A Rare Lithium Indium Siloxane: Synthesis and Crystal Structure of [InMe{(OPh₂Si)₂O}₂-*μ*-{Li(THF)₂}₂]†

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*Summary: The reaction between lithium tetramethylindate Li[InMe₄] and disilanol [(Ph₂SiOH)₂O] yields [InMe-{(OPh₂Si)₂O}₂-μ-{Li(THF)₂}₂] (**1**). Compound **1** can also be prepared starting from Ph₂Si(OH)₂ and Li[InMe₄] in good yields. The product has been characterized by elemental analysis and IR and multinuclear NMR spectroscopic studies (¹H, ⁷Li, and ²⁹Si NMR). The solid-state structure of **1**, determined by single-crystal X-ray crystallography, reveals that the central indium atom **1** is surrounded by four oxygen atoms of the two disilanolate ligands and a methyl group in a square-pyramidal geometry. The InO₄C coordination environment observed in **1** is rare among organometallic compounds of indium. The indium atom lies 0.59 Å above the rectangular plane formed by the four oxygens of the silanolate ligands.*

Introduction

The chemistry of metallosiloxanes,[1] derived from various types of silanols (R$_n$Si(OH)$_{4-n}$), has been a fertile area of research in recent times because such compounds have proven to be useful as precursors for metal silicates and also as models for silica-supported heterogeneous catalytic systems.[2] The fact that aluminosilicates are ubiquitous in nature, being the constituents of a wide range of naturally occurring minerals, makes group 13 siloxanes occupy a special place in metallosiloxane chemistry. Recent studies by Roesky,[3] Tilley,[4] and others[2] have demonstrated that soluble group 13 metallosiloxanes can serve both as model compounds for open-framework silicates[3] and as precursors for the preparation of mixed-metal oxide materials (e.g., SiO_2–Al_2O_3) under mild conditions.[4]

Studies on indium-containing silicates assume importance because of their utility in the catalytic reduction of nitrogen oxides NO_x, a process used in cleaning up exhaust gases of combustion engines.[5] Among the group 13 molecular siloxanes,[6] polycyclic or cage-like indium siloxanes are very rare, and a search of the literature reveals that only three structurally characterized polyhedral indium siloxanes have so far been reported.[7,8] All these three polyhedral indium siloxanes, for which X-ray crystal structures have been determined by Roesky et al., are derived from a kinetically stabilized N-bonded silanetriol, [RSi(OH)₃] (R = −N(2,6-*i*-Pr₂C₆H₃)-(SiMe₃)).[7,8]

In recent times, it has been shown that apart from silanetriols [RSi(OH)₃], other types of silanols[9] such as silanediols [R₂Si(OH)]₂, disiloxane-1,3-diols [(R₂SiOH)₂O], and oligomeric silasesquioxanes [(*c*-C₆H₁₁)₇Si₇O₉(OH)₃] are also excellent synthons for metallosiloxanes.[2a−c] In particular, diphenylsilanediol, Ph₂Si(OH)₂, and its primary condensation product disiloxane-1,3-diol [(Ph₂SiOH)₂O] have been studied as synthons for various metal and nonmetal siloxane derivatives.[10] Although a few gallium siloxanes derived from this class of silanols were recently reported,[11,12] quite surprisingly, there are no examples in the literature on the use of Ph₂Si(OH)₂ and [(Ph₂SiOH)₂O] in synthesizing indium siloxanes. Continuing our interest in this area, herein we report

† This work is dedicated to Professor V. Krishnan on the occasion of his 65th birthday.

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on the synthesis and structural characterization of the first indium siloxane derived from disilanol [(Ph$_2$SiOH)$_2$O].

Experimental Section

General Procedures. Standard Schlenk techniques were used for experimental manipulations, and all air-sensitive materials were handled inside a M. Braun drybox. Solvents were rigorously dried and freshly distilled by standard methods prior to their use. Starting materials, such as InCl$_3$ (Aldrich), MeLi (Acros), and Ph$_2$SiCl$_2$ (Aldrich), procured from commercial sources were used as received. The disilanol[13] and Li[InMe$_4$][14] were synthesized using reported procedures. Elemental analyses were performed on a Carlo Erba (Italy) Model 1106 elemental analyzer. The ^{1}H and ^{29}Si NMR spectra were recorded on a Bruker AS 400 instrument using Me$_4$Si as the reference for both ^{1}H and ^{29}Si spectral measurements. Infrared spectra were recorded on a Nicolet Impact 400 FT-IR spectrometer as Nujol mulls.

Synthesis of 1. To a solution of Li[InMe$_4$] (1 mmol, 182 mg) in 30 mL of dry THF at 0 °C was added slowly the disilanol (1 mmol, 414.6 mg) in THF (15 mL) via syringe over 15 min. After the addition, the reaction mixture was allowed to warm to room temperature and subsequently heated at 50 °C for 0.5 h. The solvent was removed from the resultant turbid solution, and the residue was extracted with a 2 mL:5 mL mixture of THF/petroleum ether, filtered, and left for crystallization. Large colorless single crystals of **1** formed after 72 h. Yield: 55%. Anal. Calcd for C$_{65}$H$_{75}$InLi$_2$O$_{10}$Si$_4$ (1257.31): C 62.1, H 6.0. Found: C 61.4, H 6.1. IR (cm^{-1}, Nujol): 1590w, 1428s, 1343w, 1304w, 1264w, 1184w, 1114s, 1050s, 1033s, 1019s, 1003s, 977vs, 916m, 839m, 742m, 700s. ^{1}H NMR (C$_6$D$_6$, 400 MHz): δ 0.16 (s, 3H, InCH_3), 1.17 (t, 16H, OCH$_2$CH_2, $^3J_{HH}$ = 6.4 Hz), 3.28 (t, 16H, OCH_2), 7.16−8.02 (m, 40H, C$_6$H$_5$) ppm. ^{7}Li NMR (C$_6$D$_6$, 155 MHz): δ 0.48 (s) ppm. ^{29}Si NMR (C$_6$D$_6$, 80 MHz): δ −37.4 (s) ppm.
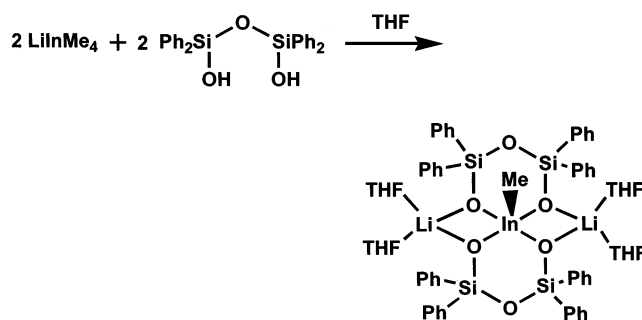
Compound **1** could also be synthesized from Li[InMe$_4$] and Ph$_2$Si(OH)$_2$ using the same procedure.

Crystal Structure Determination of 1. Single crystals of **1** were grown from a dilute THF/petroleum ether solution at room temperature over a period of several days. Crystals suitable for X-ray diffraction studies were chosen from these crops and mounted on a Siemens STOE AED2 four-circle diffractometer for the cell determination and intensity data collection. The unit cell parameters were derived and refined by using randomly selected reflections in the 2θ range 20−30°. The intensity data have been corrected for absorption effects using psi-data (max. and min. transmission factors 0.844 and 0.778). The structure was solved by direct methods using SHELXS-97 and refined by using SHELXL-97.[15] All the hydrogen atoms were placed in calculated positions and were included in the refinement using a suitable riding model. *Crystal data*: C$_{65}$H$_{75}$InLi$_2$O$_{10}$Si$_4$, M = 1257.3, monoclinic, *Pn*, a = 10.740(2) Å, b = 16.230(3) Å, c = 21.295(4) Å, β = 101.92(3)°, V = 3632(1) Å^3, d_c = 1.150 Mg/m^3, Z = 2, $F(000)$ = 1312, cryst size = 0.6 × 0.6 × 0.4 mm, λ = 0.71073 Å, μ = 0.44 mm^{-1}, total/unique reflections = 12838/12821 [R(int) = 0.005], T = 150(2) K, θ range = 3.3−25.0°, final R [$I > 2\sigma(I)$]: R$_1$ = 0.053, wR_2 = 0.150, R (all data): R$_1$ = 0.061, wR_2 = 0.158, goodness of fit = 1.11, largest difference peak and hole = 1.20 and −0.40 e·Å^{-3}.

Results and Discussion

Our initial attempts to synthesize molecular indium siloxanes from silanediol [Ph$_2$Si(OH)$_2$] (**A**) and disilanol

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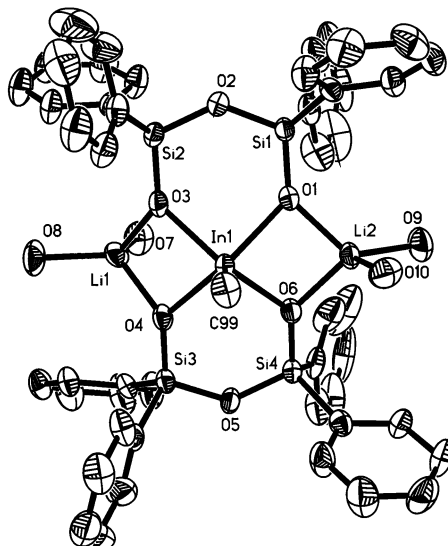
Scheme 1. Synthesis of 1

[(Ph$_2$SiOH)$_2$O] (**B**) by using InMe$_3$ as the indium source did not yield any characterizable indium-containing siloxane. This was not surprising in the light of observations made by Sullivan et al. that the reactions of **B** with precursors such as AlMe$_3$ often lead to the formation of cyclic siloxanes [R$_2$SiO]$_n$ and not the desired metallosiloxanes.[2b] In addition to the reasoning provided by Sullivan, the Lewis acidity of the group 13 alkyls may also be the reason for the facile self-condensation−cyclization reaction of the silanol.[16] Hence, it was our expectation that if a non Lewis acidic "indate complex" such as LiInMe$_4$ is used in place of InMe$_3$, the in situ cyclization of **B** could be prevented.[17,18]

Accordingly, the treatment of [LiInMe$_4$][14] with **B**[13] in dry THF leads to the formation of the title lithium indium siloxane **1** in nearly quantitative yields, from which analytically pure product is obtained as single crystals in about 55% yield (Scheme 1). Siloxane **1** has been characterized by elemental analysis and IR, ^{1}H, ^{7}Li, and ^{29}Si NMR spectroscopic studies. The molecular structure of the product has been unambiguously established by a single-crystal X-ray diffraction study.

The silicon atoms in the molecule are equivalent in solution and appear as a singlet at δ −37.4 ppm in the ^{29}Si NMR spectrum. This value compares well with the chemical shifts observed for related metallosiloxanes derived from **B**.[2b,10] In the ^{1}H NMR spectrum, the resonance due to the protons of the methyl group attached to the central indium appears as a singlet at δ 0.16 ppm. The triplets for the two types of methylene protons arising from the coordinated THF molecules appear at δ 1.17 and 3.28 ppm, respectively. The room-temperature ^{7}Li NMR spectrum shows a sharp single resonance at δ 0.48 ppm, indicating that the two lithium ions are equivalent in solution at room temperature.

The solid-state structure of **1** determined by single-crystal X-ray crystallography (Figure 1; Table 1) reveals that no siloxane chain-expansion reaction has taken place. The central indium ion in **1** is surrounded by two disilanolates (in a spirocyclic fashion) and a methyl group in a square-pyramidal geometry. Although a few five-coordinate organometallic derivatives of indium are known, the coordination environment in **1**, where the metal ion is surrounded by four oxygens and one methyl

(16) Condensation reactions of silanols are facile in the presence of acid or base impurities.

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Figure 1. ORTEP of **1** (50% probability level). The THF carbon and all the hydrogen atoms are omitted for the sake of clarity.
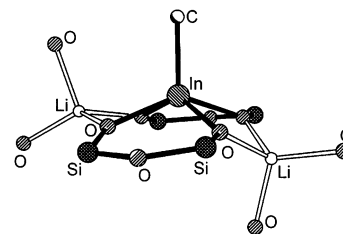

Figure 2. Core structure of **1** showing the coordination environment around In and Li ions.

four-membered rings are nonplanar, while the two six-membered $InSi_2O_3$ rings adopt a half-chair conformation. The In atom in these six-membered rings deviates considerably from the mean plane formed by the other five (two Si and three O) atoms.

The observed In−C distance of 2.138(7) Å in **1** compares well with the In−C distances observed in the only other structurally characterized cubic Li−In−siloxane, $[\{RSiO_3InMe\}\{Li(THF)\}]_4$ (**C**) (2.131(4) Å),[4] although the indium ion is pentacoordinate in **1**, while it is tetracoordinate with a tetrahedral geometry in **C**. The observed In−O distances in **1** vary over a small range, 2.134(4)−2.186(4) Å. These distances are slightly longer than those observed for **C** (2.036(3)−2.068(3) Å) but are shorter than those observed for the indium phosphinate complex $[MeIn(OH)(O_2PPh_2)(py)]_4$ (av 2.23 Å).[20] There are two types of O−In−O angles in the molecule. Expectedly, the *trans* O−In−O angles (137.3-(2)° and 141.5(1)°) are larger than the *cis* O−In−O angles (77.0(2)−88.7(1)°). The sum of angles within the two four-membered $InLiO_2$ rings (358.2° and 346.5°) indicate that one of the rings is severely puckered while the other remains almost planar (Figure 2).

The structure of compound **1** is somewhat structurally similar to the earlier reported metallosiloxanes $Me_8Si_4O_6Al_3X_6$, which have been prepared by the reaction of AlX_3 with $[Me_2SiO]_4$.[21] While the basic structural motif of homometallic $Me_8Si_4O_6Al_3X_6$ is made up of three aluminum ions which are held together by the two disiloxane ligands, in the heterometallosiloxane **1** two disiloxane ligands bridge one indium and two lithium ions.[21]

In summary, it has been shown that the change of metal source from neutral $InMe_3$ to the anionic complex $[InMe_4]^-$ allows the isolation of the indium siloxane **1** with a In−Me linkage. This method appears to be general for the generation of siloxanes of other metals, although isolation of analytically pure crystalline Al derivatives has thus far proven to be difficult. Our further studies in this area are aimed at expanding this methodology for the preparation of other bimetallic heterosiloxanes that incorporate other alkali and alkaline earth metal ions. These bimetallic siloxanes are potentially useful for the generation of the respective mixed-metal silicates through suitable decomposition reactions.

Table 1. Selected Bond Distances and Bond Angles in 1

In(1)−C(99)	2.138(7)	In(1)−O(3)	2.138(4)
In(1)−O(4)	2.155(4)	In(1)−O(6)	2.160(4)
In(1)−O(1)	2.186(4)	Si(1)−O(1)	1.591(4)
Si(1)−O(2)	1.645(4)	Si(2)−O(3)	1.596(4)
Si(2)−O(2)	1.640(4)	Si(3)−O(4)	1.600(4)
Si(3)−O(5)	1.638(4)	Si(4)−O(6)	1.610(4)
Si(4)−O(5)	1.645(4)	Li(1)−O(8)	1.925(13)
Li(1)−O(4)	1.934(11)	Li(1)−O(3)	1.947(10)
Li(1)−O(7)	1.971(13)	Li(2)−O(1)	1.923(10)
Li(2)−O(6)	1.952(10)	Li(2)−O(9)	1.989(12)
Li(2)−O(10)	1.992(13)		
O(3)−In(1)−C(99)	111.9(2)	O(3)−In(1)−O(4)	78.0(1)
C(99)−In(1)−O(4)	109.1(2)	O(3)−In(1)−O(6)	137.3(2)
C(99)−In(1)−O(6)	110.8(2)	O(4)−In(1)−O(6)	88.7(1)
O(3)−In(1)−O(1)	88.6(1)	C(99)−In(1)−O(1)	109.4(2)
O(4)−In(1)−O(1)	141.5(1)	O(6)−In(1)−O(1)	77.0(2)
O(8)−Li(1)−O(4)	119.0(6)	O(8)−Li(1)−O(3)	117.8(6)
O(4)−Li(1)−O(3)	88.2(5)	O(8)−Li(1)−O(7)	111.6(6)
O(4)−Li(1)−O(7)	108.9(6)	O(3)−Li(1)−O(7)	109.0(5)
O(1)−Li(2)−O(6)	88.6(5)	O(1)−Li(2)−O(9)	124.2(6)
O(6)−Li(2)−O(9)	122.2(5)	O(1)−Li(2)−O(10)	109.0(5)
O(6)−Li(2)−O(10)	112.3(5)	O(9)−Li(2)−O(10)	100.7(5)
Si(1)−O(1)−Li(2)	136.2(4)	Si(1)−O(1)−In(1)	132.9(2)
Li(2)−O(1)−In(1)	90.8(3)	Si(2)−O(2)−Si(1)	134.1(3)
Si(2)−O(3)−Li(1)	130.5(4)	Si(2)−O(3)−In(1)	131.9(2)
Li(1)−O(3)−In(1)	96.1(4)	Si(3)−O(4)−Li(1)	130.1(4)
Si(3)−O(4)−In(1)	131.6(2)	Li(1)−O(4)−In(1)	95.9(3)
Si(3)−O(5)−Si(4)	135.0(3)	Si(4)−O(6)−Li(2)	135.3(4)
Si(4)−O(6)−In(1)	132.3(2)	Li(2)−O(6)−In(1)	90.8(3)

group in a severely distorted square-pyramidal geometry, is rare in the organometallic chemistry of indium.[19]

The indium atom in **1** lies 0.59 Å above the rectangular plane formed by the four oxygens of the silanolate ligands. The axial methyl substituent is located 2.138-(7) Å away from the indium atom. The silanolate oxygen atoms coordinated to the In metal also bridge two Li ions on either side of the square plane, resulting in the formation of two four-membered $InLiO_2$ rings. These

Supporting Information Available: Crystallographic data for **1** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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