Synthesis and X-Ray Structure of Me₂InI(NH₂(*t*-Bu)): The First Structurally Characterized Amine Adduct of a Dialkyl Indium Iodide

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NOTE

SYNTHESIS AND X-RAY STRUCTURE OF Me$_2$InI(NH$_2$(t-Bu)): THE FIRST STRUCTURALLY CHARACTERIZED AMINE ADDUCT OF A DIALKYL INDIUM IODIDE

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INTRODUCTION

Our research involving the alkyl derivatives of gallium and indium with nitrogen-based ligands has focussed mainly on trialkyl metal amine adducts (R$_3$M^p.NRH$_2$), and alkyl metal amides, (R$_2$MNRH)$_n$.[1] Recent work has included the structural characterization of dialkyl metal halide complexes, as [Cy$_2$GaCl]$_2$,[2] which are generally used *in situ*, and are used as starting materials for the amido species.[3] To expand this work we have now isolated primary amine adducts of the dialkyl metal halide species.[4] The complex Me$_2$InI(NH$_2$(t-Bu)) (1) is one such example and represents the first structurally characterized bisalkyl indium halide amine adduct. Interestingly, 1 crystallizes with one molecule of the ammonium iodide salt, I[NH$_3$(t-Bu)] in the crystal lattice.

EXPERIMENTAL

Standard Schlenk-line techniques were employed in conjunction with an inert atmosphere glove box. Diethylether and toluene were distilled from sodium metal under purified N$_2$ prior to use. InI$_3$ was used as received from Aldrich. ^{1}H NMR spectra were recorded on a General Electric QE-300 spectrometer. X-ray diffraction data were collected on an Enraf-Nonius CAD-4 diffractometer.

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Synthesis of $Me_2InI(NH_2(t-Bu))(1)$

A solution of MeLi in Et_2O (10.39 cm³ of a 0.77 M solution, 8.00 mmol) was added dropwise to a stirring solution of InI_3 (1.98 g, 4.00 mmol) in diethylether (50 cm³) at $-78°C$. The reaction mixture was allowed to warm to room temperature and then stirred (6 h) before *tert*-butyl amine (0.84 cm³, 8.00 mmol) was added to the reaction mixture. The solution was then stirred (12 h) before volatile materials were removed *in vacuo*. The residue was extracted with toluene (100 cm³) and filtered. The filtrate was concentrated (30 cm³) and then cooled ($-20°C$) for 1 month to yield colourless, X-ray quality needles of $Me_2InI(NH_2(t-Bu))$ (1); Mp 62–64°C(dec.), yield 30% based on InI_3. ¹H NMR(300.15 MHz, C_6D_6): δ 0.22 (s, CH_3-In), 0.59, 0.85 (m, m, $t-Bu-NH_3{}^+$), 1.2 (m, $t-Bu-NH_2$).

Structural solution and refinement

Crystals of **1** were sealed in Lindemann capillaries under an atmosphere of dry argon. Intensities were collected on an Enraf-Nonius CAD-4 diffractometer at 25°C using the $\theta/2\theta$ scan technique. reflections were measured in the range $2 < 2\theta < 50°$. Of 3818 independent reflections collected, 2379 having $I > 3\sigma(I)$ were used for the structure analysis. The intensities were collected for Lorentz and polarization effects. No absorption correction was applied. Details of the data collection are given in Table I. Positional and equivalent isotropic thermal parameters are listed in Table II and selected bond lengths and angles are given in Table III.

All calculations were performed on a MICROVAX 3100 computer, using the SHELX software package.[5] The structure was solved by Patterson and Fourier methods. The hydrogen atoms were placed in their geometrically calculated positions and included in the final structure factor calculations with fixed isotropic thermal

TABLE I

Data collection and processing parameters for (1).

Formula	$C_{10}H_{29}N_2I_2In$
MW	546.03
Space group	$P2_1/c$
a	14.903(2)
b	6.5340(7)
c (Å)	20.133(2)
β (°)	94.623(8)
V (Å³)	1952(4)
Z	4
D_c (g cm³)	1.865
$F(000)$	1032
μ (cm⁻¹)	43.25
Radiation	MoK$_\alpha$
2θ range (°)	2–50
Unique reflections	3818
Reflections with $I > 3\sigma(I)$	2379
Refined parameters	136
R	0.031
R_w	0.040

TABLE II
Positional and equivalent isotropic thermal parameters for (1).

Atom	x/a	y/b	z/c	$U(eqv), Å^2$
In	0.30123(3)	0.93224(8)	0.97486(2)	0.054(1)
I(1)	0.40398(3)	0.7755(1)	1.08770(2)	0.073(24)
I(2)	0.8171(3)	0.22416(7)	0.84555(2)	0.056(6)
Me(1)	0.3329(6)	1.252(1)	0.9762(5)	0.080(28)
Me(2)	0.1794(5)	0.759(1)	0.9666(4)	0.072(15)
N(1)	0.4009(4)	0.7951(9)	0.9060(2)	0.057(16)
C(1)	0.3827(6)	0.788(1)	0.8311(3)	0.060(19)
C(2)	0.3591(5)	0.999(1)	0.8075(4)	0.071(10)
C(3)	0.3062(9)	0.647(2)	0.8134(4)	0.141(73)
C(4)	0.4684(7)	0.717(2)	0.8014(4)	0.104(43)
N(2)	0.0310(4)	0.2241(8)	0.6690(3)	0.050(5)
C(11)	0.1146(5)	0.224(1)	0.6318(3)	0.053(3)
C(12)	0.1705(6)	0.407(1)	0.6563(5)	0.087(13)
C(13)	0.1633(5)	0.025(1)	0.6507(5)	0.083(17)
C(14)	0.0837(6)	0.232(1)	0.5589(4)	0.082(24)

TABLE III
Selected bond lengths and angles for (1).

Atoms		Distance (Å)	Atoms		Distance
In	-I(1)	2.8247(7)	In	-N(1)	2.292(5)
In	-Me(1)	2.145(7)	In	-Me(2)	2.135(7)
N(1)	-C(1)	1.511(8)	N(2)	-C(11)	1.503(8)
C(1)	-C(2)	1.49(1)	C(1)	-C(3)	1.49(1)
C(1)	-C(4)	1.52(1)	C(11)	-C(12)	1.51(1)
C(11)	-C(13)	1.52(1)	C(11)	-C(14)	1.50(1)

Atoms			Angle (°)	Atoms			Angle
I(1)	-In	-N(1)	90.4(1)	I(1)	-In	-Me(1)	103.9(3)
N(1)	-In	-Me(1)	103.7(3)	I(1)	-In	-Me(2)	105.7(2)
Me(1)	-In	-Me(2)	134.8(3)	N(1)	-I	-Me(2)	109.4(3)
In	-N(1)	-C(1)	122.7(4)	N(1)	-C(1)	-C(2)	107.9(6)
N(1)	-C(1)	-C(3)	109.2(6)	C(2)	-C(1)	-C(3)	110.2(8)
N(1)	-C(1)	-C(4)	108.1(6)	C(2)	-C(1)	-C(4)	109.9(7)
C(3)	-C(1)	-C(4)	111.4(8)	N(2)	-C(11)	-C(12)	107.0(6)
N(2)	-C(11)	-C(13)	105.8(6)	C(12)	-C(11)	-C(13)	110.9(6)
N(2)	-C(11)	-C(14)	106.5(6)	C(12)	-C(11)	-C(14)	113.9(7)
C(13)	-C(11)	-C(14)	112.1(7)				

parameters. The final R value was 0.03 ($R_w = 0.040$). Full supplementary structural data are available from the authors on request.

RESULTS AND DISCUSSION

The molecular structure of **1** is shown in Figure 1. The coordination geometry about the gallium atom is approximately tetrahedral. However, the most notable deviation from T_d geometry can be seen in the Me(1)–In–Me(2) bond angle of 134.8(3)°. Large C–M–C bond angles are not unusual in dialkyl metal halide species such as $Cy_2GaBr(NH_2Ph)$[4] (124.9(4)), and the bis solvated cationic complex $[Me_2Ga(NH_2(t\text{-}Bu))_2]Br$[6] (121.2(5)). Indeed, the unsolvated $[Me_2In]Br$[7] and $[Me_2Tl]Cl$[8] species exist as separate ions wherein the Me–M–Me bond angles are perfectly linear. This trend is also seen in other main group complexes such as $Me_2Cd(bipyridyl)_2$, which has a Me(1)–Cd–Me(2) angle of 148.4(8)°.[9] One result from the widening of the Me(1)–In–Me(2) bond in **1** is a concurrent narrowing of the I–In–N(1) angle to 90.4(1)°. There is the possibility that internal hydrogen bonding between the N–H(2) group and indium may be the distorting factor in **1**. Intramolecular hydrogen bonding has been seen in $Cy_2GaBr(NH_2Ph)$ (N–H ... Br 2.84 Å). However, the wide C–M–C bond angle was not attributed to this interaction. In **1** the greater length of the In–N bond (2.292(5) Å) and In–I (2.8247(7) Å) bond places the nitrogen hydrogen and iodide beyond bonding range (> 3.6 Å).
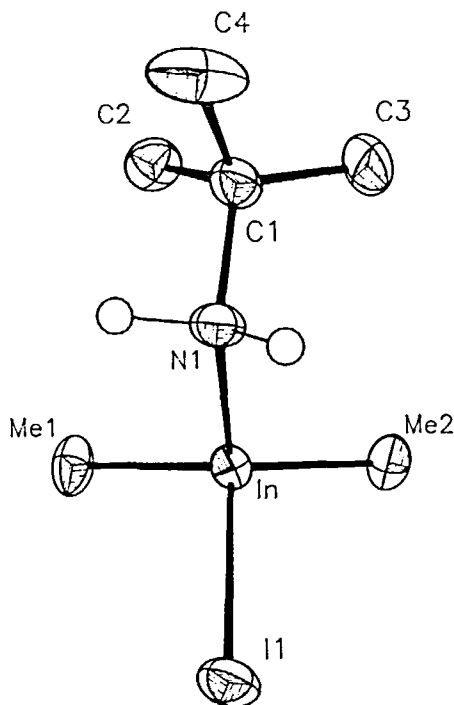

FIGURE 1   ORTEP view of $Me_2InI(NH_2(t\text{-}Bu))$ (**1**) showing the atom numbering scheme. All carbon hydrogen atoms are omitted for clarity.
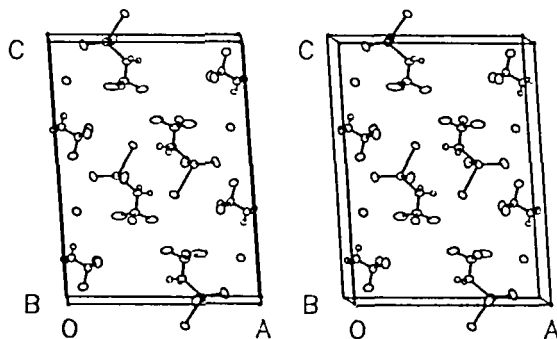
FIGURE 2   Unit cell view of compound (1) showing the location of co-crystallized [NH$_3$(t-Bu)]I.

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