State, and ZIP Code) Department of the Navy Arlington, VA 22217		
6c ADDRESS (City, State, and ZIP Code) Department of Chemistry Buffalo, NY 14214		9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-90-J-1530		
8a NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research		10 SOURCE OF FUNDING NUMBERS		
8b OFFICE SYMBOL (If applicable)		PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.
8c ADDRESS (City, State, and ZIP Code) Department of the Navy Arlington, VA 22217		WORK UNIT ACCESSION NO. 4135002		
11. TITLE (Include Security Classification) Reagents Based on Cyclopentadienyl Derivatives of the Group 14 Elements for the Synthesis of Indium(I) Derivatives. Crystal and Molecular Structure of $In(C_5H_4SiMe_3)$				
12. PERSONAL AUTHOR(S) O. T. Beachley, Jr., J. F. Lees, T. E. Glassman, Melvyn Rowen Churchill and Lisa A. Buttrey				
13a TYPE OF REPORT Technical Report		13b TIME COVERED FROM _____ TO _____		14. DATE OF REPORT (Year, Month, Day) 30 April 1990
15 PAGE COUNT 25				
16 SUPPLEMENTARY NOTATION To be published in <u>Organometallics</u>				
17 COSATI CODES			18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	SUB-GROUP	Organoindium(I) compounds, cyclopentadienylindium(I) compounds, X-ray structural study, semiconductor precursors (SJS)	
19 ABSTRACT (Continue on reverse if necessary and identify by block number)				
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20 DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION Unclassified	
22a NAME OF RESPONSIBLE INDIVIDUAL O. T. Beachley, Jr.		22b TELEPHONE (Include Area Code) 716-831-3266		22c OFFICE SYMBOL

90 05 07 031

DISTRIBUTION STATEMENT A
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Distribution Unlimited

OFFICE OF NAVAL RESEARCH
Contract N-00014-90-J-1530
R&T Code 4135002
TECHNICAL REPORT NO. 25

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Prepared for Publication

in

Organometallics

State University of New York at Buffalo
Department of Chemistry
Buffalo, New York 14214

30, April 1990

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Contribution from the Department of Chemistry,
State University of New York at Buffalo, Buffalo, New York 14214

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Abstract

The cyclopentadienyltrimethyl derivatives of the group 14 elements ($\text{C}_5\text{H}_4\text{MMe}_3$, M=Si, Ge, Sn) have been investigated for their effects in indium(I) chemistry. The compounds $\text{In}(\text{C}_5\text{H}_4\text{SiMe}_3)$ and $\text{In}(\text{C}_5\text{H}_4\text{GeMe}_3)$ have been prepared from the corresponding lithium cyclopentadienyl reagent $\text{LiC}_5\text{H}_4\text{MMe}_3$ and InCl . Characterization data have included partial elemental analyses (C,H), physical properties, IR and ^1H NMR spectroscopic data, oxidation reactions with dilute aqueous HCl and a single crystal X-ray structural study in the case of $\text{In}(\text{C}_5\text{H}_4\text{SiMe}_3)$. When cyclopentadienyltrimethyltin, $\text{C}_5\text{H}_5\text{SnMe}_3$, was combined with InCl in diethyl ether, $\text{In}(\text{C}_5\text{H}_5)$ and Me_3SnCl were formed in good yields. $\text{In}(\text{C}_5\text{H}_4\text{SiMe}_3)$ crystallizes in the centrosymmetric monoclinic space group $\text{P2}_1/\text{c}$ (C_{2h}^5 ; No. 14) with $a = 9.171(5)\text{\AA}$, $b = 9.910(6)\text{\AA}$, $c = 11.677(7)\text{\AA}$, $\beta = 97.30(5)^\circ$, $V = 1052.6(11)\text{\AA}^3$

and $Z = 4$. Diffraction data (Mo K α radiation, $2\theta = 4.5-50.0^\circ$) were collected on a Syntex P2₁ 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 $[\text{In}(\text{C}_5\text{H}_4\text{SiMe}_3)]_\infty$. Each indium atom interacts with two η^5 - $\text{C}_5\text{H}_4\text{SiMe}_3$ ligands with a centroid...In...centroid angle of 131.78° and each η^5 - $\text{C}_5\text{H}_4\text{SiMe}_3$ 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\AA . Thus, $\text{In}(\text{C}_5\text{H}_4\text{SiMe}_3)$ 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, $\text{In}(\text{C}_5\text{H}_5)^1$ and $\text{In}(\text{C}_5\text{H}_4\text{Me})^1$ exist in the solid state as zig-zag chains but with slightly different structures. The packing of the $\text{In}(\text{C}_5\text{H}_5)$ units leads to a structure in which each indium atom is 3.986(1)Å away from two other indium atoms. The structure of $\text{In}(\text{C}_5\text{H}_4\text{Me})$ has one indium atom at 3.986(1)Å from only one other indium atom. The compound $\text{In}[\text{C}_5(\text{CH}_2\text{Ph})_5]^3$ 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 $\text{In}(\text{C}_5\text{Me}_5)^4$ 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 which have the identical structure. 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 $\text{In}(\text{C}_5\text{H}_5)^1$, $\text{In}(\text{C}_5\text{H}_4\text{Me})^1$ and $\text{In}(\text{C}_5\text{Me}_5)^{4a}$. The gas phase structure of $\text{In}[\text{C}_5(\text{CH}_2\text{Ph})_5]$ has not been reported. Thus, in order to learn more about the factors which 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 $\text{In}(\text{C}_5\text{H}_4\text{SiMe}_3)$ was reported.⁵

This paper serves to report on the preparation and properties of $\text{In}(\text{C}_5\text{H}_4\text{SiMe}_3)$ and $\text{In}(\text{C}_5\text{H}_4\text{GeMe}_3)$ as well as on the crystal and molecular

structure of $\text{In}(\text{C}_5\text{H}_4\text{SiMe}_3)$. It is regrettable that crystals of $\text{In}(\text{C}_5\text{H}_4\text{GeMe}_3)$ were unsuitable for an X-ray structural study. When an attempt was made to prepare the tin analog $\text{In}(\text{C}_5\text{H}_4\text{SnMe}_3)$, transfer of the cyclopentadienyl group from tin to indium was observed. Thus, a new synthetic route to cyclopentadienylindium(I) from $\text{Me}_3\text{SnC}_5\text{H}_5$ and InCl was discovered. The synthesis of $\text{In}(\text{C}_5\text{H}_4\text{SnMe}_3)$ 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 in a purified argon atmosphere by using a Vacuum Atmospheres Dri-Lab.⁷ The cyclopentadienylindium(I) derivatives were so exceedingly sensitive to trace quantities of moisture that all glassware used for their preparation, characterization and handling were flame-heated under dynamic vacuum and then permitted to stand in the dry box for approximately 2h 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 $\text{Me}_3\text{Sn}(\text{C}_5\text{H}_5)$ ⁶ were prepared as previously described. Since the purity of the cyclopentadienyl reagents $\text{Li}(\text{C}_5\text{H}_4\text{SiMe}_3)$ and $\text{Li}(\text{C}_5\text{H}_4\text{GeMe}_3)$ is critical for the synthesis of the indium(I) compound, their preparation is described in the Experimental Section. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY. Infrared spectra of Nujol mulls were recorded by means of a Perkin-Elmer 683 spectrometer. Absorption intensities are reported with 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 by means of a Varian Gemini-300 NMR spectrometer. Chemical shifts are reported in δ units (ppm) and are referenced to SiMe_4 as δ 0.00 and benzene as δ 7.13. All NMR tubes were sealed under vacuum.

Synthesis of $\text{Li}(\text{C}_5\text{H}_4\text{SiMe}_3)$ 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 which contained 1.46 g of $\text{Li}(\text{C}_5\text{H}_5)$ (20.2 mmol) and 40 mL of THF. The

Me_3SiCl was slowly added to $\text{Li}(\text{C}_5\text{H}_5)/\text{THF}$ at room temperature over a 20 minute period. After 16 hours of vigorous stirring, the solution became orange. The THF and the product, $\text{Me}_3\text{SiC}_5\text{H}_5$, were removed from the LiCl and transferred to a clean flask by vacuum distillation. Another reaction tube which contained 8.4 mL of 2.5 M LiBu^{n} (21 mmol) was connected to the new flask which contained the $\text{Me}_3\text{SiC}_5\text{H}_5$ and THF. The lithiating reagent was then added very slowly at -78°C to $\text{Me}_3\text{SiC}_5\text{H}_5$. The solution was slowly (2h) warmed to room temperature and stirred for 12h. The excess LiBu^{n} was separated from the white solid product with pentane by using normal washing procedures to leave 2.64 g of $\text{Li}(\text{C}_5\text{H}_5\text{SiMe}_3)$, 18.3 mmol, 90.7% yield based on $\text{Li}(\text{C}_5\text{H}_5)$.

Synthesis of $\text{In}(\text{C}_5\text{H}_4\text{SiMe}_3)$

A dumper was charged with 0.879 g of InCl (5.85 mmol) and was attached to a two-neck round bottom flask which contained 0.906 g of $\text{Li}(\text{C}_5\text{H}_4\text{SiMe}_3)$ (7.93 mmol). After the distillation of 25 mL of diethyl ether, the InCl was slowly added at room temperature. Twelve hours later, the solution was light gray in color. 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, $\text{In}(\text{C}_5\text{H}_4\text{SiMe}_3)$, was separated from the 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, $\text{In}(\text{C}_5\text{H}_4\text{SiMe}_3)$, was isolated in a 91.3% yield (1.34 g, 5.34 mmol) as based on InCl . Crystallographic quality crystals were obtained by very slow sublimation in a narrow (8 mm) glass tube at 27°C .

$\text{In}(\text{C}_5\text{H}_4\text{SiMe}_3)$: 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: \bar{C} , 38.12; H, 5.20. Found: C, 38.01; H, 5.31. $\text{In}(\text{C}_5\text{H}_4\text{SiMe}_3)$ is not pyrophoric, but the compound is extremely sensitive to oxygen and water.

Hydrolysis of $\text{In}(\text{C}_5\text{H}_4\text{SiMe}_3)$

A known quantity of $\text{In}(\text{C}_5\text{H}_4\text{SiMe}_3)$, 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 3M 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 Töepler pump-gas burette assembly. The volume of H_2 collected, 15.35 cm^3 H_2 at STP, (0.733 mmol) corresponds to a 86.72% yield as based on the oxidation of indium(I) to indium(III) with formation of one mole of H_2 per mole of indium(I).

Synthesis of $\text{Me}_3\text{GeC}_5\text{H}_5$

The procedure by Davison and Rakita⁶ for the preparation of trimethylgermylcyclopentadiene was modified slightly. A two-neck Solv-SealTM flask which was charged with 0.295 g of $\text{Li}(\text{C}_5\text{H}_5)$ (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 $\text{Li}(\text{C}_5\text{H}_4\text{GeMe}_3)$.

Synthesis of $\text{Li}(\text{C}_5\text{H}_4\text{GeMe}_3)$

A flask which was equipped with a small tube containing 1.2 mL of 2.5 M LiBu^n was charged with the diethyl ether solution of $\text{Me}_3\text{GeC}_5\text{H}_5$ 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. The diethyl ether was removed then by vacuum distillation. The resulting product was washed with pentane to leave 0.510 g of $\text{Li}(\text{C}_5\text{H}_4\text{GeMe}_3)$ (2.70 mmol, 90.6% yield as based on Me_3GeBr).

$\text{Li}(\text{C}_5\text{H}_4\text{GeMe}_3)$: Colorless solid. ^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 (w), 1053 (vw), 1033 (m), 862 (vw), 829 (m), 766 (vs), 755 (sh), 655 (w), 594 (m), 570 (w), 506 (m, br).

Synthesis of $\text{In}(\text{C}_5\text{H}_4\text{GeMe}_3)$

A small dumper which was charged with 1.23 g of InCl (8.19 mmol) was connected to a two-neck flask containing 1.55 g of $\text{Li}(\text{C}_5\text{H}_4\text{GeMe}_3)$ (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 $\text{Li}(\text{C}_5\text{H}_4\text{GeMe}_3)$ reached room temperature, the InCl was added, all at once. The mixture immediately turned grey (possibly due to the formation of indium metal). This mixture was allowed to stir in the dark for 19 h, after which time the mixture was dark grey. The ether was quickly removed at 0°C . In an inert atmosphere glove box, 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 $-196\text{ }^{\circ}\text{C}$ 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 $38\text{ }^{\circ}\text{C}$. This slow sublimation provided colorless, needle-like crystals. Trimethylgermylcyclopentadienylindium(I) (2.18 g, 7.35 mmol) was isolated in 89.4% yield based on InCl. Attempts to grow crystals of $\text{In}(\text{C}_5\text{H}_4\text{GeMe}_3)$ of appropriate quality for an X-ray diffraction study were unsuccessful.

$\text{In}(\text{C}_5\text{H}_4\text{GeMe}_3)$: Colorless crystalline solid; mp $50.0 - 52.0\text{ }^{\circ}\text{C}$, $-120\text{ }^{\circ}\text{C}$ yellow color formed, $-220\text{ }^{\circ}\text{C}$ opaque yellow liquid observed. Hydrolysis: 0.927 mol of H_2 /mol of $\text{In}(\text{C}_5\text{H}_4\text{GeMe}_3)$. ^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 70eV (M/z, relative intensities): 115, 100, In^+ ; 283, 60, $m^+ - \text{Me}$; 298, 45, m^+ .

Collection of X-Ray Diffraction Data for $\text{In}(\text{C}_5\text{H}_4\text{SiMe}_3)$

The crystal chosen for the X-ray diffraction study (dimensions $\sim 0.07 \times 0.3 \times 0.7\text{ mm}$) was cut from a larger transparent colorless plate. It was sealed into a thin-walled glass capillary. The crystal was mounted and accurately aligned on a Syntex P2₁ automated four-circle diffractometer with its extended direction close to coincident with the ϕ -axis. Subsequent set-up operations and collection of the X-ray diffraction data were carried out as previously described;⁷ details are collected in Table 1.

Since the crystal was purported to be somewhat sensitive to u.v./visible light, data was collected at a fairly high scan speed (6.0 deg per min. in 2θ). The $2/m$ Laue symmetry and the systematic absences ($h0l$ for

$l = 2n + 1$ and $Ok0$ 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, $B = 4.58 \text{ \AA}^2$.

Solution and Refinement of the Structure of $\text{In}(\text{C}_5\text{H}_4\text{SiMe}_3)$

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 $w = [0(|F_o|)^2 + (0.015|F_o|)^2]^{-1}$. Discrepancy indices referred to below are defined in equations 1-3.

$$R_F(\%) = 100 \sum ||F_o| - |F_c|| / \sum |F_o| \quad (1)$$

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

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

In eqn 3, NO = number of observations and NV = number of variables.

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 $d(C-H) = 0.95\text{\AA}^9$ 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 eqn 4;

$$|F_{o,corr}| = |F_{o,uncorr}|(1.0 + gI_o) \quad (4)$$

the value determined for g was 3.2×10^{-8} .

The correctness of the structure was confirmed from a final difference-Fourier map on which the strongest feature was a peak of height $0.75 \text{ e}^-/\text{\AA}^3$ close to the position of the indium atom. An analysis of $\Sigma w\Delta^2$ 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 2.

Reaction of $\text{Me}_3\text{SnC}_5\text{H}_5$ with InCl

A side-arm dumper containing 0.254 g of InCl (1.69 mmol) was connected to a two-neck flask which contained 0.279 g of $\text{Me}_3\text{SnC}_5\text{H}_5$ (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 was protected from

light while being stirred vigorously for 12 hours. The solvent was removed by vacuum distillation while at $-20\text{ }^{\circ}\text{C}$. Cyclopentadienylindium(I) formed very fine hair-like 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 $\text{In}(\text{C}_5\text{H}_5)$, Me_3SnCl was removed by sublimation to leave pure $\text{In}(\text{C}_5\text{H}_5)$. The indium(I) product was finally sublimed at $80\text{ }^{\circ}\text{C}$ to a clean portion of the reaction flask. The pale yellow crystals of $\text{In}(\text{C}_5\text{H}_5)$ (0.131 g , 0.731 mmol) were obtained in 60.4% yield based on $\text{Me}_3\text{SnC}_5\text{H}_5$.

$\text{In}(\text{C}_5\text{H}_5)$: Pale yellow crystalline solid; mp $168.0 - 170.0\text{ }^{\circ}\text{C}$ (Lit.¹ $169.3 - 171.0\text{ }^{\circ}\text{C}$); Sublimed at $80\text{ }^{\circ}\text{C}$, 0.001 mmHg . $^1\text{H NMR}$ (benzene- d^6): δ 5.95 (s) (Lit.¹ 5.93 (s)). Me_3SnCl : Colorless crystalline solid; mp $36.2 - 38.2\text{ }^{\circ}\text{C}$ (Lit.¹⁰ $37\text{ }^{\circ}\text{C}$); sublimed at $25\text{ }^{\circ}\text{C}$, 0.001 mmHg . $^1\text{H NMR}$ (benzene- d^6): δ 0.21 (s).

Results and Discussion

The indium(I) derivatives $\text{In}(\text{C}_5\text{H}_4\text{SiMe}_3)$ and $\text{In}(\text{C}_5\text{H}_4\text{GeMe}_3)$ have been prepared from InCl and the appropriate lithium cyclopentadienyl reagent ($\text{LiC}_5\text{H}_4\text{SiMe}_3$, $\text{LiC}_5\text{H}_4\text{GeMe}_3$) in diethyl ether by using a modification of the general procedure developed by Peppe, Tuck and Victoriano.¹¹ In contrast, the cyclopentadienyl tin reagent, $\text{Me}_3\text{SnC}_5\text{H}_5$, reacts with InCl in diethyl ether to form $\text{In}(\text{C}_5\text{H}_5)$ and Me_3SnCl . The two compounds ($\text{In}(\text{C}_5\text{H}_4\text{SiMe}_3)$ and $\text{In}(\text{C}_5\text{H}_4\text{GeMe}_3)$) have been characterized by partial elemental analyses (C and H), physical properties, IR and ^1H NMR spectroscopic data and oxidation reactions with dilute aqueous HCl . In addition, $\text{In}(\text{C}_5\text{H}_4\text{SiMe}_3)$ 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 $\text{In}(\text{C}_5\text{H}_4\text{SiMe}_3)$ and $\text{In}(\text{C}_5\text{H}_4\text{GeMe}_3)$. Thus, the syntheses of $\text{In}(\text{C}_5\text{H}_4\text{SiMe}_3)$ and $\text{In}(\text{C}_5\text{H}_4\text{GeMe}_3)$ from the corresponding lithium cyclopentadienyl reagents provide the highest percent yield of any cyclopentadienylindium(I) derivative which has been prepared to date including $\text{In}(\text{C}_5\text{H}_5)$,¹ $\text{In}(\text{C}_5\text{H}_4\text{Me})$,¹ $\text{In}(\text{C}_5\text{Me}_5)$,⁴ $\text{In}[\text{C}_5(\text{CH}_2\text{Ph})_5]$.³ It is of significance to note that $\text{In}(\text{C}_5\text{H}_4\text{SiMe}_3)$ 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 $\text{In}(\text{C}_5\text{H}_4\text{SiMe}_3)$ consists of (theoretically) infinite zigzag chains based on $[\text{In}(\text{C}_5\text{H}_4\text{SiMe}_3)]_n$. The labelling of atoms in the basic $\text{In}(\text{C}_5\text{H}_4\text{SiMe}_3)$ unit is illustrated in Figure 1. In the solid state each indium atom interacts with two trimethylsilylcyclopentadienyl ligands [$\langle \text{centroid} \cdots \text{In} \cdots \text{centroid} (2-x, 1/2 + y, 1 1/2-z) = 131.78^\circ$] and each cyclopentadienyl ligand is "inversely sandwiched" between two indium atoms [$\langle \text{In} \cdots \text{centroid} \cdots \text{In} (2-x, -1/2 + y, 1 1/2-z) = 175.94^\circ$] (see Figure 2).

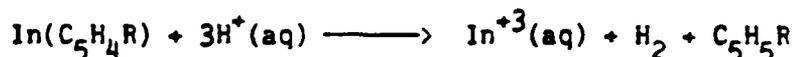
The basic carbocyclic ring, defined by atoms C(1) through C(5), is associated with In-C distances of 2.837(5)-2.953(4)Å (average = 2.872Å) and an In \cdots centroid distance of 2.609Å. The second carbocyclic ring (atoms C(1) * -C(5) * ; related to the basic asymmetric unit by the transformation $2-x, 1/2 + y, 1 1/2-z$ (i.e., a 2_1 axis)) is associated with In-C * distances of 2.930(4)-3.175(5)Å (average = 3.067Å) and an In \cdots centroid * distance of 2.822Å. These distances may be compared to those in the related zigzag polymers (InC₅H₅) $_{\infty}$ [In-C = 2.853(22)-3.091(21)Å, In-C * = 2.863(20)-2.983(17)Å, In \cdots centroid = 2.726Å, In \cdots centroid * = 2.687Å]¹ and (InC₅H₄Me) $_{\infty}$ [In-C = 2.800(5)-2.924(5)Å, In-C * = 2.952(5)-3.083(5)Å, In \cdots centroid = 2.609Å, In \cdots centroid * = 2.771Å]. Thus, differences between In-C and In-C * (or In \cdots centroid and In \cdots centroid *) distances increase in the order InC₅H₅ < InC₅H₄Me < InC₅H₄SiMe₃, i.e., the order of bulkiness of the substituent.

Unlike both [InC₅H₅] $_{\infty}$ (in which In \cdots In(min) = 3.986(1)Å) and [InC₅H₄Me] $_{\infty}$ ¹ (In \cdots In(min) = 3.986(1)Å), there are no close indium \cdots indium contacts in [InC₅H₄SiMe₃] $_{\infty}$. The shortest such distances are In \cdots In(2-x, -1/2 + y, 1 1/2 - z) and In \cdots In(2-x, + 1/2 + y, 1 1/2-z) at equivalent distances of 5.428Å. Thus, In(C₅H₄SiMe₃) is the first cyclopentadienylindium(I) derivative with no apparent indium-indium interactions.

The C₅H₄SiMe₃ 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 1.414Å. 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 = 1.858Å). Angles at Si show no chemically significant

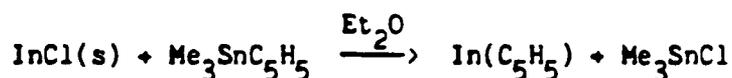
deviations from the true tetrahedral value of 109.47°; thus C(1)-Si-C(Me) = 108.75(27)-111.58(26)° and C(Me)-Si-C(Me) = 107.08(32)-110.59(32)°.

The existence of indium in the +1 oxidation state for $\text{In}(\text{C}_5\text{H}_4\text{SiMe}_3)$ and $\text{In}(\text{C}_5\text{H}_4\text{GeMe}_3)$ has been confirmed by their reactions with dilute, aqueous HCl. The ratio of mol H_2 /mol indium(I) compound was 0.867 and 0.927 for $\text{In}(\text{C}_5\text{H}_4\text{SiMe}_3)$ and $\text{In}(\text{C}_5\text{H}_4\text{GeMe}_3)$, respectively. These experimental results are consistent with the following balanced chemical equation.



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 $\text{In}(\text{C}_5\text{H}_5)$,¹ $\text{In}(\text{C}_5\text{H}_4\text{Me})$ ¹ and $\text{In}(\text{C}_5\text{Me}_5)$.⁴

The reaction of $\text{Me}_3\text{SnC}_5\text{H}_5$ with InCl in diethyl ether provides a new preparative route to InC_5H_5 . This reaction is noteworthy because elemental



indium is not observed. In contrast, grey 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 $\text{In}(\text{C}_5\text{H}_5)$ is stable to decomposition to elemental indium in dry diethyl ether. The cyclopentadienyl anion might be the apparent reducing agent of $\text{In}(\text{C}_5\text{H}_5)$ or InCl . The cyclopentadienyl anion has been proposed as a reducing agent¹² during the synthesis of $\text{In}(\text{C}_5\text{H}_5)$ from InCl_3 and NaC_5H_5 . The two products from the new reaction, $\text{In}(\text{C}_5\text{H}_5)$ 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 $\text{In}(\text{C}_5\text{H}_5)$ prepared by the new reaction was 168.0-170.0 °C (lit¹ 169.3-171.0 °C). Similarly, the melting point of Me_3SnCl , 36.2-38.2 °C, was in good agreement with the literature¹⁰ (37 °C). Thus, the Me_3SnCl elimination reaction is apparently analogous to the Me_3SiCl elimination reaction which has been used so successfully to prepare group 13-15 compounds such as $[\text{Cl}_2\text{GaAs}(\text{CH}_2\text{SiMe}_3)_2]_3$.¹³

Acknowledgement. This work was supported in part by the Office of Naval Research (O.T.B.). The authors also thank Professor Bruce M. Foxman for providing them with a copy of his IBM-PC version of the program ORTEP-II.

Supplementary Material Available. Tables of anisotropic thermal parameters and observed and calculated structure factor amplitudes (10 pages). For ordering information, see any current masthead page.

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TABLE 1

Experimental Data for the X-Ray Diffraction Study of
 $\text{In}(\text{C}_5\text{H}_4\text{SiMe}_3)$.

(A) Crystal Parameters at 21°C (294K)

Crystal system: monoclinic	Z = 4
Space group: $P2_1/c$ (No. 14)	formula = $\text{C}_8\text{H}_{13}\text{InSi}$
a = 9.171(5)Å	mol. wt = 252.1
b = 9.910(6)Å	D(calc'd) = 1.59 g/cm ⁻³
c = 11.677(7)Å	
β = 97.30(5)°	
V = 1052.6(11)Å ³	

(B) Measurement of Intensity Data

Diffractometer: Syntex P2₁

Radiation: Mo K α (λ 0.710730Å)

Monochromator: pyrolytic graphite (2θ = 12.2°), equatorial mode; assumed
50% perfect/50% ideally mosaic for polarization correction.

Reflections meas'd: +h, +k, \pm l for 2θ = 4.5-50.0° at 6.0 deg/min in 2θ ;
1972 reflections measured, yielding 1851 unique data
(R(I) = 2.19%, R(wI) = 2.68% for 121 pairs of
equivalent reflections ($Ok\bar{l}$ and $Ok\bar{l}$)).

Backgrounds: stationary crystal and counter at each end of 2θ scan, each
for 1/4 of total scan time.

Standard reflections: three approximately mutually orthogonal reflections
collected before each batch of 97 data points;

neither decay nor significant fluctuations were observed.

Absorption corrections: $\mu(\text{Mo } K\bar{\alpha}) = 22.8 \text{ cm}^{-1}$; corrected empirically by interpolation (both in 2θ and ϕ) between five normalized close-to-axial ϕ -scans: 140 ($2\theta = 17.06^\circ$, $T_{\min}/T_{\max} = 0.644$); 051 (20.92° , 0.633); 061 (25.05° , 0.605); 171 (29.66° , 0.627), 081 (33.47° , 0.624).

TABLE 2Final Positional Parameters for $\text{In}(\text{C}_5\text{H}_4\text{SiMe}_3)$.

ATOM	X	Y	Z	B, \AA^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)

TABLE 3

Interatomic Distances (Å) and Angles (°) for $\text{In}(\text{C}_5\text{H}_4\text{SiMe}_3)$

(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)
Average	2.872	Average	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)		
		Average	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-C 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 < 6Å.

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

*Atom transformation is

(2-x, +1/2 + y, 1/2-z)

**Atom transformation is

(2-x, -1/2 + y, 1 1/2-z)

CAPTIONS TO FIGURES

Figure 1.

Labelling of atoms in the basic asymmetric unit of $\text{In}(\text{C}_5\text{H}_4\text{SiMe}_3)$ (ORTEP diagram; 30% ellipsoids, with hydrogen atoms artificially reduced).

Figure 2.

Packing diagram for $\text{In}(\text{C}_5\text{H}_4\text{SiMe}_3)$ showing the infinite zigzag chains (b is vertical and c is horizontal). Only indium and silicon atoms are shaded.

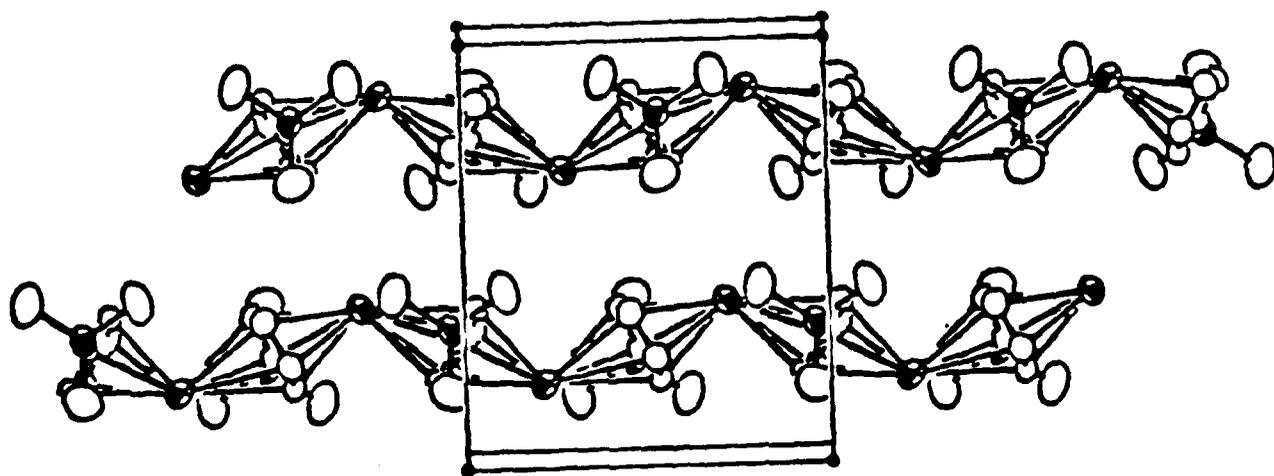


FIG. 2

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