

Synthesis and structural characterization of indium compounds with bidentate amide ligands

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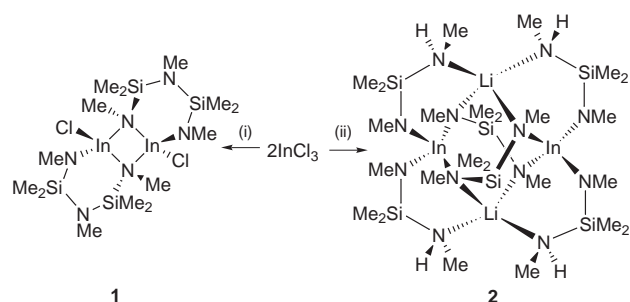
Indium trichloride reacts with 1 equivalent of $\text{MeN}(\text{SiMe}_2\text{NMeLi})_2$ to give the dimer $[\text{ClIn}(\text{NMeSiMe}_2)_2\text{NMe}]_2$ and with 4 equivalents of $\text{HNMeSiMe}_2\text{NMeLi}$ to give $[\text{Li}\{\text{In}(\text{HNMeSiMe}_2\text{NMe})(\text{MeNSiMe}_2\text{NMe})\}]_2$. In the structure of $[\text{ClIn}(\text{NMeSiMe}_2)_2\text{NMe}]_2$ a chloride and one amide group of a $[\text{MeN}(\text{SiMe}_2\text{NMe})_2]^{2-}$ ligand are bonded to each In atom in terminal positions and the other amide group of the chelating ligand is shared between two In atoms. The terminal chlorides have an *anti*-ClIn...InCl arrangement. The amine group of the $[\text{MeN}(\text{SiMe}_2\text{NMe})_2]^{2-}$ ligand does not interact with In. Variable temperature NMR spectra show $[\text{ClIn}(\text{NMeSiMe}_2)_2\text{NMe}]_2$ undergoes a fluxional process, and a mechanism involving bridge-terminal amide exchange is proposed to account for the data. The molecule $[\text{Li}\{\text{In}(\text{HNMeSiMe}_2\text{NMe})(\text{MeNSiMe}_2\text{NMe})\}]_2$ has a $\text{Li}_2\text{In}_2\text{Si}_2\text{N}_4$ adamantane-like core and overall virtual D_2 symmetry.

We recently reported the synthesis of new indium amide complexes including the neutral triamide compounds $[\text{In}\{\text{N}(\text{SiHMe}_2)(t\text{-Bu})\}_3]$ and $[\text{In}\{\text{NR}(\text{SiMe}_3)\}_3]$ where R = Ph or Bu.¹ The compounds were prepared for possible use in combination with ammonia as chemical vapor deposition (CVD) precursors to indium nitride films,² a process that would be analogous to one used to prepare GaN films at low temperature.^{3,4} Because we were interested in using the compounds for CVD studies, we restricted our synthetic work to simple amide ligands in the expectation that their complexes would have the necessary volatility to be good precursor candidates. The difficulties and successes we had while carrying out the syntheses, as well as the realization that there are only a few reported well-characterized indium complexes with multiple amide ligands,⁵⁻⁸ prompted us to take a more general approach and examine the synthesis of other types of indium amide compounds. Herein we report the syntheses and structures of two new indium complexes that contain the chelating amide ligands $[\text{MeN}(\text{SiMe}_2\text{NMe})_2]^{2-}$ and $[\text{Me}_2\text{Si}(\text{NMe})_2]^{2-}$.

Results and discussion

Syntheses

A summary of our synthetic results is presented in Scheme 1.



Scheme 1 (i) $2\text{MeN}(\text{SiMe}_2\text{NMeLi})_2$, diethyl ether, -4LiCl ; (ii) $8\text{HNMeSiMe}_2\text{NMeLi}$, diethyl ether, -6LiCl , $-2\text{Me}_2\text{Si}(\text{NMeH})_2$.

Indium trichloride reacts with 1 equivalent of the potentially tridentate ligand $\text{MeN}(\text{SiMe}_2\text{NMeLi})_2$ to give the dimer $[\text{ClIn}(\text{NMeSiMe}_2)_2\text{NMe}]_2$ **1**. The reaction between InCl_3 and 4 equivalents of $\text{HNMeSiMe}_2\text{NMeLi}$ gives $[\text{Li}\{\text{In}(\text{HNMeSiMe}_2\text{NMe})(\text{MeNSiMe}_2\text{NMe})\}]_2$ **2** in 96% yield. In the latter case, if a stoichiometry consisting of an approximately 2:1 mixture of $\text{HNMeSiMe}_2\text{NMeLi}$ and $\text{Me}_2\text{Si}(\text{NMeLi})_2$ or only 3 equivalents of $\text{HNMeSiMe}_2\text{NMeLi}$ are used the product yield is $\approx 70\%$. Interestingly, the related reaction of 2 equivalents of $\text{Me}_2\text{Si}[\text{N}(\text{SiMe}_3)\text{Li}]_2$ with InCl_3 has been reported to give a monomeric species, $[\text{Li}\{\text{In}\{\text{N}(\text{SiMe}_3)_2\text{SiMe}_2\}_2}]$.⁹

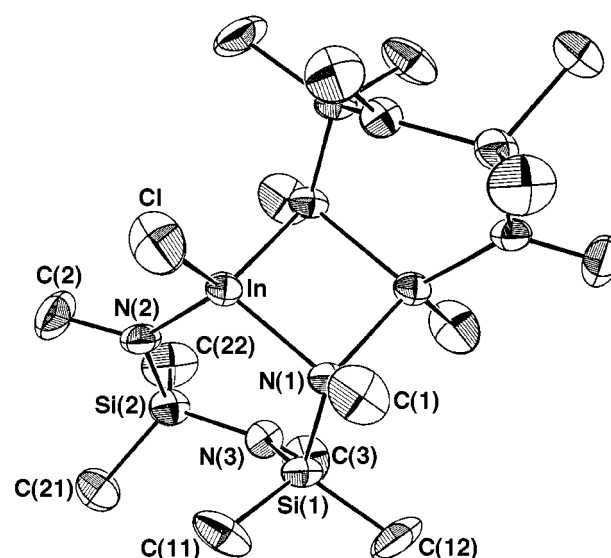


Fig. 1 View of $[\text{ClIn}(\text{NMeSiMe}_2)_2\text{NMe}]_2$ **1** showing the atom-numbering scheme (50% probability ellipsoids).

Compound **2** is partially soluble in hexane, benzene, toluene, diethyl ether, THF and CH_2Cl_2 while **1** is very soluble in the same solvents except for hexane, in which it is only partially soluble.

X-ray crystallographic studies

X-Ray crystal structure determinations of **1** (Fig. 1) and **2** (Fig. 2) were carried out. Selected bond distances and angles are presented in Tables 1 and 2. Compound **1** is situated about an inversion center and **2** lies on a two-fold axis. The amine hydrogens in **2** were located in a difference map and subsequently refined with distance constraints. Compound **1** is isomorphous with $[\text{ClAl}(\text{NMeSiMe}_2)_2\text{NMe}]_2$.¹⁰ Three other closely related

Table 1 Selected bond distances (Å) and angles (°) for [ClIn(NMeSiMe₂)₂NMe]₂ **1**

In–Cl	2.350(3)	Si1–N1	1.768(6)
In–N1	2.204(8)	Si1–N3	1.716(9)
In–N2	2.036(7)	Si2–N2	1.708(8)
In–N1'	2.199(7)	Si2–N3	1.756(9)
Cl–In–N1	110.1(2)	In–N1–In'	90.5(1)
Cl–In–N2	111.8(2)	Si1–N1–C1	114.5(6)
Cl–In–N1'	116.3(2)	Si1–N1–In'	120.1(3)
N1–In–N2	110.4(3)	C1–N1–In'	108.2(7)
N1–In–N1'	89.5(3)	In–N2–Si2	121.9(4)
N2–In–N1'	116.4(3)	In–N2–C2	119.8(6)
N1–Si1–N3	107.5(4)	Si2–N2–C2	118.3(6)
N2–Si2–N3	106.9(4)	Si1–N3–Si2	125.1(5)
In–N1–Si1	107.7(3)	Si1–N3–C3	118.4(8)
In–N1–C1	113.6(7)	Si2–N3–C3	113.9(7)

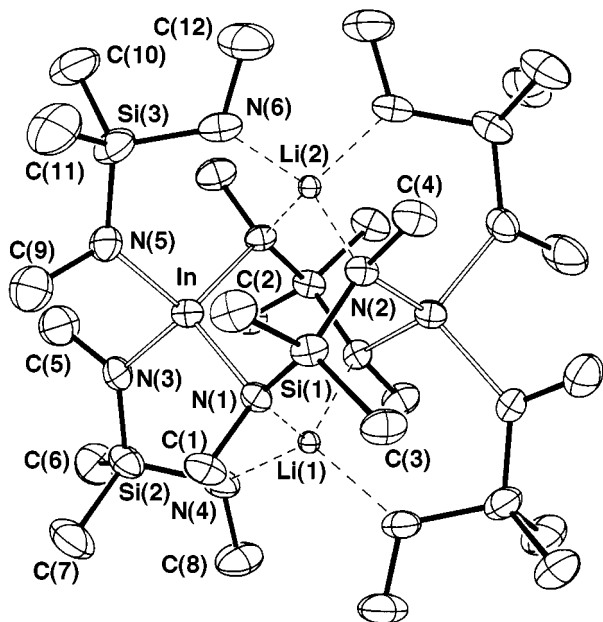
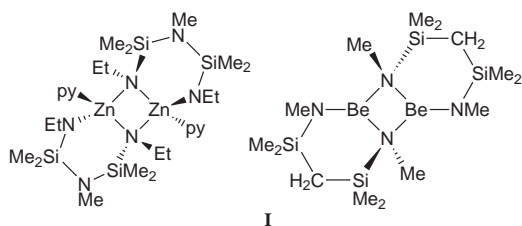


Fig. 2 View of [Li{In(HNMeSiMe₂NMe)₂(MeNSiMe₂NMe)}₂ **2** showing the atom-numbering scheme (40% probability ellipsoids).

structures are [(py)Zn(NEtSiMe₂)₂NMe]₂, [Be(NMeSiMe₂)₂-CH₂]₂ (see I), and [MeIn(NBu^t)₂SiMe₂]₂.^{11–13}



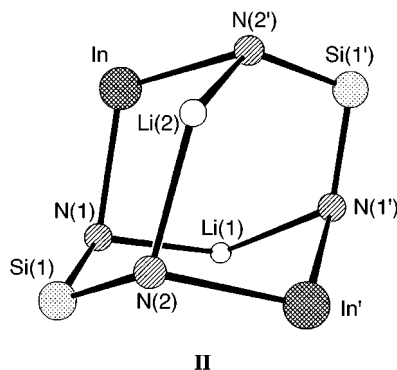
The In atom in **1** has a distorted tetrahedral geometry with the four coordination sites occupied by a Cl and three amide nitrogen atoms, one of which is terminal (N2 in Fig. 1) and the other two bridging (N1 and N1'). The amine group of the [MeN(Me₂SiNMe)₂]²⁻ ligand is not bonded to In. In the structure the indium atom is a member both of a four-membered In₂N₂ ring and a six-membered InN₃Si₂ ring.

The molecule **2** has a Li₂In₂Si₂N₄ core with an adamantane structure **II** that incorporates the bridging [MeNSiMe₂NMe]²⁻ ligands. Exocyclic to the core are four six-membered rings that include the [HNMeSiMe₂NMe]⁻ ligands. Overall, the molecule has virtual D₂ symmetry, where, in addition to the crystallographic two-fold axis passing through Li1 and Li2, there are two virtual two-fold axes, one passing through the In atoms and the other through Si1 and Si1'. Each indium atom is coordin-

Table 2 Selected bond distances (Å) and angles (°) for [Li{In(HNMeSiMe₂NMe)₂(MeNSiMe₂NMe)}₂ **2**

In–N(1)	2.165(5)	Si(2)–N(4)	1.752(5)
In–N(3)	2.107(5)	Si(3)–N(5)	1.696(6)
In–N(5)	2.109(5)	Si(3)–N(6)	1.757(6)
In–N(2')	2.161(5)	N(1)–Li(1)	2.073(8)
Si(1)–N(1)	1.719(5)	N(2)–Li(2)	2.036(8)
Si(1)–N(2)	1.730(5)	N(4)–Li(1)	2.232(8)
Si(2)–N(3)	1.697(6)	N(6)–Li(2)	2.210(9)
N(1)–In–N(3)	110.5(2)	Si(2)–N(3)–C(5)	118.3(5)
N(1)–In–N(5)	111.9(2)	Si(2)–N(4)–C(8)	114.8(4)
N(3)–In–N(5)	103.9(2)	Si(2)–N(4)–Li(1)	125.4(4)
N(1)–In–N(2')	111.7(2)	C(8)–N(4)–Li(1)	112.5(5)
N(3)–In–N(2')	110.2(2)	In–N(5)–Si(3)	130.3(3)
N(5)–In–N(2')	108.4(2)	In–N(5)–C(9)	112.1(4)
N(1)–Si(1)–N(2)	104.9(3)	Si(3)–N(5)–C(9)	117.4(5)
N(3)–Si(2)–N(4)	106.9(3)	Si(3)–N(6)–C(12)	116.6(5)
N(5)–Si(3)–N(6)	106.9(3)	Si(3)–N(6)–Li(2)	122.7(3)
In–N(1)–Si(1)	112.5(2)	C(12)–N(6)–Li(2)	113.9(5)
In–N(1)–C(1)	111.4(3)	N(1)–Li(1)–N(4)	110.4(2)
Si(1)–N(1)–C(1)	112.9(4)	N(1)–Li(1)–N(1')	109.3(6)
In–N(1)–Li(1)	93.1(3)	N(4)–Li(1)–N(1')	103.8(2)
Si(1)–N(1)–Li(1)	124.5(3)	N(1)–Li(1)–N(4')	103.8(2)
C(1)–N(1)–Li(1)	100.6(4)	N(4)–Li(1)–N(4')	119.0(6)
Si(1)–N(2)–C(4)	113.3(4)	N(1')–Li(1)–N(4')	110.4(2)
Si(1)–N(2)–Li(2)	125.3(3)	N(2)–Li(2)–N(6)	100.7(2)
C(4)–N(2)–Li(2)	100.0(4)	N(2)–Li(2)–N(2')	110.1(6)
Si(1)–N(2)–In'	112.8(2)	N(6)–Li(2)–N(2')	114.5(2)
C(4)–N(2)–In'	110.4(4)	N(2)–Li(2)–N(6')	114.5(2)
Li(2)–N(2)–In'	92.7(3)	N(6)–Li(2)–N(6')	116.9(6)
In–N(3)–Si(2)	128.8(3)	N(2')–Li(2)–N(6')	100.7(2)
In–N(3)–C(5)	112.8(4)		

ated to the amide end of two [HNMeSiMe₂NMe]⁻ ligands and also shares two bridging [MeNSiMe₂NMe]²⁻ ligands, resulting in an In atom surrounded by four amide groups (N1, N2', N3 and N5 in Fig. 2) in a tetrahedral arrangement. The amine ends of the [HNMeSiMe₂NMe]⁻ ligands (N4 and N6) are coordinated to lithium, which also interacts with the bridging [MeNSiMe₂NMe]²⁻ ligands. The cation has a distorted tetrahedral geometry with widely varying angles (101–119°). Charge separation in the complex can be described as [In(NRR')₄]⁻ and Li⁺.



In **1** the angles around indium vary from 90° to 116° with the smallest angle associated with the bridging amide groups, N1–In–N1', but in **2** the N–In–N angles are in the narrow range 104–112°. The terminal amide nitrogens in both structures have essentially planar geometries. The angles about these nitrogens span a narrow range (118–122°) in **1** but vary more widely (112–130°) in **2** with the larger angles (129 and 130°) being associated with In–N–Si and the smaller with In–N–C (112 and 113°). In **2** the amine nitrogens, N4 and N6, and the amide nitrogens that interact with the Li⁺, N1 and N2, have distorted tetrahedral geometries.

The terminal In–N amide distances, In–N3 [2.107(5) Å] and In–N5 [2.109(5) Å] in **2** and In–N2 [2.036(7) Å] in **1**, are similar to those found in [In{N^t-Bu(SiHMe₂)₃}(p-Me₂NC₅H₄N)] [average 2.125(3) Å], [In{NPh(SiMe₃)₃}(OEt₂)] [average 2.095(2)

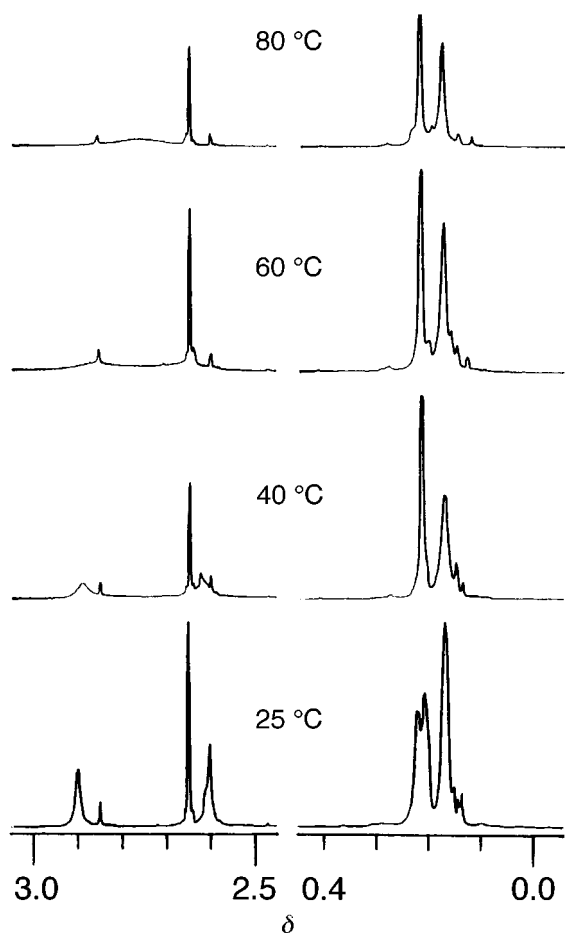


Fig. 3 The *NMe* (left) and *SiMe* (right) regions of the ^1H NMR spectra for $[\text{ClIn}(\text{NMeSiMe}_2)_2\text{NMe}]_2$ (toluene- d_6) recorded at various temperatures.

\AA], $[\text{In}(\text{NPh}_2)_3(\text{py})]$ [average 2.083(3) \AA],¹ $[\text{In}\{\text{N}(\text{SiMe}_3)_2\}_3]$ [2.049(1) \AA], $[(\text{Me}_3\text{C})_2\text{In}\{\text{NSiPh}_3(2,6\text{-}i\text{-Pr}_2\text{Ph})\}]$ [2.104(3) \AA],⁶ $[\text{InL}_3]$ (HL = 2,2,6,6-tetramethylpiperidine) [average 2.078(5) \AA],⁸ $[\text{MeIn}(\text{N}t\text{-Bu})_2\text{SiMe}_2]$ [2.107(3) \AA]¹³ and $[\text{Et}_2\text{In}(\text{NC}_5\text{H}_4)]$ [2.166(4) \AA].¹⁴ The In–N1 and N1' distances in **1** [average 2.202(8) \AA] are slightly shorter than the In–N_{bridge} distances in $[\text{MeIn}(\text{NBu}^t)_2\text{SiMe}_2]$ [average 2.267(4)].¹³ In **2** the interaction of the amide nitrogens N1 and N2' with the lithium cations lengthens their In–N distances about 0.05 \AA compared to In–N3 and In–N5, and causes them to be almost as long as the In–N1 [2.204(8) \AA] and In–N1' [2.199(7) \AA] bridging amide distances in **1**. The Li–N1 and –N2 distances in **2**, which involve the nitrogens associated with the long In–N distances, are significantly shorter than the Li–N distances involving the amine N4 and N6 atoms.

Spectroscopic characterization

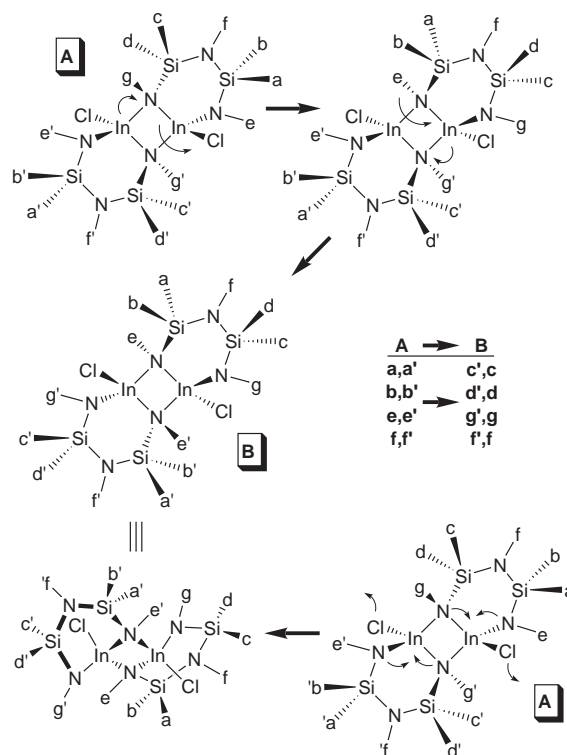
In the ^1H NMR spectrum of **2** there are five sharp singlets and a doublet, all with equal intensity, and a quartet with one-third relative intensity. The five singlets arise from three sets of four methyl groups attached to Si and two sets of four methyl groups attached to nitrogen, and the quartet (*NH*) and doublet (*NMe*) arise from the amine groups of the $[\text{HNMeSiMe}_2\text{NMe}]^-$ ligands. In the $^{13}\text{C}\{-^1\text{H}\}$ NMR spectrum there are six singlets. These data are consistent with the solid state structure (*i.e.*, with the molecule having virtual D_2 symmetry). A medium intensity band at 3310 cm^{-1} is observed in the IR spectrum that can be assigned to the N–H stretch.

At room temperature the ^1H spectrum of **1** consists of three closely spaced singlets in the *SiMe*₂ region in a 1:1:2 ratio and one sharp singlet and two slightly broad singlets in a 1:1:1 ratio in the *NMe* region (Fig. 3). The *SiMe*₂ singlet of relative

intensity 2 is composed of two accidentally degenerate singlets of equal intensity. The $^{13}\text{C}\{-^1\text{H}\}$ spectrum has seven singlets, four in the *SiMe*₂ region and three in the *NMe* region. These data are consistent with the solid state structure.

Variable temperature NMR (Fig. 3) was used to determine why two of the *NMe* resonances in the room temperature spectrum of **1** are broad. As the temperature of the NMR sample is raised, the two broad *NMe* resonances broaden further, collapse into the baseline at $\approx 60^\circ\text{C}$ ($\Delta G^\ddagger = 16 \text{ kcal mol}^{-1}$ at 60°C),¹⁵ and re-emerge at $70\text{--}80^\circ\text{C}$ as a broad hump. At 90°C , the highest temperature examined, the coalesced resonances are beginning to sharpen back into a singlet. The sharp *NMe* resonance observed in the room temperature spectrum remains sharp in the entire temperature range examined. In the *SiMe*₂ region, the two separated singlets merge into one peak as the temperature is raised while the accidentally degenerate peaks never separate and presumably merge, thereby resulting in two singlets being observed in the region at high temperatures. Conversely, as the NMR sample is cooled below room temperature, the two broad *NMe* resonances sharpen and the resonances in the *SiMe*₂ region sharpen and shift slightly; thus, at -10°C there are three sharp singlets in the *NMe* region and four sharp equal intensity singlets in the *SiMe*₂ region, as is consistent with the solid state structure.

The variable temperature data indicate that the two amide methyl groups and, separately, two sets of two methyl groups attached to Si of the $[\text{MeN}(\text{SiMe}_2\text{NMe})_2]^{2-}$ ligands are made equivalent by a dynamic process. Possible mechanisms to account for the NMR data include a concerted bridge–terminal amide exchange mechanism (Scheme 2, reading bottom to top)



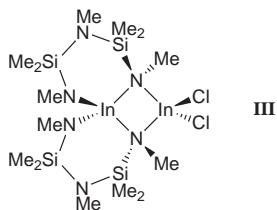
Scheme 2

or, more likely, a mechanism involving In–N bond opening and rotation that passes through an intermediate with C_2 symmetry (Scheme 2, reading top to bottom). A dimer–monomer equilibrium does not account for the data if the reasonable assumptions are made that the monomer would have a C_{2v} trigonal planar ClInN_2 core and the amine nitrogen undergoes rapid inversion in the temperature range examined.

In contrast to the solution dynamic behavior of **1** the aluminium analog $[\text{ClAl}(\text{NMeSiMe}_2)_2\text{NMe}]_2$ is reported to be

stereochemically rigid on the NMR time scale near room temperature.¹⁰ The related compounds [(py)Zn(NEtSiMe₂)₂NMe]₂, [Be(NMeSiMe₂)₂CH₂]₂ (see **1**) and [MeIn(NBu^t)₂SiMe₂]₂, however, all exhibit fluxional NMR behavior,^{11–13} which was attributed, respectively, to a monomer–dimer interconversion, an interconversion among oligomers, and an intramolecular dynamic process.

In the room temperature ¹H NMR spectrum of a CD₂Cl₂ solution of **1** there are in addition to the primary resonances discussed above four equal intensity sharp singlets in the SiMe₂ region and three equal intensity sharp singlets in the NMe region. The relative intensities of these resonances are approximately 10% of the primary resonances. The resonances are present with about the same intensities in samples prepared from different batches of crystals and from crystals grown from disparate solvent systems as well as when toluene-*d*₈ or benzene-*d*₆ is used as the NMR solvent instead of CD₂Cl₂, although there is more overlap of the resonances with the primary resonances in the hydrocarbon solvents, *e.g.*, see Fig. 3. The intensities of the resonances do not change nor do the resonances change shape as a function of temperature (*e.g.*, they do not broaden at high temperatures). From the observations it can not be determined whether the resonances are due to an isomer of **1** or a persistent impurity, but an isomer that would plausibly account for the data is **III**. A referee suggested that one might expect **III** to be fluxional, which is not observed.



Conclusion

Indium trichloride reacts with 1 equivalent of MeN(SiMe₂NMeLi)₂ to give the dimer **1** and with 4 equivalents of HNMeSiMe₂NMeLi to give **2**. In the structure of **1**, which is isomorphous with the known Al derivative, a chloride and one amide group of a [MeN(SiMe₂NMe)₂]²⁻ ligand are bonded to each In atom in terminal positions and the other amide group of the chelating ligand is shared between two In atoms. The terminal chlorides have an *anti*-ClIn...InCl arrangement. The amine group of the [MeN(SiMe₂NMe)₂]²⁻ ligand does not interact with In. Variable temperature NMR spectra show **1** undergoes a fluxional process that makes the bridging and terminal amide groups and, separately, two sets of two methyl resonances of the [MeN(SiMe₂NMe)₂]²⁻ ligand equivalent at high temperatures. A mechanism involving bridge–terminal amide exchange is proposed to account for the data. The molecule **2** has an adamantane-like Li₂In₂Si₂N₄ core with four InNSiNLiN rings fused to the core in such a way as to give the molecule virtual D₂ symmetry.

Experimental

General techniques and reagents

All manipulations were carried out in a glove box or by using Schlenk techniques. Solvents were purified by using standard techniques after which they were stored in the glove box over 4-Å molecular sieves until needed. H₂NMe was purchased from Matheson and Me₂SiCl₂ from Aldrich. The former was used as received and the latter was degassed with an argon stream before it was used. The lithium salts of the amines were prepared by reacting the amines in hexanes with the appropriate amount of *n*-BuLi, washing the resulting solid with hexanes, and then

drying *in vacuo*. NMR spectra were collected on a 300 MHz instrument.

Syntheses

The amines MeN(SiMe₂NHMe)₂ and Me₂Si(NHMe)₂. These compounds were prepared by using a slight modification of the literature procedure.¹⁶ Methylamine was added *via* a syringe needle over the surface of a stirred solution of Me₂SiCl₂ (30 cm³, 0.25 mol) in cold (5–10 °C) diethyl ether (300 cm³). The amine addition continued for 4 h during which time a white solid formed. After the amine addition was stopped, the reaction mixture was refluxed for 1 h. The mixture was then cold-filtered (0 °C). The solvent was removed *in vacuo* from the filtrate, and the residue was fractionally distilled at atmospheric pressure, giving Me₂Si(NHMe)₂ as a colorless liquid (bp 107 °C at 760 mmHg). Yield, 12 g (40%). Low pressure distillation of the residue gave MeN(SiMe₂NHMe)₂ as a colorless liquid (bp 70 °C at 0.01 mmHg). Yield, 3.8 g (7.4%). ¹H NMR (C₆D₆) for MeN(SiMe₂NHMe)₂: δ 0.085 (s, 12, SiMe₂), 0.28 (broad, 2, NH), 2.37 (slightly br s, 6, NMe), 2.43 (s, 3, NMe). ¹H NMR (C₆D₆) for Me₂Si(NHMe)₂: δ -0.056 (s, 6, SiMe₂), 0.21 (broad, 2, NH), 2.39 (d, J_{HH} = 6.6 Hz, 6, NMe).

The dimer [ClIn(NMeSiMe₂)₂NMe]₂. A diethyl ether solution (5 cm³) of MeN(SiMe₂NMeLi)₂ (0.22 g, 1.0 mmol) was added dropwise to a slurry of InCl₃ (0.22 g, 1.0 mmol) in cold (-78 °C) ether (25 cm³). The mixture was stirred for 24 h while the temperature was allowed slowly to warm to room temperature. A white precipitate formed. The ether was removed by vacuum distillation and the residue was extracted with hexane (3 × 10 cm³). The extracts were combined and filtered through Celite. The hexane was removed *in vacuo* and the residue, a white solid, was held *in vacuo* for 24 h. This material is pure product by ¹H NMR. Yield, 0.20 g (57%). Colorless cubic crystals can be grown from ether at low temperature (-35 °C). A satisfactory nitrogen analysis was not obtained (Found: C, 23.76; H, 6.13; N, 10.83. C₁₄H₄₂N₆Cl₂In₂Si₄ requires C, 23.76; H, 6.00; N, 11.88). See the text for complete details regarding the ¹H NMR spectra of this compound. ¹H NMR (C₆D₆): δ 0.16 (s, 12, SiMe₂), 0.20 (s, 6, SiMe₂), 0.22 (s, 6, SiMe₂), 2.60 (s, 6, NMe), 2.66 (s, 6, NMe), 2.91 (s, 6, NMe). ¹³C-¹H NMR (C₆D₆): δ -2.19 (SiMe₂), -0.74 (SiMe₂), 0.04 (SiMe₂), 1.36 (SiMe₂), 32.5 (NMe), 33.1 (NMe), 34.3 (NMe). IR (Nujol, CsI, cm⁻¹): 1307w, 1257s, 1219w, 1170m, 1151w, 1130w, 1076m, 1045m, 997w, 893m, 856m, 819w, 792m, 760w, 680w, 669w, 642w, 542w, 488w, 453w and 407w.

The dimer [Li{In(HNMeSiMe₂NMe)₂(MeNSiMe₂NMe)}]₂. A diethyl ether solution (5 cm³) of HNMeSi(Me₂)NMeLi (0.50 g, 4.0 mmol) was added dropwise to a slurry of InCl₃ (0.22 g, 1.0 mmol) in ether (25 cm³) at room temperature. The mixture was stirred for 24 h and then the ether was removed by vacuum distillation. The residue was dried for 24 h after which it was extracted with hexane (10 × 10 cm³). The extracts were combined and filtered through Celite, and the hexane was removed *in vacuo* from the filtrate. The residue, a white solid, is pure product by ¹H NMR. Yield, 0.45 g (96%). If the reaction is carried out by using a 2 : 1 mixture of HNMeSiMe₂NMeLi and Me₂Si(NMeLi)₂ or only 3 equivalents of HNMeSiMe₂NMeLi the yield is about 70%. Colorless crystals of the product can be formed by dissolving the solid in a hexane–ether mixture (1 : 9) and cooling (-35 °C for 24 h) (Found: C, 30.03; H, 8.15; N, 17.52. C₂₄H₇₆N₁₂In₂Li₂Si₆ requires C, 30.50; H, 8.12; N, 17.79). ¹H NMR (C₆D₆): δ 0.22 (s, 12, SiMe₂), 0.36 (s, 12, SiMe₂), 0.46 (s, 12, SiMe₂), 0.51 (q, J_{HH} = 6.6, 4, NH), 2.21 (d, J_{HH} = 6.6 Hz, 12, NMe), 2.79 (s, 12, NMe), 3.06 (s, 12, NMe). ¹³C-¹H NMR (C₆D₆): δ -1.91 (SiMe₂), -1.07 (SiMe₂), 0.48 (SiMe₂), 30.1 (NMe), 34.0 (NMe), 34.6 (NMe). IR (Nujol, CsI, cm⁻¹): 3310m, 1246m, 1168m, 1062m, 1026m, 1003m, 854m, 823m, 763m, 690m, 671m, 511w, 474w and 443w.

Crystal structure determination of [ClIn(NMeSiMe₂)₂NMe]₂

Crystal data. C₁₄H₄₂Cl₂In₂N₆Si₄, $M = 707.42$, triclinic, $a = 8.313(2)$, $b = 9.550(2)$, $c = 10.244(2)$ Å, $\alpha = 102.06(2)$, $\beta = 97.98(2)$, $\gamma = 110.03(2)^\circ$, $U = 727.4$ Å³, $T = 23$ °C, space group $P\bar{1}$, Mo-K α ($\lambda = 0.71073$ Å), $Z = 1$, $D_c = 1.62$ g cm⁻³, $F(000) = 356$. Colorless rods. Crystal dimensions: $0.08 \times 0.11 \times 0.41$ mm, $\mu = 19.2$ cm⁻¹.

Data collection. The crystal was mounted in a capillary under an argon atmosphere. Enraf-Nonius CAD-4F (κ geometry) diffractometer. θ - 2θ scan mode with scan width $\Delta\theta = 0.8 + 0.35\tan\theta$, scan speed range 0.67 – 8° min⁻¹, graphite-monochromated Mo-K α radiation; 1766 reflections measured ($3^\circ \leq 2\theta \leq 44^\circ$, $h, \pm k, \pm l$), 1766 unique, 1437 observed with $F > 6\sigma(F)$. Lorentz and polarization corrections were applied. A semi-empirical absorption correction was applied based on ψ scans of 5 reflections having χ angles between 70 and 90° . Three standard reflections were measured every 3600, and these showed no significant variation.

Structure solution and refinement. The Laue symmetry was determined to be $\bar{1}$, and the space group was shown to be $P\bar{1}$ or $P\bar{1}$. $P\bar{1}$ was assumed to be the correct setting, which was confirmed subsequently by successful refinement. The structure was solved by using the MolEN Patterson interpretation program, which revealed the position of the In atom. The remaining non-hydrogen atoms were located in subsequent difference Fourier syntheses. The usual sequence of isotropic and anisotropic refinement was followed. Hydrogen atoms attached to carbon were then entered in ideal calculated positions and constrained to a riding motion such that $U(H) = 1.3U(\text{attached C})$. After all shift/esd ratios were less than 0.01, convergence was reached with $R, R' = 0.040, 0.048$ (goodness-of-fit = 1.27). The weighting scheme was $w = [0.04F^2 + (\sigma(F))^2]^{-1}$. No unusually high correlations were noted between any of the variables in the last cycle of full-matrix least squares refinement, and the final difference map showed a maximum peak of about 0.62 e Å⁻³ located near In. All calculations were made using the MolEN package of programs.¹⁷

Crystal structure determination of [Li{In(HNMeSiMe₂)NMe)₂(MeNSiMe₂)NMe}]₂

Crystal data. 2Li⁺·C₂₄H₇₆N₁₂Si₆In₂²⁻, $M = 945.18$, monoclinic, $a = 17.736(6)$, $b = 12.778(4)$, $c = 21.201(7)$ Å, $\beta = 103.64(2)^\circ$, $U = 4669$ Å³, $T = -50$ °C, space group $I2/a$, Mo-K α ($\lambda = 0.71073$ Å), $Z = 4$, $D_c = 1.34$ g cm⁻³, $F(000) = 492$. Crystal dimensions: $0.20 \times 0.25 \times 0.35$ mm, $\mu = 11.5$ cm⁻¹.

Data collection. The crystals were handled under mineral oil. The crystal chosen for analysis was transferred to a cold nitrogen stream for data collection on a Nicolet R3m/V diffractometer equipped with an LT-1 low-temperature device, ω mode with scan width $\Delta\theta = 1.30 + (K\alpha_2 - K\alpha_1)^\circ$, scan speed range 1.5 – 15.0° min⁻¹, graphite-monochromated Mo-K α radiation; 3329 reflections measured ($4^\circ \leq 2\theta \leq 45^\circ$, $\pm h, k, l$), 2327 independent with $I > 3\sigma(I)$. Lorentz and polarization corrections were applied; however, no correction for absorption was made due to the small absorption coefficient. Two standard reflections were measured every 2 h or after every 100 data points collected, and these showed no significant variation.

Structure solution and refinement. The Laue symmetry was determined to be $2/m$, and the space group was shown to be Ia or $I2/a$. Because the unitary structure factors displayed centric statistics, $I2/a$ was assumed to be the correct setting from the outset, which was confirmed subsequently by successful refinement. The structure was solved by using the SHELXTL Patterson interpretation program, which revealed the position of the In atom in the asymmetric unit, consisting of one-half

molecule situated about a two-fold axis. The remaining non-hydrogen atoms were located in subsequent difference Fourier syntheses. The usual sequence of isotropic and anisotropic refinement was followed. Hydrogen atoms attached to carbon were then entered in ideal calculated positions and constrained to a riding motion with a single variable isotropic thermal parameter for the SiMe₃ hydrogens and a separate variable for the NMe hydrogens. The two amino hydrogens were located in difference maps and allowed to refine with distance constraints. All non-Li atoms occupy general positions, and both the Li atoms lie in special positions on a two-fold axis. The isotropic thermal parameters of both Li atoms refined to unreasonably small values (average 0.002 Å²); therefore, in the final least squares refinement the Li isotropic thermal parameters were fixed.

The possibility that some other cationic species occupies the Li positions was considered because of the irregularity in the Li refinement. Based on the way in which the compound was synthesized the only other species that can reasonably be considered to occupy the Li positions is Na. Whether the atoms are Li or Na, charge balance requires the cation-to-In atom ratio be one (*i.e.*, the positions cannot be half occupied). The possibility that the salt contains Na rather than Li was excluded for the following reasons: (1) a search of the Cambridge Crystallographic database for Li–N and Na–N distances where nitrogen is attached to at least two carbon atoms revealed that the distances are in the range 1.89 – 2.56 and 2.34 – 3.44 Å, respectively. In the present case, the Li–N distances range from 2.04 to 2.23 Å. This suggests that Li at 100% occupancy is the more reasonable choice. (2) The compound was synthesized in high yield using the Li salt HNMeSi(Me₂)NMeLi. A high yield would not be expected if the Na came from a contamination source, such as the Li amide salt, Celite filter aid or glassware. (3) When Na was refined in the Li positions the isotropic thermal parameters became unreasonably large (average 0.14 Å²).

After all shift/esd ratios were less than 0.2, convergence was reached with $R, R' = 0.034, 0.036$. The weighting scheme was $w = [\sigma(F)]^{-2}$. No unusually high correlations were noted between any of the variables in the last cycle of full-matrix least squares refinement, and the final difference map showed a maximum peak of about 0.7 e Å⁻³ located 0.47 Å away from Li(1). There was also a peak of about 0.5 e Å⁻³ located 0.7 Å away from Li(2). Calculations were made using Nicolet's SHELXTL PLUS (1987) package of programs.¹⁸

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