Sterically demanding organoindium compounds. Synthesis and molecular structure of bis[(2,6-dimesitylphenyl)indium dichloride], $[(Mes_2C_6H_3)InCl_2]_2$ $(Mes = 2,4,6-Me_3C_6H_2)$ [*]

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Abstract

The sterically demanding arylindium dichloride bis[(2,6-dimesitylphenyl)indium dichloride] $[(Mes_2C_6H_3)InCl_2]_2$ $(Mes = 2,4,6-Me_3C_6H_2)$ prepared by reaction of (2,6-dimesitylphenyl)lithium $(Me_2C_6H_3Li)$ with indium chloride and characterized by ^{1}H NMR, elemental analyses and single-crystal X-ray diffraction, crystallizes in the monoclinic space group $P2_1/n$ (No. 14) with unit-cell parameters $a = 11.094$ (4) Å, $b = 16.902$ (4) Å, $c = 13.762$ (3) Å, $\beta = 96.69$ (2)°, $V = 2563$ Å^3 for $Z = 2$ and $D_{calc} = 1.40$ g cm^{-3}. Refinement based upon 1980 observed reflections converged at $R = 0.039$ and $R_w = 0.046$. The title compound, residing about a center of symmetry, contains a planar and slightly asymmetric In_2Cl_2 four-membered ring with an In–Cl bond distances of 2.519 (2) and 2.514 Å. The terminal In–Cl bond distance is shown to be 2.334 (3) Å while the In–C bond distance is 2.138 (8) Å. The independent In–C bond distance is determined to be 2.138 (8) Å. The title compound represents only the second example of a dimeric organoindium halide.

Keywords: Indium; Sterically demanding organoindium compounds; X-ray structure

1. Introduction

Ligand steric loading has proven to be a useful practice throughout inorganic chemistry as particularly sensitive or reactive molecules may often be stabilized by saturating the coordination sphere of the metal. An additional benefit of large ligands is that they often sterically inhibit decomposition pathways. The utilization of sterically demanding ligands has also become a popular routine in the organometallic chemistry of the heavier congeners of Group 13. In an effort to examine a particularly bulky ligand we endeavored to utilize the 2,6-dimesitylphenyl moiety relative to organoindium chemistry. Herein we report the synthesis and structure of bis[(2,6-dimesitylphenyl)indium dichloride], $[(Mes_2C_6H_2)InCl_2]_2$ (I), isolated from reaction of

(2,6-dimesitylphenyl)lithium $Mes_2C_6H_3Li$ $(Mes = 2,4,6-Me_3C_6H_2)$ with indium chloride in diethyl ether:

(I)
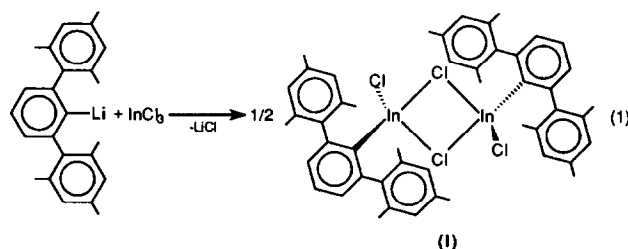
Despite the steric demands imposed by the 2,6-dimesitylphenyl ligand, the indium chloride is isolated as a μ^2-Cl bridged dimer.

2. Experimental details

2.1. General comments

Standard Schlenk techniques were employed in conjunction with an inert atmosphere dry-box (Vacuum

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Atmosphere HE-43 Dri-Lab). Solvents were distilled from sodium benzophenone under an atmosphere of argon prior to use. NMR spectra were recorded on a Bruker AC300 Fourier transform NMR spectrometer. X-ray diffraction data were collected on a Rigaku AFC7R single-crystal diffractometer. Indium chloride was purchased from Strem Chemical Co. and used as received. (2,6-Dimesitylphenyl)lithium was prepared by published procedures [1]. Elemental analyses were performed by E + R Microanalytical Laboratories (Corona, NY).

2.2. Synthesis of [(Mes₂C₆H₃)InCl₂]₂ (I)

In a dry-box a 100 ml flask was charged with $InCl_3$ (0.88 g, 4 mmol) and ether (40 cm³). To this solution at −78°C an ether solution (40 cm³) of $(Mes_2C_6H_3)Li$ (1.28 g, 4 mmol) was added dropwise with vigorous stirring. The mixture was stirred for 3 h at this temperature and then allowed to warm slowly to room tempera-

ture. After stirring for an additional 24 h the white precipitate (LiCl) was separated by filtration. The colorless filtrate was dried in vacuo and extracted with a toluene–benzene mixture (25 cm³: 5 cm³) and filtered. Cooling the filtrate at −20°C for 2 days gives cubic colorless crystals from which a single crystal was chosen directly for X-ray analysis. For other analyses the compound was separated from the solvent and dried in vacuo, (yield, 65%; melting point, 137–138°C). Anal. Found: C, 58.33; H, 5.37. $C_{24}H_{25}Cl_2In$ calc.: C, 57.70; H, 5.00%. ¹H NMR ($C_2D_5OC_2D_5$ 300 MHz, 297 K): 7.30–7.37 (m, 1H, p-CH₃), 6.93–6.96 (m, 2H, m-CH₃), 6.75 (s, 4H, m'-CH₃), 2.15 (s, 6H, p'-CH₃), 1.95 (s, 9H, o'-CH₃), 1.90 (s, 3H, o'-CH₃) ppm. ¹³C NMR: δ 137.13, 136.03, 130.52, 129.32, 128.94, 128.74, 128.26, 127.98 ppm.

2.3. Crystal structure determination

A colorless parallelepiped crystal of [(Mes₂C₆H₃)-InCl₂]₂ was mounted in a glass capillary under an

Table 1
Crystallographic data for [Mes₂C₆H₃)InCl₂]² (I)

|	
Crystal data	
Empirical formula	$C_{54}H_{56}Cl_4In_2$
Formula weight (g mol)	1076.43
Color; habit	Colorless; parallelepiped
Size (mm)	0.21 × 0.24 × 0.37
Space group	Monoclinic, $P2_1/n$ (No. 14)
Unit-cell dimensions	
a (Å)	11.094(4)
b (Å)	16.902(4)
c (Å)	13.762(3)
β (°)	96.69(2)
V (Å³)	2563(1)
Formula units per cell	2
D_{calc} (g cm³)	1.40
$F(000)$	1092
Data collection	
Number of unit-cell reflections	42 (25.50° < 2θ < 41.02°)
2θ range (°)	3.5–45.0
Scan type	ω–2θ
Scan speed (° mm⁻¹)	Variable; 2.09–14.65
Number of reflections collected	3790
Number of reflections unique/R_{int}	3366 (0.024)
Indices	(12 9 ± 15)
Crystal decomposition	Negligible (2%)
Absorption coefficient (mm⁻¹)	1.14
Minimum transmission; maximum transmission	0.83; 1.00
Refinement	
Final residuals	
R	0.0389
R_w	0.0456
Goodness of fit S	1.12
Largest Δ/σ	0.0009
Number of reflections observed ($I > 3\sigma(I)$)	1980
Number of parameters refined	136
Data-to-parameter ratio	14.6 to 1
Maximum difference peaks; minimum difference peaks (electrons Å⁻³)	0.63; − 0.90
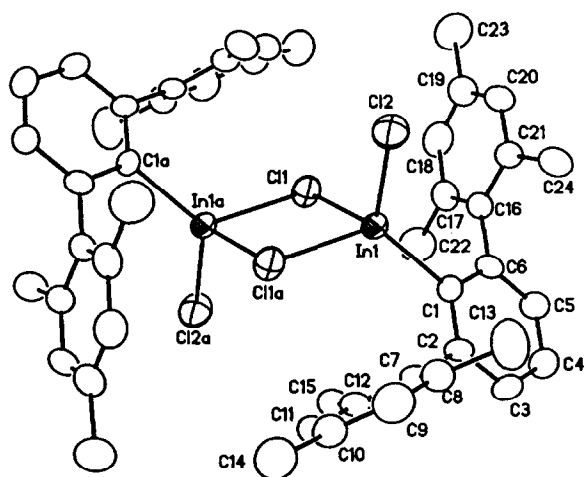
Fig. 1. A thermal ellipsoid plot of [(Mes$_2$C$_6$H$_3$)InCl$_2$]$_2$ (I) showing the atom-labeling scheme. Thermal ellipsoids show 35% probability levels; hydrogen atoms have been omitted. Selected bond distances and angles are as follows: In(1)–Cl(1), 2.519(2) Å; In(1)–Cl(2), 2.344(3) Å; In(1)–Cl(1), 2.138(8) Å; In(1)–Cl(1a), 2.514(2) Å; Cl(1)–In(1)–Cl(2), 103.7(1)°; Cl(1)–In(1)–C(1), 116.4(2)°; Cl(2)–In(1)–C(1), 124.2(2)°; Cl(1)–In(1)–Cl(1a), 83.7(1)°; Cl(2)–In(1)–Cl(1a), 97.7(1)°; C(1)–In(1)–Cl(1a), 122.7(2)°; In(1)–Cl(1) –In(1a), 96.3(1)°; In(1)–C(1)–C(2), 122.7(5)°; In(1)–C(1)–C(6), 116.5(6)°.

atmosphere of argon. X-ray intensity data were collected on a Nicolet R3mV diffractometer, with graphite-monochromated Mo Kα radiation ($\lambda = 0.710$ 73 Å) at 21°C, using the ω-2θ scan technique to a maximum 2θ value of 45°. The structure was solved by direct methods using the TEXSAN [2] and SHELXTL [3] package of computer programs. The gallium and chlorine atoms were refined using anisotropic thermal parameters while the carbon atoms were refined isotropically. Hydrogen atoms were located by standard difference Fourier techniques and were included in the structure factor calculation at idealized positions ($d_{C-H} = 0.96$ Å) and were allowed to ride on the atoms to which they were bonded. An isotropic group thermal parameter ($U_{iso} = 0.115(8)$ Å^2) was refined for all the hydrogen atoms. The final cycle of full-matrix least-squares refinement was based on 1980 observed reflections ($I > 2\sigma(I)$). Refinement converged at $R = 0.039$ and $R_w = 0.046$. The asymmetric unit contains one (Mes$_2$C$_6$H$_3$)-InCl$_2$ monomer situated about an inversion center (0, $\frac{1}{2}$, $\frac{1}{2}$) which generates the other half of the dimer. In addition, the asymmetric unit contains half a benzene solvent molecule which is also situated about an inversion center ($\frac{1}{2}$, $\frac{1}{2}$, 0). The X-ray crystal structure of

Table 2
Atomic coordinates and equivalent isotropic displacement coefficients for [Mes$_2$C$_6$H$_3$)InCl$_2$]$_2$ (I)

	x ($\times 10^{-4}$)	y ($\times 10^{-4}$)	z ($\times 10^{-4}$)	U_{eq} [a] ($\times 10^{-3}$ Å^2)
In(1)	930(1)	5178(1)	3969(1)	45(1)
Cl(1)	−1259(2)	5266(2)	4277(1)	63(1)
Cl(2)	1643(3)	6477(2)	4210(2)	87(1)
C(1)	1312(7)	4439(5)	2781(5)	38(3)
C(2)	2152(7)	3812(5)	2897(5)	42(3)
C(3)	2336(8)	3350(6)	2095(6)	56(4)
C(4)	1695(9)	3514(6)	1185(6)	65(4)
C(5)	898(10)	4132(6)	1072(6)	60(4)
C(6)	696(7)	4617(5)	1862(6)	42(3)
C(7)	2867(8)	3641(5)	3882(6)	45(3)
C(8)	4036(8)	3934(6)	4096(6)	56(4)
C(9)	4663(9)	3764(7)	4995(7)	75(5)
C(10)	4193(10)	3318(7)	5691(7)	71(4)
C(11)	3029(10)	3032(6)	5453(7)	66(4)
C(12)	2367(9)	3170(5)	4559(6)	52(4)
C(13)	4622(10)	4440(8)	3360(8)	96(5)
C(14)	4861(10)	3191(7)	6697(7)	95(5)
C(15)	1078(9)	2845(6)	4353(7)	72(4)
C(16)	−136(7)	5306(6)	1757(5)	45(3)
C(17)	−1389(8)	5234(7)	1786(5)	57(3)
C(18)	−2098(10)	5912(9)	1712(7)	76(5)
C(19)	−1616(11)	6659(8)	1612(7)	74(5)
C(20)	−387(11)	6717(6)	1548(6)	67(4)
C(21)	353(9)	6065(6)	1621(6)	51(4)
C(22)	−1961(10)	4419(7)	1905(9)	90(5)
C(23)	−2430(12)	7377(8)	1536(9)	122(7)
C(24)	1666(9)	6173(6)	1492(7)	69(4)
C(25)	4426(13)	5618(10)	370(11)	115(7)
C(26)	4195(11)	4853(11)	639(9)	94(5)
C(27)	4744(12)	4242(8)	286(11)	102(6)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

$[(Mes_2C_6H_3)InCl_2]_2$ is given in Fig. 1. Table 1 provides a summary of crystallographic data, data collection and structural refinement while atomic coordinates are given in Table 2.

3. Results and discussion

Trimethylindium-based compounds have recently been the subject of some interesting studies. For example, this laboratory reported the synthesis and molecular structure of the trimeric phosphinoindane $[Me_2In-PPh_2]_3$ isolated from reaction of Me_3In with diphenylphosphine [4]. Furthermore, the dimeric phosphinogallane $[Me_2In-P(SiMe_3)_2]_2$, isolated from reaction of Me_3In with $P(SiMe_3)_3$, has been shown to afford indium phosphine at 400°C [5].

Relative to aryl-based organoindium compounds, considerable attention has been focused on the substituted phenyl derivatives such as mesityl, Mes, (2,4,6-$Me_3C_6H_2$) and the so-called super-mesityl—the *tert*-butyl derivative of mesityl—Mes* (2,4,6-$^tBu_3C_6H_2$) ligand systems. The utilization of these sterically demanding ligands has afforded the isolation of the dimer $[Mes_2InCl]_2$ [6] while the bulkier *tert*-butyl-substituted derivative yields the dichloride monomer Mes*$InCl_2$ [7]. As the (2,6-dimesitylphenyl) ligand is considerably more sterically demanding than the mesityl ligand, it is quite surprising that I assumes a dimeric form. Furthermore, it is interesting that the bridging In–Cl bond distances in I (2.519(2) and 2.514(2) Å) are slightly shorter than the corresponding bridging In–Cl bond distances in $[Mes_2InCl]_2$ (2.585(3) and 2.584(3) Å). In addition, it is surprising that the terminal In–Cl bond distance of 2.344(3) Å in I is noticeably shorter than the aforementioned In–Cl distances and even shorter than the In–Cl bond distance reported for Mes*$InCl_2$. Indeed, the terminal In–Cl bond distance is among the shortest distances reported.

For perspective, this sterically demanding ligand system has been applied to the organometallic chemistry of the Group 13 elements only recently. This ligand was employed by this laboratory to prepare bis(2,6-dimesitylphenyl)gallium chloride $(Mes_2C_6H_3)_2GaCl$) (II) [8]:
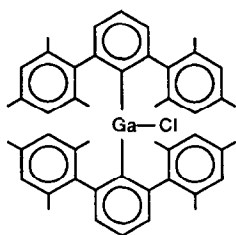
(II)

Compound II is note worthy as the steric demands of the ligand were sufficient so as to afford the first T-shaped geometry about the gallium atom. Compound I resides about a planar and yet slightly asymmetric, In_2Cl_2 four-membered ring with In–Cl bond distances of 2.519(2) Å and 2.514(2) Å. While the In–Cl bonds to the μ^2-Cl atoms are well within the range of previously reported interactions (2.40–2.67 Å) [9], the terminal In–Cl bond distance must be considered reasonably short at a distance of 2.344(3) Å. The steric demands of the ligands are also manifest prominently as evidenced by the Cl(2)–In(1)–C(1) bond angle of 124.2(2)°.

This sterically demanding arylindium dichloride dimer is note worthy as it incorporates one of the most sterically demanding ligands so far examined and as such affords unique opportunities as to the synthetic possibilities of this compound.

4. Supplementary material available

A textual summary of data collection and refinement, and tables of crystal data, bond distances and angles, final fractional coordinates, and thermal parameters (16 pages). Ordering information is given on any current masthead page.

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