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The golden yellow compound $In(C_5Me_5)$ has been prepared in only 62% yield from InCl and $Li(C_5Me_5)$ in diethyl ether and fully characterized according to its physical and solubility properties, its reaction with dilute aqueous HCl, a cryoscopic molecular weight study in cyclohexane, IR and $^1H$ NMR spectroscopic properties, a single-crystal X-ray diffraction study and a gas-phase electron diffraction study. The other products of this reaction have been identified as $In(C_5Me_5)_2Cl$, indium metal and $(C_5Me_5)_2$ in 5.0, 21 and 2.5% yields, respectively. The identity of the yellow indium(III) product, $In(C_5Me_5)_2Cl$,

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ABSTRACT (continued)

was confirmed by its independent synthesis from $InCl_3$ and $LiC_5Me_5$ in a 1:2 mol ratio and full characterization. The orange-yellow compound $In(C_5Me_5)Cl_2$ has also been synthesized from $InCl_3$ and $Li(C_5Me_5)$ in a 1:1 mol ratio in order to distinguish it from $In(C_5Me_5)_2Cl$. However, the attempted preparation of $In(C_5Me_5)_3$ from $InCl_3$ and either $Li(C_5Me_5)$ or $Na(C_5Me_5)$ was unsuccessful. A noteworthy observation of the chemical properties of the pentamethylcyclopentadienyl-indium(I) and -indium(III) compounds was their decomposition in benzene solution to form $(C_5Me_5)_2$ and other products. Additional studies of prepurified $In(C_5Me_5)$ confirmed decomposition in THF and pyridine but demonstrated its stability in cyclohexane. The compound $In(\eta^5-C_5Me_5)$ crystallizes in the rhombohedral space group $R\bar{3}$ ($C_{3i}^2$;No. 148) with unit cell parameters (hexagonal setting) *a*=20.182(4)Å, *c*=13.436(3)Å, V=4739(2)Å$^3$ and Z=18. Single-crystal X-ray diffraction data (Mo Kα, 2θ = 4.5-50.0°) were collected with a Syntex $P2_1$ automated four-circle diffractometer; the structure was solved and refinement converged with $R_F$ = 3.6% and $R_{wF}$ 3.3% for all 1870 symmetry-independent data (none rejected) and $R_F$ = 2 [illegible] and $R_{wF}$ = 2.9% for those 1444 reflections with $|F_o| > 6\sigma(|F_o|)$. The $\eta^5-C_5Me_5$ ligand is symmetrically bound to indium with In-C = 2.581(4)-2.613(4)Å (average = 2.595Å) and In•••centroid = 2.302Å. The $In(\eta^5-C_5Me_5)$ units are arranged about centers of $\bar{3}$ ($S_6$) symmetry, with indium atoms on the interior and $\eta^5-C_5Me_5$ units on the exterior of hexameric units in which In-In distances are 3.942(1)-3.963(1)Å. The "centroid" → indium vectors do not point toward the center of the hexaindium cluster as in other main-group clusters. The molecular structure of $In(C_5Me_5)$ in the gas phase consists of discrete monomeric units with the indium(I) atom being situated 2.288Å above the ring centroid. *Ab initio* calculations were carried out on $In(C_5H_5)$ and $In(C_5Me_5)$ in an attempt to understand the effects of methyl groups on the bonding between indium(I) and the cyclopentadienyl ring.

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# Pentamethylcyclopentadienyl-indium(I) and -indium(III) Compounds--Syntheses, Reactivities and X-Ray Diffraction and Electron Diffraction Studies of In($C_5Me_5$).

by

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# Pentamethylcyclopentadienyl-indium(I) and -indium(III) Compounds--Syntheses, Reactivities and X-Ray Diffraction and Electron Diffraction Studies of In($C_5Me_5$).

by

O. T. Beachley, Jr.[1a], Richard Blom[1b], Melvyn Rowen Churchill[1a], Knut Faegri, Jr., James C. Fettinger[1a], J. C. Pazik[1a] and L. Victoriano[1a]

## Abstract

The golden yellow compound In($C_5Me_5$) has been prepared in only 62% yield from InCl and Li($C_5Me_5$) in diethyl ether and fully characterized according to its physical and solubility properties, its reaction with dilute aqueous HCl, a cryoscopic molecular weight study in cyclohexane, IR and $^1$H NMR spectroscopic properties, a single-crystal X-ray diffraction study and a gas-phase electron diffraction study. The other products of this reaction have been identified as In($C_5Me_5$)$_2$Cl, indium metal and ($C_5Me_5$)$_2$ in 5.0, 21 and 2.5% yields, respectively. The identity of the yellow indium(III) product, In($C_5Me_5$)$_2$Cl, was confirmed by its independent synthesis from InCl$_3$ and LiC$_5$Me$_5$ in a 1:2 mol ratio and full characterization. The orange-yellow compound In($C_5Me_5$)Cl$_2$ has also been synthesized from InCl$_3$ and Li($C_5Me_5$) in a 1:1 mol ratio in order to distinguish it from In($C_5Me_5$)$_2$Cl. However, the attempted preparation of In($C_5Me_5$)$_3$ from InCl$_3$ and either Li($C_5Me_5$) or Na($C_5Me_5$) was unsuccessful. A

noteworthy observation of the chemical properties of the pentamethylcyclopentadienyl-indium(I) and -indium(III) compounds was their decomposition in benzene solution to form $(C_5Me_5)_2$ and other products. Additional studies of prepurified $In(C_5Me_5)$ confirmed decomposition in THF and pyridine but demonstrated its stability in cyclohexane. The compound $In(\eta^5-C_5Me_5)$ crystallizes in the rhombohedral space group $R\bar{3}$ ($C_{3i}^2$;No. 148) with unit cell parameters (hexagonal setting) $\underline{a}$=20.182(4)Å, $\underline{c}$=13.436(3)Å, V=4739(2)$Å^3$ and Z=18. Single-crystal X-ray diffraction data (Mo Kα, 2θ = 4.5-50.0°) were collected with a Syntex $P2_1$ automated four-circle diffractometer; the structure was solved and refinement converged with $R_F$ = 3.6% and $R_{wF}$ = 3.3% for all 1870 symmetry-independent data (none rejected) and $R_F$ = 2.5% and $R_{wF}$ = 2.9% for those 1444 reflections with $|F_o| > 6\sigma(|F_o|)$. The $\eta^5-C_5Me_5$ ligand is symmetrically bound to indium with In-C = 2.581(4)-2.613(4)Å (average = 2.595Å) and In•••centroid = 2.302Å. The $In(\eta^5-C_5Me_5)$ units are arranged about centers of $\bar{3}$ ($S_6$) symmetry, with indium atoms on the interior and $\eta^5-C_5Me_5$ units on the exterior of hexameric units in which In-In distances are 3.942(1) [illegible](1)Å. The "centroid" - indium vectors do not point toward the center of the hexaindium cluster as in other main-group clusters. The molecular structure of $In(C_5Me_5)$ in the gas phase consists of discrete monomeric units with the indium(I) atom being situated 2.288Å above the ring centroid. <u>Ab initio</u> calculations were carried out on $In(C_5H_5)$ and $In(C_5Me_5)$ in an attempt to understand the effects of methyl groups on the bonding between indium(I) and the cyclopentadienyl ring.

## Introduction

The chemistry of indium is of particular importance for elucidating the chemical relationships between group 13 derivatives in typical and low oxidation states. Even though simple indium(III) and indium(I) halides are available as starting materials for synthetic reactions, the only organic substituents which have been utilized for both classes of indium compounds are the cyclopentadienyl groups, $C_5H_5$ and $C_5H_4Me$. The indium(III) derivatives $In(C_5H_5)_3$[2,3] and $In(C_5H_4Me)_3$[3] were prepared from $InCl_3$ and a slight stoichiometric excess of $M(C_5H_4R)(M{=}Li,Na;\ R{=}H,Me)$. However, only $In(C_5H_5)_3$ has been investigated by an X-ray structural study.[4] The compound was reported to exist as infinite chains with each indium $\sigma$-bonded to two terminal and two bridging cyclopentadienyl groups. The indium(I) derivatives have been prepared by two routes, reduction reactions[2] of indium(III) and metathetical reactions of indium(I).[5] The initial preparation of $In(C_5H_5)$, the first organometallic indium(I) compound,[2] involved an apparent reduction reaction since the reagents were $InCl_3$ and $NaC_5H_5$ in a 1:4 mol ratio. Thermolysis of the reaction product mixture at 100°C produced $In(C_5H_5)$. The early workers[2] believed that $In(C_5H_5)_3{\bullet}OEt_2$ decomposed to form $In(C_5H_5)$. Later research[3] showed that $In(C_5H_5)$ was only formed from $In(C_5H_5)_3$ in significant amounts when the temperature was above 150°C. Thus, the cyclopentadienyl anion was suggested as the apparent reducing agent. When $Na(C_5H_5)$ was replaced by $Li(C_5H_5)$, the yield of $In(C_5H_5)$ was significantly lower and the yield of $In(C_5H_5)_3$ was correspondingly higher.[3] It is also of significance that methylcyclopentadienyl indium(III) compounds required lower temperatures for reductive thermolysis than those used in the cyclopentadienyl system. The most useful preparative route to indium(I) derivatives has involved a simple metathetical reaction between InCl and $Li(C_5H_4R)$. The yields[6] of $In(C_5H_5)$ and $In(C_5H_4Me)$ were typically greater than 80%. X-ray structural studies[6] have defined zig-zag polymeric structures with $In(\eta^5\text{-}C_5H_4R)$ (R=H,Me) units and apparent indium-indium interactions. In the crystal structure of $In(C_5H_5)$ each indium was separated from two other indium atoms by 3.986(1)Å whereas in the $In(C_5H_4Me)$ structure,[6] each indium had only one neighbor at 3.986(1)Å.

The synthesis and characterization of $In(C_5Me_5)$ has been reported recently.[7] This communication revealed that the compound was prepared in only 58% yield but the disposition of the remaining indium remained undefined. We herein report our studies which have been used to define (1) the products from the reaction between InCl and $Li(C_5Me_5)$, (2) the nature of pentamethylcyclopentadienyl indium(III) compounds and (3) the chemical relationships between indium(I) and indium(III) pentamethylcyclopentadienyl derivatives. The isolable products from the InCl - $Li(C_5Me_5)$ reaction include $In(C_5Me_5)$, indium metal, LiCl, $In(C_5Me_5)_2Cl$ and $(C_5Me_5)_2$. These compounds have been characterized by elemental analysis, IR and $^1H$ NMR spectroscopy and cryoscopic molecular weight studies in cyclohexane, as appropriate. In addition, the structures of $In(C_5Me_5)$ in both the solid and gas phases have been determined by X-ray and electron diffraction studies, respectively. The structural parameters of $In(C_5Me_5)$ are in turn compared with those for $In(C_5H_4Me)$ and $In(C_5H_5)$ in order to elucidate the experimentally observable effects of methyl groups on cyclopentadienyl ring-indium(I) bonding interactions. *Ab initio* calculations for $In(C_5Me_5)$ and $In(C_5H_5)$ have been used to understand more fully the bonding interactions responsible for our experimental observations.

## 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) derivative was so exceedingly sensitive to trace quantities of moisture that all glassware used for its preparation, characterization and handling was flame heated under dynamic vacuum prior to use. Indium(I) chloride was purchased from Strem Chemicals, Inc., indium(III) chloride from Aesar and both were used without further purification. All solvents were purified before use. Diethyl ether was refluxed and stored over sodium diphenylketyl. Pentane and cyclohexane were refluxed over $CaH_2$ and stored over a sodium mirror. Pentamethylcyclopenta-diene was vacuum distilled immediately before use. Since the purity of $Li(C_5Me_5)$ and $Na(C_5Me_5)$ is of significance to the synthesis of the indium(I) derivative, 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 90MHz by means of either a Varian Model EM-390 or a Joel 90Q spectrometer. Chemical shifts are reported in $\delta$ units(ppm) and are referenced to $SiMe_4$ as $\delta$ 0.00 and benzene as $\delta$ 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.[8]

Preparation of Li($C_5Me_5$). A 100mL two-necked flask was charged with 12.5mL of 2.5M Li(n-Bu) (31.2mmol) and 4.06g of pentamethylcyclopentadiene (29.8mmol) was added to a side-arm dumper. The appartus was assembled and 40mL of pentane was vacuum distilled into the flask containing the $C_5Me_5H$. The reagents were mixed at room temperature and a white precipitate formed. After stirring for 18h, the volatile components were removed by vacuum distillation. The reaction flask was fitted with a medium frit connected to a 100mL side-arm flask. Pentane (50mL) was vacuum distilled into the flask containing the off-white Li($C_5Me_5$) and the product was washed 5 times with the pentane. The off-white insoluble product, Li($C_5Me_5$) (4.09g, 28.8mmol) was isolated in 96.7% yield based on $C_5Me_5H$.

Li($C_5Me_5$). IR (Nujol mull, $cm^{-1}$): 2722(m), 1300(vw), 1070(vw), 791(w), 763(vw), 533(vs, br), 388(vw), 321(w).

Preparation of Na($C_5Me_5$). The compound, $NaC_5Me_5$, was prepared according to a modification of a previous method.[9] Finely divided sodium was obtained by removing toluene, by vacuum distillation, from a 30% Na/toluene dispersion (Alfa Products). The sodium (2.04g, 83.95mmol) was added to a 100mL two-necked flask and $C_5Me_5H$ (5.079g, 37.2mmol) was pipetted into a tube sealed with a Teflon valve. Fifty milliliters of THF was vacuum distilled into the flask containing the sodium with 20mL being distilled into the tube containing the $C_5Me_5H$. Both vessels were purged with argon and the sealed tube and condenser were connected to the two neck flask. The solution of $C_5Me_5H$ was added to the sodium dispersion in THF and the reaction mixture was refluxed for 2d. The THF was removed by vacuum distillation. In the dry box, a fresh portion of THF was added to the reaction mixture. The dispersion was allowed to settle and the supernatant liquid was removed. This extraction was repeated an additional time with a fresh portion of THF. Both solutions were combined and then filtered through a medium glass frit into a 100mL side arm flask. The THF was removed by vacuum distillation and the product was washed three times with pentane. The compound, $Na(C_5Me_5)$, was isolated as a colorless, granular solid in 43.56% yield (2.57g, 16.2mmol) based on $C_5Me_5H$.

$Na(C_5Me_5)$. $^1H$ NMR ($d^8$-THF, $\delta$): 1.95 (s). IR (Nujol mull, $cm^{-1}$): 2730(m), 1075(vw), 1022(vw), 985(vw), 789(w), 461(vw), 403(w), 330(vs), 281(w), 272(m).

Synthesis of $In(C_5Me_5)$. Finely ground indium(I) chloride (1.438g, 9.572mmol) was weighed and transferred to a side-arm dumper. The side-arm dumper was connected to a 100mL two neck flask containing 1.419g of $Li(C_5Me_5)$ (9.989mmol). The apparatus was evacuated and 50mL of $Et_2O$ was vacuum distilled into the flask containing the $Li(C_5Me_5)$. After a suspension of $Li(C_5Me_5)$ was obtained by rapid stirring, the InCl was added, all at once, to the suspension. A gray precipitate of indium metal was observed after the addition. The reaction mixture was stirred at room temperature for 5h and then the solution was filtered through a medium glass frit. The light gray ether-insoluble product was washed four times with the ether. A total of 2.000g of a yellow ether-soluble product was isolated and transferred to a Solv-seal sublimation tube. Golden yellow crystals of $In(C_5Me_5)$ (1.485g, 5.938mmol, 62.01% yield based on InCl) were separated from the ether-soluble solid by sublimation at 55°C. Pentane was then vacuum distilled onto the nonvolatile, ether soluble residue and the resulting pentane insoluble portion was extracted three times. A 0.302g sample of a pentane soluble material was isolated and purified by washing it with one 20mL portion of pentane to yield 0.0849g of analytically pure

$In(C_5Me_5)_2Cl$ (0.202mmol, 2.11% yield based on InCl). The remaining pentane-soluble portion contained an additional 0.112g of $In(C_5Me_5)_2Cl$ (0.276mmol) and 0.0337g of $(C_5Me_5)_2$ (0.125mmol) which were identified by $^1H$ NMR spectroscopy. Both the ether-soluble but pentane-insoluble material (0.0366g) and the ether-insoluble fraction (0.6545g) contained LiCl, $In^0$ and excess $Li(C_5Me_5)$. Calculations which considered the stoichiometric excess of $Li(C_5Me_5)$ over the mol quantity of InCl and the assumption that all chlorine in InCl formed LiCl indicated that 0.226g of indium metal (1.97mmol, 20.6% of the initially available indium) was produced.

$In(C_5Me_5)$. Golden-yellow crystalline solid; mp 92.0-93.0°C. $^1H$ NMR ($C_6H_6$, $\delta$): 2.02 (s) Refer to Results and Discussion for further details of the $^1H$ NMR spectra. IR (Nujol mull, $cm^{-1}$): 2720(vw), 1727(w), 1412(m), 1152(vw), 1014(w), 790(m), 583(m), 466(vw), 345(w), 285(sh), 280(vs), 268(vs). Anal. Calcd.: C, 48.03; H, 6.06. Found: C, 47.74; H, 6.04. Cryoscopic molecular weight, cyclohexane solution, formula weight 250 (obsd. molality, obsd. mol. wt., association): 0.136, 260, 1.04; 0.0978, 266, 1.06; 0.0622, 273, 1.09.

$In(C_5Me_5)_2Cl$. Yellow crystalline solid; mp decomposes at 97°C. $^1H$ NMR ($C_6H_6$, $\delta$): 1.88 (s). IR (Nujol mull, $cm^{-1}$): 1734(w), 1728(w), 1590(vw), 1276(m), 1237(m), 1142(w), 1128(w), 1050(w), 1035(w), 1005(vw), 940(w), 798(w), 787(w), 592(m), 561(w), 420(w), 254(vs). Anal. Calcd.: C, 57.10; H, 7.19. Found: C, 56.96; H, 7.25.

Hydrolysis of $In(C_5Me_5)$. A 0.243g (0.972mmol) sample of $In(C_5Me_5)$ was added to a tube equipped with a Teflon valve. The tube was evacuated and approximately 8mL of a dilute HCl solution was added through the neck of the tube. The $In(C_5Me_5)$ formed a ball of indium metal upon addition of the acid solution. Gas evolution was observed at the surface of the indium metal.

The tube was placed in a 100°C oil bath and the reaction mixture was stirred for 2h to form a clear pink solution. Hydrogen gas (0.819mmol) was later collected by means of a Toepler pump-gas buret assembly for an 84.3% yield based on the oxidation of $In^{+1}$ to $In^{+3}$.

### Identification of Initial Products From the Hydrolysis of $In(C_5Me_5)$.

In the dry box, a 0.131g (0.524mmol) sample of $In(C_5Me_5)$ was transferred to a 125mL Erlynmeyer flask. The top of the flask was covered with Parafilm and removed from the dry box. Dilute HCl (10mL) was added to the flask containing the $In(C_5Me_5)$. After 15 min of reaction, 10mL of benzene was added to the aqueous solution. The benzene/$H_2O$ mixture was transferred to a separatory funnel. The bottom aqueous phase was discarded and a $^1H$ NMR spectrum of the yellow benzene solution was obtained. The spectrum exhibited lines at δ1.77 (s), 1.72 (s), 1.00 (d, J=8.1Hz) and a small line at δ0.42 (s). Except for the small line at δ0.42 (believed due to an impurity), the spectrum was identical to that of an authentic sample of $C_5Me_5H$.

### Relative Rates of Decomposition of $In(C_5Me_5)$ in Different Solvents.

The decomposition of cyclohexane, benzene, pyridine and THF solutions of $In(C_5Me_5)$ to indium metal and $(C_5Me_5)_2$ was studied by $^1H$ NMR spectroscopy. All NMR tubes were flame sealed under vacuum and the initial spectra were recorded immediately after the solutions were warmed to room temperature. Observed rate constants were calculated as described in the following section for "Benzene".

Benzene: A 0.0436g sample of $In(C_5Me_5)$ (0.174mmol) was placed in an NMR tube and 0.7mL of $C_6D_6$ was vacuum distilled onto the sample. The initial spectrum exhibited a single resonance at δ2.02. With time, resonances at 1.72 (s), 1.64 (s) and 1.12ppm (s), indicative of $(C_5Me_5)_2$, grew into the spectrum. Upon increasing the amplitude of the initial spectrum, small lines at 1.77 (s), 1.72 (s) and 0.96ppm (d) corresponding to $C_5Me_5H$ were observed. These resonances did not continue to grow and their area was eliminated in subsequent calculations. The relative areas of the $In(C_5Me_5)$ and $(C_5Me_5)_2$ resonances were normalized and an observed rate constant was calculated based on the disappearance of the $In(C_5Me_5)$ resonance.

<u>THF</u>: In a similar manner, an NMR tube was charged with 0.0446g of $In(C_5Me_5)$ (0.178mmol) and 0.7mL of $d^8$-THF. At time zero, the $^1H$ NMR spectrum consisted of one line at 2.05ppm (s). Throughout the time frame of the experiment, two new resonances at 1.65 (s) and 1.07ppm (s) appeared and grew in intensity. These lines coincided with those for an authentic spectrum of $(C_5Me_5)_2$ in THF solution. The initial spectrum also revealed a trace amount of $C_5Me_5H$.

<u>Pyridine</u>: An NMR tube was charged with 0.044g of $In(C_5Me_5)$ (0.18mmol) and 0.7mL of pyridine. The initial spectrum consisted of one resonance at 2.06ppm (s, $In(C_5Me_5)$). Lines coinciding with those of an authentic sample of $C_5Me_5H$ were observed at higher amplitudes. With time, resonances for $(C_5Me_5)_2$ at 1.72 (s), 1.67 (s) and 1.12ppm (s) began to appear and increase in intensity in the spectra.

<u>Cyclohexane</u>: An NMR tube was charged with 0.0439g of $In(C_5Me_5)$ (0.176mmol) and 0.7mL of $d^{12}$-cyclohexane. The $^1H$ NMR spectra exhibited a singlet at 2.05ppm ($In(C_5Me_5)$) and a small broad line at 1.38ppm (residual $C_6H_{12}$). The spectrum was monitored for 5d with virtually no change in the relative areas of the resonances initially observed and no new resonances appeared.

<u>Synthesis of $In(C_5Me_5)_2Cl$ from $InCl_3$</u>. A 100mL side-arm flask was charged with 1.794g of $InCl_3$ (8.111mmol) and 2.371g of $Li(C_5Me_5)$

(16.68mmol). The flask was evacuated and 50mL of diethyl ether was distilled onto the reaction mixture. After stirring at room temperature for 14h the ether was removed by vacuum distillation. Pentane (50mL) was distilled onto the products and the resulting solution was filtered through a medium glass-frit. The compound, $In(C_5Me_5)_2Cl$, was separated from the LiCl by repeated (~20) pentane washings. A yellow solid, $In(C_5Me_5)_2Cl$, was isolated from the pentane in 77.6% yield (2.649g, 6.297mmol) based on $InCl_3$. The pentane insoluble product consisted of LiCl and excess $Li(C_5Me_5)$. Lithium chloride (0.680g, 16.0mmol) was obtained in 98.9% yield after accounting for the excess $Li(C_5Me_5)$ over $InCl_3$. The indium(III) compound was purified by washing it once with 20mL of pentane.

$In(C_5Me_5)_2Cl$. Yellow crystalline solid; mp. decomposes at 98.5°C to a brown material; at 103°C the sample turns opaque white. $^1H$ NMR (ppm): $C_6H_6$, 1.87 (s); $d^8$-THF 1.78 (s). Refer to Results and Discussion for further details of the NMR spectra. IR (Nujol, $cm^{-1}$): 1725(vw), 1618(w), 1590(vw), 1275(m), 1235(m), 1140(w), 1128(w), 1050(m), 1035(w), 1008(w), 940(m), 815(vw), 798(w), 788(w), 694(w), 650(w), 592(m), 560(w), 420(m), 398(w), 278(m), 254(vs). Anal. Calcd.: C, 57.10; H, 7.19. Found: C, 57.36; H, 7.45. Solubility: very soluble in $Et_2O$ and THF, limited solubility in benzene and pentane.

Reaction of $InCl_3$ with $Li(C_5Me_5)$ in a 1:3 Mole Ratio. Freshly prepared $Li(C_5Me_5)$ (2.020g, 14.22mmol) was added to a 100mL two-necked flask and a side-arm dumper was charged with 1.000g of $InCl_3$ (4.521mmol). The apparatus was assembled, evacuated and 50mL of diethyl ether was vacuum distilled into the flask containing the $Li(C_5Me_5)$. The $InCl_3$ was added to the suspension of $Li(C_5Me_5)$. After stirring at room temperature for 24h, the $Et_2O$ was removed and 50mL of pentane were vacuum distilled into the flask containing the reaction products. A yellow, pentane soluble solid was extracted from the insoluble LiCl. The yellow product was identified as In(C$_5$Me$_5$)$_2$Cl (1.461g, 3.473mmol, 76.80% yield based on InCl$_3$) by its melting point, $^1$H NMR spectrum and elemental analysis.

Reaction of InCl$_3$ with Na(C$_5$Me$_5$) in a 1:3 Mole Ratio. Indium trichloride (0.348g, 1.57mmol) was added to a side arm dumper and the dumper was connected to a 100mL two-necked flask containing 0.788g of Na(C$_5$Me$_5$) (4.98mmol). Tetrahydrofuran (50mL) was vacuum distilled onto both reactants. The reagents were mixed and a deep yellow solution formed immediately. Within 5.5h the deep yellow solution turned pale yellow. After stirring for 18h a trace amount of indium metal was observed. The THF was removed and 50mL of pentane was distilled onto the reaction products. The pentane insoluble material contained NaCl and excess Na(C$_5$Me$_5$) (0.299g, 94.0% yield of NaCl as based on complete reaction and by accounting for excess Na(C$_5$Me$_5$) over InCl$_3$). The pentane soluble portion contained a mixture of In(C$_5$Me ) and (C$_5$Me$_5$)$_2$. Golden yellow crystals of In(C$_5$Me$_5$) (0.221g, 0.886mm [illegible] .4% yield based on InCl$_3$) were sublimed from the pentane soluble mixture. A $^1$H NMR spectrum of a 0.394g sample of the pentane soluble portion was obtained after most of the In(C$_5$Me$_5$) was removed. The spectrum exhibited resonances at 2.00ppm (s), 1.72ppm (s), 1.63ppm (s) and 1.11ppm (s) relative to benzene at 7.13ppm. Integration values indicated that 90.5% of the sample was (C$_5$Me$_5$)$_2$ (0.356g 1.32mmol, 83.9% yield based on InCl$_3$). The line at 2.00ppm was assigned to In(C$_5$Me$_5$) indicating an additional 0.0378g (0.151mmol, 9.5%) for a total yield of 65.9% yield based on InCl$_3$. Refer to Results and Discussion for additional details.

Reaction of $Li(C_5Me_5)$ with $InCl_3$ in a 1:1 Mole Ratio. An apparatus consisting of a 100mL two-neck flask with $Li(C_5Me_5)$ (0.757g, 5.33mmol) and a side-arm dumper with 1.183g of $InCl_3$ (5.349mmol) was assembled, evacuated and diethyl ether (50mL) was vacuum distilled onto the $Li(C_5Me_5)$. The $InCl_3$ was added to the resulting suspension. After stirring for 24h at room temperature, the solution was filtered to yield 0.0689g of LiCl, an ether-insoluble product. The ether was removed by vacuum distillation and 50mL of pentane was distilled onto the ether-soluble, orange-yellow solid. After 4 extractions, a total of 1.03g of impure $In(C_5Me_5)Cl_2$ (3.21mmol, 60.2% yield based on $InCl_3$) was isolated from the pentane-soluble portion. An additional 0.581g of LiCl was isolated as a pentane-insoluble product for a total yield of greater than 100%. It was evident that the pentane-insoluble material contained additional $In(C_5Me_5)Cl_2$. Attempted purifications, which included washing the final product with pentane and recrystallization from a saturated pentane solution, were unsuccessful.

$In(C_5Me_5)Cl_2$. Orange-yellow solid; mp sample turned purple at 98.5°C and by 176°C the material was black. $^1H$ NMR ($C_6H_6$, $\delta$): 1.89 (s, $In(C_5Me_5)_2Cl$), 1.84 (s, $In(C_5Me_5)Cl_2$), 1.72 (s, $(C_5Me_5)_2$), 1.64 (s, $(C_5Me_5)_2$), and 1.12 (s, $(C_5Me_5)_2$). The resonances for the impurities, $In(C_5Me_5)_2Cl$ and $(C_5Me_5)_2$, were only of minor intensity.

Relative Rates of Decomposition of $In(C_5Me_5)_2Cl$ and $In(C_5Me_5)Cl_2$. The rates of decomposition of $In(C_5Me_5)_2Cl$ and $In(C_5Me_5)Cl_2$ were studied by $^1H$ NMR spectroscopy. NMR tubes were flame sealed under vacuum and the initial spectra were recorded immediately after the solutions warmed to room temperature. Relative integration values were monitored and treated as absorbances. $In(C_5Me_5)_2Cl$: A saturated benzene solution of the compound was prepared and the initial spectrum exhibited one resonance at 1.88ppm (s).

With time resonances due to the formation of $(C_5Me_5)_2$ at 1.73, 1.64 and 1.12ppm were monitored. In addition to these resonances, lines at 2.00, 1.93 and 1.90ppm appeared in later spectra. These observations suggest that multiple species were being formed. <u>$In(C_5Me_5)Cl_2$</u>: The spectrum of a saturated benzene solution of the compound was recorded at various time intervals. The intensity of the resonance at 1.83ppm associated with $In(C_5Me_5)_2Cl$ decreased with time while resonances at 1.73, 1.65 and 1.13ppm ($(C_5Me_5)_2$) grew in intensity. Relative integration values were normalized and an observed rate constant was calculated. (See Results and Discussion)

<u>Collection of X-Ray Diffraction Data for $In(\eta^5\text{-}C_5Me_5)$</u>. A clear golden yellow crystal of approximate dimensions 0.3x0.3x0.45 $mm^3$ was mounted in a thin-walled glass capillary under an inert atmosphere. The capillary was sealed and the crystal was accurately centered and aligned on a eucentric goniometer on a Syntex $P2_1$ automated four-circle diffractometer. All subsequent operations *involved in determining the crystal's* lattice parameters and orientation matrix and in collecting intensity data were carried out as described previously.[10] Details are given in Table I. The following points should be noted. (1) The crystal belongs to the rhombohedral sub-set of the trigonal/hexagonal crystal system. It has only $\bar{3}$ ($S_6$ or $C_{3i}$) diffraction symmetry as determined by (a) axial photographs and (b) unsuccessful attempts to average data using the higher $\bar{3}m$ ($D_{3d}$) Laue group. Averaging statistics were $R(I) = 4.1\%$ and $R(wI) = 5.1\%$ for three averaged forms under $\bar{3}$ symmetry (cf. $R(I) = 39\%$ and $R(wI) = 50\%$ under $\bar{3}m$ symmetry). (2) We elected to use the hexagonal axes rather than the rhombohedral axes for cell parameters. (3) With the systematic presence of data for $-h+k+\ell = 3n$ only and no other systematic absences, possible space groups are the centrosymmetric $R\bar{3}$ ($C_{3i}^2$; No. 148)[11a] or the

noncentrosymmetric R3 ($C_3^4$; No. 146).[11b] The former was found to be the correct choice by successful solution of the structure in that higher-symmetry group.

All data were corrected for the effects of absorption and for Lorentz and polarization effects; the 5770 data collected (representing three equivalent forms) were merged to 1870 point group independent data. Data were converted to $|F_o|$ values and placed on an approximately absolute scale by means of a Wilson plot. All 1870 data were used in the subsequent refinement.

<u>Solution of the Structure of In($\eta^5$-$C_5Me_5$).</u> All calculations were carried out using the SUNY-Buffalo modified version of the Syntex XTL interactive crystallographic program package.[12] Calculated structure factors were based upon the analytical expression for the neutral atoms' scattering factors;[13a] these were corrected for both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion.[13b] The function minimized during least-squares refinement procedures was $\Sigma w(|F_o|-|F_c|)^2$, with $1/w = [\sigma(|F_o|)]^2 + [0.015|F_o|]^2$.

The location of the heavy atom (In) was determined from a Patterson map. All other atoms (including all hydrogen atoms) were found from difference-Fourier maps. Refinement converged ($\Delta/\sigma > 0.01$) with $R_F = 3.6\%$, $R_{wF} = 3.3\%$ and GOF = 0.997[14] for all 1870 reflections ($R_F = 2.8\%$ and $R_{wF} = 3.2\%$ for the 1619 reflections with $|F_o| > 3\sigma(|F_o|)$; $R_F = 2.5\%$ and $R_{wF} = 2.9\%$ for those 1444 reflections with $|F_o| > 6\sigma(|F_o|)$). The function $\Sigma w|\Delta F|^2$ showed no significant dependence upon $|F_o|$, $(\sin\theta)/\lambda$, sequence number or identity or parity of the Miller indicies; the weighting scheme is thus appropriate. A final difference-Fourier synthesis showed no features above $0.18e^-/\AA^3$; the structure is thus both correct and complete.

A correction for secondary extinction was applied to all data, based upon the approximate Zachariasen equation,[15] $|F_{o,cor}| = |F_{o,uncor}| (1.0 + gI_o)$; the value determined for g was $3.7 \times 10^{-8}$.

Final atomic coordinates are collected in Table II.

*Electron Diffraction Study of In($C_5Me_5$).* The electron scattering pattern of In($C_5Me_5$) were recorded on Balzers Eldigraph KDG-2[16] with nozzle and reservoir temperatures of 92(5)°C. A torus shaped nozzle, which permitted the scattering pattern to be recorded with a reservoir vapor pressure of about 1 torr[17] was used. The electronic wavelength was calibrated against scattering patterns of benzene ($\underline{r}$(C-C)=139.75 pm) with an estimated standard deviation of 0.1%. The nozzle-to-plate distances were 497.97 and 248.03 mm with five (5) plates being used at each distance. The data extended from $s = 21.25$ to $150.0\ nm^{-1}$ with $\Delta s = 1.25\ nm^{-1}$ (50 cm) and from $s = 40.25$ to $260.0\ nm^{-1}$ with $\Delta s = 2.5\ nm^{-1}$. Complex atomic scattering functions, f'(s), for H and C were calculated from an analytical representation of the atomic potential.[18] For In, tabulated values were used,[19] interpolated to 42 kV. The data reduction was carried out by established procedures.[20] 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 a least-squares fitting of the sum of a polynomial and a theoretical molecular intensity curve to the experimental levelled intensity curve. The degree of the polynomial was 6 for the long nozzle-to-plate distance set and 8 for the short nozzle-to-plate distance set. Individual curves of each set were averaged, but the average curves were not connected in the least-squares refinements. A non-diagonal weight matrix was used in the final refinement in order to correct for data correlation.[21]

The molecular model of $In(C_5Me_5)$ is shown in Figure 5. The $In(C_5C_5)$ skeleton was assumed to be of $C_{5v}$ symmetry, and the $CCH_3$ fragment of $C_{3v}$ symmetry fixed in a position with one InCCH torsion angle of 90°. With these assumptions the molecular structure can be described by six independent parameters; the In-ring centroid height, h, the C1-C2, C1-C11 and C-H bond distances and the two angles, <CCH of the methyl groups, and the angle between the ring plane and the C-C(Me) bonds, $<C_5$,C-C(Me). The latter is defined as positive when the ring substituents are bent towards the metal atom. In addition to these six geometrical parameters, ten root-mean-square amplitudes of vibration (l-values) were included in the refinements.

The theoretical molecular intensity curves with experimental points are shown in Figure 6, and the corresponding experimental radial distribution curve is shown in Figure 7.

Ab initio Calculations. All calculations were carried out by using the DISCO program which takes full advantage of the molecular symmetry.[22] Calculations were carried out on $In(C_5H_5)$ and $In(C_5Me_5)$ with assumed $C_{5v}$ symmetry. The indium-ring centroid distance was the only geometrical parameter that was varied to yield an optimum energy for each basis set. The ring geometries were fixed with r(C-C) = 1.422 Å and r(C-H) = 1.080 Å for $C_5H_5$, and r(C-C) = 1.422 Å, r(C-C(Me)) = 1.500 Å, and r(C-H) = 1.080 Å for $C_5Me_5$. The ring substituents were bent out of the ring plane by 5° away from the metal atom. The different sets of basis functions were used: The M-basis set[23] is for In a 15s11p6d basis set contracted to 10s8p4d, for C a 7s3p basis set contracted to 4s2p and for H a 4s basis set contracted to 2s. The L-basis set[24] is for In a 18s14p8d basis set contracted to 16s12p8d, for C a 10s6p basis set contracted to 6s4p and for H a 4s basis set contracted to 2s.

## Results and Discussion

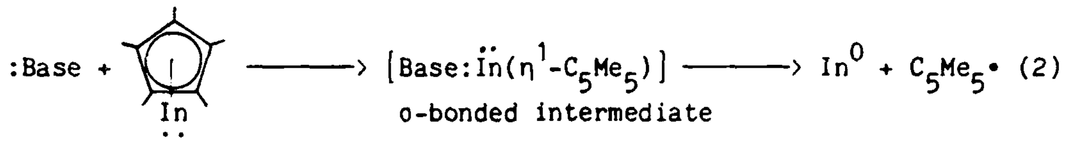
The third example of an indium(I) derivative, $In(C_5Me_5)$, has been prepared from InCl and $Li(C_5Me_5)$ in diethyl ether by using a modification of the general procedure of Peppe, Tuck and Victoriano.[5] The compound has been fully characterized by elemental analyses (C,H), physical properties, IR and $^1H$ NMR spectroscopic data, oxidation reactions with dilute aqueous HCl, stability studies in a variety of solvents, cryoscopic molecular weight studies in cyclohexane as well as X-ray and electron diffraction structural studies of the solid and gas phases, respectively. The use of high purity reagents and very clean, dry glassware lead to a 62% yield of $In(C_5Me_5)$. Similar reaction conditions provided $In(C_5H_5)$ and $In(C_5H_4Me)$ in approximately 80 and 85% percent yields, respectively.[6]

The fate of the indium after the reaction of InCl with $Li(C_5Me_5)$ in diethyl ether has been investigated in detail. The products of the reaction were separated initially by their solubility in ether, the reaction solvent. The insoluble material included indium metal (~ 20% of the initially available indium), LiCl (assumed to be stoichiometric) and the slight excess of $Li(C_5Me_5)$. The ether-soluble products were $In(C_5Me_5)$, $In(C_5Me_5)_2Cl$ and $(C_5Me_5)_2$. The indium(I) product was isolated by sublimation at 55°C. After all $In(C_5Me_5)$ had been removed from the ether-soluble material, repeated pentane extractions provided a mixture of $In(C_5Me_5)_2Cl$ and $(C_5Me_5)_2$. A partial extraction of this mixture with pentane provided an analytically pure sample of $In(C_5Me_5)_2Cl$. The identity of this compound was confirmed by its independent synthesis from $InCl_3$ and $Li(C_5Me_5)$ and comparisons of spectral and physical properties.

Our data suggest that the decomposition of purified $In(C_5Me_5)$ leads to the formation of indium metal and decamethylfulvalene,[25] $(C_5Me_5)_2$

$$2In(C_5Me_5) \longrightarrow 2In^0 + (C_5Me_5)_2 \qquad (1)$$

(Equation 1). In order to more fully understand this process, the relative rates of decomposition of $In(C_5Me_5)$ in benzene, THF, pyridine and cyclohexane were studied by $^1H$ NMR spectroscopy. These solvents were selected because they would include a range of basicities and their resonances would not interfere with those of either $In(C_5Me_5)$ or $(C_5Me_5)_2$. The observed pseudo first order rate constants for the decomposition of $In(C_5Me_5)$ suggest the following order: cyclohexane (no decomposition over 5 days) < benzene ($2.4 \times 10^{-3}$ $hr^{-1}$), < THF ($4.1 \times 10^{-3}$ $hr^{-1}$) < pyridine ($7.0 \times 10^{-3}$ $hr^{-1}$). Thus, as the Lewis base strength of the solvent increased, the observed rate of decomposition increased. Two mechanisms are consistent with our data. Both involve the initial coordination of the base to a Lewis acid site in $In(C_5Me_5)$ with slippage of the cyclopentadienyl ring from $\eta^5$ to $\eta^1$ (Equation 2). (Benzene would have to form a π-complex with indium(I).) If the Base:$In(\eta^1\text{-}C_5Me_5)$ intermediate decomposed by a homolytic cleavage of



the indium-carbon σ-bond, indium atoms and $C_5Me_5$ radicals would form. Subsequent dimerization of the $C_5Me_5$ radical would form the observed fulvalene, the major product. Pentamethylcyclopentadiene was only observed during the initial minutes of the decomposition. It is noteworthy that $In[CH_2(SiMe_3)_2]$ and $In[N(SiMe_3)_2]$ also have been suggested to decompose rapidly by a radical path.[26] An alternate pathway for the formation of indium metal and $(C_5Me_5)_2$ from Base:$\ddot{In}(\eta^1\text{-}C_5Me_5)$ could involve an initial disproportionation reaction to form indium metal and $In(C_5Me_5)_3$. This reaction would have to be followed by either a rapid reductive elimination and/or a radical decomposition reaction(s) (Equation 3-4) as $In(C_5Me_5)_3$ is

$$3Base{:}\ddot{I}n(\eta^1\text{-}C_5Me_5) \longrightarrow 2In^0 + \underset{\text{unstable}}{[In(C_5Me_5)_3]} \qquad (3)$$

$$[In(C_5Me_5)_3] \longrightarrow In(C_5Me_5) + (C_5Me_5)_2 \qquad (4)$$

not an observed product. Even though the indium(III) compounds $In(C_5Me_5)_2Cl$ and $In(C_5Me_5)Cl_2$ have been observed to form $(C_5Me_5)_2$, our experimental data do not permit us to distinguish between the two mechanisms.

The identity of $In(C_5Me_5)_2Cl$ among the products of the reaction of InCl with $Li(C_5Me_5)$ has been confirmed by the independent synthesis of bis(pentamethylcyclopentadienyl)indium(III) chloride. The new compound was prepared from $InCl_3$ and $Li(C_5Me_5)$ in a 1:2 mol stoichiometry (Equation 5) in $Et_2O$ solution. The compound $In(C_5Me_5)_2Cl$ was isolated as a bright yellow

$$InCl_3 + 2Li(C_5Me_5) \longrightarrow In(C_5Me_5)_2Cl + 2LiCl \qquad (5)$$

solid in 77.6% yield and has been fully characterized by elemental analyses, melting point data and IR and $^1H$ NMR spectroscopy. Bis(pentamethylcyclopentadienyl)indium(III) chloride is soluble in ethereal solvents but has limited solubility in benzene and pentane. In addition, $In(C_5Me_5)_2Cl$ decomposed in benzene. (See later discussion.) Consequently, the structure of $In(C_5Me_5)_2Cl$ in solution could not be studied by cryoscopic molecular weight measurements. The sample of $In(C_5Me_5)_2Cl$ obtained from the reaction of $InCl_3$ and $Li(C_5Me_5)$ had properties which were identical to those of a sample isolated from the reaction of InCl and $Li(C_5Me_5)$.

(Pentamethylcyclopentadienyl)indium(III) dichloride ($In(C_5Me_5)Cl_2$) was also independently synthesized in order to distinguish it from $In(C_5Me_5)_2Cl$. The compound $In(C_5Me_5)Cl_2$ was isolated as an orange-yellow solid from the reaction of $InCl_3$ and $Li(C_5Me_5)$ in a 1:1 mol stoichiometry in diethyl ether. Unfortunately, satisfactory elemental analyses could not be obtained. The experimental percent composition of carbon and hydrogen were significantly higher than the calculated value, but not nearly as high as required if significant quantities of $In(C_5Me_5)_2Cl$ were also present. The poor analytical results are consistent with the apparent ease of decomposition of $In(C_5Me_5)Cl_2$ in solution. The $^1H$ NMR spectra of $In(C_5Me_5)Cl_2$ always exhibited resonances for the fulvalene derivative $(C_5Me_5)_2$ which grew in intensity relative to the singlet at 1.83ppm assigned to $In(C_5Me_5)Cl_2$. The nature of $In(C_5Me_5)Cl_2$ and $In(C_5Me_5)_2Cl$ will be discussed more fully in a later paragraph.

Attempts have been made to prepare tris(pentamethylcyclopentadienyl)-indium(III) ($In(C_5Me_5)_3$) by metathatical reactions between $InCl_3$ and $Li(C_5Me_5)$ or $Na(C_5Me_5)$ in a 1:3 mol stoichiometry in order to test the hypothesis that $In(C_5Me_5)_3$ is an intermediate in the preparation or decomposition of $In(C_5Me_5)$. Reaction of $InCl_3$ and $Li(C_5Me_5)$ in a 1:3 mol ratio led to the formation of $In(C_5Me_5)_2Cl$. No $In(C_5Me_5)_3$ was observed. It is of interest that attempts to prepare $Ga(C_5Me_5)_3$ from $GaCl_3$ and $Li(C_5Me_5)$ (1:3 mol ratio) resulted in the formation of $Ga(C_5Me_5)_2Cl$.[9] However, upon utilizing the stronger alkylating agent $Na(C_5Me_5)$, $Ga(C_5Me_5)_3$ was obtained. Therefore, the reaction of $InCl_3$ and $Na(C_5Me_5)$ in a 1:3 mol ratio was examined in an attempt to prepare $In(C_5Me_5)_3$. However, the reaction of $InCl_3$ with $Na(C_5Me_5)$ gave $In(C_5Me_5)$, $(C_5Me_5)_2$ and NaCl as isolable products. In this reaction, $Na(C_5Me_5)$ is apparently acting as a alkylating agent and possibly as a reducing agent (Equation 6). The observed percent yields of $In(C_5Me_5)$, $(C_5Me_5)_2$ and NaCl (65.9%, 83.9% and 94.0%, respectively, based on

$$InCl_3 + 3Na(C_5Me_5) \longrightarrow In(C_5Me_5) + (C_5Me_5)_2 + 3NaCl \quad (6)$$

$InCl_3$) are in agreement with the stoichiometry of Equation 6. In this reaction $In(C_5Me_5)_3$ can be considered to be an intermediate which either decomposes to form $In(C_5Me_5)$ and $(C_5Me_5)_2$ or which reacts immediately with excess $Na(C_5Me_5)$ to form $In(C_5Me_5)$ and $(C_5Me_5)_2$ (Equation 7). The suggestion that $Na(C_5Me_5)$ is the apparent reducing agent would be consistent

$$In(C_5Me_5)_3 + Na(C_5Me_5) \longrightarrow In(C_5Me_5) + (C_5Me_5)_2 + Na(C_5Me_5) \quad (7)$$

with the earlier work of Tuck and Poland[3] with the indium-$C_5H_5$ system.

The nature of the pentamethylcyclopentadienylindium(III) compounds $In(C_5Me_5)Cl_2$ and $In(C_5Me_5)_2Cl$ in benzene and THF solutions has been investigated. In benzene solution, $In(C_5Me_5)Cl_2$ completely decomposes within 24h to form $(C_5Me_5)_2$ and presumably "$InCl_2$" (Equation 8). This

$$2In(C_5Me_5)Cl_2 \xrightarrow{C_6H_6} 2"InCl_2" + (C_5Me_5)_2 \quad (8)$$

decomposition was monitored by $^1H$ NMR spectroscopy. By monitoring the growth of the $(C_5Me_5)_2$ resonances with respect to time, an observed rate constant of $1.6 \times 10^{-1}$ $hr^{-1}$ was calculated. The complete disappearance of the resonance at 1.83ppm corresponding to $In(C_5Me_5)Cl_2$ within 24h indicated that decomposition was complete. In an attempt to identify the indium containing product, the $^{115}$In NMR spectrum of the product believed to be "$InCl_2$" in $CH_2Cl_2$/benzene was investigated. However, no signal was observed. The sample of "$InCl_2$" did not melt at temperatures up to 380°C or appear to sublime at 250°C. For comparison, reaction of yellow InCl with $InCl_3$ in a $CH_2Cl_2$/benzene solution produced a colorless compound which exhibited no resonances in its $^{115}$In NMR spectrum. This product did not melt up to 330°C but did appear to sublime at 235°C. The apparent ease of decomposition of $In(C_5Me_5)Cl_2$ may be responsible for our inability to obtain an analytically pure sample of the compound. In THF solution, $In(C_5Me_5)Cl_2$ is apparently stable to decomposition, showing little sign of decomposition even after four days. The compound, $In(C_5Me_5)_2Cl$, exhibits a behavior in solution which is very similar to that observed for $In(C_5Me_5)Cl_2$. In THF solution, $In(C_5Me_5)_2Cl$ is stable to decomposition for several days but in benzene solution it readily decomposes to $(C_5Me_5)_2$ and several other products. The nature of the decomposition of $In(C_5Me_5)_2Cl$ is not as simple as that postulated for $In(C_5Me_5)Cl_2$. Not only are the $^1$H NMR resonances for $(C_5Me_5)_2$ observed, but with time several other new resonances also grow into the spectrum. The formation of multiple products did not permit a calculation of an observed rate constant, but the rate of decomposition of $In(C_5Me_5)_2Cl$ in benzene solution is qualitatively slower than that of $In(C_5Me_5)Cl_2$. The decomposition of $In(C_5Me_5)_2Cl$ may proceed initially to produce InCl and $(C_5Me_5)_2$. The InCl might then react with $In(C_5Me_5)_2Cl$ to form an indium-indium bonded derivative. A variety of other reactions can also be postulated resulting in a substantial number of possible products. The observations that Lewis bases inhibit decomposition of $In(C_5Me_5)_2Cl$ and $In(C_5Me_5)Cl_2$ suggest that a vacant coordination site is a prerequisite.

Unfortunately, our limited data do not warrant further discussion of possible decomposition mechanisms.

The preparative reaction for (pentamethylcyclopentadienyl)indium(I) was studied extensively in order to define and understand the origins of the various products, $In(C_5Me_5)_2Cl$, $In^0$ and $(C_5Me_5)_2$. The reaction of InCl and $Li(C_5Me_5)$ does not appear to be as simple as the reactions of InCl and $Li(C_5H_4R)$ (R=H,Me).[6] The combination of low yields of $In(C_5Me_5)$ and the isolation and identification of multiple products suggests that significant side reactions are occurring. Indium metal can be envisioned to be formed by at least three different routes 1) the disproportionation of the starting material InCl in $Et_2O$ as has been previously observed[27], 2) the disproportionation of $In(C_5Me_5)$ and 3) homolytic cleavage of the $In-C_5Me_5$ bonds. The formation of small quantities of $In(C_5Me_5)_2Cl$ can occur by the reaction of $InCl_3$ with $Li(C_5Me_5)$ or by an exchange reaction between $In(C_5Me_5)_3$ and InCl or LiCl. The fulvalene $(C_5Me_5)_2$ can be obtained from the decomposition of $In(C_5Me_5)$, $In(C_5Me_5)_2Cl$ and/or $In(C_5Me_5)_3$. Our observations that $In(C_5Me_5)_3$ cannot be prepared suggest that reactions of $In(C_5Me_5)_3$ might be unlikely.

With $In(C_5Me_5)$ being soluble and stable to decomposition in cyclohexane solution, the nature of the species in solution was investigated by cryoscopic molecular weight studies. Our data suggest that $In(C_5Me_5)$ exhibits no apparent association over the concentration range of 0.0622m - 0.136m. In contrast $In(C_5H_4Me)$ exists as a monomer-dimer equilibrium mixture in cyclohexane whereas $In(C_5H_5)$ is not sufficiently soluble to study.[6] Apparently, the different structures are related to the effects of five methyl groups on the cyclopentadienyl ring. If the methyl groups are electron donating, the indium-pentamethylcyclopentadienyl "π-bond" might be sufficiently strong to minimize the tendency for ring slippage and dimer formation as observed for In($C_5H_4$Me).

In($\eta^5$-$C_5Me_5$) crystallizes in the rhombohedral space group R$\bar{3}$ with 18 In($\eta^5$-$C_5Me_5$) units in the hexagonal "triple-cell". The labelling of atoms in the basic crystallographic asymmetric unit is illustrated in Figure 1. The individual In($\eta^5$-$C_5Me_5$) units are arranged about points of crystallographic $\bar{3}$ ($S_6$) symmetry such that the indium atoms are on the interior and the $\eta^5$-$C_5Me_5$ units are on the exterior of hexameric "clusters". The two independent indium-indium distances are essentially chemically equivalent, with values of 3.963(1)Å around the $C_3$ axis and 3.942(1)Å between atoms of the two distinct opposed $In_3$ units of crystallographically-imposed 3 ($C_3$) symmetry. The octahedral hexameric cluster is shown in Figure 2. Stereoscopic views of the cluster and of the packing of these clusters in the unit cell are given in Figures 3 and 4. Intramolecular distances, angles and planes are collected in Tables III-V.

It is difficult to assess the importance of the In-In interactions of 3.942(1)-3.963(1)Å. Very similar In-In distances are observed in In($\eta^5$-$C_5H_5$) (a zig-zag polymer of [In($\eta^5$-$C_5H_5$)]$_\infty$ units with inter-chain In-In distances of 3.986(1)Å) and In($\eta^5$-$C_5H_4$Me) (a zig-zag polymer of [In($\eta^5$-$C_5H_4$Me)]$_\infty$ units, with a different pattern of inter-chain In-In contacts, having the same In-In distance of 3.986(1)Å).[6] However, it is unlikely that any of these In-In interactions are of much energetic significance (vide infra).

Each In($\eta^5$-$C_5Me_5$) unit has a very simple geometry (see Figure 1). It consists of a "half-sandwich" geometry in which an indium(I) atom is symmetrically bonded to an $\eta^5$-$C_5Me_5$ ring. The individual In-C distances range from 2.581(4)Å through 2.613(4)Å, averaging 2.595 Å and the In-"centroid" distance is 2.302 Å. Carbon-carbon distances within the carbocyclic ring range from 1.397(6)Å through 1.417(6)Å, averaging 1.409 Å, while C-Me distances range from 1.496(10)Å through 1.515(9)Å, averaging 1.508 Å.

The carbon-atom skeleton of the $C_5Me_5$ ring has $C_{5v}$ rather than $D_{5h}$ symmetry, since all methyl groups are displaced from the carbocyclic ring in a direction away from the indium atom. As shown in Table V, the $C_5$ ring is planar within the limits of experimental error (rms deviations of atoms from the least-squres plane is only 0.002 Å!). The indium atom lies +2.3019(3)Å from the $C_5$ plane, while the deviations of the methyl carbon atoms are -0.098(8)Å for C(6), -0.107(8)Å for C(7), -0.110(7)Å for C(8), -0.092(8)Å for C(9) and -0.097(9)Å for C(10). The average deviation of -0.101 Å taken with the average C(ring)-Me bond length of 1.508 Å corresponds to a bending of the methyl groups out of the plane of the ring and away from the indium atom by 3.84°.

All hydrogen atoms were located and refined; although the range of C-H distances is large (0.69(8) through 1.19(11)Å), the average value of 0.95 Å is identical to the accepted "X-ray determined" C-H distance[28] and the geometry about the carbon atom is tetrahedral, as expected.

The volatility of $In(C_5Me_5)$ suggests and the electron diffraction data confirm that the octahedral arrangement observed in the solid state dissociates readily in the gas phase to form monomeric species. However, some type of bonding interaction is required to counteract the repulsions between the ends of the dipole moments associated with bringing six monomeric pentamethylcyclopentadienylindium(I) units together in the solid state. Cyclopentadienylindium(I) has a significant experimental dipole moment[29] of 2.2D with the indium atom and its associated lone pair being the negative end of the molecule. It is also of interest that the structure of the hexaindium cluster $In_6(C_5Me_5)_6$ is significantly different from that observed for other stable main-group element clusters such as those for boron hydrides[30,31,32] and boron subhalides.[33,34] All boron containing clusters have hydrogen→boron and halogen→boron vectors which point toward the centers of the clusters. The centroid→indium vectors do not point toward the center of the $In_6$ cluster (see Figure 2). The only fully characterized octahedral boron cluster[35] is $B_6H_6^{2-}$ and the related isoelectronic carborane $B_4C_2H_6$.[36] The boron subhalide $B_6Br_6$ has been observed but the compound has not been fully characterized.[34] Similarly, $B_6[NMe_2AlMe_2]_6$ has been reported, but no structural data are available.[37] Orbital and skeletal electron counting conventions by Wade[30] and Williams[31] require each skeletal atom to provide one sp hybrid orbital and two p atomic orbitals for cluster bonding. Thus, the octahedral boron cluster, $B_6H_6^{2-}$, has seven pairs of skeletal bonding electrons whereas $In_6(C_5Me_5)_6$ has only six apparent electron pairs. The resulting disparities between the structural characteristics and the thermodynamic stabilities of these octahedral clusters could originate with the atomic orbitals which each skeletal atom provides for cluster bonding and/or with the number of available skeletal bonding electrons.

Electron diffraction studies identify monomeric $In(\eta^5\text{-}C_5Me_5)$ species in the gas phase at 92(5)°C. The molecular model is shown in Figure 5. The geometrical parameters and root-mean-square amplitudes of vibration (l-values) obtained in the electron diffraction study of $In(C_5Me_5)$ are listed in Table VI. The In-C bond distance of 2.592(7)Å is indistinguishable from that observed in the solid state (2.595±0.016Å) but is slightly shorter than the In-C bond distances in $In(C_5H_4Me)$[6] and $In(C_5H_5)$,[38] 2.607(5) and 2.619(5)Å, respectively. A similar trend is observed for the In-centroid distance in the solid state (Table VII). Results from the ab initio calculations are presented in Table VIII, which lists the optimized total energies and metal-ring centroid distances, as well as gross atomic charges and overlaps from a Mulliken population analysis. The metal-ring distance shows a marked basis set dependence with a (fortuitously) good agreement between the M-basis results and the experimental value. The L-basis set yields considerably longer metal-ring distances, indicating that the smaller basis set may be affected by a superposition of errors. This basis set dependence is somewhat unexpected considering the apparent basis set insensitivity of ferrocene at this level of accuracy,[39] the reason may be an inadequate description of the In atom in the M-basis set. By analogy with calculations on magnesocene,[40] inclusion of d-orbitals on the ring carbons may reduce the metal-ring distance somewhat, but unfortunately this is beyond our present computational capabilities. Similar discrepancies between calculated and experimental metal-ring distances are also found in other metallocenes,[40] and have been ascribed to problems inherent in the Hartree-Fock description of these complexes.[41] It is, however, interesting to note that the decrease of this distance upon permethylation is qualitatively correctly described, supporting the assumption that qualitative insight into the bonding in these compounds may be obtained from the calculations. For the L-basis set relativistic energy corrections from first-order perturbation theory have been included but they do not affect the optimum metal-ring distance.

The molecular orbital energies calculated using the L-basis set for $In(C_5H_5)$ and $In(C_5Me_5)$ as well as the orbitals of the two neutral ligands,

$C_5H_5$ and $C_5Me_5$, and the neutral In metal atom, are listed in Table IX. Orbital energies of the permethylated compound are lowered in comparison to those for the non-methylated one. This effect has previously been observed in PES studies for a variety of methylated cyclopentadienyl complexes.[42] The In lone pair ($6a_1$, our numbering scheme) is destabilized for both compounds by approximately 2eV in comparison to an isolated indium atom. For both $In(C_5H_5)$ and $In(C_5Me_5)$ bonding is mainly due to the overlap between the metal $5p_{x,y}$ orbital and the $6e_1$ orbital of the ring and between a metal orbital of $a_1$ character and the $5a_1$ orbital of the ring. Because of the higher $6e_1$ orbital energy of the permethylated ring, interaction with the In $p_{x,y}$ orbitals increases, which leads to increased stabilization of this molecular orbital compared to that for the nonmethylated compound. For $In(C_5Me_5)$ there is an additional bonding capability between an In orbital of $a_1$ type and the ring $4a_1$ orbital, as seen by the stabilization of the latter by nearly 0.6 eV. The stabilization of the $5a_1$ orbital of the ring is about 0.2 eV less for the permethylated ring due to the nonbonding interaction between the metal and the methyl groups. For $In(C_5H_5)$ the order of the $6a_1$ and $6e_1$ orbitals are reversed in comparison to recent Xα-SW[43] and pseudopotential SCF[44] calculations on this compound.

As seen in Table VIII, the charge on the In atom is about +0.5 in both molecules and the electron density in the valence region is only modestly increased when methyl groups are introduced on the ring. The most striking differences in the atomic charges on going from the nonmethylated to the permethylated cyclopentadienyl ring is that in the latter the negative charge positioned on the ring carbon atoms is decreased from -0.34 to -0.16 due to methylation of the ring. The charge on each ring substituent is +0.24 for the nonmethylated compound and +0.07 for each methyl group in the permethylated compound. The deshielding of a ring carbon when alkyl groups are introduced on the ring can be observed by $^{13}C$ NMR by increased chemical shift of this carbon. This effect has been observed for unsubstituted and non-alkyl substituted ferrocenes,[45] where the chemical shift of a ring carbon increases from $\delta 67.8$ to $\delta 83.1$ppm when a hydrogen is substituted by a methyl group. The stabilization of charge by polarization of the whole molecule (ion) has a parallel in the increased gas phase acidity of alcohols when the number of carbon atoms increases.[46] The reverse trend is observed for the acidities of cyclopentadiene and pentamethylcyclopentadiene in solution where the latter is the weakest acid. This decreased acidity in solution due to methylation has been rationalized by methyl hyperconjugative stabilization of the undissociated molecule and methyl steric inhibition of solvation of the anion.[47]

In a simple electrostatic model, the shorter metal-ring distance found in $In(C_5Me_5)$ may be seen as a consequence of the shift of negative charge towards the ring substituents. This allows for a closer approach of the ring to the center of positive charge before the equilibrium of repulsive and attractive forces is established, as compared to $In(C_5H_5)$. The harmonic In-ring force constants for the two molecules as calculated from the optimal energy for three different In-ring distances are $1.436 \times 10^{-2}$ Nm$^{-1}$ and $1.488 \times 10^{-2}$ Nm$^{-1}$ for $In(C_5H_5)$ and $In(C_5Me_5)$, respectively. It is of interest that the In-ring force constant calculated from spectroscopic data[48] for $In(C_5H_5)$ ($1.41 \times 10^{-2}$ Nm$^{-1}$) is not very different from our ab initio result. These values indicate a somewhat stiffer In-ring bond in $In(C_5Me_5)$ than in $In(C_5H_5)$, which is consistent with the shortening of the In-C bond observed in the former. The increase in the force constant in the electron diffraction study should result in a decrease in l(In-C) when going from $In(C_5H_5)$ via $In(C_5H_4Me)$ to $In(C_5Me_5)$.[49] However, the experimental l-values for the three compounds are 0.077(7)Å, 0.096(5)Å and 0.090(5)Å, respectively.

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Supplementary Materials Available. A table of observed and calculated structure factor amplitudes (10pp). Ordering information is given on any current masthead page.

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## Table I

## Experimental Data for the X-Ray Diffraction Study of In($\eta^5$-$C_5Me_5$)

(A) Unit Cell Data at 24°C (297K)

| | |
|---|---|
| Crystal system: trigonal | $V = 4739(2) Å^3$ |
| Laue symmetry: $\bar{3}$ | $Z = 18$ |
| Space group: R$\bar{3}$ ($C_{3i}^2$; No. 148)<br>(hexagonal setting) | formula = $C_{10}H_{15}In$ |
| $\underline{a}$ = 20.182(4)Å | mol wt = 250.05 |
| $\underline{c}$ = 13.436(3)Å | D(calc'd) = 1.58 g/cm$^3$ |

(B) Collection of X-Ray Diffraction Data

Diffractometer: Syntex $P2_1$

Radiation: Mo Kα ($\lambda$ 0.710730 Å)

Monochromator: highly oriented (pyrolytic) graphite; equatorial mode with 2θ(m) = 12.160°; assumed to be 50% perfect/50% ideally-mosaic for polarization correction

Reflections measured: +h,±k,±ℓ for 2θ = 4.5°-50.0°. Only data with -h+k+ℓ = 3n were collected (i.e., obverse rhombohedral condition). A total of 5770 reflections were collected (3 equivalent forms) and were merged to 1870 unique data

Scan type: coupled θ(crystal)-2θ(counter) at 2.0 deg/min in 2θ over a range $[2\theta(K\alpha_1)-0.9]° \rightarrow [2\theta(K\alpha_2) + 0.9]°$

Backgrounds: stationary-crystal, stationary-counter at each extreme of the $2\theta$ scan, each for one-fourth total scan time

Standard reflections: three approximately mutually orthogonal reflections were recollected after each batch of 97 data points. A slight monotonic decrease in intensity (to ~95% of initial values) was noted and was corrected for.

Absorption correction: $\mu(\mathrm{Mo\ K}\alpha) = 21.7\ \mathrm{cm}^{-1}$; data were corrected empirically based upon interpolation (in $2\theta$ and $\phi$) between $\psi$-scans of six close-to-axial (i.e. $\psi_o = 90\pm10°$) reflections at well separated $2\theta$ values. $I_{max}/I_{min}$ values ranged from 1.194 down to 1.135 for the six scans.

## Table II

## Final Atomic Parameters for In($\eta^5$-$C_5Me_5$)

| ATOM | x | y | z | B,$Å^2$ |
|---|---|---|---|---|
| In | 0.08071(1) | 0.12962(1) | 0.11951(2) | |
| C(1) | 0.14185(20) | 0.26989(19) | 0.18523(30) | |
| C(2) | 0.12459(20) | 0.22349(19) | 0.27085(27) | |
| C(3) | 0.04391(20) | 0.17761(19) | 0.27698(26) | |
| C(4) | 0.01195(20) | 0.19631(19) | 0.19596(26) | |
| C(5) | 0.07286(22) | 0.25290(20) | 0.13978(27) | |
| C(6) | 0.22020(38) | 0.33160(37) | 0.15258(69) | |
| C(7) | 0.18352(41) | 0.22938(46) | 0.34344(55) | |
| C(8) | 0.00086(45) | 0.12421(36) | 0.36227(47) | |
| C(9) | -0.07177(29) | 0.16602(45) | 0.17547(59) | |
| C(10) | 0.06373(54) | 0.29305(45) | 0.05003(49) | |
| H(6A) | 0.2545(40) | 0.3130(36) | 0.1663(55) | 10.1(19) |
| H(6B) | 0.2214(46) | 0.3164(45) | 0.0720(70) | 13.7(23) |
| H(6C) | 0.2264(41) | 0.3673(43) | 0.1645(55) | 10.4(21) |
| H(7A) | 0.1996(46) | 0.2801(49) | 0.3728(64) | 13.1(23) |
| H(7B) | 0.2262(53) | 0.2232(52) | 0.3109(71) | 15.6(28) |
| H(7C) | 0.1616(40) | 0.1933(40) | 0.3863(56) | 10.5(22) |
| H(8A) | -0.0568(39) | 0.1038(38) | 0.3313(56) | 11.2(18) |
| H(8B) | 0.0178(72) | 0.0946(65) | 0.3703(85) | 19.1(40) |
| H(8C) | -0.0087(54) | 0.1357(54) | 0.4461(84) | 16.9(29) |
| H(9A) | -0.1033(48) | 0.1326(48) | 0.2294(73) | 13.9(27) |
| H(9B) | -0.0748(39) | 0.2065(42) | 0.1762(56) | 11.0(20) |
| H(9C) | -0.0979(40) | 0.1241(43) | 0.1251(63) | 11.8(19) |
| H(10A) | 0.0782(43) | 0.2850(44) | -0.0207(65) | 12.9(22) |
| H(10B) | 0.0128(64) | 0.2668(59) | 0.0391(83) | 17.3(41) |
| H(10C) | 0.0516(42) | 0.3215(42) | 0.0662(57) | 11.5(21) |

| ATOM | B11 | B22 | B33 | B12 | B13 | B23 |
|---|---|---|---|---|---|---|
| In | 5.329(15) | 4.806(14) | 5.065(15) | 3.012(10) | -0.2503(88) | -1.1042(86) |
| C(1) | 5.20(16) | 3.88(14) | 6.07(18) | 1.81(12) | 0.74(14) | -0.87(13) |
| C(2) | 5.07(15) | 5.05(15) | 5.22(17) | 2.87(13) | -1.05(12) | -1.73(13) |
| C(3) | 5.57(16) | 4.50(14) | 3.90(14) | 2.35(12) | 0.67(12) | -0.46(11) |
| C(4) | 4.79(14) | 4.92(15) | 4.83(16) | 2.95(13) | -0.34(13) | -1.29(12) |
| C(5) | 6.48(18) | 4.66(15) | 4.72(15) | 3.56(14) | 0.19(14) | -0.34(12) |
| C(6) | 6.91(28) | 5.31(25) | 13.21(56) | 1.08(22) | 3.55(31) | -1.45(29) |
| C(7) | 8.24(30) | 9.22(36) | 8.03(33) | 5.63(29) | -3.77(27) | -3.62(31) |
| C(8) | 10.02(37) | 7.46(28) | 6.16(26) | 3.57(27) | 2.89(26) | 1.41(22) |
| C(9) | 5.52(21) | 9.34(33) | 10.44(40) | 4.71(24) | -1.39(25) | -3.68(33) |
| C(10) | 14.02(61) | 8.55(34) | 6.31(28) | 7.96(43) | 0.36(30) | 1.07(24) |

## Table III

## Intramolecular Distances (Å) for In($\eta^5$-$C_5Me_5$)

(A) Indium-Carbon Distances

| | | | |
|---|---|---|---|
| In-C(1) | 2.612(3) | In•••cent | 2.302 |
| In-C(2) | 2.613(4) | | |
| In-C(3) | 2.586(4) | | |
| In-C(4) | 2.581(4) | | |
| In-C(5) | 2.585(4) | | |
| Av. In-C | 2.595±0.016 | | |

(B) Carbon-Carbon Distances

| | | | |
|---|---|---|---|
| C(1)-C(2) | 1.413(5) | C(1)-C(6) | 1.508(9) |
| C(2)-C(3) | 1.417(6) | C(2)-C(7) | 1.496(10) |
| C(3)-C(4) | 1.409(5) | C(3)-C(8) | 1.514(7) |
| C(4)-C(5) | 1.408(5) | C(4)-C(9) | 1.507(9) |
| C(5)-C(1) | 1.397(6) | C(5)-C(10) | 1.515(9) |
| Av. C-C(ring) | 1.409±0.007 | Av. C-Me | 1.508±0.008 |

(C) Carbon-Hydrogen Distances

| | | | |
|---|---|---|---|
| C(6)-H(6A) | 0.96(9) | C(8)-H(8C) | 1.19(11) |
| C(6)-H(6B) | 1.13(9) | C(9)-H(9A) | 0.98(9) |
| C(6)-H(6C) | 0.69(8) | C(9)-H(9B) | 0.85(8) |
| C(7)-H(7A) | 0.99(9) | C(9)-H(9C) | 1.00(8) |
| C(7)-H(7B) | 1.03(12) | C(10)-H(10A) | 1.03(9) |
| C(7)-H(7C) | 0.86(7) | C(10)-H(10B) | 0.90(13) |
| C(8)-H(8A) | 1.10(9) | C(10)-H(10C) | 0.76(9) |
| C(8)-H(8B) | 0.83(14) | | |
| | | av. C-H | 0.95±0.14 |

## Table IV

## Interatomic Angles (in Degrees) for In($\eta^5$-$C_5Me_5$)

### (A) C-In-C Angles

| | | | |
|---|---|---|---|
| C(1)-In-C(2) | 31.37(12) | C(2)-In-C(4) | 52.26(12) |
| C(1)-In-C(3) | 52.12(12) | C(2)-In-C(5) | 51.83(12) |
| C(1)-In-C(4) | 52.13(12) | C(3)-In-C(4) | 31.66(12) |
| C(1)-In-C(5) | 31.18(13) | C(3)-In-C(5) | 52.12(12) |
| C(2)-In-C(3) | 31.63(12) | C(4)-In-C(5) | 31.62(12) |

### (B) In-C-C Angles

| | | | |
|---|---|---|---|
| In-C(1)-C(2) | 74.37(23) | In-C(3)-C(8) | 121.51(35) |
| In-C(1)-C(5) | 73.35(23) | In-C(4)-C(3) | 74.36(22) |
| In-C(1)-C(6) | 121.92(38) | In-C(4)-C(5) | 74.36(23) |
| In-C(2)-C(1) | 74.26(23) | In-C(4)-C(9) | 120.13(36) |
| In-C(2)-C(3) | 73.11(22) | In-C(5)-C(1) | 75.47(23) |
| In-C(2)-C(7) | 122.17(38) | In-C(5)-C(4) | 74.01(22) |
| In-C(3)-C(2) | 75.27(22) | In-C(5)-C(10) | 120.89(40) |
| In-C(3)-C(4) | 73.98(22) | | |

### (C) C-C-C(Ring) Angles

| | | | |
|---|---|---|---|
| C(5)-C(1)-C(2) | 107.9(4) | C(3)-C(4)-C(5) | 107.5(3) |
| C(1)-C(2)-C(3) | 107.6(3) | C(4)-C(5)-C(1) | 108.9(4) |
| C(2)-C(3)-C(4) | 108.1(3) | | |

### (D) C-C-Me Angles

| | | | |
|---|---|---|---|
| C(5)-C(1)-C(6) | 125.5(5) | C(4)-C(3)-C(8) | 126.8(4) |
| C(2)-C(1)-C(6) | 126.4(5) | C(3)-C(4)-C(9) | 127.1(4) |
| C(1)-C(2)-C(7) | 123.7(5) | C(5)-C(4)-C(9) | 125.3(4) |
| C(3)-C(2)-C(7) | 128.5(5) | C(4)-C(5)-C(10) | 124.8(5) |
| C(2)-C(3)-C(8) | 124.9(4) | C(1)-C(5)-C(10) | 126.1(5) |

(E) C-C-H and H-C-H Angles

| | | | |
|---|---|---|---|
| C(1)-C(6)-H(6A) | 107(5) | H(6A)-C(6)-H(6B) | 88(7) |
| C(1)-C(6)-H(6B) | 102(5) | H(6A)-C(6)-H(6C) | 125(8) |
| C(1)-C(6)-H(6C) | 111(7) | H(6B)-C(6)-H(6C) | 119(8) |
| C(2)-C(7)-H(7A) | 100(5) | H(7A)-C(7)-H(7B) | 116(8) |
| C(2)-C(7)-H(7B) | 113(6) | H(7A)-C(7)-H(7C) | 112(8) |
| C(2)-C(7)-H(7C) | 109(5) | H(7B)-C(7)-H(7C) | 107(8) |
| C(3)-C(8)-H(8A) | 96(4) | H(8A)-C(8)-H(8B) | 121(10) |
| C(3)-C(8)-H(8B) | 108(9) | H(8A)-C(8)-H(8C) | 101(7) |
| C(3)-C(8)-H(8C) | 132(5) | H(8B)-C(8)-H(8C) | 101(10) |
| C(4)-C(9)-H(9A) | 111(6) | H(9A)-C(9)-H(9B) | 109(8) |
| C(4)-C(9)-H(9B) | 102(5) | H(9A)-C(9)-H(9C) | 92(7) |
| C(4)-C(9)-H(9C) | 118(5) | H(9B)-C(9)-H(9C) | 124(7) |
| C(5)-C(10)-H(10A) | 122(5) | H(10A)-C(10)-H(10B) | 95(9) |
| C(5)-C(10)-H(10B) | 103(8) | H(10A)-C(10)-H(10C) | 127(8) |
| C(5)-C(10)-H(10C) | 110(6) | H(10B)-C(10)-H(10C) | 78(10) |

## Table V

## Deviations of Non-Hydrogen Atoms (in Å) from the Pentaatomic Carbocyclic Ring in In($\eta^5$-$C_5Me_5$)

Equation of Plane: $0.4446X - 0.7088Y - 0.5477Z = -4.6444$

| Atom | Dev. | Atom | Dev. |
|---|---|---|---|
| C(1)* | 0.00(4) | C(6) | -0.098(8) |
| C(2)* | -0.002(4) | C(7) | -0.107(8) |
| C(3)* | 0.003(4) | C(8) | -0.110(7) |
| C(4)* | -0.003(4) | C(9) | -0.092(8) |
| C(5)* | 0.002(4) | C(10) | -0.097(9) |
| In | 2.3019(3) | | |

Table VI

The Geometrical Parameters and Root Mean Square Amplitudes of Vibration of (l-values) for $In(C_5Me_5)$ in the Gas Phase.

| | $In(C_5Me_5)$ | |
|---|---|---|
| | $r_a$/Å | l/Å |
| bond distances | | |
| In-C | 2.592(4) | 0.090(7) |
| h[a] | 2.288(4) | - |
| C1-C2 | 1.432(4) | 0.040(5)[b] |
| C-C(Me) | 1.505(5) | 0.045(5)[b] |
| C-H | 1.103(6) | 0.082(7) |
| other distances | | |
| In•••C(Me) | 3.62 | 0.143(6) |
| In•••H(range) | 3.65-4.57 | 0.32(8) |
| C1•••C3 | 2.32 | 0.058(9) |
| C2•••C11 | 2.62 | 0.065(5) |
| C3•••C11 | 3.78 | 0.074(4) |
| C(Me)•••C(Me) (short) | 3.20 | 0.135(12) |
| C(Me)•••C(Me) (long) | 5.17 | 0.099(8) |
| angles (°): | | |
| $<C_5$,C(Me) | 0.041(3) | - |
| <CCH | 1.161(10) | - |

[a] The perpendicular height from the metal atom to the ring centroid.

[b] l-values with identical index were refined with constant difference.

## Table VII

## Comparison of Some Properties of In($C_5H_5$), In($C_5H_4$Me) and In($C_5Me_5$)

| | In($C_5H_5$) | In($C_5H_4$Me) | In($C_5Me_5$) |
|---|---|---|---|
| Color | Pale yellow | Colorless | Golden yellow |
| Melting Point (°C) | 169.3-170.7 | 49.0-49.7 | 92.0-93.0 |
| Sublimation Temp. (°C) | 35 | 35 | 55 |
| Solubility[a] | Soluble: THF, $Et_2O$<br>Sparingly sol.:$C_6H_{12}$ | Soluble: THF, $Et_2O$, $C_6H_{12}$, $C_6H_6$ | Soluble: THF, $Et_2O$, $C_6H_{12}$, $C_6H_6$ |
| Association ($C_6H_{12}$) | - | monomer-dimer | monomer |
| Acid Hydrolysis (mol $H_2$/mol In(I)) | 0.94 | 0.95 | 0.85 |
| Indium-Centroid(Å): | | | |
| Gas Phase | 2.322 | 2.310 | 2.288 |
| Solid State | 2.726 | 2.609 | 2.302 |
| In-In distance (Å)(Solid) | 3.986(1) | 3.986(1) | 3.963(1), 3.943(1) |

---

[a] Some of these solvents accelerate decomposition.

## Table VIII

### Optimal Energies with Corresponding Metal-Ring Centroid Distance, and Mulliken Population Analysis for $In(C_5H_5)$ and $In(C_5Me_5)$ with the Two Different Basis Sets.

| | $In(C_5H_5)$ | | $In(C_5Me_5)$ | |
|---|---|---|---|---|
| | M-basis | L-basis | M-basis | L-basis |
| $E_{min}$/a.u. | -5931.0482 | -5932.2917[a] | -6125.9628 | -6127.3829[a] |
| h/Å | 2.317 | 2.412 | 2.270 | 2.359 |
| $Q_{In}$ | +0.54 | +0.49 | +0.58 | +0.48 |
| $Q_{C(ring)}$ | -0.36 | -0.34 | -0.26 | -0.16 |
| $Q_H$ | +0.25 | +0.24 | +0.21 | +0.20[b] |
| $Q_{C(Me)}$ | - | - | -0.48 | -0.53[b] |
| $P_{In-C}$ | 0.10 | 0.07 | 0.10 | 0.10 |
| $P_{C-C(in\ ring)}$ | 0.37 | 0.46 | 0.33 | 0.50 |
| $P_{C-H}$ | 0.39 | 0.38 | 0.40 | 0.39 |
| $P_{C-C(Me)}$ | - | - | 0.23 | 0.23 |

---

[a] Relativistic correction energies were calculated in the L-basis calculations. The relativistic correction energies were -130.3336 a.u. and -130.4063 a.u. for $In(C_5H_5)$ and $In(C_5Me_5)$ respectively.

[b] The total methyl group charge is then +0.07.

## Table IX

## Orbital Energies in eV for In($C_5H_5$) and In($C_5Me_5$) Along With the Neutral Framents In, $C_5H_5$ and $C_5Me_5$ Calculated With The L-basis Set

| | $C_5H_5$ | In($C_5H_5$) | In | In($C_5Me_5$) | $C_5Me_5$ |
|---|---|---|---|---|---|
| $6a_1$ | | -8.33 | -10.08(In5s) | -7.89 | |
| $6e_1$ | -8.24 | -8.52 | -5.57(In5p) | -7.64 | -7.16 |
| $5e_2$ | -14.44 | -14.19 | | -12.76 | -12.75 |
| $5e_1$ | -15.14 | -14.98 | | -14.07 | -13.98 |
| $5a_1$ | -13.22 | -15.00 | | -13.18 | -11.63 |
| $1a_2$ | | | | -14.39 | -14.37 |
| $4e_1$ | | | | -14.90 | -14.88 |
| $4e_2$ | | | | -15.04 | -15.00 |
| $3e_1$ | | | | -15.58 | -15.45 |
| $3e_2$ | | | | -16.00 | -15.99 |
| $4a_1$ | | | | -16.79 | -16.21 |
| $3a_1$ | -19.41 | -19.25 | | -17.48 | -17.41 |
| $2e_2$ | -20.24 | -20.04 | | -19.16 | -19.12 |
| $2e_1$ | -26.11 | -26.03 | | -23.45 | -23.30 |
| $2a_1$ | | | | -26.42 | -26.36 |
| $1e_2$ | | | | -26.81 | -26.80 |
| In4d | | -28.56($4d_{z^2}$)<br>-28.65($4d_\delta$)<br>-28.69($4d_\pi$) | -28.80 | -28.05($4d_\delta$)<br>-28.16($4d_{z^2}$)<br>-28.22($4d_\pi$) | |
| $1e_1$ | | | | -28.64 | -28.37 |
| $1a_1$ | -31.78 | -31.99 | | -32.19 | -31.76 |
| In4p | | -95.13 | -95.30 | -94.70 | |
| In4s | | -135.10 | -135.27 | -134.65 | |
| $C1s^a$ | 306.21 | -305.87 | | -304.85 | -304.83 |
| | | | | -305.59 | -305.67 |
| In3d | | -478.22 | -478.26 | -477.77 | |
| In3p | | -690.17 | -690.11 | -689.72 | |
| In3s | | -805.82 | -805.72 | -805.37 | |
| In2p | | -3786.85 | -3785.48 | -3786.40 | |
| In2s | | -4065.05 | -4063.58 | -4064.59 | |
| In1s | | -27151.39 | -27140.05 | -27150.93 | |

---

[a] Mean values.

## Captions to Figures

Figure 1. Labelling of atoms in the asymmetric unit of $In(\eta^5-C_5Me_5)$, with hydrogen atoms artificially reduced.

Figure 2. Geometry of the $[In(\eta^5-C_5Me_5)]_6$ unit. Note that the vectors from the centroids of the $\eta^5-C_5Me_5$ ligands to the indium atoms do not point to the center of the hexaindium framework.

Figure 3. Stereoscopic view of the $[In(\eta^5-C_5Me_5)]_6$ unit.

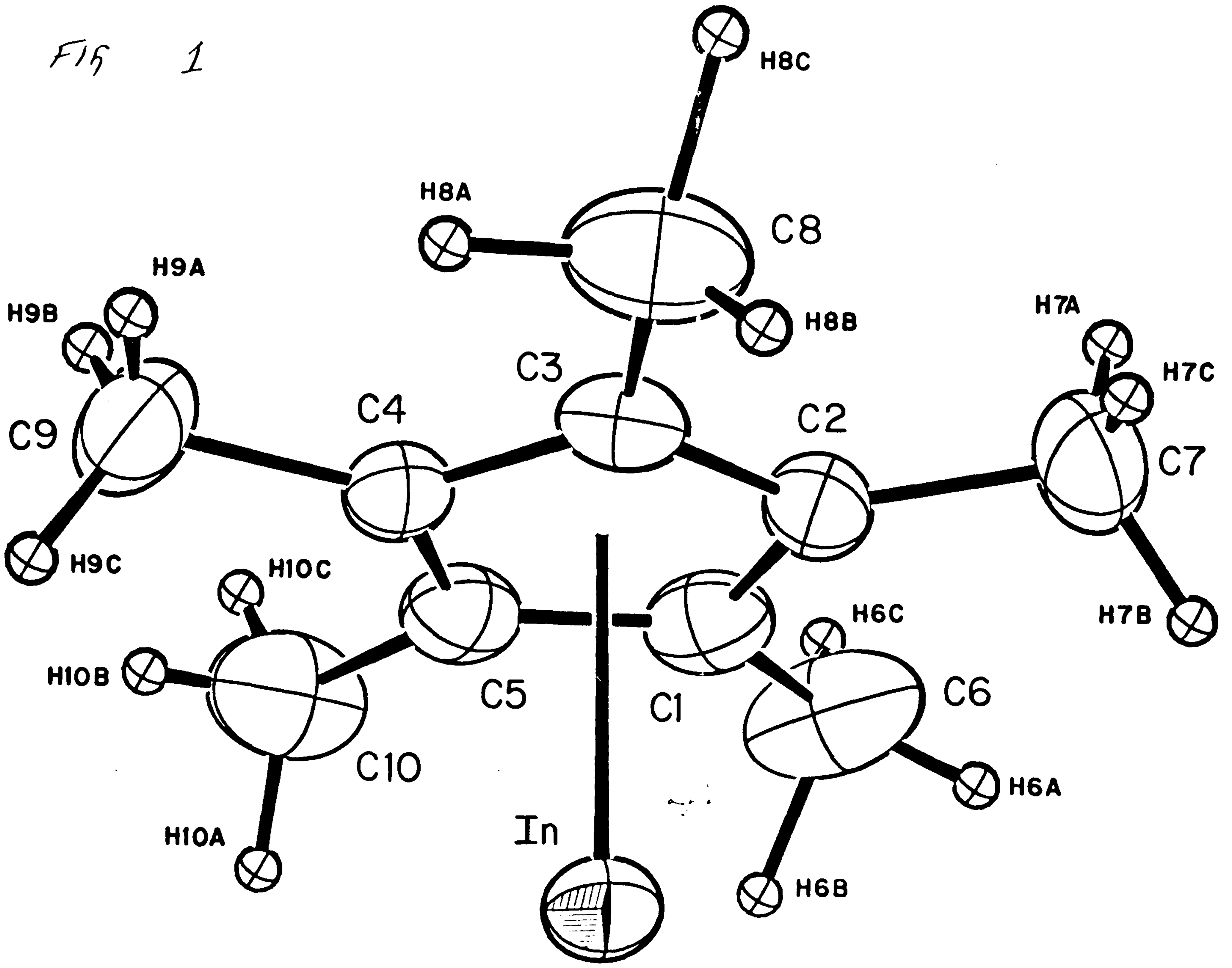
Figure 4. Packing of $[In(\eta^5-C_5Me_5)]_6$ units within the unit cell.

Figure 5. Molecular model for $In(C_5Me_5)$ in the gas phase for electron diffraction study.

Figure 6. Theoretical molecular intensity curves with experimental points for the electron diffraction study on $In(C_5Me_5)$. The difference between experimental and theoretical curves for the best model are drawn in the lower part of the figure.

Figure 7. Experimental RD curve for the electron diffraction study on $In(C_5Me_5)$. 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 $pm^2$.

Fig 1


H8C
H8A
C8
H9A
H9B
H8B
H7A
C3
H7C
C4
C2
C9
C7
H9C
H10C
H6C
H7B
H10B
C5
C1
C6
C10
H6A
H10A
In
H6B

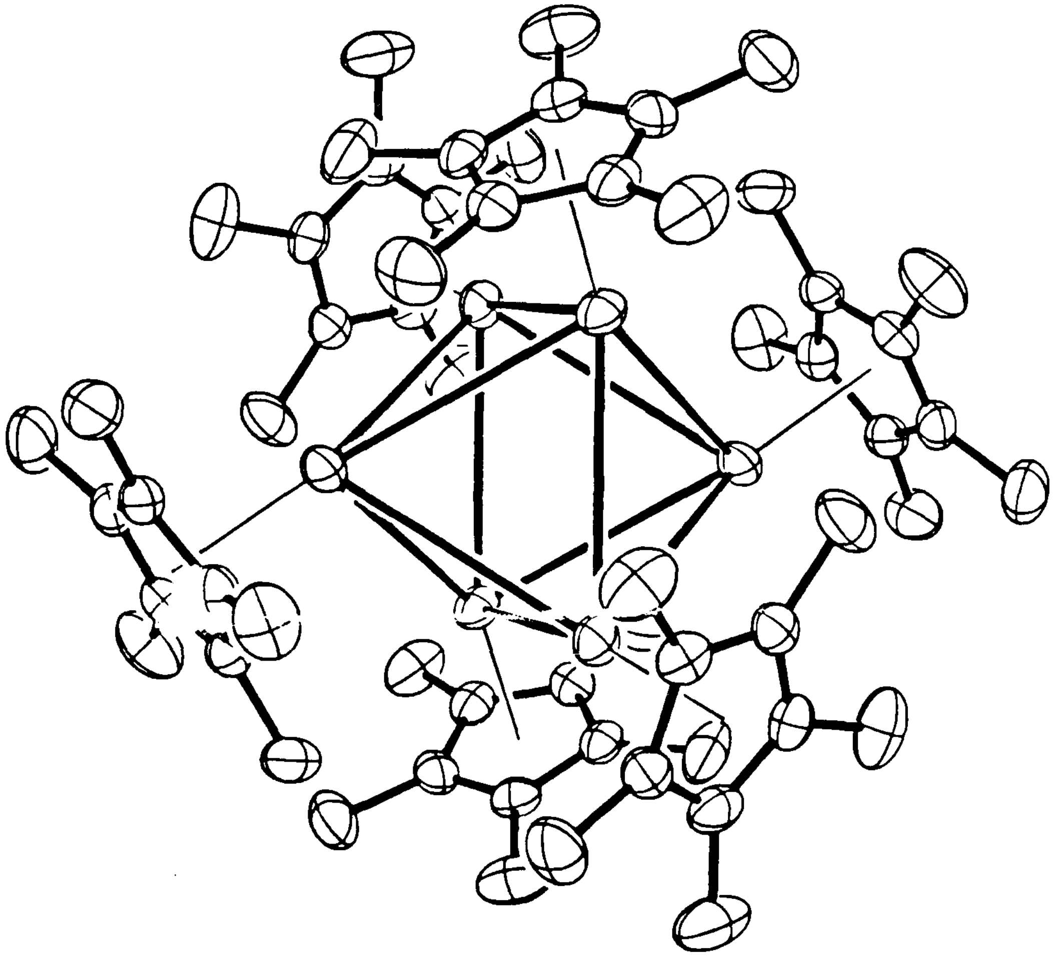


Fig. 2

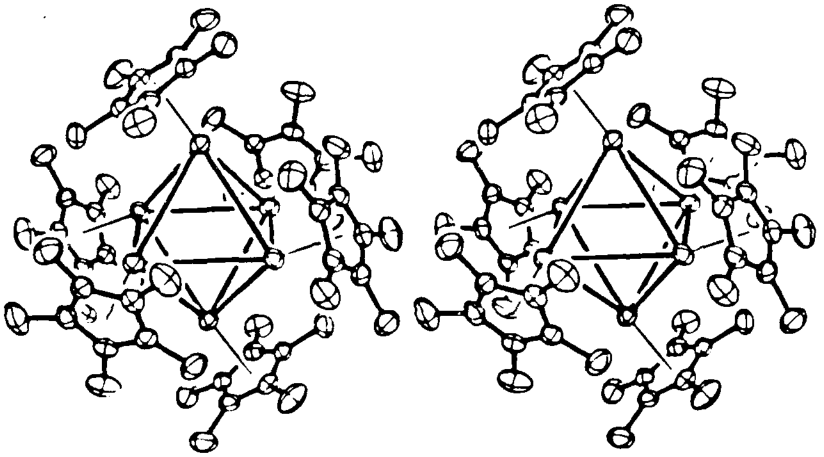


Fig 3
CORRECT SIZE
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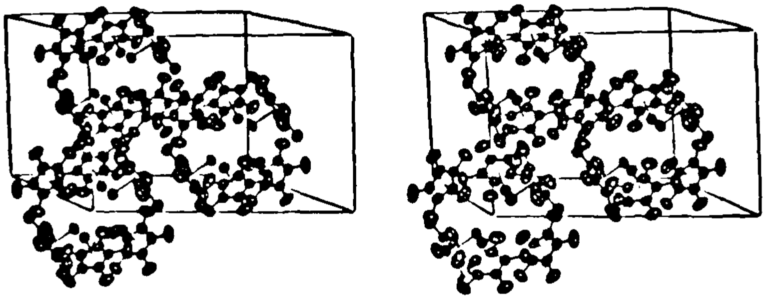

Fig 4
CORRECT SIZE
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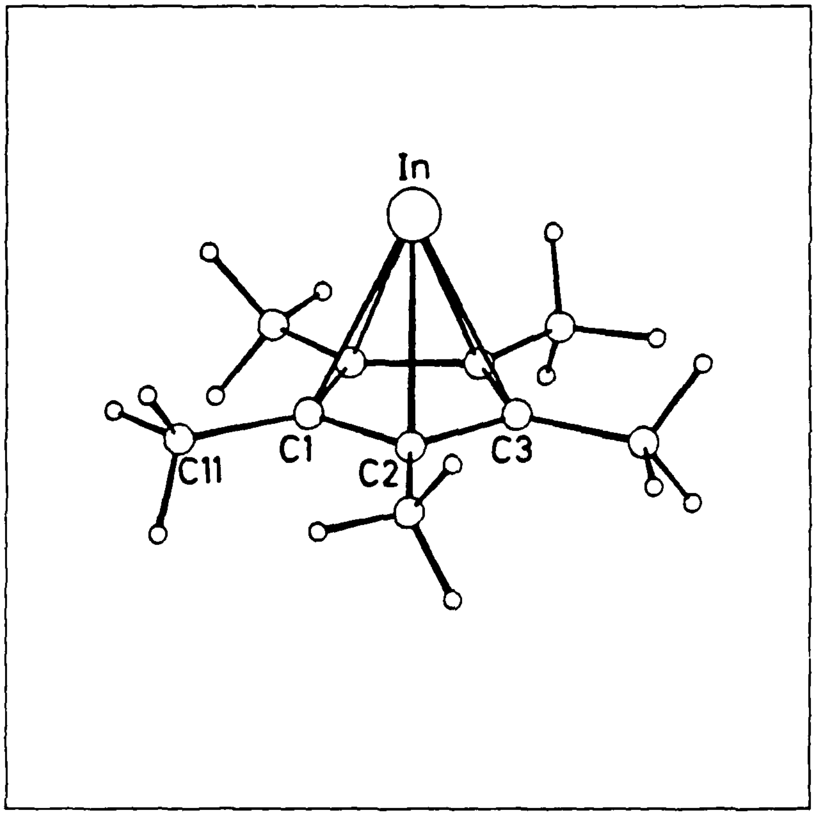

FIG 5

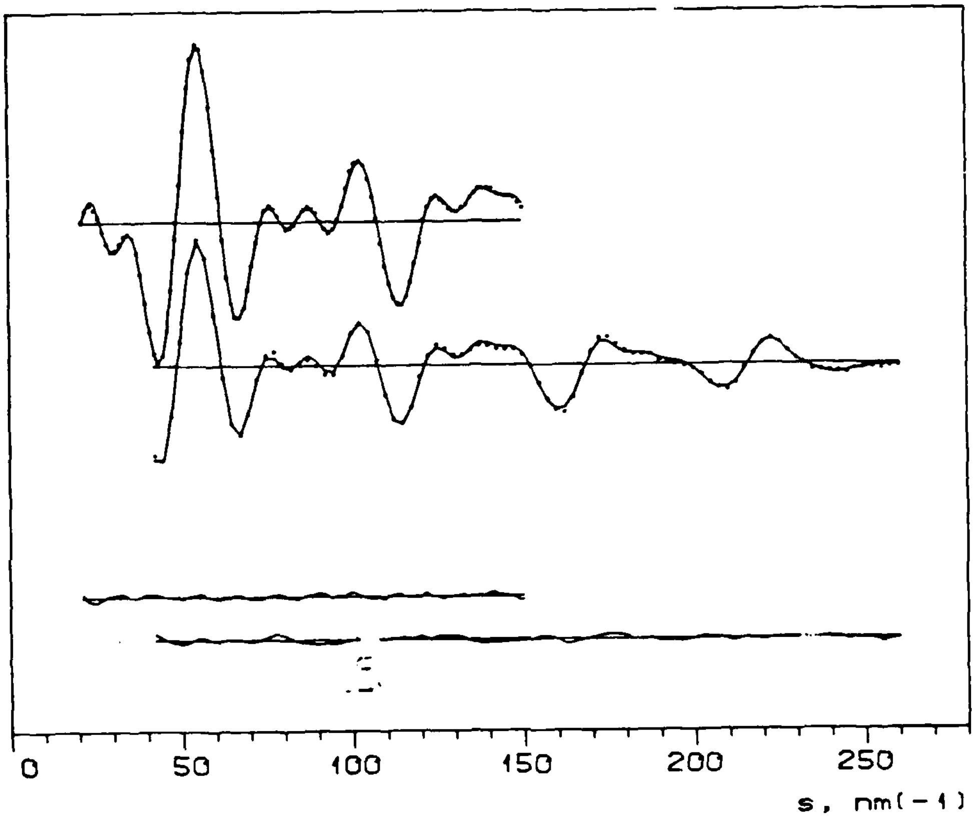

FIG 6

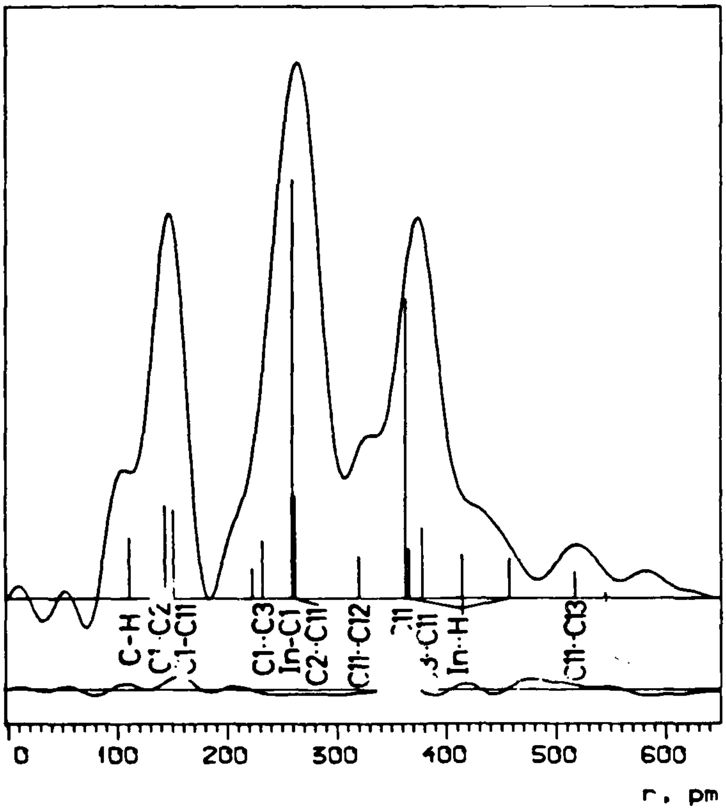
C-H
C1-C2
C1-C11
C1-C3
In-C1
C2-C11
C11-C12
11
3-C11
In-H
C11-C13
0
100
200
300
400
500
600
r, pm

FIG. 7

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