Organometallics 1988, *7*, 1051–1059

Synthesis, Characterization, and Structural Studies of $In(C_5H_4Me)$ by X-ray Diffraction and Electron Diffraction Techniques and a Reinvestigation of the Crystalline State of $In(C_5H_5)$ by X-ray Diffraction Studies

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Received July 14, 1987

The compound $In(C_5H_4Me)$ has been prepared from InCl and $Li(C_5H_4Me)$ in diethyl ether and fully characterized according to its physical and solubility properties, reaction with dilute HCl, a cryoscopic molecular weight study in cyclohexane, infrared and ^1H NMR spectroscopic properties, an X-ray structural study, and a gas-phase electron diffraction study. In addition, a quantitative X-ray structural study has been used to reinvestigate the nature of the solid state of $In(C_5H_5)$. The compound $In(C_5H_4Me)$ crystallizes in the centrosymmetric space group $P2_1/n$ (No. 14, variation) with $a = 6.1636$ (14) Å, $b = 11.5684$ (17) Å, $c = 9.1723$ (15) Å, $\beta = 103.561$ (15)°, $V = 635.78$ (19) Å^3, and $Z = 4$. Diffractometer data (Mo Kα, $2\theta = 4.0$–$50.0°$) were collected, and the structure was refined to $R_F = 4.0\%$ and $R_{wF} = 3.9\%$ for all 1115 independent reflections. The parent compound $In(C_5H_5)$ crystallizes in the acentric monoclinic space group Cc (No. 9) with $a = 9.1480$ (2) Å, $b = 10.0875$ (19) Å, $c = 5.9116$ (25) Å, $\beta = 102.795$ (26)°, $V = 531.98$ (27) Å^3, and $Z = 4$. Diffractometer data (Mo Kα, $2\theta = 5.0$–$55.0°$) were collected, and the structure was refined to $R_F = 4.4\%$ and $R_{wF} = 5.3\%$ for all 1226 independent reflections. Each structure consists of zigzag chains of InCp units (Cp = C_5H_5 or C_5H_4Me) in which indium atoms interact with each side of the Cp ring and two Cp rings interact with each indium atom. For $In(C_5H_5)$, the centroid–In–centroid′ angle is 128.02°, the In–centroid–In′ angle is 176.99° (centroid = centroid of carbocyclic C_5 system), and In–C distances are 2.853 (22)–3.091 (21) Å; for $In(C_5H_4Me)$, the centroid–In–centroid′ angle is 130.66°, the In–centroid–In′ angle is 179.74°, and In–C distances are 2.800 (5)–2.924 (5) Å. Weak interchain In–In interactions at 3.986 (1) Å are observed for both $In(C_5H_5)$ and $In(C_5H_4Me)$, although they crystallize in different space groups. The molecular structure of $In(C_5H_4Me)$ in the gas-phase consists of discrete monomeric units with the indium(I) atom being situated above the ring centroid. The available data permit comparisons of the properties and structural parameters of $In(C_5H_5)$, $In(C_5H_4Me)$, and $In(C_5Me_5)$.

Introduction

The synthesis and characterization of organometallic derivatives of main-group elements in low oxidation states provide the focus for an interesting area of chemistry. In group 13 chemistry, derivatives which incorporate organic moieties which exhibit multihapto coordination have been described. The limited number of such compounds in indium chemistry can be separated into two general classes, cyclopentadienyl- and arene-type derivatives. Only two cyclopentadienyl indium(I) derivatives, $In(C_5H_5)$ and $In(C_5Me_5)$, have been fully characterized. The first compound[2] to be identified was $In(C_5H_5)$. A gas-phase structural study by electron diffraction techniques confirmed the existence of an "open-faced half-sandwich" structure in the vapor phase.[3] A semiquantitative X-ray diffraction study[4] suggested a zigzag polymeric chain of $In(\eta^5\text{-}C_5H_5)$ units in the solid state. In contrast, our recent structural study[5] of $In(C_5Me_5)$ revealed the presence of apparent octahedral clusters with indium atoms on the interior and $\eta^5\text{-}C_5Me_5$ units on the exterior. The only other indium(I) derivative to be described in the literature is $In(C_5H_4Me)$.[6] However, the compound's apparent ease of decomposition prevented characterization except for an indium analysis. Only one arene–indium(I) compound $(Me_3C_6H_3)_2In(InBr_4)$ has been prepared and fully characterized.[7] The X-ray structural study revealed the presence of η^6-coordination of mesitylene to indium(I). It is noteworthy that additional X-ray structural studies of other arene–main-group metal (group 13) compounds[8] identify the increasing basicity of the arene ligands, $C_6H_6 < C_6Me_3H_3 < C_6Me_6$.

In this paper, we report the synthesis and complete characterization of $In(C_5H_4Me)$ by elemental analyses, cryoscopic molecular weight measurements in cyclohexane solution, and IR and ^1H NMR spectroscopic data as well as gas-phase electron diffraction and X-ray solid-state structural studies. In addition, the properties and structure of $In(C_5H_5)$ in the solid state have been reinvestigated. Consequently, the new data permit accurate comparisons of the properties and structural parameters for the three known cyclopentadienylindium(I) derivatives $In(C_5H_5)$, $In(C_5H_4Me)$, and $In(C_5Me_5)$.

Experimental Section

General Data. All compounds described in this investigation were exceedingly sensitive to oxygen and moisture and were manipulated in a standard high vacuum line or in 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

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0276-7333/88/2307-1051$01.50/0

preparation, characterization, and handling was flame-heated under dynamic vacuum prior to use. Indium(I) chloride was purchased from Strem Chemicals, Inc., and was used without further purification. All solvents were purified before use. Diethyl ether was refluxed and stored over sodium diphenyl ketyl. Pentane and cyclohexane were refluxed over CaH_2 and stored over a sodium mirror. Cyclopentadiene and methylcyclopentadiene dimers were cracked immediately before use. The cyclopentadienyllithium reagents, $Li(C_5H_5)$ and $Li(C_5H_4Me)$, were either purchased from Alfa Products and used as received or prepared in our laboratory and isolated as colorless powders after repeated washings with pentane. Since the purity of the lithium cyclopentadienyl reagents is of significance to the synthesis of the indium(I) derivatives, their preparations are described in the appropriate paragraphs of this Section. Analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY. Infrared spectra of Nujol mulls between CsI plates 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 90 MHz by means of either a Varian Model EM-390 or a JEOL FX-90Q 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. Molecular weights were determined cryoscopically in cyclohexane solution by using an instrument similar to that described by Shriver.[9]

Preparation of $Li(C_5H_5)$. Dicyclopentadiene was cracked just prior to use. A Solva-seal flask with a 9-mm side arm was charged with 31.0 mL of 2.5 M Li(*n*-Bu) (78 mmol) in hexanes. The cyclopentadiene (5.062 g, 76.58 mmol) was pipetted into a 9-mm Solva-seal side-arm dumper. Pentane (20 mL) was vacuum distilled into the flask containing the Li(*n*-Bu). The reagents were mixed at room temperature, and the ensuing exothermic reaction prompted the cooling of the system in an ice bath. After the reaction mixture was stirred for 18 h, the volatile components were removed by vacuum distillation. The reaction flask was then fitted with a medium glass frit connected to a 100-mL Solva-seal side-arm flask. Pentane (60 mL) was vacuum distilled into the flask containing the $Li(C_5H_5)$, and the product was washed three times. Lithium cyclopentadienide $Li(C_5H_5)$ (5.00 g, 69.4 mmol) was isolated as a colorless powder in 90.6% yield based on cyclopentadiene.

$Li(C_5H_5)$: colorless solid; IR (Nujol mull, cm^{-1}) 3940 (w), 3680 (vw), 3090 (m), 2728 (w), 2680 (w), 2398 (w), 2243 (vw), 2060 (vw), 1758 (w), 1702 (vw), 1690 (m), 1530 (w), 1300 (w), 1258 (w), 1168 (w), 1150 (w), 1110 (w), 1003 (vs), 888 (vw), 849 (w), 744 (vs), 698 (sh), 512 (s), 380 (m), 268 (m).

Preparation of $Li(C_5H_4Me)$. Methylcyclopentadiene dimer was cracked prior to use to yield monomeric C_5H_4Me, bp 72 °C. A Solva-seal flask with a 9-mm side arm was charged with 27.9 mL of 2.5 M Li(*n*-Bu) (70 mmol) in hexanes, and methylcyclopentadiene (5.60 g, 69.7 mmol) was pipetted into a 9-mm Solva-seal side-arm dumper. The apparatus was assembled, and 30 mL of pentane was vacuum distilled into the flask containing the Li(*n*-Bu). The reagents were mixed at 0 °C, and after 15 min the reaction mixture was warmed to room temperature and stirred for 24 h. The product $Li(C_5H_4Me)$ was purified by repeated washings with pentane. The colorless powder, $Li(C_5H_4Me)$ (5.27 g, 61.2 mmol), was isolated in 87.8% yield based on methylcyclopentadiene.

$Li(C_5H_4Me)$: colorless solid; IR (Nujol mull, cm^{-1}) 3944 (vw), 3095 (sh), 3080 (m), 2738 (m), 2705 (w), 2668 (w), 2395 (vw), 2195 (vw), 1738 (vw), 1693 (w), 1640 (sh), 1628 (w), 1578 (w), 1334 (m), 1302 (m), 1231 (m), 1225 (w), 1166 (w), 1151 (w), 1058 (m), 1036 (s), 1024 (s), 1004 (w), 968 (w), 931 (m), 887 (vw), 860 (w), 824 (s), 736 (vs), 645 (m), 507 (s, br), 390 (m, br), 332 (m), 270 (m).

Synthesis of $In(C_5H_5)$. Cyclopentadienylindium(I) was prepared according to a modification of the literature method.[10] The compound $In(C_5H_5)$ was so exceedingly sensitive to oxygen and moisture that all glassware that came in contact with this compound had to be flame-dried under dynamic vacuum prior to use. In a typical experiment, 0.699 g of $Li(C_5H_5)$ (9.70 mmol) was added to a 100-mL two-neck flask. A side-arm dumper was charged with 1.510 g of InCl (10.05 mmol) that had been previously ground to a fine yellow powder. The apparatus was assembled in the drybox, and then 50 mL of Et_2O was vacuum distilled into the flask containing the $Li(C_5H_5)$. The InCl was added to the suspension of $Li(C_5H_5)$ in one motion, and the reaction mixture was stirred at room temperature. After 17 h, the ether was removed by vacuum distillation and the resulting grayish yellow product was subjected to dynamic vacuum for only 15 min to remove the final traces of ether. (Extended pumping was observed to result in the loss of volatile $In(C_5H_5)$.) The reaction flask was fitted with an 85° bent elbow connected to a 100-mL side-arm flask. Cyclopentadienylindium(I) was sublimed at 55 °C, under dynamic vacuum, and collected in a side-arm flask that was cooled to −196 °C. The pale yellow final product $In(C_5H_5)$ was isolated in 81.9% yield (1.429 g, 7.94 mmol) based on $Li(C_5H_5)$. Additional purification was accomplished by sublimation in a sealed tube at 45 °C. Crystals of $In(C_5H_5)$ suitable for the X-ray structural determination were obtained by slow sublimation at 45 °C in a sealed tube.

$In(C_5H_5)$: pale yellow crystalline solid at room temperature; mp 169.3–171.0 °C. The compound is soluble without any significant decomposition to indium metal in Et_2O, THF, C_6H_6, and $CHCl_3$ but is only very slightly soluble in cyclohexane and pentane. Dry glassware and solvents are necessary to minimize the formation of indium metal. ^1H NMR: C_6D_6, δ 5.93 (s); THF-d_8, δ 5.93 (s); $CDCl_3$, δ 6.10 (s). IR (Nujol mull, cm^{-1}): 1003 (w), 973 (w), 768 (m), 737 (m) (bands for Nujol have been omitted).

Hydrolysis of $In(C_5H_5)$. A tube equipped with a Teflon valve was charged with 0.2471 g (1.373 mmol) of $In(C_5H_5)$, cooled to −196 °C, and then evacuated. Approximately 8 mL of dilute HCl was slowly added at room temperature to the $In(C_5H_5)$. The $In(C_5H_5)$ immediately formed a ball of indium metal, and gas evolution was observed at the surface of the metal. The tube was placed in a 100 °C oil bath, and the reaction mixture was heated and stirred for 4 days. Hydrogen gas was removed and collected in a calibrated portion of the vacuum line by means of a Toepler pump and gas buret assembly. A total of 1.29 mmol of H_2 was collected for a 94.2% yield based on the oxidation of indium(I) to indium(III).

Synthesis of $In(C_5H_4Me)$. (Monomethylcyclopentadienyl)indium(I) is a compound extremely sensitive to oxygen and moisture. All glassware which came in contact with the material had to be dried with a gas flame while under dynamic vacuum to remove trace amounts of moisture prior to use. A freshly prepared sample of $Li(C_5H_4Me)$ (0.6413 g, 7.452 mmol) was weighed and transferred to a 100-mL two-necked flask equipped with a side-arm dumper containing 1.070 g of finely ground InCl (7.125 mmol). A suspension of $Li(C_5H_4Me)$ was obtained by rapidly stirring the $Li(C_5H_4Me)$ in 50 mL of diethyl ether. The InCl was then added in one motion to the suspension, and the resulting light gray mixture was stirred for 18 h. The ether was removed by vacuum distillation taking care not to subject the products to extended periods of dynamic vacuum. The reaction flask was fitted with an 85° bent elbow connected to a 100-mL side-arm flask. A colorless solid, $In(C_5H_4Me)$, was sublimed under dynamic vacuum at room temperature into the side-arm flask which was cooled to −196 °C. The indium(I) compound was isolated as a grayish white solid (1.213 g, 6.256 mmol, 87.80% yield based on InCl). The existence of a grayish solid suggested trace decomposition to indium metal. Colorless crystals of $In(C_5H_4Me)$ were obtained by vacuum sublimation in a Solva-seal tube at 35 °C. In addition, colorless crystals were also obtained by recrystallization from pentane at −5 °C. The nonvolatile product from the reaction, impure LiCl, was washed with pentane and collected as a light gray solid (0.2741 g, 6.466 mmol, 90.75% yield based on InCl).

$In(C_5H_4Me)$: colorless crystalline solid at room temperature; mp 48.5–51.0 °C (melts to a yellow liquid). The compound is soluble in benzene, Et_2O, THF, $CHCl_3$, and cyclohexane. Cyclohexane solutions formed only trace amounts of indium metal provided the glassware had been previously flame-dried. Solutions in THF and C_6H_6 produced an indium mirror. The extreme moisture sensitivity of $In(C_5H_4Me)$ makes it difficult to determine

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Table I. Experimental Data for the X-ray Diffraction Studies of In(C_5H_5) and In(C_5H_4Me)

(A) Crystal Parameters at 24 °C (297 K)

	In(C_5H_5)	In(C_5H_4Me)		In(C_5H_5)	In(C_5H_4Me)
cryst system	monoclinic	monoclinic	V, Å^3	531.98 (27)	635.78 (19)
space group	Cc (No. 9)	$P2_1/n$ (No. 14)	Z	4	4
a, Å	9.1480 (20)	6.1636 (14)	formula	C_5H_5In	C_6H_7In
b, Å	10.0875 (19)	11.5684 (17)	mol wt	179.93	193.95
c, Å	5.9116 (25)	9.1723 (15)	D(calcd), g/cm^3	2.25	2.03
β, deg	102.795 (26)	103.561 (15)	μ(Mo Kα), cm^{-1}	42.5	35.6

(B) Collection of X-ray Diffraction Data

	In(C_5H_5)	In(C_5H_4Me)
radiatn	Mo K$\bar{\alpha}$ (λ = 0.710 730 Å)	^{a}
diffractometer	Syntex P2$_1$	^{a}
monochromator	pyrolytic graphite ($2\theta_m$ = 12.160°); assumed 50% perfect/50% ideally imperfect for polarization correction	^{a}
scan type	coupled θ(crystal)–2θ(counter)	^{a}
scan range	$[2\theta(K\alpha_1) - 1.1]° \rightarrow [2\theta(K\alpha_2) + 1.1]°$	$[2\theta(K\alpha_1) - 1.0] \rightarrow [2\theta(K\alpha_2) + 1.0]$
scan speed	5.0 deg/min	4.0 deg/min
bkgd	stationary crystal and counter at each end of 2θ scan, each for one-fourth of scan time	^{a}
reflctns measd	$\pm h,\pm k,\pm l$ for 2θ = 5.0–55.0; 2534 data merged to 1226 point-group independent reflections	$\pm h,\pm k,\pm l$ for 2θ = 4.5–50.0°; 1352 data merged yielding 1115 independent reflections
stds	3 approximately mutually orthogonal reflections collected before each batch of 97 data points; no significant fluctuations nor decay were observed	^{a}
absorptn	corrected empirically by interpolation (in 2θ and ϕ) between four close-to-axial reflections $\bar{4}0\bar{2}$, 2θ = 25.6°, T_{min}/T_{max} = 0.738; $\bar{5}\bar{1}\bar{2}$, $\bar{5}1\bar{2}$, 2θ = 29.9°, average (T_{min}/T_{max}) = 0.731; $\bar{6}0\bar{2}$, 2θ = 33.9°, T_{min}/T_{max} = 0.728	corrected empirically by interpolation (in 2θ and ϕ) between four close-to-axial reflections 113, 2θ = 17.1°, T_{min}/T_{max} = 0.671; 204, 2θ = 25.3°, T_{min}/T_{max} = 0.717; 215, 2θ = 29.6°, T_{min}/T_{max} = 0.727; 206, 2θ = 33.7°, T_{min}/T_{max} = 0.727

[a] Entry same as for column on left.

whether metal formation is caused by the solvent or by trace quantities of moisture: ^{1}H NMR (C_6D_6) δ 2.04 (s, 3 H, CH_3), 5.82 (m, 4 H, C_5H_4); IR (Nujol mull, cm^{-1}): 1310 (vw), 1039 (vw), 1025 (w), 997 (w), 972 (vw), 928 (vw), 813 (s) 781 (s), 759 (s), 722 (s), 668 (m), 614 (m), 605 (m) (bands for Nujol have been omitted). Anal. Calcd: C, 37.16; H, 3.64. Found: C, 37.26; H, 4.02. Cryoscopic molecular weight, cyclohexane solution, formula weight 193.9 (observed molality, observed molecular weight, association): 0.0921, 313, 1.62; 0.0722, 335, 1.73; 0.0626, 308, 1.59; 0.0527, 304, 1.57; 0.0340, 286, 1.47; 0.0335, 291, 1.49.

Hydrolysis of (C_5H_4Me). Hydrolysis of a 0.2283 g sample of In(C_5H_4Me) (1.177 mmol) with dilute HCl at room temperature produced 1.12 mmol (PVT measurements) of noncondensable gas (H_2). Upon addition of the dilute HCl, a ball of indium metal formed in the reaction tube. Gas evolution was observed at the surface of the metal. Hydrogen gas was obtained in 95.5% yield based on the oxidation of indium(I) to indium(III).

X-ray Diffraction Study of In(C_5H_5). A clear, very pale yellow, irregularly shaped crystal of approximate orthogonal dimensions 0.15 × 0.3 × 0.4 mm^3 was sealed inside a thin-walled glass capillary under an argon atmosphere. It was aligned (with its extended direction approximately parallel with the instrumental ϕ axis) on a Syntex P2$_1$ automated four-circle diffractometer. All subsequent setup operations (i.e., determination of the lattice constants and orientation matrix) and collection of the intensity data were performed as described previously;[11] details are given in Table I. The final unit cell parameters were based on a least-squares analysis of the setting angles (2θ, ω, χ) of the unresolved Mo K$\bar{\alpha}$ components of 25 automatically centered reflections with 2θ = 30–38°.

The systematic absences hkl for $h + k = 2n + 1$ and $h0l$ for $l = 2n + 1$ are consistent with the noncentrosymmetric monoclinic space group Cc (C_s^4; No. 9) or the centrosymmetric monoclinic space group $C2/c$ (C_{2h}^6; No. 15). With Z = 4, the crystallographic asymmetric unit is one formula unit of In(C_5H_5) in space group Cc or one-half an In(C_5H_5) unit (with crystallographically imposed C_2 or C_i symmetry on the observed ensemble) in space group $C2/c$.

Table II. Intensity Statistics for X-ray Diffraction Data of In(C_5H_5) and In(C_5H_4Me)

function	In(C_5H_5) (obsd)	acentric (theor)	In(C_5H_4Me) (obsd)	centric (theor)
$\langle \lvert E \rvert \rangle$	0.904	0.886	0.810	0.798
$\langle \lvert E^2 \rvert \rangle$	1.000	1.000	1.000	1.000
$\langle \lvert E^2 \rvert - 1 \rangle$	0.648	0.736	0.935	0.968
% $\lvert E \rvert > 1.0$	42.99	36.79	33.54	31.73
% $\lvert E \rvert > 1.8$	0.49	3.92	6.64	7.19
% $\lvert E \rvert > 2.0$	0.00	1.89	4.30	4.55
% $\lvert E \rvert > 2.5$	0.00	0.19	0.36	1.24
% $\lvert E \rvert > 3.0$	0.00	0.01	0.09	0.27

Intensity statistics (Table II) and the successful solution of the structure revealed that Cc was the true space group.

A full shell of data (±h,±k,±l for 2θ = 5.0–55.0°) was collected; these data were corrected for absorption and Lorentz–polarization effects and were merged to a single set of point-group independent reflections. (Allowing for anomalous dispersion we have $hkl = h\bar{k}l \neq \bar{h}k\bar{l} = \bar{h}\bar{k}\bar{l}$ and $\bar{h}kl = \bar{h}\bar{k}l \neq hk\bar{l} = h\bar{k}\bar{l}$.) Any reflection with I(net) < 0 was assigned the value $|F_0| = 0$.

All calculations were performed by using our in-house NOVA 1200 computer operated under the SUNY—Buffalo modified version of the Syntex XTL interactive crystallographic program package.[12] The calculated structure factors were based upon the analytical form of the neutral atoms scattering factors and were corrected for both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion.[13] The function minimized during least-squares refinement was $\sum w(|F_o| - |F_c|)^2$ where the weighting scheme is based upon counting statistics along with an "ignorance factor" of 0.015.

The position of the indium atom was determined from a Patterson map. The remaining non-hydrogen atoms were located from a difference Fourier synthesis. Attempts to locate directly the positions of the hydrogen atoms were unsuccessful, probably

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(12) *Syntex XTL Operations Manual*, 2nd ed.; Syntex Analytical Instruments: Cupertino, CA, 1976.

(13) *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. 4, pp 99–100, 149–150.

Table III. Final Atomic Coordinates for $In(C_5H_5)$

atom	*x*	*y*	*z*
In	0.00000 (0)	0.13256 (3)	0.00000 (0)
C(1)	0.3265 (20)	0.1467 (19)	0.2856 (44)
C(2)	0.2454 (25)	0.1929 (20)	0.4166 (23)
C(3)	0.1741 (17)	0.3052 (16)	0.3498 (39)
C(4)	0.2106 (23)	0.3397 (20)	0.1557 (55)
C(5)	0.3059 (16)	0.2443 (31)	0.0939 (23)
H(1)[a]	0.3858	0.0684	0.3058
H(2)[a]	0.2365	0.1489	0.5550
H(3)[a]	0.1092	0.3516	0.4272
H(4)[a]	0.1774	0.4178	0.0698
H(5)[a]	0.3475	0.2425	−0.0396

[a] *B*(iso) = 8.0 Å^2.

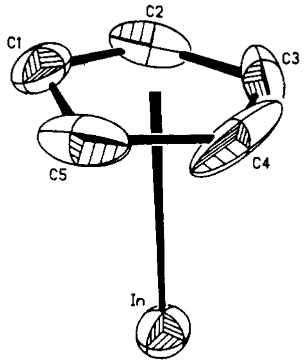

Figure 1. Labeling of atoms and atomic vibration ellipsoids for the crystallographic asymmetric unit of $In(C_5H_5)$. Note the large amplitude of libration in the plane of the C_5H_5 ring, perpendicular to the C(ring)···centroid vector (ORTEP2 diagram, 30% vibration ellipsoids).

due to the large amplitude of libration associated with the cyclopentadienyl ligand. Hydrogen atoms were therefore included in calculated positions based upon an externally bisecting geometry around the C_5 ring and *d*(C–H) = 0.95 Å.[14]

Full-matrix least squares refinement of positional and anisotropic thermal parameters for all non-hydrogen atoms led to convergence with[15] R_F = 4.4%, R_{wF} = 5.3%, and GOF = 1.95 for all 1226 independent reflections (R_F = 4.2% and R_{wF} = 5.2% for those 1135 data with $|F_o| > 6\sigma(|F_o|)$). A final difference Fourier synthesis was essentially featureless; the structure is therefore both correct and complete. Inversion of coordinates and refinement to convergence gave slightly higher residuals. The original choice of coordinates thus defines the correct crystal chirality. Final positional parameters are collected in Table III. Labeling of atoms in the crystallographic asymmetric unit is shown in Figure 1.

X-ray Diffraction Study of $In(C_5H_4Me)$. An opaque white crystal of approximate dimensions 0.1 × 0.2 × 0.5 mm^3 was sealed into a thin-walled glass capillary under argon. The diffraction experiment was carried out in a manner similar to that described above for $In(C_5H_5)$. Conditions for data collection and cell parameters are given in Table I. (Cell parameters were based on 25 reflections with 2θ = 29.0–31.5°.)

The systematic absences *h*0*l* for $h + l = 2n + 1$ and 0*k*0 for $k = 2n + 1$ are indicative of the centrosymmetric monoclinic space group $P2_1/n$ (C_{2h}^5 variation; No. 14).

The position of the indium atom was determined from a Patterson map; a difference Fourier map revealed the positions of the six independent carbon atoms. Full-matrix least-squares refinement of positional and isotropic thermal parameters led to R_F = 17.5% and R_{wF} = 20.8%. The use of anisotropic thermal parameters led to R_F = 4.6% and R_{wF} = 4.8%. Hydrogen atoms were located from a difference Fourier map, and a minor correction for secondary extinction was carried out ($g = 7.5 \times 10^{-9}$, where $|F_{o,cor}| = |F_{o,uncor}|\,(1.0 + gI_o)$). Final convergence was reached with R_F = 4.0%, R_{wF} = 3.9%, and GOF = 1.56 for all 1115 reflections (R_F = 3.0% and R_{wF} = 3.6% for those 908 data with $|F_o| > 6\sigma(|F_o|)$). A final difference Fourier synthesis was "clean". Positional parameters are collected in Table IV. Labeling of atoms in the crystallographic asymmetric unit is shown in Figure 2.

Table IV. Final Atomic Coordinates for $In(C_5H_4Me)$

atom	*x*	*y*	*z*	*B*(iso), Å^2
In	0.15291 (7)	0.15296 (3)	0.02900 (4)	
C(1)	0.04605 (71)	0.32399 (38)	−0.19844 (48)	
C(2)	0.04088 (82)	0.22158 (43)	−0.28417 (48)	
C(3)	−0.14391 (91)	0.15655 (44)	−0.27083 (55)	
C(4)	−0.25511 (90)	0.21619 (50)	−0.17875 (61)	
C(5)	−0.13800 (77)	0.31843 (45)	−0.13303 (52)	
C(6)	0.2081 (11)	0.42252 (60)	−0.18770 (87)	
H(2)	0.1328 (77)	0.2054 (46)	−0.3437 (52)	3.8 (10)
H(3)	−0.1876 (74)	0.0822 (47)	−0.3132 (50)	4.0 (10)
H(4)	−0.366 (10)	0.2027 (59)	−0.1609 (67)	5.8 (16)
H(5)	−0.184 (11)	0.3743 (70)	−0.0657 (80)	8.0 (18)
H(6A)	0.234 (17)	0.4677 (88)	−0.103 (11)	11.5 (29)
H(6B)	0.352 (23)	0.409 (13)	−0.137 (15)	15.2 (38)
H(6C)	0.181 (17)	0.462 (11)	−0.306 (12)	14.4 (32)

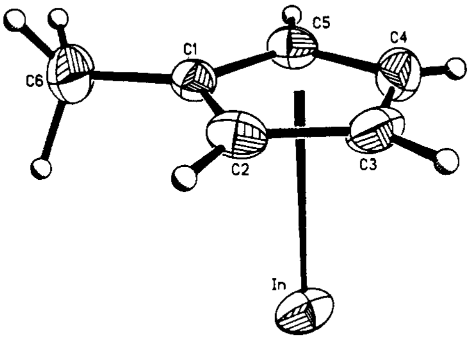

Figure 2. Labeling of atoms and atomic vibration ellipsoids for the crystallographic asymmetric unit of $In(C_5H_4Me)$. Note the reduced size of the carbon atom ellipsoids relative to those in Figure 1 (ORTEP2 diagram, 30% vibration ellipsoids; those of the hydrogen atoms are artificially reduced for clarity.)

Electron Diffraction Study of $In(C_5H_4Me)$. The electron scattering pattern of $In(C_5H_4Me)$ was recorded on a Balzers Eldigraph KDG-2[16] with nozzle and reservoir temperatures of approximately 30 °C. A use of a torus shaped nozzle permitted the scattering pattern to be recorded with a reservoir vapor pressure of about 1 Torr.[17] The electronic wavelength was calibrated against scattering patterns of benzene (*r*(C–C) = 139.75 pm) with an estimated standard deviation of 0.1%. The nozzle-to-plate distances were approximately 50 and 25 cm. Five plates at 50 cm and six plates at 25 cm were used. The data extended from *s* = 21.25 to 145.0 nm^{-1} with Δs = 1.25 nm^{-1} (50 cm) and from *s* = 40.25 to 260.0 nm^{-1} with Δs = 2.5 nm^{-1}. Complex atomic scattering functions *f*′(*s*) for H and C were calculated from an analytical representation of the atomic potential[18] by using a program written by Yates.[19] For In, tabulated values were used,[20] interpolated to 42 kV. The data reduction was carried out by established procedures.[21] A blackness correction of $1 + 0.03D + 0.09D^2 + 0.03D^3$ was used. The molecular intensities were modified by multiplication with $s/|f'_{In}||f'_C|$. The backgrounds were computer drawn by least-squares fitting of the sum of a polynomial and a theoretical molecular intensity curve to the experimental

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(14) Churchill, M. R. *Inorg. Chem.* **1973**, *12*, 1213.

(15) R_F (%) = $100\sum||F_o||/\sum|F_o|$; R_{wF} (%) = $100[\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; GOF = $[\sum w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$, where NO = number of observations and NV = number of variables.

(16) Zeil, W.; Haase, J.; Wegmann, L. Z. *Instrumentenkd* **1966**, *74*, 84. Bastiansen, O.; Graber, R.; Wegmann, L. *Balzers High Vacuum Report* **1969**, *25*, 1. Balzers A-G fur Hochvakuumtechnik and dunne Schichten, 9496 Balzers, Lichtenstein.

(17) Ashby, E. C.; Fernholt, L.; Haaland, A.; Seip, R.; Scott Smith, R. *Acta Chem. Scand. Ser. A* **1980**, *A34*, 213. Annual Report of Norwegian Electron Diffraction Group, 1980.

(18) Strand, T.; Bonham, R. A. *J. Chem. Phys.* **1964**, *40*, 1686.

(19) Yates, A. C. *Comput. Phys. Commun.* **1971**, *2*, 175.

(20) *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. 4, section 2.5.

(21) Andersen, B.; Seip, H. M.; Strand, T.; Stolevik, R. *Acta Chem. Scand.* **1969**, *23*, 3224.

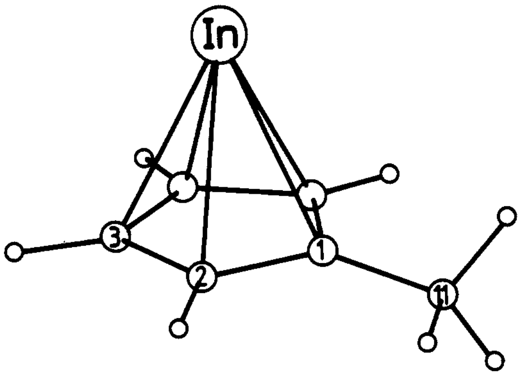

Figure 3. Molecular model for $In(C_5H_4Me)$ in the gas phase for electron diffraction study.

leveled intensity curve. The degree of the polynomial was 6 for the 50 cm data and 8 for the 25 cm data. Individual curves of each nozzle-to-plate distance were averaged, but the average curves were not connected in the least-squares refinements. A nondiagonal weight matrix was used in the final refinement in order to correct for data correlation.[22]

The molecular model of $In(C_5H_4Me)$ in the gas phase is shown in Figure 3. The model can be made from $In(C_5H_5)$ of C_{5v} symmetry by substituting one H atom with a CH_3 group. The CCH_3 fragment were assumed to be of C_{3v} symmetry fixed in a position with one InC(1)C(11)H torsion angle of 90°. With these assumptions the molecular structure can be described by eight independent parameters: the In–ring centroid height h, the C(1)–C(2), C(1)–C(11), C(2)–H, and C(11)–H bond distances, the CCH angle of the methyl group, and two angles, one between the ring plane and the C–H bonds, C_5, C–H, and the second between the ring plane and the C–C(Me) bond, C_5,C–C(Me). The latter two angles are defined as positive when the ring substituents are bent toward the metal atom. The fixed l values are normal for this kind of compound, and were taken from an electron diffraction study of $In(C_5Me_5)$ that will be published in the near future.

In order to test the assumed C_{5v} symmetry of the InC_5 skeleton, we performed some refinements where the position of the metal atom relative to the ring was determined not only by h but also by a second coordinate that allowed the metal atom to be displaced from the C_5 axis. The displacement was restricted to the plane defined by the In atom, the ring centroid, and the C1 atom. The introduction of this new independent parameter did not lead to improved fit of the theoretical curve to the experimental ones, and the horizontal movement of the In atom was in no cases larger than 0.07 Å with an estimated standard deviation twice this value. Our conclusion is that the In atom is positioned at or very close to the C_5 axis of the ring. In Table VIII the results obtained with the In atom fixed at the C_5 axis are listed. The theoretical molecular intensity curves with experimental points are shown in Figure 4, and the corresponding experimental radial distribution curve is shown in Figure 5.

Results and Discussion

The two compounds $In(C_5H_5)$ and $In(C_5H_4Me)$ have been prepared from indium(I) chloride and the appropriate lithium cyclopentadienide in diethyl ether by using a modification of the general procedure of Peppe, Tuck, and Victoriano.[10] Both compounds have been fully characterized according to their physical and solubility properties, reactions with dilute aqueous HCl, cryoscopic molecular weight studies in cyclohexane ($In(C_5H_4Me)$ only), infrared, and ^1H NMR spectroscopic properties and X-ray structural studies. In addition, the molecular structure of $In(C_5H_4Me)$ in the gas phase has been investigated by an electron diffraction study. Both compounds are exceedingly sensitive to oxygen and moisture. The new compound $In(C_5H_4Me)$ is so readily decomposed by moisture that extreme care must be used for all manipulations. Excellent technique can lead to colorless crystals. In contrast, the presence of apparent moisture, even on the walls of clean glassware which has not been flame-dried under dynamic vacuum, leads to the formation of indium metal. Thus, the presence of a gray color in samples of these indium(I) cyclopentadienyl derivatives is a clear indication of trace decomposition. Consequently, it is not surprising that a previous report[6] described $In(C_5H_4Me)$ to be so unstable that it was not possible to fully characterize the compound.

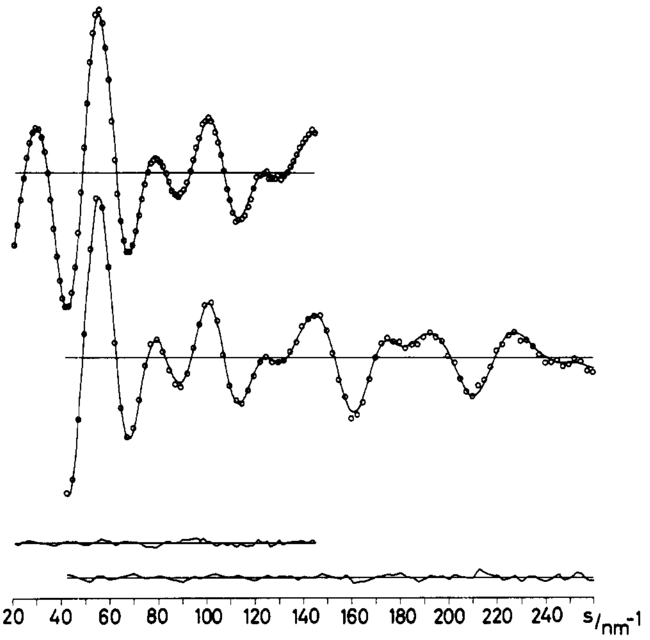

Figure 4. Theoretical molecular intensity curves with experimental points for the electron diffraction study on InC_5H_4Me. The difference between experimental and theoretical curves for the best model are drawn in the lower part of the figure.

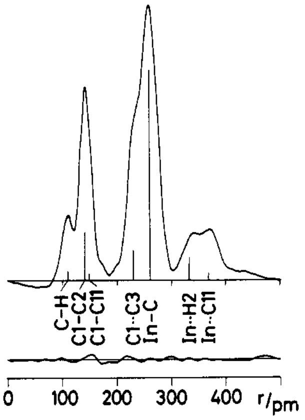

Figure 5. Experimental RD curve for the electron diffraction study on InC_5H_4Me. The difference between the experimental and theoretical RD curve calculated for the best model are drawn in the lower part of the figure. The most important distances are indicated by bars of height approximately proportional to the area under the corresponding peak. Artificial damping constant, k, is 20 pm^2.

A variety of experimental conditions including the purity of the lithium cyclopentadienide reagent and the $Li(C_5H_4R)$ (R = H, Me)/InCl mole ratio were varied in order to determine the optimum conditions for the syntheses of the indium(I) cyclopentadienyl derivatives. Our experimental observations suggest that freshly prepared, colorless samples of $Li(C_5H_4R)$, a stoichiometric ratio of reagents

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[22] Seip, H. M.; Strand, T. G.; Stolevik, R. *Chem. Phys. Lett.* **1969**, *3*, 617.

as based on eq 1, and very clean, dry glassware provide the

$$\mathrm{Li(C_5H_4R) + InCl(s) \xrightarrow[R\,=\,H,\,Me]{Et_2O} In(C_5H_4R) + LiCl(s)} \tag{1}$$

highest yields of the organoindium(I) derivatives (Table V). A large excess of $Li(C_5H_4R)$ over InCl does not significantly increase the yield of $In(C_5H_4R)$, provided that $Li(C_5H_4R)$ is freshly prepared, pure and colorless. The isolation of $In(C_5H_4R)$ (R = H, Me) in high yield (80–90%) suggests that no significant competing reactions are occurring during the preparative reactions.

The current crystal structure of $In(C_5H_5)$, based upon data from a complete shell of reciprocal space ($\pm h,\pm k,\pm l$ for $2\theta = 5.0–55.0°$ with Mo $K\bar{\alpha}$ radiation), confirms the earlier semiquantitative report by Frasson, Menegus, and Panattoni (based upon photographic *h*0*l*, 0*kl*, and *hk*0 data only).[4] Accurate interatomic distances and angles for this species are collected in Table VI.

The structure of $In(C_5H_5)$ consists of (theoretically) infinite zigzag chains based on $[In(\eta^5\text{-}C_5H_5)]_\infty$ (Figure 6). Each indium atom interacts with two cyclopentadienyl ligands (<centroid–In–centroid′ = 128.02°), and each cyclopentadienyl ligand is linked to two indium atoms (<In–centroid–In′ = 176.99°) (Figure 7). In addition to this, there are possible weak In–In interactions between the individual chains defined, in a zigzag fashion, by the *c*-glide operations such that In–In $(x, -y, \pm^1/_2 + z)$ = 3.986 (1) Å and <In$[x, -y, -^1/_2 + z]$–In–In$[x, -y, +^1/_2 + z]$ = 95.72 (1)° (Figure 6). [Note that each indium atom interacts with *two* others: cf. structure of $In(C_5H_4Me)$, below.]

The defined cyclopentadienyl system, C(1)→C(5), is associated with C–In distances of 2.853 (22)–3.091 (21) Å and a centroid–In distance of 2.726 Å; it is also in contact with a second indium atom, In$[^1/_2 + x, ^1/_2 - y, ^1/_2 + z]$ (related to the defined In by an *n*-glide perpendicular to *b* at $y = ^1/_4$ in space group *Cc*), such that C–In′ distances are 2.863 (20)–2.983 (17) Å and centroid–In′ = 2.687 Å. These indium(I)–C(cyclopentadieny) distances in the solid state are all far greater than typical In(III)–C(sp³) distances (e.g. 2.153 (5) Å for $[(CH_3)_2InN(CH_3)(C_6H_5)]_2$[23] and 2.161 (3) Å for $InMe_3$[24]) and are consistent with either very weak covalent bonding or an ionic structure.

The cyclopentadienyl ligand is ordered (thereby negating a possible centrosymmetric structure) but is undergoing substantial librational motion as is evidenced by the large anisotropic thermal parameters (see Figure 1). Individual C–C distances range from 1.27 (3) through 1.48 (3) Å, averaging 1.36 Å. This value is lower than the normal $C–C(\eta^5\text{-}C_5H_5)$ bond length of 1.43 Å, but is consistent with an artificial shortening due to libration of the ring about its C_5 axis.

The crystal structure of $In(C_5H_4Me)$ bears a similarity to that of $In(C_5H_5)$ but has certain minor differences. The packing of $In(C_5H_4Me)$ units is illustrated in Figures 8 and 9. Interatomic distances and angles are presented in Table VII. Each indium atom interactions with two C_5H_4Me ligands (<centroid–In–centroid′ = 130.66°), and each C_5H_4Me ligand is linked to two indium atoms (<In–centroid–In′ = 179.74°). The structure thus contains zigzag chains of $[In(\eta^5\text{-}C_5H_4Me)]_\infty$ molecules. There are additional weak In–In interactions between the chains, operating now through *inversion* centers such that In–In$(-x, -y, -z)$ = 3.986 (1) Å. [Note that, in contrast to the structure of $In(C_5H_5)$ (above), each indium atom in $In(C_5H_4Me)$ interacts with only *one* other indium atom.]

Table V. Reaction Conditions for Synthesis of $In(C_5H_4R)$ (R = H, Me)

R	InCl, mmol	$Li(C_5H_4R)$, mmol	$In(C_5H_4R)$, mmol	% yield
H	10.05	9.70	7.94	81.9
H	4.85	4.93[a]	3.62	74.6
H	4.94	24.8	4.39	88.9
Me	7.12	7.45	6.26	87.9
Me	7.93	7.99	6.34	79.9

[a] Commercial sample of $Li(C_5H_5)$.

Table VI. Interatomic Distances (Å) and Angles (deg) from the X-ray Diffraction Study of $In(C_5H_5)$

(A) Indium–Indium Distances			
In–In$[x, -y, -^1/_2 + z]$	3.986 (1)		
In–In$[x, -y, ^1/_2 + z]$	3.986 (1)		
(B) Carbon–Indium Distances			
C(1)–In	3.091 (21)	C(1)–In$[^1/_2 + x, ^1/_2 - y, ^1/_2 + z]$	2.863 (20)
C(2)–In	3.004 (18)	C(2)–In$[^1/_2 + x, ^1/_2 - y, ^1/_2 + z]$	2.874 (22)
C(3)–In	2.896 (19)	C(3)–In$[^1/_2 + x, ^1/_2 - y, ^1/_2 + z]$	2.983 (17)
C(4)–In	2.853 (22)	C(4)–In$[^1/_2 + x, ^1/_2 - y, ^1/_2 + z]$	2.974 (27)
C(5)–In	2.953 (19)	C(5)–In$[^1/_2 + x, ^1/_2 - y, ^1/_2 + z]$	2.927 (18)
centroid–In	2.726	centroid–In$[^1/_2 + x, ^1/_2 - y, ^1/_2 + z]$	2.687
(C) Carbon–Carbon Distances			
C(1)–C(2)	1.27 (3)	C(4)–C(5)	1.40 (3)
C(2)–C(3)	1.32 (3)	C(5)–C(1)	1.48 (3)
C(3)–C(4)	1.31 (4)		
(D) In–Centroid–In, Centroid–In–Centroid, and In–In–In Angles			
In–centroid–In$[^1/_2 + x, ^1/_2 - y, ^1/_2 + z]$	176.99		
centroid–In–centroid$[-^1/_2 + x, ^1/_2 - y, -^1/_2 + z]$	128.02		
In$[x, -y, -^1/_2 + z]$–In–In$[x, -y, ^1/_2 + z]$	95.72 (1)		
(E) C–C–C Angles			
C(5)–C(1)–C(2)	103.3 (19)	C(3)–C(4)–C(5)	109.8 (21)
C(1)–C(2)–C(3)	116.6 (19)	C(4)–C(5)–C(1)	103.8 (19)
C(2)–C(3)–C(4)	106.5 (19)		

The basic C_5H_4Me ligand is associated with C–In distances of 2.800 (5)–2.924 (5) Å with centroid–In = 2.609 Å; it also interacts with In$(-^1/_2 + x, ^1/_2 - y, -^1/_2 + z)$ (related to the basic In by an *n*-glide perpendicular to *b* at $y = ^1/_4$ in space group $P2_1/n$) such that C–In′ = 2.952 (5)–3.083 Å and centroid–In′ = 2.711 Å. The C_5H_4Me group is thus less symmetrically disposed between indium atoms than is the C_5H_5 group in $In(C_5H_5)$.

The C_5H_4Me group is more rigidly held in the crystal lattice than is the C_5H_5 group, so librational effects are much less severe. Individual C–C distances in the ring range from 1.389 (8) through 1.418 (7) Å, averaging 1.401 Å, while the C(ring)–Me bond length is 1.503 (8) Å. All hydrogen atoms in this structure were located and refined, resulting in C–H(ring) = 0.76 (6)–0.98 (8) Å and C–H(Me) = 0.91 (10)–1.15 (11) Å (cf. 0.95 Å as the accepted "X-ray determined" C–H distance).[14]

A most interesting feature of the structures of $In(C_5H_5)$, $In(C_5H_4Me)$, and $In(C_5Me_5)$ relates to the existence of structures that place the indium atoms at very similar internuclear distances even though these three compounds exhibit two distinctly different types of structures. The two zigzag polymeric structures of $In(C_5H_5)$ and $In(C_5H_4Me)$ have alternating metal atoms and organic ligands with each of the two faces of the carbocyclic ligand interacting with an indium atom. In contrast to this, In-

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[23] Beachley, O. J., Jr.; Bueno, C.; Churchill, M. R.; Hallock, R. B.; Simmons, R. G. *Inorg. Chem.* **1981**, *20*, 2423.

[24] Fjeldberg, T.; Haaland, A.; Seip, R.; Shen, Q.; Weidlein, J. *Acta Chem. Scand., Ser. A.* **1982**, *A36*, 495.

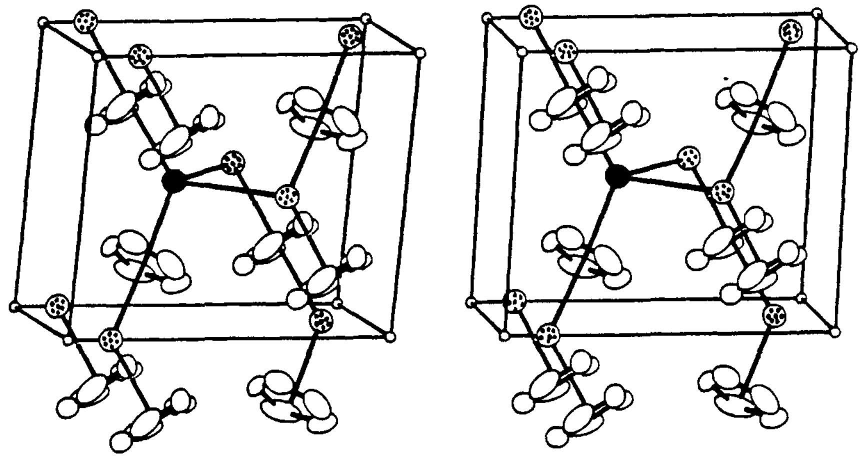


Figure 6. Stereoscopic view of the crystal structure for $[In(\eta^5\text{-}C_5H_5)]_\infty$, with "*c*" toward the viewer, *b* horizontal, and *a* vertical. It essentially consists of infinite zigzag strands of $-In-C_5H_5-In-C_5H_5-$ with interstrand In···In contacts of 3.986 (1) Å. Note that each indium atom is in contact with *two* other indium atoms. (This is shown clearly only for the darkened indium atom.)

Table VII. Interatomic Distances (Å) and Angles (deg) from the X-ray Diffraction Study of In(C_5H_4Me)

(A) Indium–Indium Distances			
In–In($-x, -y, -z$)	3.986 (1)		
(B) Carbon–Indium Distances			
C(1)–In	2.838 (4)	C(1)–In($-^1/_2 + x, {}^1/_2 - y, -^1/_2 + z$)	3.058 (4)
C(2)–In	2.903 (5)	C(2)–In($-^1/_2 + x, {}^1/_2 - y, -^1/_2 + z$)	2.973 (4)
C(3)–In	2.924 (5)	C(3)–In($-^1/_2 + x, {}^1/_2 - y, -^1/_2 + z$)	2.952 (5)
C(4)–In	2.871 (6)	C(4)–In($-^1/_2 + x, {}^1/_2 - y, -^1/_2 + z$)	3.014 (6)
C(5)–In	2.800 (5)	C(5)–In($-^1/_2 + x, {}^1/_2 - y, -^1/_2 + z$)	3.083 (5)
centroid–In	2.609	centroid–In($-^1/_2 + x, {}^1/_2 - y, -^1/2 + z$)	2.771
(C) Carbon–Carbon Distances			
C(1)–C(2)	1.418 (7)	C(4)–C(5)	1.398 (8)
C(2)–C(3)	1.394 (8)	C(5)–C(1)	1.404 (7)
C(3)–C(4)	1.389 (8)	C(1)–C(6)	1.503 (8)
(D) Carbon–Hydrogen Distances			
C(2)–H(2)	0.89 (5)	C(6)–H(6A)	0.92 (10)
C(3)–H(4)	0.96 (5)	C(6)–H(6B)	0.91 (14)
C(4)–H(4)	0.76 (6)	C(6)–H(6C)	1.15 (11)
C(5)–H(5)	0.98 (8)		
(E) In–Centroid–In and Centroid–In–Centroid Angles			
In–Centroid–In ($-^1/_2 + x, {}^1/_2 - y, -^1/_2 + z$)	179.74		
Centroid–In–Centroid ($+^1/_2 + x, {}^1/_2 - y, +^1/_2 + z$)	130.66		
(F) C–C–C Angles			
C(5)–C(1)–C(2)	106.5 (4)	C(2)–C(1)–C(6)	126.7 (5)
C(1)–C(2)–C(3)	108.4 (4)	C(5)–C(1)–C(6)	126.7 (5)
C(2)–C(3)–C(4)	108.4 (5)		
C(3)–C(4)–C(5)	108.0 (5)		
C(4)–C(5)–C(1)	108.8 (4)		
(G) C–C–H Angles			
C(1)–C(2)–H(2)	125 (3)	C(1)–C(5)–H(5)	128 (4)
C(3)–C(2)–H(2)	126 (3)	C(4)–C(5)–H(5)	123 (4)
C(2)–C(3)–H(3)	127 (3)		
C(4)–C(3)–H(3)	124 (3)	C(1)–C(6)–H(6A)	118 (7)
C(3)–C(4)–H(4)	129 (5)	C(1)–C(6)–H(6B)	117 (9)
C(5)–C(4)–H(4)	123 (5)	C(1)–C(6)–H(6C)	107 (6)

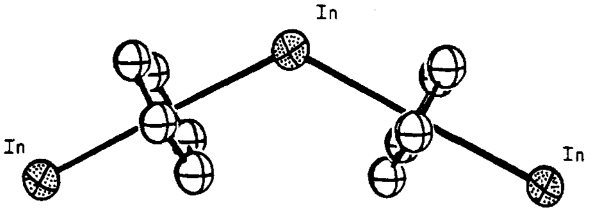


Figure 7. The environment of the indium atom projected onto the centroid–In–centroid′ plane. The centroid–In–centroid′ angle is 128.02°.

Table VIII. Geometrical Parameters and Root-Mean-Square Amplitudes of Vibration (*l* Values) for In(C_5H_5) and In(C_5H_4Me) in the Gas Phase

	In(C_5H_5)[b]		In(C_5H_4Me)	
	r	*l*/Å	*r*	*l*/Å
bond distances (r_a/Å)				
In–C	2.619 (5)	0.077 (7)	2.607 (5)	0.096 (5)
h[a]	2.322 (–)	0.040 (9)	2.309 (5)	
C(1)–C(2)	1.425 (7)	0.040 (9)	1.424 (3)	0.047 (5)[d]
C(1)–C(11)			1.512 (15)	0.052 (5)[d]
C–H(Cp)	1.10 (6)	0.07 (6)	1.101 (14)	0.053 (21)
C–H(Me)			1.103[c]	0.082[c]
other distances (r_a/Å)				
In···C(11)			3.69	0.15 (4)
In···H(Cp)	3.34	0.11 (3)	3.34	0.13 (5)
In···H(Me)-(range)			3.69–4.60	0.32[c]
C(1)···C(3)	2.314	0.044 (13)	2.30	0.055 (6)
C(2)···C(11)			2.61	0.065[c]
C(3)···C(11)			3.76	0.074[c]
angles (deg)				
C_5,C–H	–4.5 (20)		–5 (4)	
C_5,C–C(Me)			–7 (3)	
CCH			112 (6)	

[a] The perpendicular height from the metal atom to the ring centroid. [b] r_g values from ref 3, converted to r_a values by $r_a = r_g - l^2/r_e$. [c] Fixed values. [d] Values with identical index were refined with constant difference.

(C_5Me_5) has fragments which agglomerate into discrete hexameric clusters.[5] The indium–indium distances in the three compounds are 3.986 (1) Å in In(C_5H_5), 3.986 (1) Å in In(C_5H_4Me), and 3.943 (1) and 3.963 (1) Å in In(C_5Me_5). The significance of these observations relative to the bonding in these cyclopentadienylindium(I) derivatives remains to be clearly defined, but it may suggest the existence of weak indium–indium bonding. It is of interest that Frasson, Menegus, and Panattoni[4] originally proposed the existence of indium–indium interactions in In(C_5H_5).

The structure of In(C_5H_4Me) in the gas phase consists of discrete monomeric units with the indium(I) atom being situated over the ring centroid. The molecular model for the gas phase is shown in Figure 3. Even though the gas-phase structures of In(C_5H_4Me) and In(C_5H_5)[3] are very similar, differences do exist. The geometrical parameters and root-mean-square amplitudes of vibration (*l* values)

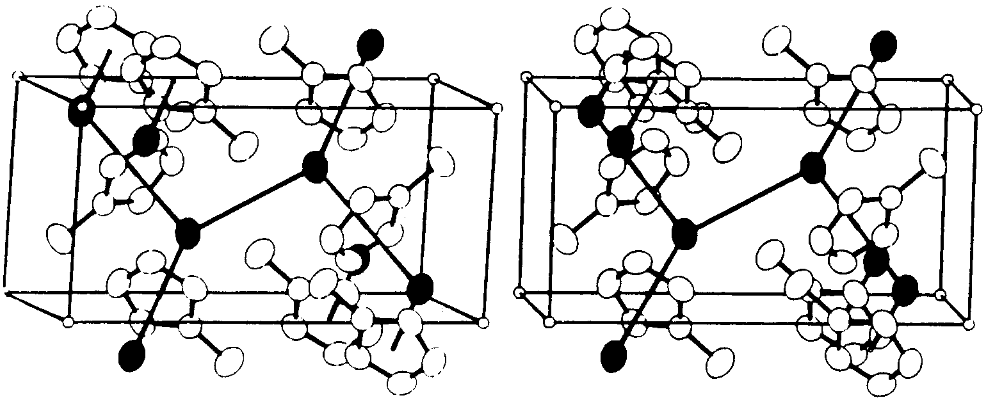


Figure 8. Stereoscopic view of the crystal structure of $[\mathrm{In}(\eta^5\text{-}C_5H_4Me)]_\infty$, viewed with *c* toward the viewer, *b* horizontal, and *a* vertical. The structure consists of infinite zigzag strands of $-\mathrm{In}-C_5H_4Me-\mathrm{In}-C_5H_4Me-$ with interstrand In···In contacts of 3.986 (1) Å. Note that each indium atom is in contact with only *one* other indium atom.

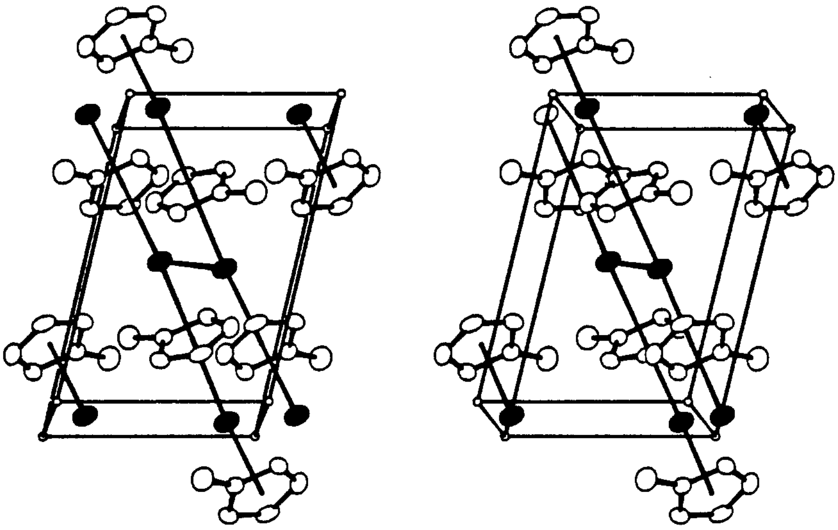
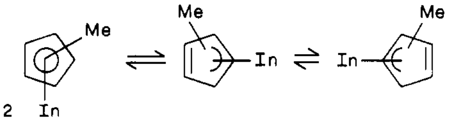


Figure 9. A stereoscopic view of the crystal structure of $[\mathrm{In}(\eta^5\text{-}C_5H_4Me)]_\infty$, viewed with *b* toward the viewer, *a* horizontal, and *c* vertical. Note the double strand of $-\mathrm{In}-C_5H_4-\mathrm{In}-C_5H_4-$ molecules linked by weak In···In interactions.

for both compounds are listed in Table VIII. The most significant difference between the structures of $\mathrm{In}(C_5H_5)$ and $\mathrm{In}(C_5H_4Me)$ relates to the shortening of In–centroid distance upon substituting one hydrogen by a methyl group. A similar change is observed between the solid-state structures. These observations suggest that the methyl group acts as an electron-donating substituent which makes $C_5H_4Me^-$ a better ligand than $C_5H_5^-$ toward indium(I). The ring H atoms and the methyl group are bent away from the indium atom in $\mathrm{In}(C_5H_4Me)$ by 5 (4)° and 7 (3)°, respectively. Similar observations[3] have been made for $\mathrm{In}(C_5H_5)$ and for the isoelectronic $\mathrm{Sn}(C_5Me_5)^+$ ion.[25] The decreased antibonding s–a_1 (π) interaction between the metal and the ring[26] is believed to be responsible. The ligand geometry in $\mathrm{In}(C_5H_4Me)$ is similar to that found in $\mathrm{Ge}(C_5H_4Me)_2$ and $\mathrm{Sn}(C_5H_4Me)_2$.[27]

The nature of $\mathrm{In}(C_5H_4Me)$ in cyclohexane solution has been examined by cryoscopic molecular weight experiments. Cyclohexane was selected as the best solvent for these studies. The compound is readily soluble, and this solvent can be thoroughly and completely dried in order to minimize the formation of metal. The compound $\mathrm{In}(C_5H_4Me)$ exhibits an apparent degree of association of 1.49–1.62 in the concentration range of 0.0335–0.0921 m. These data are consistent with the existence of an equilibrium between monomeric and dimeric molecules in the simplest case. Dimeric molecules can be envisioned to be formed from monomeric molecules either by the formation of donor–acceptor bonds between indium atoms or by association as in the solid state. If double bonds between indium atoms do occur by donor–acceptor interactions, η^3-coordination of the cyclopentadienyl rings would be required.



(2)

The proposed dimeric molecule with indium–indium bonds would have to be of marginal stability because a structural change would have to occur to form the solid as a zigzag polymer of alternating indium(I) atoms and carbocyclic ligands.

Oxidation–reduction reactions occur when dilute aqueous hydrochloric acid is added to both $\mathrm{In}(C_5H_5)$ and $\mathrm{In}(C_5H_4Me)$ as solids. The final products are indium(III) (oxidation) and 1 mol of H_2/mol of $\mathrm{In}(C_5H_4R)$ (reduction). However, in the case of both indium(I) cyclopentadienyl derivatives, indium metal is observed before H_2 generation occurs. Thus, indium(I) is apparently initially reduced and

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then the indium metal is oxidized. Since only 1 mol of H_2 is formed per mol of indium(I), only two-thirds of the initial indium(I) can be converted to indium metal. One possible reaction sequence (eq 3–5) that would be consistent with all observations involves the initial hydrolytic cleavage of $In(C_5H_4R)$ with the subsequent rapid disproportionation of the resulting indium(I) species to form indium metal and indium(III). The disproportionation reaction provides $^2/_3$ mol of indium metal/mol of indium(I) as required by the H_2 evolution measurements. An alternative sequence of reactions begins with the disproportionation of $In(C_5H_4R)$ (eq 6). Then, $In(C_5H_4R)_3$ would hydrolyze, and indium metal would be oxidized by H^+ to form the observed products. Our limited data do not permit us to distinguish between the two hypotheses. However, the persistence of the indium(I) derivative in aqueous HCl for sufficient time to form $In(C_5H_4R)_3$ would seem unlikely.

$$In(C_5H_4R)(s) + H^+(aq) \rightarrow In^+(aq) + C_5H_5R \quad (3)$$

$$In^+(aq) \rightarrow {}^2/_3In^0 + {}^1/_3In^{3+}(aq) \quad (4)$$

$$^2/_3In^0 + 2H^+ \rightarrow {}^2/_3In^{3+}(aq) + H_2(g) \quad (5)$$

$$3In(C_5H_4R) \rightarrow 2In^0 + In(C_5H_4R)_3 \quad (6)$$

The physical properties of $In(C_5H_5)$ and $In(C_5H_4Me)$ are surprisingly different. The parent compound $In(C_5H_5)$ is a pale yellow solid with the surprisingly high melting point of 169.3–171.0 °C. In contrast, $In(C_5H_4Me)$ is a colorless solid with the relatively low melting point of 48.5–51.0 °C. It is also noteworthy that $In(C_5H_4Me)$ is more volatile than $In(C_5H_5)$. These observations of volatility at room temperature suggest that the bonding between $In(C_5H_4R)$ units in the solid state is relatively weak. However, the interactions between $In(C_5H_5)$ are strong enough to substantially reduce the solubility of the compound in the nonpolar solvent cyclohexane. The compound $In(C_5H_4Me)$ is soluble in cyclohexane. The properties of solid $In(C_5H_5)$ and its long indium–cyclopentadienyl distances would be consistent with the earlier conclusion of significant ionic character to the bonds. The addition of a methyl group would appear to increase the covalent bonding contribution to the bonds between indium and the ring, decrease the metal–ring distance, and change the properties. In an upcoming paper additional comparisons between the significant features of $In(C_5H_5)$, $In(C_5H_4Me)$, and $In(C_5Me_5)$ will be fully discussed.

Acknowledgement is made to donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Office of Naval Research for partial support of this research. R.B. thanks Professor Arne Haaland, University of Oslo, for bringing him into the interesting field of cyclopentadienyl chemistry. We thank Dr. J. W. Ziller for assistance with the ORTEP diagrams.

Registry No. InCl, 13465-10-6; $In(C_5H_5)$, 34822-89-4; $In(C_5H_4Me)$, 38181-22-5; $Li(C_5H_5)$, 16733-97-4; $Li(C_5H_4Me)$, 54061-45-9; cyclopentadiene, 542-92-7; methylcyclopentadiene, 26519-91-5.

Supplementary Material Available: Tables of anisotropic thermal parameters (2 pages); listings of observed and calculated structure factor amplitudes (12 pages). Ordering information is given on any current masthead page.

Kinetic Study of the Formation of Dihydrogen from the Reaction of [1.1]Ferrocenophanes with Strong Acids. 2.[1] Tensiometry, Spectrometry, and Deuterium Exchange Studies

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Received July 14, 1987

The kinetics of the reactions [1.1]ferrocenophane (I), 3,3′-trimethylene[1.1]ferrocenophane (II), and 2,2′-trimethylene[1.1]ferrocenophane (III) were studied by using tensiometric and spectrometric techniques at acid strengths that were lower than those used in the electrochemical investigation.[1] The results of these measurements are consistent with the three-step mechanism proposed for the formation of dihydrogen: a very fast initial protonation, a slower second protonation, and the elimination of dihydrogen as the rate-determining step. However, at the lower acid strengths, competing reactions occur. One of these very likely involves the comproportionation of the ferrocenophane and the dication followed by the decomposition of the resulting monocation. The nature of other competing reactions remains as an open question. Kinetic studies using deuteriated acids established a primary kinetic isotope effect, k_H/k_D, between 3 and 5, for compound I. The ring protons of the ferrocenophane undergo complete exchange in these media at a rate much faster than the rate for dihydrogen formation. No exchange of the methylene protons was observed.

Introduction

Bitterwolf and Ling reported that compound I (see Figure 1 for the structures) reacts quantitatively with a strong acid, e.g. $BF_3{\cdot}H_2O$, to yield the ferrocenophane dication and dihydrogen.[2] Since ferrocene derivatives are known to be protonated on the iron atom under these conditions,[2,3] it was assumed[2] that the mechanism involves

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