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(Tert-butyl)cyclopentadienylindium(I), In($C_5H_4CMe_3$): synthesis, characterization and X-ray structural study

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Abstract

The indium(I) compound, In($C_5H_4CMe_3$), has been prepared from the corresponding lithium cyclopentadienyl reagent Li($C_5H_4CMe_3$) and InCl in OEt_2. Characterization data have included partial elemental analyses (C, H), physical properties, IR, ^1H NMR and mass spectroscopic data, oxidation reactions with dilute aqueous HCl and a single-crystal X-ray structural study. The colorless crystal of In($C_5H_4CMe_3$) consists of infinite zigzag chains. There are no interstrand In ··· In interactions. The compound crystallizes in the monoclinic space group $P2_1/n$ with four formula units in the unit cell with dimensions of a 6.139(1), b 9.765(6), c 15.543(3) Å, β 92.87(1) and ρ_{calcd} 1.68 g/cm^3.

Compounds which have a group 13 element in a low oxidation state are an interesting but little studied class of compounds. The most common indium(I) derivatives incorporate a cyclopentadienyl substituent and include In(C_5H_5) [1–3], In(C_5H_4Me) [3], In($C_5H_4SiMe_3$) [4], In($C_5H_4GeMe_3$) [4], In (C_5Me_5) [5,6] and In[$C_5(CH_2Ph)_5$] [7]. It is noteworthy that the crystalline state of all of these compounds except In($C_5H_4GeMe_3$) have been studied and five different structures have been observed for the five compounds studied. Three compounds, In(C_5H_5) [3], In(C_5H_4Me) [3] and In($C_5H_4SiMe_3$) [4], exist in the solid state as zigzag chains but with different numbers of short interstrand In ··· In interactions. Each indium in In(C_5H_5) is 3.986(1) Å away from two other indium atoms [3] whereas In(C_5H_4Me) has an indium atom at 3.986(1) Å from only one other indium atom [3]. The trimethylsilyl derivative In($C_5H_4SiMe_3$) has no interstrand interactions [4]. Pentamethylcyclopentadienylindium(I) [5,6] exists as a hexameric (octahedral) cluster with In ··· In interactions of 3.963(1) and 3.943(1) Å. The compound In[$C_5(CH_2Ph)_5$] [7] forms quasi-dimeric units with indium–indium distances of 3.631(2) Å, the shortest observed to date. In this paper we extend this series with synthesis and complete characterization of In($C_5H_4CMe_3$).

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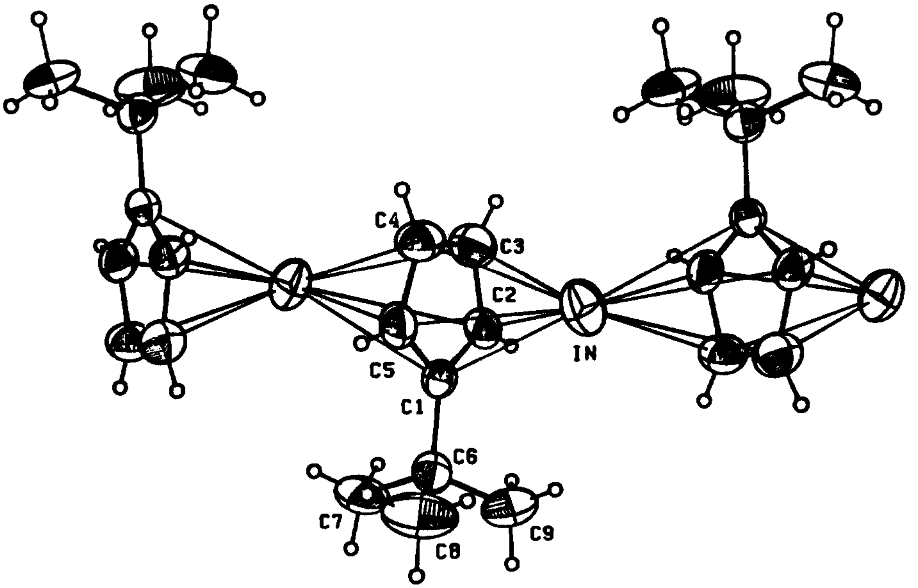

Fig. 1. Labeling of atoms in In($C_5H_4CMe_3$) (ORTEP diagram; 50% ellipsoids with hydrogen atoms artifically reduced.

The compound In($C_5H_4CMe_3$) was prepared from InCl and Li($C_5H_4CMe_3$) in diethyl ether by using the method of Peppe et al. [2] and was fully characterized by its physical properties, partial elemental analyses (C, H), reaction with dilute aqueous HCl, IR, ^{1}H NMR and mass spectroscopy and a single crystal X-ray structural study. The synthesis of the compound according to the following equation was observed to be typical of indium(I) compounds. Upon addition of

$$\mathrm{InCl} + \mathrm{Li(C_5H_4CMe_3)} \xrightarrow{\mathrm{OEt_2}} \mathrm{In(C_5H_4CMe_3)} + \mathrm{LiCl}$$

Li($C_5H_4CMe_3$), a gray colored material, possibly indium metal, was observed. The lithium cyclopentadienide reagent apparently acts as a reducing agent or the indium(I) disproportionates to a slight extent [8]. However, the extent of decomposition was small. The colorless, crystalline indium(I) product was isolated in ~ 90% yield.

The structure of In($C_5H_4CMe_3$) consists of (theoretically) infinite zigzag chains based on $[\mathrm{In(C_5H_4CMe_3)}]_\infty$ with no interstrand In · · · In interactions. The structure is very similar to that observed for $[\mathrm{In(C_5H_4SiMe_3)}]_\infty$. The labelling of atoms in the basic In($C_5H_4CMe_3$) unit is illustrated in Fig. 1 whereas the packing diagram is shown in Fig. 2. Bond distances and bond angles are collected in Table 1. In the solid state each indium atom interacts with two (t-butyl)cyclopentadienyl ligands (centroid · · · In · · · centroid = 128.2°) and each cyclopentadienyl ligand is "inversely sandwiched" between two indium atoms (In · · · centroid · · · In = 173.4°). The corresponding angles in In($C_5H_4SiMe_3$) [4], In(C_5H_4Me) [3] and In(C_5H_5) [3] are 131.78 and 175.94°, 130.66 and 179.74°, and 128.02 and 176.99°, respectively. Thus, these intrachain angles are very similar for all compounds with zigzag chains (see Table 2).

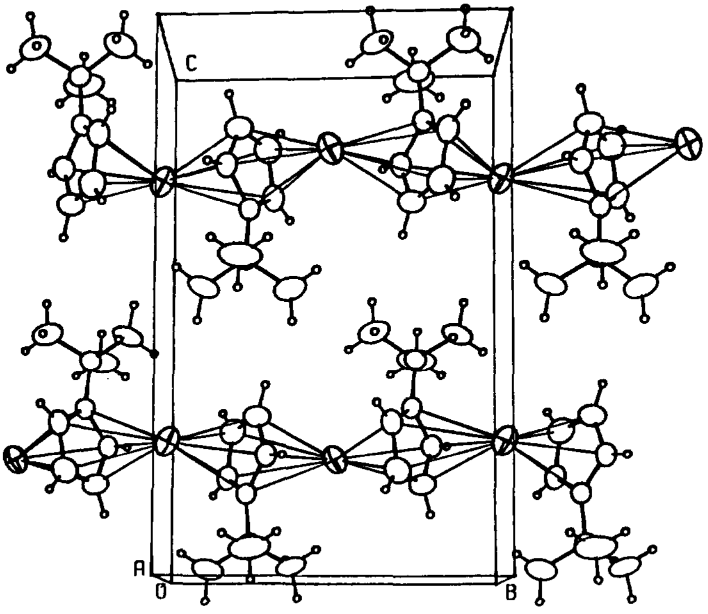

Fig. 2. Packing diagram for In($C_5H_4CMe_3$) showing the infinite zigzag chains.

The basic carbocyclic ring, defined by atoms C(1) through C(5), is associated with In–C distances of 2.71(1)–2.911(9) Å (average 2.81 Å) and an In · · · centroid distance of 2.53 Å. These distances for In($C_5H_4CMe_3$) are shorter than for

Table 1

Bond distances (Å) and angles (deg) for In($C_5H_4CMe_3$)

Bond distances			
In–C(1)	2.837(8)	In–C(2)	2.738(9)
In–C(3)	2.71(1)	In–C(4)	2.84(1)
In–C(5)	2.911(9)	In–C(1)*	3.207(9)
In–C(2)*	3.310(9)	In–C(3)*	3.20(1)
In–C(4)*	2.98(1)	In–C(5)*	2.98(1)
C(1)–C(2)	1.42(1)	C(1)–C(5)	1.43(1)
C(1)–C(6)	1.51(1)	C(2)–C(3)	1.40(1)
C(3)–C(4)	1.42(1)	C(4)–C(5)	1.41(1)
C(6)–C(7)	1.52(1)	C(6)–C(8)	1.51(1)
C(6)–C(9)	1.53(1)	Cent–In	2.53
Cent*–In	2.85		
Bond angles			
C(2)–C(1)–C(5)	107.5(8)	C(2)–C(1)–C(6)	125.7(8)
C(5)–C(1)–C(6)	126.6(8)	C(1)–C(2)–C(3)	108.2(9)
C(2)–C(3)–C(4)	108.4(9)	C(3)–C(4)–C(5)	107.8(9)
C(1)–C(5)–C(4)	108.1(9)	C(1)–C(6)–C(7)	111.6(8)
C(1)–C(6)–C(8)	109.7(8)	C(7)–C(6)–C(8)	110(1)
C(1)–C(6)–C(9)	110.0(8)	C(7)–C(6)–C(9)	107.6(9)
C(8)–C(6)–C(9)	108(1)	Cent–In–Cent*	128.2
In–Cent–In*	173.4		

Table 2

Comparisons of structural features of cyclopentadienylindium(I) compounds

	$In(C_5H_5)$ [a]	$In(C_5H_4Me)$ [a]	$In(C_5H_4SiMe_3)$ [b]	$In(C_5H_4CMe_3)$
In–C(av) (Å)	2.959	2.867	2.872	2.81
In–C*(av) (Å)	2.924	3.016	3.067	3.14
In–centroid (Å)	2.726	2.609	2.609	2.53
In–centroid* (Å)	2.687	2.771	2.822	2.85
centroid–In–centroid (°)	128.02	130.66	131.78	128.2
In–centroid–In* (°)	176.99	179.74	175.94	173.4
M.p. (°C)	169.3–171.0	48.5–51.0	51.4–51.8	47.5–48.5
mmol H_2/mmol In^I	0.942	0.955	0.867	0.956

[a] Reference 3. [b] Reference 4.

$In(C_5H_4SiMe_3)$ [4] of In–C(average) of 2.872 Å and In ··· centroid of 2.609 Å. The second carbocyclic ring (atoms C(1)*–C(5)* is associated with In–C* distances of 2.98(1)–3.310(9) Å (average 3.14 Å) and an In ··· centroid* distance of 2.85 Å. The corresponding distances in $In(C_5H_4SiMe_3)$ [4] are shorter. Thus, $In(C_5H_4CMe_3)$ has the shortest In–C (In–centroid) and longest In–C* (In–centroid*) for any cyclopentadienylindium(I) derivative (Table 2) with a zigzag structure.

The existence of indium in the +1 oxidation state for $In(C_5H_4CMe_3)$ has been confirmed by its reactions with dilute aqueous HCl. The ratio of mol of H_2/mol of In^I compound was 0.957. These results are consistent with the following balanced chemical equation. However, it must be noted that indium metal was found upon exposure of $In(C_5H_4CMe_3)$ to the acid. Then, the metal appeared to react with the acid to liberate H_2. Similar observations have been noted for other cyclopentadienylindium(I) compounds [3–6].

$$In(C_5H_4CMe_3) + 3H^+ \rightarrow In^{+3}_{(aq)} + H_{2(g)} + C_5H_5(CMe_3)$$

The mass spectrum of $In(C_5H_4CMe_3)$, which readily sublimes at 35 °C, suggests the presence of a monomeric species in the gas phase as has been observed by electron diffraction studies for $In(C_5H_5)$ [3,12], $In(C_5H_4Me)$ [3] and $In(C_5Me_5)$ [5]. The primary ions detected in the mass spectrum were In^+ (115 m/z) and $In(C_5H_4CMe_3)^+$ (236 m/z). Thus, one of the indium-cyclopentadienyl ring interactions of the solid must be quite weak.

Experimental section

All compounds described in this investigation were exceedingly sensitive to oxygen and water and were manipulated in a standard vacuum line or under a purified argon atmosphere by using Vacuum/Atmospheres Dri-Lab. The cyclopentadienylindium(I) derivative was so exceedingly sensitive to trace quantities of moisture that all glassware used for their preparation, characterization, and handling was flame-heated under dynamic vacuum and then permitted to stand in the drybox for approximately 2 h prior to use. All solvents were purified by standard techniques. Indium(I) chloride was purchased from Strem Chemicals, Inc. and was used without further purification. The reagent $Li(C_5H_4CMe_3)$ was prepared from 6,6-dimethylfulvene and LiMe in OEt_2 as previously described [9]. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY. Infrared spectra of Nujol mulls were recorded with a Perkin–Elmer 683 spectrometer. Absorption intensities are reported with the 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 300 MHz with a Varian Gemini-300 NMR spectrometer. Chemical shifts are reported in δ units (ppm) and are referenced to $SiMe_4$ at δ 0.00 and benzene at δ 7.13. All NMR tubes were sealed under vacuum. Mass spectra of the samples contained in capillary tubes were recorded with a VG Model 70-SE spectrometer equipped with Electron Impact (E) capabilities.

Synthesis of $In(C_5H_4CMe_3)$

A side-arm dumper charged with 0.712 g (4.74 mmol) of finely ground InCl was connected to a two-neck flask containing 0.602 g (4.70 mmol) of lithium t-butylcyclopentadienide. Twenty-five mL of dry diethyl ether was distilled into the flask. While the solution was at room temperature, the InCl powder was added all at once to the rapidly stirred mixture. Some of the InCl decomposed to form a grey colored material, possibly indium metal. The mixture was then stirred for 19 h in the dark. The ether was removed very quickly by vacuum distillation. (No hot water bath was used to assist the distillation.) An 80 ° elbow equipped with a Schlenk flask was attached to the original two-neck reaction flask in the dry box. The clean flask was placed in a −196 °C bath and the product was dynamically sublimed from the reaction flask into the clean Schlenk flask. This isolation procedure took only 1 h because of the volatility of t-butylcyclopentadienylindium(I). The product was then transferred to a straight 20 mm Solv-Seal^{TM} tube. The tube was evacuated and was placed in a 35 °C oil bath for 6 h. The product sublimed under static vacuum as clear colorless crystals. The compound t-butylcyclopentadienylindium(I), $In(C_5H_4CMe_3)$ (1.006 g, 4.26 mmol), was isolated in 90.6% yield as based on $Li(C_5H_4CMe_3)$.

$In(C_5H_4CMe_3)$. Colorless crystalline solid; m.p. 44.5 °C (glass transition), 47.5–48.5 °C (melting), ~ 300 °C (decomposition) pale yellow/brown. ^{1}H NMR (C_6D_6, δ): 1.18 (s, 9H, CMe_3); 5.79 (t, 2H, CH, ^3J(HCCH) = 2.8 Hz); 5.96 (t, 2H, CH, ^3J(HCCH) = 2.9 Hz). IR (Nujol mull, cm^{-1}): 3091m, 1672vw, br, 1608w, br, 1562w, br, 1475s, sh, 1400m, 1270s, 1195m, 1181m, 1145vs, 1040m, 1030m, 1014m, 909m, 845w, 845w, 814vs, br, 754vs, br, 665vs, 575vw, 460w, 442s, 350m. Anal. Found: C, 45.49; H, 5.49. $C_9H_{13}In$ calcd: C, 45.79; H, 5.55%. MS EI 10 V (m/z, relative intensity): 115, 100%, In^+; 236, 40%, $In(C_5H_4CMe_3)^+$.

Hydrolysis of $In(C_5H_4CMe_3)$

A quantity of $In(C_5H_4CMe_3)$ (0.104 g, 0.440 mmol), was placed in a 100 mL round bottom flask. After this flask was evacuated while at −196 °C, ≈ 20 mL of 3 *M* HCl was added through an addition tube. Immediately upon exposure to aqueous acid, the compound decomposed to indium metal. Then, the metal apparently reacted with the acid. The hydrolysis was allowed to proceed for 3 days at ~ 100 °C. The noncondensable gas was isolated and measured by means of a Toepler pump–gas burette assembly. The volume of H_2 collected, 8.8 cmHg at STP, (0.421 mmol) corresponds to a 95.7% yield as based on the oxidation of indium(I) to indium(III) with formation of one mole of H_2 per mole of indium(I).

Table 3

Crystal data and summary of intensity data collection and structure refinement

Compound	$In(C_5H_4CMe_3)$
Color/Shape	colorless/parallelepiped
Mol. Wt.	236.02
Space group	$P2_1/n$
Temp. (°C)	20
Cell constants [a]	
a (Å)	6.139(1)
b (Å)	9.765(6)
c (Å)	15.543(3)
β (deg)	92.87(1)
Cell vol. (Å^3)	930.6
Molecules/unit cell (Z)	4
ρ_{calc}, g cm^{-3}	1.68
μ_{calc}, cm^{-1}	24.5
Diffractometer/scan	Enraf–Nonius CAD-4/$\omega-2\theta$
Range of relative transm. factors (%)	81/100
Radiation, graphite monochromator	Mo-K_α ($\lambda = 0.71073$)
Max crystal dimensions (mm)	$0.13 \times 0.35 \times 0.53$
Scan width (°)	$0.80 + 0.35 \tan\theta$
Std reflections	200; 0, 10; 0; 0, 0, 12
Decay of standards	±2%
Reflections measured	1939
2θ range (°)	$2 \leqslant 2\theta \leqslant 50$
Range of h, k, l	+7, +11, ±18
Observed reflections	1370
Computer programs [c]	SHELX [10]
Structure solution	Heavy atom techniques
No. of parameters varied	100
Weights	$[\sigma(F_o)^2 + 0.00001F_o^2]^{-1}$
GOF	15.5
$R = \Sigma \lVert F_o\rvert - \lvert F_c\rVert / \Sigma\lvert F_o\rvert$	0.071
R_w	0.072
Largest feature final diff. map, eÅ^{-3}	1.0 (near In)

[a] Least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 25 reflections $\theta > 20°$. [b] Corrections: Lorentz-polarization and absorption (empirical, ψ scan). [c] Neutral scattering factors and anomalous dispersion corrections from ref. 11.

Table 4

Final fractional coordinates for $In(C_5H_4CMe_3)$

Atom	x	y	z	B_{eq} [a]
In	0.9420(1)	0.49343(8)	0.74940(5)	3.58
C(1)	0.789(1)	0.2599(9)	0.6661(6)	1.96
C(2)	0.608(2)	0.3251(9)	0.7025(6)	2.44
C(3)	0.628(2)	0.308(1)	0.7921(7)	3.41
C(4)	0.817(2)	0.228(1)	0.8125(7)	3.15
C(5)	0.916(2)	0.198(1)	0.7349(6)	2.67
C(6)	0.828(2)	0.250(1)	0.5710(6)	2.42
C(7)	0.715(2)	0.126(1)	0.5302(7)	4.45
C(8)	1.070(2)	0.241(2)	0.5583(8)	4.89
C(9)	0.739(3)	0.377(1)	0.5240(7)	4.90

[a] $B_{eq} = 4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

X-Ray data collection, structure determination and refinement for $In(C_5H_4CMe_3)$

A transparent single crystal was mounted in a thin-walled glass capillary and transferred to the goniometer. The space group was determined to be the centric $P2_1/n$ from the systematic absences. A summary of data collection parameters is given in Table 3.

The poor quality of the crystalline material available for study resulted in high esd's and a very poor goodness of fit parameter. The geometrically constrained hydrogen atoms were placed in calculated positions 0.95 Å from the bonded carbon atom and allowed to ride on that atom with B fixed at 5.5 $Å^2$. The methyl hydrogen atoms were included as a rigid group with rotational freedom at the bonded carbon atom ($C-H = 0.95$ Å, $B = 5.5$ $Å^2$). Refinement of nonhydrogen atoms with anisotropic temperature factors led to the final values of $R = 0.071$ and $R_w = 0.072$. The final values of the positional parameters are given in Table 4.

Acknowledgements

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