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

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The golden yellow compound $In(C_5Me_5)$ has been prepared in 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 $In(C_5Me_5)_2Cl$ was confirmed by its independent synthesis from $InCl_3$ and $Li(C_5Me_5)$ 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 $In(\eta^5\text{-}C_5Me_5)$ 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, $2\theta = 4.5$–$50.0°$) 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 $\eta^5\text{-}C_5Me_5$ ligand is symmetrically bound to indium with In–C = 2.581 (4)–2.613 (4) Å (average = 2.595 Å) and In···centroid = 2.302 Å. The $In(\eta^5\text{-}C_5Me_5)$ units are arranged about centers of $\bar{3}$ (S_6) symmetry, with indium atoms on the interior and $\eta^5\text{-}C_5Me_5$ 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 2.288 Å 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.

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 that 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 σ-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 $In(C_5H_5)_3\cdot OEt_2$ 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 zigzag 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 $In(C_5Me_5)$ have been reported recently.[7] This communication revealed that the compound was prepared in only 58% yield, but

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the disposition of the remaining indium remained undefined. We herein report our studies that 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)$_2$Cl, and (C_5Me_5)$_2$. These compounds have been characterized by elemental analysis, IR and ^{1}H 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 exeedingly 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. Pentamethylcyclopentadiene 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 ^{1}H NMR spectra were recorded immediately after sample preparation at 90 MHz by means of either a Varian Model EM-390 or a JEOL 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.[8]

Preparation of Li(C_5Me_5). A 100-mL two-neck flask was charged with 12.5 mL of 2.5 M Li(n-Bu) (31.2 mmol) and 4.06 g of pentamethylcyclopentadiene (29.8 mmol) was added to a side-arm dumper. The apparatus was assembled, and 40 mL 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 18 h, the volatile components were removed by vacuum distillation. The reaction flask was fitted with a medium frit connected to a 100-mL side-arm flask. Pentane (50 mL) was vacuum distilled into the flask containing the off-white Li(C_5Me_5), and the product was washed five times with the pentane. The off-white insoluble product Li(C_5Me_5) (4.09 g, 28.8 mmol) 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 Na(C_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 (2.045 g, 88.95 mmol) was added to a 100-mL two-necked flask and C_5Me_5H (5.079 g, 37.2 mmol) was pipetted into a tube sealed with a Teflon valve. Fifty milliliters of THF was vacuum distilled into the flask containing the sodium with 20 mL 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 2 days. The THF was removed by vacuum distillation. In the drybox, 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 100-mL 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 (2.57 g, 16.2 mmol) based on C_5Me_5H.

Na(C_5Me_5): ^{1}H NMR (THF-d_8, δ) 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 (1.438 g, 9.572 mmol) was weighed and transferred to a side-arm dumper. The side-arm dumper was connected to a 100-mL two-neck flask containing 1.419 g of Li(C_5Me_5) (9.989 mmol). The apparatus was evacuated, and 50 mL 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 5 h, 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 2.000 g of a yellow ether-soluble product was isolated and transferred to a Solv-seal sublimation tube. Golden yellow crystals of In(C_5Me_5) (1.485 g, 5.938 mmol, 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 0.302-g sample of a pentane-soluble material was isolated and purified by washing it with one 20-mL portion of pentane to yield 0.0849 g of analytically pure In(C_5Me_5)$_2$Cl (0.202 mmol, 2.11% yield based on InCl). The remaining pentane-soluble portion contained an additional 0.112 g of In(C_5Me_5)$_2$Cl (0.276 mmol) and 0.0337 g of (C_5Me_5)$_2$ (0.125 mmol) which were identified by ^{1}H NMR spectroscopy. Both the ether-soluble but pentane-insoluble material (0.0366 g) and the ether-insoluble fraction (0.6545 g) contained LiCl, In^0, and excess Li(C_5Me_5). Calculations that considered the stoichiometric excess of Li(C_5Me_5) over the mole quantity of InCl and the assumption that all chlorine in InCl formed LiCl indicated that 0.226 g of indium metal (1.97 mmol, 20.6% of the initially available indium) was produced.

In(C_5Me_5): golden yellow crystalline solid; mp 92.0–93.0 °C; ^{1}H NMR (C_6H_6, δ) 2.02 (s) (refer to Results and Discussion for further details of the ^{1}H 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)$_2$Cl: yellow crystalline solid; mp decomposes at 97 °C; ^{1}H NMR (C_6H_6, δ) 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.

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Hydrolysis of $In(C_5Me_5)$. A 0.243-g (0.972-mmol) sample of $In(C_5Me_5)$ was added to a tube equipped with a Teflon valve. The tube was evacuated, and approximately 8 mL 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 2 h to form a clear pink solution. Hydrogen gas (0.819 mmol) was later collected by means of a Toepler pump–gas buret assembly for an 84.3% yield based on the oxidation of In^+ to In^{3+}.

Identification of Initial Products from the Hydrolysis of $In(C_5Me_5)$. In the drybox, a 0.131-g (0.524-mmol) sample of $In(C_5Me_5)$ was transferred to a 125-mL Erlynmeyer flask. The top of the flask was covered with Parafilm and removed from the drybox. Dilute HCl (10 mL) was added to the flask containing the $In(C_5Me_5)$. After 15 min of reaction, 10 mL 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 δ 1.77 (s), 1.72 (s), 1.00 (d, J = 8.1 Hz) and a small line at δ 0.42 (s). Except for the small line at δ 0.42 (believed due to an impurity), the spectrum was identical with 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 0.0436-g sample of $In(C_5Me_5)$ (0.174 mmol) was placed in an NMR tube, and 0.7 mL of C_6D_6 was vacuum distilled onto the sample. The initial spectrum exhibited a single resonance at δ 2.02. With time, resonances at 1.72 (s), 1.64 (s), and 1.12 ppm (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 0.96 ppm (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 on the basis of the disappearance of the $In(C_5Me_5)$ resonance.

THF. In a similar manner, an NMR tube was charged with 0.0446 g of $In(C_5Me_5)$ (0.178 mmol) and 0.7 mL of THF-d_8. At time zero, the ^1H NMR spectrum consisted of one line at 2.05 ppm (s). Throughout the time frame of the experiment, two new resonances at 1.65 (s) and 1.07 ppm (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.

Pyridine. An NMR tube was charged with 0.044 g of $In(C_5Me_5)$ (0.18 mmol) and 0.7 mL of pyridine. The initial spectrum consisted of one resonance at 2.06 ppm (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.

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

Synthesis of $In(C_5Me_5)_2Cl$ from $InCl_3$. A 100-mL side-arm flask was charged with 1.794 g of $InCl_3$ (8.111 mmol) and 2.371 g of $Li(C_5Me_5)$ (16.68 mmol). The flask was evacuated, and 50 mL of diethyl ether was distilled onto the reaction mixture. After stirring at room temperature for 14 h the ether was removed by vacuum distillation. Pentane (50 mL) 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 (2.649 g, 6.297 mmol) based on $InCl_3$. The pentane-insoluble product consisted of LiCl and excess $Li(C_5Me_5)$. Lithium chloride (0.680 g, 16.0 mmol) 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 20 mL 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); ^1H NMR (ppm, THF-d_8) 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 $Li(C_5Me_5)$ (2.020 g, 14.22 mmol) was added to a 100-mL two-necked flask, and a side-arm dumper was charged with 1.000 g of $InCl_3$ (4.521 mmol). The apparatus was assembled and evacuated, and 50 mL 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 the solution was stirred at room temperature for 24 h, the Et_2O was removed and 50 mL 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 $In(C_5Me_5)_2Cl$ (1.461 g, 3.473 mmol, 76.80% yield based on $InCl_3$) by its melting point, ^1H NMR spectrum, and elemental analysis.

Reaction of $InCl_3$ with $Na(C_5Me_5)$ in a 1:3 Mole Ratio. Indium trichloride (0.348 g, 1.57 mmol) was added to a side-arm dumper, and the dumper was connected to a 100-mL two-neck flask containing 0.788 g of $Na(C_5Me_5)$ (4.98 mmol). Tetrahydrofuran (50 mL) was vacuum distilled onto both reactants. The reagents were mixed, and a deep yellow solution formed immediately. Within 5.5 h the deep yellow solution turned pale yellow. After the mixture was stirred for 18 h, a trace amount of indium metal was observed. The THF was removed, and 50 mL of pentane was distilled onto the reaction products. The pentane-insoluble material contained NaCl and excess $Na(C_5Me_5)$ (0.299 g, 94.0% yield of NaCl as based on complete reaction and by accounting for excess $Na(C_5Me_5)$ over $InCl_3$). The pentane-soluble portion contained a mixture of $In(C_5Me_5)$ and $(C_5Me_5)_2$. Golden yellow crystals of $In(C_5Me_5)$ (0.221 g, 0.886 mmol, 56.4% yield based on $InCl_3$) were sublimed from the pentane-soluble mixture. A ^1H NMR spectrum of a 0.394 g sample of the pentane-soluble portion was obtained after most of the $In(C_5Me_5)$ was removed. The spectrum exhibited resonances at 2.00 (s), 1.72 (s), 1.63 (s), and 1.11 ppm (s) relative to benzene at 7.13 ppm. Integration values indicated that 90.5% of the sample was $(C_5Me_5)_2$ (0.356 g 1.32 mmol, 83.9% yield based on $InCl_3$). The line at 2.00 ppm was assigned to $In(C_5Me_5)$ indicating an additional 0.0378 g (0.151 mmol, 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 100-mL two-neck flask with $Li(C_5Me_5)$ (0.757 g, 5.33 mmol) and a side-arm dumper with 1.183 g of $InCl_3$ (5.349 mmol) was assembled and evacuated, and diethyl ether (50 mL) was vacuum distilled onto the $Li(C_5Me_5)$. The $InCl_3$ was added to the resulting suspension. After being stirred for 24 h at room temperature, the solution was filtered to yield 0.0689 g of LiCl, an ether-insoluble product. The ether was removed by vacuum distillation, and 50 mL of pentane was distilled onto the ether-soluble, orange-yellow solid. After four extractions, a total of 1.03 g of impure $In(C_5Me_5)Cl_2$ (3.21 mmol, 60.2% yield based on $InCl_3$) was isolated from the pentane-soluble portion. An additional 0.581 g 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, δ) 1.89 (s, $In(C_5Me_5)_2Cl$), 1.84 (s, $In(C_5Me_5)Cl_2$), 1.72 (s, $(C_5Me_5)_2$),

Table I. Experimental Data for the X-ray Diffraction Study of In(η^5-C_5Me_5)

(A) Unit-Cell Data at 24 °C (297 K)

cryst system: trigonal
Laue symmetry: $\bar{3}$
space group: $R\bar{3}$ (C_{3i}^2; No. 148) (hexagonal setting)
a = 20.182 (4) Å
c = 13.436 (3) Å
V = 4739 (2) Å^3
Z = 18
formula: $C_{10}H_{15}In$
mol wt 250.05
D(calcd) = 1.58 g/cm^3

(B) Collection of X-ray Diffraction Data

diffractometer: Syntex $P2_1$
radiatn: Mo Kα ($\bar{\lambda}$ = 0.710 73 Å)
monochromator: highly oriented (pyrolytic) graphite; equatorial mode with $2\theta(m)$ = 12.160°; assumed to be 50% perfect/50% ideally mosaic for polarization correction
reflctns measd: $+h,\pm k,\pm l$ for 2θ = 4.5–50.0°; only data with $-h+k+l = 3n$ were collected (i.e., obverse rhombohedral condition); a total of 5770 reflctns 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 $[2\theta(K\alpha_1) - 0.9]° \rightarrow [2\theta(K\alpha_2) + 0.9]°$
bkgds: stationary-crystal, stationary-counter at each extreme of the 2θ scan, each for one-fourth total scan time
std reflctns: three approximately mutually orthogonal reflections were recollected after each batch of 97 data points; a slight monotonic decrease in (to ~95% of initial values) was noted and was corrected for
absorptn correctn: μ(Mo Kα) = 21.7 cm^{-1}; data were corrected empirically based upon interpolation (in 2θ and ϕ) between ψ scans of six close-to-axial (i.e., $\psi_0 = 90 \pm 10°$) reflections at well separated 2θ values; I_{max}/I_{min} values ranged from 1.194 down to 1.135 for the six scans

1.64 (s, $(C_5Me_5)_2$), 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 1.88 ppm (s). With time resonances due to the formation of $(C_5Me_5)_2$ at 1.73, 1.64, and 1.12 ppm were monitored. In addition to these resonances, lines at 2.00, 1.93, and 1.90 ppm appeared in later spectra. These observations suggest that multiple species were being formed. **$In(C_5Me_5)Cl_2$.** The spectrum of a saturated benzene solution of the compound was recorded at various time intervals. The intensity of the resonance at 1.83 ppm associated with $In(C_5Me_5)_2Cl$ decreased with time while resonances at 1.73, 1.65, and 1.13 ppm ($(C_5Me_5)_2$) grew in intensity. Relative integration values were normalized, and an observed rate constant was calculated. (See Results and Discussion.)

Collection of X-ray Diffraction Data for In(η^5-C_5Me_5). A clear golden yellow crystal of approximate dimensions 0.3 × 0.3 × 0.45 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 subset 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 $-h+k+l = 3n$ 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.

Solution of the Structure of In(η^5-C_5Me_5). All calculations were carried out by 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 $\sum w(|F_o| - |F_c|)^2$, 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 $\sum w|\Delta F|^2$ 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 0.18 e/Å^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 3.7×10^{-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 (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 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] 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

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

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Table II. Final Atomic Parameters for $In(\eta^5\text{-}C_5Me_5)$

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

atom	*B*(11)	*B*(22)	*B*(33)	*B*(12)	*B*(13)	*B*(23)
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)

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 nondiagonal 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 C(1)–C(2), C(1)–C(11) 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, $\angle C_5$,C–C(Me). The later is defined as positive when the ring substituents are bent toward 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] 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] 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, and 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] $(C_5Me_5)_2$ (eq 1). In order to more

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

fully understand this process, we studied the relative rates of decomposition of $In(C_5Me_5)$ in benzene, THF, pyridine, and cyclohexane by ^1H NMR spectroscopy. These solvents

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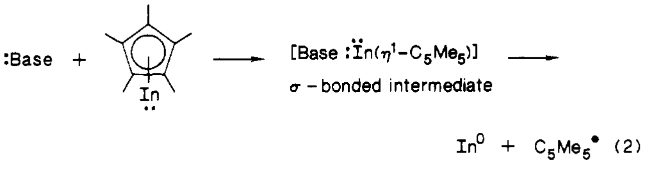
were selected because they would include a range of basicities and their resonances would not interfere with those of either In(C_5Me_5) or (C_5Me_5)$_2$. The observed pseudo-first-order rate constants for the decomposition of In(C_5Me_5) suggest the following order: cyclohexane (no decomposition over 5 days) < benzene (2.4×10^{-3} h^{-1}) < THF (4.1×10^{-3} h^{-1}) < pyridine (7.0×10^{-3} h^{-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 η^5 to η^1 (eq 2). (Benzene would have to form a π-complex with indium(I).) If the base:In(η^1-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:$\dot{\text{I}}\text{n}$(η^1-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) (eq 3 and 4) as In(C_5Me_5)$_3$ is not an observed product. Even though the indium(III) compounds In(C_5Me_5)$_2$Cl 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.



$$3\text{base:}\dot{\text{I}}\text{n}(\eta^1\text{-}C_5Me_5) \rightarrow 2\text{In}^0 + \underset{\text{unstable}}{[\text{In}(C_5Me_5)_3]} \quad (3)$$

$$[\text{In}(C_5Me_5)_3] \rightarrow \text{In}(C_5Me_5) + (C_5Me_5)_2 \quad (4)$$

The identity of In(C_5Me_5)$_2$Cl 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 (eq 5) in Et$_2$O solution. The compound In(C_5Me_5)$_2$Cl was isolated as a bright yellow solid in 77.6% yield and has been fully characterized by elemental analyses, melting point data, and IR and ^{1}H 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)$_2$Cl decomposed in benzene. (See later discussion.) Consequently, the structure of In(C_5Me_5)$_2$Cl in solution could not be studied by cryoscopic molecular weight measurements. The sample of In(C_5Me_5)$_2$Cl obtained from the reaction of InCl$_3$ and Li(C_5Me_5) had properties that were identical with those of a sample isolated from the reaction of InCl and Li(C_5Me_5).

$$\text{InCl}_3 + 2\text{Li}(C_5Me_5) \rightarrow \text{In}(C_5Me_5)_2\text{Cl} + 2\text{LiCl} \quad (5)$$

(Pentamethylcyclopentadienyl)indium(III) dichloride (In(C_5Me_5)Cl$_2$) was also independently synthesized in order to distinguished it from In(C_5Me_5)$_2$Cl. 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)$_2$Cl 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 ^{1}H 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 1.83 ppm assigned to In(C_5Me_5)Cl$_2$. The nature of In(C_5Me_5)Cl$_2$ and In(C_5Me_5)$_2$Cl 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)$_2$Cl. 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)$_2$Cl.[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 (eq 6).

$$\text{InCl}_3 + 3\text{Na}(C_5Me_5) \rightarrow \text{In}(C_5Me_5) + (C_5Me_5)_2 + 3\text{NaCl} \quad (6)$$

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$_3$) are in agreement with the stoichiometry of eq 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)$_2$ (eq 7). The suggestion that Na(C_5Me_5) is the apparent reducing agent would be consistent with the earlier work of Tuck and Poland[3] with the indium-C_5H_5 system.

$$\text{In}(C_5Me_5)_3 + \text{Na}(C_5Me_5) \rightarrow \text{In}(C_5Me_5) + (C_5Me_5)_2 + \text{Na}(C_5Me_5) \quad (7)$$

The nature of the pentamethylcyclopentadienylindium(III) compounds In(C_5Me_5)Cl$_2$ and In(C_5Me_5)$_2$Cl in benzene and THF solutions has been investigated. In benzene solution, In(C_5Me_5)Cl$_2$ completely decomposes within 24 h to form (C_5Me_5)$_2$ and presumably "InCl$_2$" (eq 8). This decomposition was monitored by ^{1}H NMR spectroscopy. By monitoring the growth of the (C_5Me_5)$_2$ resonances with respect to time, an observed rate constant of 1.6×10^{-1} h^{-1} was calculated. The complete disappearance of the resonance at 1.83 ppm corresponding to In(C_5Me_5)Cl$_2$ within 24 h 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$_2$Cl$_2$/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.

$$2\text{In}(C_5Me_5)\text{Cl}_2 \xrightarrow{C_6H_6} 2\text{“InCl}_2\text{”} + (C_5Me_5)_2 \quad (8)$$

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[26] Carty, A. J.; Gynane, M. J. S.; Lappert, M. F.; Miles, S. J.; Singh, A.; Taylor, N. J. *Inorg. Chem.* **1980**, *19*, 3637.

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 4 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 ^1H 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 0.0622–0.136 *m*. 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 $In(C_5H_4Me)$.

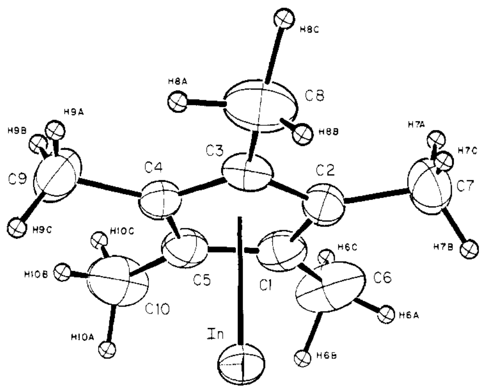

Figure 1. Labeling of atoms in the asymmetric unit of $In(\eta^5-C_5Me_5)$, with hydrogen atoms artificially reduced.

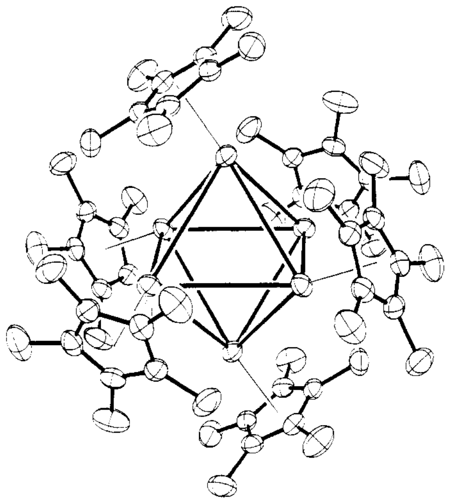

Figure 2. Geometry of the $[In(\eta^5-C_5Me_5)]_6$ unit. Note that the vectors from the centroids of the $\eta^5-C_5Me_5$ ligands to the indium atoms do *not* point to the center of the hexaindium framework.

$In(\eta^5-C_5Me_5)$ 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 zigzag polymer of $[In(\eta^5-C_5H_5)]_\infty$ units with interchain In–In distances of 3.986 (1) Å) and $In(\eta^5-C_5H_4Me)$ (a zigzag polymer of $[In(\eta^5-C_5H_4Me)]_\infty$ units, with a different pattern of interchain 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

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[27] Peppe, C.; Tuck, D. G.; Victoriano, L. *J. Chem. Soc., Dalton Trans.* **1982**, 2165.

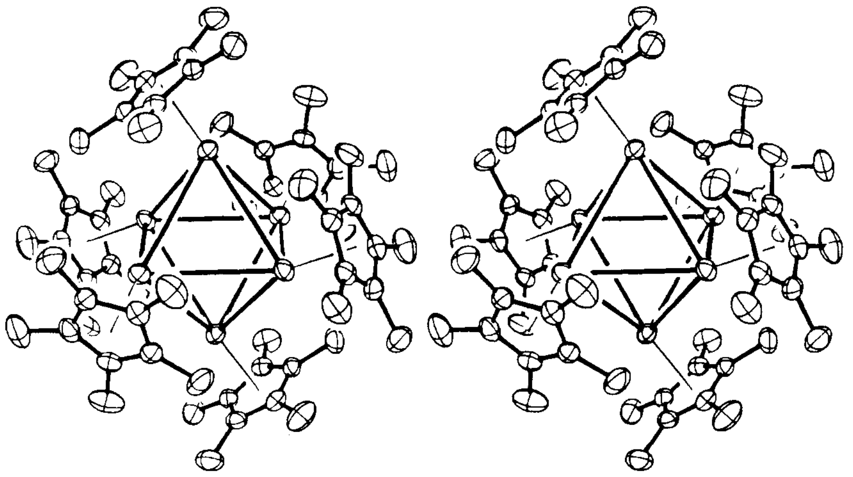

Figure 3. Stereoscopic view of the [In(η^5-C_5Me_5)]$_6$ unit.

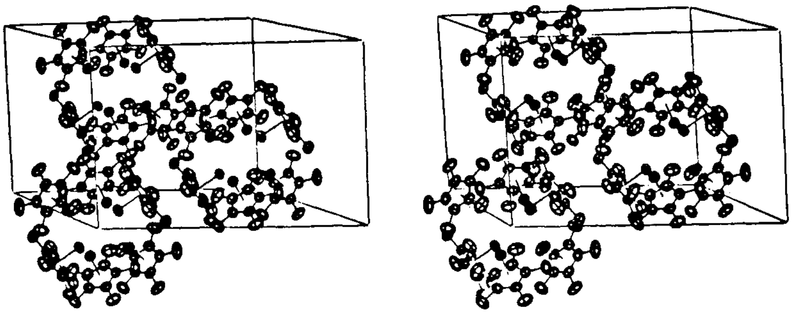

Figure 4. Packing of [In(η^5-C_5Me_5)]$_6$ units within the unit cell.

Table III. Intramolecular Distances (Å) for In(η^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)		
In–C(av)	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)
C–C(ring)(av)	1.409 ± 0.007	C–Me(av)	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)	C–H(av)	0.95 ± 0.14

Table IV. Interatomic Angles (deg) for In(η^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)–H6B)	88 (7)
C(1)–C(6)–C(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)–C(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)

η^5-C_5Me_5 ring. The individual In–C distances range from 2.581 (4) 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) through 1.417 (6) Å, averaging 1.409 Å, while C–Me distances range from 1.496 (10) 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 (root-mean-square deviations of atoms from the least-squares

Table V. Deviations of Non-Hydrogen Atoms (in Å) from the Pentaatomic Carbocyclic Ring in In(η^5-C_5Me_5)

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

atom	dev	atom	dev
C(1)*	0.000 (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)		

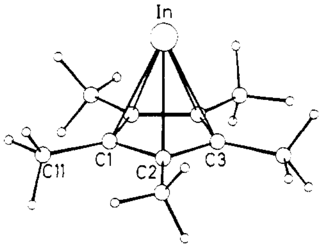

Figure 5. Molecular model for In(C_5Me_5) in the gas phase for electron diffraction study.

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 with 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 (pentamethylcyclopentadienyl)indium(I) units together in the solid state. Cyclopentadienylindium(I) has a significant experimental dipole moment[29] of 2.2 D 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[30-32] 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

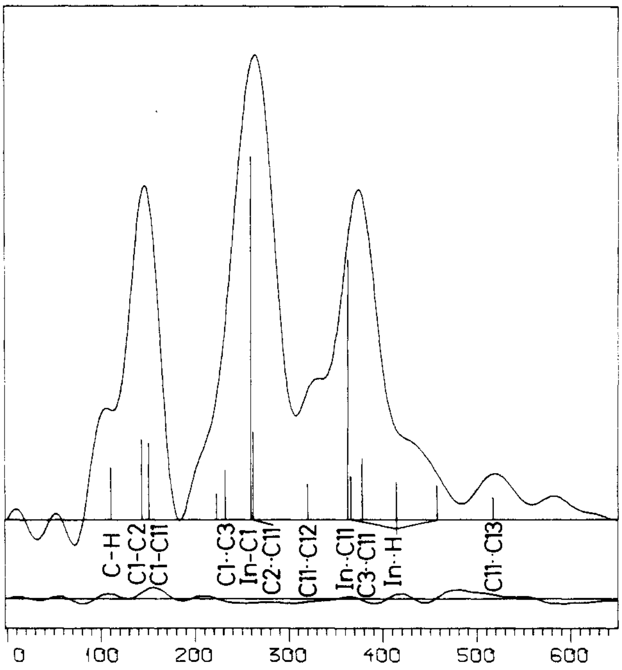

Figure 6. Theoretical molecular intensity curves with experimental points for the electron diffraction study on In(C_5Me_5). The difference between experimental and theoretical curves for the best model are drawn in the lower part of the figure.

Table VI. 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)···(Me) (long)	5.17	0.099 (8)
angles (deg)		
∠C_5,C(Me)	4.1 (3)	
∠CCH	116.1 (10)	

^{a} The perpendicular height from metal atom to the ring centroid. ^{b} Values with identical index were refined with constant difference.

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Table VII. Comparison of Some Properties of In(C_5H_5), In(C_5H_4Me), and In(C_5Me_5)

	In(C_5H_5)	In(C_5H_4Me)	In(C_5Me_5)
color	pale yellow	colorless	golden yellow
mp (°C)	169.3–170.7	49.0–49.7	92.0–93.0
sublimatn temp (°C)	35	35	55
solubility[a]	soluble in THF, Et_2O; sparingly soluble in C_6H_{12}	soluble in THF, Et_2O, C_6H_{12}, C_6H_6	soluble in THF, Et_2O, C_6H_{12}, C_6H_6
association (C_6H_{12})		monomer–dimer	monomer
acid hydrolysis (mol of H_2/mol of 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.

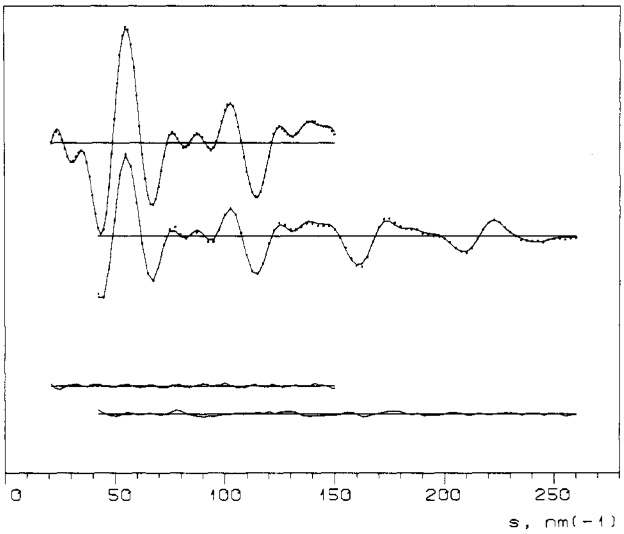

Figure 7. Experimental RD curve for the electron diffraction study on In(C_5Me_5). The difference between the experimental and theoretical RD curve calculated for the best model are drawn in the lower part of the figure. The most important distances are indicated by bars of height approximately proportional to the area under the corresponding peak. Artificial damping constant, *k*, is 20 pm^2.

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}/au	−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 au and −130.4063 au for In(C_5H_5) and In(C_5Me_5), respectively. [b] The total methyl group charge is then +0.07.

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(η^5-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 ± 0.016 Å) 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 by using the L basis set for In(C_5H_5) and In(C_5Me_5) as well as the or-

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Table IX. Orbital Energies (eV) for In(C_5H_5) and In(C_5Me_5) Along with the Neutral Fragments 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 (In 5s)	−7.89	
$6e_1$	−8.24	−8.52	−5.57 (In 5p)	−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
		−28.56		−28.05	
		($4d_{z^2}$)		($4d_\delta$)	
In 4d		−28.65	−28.80	−28.16	
		($4d_\delta$)		($4d_{z^2}$)	
		−28.69		−28.22	
		($4d_\pi$)		($4d_\pi$)	
$1e_1$				−28.64	−28.37
$1a_1$	−31.78	−31.99		−32.19	−31.76
In 4p		−95.13	−95.30	−94.70	
In 4s		−135.10	−135.27	−134.65	
C 1s[a]	306.21	−305.87		−304.85	−304.83
				−305.59	−305.67
In 3d		−478.22	−478.26	−477.77	
In 3p		−690.17	−690.11	−689.72	
In 3s		−805.82	−805.72	−805.37	
In 2p		−3786.85	−3785.48	−3786.40	
In 2s		−4065.05	−4063.58	−4064.59	
In 1s		−27151.39	−27140.05	−27150.93	

[a] Mean values.

bitals 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 2 eV 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 non-methylated 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 δ 67.8 to 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 toward 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 1.436×10^{-2} N m^{-1} and 1.488×10^{-2} N m^{-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) (1.41×10^{-2} N m^{-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) in In(C_5Me_5).[49] However, the experimental *l* values for the three compounds are 0.077 (7), 0.096 (5), and 0.090 (5) Å, respectively.

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Registry No. THF, 109-99-9; Li(C_5Me_5), 51905-34-1; Na(C_5Me_5), 40585-51-1; In(C_5Me_5), 102920-51-4; In(C_5Me_5)$_2$Cl, 117469-41-7; C_5Me_5H, 4045-44-7; InCl, 13465-10-6; $InCl_3$, 10025-82-8; In(C_5Me_5)Cl_2, 117469-42-8; In(C_5H_5), 34822-89-4; benzene, 71-43-2; pyridine, 110-86-1; cyclohexane, 110-82-7.

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

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