Synthesis and Crystal and Molecular Structure of a Sterically Unhindered Organoindium Hydride Compound, $[Li(tmeda)_2][Me_3In-H-InMe_3]$

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Summary: The reaction of either $InMe_3{\cdot}Et_2O$ *or* $InMe_2Cl$ *with a large excess of lithium hydride affords the organoindium hydride compound,* $[Li(tmeda)_2][Me_3In-H-InMe_3]$*, the X-ray crystal structure of which shows the anion to have a bent hydride bridge.*

Introduction

Aluminum and gallium hydride complexes have received considerable attention in recent years due to their usefulness in a variety of areas ranging from organic synthesis to Chemical Vapor Deposition (CVD).[1,2] In contrast, the inherent weakness of the In−H bond has led to corresponding indium hydride compounds being poorly investigated. Indeed, to date there have been only five structurally characterized indium hydride compounds, four of which are sterically stabilized by the incorporation of very bulky alkyl ligands (*viz.* $[Li(thf)_2][\{(Me_3Si)_3C\}_2In_2H_5]$ (**1**),[3] $K[H\{In(CH_2CMe_3)_3\}_2]$ (**2**),[4] $K_3[K(Me_2SiO)_7][InH(CH_2CMe_3)_3]_4$ (**3**),[5] and $[InH\{2\text{-}Me_2NCH_2(C_6H_4)\}_2]$ (**4**)[6]). The stability of the fifth species, $[Me_2InB_3H_8]$ (**5**),[7] is probably due to a largely ionic formulation, *viz.* $[Me_2In]^+[B_3H_8]^-$, in the solid state at least. Despite their instability, organoindium hydride complexes are beginning to find applications as, for example, mild reducing agents in organic synthesis[8] and in the preparation of potential CVD precursors.[9] As part of a study underway in our laboratory which is aimed at examining the stabilization and applications potential of indium hydride complexes, we report here the synthesis and structural characterization of a sterically unhindered organoindium hydride complex, $[Li(tmeda)_2][Me_3In-H-InMe_3]$ (**6**).

Results and Discussion

The reaction of a diethyl ether solution of $InMe_3{\cdot}Et_2O$ with a 20-fold excess of LiH at 0 °C over 16 h, followed by treatment of the resulting solution with an excess of tmeda, led to a moderate yield (52%) of **6** after recrystallization from diethyl ether (Scheme 1). Interestingly, the reaction of $InMe_2Cl$ with an excess of LiH in ether also led to the formation of **6** in 22% yield. This probably results from the fact that $InMe_2Cl$ exists in equilibrium with $InMe_3$ and $InCl_3$ in solution,[10] which would lead to some $LiInH_4$ being formed (*via* $InCl_3$) in the reaction with LiH. This is, however, unstable at 0 °C, depositing indium metal and thereby driving the overall reaction equilibrium to the formation of **6** (*via* $InMe_3$). It is noteworthy that treatment of the closely related system **2** with an excess of KH resulted in the formation of the mononuclear species $K[InH(CH_2CMe_3)_3]$,[4] whereas **6** did not react with excess LiH to give $[Li(tmeda)_2][InHMe_3]$, even after 16 h.

Compound **6** is a colorless crystalline solid that is stable in solution and the solid state for days at 0 °C but readily decomposes at room temperature. This decomposition process yields $[Li(tmeda)_2][InMe_4]$ as the only ether-soluble product, in addition to indium metal and a gas. The gas has not been identified but is presumably either hydrogen or methane. In addition, our efforts to determine the mechanism of decomposition for **6** have not been successful, but seemingly this involves a series of redistribution reactions.

The molecular structure of the anion of **6** is depicted in Figure 1 (Table 1). The cation, $[Li(tmeda)_2]^+$, has been structurally characterized in a number of other compounds, e.g. $[Li(tmeda)_2][AlH_4]$,[11] and has no interaction with the anion in this case. During the course of the structural refinement the bridging hydride, H(19), was located from difference maps but not refined. Therefore, its position can only be considered as approximate. Despite this, it is clear that the anion is bent (In(1)−H(19)−In(2) = 148.6(10)°, as is the case in **2** (In−H−In = 151.3(49) and 160.6(46)°).[4] Although the In-

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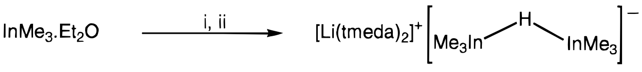
Scheme 1[a]



[a] Reagents and conditions: (i) LiH, Et_2O, 0 °C, 16 h; (ii) tmeda.

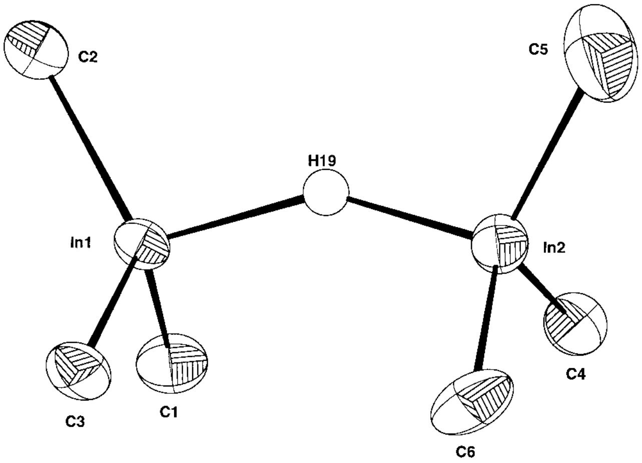


Figure 1. Molecular structure of the anion of $[Li(tmeda)_2][Me_3In{-}H{-}InMe_3]$ (**6**). Selected bond lengths (Å) and angles(deg): In(1)−In(2), 3.591(4); In(1)−C(1), 2.171(6); In(1)−C(2), 2.176(6); In(1)−C(3), 2.187(6); In(1)−H(19), 1.91(4); In(2)−C(4), 2.156(7); In(2)−C(5), 2.157(7); In(2)−C(6), 2.183(7); In(2)−H(19), 1.82(4); In(1)−H(19)−In(2), 148.6(10); C(1)−In(1)−C(2), 113.2(3); C(1)−In(1)−C(3), 112.8(2); C(2)−In(1)−C(3), 118.4(3); C(1)−In(1)−H(19), 101.8(11); C(2)−In(1)−H(19), 104.6(11); C(3)−In(1)−H(19), 103.6(12); C(4)−In(2)−C(5), 112.0(3); C(4)−In(2)−C(6), 113.4(3); C(5)−In(2)−C(6), 118.6(3); C(4)−In(2)−H(19), 101.1(13); C(5)−In(2)−H(19) 104.3(11); C(6)−In(2)−H(19), 105.1(12).

Table 1. Crystal Data for $[Li(tmeda)_2][Me_3In{-}H{-}InMe_3]$ (6)

chem formula	$C_{18}H_{51}In_2LiN_4$
fw	560.21
space group	$P2_1/c$
a (Å)	10.7080(10)
b (Å)	15.254(4)
c (Å)	17.466(2)
β (deg)	102.520(6)
V (Å^3)	2785.1(8)
Z	4
T (K)	150(2)
λ (Å)	0.710 69
ρ_{calcd} (g cm^{-3})	1.336
μ(Mo Kα) (cm^{-1})	16.63
DIFABS abs corr T(max), T(min)	1.18, 0.81
F(000)	1152
no. of reflns collected	10 935
no. of unique reflns	4157
cryst size (mm)	0.15 × 0.20 × 0.20
θ range (deg)	1.79−25.04
R(all data)[a]	0.0896
$R(I > 2\sigma(I))$[a]	0.0373
R_w(all data)[b]	0.0714
$R_w(I > 2\sigma(I))$[b]	0.0642

[a] $R = \Sigma(\Delta F)/\Sigma(F_o)$. [b] $R_w = [\Sigma\{w(\Delta F^2)^2\}/\Sigma\{w(F_o2)^2\}]^{1/2}$; $w = 1/[\sigma^2(F_o2) + (aP)^2]$, where $P = [\max(F_o^2) + 2(F_c^2)]/3$ and $a = 0.000$.

(1)···In(2) distance in **6** (3.591(4) Å; *cf.* 3.482(3) Å in **1**) is shorter than the sum of the van der Waals radii for two indium atoms (3.8 Å),[2] it is unlikely that there is any significant metal−metal interaction occurring. This is also the case in the aluminum analogue of **6**, $Na[Me_3Al{-}H{-}AlMe_3]$, which, interestingly, displays an Al−H−Al angle of 180° in the solid state.[12] The In−H distances in **6** (In(1)−H(19) = 1.91(4) Å, In(2)−H(19) = 1.82(4) Å), although inaccurate, can be compared with the bridging In−H distances in **2** (1.94 Å average)[4] which, not surprisingly, are longer than terminal In−H distances (*e.g.* 1.69(3) Å in **4**).[6] The In−C bond lengths in **6** are in the normal range.

The infrared spectrum of **6** (Nujol mull) displays a very strong, broad peak centered at 1610 cm^{-1} which has been attributed to its In−H−In stretching modes (cf. 1800−980 cm^{-1} in **2**[4]). In the ^{1}H NMR spectrum of **6** all the indium-bound methyl groups remain equivalent, even at −40 °C, and a broad signal, integrated for one hydrogen, was observed at 4.09 ppm. This has been assigned as the hydride resonance (*cf.* 3.09 ppm in **2**[4]), the broadness of which is due to the high quadrupole moment of the indium centers (^{115}In 95%, $I = {}^9/_2$, ^{113}In 5%, $I = {}^9/_2$) to which it is attached. This, combined with the lack of spherical symmetry at each indium center, also accounts for the fact that no signal was observed in the solution ^{115}In NMR spectrum of **6**.

Conclusion

In summary, we have described the synthesis and structural characterization of a novel organoindium hydride compound that possesses moderate thermal stability despite being substituted with alkyl groups of low steric bulk. The X-ray crystal structure of this compound shows it to possess an anion, $[Me_3In{-}H{-}InMe_3]^-$, with a bent hydride bridge. This contrasts sharply with the case for its aluminum analogue, $[Me_3Al{-}H{-}AlMe_3]^-$, which has previously been shown to be linear. Work continues in our laboratory on the stabilization of indium hydride complexes.

Experimental Section

General Considerations. All manipulations were carried out using standard Schlenk and glovebox techniques under an atmosphere of high-purity argon or dinitrogen. The solvents toluene and diethyl ether were distilled over Na/K alloy and then freeze/thaw degassed prior to use. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker WM-250 spectrometer in CD_2Cl_2 and were referenced to the residual ^{1}H resonances of the solvent used (^{1}H NMR) or the ^{13}C resonance of the deuterated solvent (^{13}C NMR), respectively. Microanalysis of **6** was not possible because of its thermal instability at room temperature. The starting materials, $InMe_3{\cdot}Et_2O$ and $InMe_2Cl$, were prepared by published procedures.[10] All other reagents were used as received.

Preparation of $[Li(tmeda)_2][Me_3In{-}H{-}InMe_3]$ (6). (a) LiH (0.50 g, 63 mmol) was added to a solution of $InMe_3{\cdot}Et_2O$ (0.90 g, 3.9 mmol) in Et_2O (40 mL) at −20 °C. The resulting suspension was warmed to 0 °C and stirred for 16 h after which time it was filtered and volatiles were removed *in vacuo*. The residue was redissolved in toluene (5 mL) at −10 °C and tmeda (2.0 g, 18 mmol) added. A white precipitate deposited, which was filtered off and recrystallized from Et_2O (30 mL) at −30 °C to yield **6** as colorless rods (yield 1.12 g, 52%).

(b) LiH (0.30 g, 38 mmol) was added to a solution of $InMe_2Cl$ (1.13 g, 6.3 mmol) in Et_2O (40 mL) at −20 °C. The resulting gray suspension was warmed to 0 °C and stirred for 16 h, after which time it was filtered and volatiles were removed *in vacuo*.

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The residue was redissolved in toluene (5 mL) at −10 °C and tmeda (2.0 g, 18 mmol) added. A white precipitate deposited, which was filtered off and recrystallized from Et_2O (30 mL) at −30 °C to yield **6** as colorless rods (yield 0.78 g, 22%). ^1H NMR (250 MHz, CD_2Cl_2, $SiMe_4$, 243 K): δ −0.61 (s, 18H, InMe), 2.26 (br s, 24H, NMe), 2.44 (s, 8H, NCH_2), 4.09 (br s, 1H, In−H). ^{13}C NMR (100.6 MHz, CD_2Cl_2, 243 K): δ −10.0 (s, InMe), 45.8 (br s, NMe), 56.0 (br s, NCH_2). IR: ν 1610 cm^{-1} (br s, In−H−In str).

Crystal Structure Determination of 6. Crystals of **6** were grown from an Et_2O solution and were mounted in silicone oil. All crystallographic measurements were made using a FAST area detector diffractometer following previously described procedures.[13] The structure was solved by heavy-atom methods (SHELXS86)[14] and refined on F^2 by full-matrix least squares (SHELX93)[15] using all unique data. Crystal data, details of data collections and refinement are given in Table 1. All non-hydrogen atoms are anisotropic with H atoms (except H(19)) included in calculated positions (riding model). H(19) was located from difference maps and could not be refined satisfactorily, and so its positional and isotropic displacement parameters were fixed. Neutral-atom complex scattering factors were employed.[16] Empirical absorption corrections were carried out by the DIFABS method.[17]

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Supporting Information Available: For **6**, figures giving views of the cation and the unit cell and tables of crystal data and structure refinement details, positional and thermal parameters, and bond distances and angles (9 pages). Ordering information is given on any current masthead page.

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