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# Synthesis, Properties, and X-ray Structural Study of $Me_2In(C_5H_5)$

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*Summary: The compound $Me_2In(C_5H_5)$ has been prepared by a metathetical reaction between $Me_2InCl$ and $Li(C_5H_5)$ in THF solution and by a methane elimination reaction between $InMe_3$ and $C_5H_6$ at 145−160 °C in a sealed tube and fully characterized. An X-ray structural study identified an infinite linear polymer with cyclopentadienide units bridging $InMe_2$ moieties through the 1 and 3 positions of the ring. Bridging is sufficiently strong to prevent melting before thermal decomposition at 195−200 °C and to make the compound insoluble in all solvents except those that are good Lewis bases such as THF. The compound exists in THF solution as an equilibrium mixture of $Me_2In(C_5H_5)\cdot THF$, $MeIn(C_5H_5)_2\cdot THF$, and $InMe_3\cdot THF$ according to its $^1H$ NMR spectrum.*

The synthesis, properties, and reactions of organogroup 13 compounds with two different substituents is of current interest. Pure compounds typically cannot be prepared because they undergo ligand redistribution reactions to form mixtures. However, the gallium compounds $Me_2Ga(C_5H_5)$[1] and $Et_2Ga(C_5H_5)$[2] have been isolated as pure single compounds in the solid state, but they form equilibrium mixtures of multiple species in solution (eq 1).

$$2R_2Ga(C_5H_5) \rightleftharpoons RGa(C_5H_5)_2 + GaR_3 \qquad (1)$$

The corresponding indium compound $Me_2In(C_5H_5)$ has been reported[3−5] also, but the characterization data suggest the possibility of an impure compound. Furthermore, the characterization data are insufficient to fully understand the nature of $Me_2In(C_5H_5)$ in solution so that it can be compared with the corresponding gallium derivatives. Early workers used both metathetical[3,4] and elimination reactions[5] to prepare $Me_2In(C_5H_5)$. The reaction between $Me_2InCl$ and $Na(C_5H_5)$[3,4] in hydrocarbon solvents provided the crude product in low yield, but the analytical data[4] suggest the compound was impure. The best solvent for this metathetical reaction according to these early studies was cyclohexane, as neither benzene nor toluene could be removed quantitatively.[4] However, other workers have described the synthesis of $Me_2In(C_5H_5)$[5] from a toluene solution by utilizing the elimination of methane from $InMe_3$ and $C_5H_6$ at room temperature. The third synthetic reaction to prepare $Me_2In(C_5H_5)$ involved the elimination of $NMe_2H$ from a toluene solution of $[Me_2InNMe_2]_2$ and $C_5H_6$, but neither the technique for purification nor elemental analysis data for the product were described.[5] Thus, our need for a good preparative route to pure $Me_2In(C_5H_5)$ in high yield and for a more thorough understanding of the structure of the compound in the solid state and its properties in solution including its propensity to undergo a ligand redistribution reaction prompted our reinvestigation.

Two reactions, a metathetical reaction between $Me_2InCl$ and $Li(C_5H_5)$ in THF solution and a methane elimination reaction between $InMe_3$ and $C_5H_6$ at 145−160 °C in a sealed tube, have been found to be useful for the preparation of pure $Me_2In(C_5H_5)$. Even though both reactions provide high yields of the desired product, the preferred method involves the metathetical reaction in THF solution (eq 2). All reactants and all products in the metathetical reaction are soluble, and the THF can be quantitatively removed from $Me_2In(C_5H_5)$. Isolation and purification of the product involved removal of THF by vacuum distillation at room temperature and then vacuum sublimation at 120 °C. The purified product was isolated in 85% yield. Initiation of the methane elimination reaction (eq 3) required temperatures of approximately 120 °C, whereas a rate suitable for synthesis occurred at 145−160 °C. Even though this preparative method is simple and gives better than a 75% yield of the purified product, it suffers two distinct disadvantages. First, the temperature must be carefully controlled and the time of heating, typically about 3 h, must be minimized. Slow decomposition of $Me_2In(C_5H_5)$ occurs at the preparative reaction temperature. Thus, the observed yield of methane was greater than that expected on the basis of the balanced equation. Second, the volume of the sealed tube limits the amount of product that can be prepared safely.

$$Me_2InCl + Li(C_5H_5) \xrightarrow{THF} Me_2In(C_5H_5) + LiCl \qquad (2)$$

$$InMe_3 + C_5H_6 \xrightarrow[\text{sealed tube}]{145-160\ °C} Me_2In(C_5H_5)_8 + CH_4 \qquad (3)$$

The reaction between $InMe_3$ and $C_5H_6$ in aromatic solvents has been reinvestigated. The earlier literature described the synthesis of $Me_2In(C_5H_5)$ in 73% yield at

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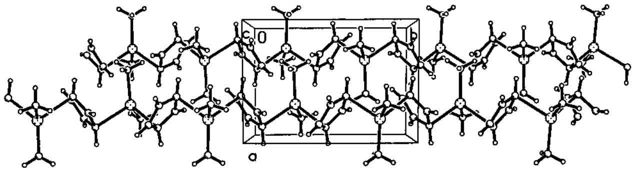

**Figure 1.** Unit cell of $[Me_2In(C_5H_5)]_\infty$.

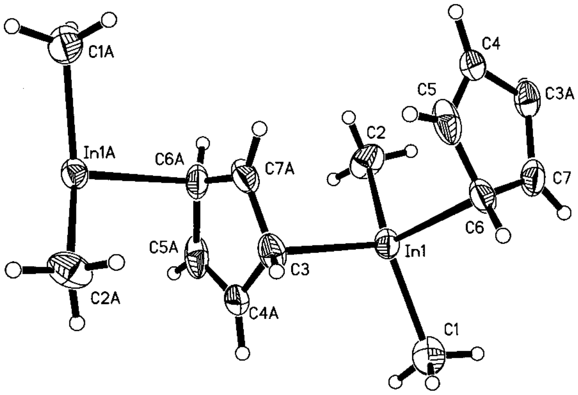

**Figure 2.** Structure of a portion of the polymeric chain of $[Me_2In(C_5H_5)]_\infty$ with labeling of atoms.

room temperature by using a toluene solution.[5] We observed no $Me_2In(C_5H_5)$ to be formed when $InMe_3$ and $C_5H_6$ were allowed to react either in a benzene solution at room temperature or at the temperature of a refluxing benzene solution in the exclusion of air. When $InMe_3$ and $C_5H_6$ were combined in a toluene solution as described in the literature,[5] variable results were obtained. When the reagents were pure and air was excluded rigorously, a trace of a colorless insoluble solid was observed, but the quantity was too small for conclusive identification as $Me_2In(C_5H_5)$. However, when a small amount of air had leaked accidentally into the reaction vessel, the insoluble product was identified as $Me_2In(C_5H_5)$. In one case, a pinched O-ring, which had been used with Solv-Seal glassware, permitted air to enter the previously evacuated reaction flask. The yield of $Me_2In(C_5H_5)$ was 17%. In another experiment, when air leaked into the reaction flask through a silicone-greased joint, the yield of $Me_2In(C_5H_5)$ was about 24%.

The Lewis acidity of $Me_2In(C_5H_5)$ with THF, $Et_2O$, and $NMe_3$ was investigated by tensimetric titrations at 0 °C. Both $NMe_3$ and THF formed 1:1 adducts according to the titration data, but each adduct exhibited a dissociation pressure of the base in equilibrium with the adduct. Thus, these bases can be quantitatively removed from their adducts by vacuum distillation at room temperature. In contrast diethyl ether does not form an adduct with $Me_2In(C_5H_5)$. The order of Lewis basicity as determined by dissociation pressure was $NMe_3 > THF \gg OEt_2$.

**Table 1. Bond Lengths (Å) and Angles (deg) for $[Me_2In(C_5H_5)]_\infty$[a]**

| | | | |
|---|---|---|---|
| In(1)−C(1) | 2.118(14) | In(1)−C(2) | 2.129(13) |
| In(1)−C(3) | 2.457(12) | In(1)−C(6) | 2.484(12) |
| C(3)−C(7)#1 | 1.38(2) | C(3)−C(4)#1 | 1.41(2) |
| C(4)−C(5) | 1.33(2) | C(4)−C(3)#2 | 1.41(2) |
| C(5)−C(6) | 1.41(2) | C(6)−C(7) | 1.36(2) |
| C(7)−C(3)#2 | 1.38(2) | | |
| C(1)−In(1)−C(2) | 133.2(6) | C(1)−In(1)−C(3) | 105.4(5) |
| C(2)−In(1)−C(3) | 108.8(5) | C(1)−In(1)−C(6) | 97.4(5) |
| C(2)−In(1)−C(6) | 110.8(5) | C(3)−In(1)−C(6) | 94.1(5) |
| C(7)#1−C(3)−C(4)#1 | 106.0(12) | C(7)#1−C(3)−In(1) | 96.5(8) |
| C(4)#1−C(3)−In(1) | 90.2(8) | C(5)−C(4)−C(3)#2 | 109.5(13) |
| C(4)−C(5)−C(6) | 107.6(13) | C(7)−C(6)−C(5) | 107.8(12) |
| C(7)−C(6)−In(1) | 90.6(9) | C(5)−C(6)−In(1) | 102.9(9) |
| C(6)−C(7)−C(3)#2 | 108.8(11) | | |

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x+3/2$, $y-1/2$, $-z+3/2$; #2 $-x+3/2$, $y+1/2$, $-z+3/2$.

An X-ray structural study of $Me_2In(C_5H_5)$ identified a linear polymer as depicted in Figure 1. A portion of the chain with the labeling of the atoms is shown in Figure 2. Interatomic distances and angles are collected in Table 1. Even though this structure is of limited precision, it is readily apparent that each indium atom is in contact with four carbon atoms with two terminal $In-CH_3$ bonds and two bridging $In-C(C_5H_5)$ bonds. The two terminal methyl groups have In−C bond lengths of 2.118(14) and 2.129(13) Å. These bond distances are similar to the distances in $InMe_3$[7] of 2.179(12), 2.121(14), and 2.136(13) Å. The two indium−carbon bonds to bridging cyclopentadienide groups have distances of 2.457(12) and 2.484(12) Å. The corresponding bridging $In-C(C_5H_5)$ distances in $In(C_5H_5)_3$[8] are 2.466(8) and 2.374(7) Å. Thus, the average $In-C(C_5H_5)$ contact distance is 0.347 Å longer than the average $\sigma$-bonding In−Me distance. Although each In(III) center appears to be in a typical distorted tetrahedral environment, the C(Me)−In−C(Me) angle is larger than the ideal *trigonal* value of 120° with a value of 133.2°, while the $C(C_5H_5)-In-C(C_5H_5)$ angle is less than the ideal *tetrahedral* angle of 109.5° at 94.1°. Thus, each indium(III) atom can be considered to have two normal $\sigma$-bonds to the methyl groups and a two-electron three-centered bond across the $C(C_5H_5)-In-C(C_5H_5)$ system. Distances within each $C_5H_5$ system show the appropriate systematic pattern. The shortest C−C distance in each ring (i.e., C(4)−C(5) = 1.33(2) Å) is for that carbon−carbon bond to which neither of the carbon atoms interacts with an indium(III) center. The longest C−C distances are C(5)−C(6) = 1.41(2) Å and C(3)#2−C(4) = 1.41(2) Å, whereas C(6)−C(7) = 1.36(2) Å and C(7)−C(3)#2 = 1.38(2) Å are of intermediate length. Thus, the molecular structures of $Me_2In(C_5H_5)$, $Me_2Ga(C_5H_5)$,[6] $Et_2Ga(C_5H_5)$,[2] and $In(C_5H_5)_3$[8] bear many close resemblances. However, the $C(C_5H_5)-In-C(C_5H_5)$ angle for the terminal cyclopentadienide groups in $In(C_5H_5)_3$[8] is 118.7(3)°, the C(Et)−Ga−C(Et) angle for $Et_2Ga(C_5H_5)$[2] is 125.0(3)°, and the C(Me)−Ga−C(Me) angle for $Me_2Ga(C_5H_5)$[6] is 127.0(2)°.

Solvents for $Me_2In(C_5H_5)$ are strong Lewis bases such as THF and $NMe_3$. Since the pure compound exists as a polymer with four-coordinate indium, dissolution requires cleavage of the polymer and coordination with the base. Thus, the solvent must have a donor ability that is comparable to that of the cyclopentadienide−indium bridge. Since $Me_2In(C_5H_5)$ is insoluble in diethyl ether, ether is apparently too weak a base to break the bridge. In contrast THF cleaves the bridge and dissolves $Me_2In(C_5H_5)$, but pure $Me_2In(C_5H_5)\cdot THF$ does not exist in THF solution. Ligand redistribution reactions occur to form an equilibrium mixture of $Me_2In(C_5H_5)\cdot THF$,

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$MeIn(C_5H_5)_2\cdot THF$, and $InMe_3\cdot THF$ (eq 4). Three in-

$$2Me_2In(C_5H_5)\cdot THF \xrightleftharpoons{THF} MeIn(C_5H_5)\cdot THF + InMe_3\cdot THF \quad (4)$$

dium−methyl resonances, one for each compound, are observed by $^1H$ NMRspectroscopy at the normal operating temperature of the instrument. Removal of THF leads to reformation of pure $Me_2In(C_5H_5)$ as the polymer. Thus, the chemistry of $Me_2In(C_5H_5)$ and $Me_2Ga(C_5H_5)$[1] has many similarities, but the apparently stronger cyclopentadienide bridge for the indium compound renders it less volatile, less soluble, and higher melting than its gallium analogue.

## Experimental Section

All compounds described in this investigation were manipulated in a standard vacuum line or in a purified argon atmosphere. The reagent $InMe_3$ was prepared by using the literature procedure,[9] whereas $InMe_2Cl$[10] was prepared by a stoichiometric ligand redistribution reaction between $InMe_3$ and $InCl_3$ in pentane at room temperature. Lithium cyclopentadienide was prepared by adding a hexane solution of LiBu to excess $C_5H_6$ in pentane by using the literature procedure.[11] All solvents were dried by conventional procedures. Elemental analyses were performed by E+R Microanalytical Laboratories, Inc., Corona, NY. The $^1H$ NMR spectra were recorded at 400 MHz by using a Varian Unity-Inova 400 spectrometer. Proton chemical shifts are reported in $\delta$ (ppm) units and are referenced to $SiMe_4$ at 0.00 ppm and THF at 3.58 and 1.73 ppm. All samples for NMR spectroscopy were contained in sealed NMR tubes. Melting points were observed with a Mel-Temp by using flame-sealed capillaries filled with purified argon and are uncorrected.

**Synthesis of $Me_2In(C_5H_5)$ by a Metathesis Reaction.** A 1.934 g (10.73 mmol) sample of $Me_2InCl$ and 0.790 g (11.0 mmol) of $Li(C_5H_5)$ were contained in flasks connected by a glass elbow. Then, approximately 10 mL of THF was vacuum distilled into each flask. The colorless solution of $Li(C_5H_5)$ was added slowly to the colorless solution of $Me_2InCl$ at 0 °C over 30 min. The resulting solution was stirred at room temperature overnight, and then the solvent was removed by vacuum distillation. The crude product was triply vacuum sublimed at 120 °C to give 1.93 g (9.17 mmol) (85.5% yield based on $Me_2InCl$) of $Me_2In(C_5H_5)$ as a colorless solid. $Me_2In(C_5H_5)$: mp 195−200 °C (dec); $^1H$ NMR (THF-$d_8$, $\delta$) 6.05 (s, $(C_5H_5)$, 2.19 H); 0.11 (s, $In\mathit{Me}_3$, 0.48 H); −0.52 (s, $\mathit{Me}_2In(C_5H_5)$, 6.0 H); −1.11 (s, $\mathit{Me}In(C_5H_5)_2$, 0.11 H). Anal. Calcd for $C_7H_{11}In$: C 40.04, H 5.28. Found: C 40.10, H 5.14.

**Synthesis of $Me_2In(C_5H_5)$ by Methane Elimination (Sealed Tube Reaction).** After a 0.774 g (4.84 mmol) sample of $InMe_3$ was placed in a break-seal tube fitted with an adapter, freshly cracked $C_5H_6$ (0.361 g, 5.46 mmol) was added by vacuum distillation. The tube was sealed and then placed in a tube furnace at 145−160 °C for 3 h. The evolved methane was removed while the tube was at −196 °C and was measured by use of a Toepler pump-gas buret assembly (6.05 mmol). Material volatile at room temperature, typically only excess $C_5H_6$, was removed by vacuum distillation. The remaining product was sublimed at 120 °C and 0.792 g $Me_2In(C_5H_5)$ (3.77 mmol, 77.9% yield based on $InMe_3$) was obtained. The characterization data for $Me_2In(C_5H_5)$ prepared by this pryolytic method were identical to that observed for the compound prepared by the metathetical reaction in THF.

**Table 2. Data for the X-ray Crystallographic Study of $[Me_2In(C_5H_5)]_\infty$**

| | |
|---|---|
| empirical formula | $C_7H_{11}In$ |
| cryst syst | monoclinic |
| space group | $P2_1/n$ |
| $a$, Å | 6.7966(6) |
| $b$, Å | 9.5184(9) |
| $c$, Å | 12.2013(11) |
| $\beta$, deg | 99.091(2) |
| $V$, Å$^3$ | 779.42(12) |
| $Z$ | 4 |
| fw | 209.98 |
| $D$, g/cm$^3$ | 1.789 |
| temp (K) | 298(2) |
| $\mu$(Mo K$\alpha$), mm$^{-1}$ | 2.934 |
| $F$(000) | 408 |
| $\theta$ range for data solution, deg | 2.73−19.99 |
| $h$ | −7 to 9 |
| $k$ | −12 to 12 |
| $l$ | −15 to 16 |
| no. of reflns collected | 2228 |
| no. of indep reflns | 723 ($R_{int} = 1.865\%$) |
| refinement method | full-matrix least-squares on $F^2$ |
| no. of data/restraints/params | 718/0/73 |
| final $R$ indices [$I > 2\sigma(I)$] | R1 = 0.0523, wR2 = 0.1318 |
| $R$ indices (all data) | R1 = 0.0729, wR2 = 0.1522 |
| goodness-of-fit on $F^2$ | 1.054 |
| largest diff peak, e Å$^{-3}$ | 0.886 |
| largest diff hole, e Å$^{-3}$ | −1.335 |

**Attempted Synthesis of $Me_2In(C_5H_5)$ by Methane Elimination (Reactions in Solution).** A break-seal apparatus was charged with $InMe_3$ (0.566 g, 3.54 mmol) and freshly cracked and vacuum-distilled $C_5H_6$ (0.257 g, 3.89 mmol). Toluene (~10 mL) was distilled into the tube, and the apparatus was flame-sealed. After the solution was allowed to sit at room temperature for 48 h, the break-seal was opened and all material volatile at room temperature was removed by vacuum distillation to leave 0.057 g of a colorless solid. If this solid were pure $Me_2In(C_5H_5)$, the yield would be 0.27 mmol or 7.6% based on $InMe_3$.

In another experiment, a flask with silicone-greased joints was charged with $InMe_3$ (1.021 g, 6.38 mmol), freshly cracked and vacuum-distilled $C_5H_6$ (0.465 g, 7.03 mmol), and a stir bar. After toluene (~15 mL) was vacuum distilled into the flask, the resulting solution was allowed to stir at room temperature for 4 days. Noncondensable gas other than $CH_4$ was observed to be present in the flask at −196 °C. All material volatile at room temperature was removed by vacuum distillation. The resulting pale yellow solid was sublimed under vacuum at 120 °C to produce a colorless solid which was shown to be $Me_2In(C_5H_5)$ (0.319 g, 1.52 mmol, 23.8% yield based on $InMe_3$) by its decomposition temperature and $^1H$ NMR spectrum in THF solution.

A third experiment used a Solv-Seal flask that had been charged with $InMe_3$ (0.977 g, 6.11 mmol), freshly cracked and vacuum-distilled $C_5H_6$ (0.437 g, 6.61 mmol), and a stir bar. Toluene (~15 mL) was vacuum distilled into the flask, and the solution was allowed to stir at room temperature for 2 days. Noncondensable gas other than $CH_4$ was observed at −196 °C. After all material volatile at room temperature had been removed, the resulting pale yellow solid was sublimed at 120 °C to produce $Me_2In(C_5H_5)$ as a colorless solid (0.221 g, 1.05 mmol, 17.2% based on $InMe_3$).

**Lewis Acidity Studies of $Me_2In(C_5H_5)$ by Tensimetric Titrations.** In a typical tensimetric titration, a weighed quantity of $Me_2In(C_5H_5)$ was placed in a tensimeter, and then small increments of the base were added by vacuum distillation at −196 °C. The apparatus was warmed to 0 °C and permitted to stand until no change in pressure as measured on a mercury manometer was observed. Then the next incre-

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ment of base was added. The experimental data include the quantity of $Me_2In(C_5H_5)$, the incremental addition of base as the mol ratio of base to $Me_2In(C_5H_5)$, and the observed pressure in mmHg. $NMe_3$: 0.144 g of $Me_2In(C_5H_5)$ (0.685 mmol); 0.126, 1.0; 0.257, 1.0; 0.334, 1.0; 0.408, 1.0; 0.509, 1.0; 0.608, 1.0; 0.697, 1.5; 0.826, 2.0; 0.974, 4.5; 1.00, 8.5; 1.387, 32. THF: 0.144 g of $Me_2In(C_5H_5)$ (0.685 mmol); 0.113, 9.0; 0.212, 13.0; 0.374, 15.0; 0.408, 17.0; 0.536, 24.0; 0.657, 36.0, 0.804, 39.0; 0.895, 39.0, 1.00, 40.0; 1.117, 42.0. $Et_2O$: 0.141 g of $Me_2In(C_5H_5)$ (0.673 mmol); 0.174, 20.0, 0.361, 42.0; 0.631, 64.0; 1.00, 102.0.

**Determination of the Crystal Structure.** A crystal that formed during the preparation of $Me_2In(C_5H_5)$ from $InMe_3$ and $C_5H_6$ in a sealed tube at 145−160 °C and appeared as a portion of a large, flat, thin sheet was cut into smaller parts. One part was sealed into a thin-walled glass capillary under an argon atmosphere inside the drybox maintained under anaerobic and moisture-free conditions and then used for the X-ray structural study. The selected crystal was the one of maximum thickness of those obtained from multiple synthetic experiments. The diffraction data, as summarized in Table 2, were collected by using a Siemens SMART CCD diffractometer and graphite-monochromated Mo Kα (0.71073 Å) radiation. A full data set ($2\theta = 55°$) was collected, but no useful data were observed beyond 40°. Thus, this structural determination is of limited precision, and the esd's on the bond parameters are probably underestimated by a factor of 2. A routine absorption correction was applied by using SADABS and any decay correction was made with the SAINT program. All calculations were performed on a personal computer by using the Siemens software package SHELXTL-Plus 5.03. A Patterson map was used to locate the indium atoms, and then the structure was solved by direct methods and successive interpretation of difference Fourier maps, followed by least-squares refinement. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in the refinement in calculated positions using fixed isotropic parameters.

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**Supporting Information Available:** Complete tables of positional parameters, interatomic distances and angles, anisotropic thermal parameters, and calculated positions for hydrogen atoms for the X-ray study. This material is available free of charge via the Internet at http://pubs.acs.org.

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