

Organometallic compounds of Group 13 elements containing the ligand $C(SiMe_3)_2(SiMe_2C_5H_4N-2)$

James Howson^a, Colin Eaborn^a, Peter B. Hitchcock^a, Michael S. Hill^{b,*},
J. David Smith^{a,*}

^a Department of Chemistry, School of Life Sciences, University of Sussex, Brighton BN1 9QJ, UK

^b Department of Chemistry, Imperial College London, South Kensington, London SW7 2AZ, UK

Received 9 July 2004; accepted 18 August 2004

Available online 23 September 2004

Abstract

The lithium derivative $\overline{Li(THF)C(SiMe_3)_2(SiMe_2C_5H_4N-2)}$ (**1**) reacted with $AlCl_3$ or Me_2AlCl to give, respectively, the monomeric compounds $\overline{AlCl_2C(SiMe_3)_2(SiMe_2C_5H_4N-2)}$ (**2a**) and $\overline{AlMe_2C(SiMe_3)_2(SiMe_2C_5H_4N-2)}$ (**2b**). The product from reaction with commercially available $GaBr_3$ was the analytically pure monomeric heterocycle $\overline{GaBr(OH)C(SiMe_3)_2(SiMe_2C_5H_4N-2)}$ (**3**), indicating that the starting halide had been partially hydrolysed before use. The reaction between **1** and commercially available $InCl_3$ gave a homogenous white solid $[\overline{InCl(\mu-X)C(SiMe_3)_2(SiMe_2C_5H_4N-2)}]_2$ (**4**) with X = Cl (59%) or OH (41%). The X-ray crystal structures of **2a**, **3**, and **4** have been determined.

© 2004 Elsevier B.V. All rights reserved.

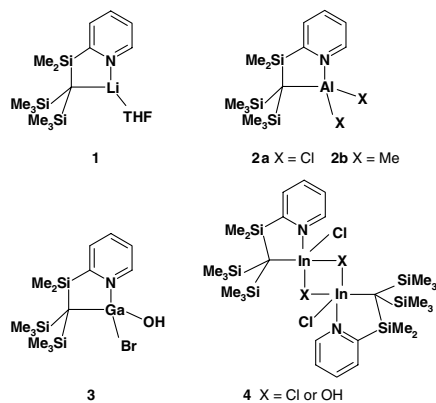
Keywords: Aluminium; Gallium; Indium; Organosilicon; Metallacycles

1. Introduction

During the last 20 years, we and others have shown that main group organometallic compounds containing the trisyl ligand $[C(SiMe_3)_3]$ show unusual structures and chemical properties [1]. By replacement of the methyl groups within the ligands with groups bearing lone pairs we have been able to expand the range of isolable compounds to include derivatives of the transition metals and to study how the molecular parameters of the ligand vary in similar compounds of a wide range of metals. Derivatives of the ligand $C(SiMe_3)_2(SiMe_2C_5H_4N-2)$ (**R**) form one of the most extensively studied series of this type [2–6]. Most are derived from the lithium precursor $LiR(THF)$ (**1**). Compounds of Groups 10 [4], 11, 12 [5], and 14 [6] have been described

previously; here we report some preliminary studies on compounds of Group 13 elements.

Our aim was to obtain dihalides RMX_2 , where M is a Group 13 element, as potential precursors for syntheses



* Corresponding authors. Tel.: +12 736 78124; fax: +12 736 77196.

E-mail address: j.d.smith@sussex.ac.uk (J.D. Smith).

of organometallic compounds (RM)_n, in which the metal is in a formal oxidation state 1. It has been shown that reduction of compounds RMCl₂ [R = C(SiMe₃)₃] gives tetrameric compounds (RM)₄ [7]. When R = C(SiMe₃)₂(SiMe₂C₅H₄N-2), the ligand is potentially bidentate, so compounds in which *n* < 4 might be formed. Precedents for such compounds in the literature include the unstable aryl derivative (AlAr)₂ [Ar = C₆H₃{C₆H₃ⁱPr₂-2,6}]-2,6, characterised as a [2 + 4] Diels–Alder cycloaddition product with toluene [8], the weakly bound (InAr)₂ [9], and a series of monomeric carbene analogues RM:, in which R is a bulky organic group or a crowded monovalent bidentate diketiminato or related ligand [10]. The aluminium compound **2a** and the related dimethyl derivative **2b** were isolated as analytically pure samples, with clean spectroscopic data. We found, however, that reactions of the lithium derivative **1** with commercially available samples of GaBr₃ and InCl₃ gave products that contained oxygen, indicating that moisture had been unintentionally admitted. Since we exercised care in drying solvents and encountered no problem in the synthesis of **2a** and **2b**, we think that the starting halides, which were used without purification, had partially hydrolysed. The new gallium compound **3** was well defined and analytically pure but in the lattice of the indium compound **4** OH and Cl were disordered over bridging positions. Although we plan to study the reactions of the lithium compound **1** with carefully purified gallium and indium halides in an attempt to obtain oxygen-free dihalides, we describe the structures of **3** and **4** at this stage, since these are of interest in themselves and **3** is the first bromo(hydroxido)organogallium derivative to be structurally characterised.

2. Experimental

Attempts were made to exclude air and moisture as far as possible by use of Schlenk techniques, flame-dried glassware, and argon as blanket gas. Solvents were purified by standard procedures, distilled and stored in Young's ampoules either over a potassium mirror (toluene, hexane, diethyl ether) or activated molecular sieves (THF). NMR spectra from samples in C₆D₆ were recorded at 300.13 (¹H), 125.8 (¹³C), 130.4 (²⁷Al) and 99.4 (²⁹Si) MHz. EI mass spectra were obtained at 70 eV and data are given for species containing ²⁸Si, ³⁵Cl and ⁶⁹Ga; in assignments R = C(SiMe₃)₂(SiMe₂C₅H₄N).

2.1. $\overline{\text{AlCl}_2\text{C}(\text{SiMe}_3)_2(\text{SiMe}_2\text{C}_5\text{H}_4\text{N}-2)}$ (**2a**)

A solution of **1** (5.0 mmol) in THF (30 cm³) was added slowly to a solution of AlCl₃ (0.67 g, 5.0 mmol) in THF (25 cm³) at –78 °C. Solvents were removed and the residue was extracted with hexane (50 cm³).

The extract was filtered and the volume of the solution was reduced to 10 cm³ to give colourless crystals of **2a** (1.10 g, 56%). Anal. Calc. for C₁₄H₂₈AlCl₂NSi₃: C, 42.84; H, 7.19; N, 3.57. Found: C, 41.66; H, 6.94; N, 3.41%. ¹H NMR: δ 0.33 (SiMe₃), 0.37 (SiMe₂), 6.33 (1H, m, 4-H), 6.77–6.85 (2H, m, 3- and 5-H), 8.30 (1H, d, 6-H). ¹³C NMR: δ 3.4 (SiMe₂), 5.9 (SiMe₃), 124.9 (4-C), 129.1 (5-C), 139.9 (3-C), 146.1 (6-C), 172.0 (*i*-C). The signal from the carbon atom attached to aluminium could not be observed. ²⁷Al NMR: δ 126.6, Δ*v*_{1/2} = 1.2 kHz. ²⁹Si NMR: δ –1.7 (SiMe₃), –0.4 (SiMe₂). MS: *m/z*: 376 (70, M – Me), 356 (20, M – Cl), 294 (10, R), 280 (30, RH – Me), 264 (100, Me₂Si=C(SiMe₂C₅H₄N)SiMe₂), 136 (15, C₅H₄NSiMe₂), 125 (50), 73.

2.2. $\overline{\text{AlMe}_2\text{C}(\text{SiMe}_3)_2(\text{SiMe}_2\text{C}_5\text{H}_4\text{N}-2)}$ (**2b**)

A solution of AlMe₂Cl (3.5 mmol) in hexane (3.5 cm³) was added to a solution of **1** (3.5 mmol) in THF (30 cm³) at –78 °C. The mixture was stirred for 2 h at –78 °C, then allowed to warm to room temperature. Solvents were removed in vacuum and the residue was extracted with toluene (20 cm³). The extract was filtered and the volume of the solution was reduced to 10 cm³ to give colourless crystals of **2b** (0.87 g, 70%). Anal. Calc. for C₁₆H₃₄AlNSi₃: C, 54.64; H, 9.74; N, 3.98. Found: C, 54.36; H, 9.53; N, 4.21%. ¹H NMR: δ –0.20 (6H, s, AlMe₂), 0.28 (18H, s, SiMe₃), 0.40 (6H, s, SiMe₂), 6.34 (1H, t, 4-H), 6.79 (1H, t, 5-H), 6.91 (1H, d, 3-H), 7.92 (d, 1H, 6-H). ¹³C NMR: δ –3.5 (b, AlMe₂), –0.3 (CSi₃), 3.9 (SiMe₂), 6.2 (SiMe₃), 124.0 (4-C), 128.8 (5-C), 138.0 (3-C), 145.5 (6-C), 173.6 (*i*-C). ²⁷Al NMR: δ 174 (Δ*v*_{1/2} = 2.6 kHz). ²⁹Si NMR: δ –2.8 (SiMe₃), –0.6 (SiMe₂). MS: *m/z*: 368 (20, RAl(OMe)₂ – Me), 352 (95, RAlMe(OMe) – Me), 336 (80, RAlMe) 295 (10, RH) 280 (40, RH – Me) 264 (100), 248 (20), 194 (20), 136 (20), 73(20).

2.3. $\overline{\text{GaBr}(\text{OH})\text{C}(\text{SiMe}_3)_2(\text{SiMe}_2\text{C}_5\text{H}_4\text{N}-2)}$ (**3**)

A solution of **1** (2.46 mmol) in THF (20 cm³) was added slowly to a solution of GaBr₃ (1.00 g) in THF (20 cm³) at –78 °C. Solvents were removed and the residue was extracted with hexane (50 cm³). The extract was filtered and the volume of the solution was reduced to 10 cm³ to give yellow crystals of **3** (0.96 g, 85%), m.p. 266 °C (softens 140 °C). Anal. Calc for C₁₄H₂₉GaBrNOSi₃: C, 36.42; H, 6.29; N, 3.04. Found: C, 36.55; H, 6.41; N, 2.87. ¹H NMR: δ –0.05 and 0.46 (9H, s, SiMe₃), 0.31 and 0.55 (3H, s, SiMe₂), 6.41 (1H, m, 4-H), 6.80–6.89 (2H, m, 3- and 5-H), 8.06 (1H, d, 6-H). ¹³C NMR: δ 2.9 and 4.2 (SiMe₂), 5.3 and 6.2 (SiMe₃), 124.7 (4-C), 129.1 (5-C), 138.5 (3-C), 145.5 (6-C), 172.2 (*i*-C). ²⁹Si NMR: δ: –1.7 and –0.4 (SiMe₃), 4.4 (SiMe₂). MS: *m/z*: 444 (20, M – OH), 380 (30, M – Br),

295 (70, RH), 280 (100, RH – Me), 264 (80), 217, 192, 136, 73, 59.

2.4. $[\overline{\text{InCl}\{Cl_{0.59}(\text{OH})_{0.41}\}C(\text{SiMe}_3)_2(\text{SiMe}_2\text{C}_5\text{H}_4\text{N}-2)}]_2$ (**4**)

A solution of **1** (4.0 mmol) in THF (30 cm³) was added slowly to a solution of InCl₃ (0.89 g, 4.0 mmol) in THF (25 cm³) at –78 °C. The mixture was allowed to warm to room temperature, solvents were removed, and the residue was extracted with hexane (50 cm³). The extract was filtered and the volume of the solution was reduced to 10 cm³ to give colourless crystals of **4**. The ¹H NMR spectrum of a sample of **4** in C₆D₆ was complex, indicating that several species were present.

2.5. Crystallography

Data were collected on a Nonius-Kappa CCD diffractometer and structure solutions and refinements were by SHELXL-97 as incorporated in the package WINGX. No absorption correction was applied for **2a**, and MULTISCAN was used for **3** and **4**. Non-hydrogen atoms were anisotropic and hydrogen atom positions were included in riding mode. Further details are given in Table 1. In the structure of **3** there are two independent molecules in the asymmetric unit; one of these showed disorder in one of the SiMe₃ groups with alternative sites for C9–C11. The hydrogen atoms attached to oxygen were not located. The structure determination of **4** showed peaks in a difference map attributed to partial replacement of bridging Cl by OH (occupancy 0.41) and a hydrogen-bonded water molecule (occupancy 0.09).

3. Results and discussion

The compounds **2a**, **2b**, **3**, and **4** were obtained by treatment of commercial samples of Group 13 metal halides with the lithium reagent **1**. In the case of **3** and **4**, oxygen was inadvertently incorporated into the products. The susceptibility of organogallium and -indium dihalides to hydrolysis is well known and has led to misinterpretation of X-ray structural data [11]. The fact that compound **3** was isolated in good yield as an analytically pure sample indicated (a) that at least one molar equivalent of water must have been present in the initial halide and (b) that attack of water on the final Ga–Br bond is slow.

The molecular structure of the aluminium compound **2a** is shown in Fig. 1 and that of the unordered molecule of the gallium derivative **3** in Fig. 2; important bond lengths and angles given in Table 2. The structures are very similar; both compounds are monomeric and solvent-free in the solid state. In each case the pyridyl nitrogen is a sufficiently strong donor to displace THF from the coordination sphere of the metal and give a $\overline{\text{MC1SiC4N}}$ chelate ring. As in the compounds RMgBr(THF) [R = C(SiMe₃)₂(SiMe₂C₅H₄N)], CrR₂ and (RCrCl)₂, the MNC4Si sequence is essentially planar with the SiC1M plane at an angle of about 30°. An X-ray crystal structure determination of the dimethyl compound **2b** showed that the lattice was disordered. Not surprisingly, it was impossible to distinguish between SiMe₂ and AlMe₂ groups or between the C5 and N atoms in the pyridyl group. There was, however, no doubt that the structure was the same as that of the dichloride **2a**.

Table 1
X-ray structure determinations

	2a	3	4
Chemical formula	C ₁₄ H ₂₈ AlCl ₂ NSi ₃	C ₁₄ H ₂₉ BrGaNOSi ₃	C ₂₈ H ₅₆ Cl ₄ In ₂ N ₂ Si ₆ ^a
Formula weight	392.5	461.3	960.7
T (K)	173(2)	173(2)	173(2)
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i> (no. 14)	<i>P</i> 2 ₁ / <i>c</i> (no. 14)	<i>P</i> $\bar{1}$ (no. 2)
<i>a</i> (Å)	8.9650(2)	32.0315(11)	9.1647(7)
<i>b</i> (Å)	9.3044(2)	9.1134(2)	9.5708(6)
<i>c</i> (Å)	25.6527(7)	15.2767(5)	12.5915(9)
α (°)	90	90	73.211(4)
β (°)	94.170(2)	93.440(1)	80.623(5)
γ (°)	90	90	86.806(5)
<i>U</i> (Å ³)	2134.1(1)	4451.5(2)	1043.2(1)
<i>Z</i>	4	8	1
μ (mm ^{–1})	0.51	3.19	1.56
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.040, 0.100	0.057, 0.124	0.056, 0.127
All data	0.052, 0.107	0.100, 0.141	0.066, 0.131
Measured/independent reflections/ <i>R</i> _{int}	13,585/4974/0.035	19,218/7755/0.070	12,565/3643/0.061
Reflections with <i>I</i> > 2 σ (<i>I</i>)	4071	5105	3157

^a For main component.

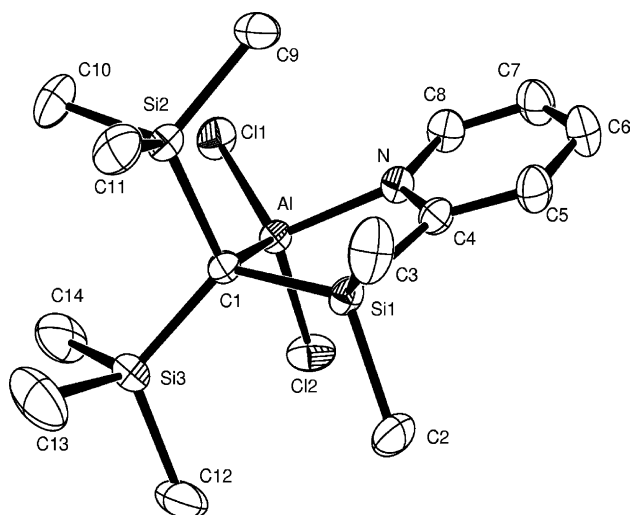


Fig. 1. The molecular structure of **2a** with 50% thermal ellipsoids.

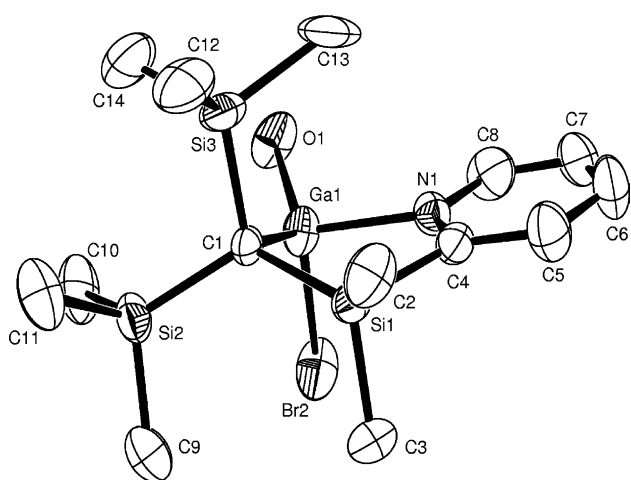
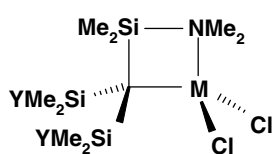
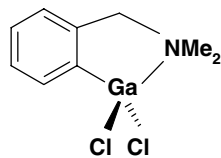


Fig. 2. The structure of the undisordered molecule of **3** with 20% thermal ellipsoids.



5a M = Al, Y = Me; **5b** M = Al, Y = NMe₂;

5c M = Ga, Y = Me

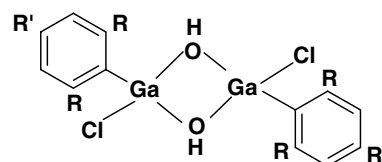


6

For compounds of the general type $\overline{LL'AlCl_2}$ (where LL' is a bidentate ligand having C and N as donor atoms), those with four-membered chelate

rings, e.g. $\overline{AlCl_2C(SiMe_3)_2(SiMe_2NMe_2)}$ (**5a**) [12] or $\overline{AlCl_2C(SiMe_2NMe_2)_2(SiMe_2NMe_2)}$ (**5b**) [13] have dative Al–N bond lengths in the range 1.968(4)–1.975(2) Å. The bonds in compounds with five- or six-membered rings are usually (but not always [14]) longer [1.960(2)–2.085(4) Å] [14–17]. The dative Al–N bond length from the pyridyl nitrogen in **2a** [1.9383(16) Å] is shorter than any of these and similar to those in amine adducts of $AlCl_3$ [18].

There is a significant difference (29σ) between the Al–Cl1 and the Al–Cl2 bond lengths in **2**, indicating that the Al–Cl2 bond perpendicular to the plane of the $\overline{AlClSiC_4N}$ ring is weaker than the other one (Al–Cl1). There is no such difference between the Al–Cl bonds in the structures of other compounds of the type $\overline{LL'AlCl_2}$ determined by X-ray diffraction [12,13] and no evidence from Cl···C distances that Cl1 in **2** is less crowded than Cl2. However, a similar significant difference between Ga–Cl bond lengths has been observed in the compound (*o*-Me₂NCH₂)C₆H₄GaCl₂ (**6**) [15]. Because anomalously short M–μ–Cl bonds in dimeric Group 13 compounds have previously been attributed to partial replacement of Cl by OH [11,19], we considered whether the difference between the Al–Cl1 and Al–Cl2 bonds in **2a** could be ascribed to partial hydrolysis with preferential locations of OH at Cl1 sites. There is, however, no crystallographic evidence for this; no anomalies were found in the Cl thermal ellipsoids.



7a R = C₆H₂Pr₃-2,4,6, R' = H;

7b R = C₆H₂Me₃-2,4,6, R' = H;

7c R = R' = CF₃

The Al–C bond [1.9784(19) Å] is in the usual range for four-coordinate aluminium [20]. We showed earlier [6] that the value of $r_{MC} - r_{MN}$ in organometallic compounds containing the ligand $C(SiMe_3)_2(SiMe_2C_5H_4N)$ is a sensitive measure of the acceptor strength of the metal. The values (Å) for M = Al (0.04) and Ga (–0.02) derived from **2a** and **3**, respectively, may be compared with values for M = Li (0.11), Mg (0.09), Ni (0.02), Sn (–0.01) and Zn (–0.04) [2,4–6]. The experimental values can be expected to show some scatter since the ligands attached to the metal are not in every case the same; nevertheless the crystallographic data from the present and other recent papers [2,4–6] rank the metals in an order that parallels the widely used electrochemical series.

Table 2
Selected bond lengths (Å) and angles (°) in $\overline{\text{AlCl}_2\{\text{C}(\text{SiMe}_3)_2(\text{SiMe}_2\text{C}_5\text{H}_4\text{N}-2)\}}$ (**2a**) and $\overline{\text{GaBr}(\text{OH})\{\text{C}(\text{SiMe}_3)_2(\text{SiMe}_2\text{C}_5\text{H}_4\text{N}-2)\}}$ (**3**)

	2a	3^b
<i>Bond lengths</i>		
M–C ^a	1.9784(19)	2.008(5)
M–N	1.9383(16)	2.047(5)
Al–Cl1 or Ga–O	2.1295(8)	2.099(4)
Al–Cl2 or Ga–Br	2.1529(8)	2.4028(9)
Si1–C1	1.8785(18)	1.872(5)
Si2–C1	1.9047(19)	1.888(5)
Si3–C1	1.8934(19)	1.905(5)
Si–Me	1.860(2)–1.887(2)	1.864(7) ^c
Si–C4	1.920(2)	1.909(6)
N–C4	1.363(2)	1.344(7)
<i>Bond angles</i>		
N–M–C	100.07(7)	95.79(19)
N–Al–Cl1 or N–Ga–O	105.81(6)	109.06(19)
N–Al–Cl2 or N–Ga–Br	101.37(6)	98.82(13)
C–Al–Cl1 or C–Ga–O	122.82(6)	130.08(19)
C–Al–Cl2 or C–Ga–Br	116.81(6)	113.87(15)
Cl1–Al–Cl2 or O–Ga–Br	106.80(3)	104.41(13)
C2–Si1–C3	104.76(12)	106.5(3)
C1–Si–C2,3	117.47(10), 119.41(9)	117.9(3), 118.2(3)
C4–Si–C2,3	106.21(10), 104.70(10)	106.7(3), 103.7(3)
C1–Si–C4	102.84(8)	102.3(2)
Me–Si–Me	104.36(14)–108.35(15)	104.5(4)–107.8(3)
Si–C–Si	108.53(9), 111.99(9), 119.13(10)	118.0(3), 110.8(3), 110.9(3)
Si–C1–M	99.24(8), 108.97(9), 107.92(9)	101.0(2), 110.0(3), 104.9(3)
Si1–C4–N	115.23(13)	115.2(4)
C4–N–M	112.72(13)	114.1(4)
Fold angle at M···Si	30	34

^a M = Al or Ga.

^b Values for the unordered molecule; those for the other molecule do not differ significantly.

^c Mean value with e.s.d. for individual measurements in parentheses. No individual value differs significantly from the mean.

As far as we are aware, the structures of only three compounds of the general type RGaXOH have been determined [11,21]. In contrast to compound **3**, all these ($[\text{2,6-R}_2\text{-4-R}'\text{C}_6\text{H}_2\text{GaCl}(\mu\text{-OH})]_2$ **7a**, $\text{R} = \text{C}_6\text{H}_2\text{Pr}_{3-2,4,6}$, $\text{R}' = \text{H}$; **7b**, $\text{R} = \text{C}_6\text{H}_2\text{Me}_{3-2,4,6}$, $\text{R}' = \text{H}$ and **7c**, $\text{R} = \text{R}' = \text{CF}_3$), are dimeric. The OH group in **3** occupies the position of the more strongly bound Cl in **2a** and the bromine that of the less strongly bound atom. In the compounds $\overline{\text{LL}'\text{GaCl}_2}$, Ga–N bonds are usually longer than Ga–C bonds (for an exception see [22]). The Ga–N [2.047(5) Å] and Ga–C bond lengths [2.008(5) Å] in **3** are within the reported ranges [Ga–N 2.013(2)–2.092(5) Å and Ga–C 1.936(6)–2.013(7) Å [15,16,23]] and close to the values [Ga–N 2.057(4), Ga–C 2.000(4) Å] found for the compound $\overline{\text{GaCl}_2\text{C}(\text{SiMe}_3)_2(\text{SiMe}_2\text{NMe}_2)}$ (**5c**) [13]. The Ga–O distance in **3** [2.099(4) Å] is a little longer than the sum of the covalent radii (1.93 Å) and at the upper end of the range found in organogallium hydroxides [1.892(5)–2.033(5) Å] [11,21,24]. The Ga–Br distance [2.4028(9) Å] is likewise longer than the sum of the covalent radii (2.34 Å) and Ga–Br(terminal) distances [2.300(1)–2.311(2) Å] found in organogallium compounds containing the GaBr_4 fragment [25]. The long Ga–O and GaBr distances in **3**

suggest that the crowding at the gallium is greater than that in previously reported compounds. The pyridyl nitrogen atom appears to be a sufficiently strong donor to prevent formation of a dimeric structure like that found for the chloro(hydroxido) compounds **7a** and **7b**. In both **2a** and **3** the coordination at the metal is that of a distorted tetrahedron with two interbond angles (those between C and Cl, Br or O) considerably greater, and the other four angles less, than the tetrahedral value.

Only one signal is observed for the SiMe_3 group and one for the SiMe_2 group in the ^1H , ^{13}C and ^{29}Si spectra of **2a** and **2b**, indicating that in solution the SiMe_3 groups on either side of the ring are interchanging on the NMR time scale. Two signals for Me_3Si groups are observed in the ^1H , ^{13}C , and ^{29}Si NMR spectra of **3**, showing that the groups on either side of the ring are inequivalent in solution and that the cyclic structure shown in Fig. 2, with nitrogen firmly bound to gallium, is preserved. When the exocyclic atoms attached to the metal are the same, as in **2a** and **2b**, interchange between Si2 and Si3 may be effected by ring inversion. When the exocyclic groups are different, as in **3**, the inequivalence is maintained during inversion and complete dissociation

of the metal–nitrogen bond is required to make the environments of Si2 and Si3 the same. The X-ray data confirm that metal–nitrogen bond dissociation is less likely in **2a** or **2b** than in **3**, so it is probable that SiMe₃ groups in **2a** and **2b** are made equivalent by ring-inversion rather than by dissociation.

By drawing together the results from **2a**, **2b** and **3** and those from previously reported compounds containing the ligand R = C(SiMe₃)₂(SiMe₂C₅H₄N-2), it is possible to generalise as follows. The metallacycles readily invert without dissociation, as shown by single SiMe₃ peaks in spectra of **2a**, **2b**, Li(THF)₃(μ-Br)MgBrR [3] and (RZnBr)₂ [5]. The inversion is masked in **3**, RMgBr(THF) [2] and RSnCl [6], in which SiMe₃ environments are different for both possible ring configurations. For compounds of metals with low Lewis acidity, e.g. RPbCl [6] and RHgCl [5], ring dissociation leads to single SiMe₃ peaks, even when different groups are attached to the metal.

The reaction between the lithium compound **1** and indium(III) chloride gave a colourless crystalline solid identified as the organoindium chloride/hydroxide **4** by an X-ray structure determination. Pure samples of the dichloride RInCl₂ or the hydroxidochloride RIn(OH)Cl could not be obtained, but it was clear that both formed molecules, in which the indium was five-coordinate. These crystallised randomly in the same lattice with electron density from bridging hydroxide groups appearing within the planar In₂Cl₂-ring, as shown in Fig. 3. (The compounds [(Me₃Si)₂CH]₂InCl]₂ and [(Me₃Si)₂CH]₂In(OH)₂ also have similar crystal structures [26].) Apart from the disorder in the bridging bonds, the rest of the molecule is well defined so that reasonably precise selected bond lengths and angles can be given in Table 3. We do not discuss the bridge bonds further because of the uncertainty arising from the crystallographic disorder but the In–Cl and In–O bond lengths are similar

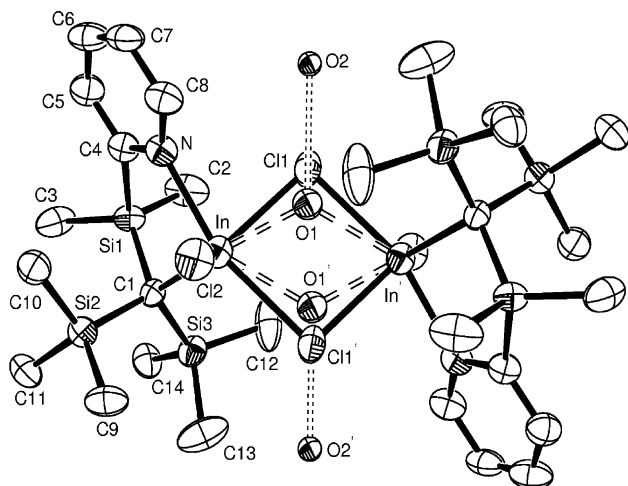


Fig. 3. The molecular structure of $[\text{InCl}(\text{Cl}_{0.59}(\text{OH})_{0.41})\text{C}(\text{SiMe}_3)_2\text{-(SiMe}_2\text{C}_5\text{H}_4\text{N-2)}]_2$ (**4**), with 50% thermal ellipsoids and showing the hydrogen bonds from the hydroxyl group to the oxygen of the water molecule with occupancy 0.09.

Table 3
Selected bond lengths and angles in **4**

Bond lengths			
In–C	2.221(6)	In–Cl2	2.4032(19)
In–N	2.313(6)	In–O	2.090(15)
In–Cl1	2.574(5)	In–O'	2.216(15)
In–Cl1'	2.658(4)	Si–C1	1.887(7) ^a
Bond angles			
		C1–In–Cl2	122.22(18)
		C1–Si–C4	107.7(3)
N–In–C1	89.4(2)	In–C1–Si1	101.5(3)
		In–C1–Si2	104.4(3)
N–In–Cl2	89.45(14)	In–C1–Si3	113.4(3)
		Si–C–Si ^a	112.3(3)
		C4–N–In	114.2(4)
		Si–C4–N	116.0(5)

^a Mean value with e.s.d. of single measurements in parentheses. No individual value differs significantly from the mean.

to those reported for other organoindium derivatives [26,28]. The coordination number of the metal in **4** is higher than that in **2a**, reflecting the larger radius of indium. Many organoindium dihalides RInX₂ (X = Cl, Br or I) adopt 'stair-step' polymeric structures containing five-coordinate indium atoms linked into infinite strands by (μ-X)₂ bridges [26,27,29]. Dimers are formed when R = C₆H₃{C₆H₂R'}₂ (R' = Me [30] or ⁱPr [11]) and monomers when R is C₆H₂'Bu₃ [31]. In **4** the ligand is bidentate, so that indium achieves five-coordination in the dimer and further association to give polymers is prevented.

The structures reported here reflect the effects of size and Lewis acidity of Group 13 elements. The syntheses of the oxygen-free dihalides and their reactions with reducing agents are worthy of further study.

4. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre CCDC nos. 233775–233777 for compounds **2a**, **3** and **4**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

Acknowledgement

The authors thank the EPSRC for financial support.

References

- [1] C. Eaborn, J.D. Smith, J. Chem. Soc., Dalton Trans. (2001) 1541.
- [2] S.S. Al-Juaid, C. Eaborn, P.B. Hitchcock, M.S. Hill, J.D. Smith, Organometallics 19 (2000) 3224.

- [3] S.S. Al-Juaid, A.G. Avent, C. Eaborn, S.M. El-Hamruni, S.A. Hawkes, M.S. Hill, M. Hopman, P.B. Hitchcock, J.D. Smith, *J. Organomet. Chem.* 631 (2001) 76.
- [4] C. Eaborn, M.S. Hill, P.B. Hitchcock, J.D. Smith, *Chem. Commun.* (2000) 691.
- [5] C. Eaborn, M.S. Hill, P.B. Hitchcock, J.D. Smith, *J. Chem. Soc., Dalton Trans.* (2002) 2467.
- [6] S.S. Al-Juaid, A.G. Avent, C. Eaborn, M.S. Hill, P.B. Hitchcock, D.J. Patel, J.D. Smith, *Organometallics* 20 (2001) 1223.
- [7] W. Uhl, W. Hiller, M. Layh, W. Schwarz, *Angew. Chem., Int. Ed. Engl.* 31 (1992) 1364;
W. Uhl, R. Graupner, M. Layh, U. Schütz, *J. Organomet. Chem.* 493 (1995) C1;
R.D. Schluter, A.H. Cowley, D.A. Atwood, R.A. Jones, J.L. Atwood, *J. Coord. Chem.* 30 (1993) 25;
W. Uhl, A. Jantschak, *J. Organomet. Chem.* 555 (1998) 263;
C. Schnitter, H.W. Roesky, C. Röpken, R. Herbst-Irmer, H.-G. Schmidt, M. Noltemeyer, *Angew. Chem., Int. Ed.* 37 (1998) 1952;
W. Uhl, S.U. Keimling, K.W. Klinkhammer, W. Schwarz, *Angew. Chem., Int. Ed. Engl.* 36 (1997) 64;
W. Uhl, A. Jantschak, W. Saak, M. Kaupp, R. Wartchow, *Organometallics* 17 (1998) 5009.
- [8] R.J. Wright, A.D. Phillips, P.P. Power, *J. Am. Chem. Soc.* 125 (2003) 10784.
- [9] R.J. Wright, A.D. Phillips, N.J. Hardman, P.P. Power, *J. Am. Chem. Soc.* 124 (2002) 8538.
- [10] N.J. Hardman, R.J. Wright, A.D. Phillips, P.P. Power, *J. Am. Chem. Soc.* 125 (2003) 2667;
A. Haaland, K.-G. Martinsen, H.V. Volden, W. Kaim, E. Waldhör, W. Uhl, U. Schütz, *Organometallics* 15 (1996) 1146;
C. Cui, H.W. Roesky, H.-G. Schmidt, M. Noltemeyer, H. Hao, F. Cimpoesu, *Angew. Chem., Int. Ed.* 39 (2000) 4274;
N.J. Hardman, B.E. Eichler, P.P. Power, *Chem. Commun.* (2000) 1991;
M.S. Hill, P.B. Hitchcock, *Chem. Commun.* (2004) 1818.
- [11] B. Twamley, P.P. Power, *Chem. Commun.* (1999) 1805.
- [12] S.S. Al-Juaid, C. Eaborn, S.M. El-Hamruni, P.B. Hitchcock, J.D. Smith, *Organometallics* 18 (1999) 45.
- [13] C. Eaborn, A. Farook, P.B. Hitchcock, J.D. Smith, *Organometallics* 17 (1998) 3135.
- [14] W. Zheng, N.C. Mösch-Zanetti, T. Blunck, H.W. Roesky, M. Noltemeyer, H.-G. Schmidt, *Organometallics* 20 (2001) 3299.
- [15] H.S. Isom, A.H. Cowley, A. Decken, F. Sissingh, S. Corbelin, R.J. Lagow, *Organometallics* 14 (1995) 2400.
- [16] S. Bensiok, M. Bangel, B. Neumann, H.-G. Stammer, P. Jutzi, *Organometallics* 19 (2000) 1292.
- [17] M.A. Dam, O.S. Akkerman, F. Bickelhaupt, H. Veldman, A.L. Spek, *Main Group Met. Chem.* 18 (1995) 633.
- [18] A. Haaland, in: G.H. Robinson (Ed.), *Coordination Chemistry of Aluminum*, VCH, New York, 1993, p. 1.
- [19] J. Su, X.-W. Li, G.H. Robinson, *Chem. Commun.* (1998) 2015.
- [20] C.E. Holloway, M. Melnik, *J. Organomet. Chem.* 543 (1997) 1.
- [21] R.D. Schluter, H.S. Isom, A.H. Cowley, D.A. Atwood, R.A. Jones, F. Olbrich, S. Corbelin, R.J. Lagow, *Organometallics* 13 (1994) 4058;
R.J. Wehmschulte, J.M. Steele, M.A. Khan, *Organometallics* 22 (2003) 4678.
- [22] K.S. Klimek, C. Cui, H.W. Roesky, M. Noltemeyer, H.-G. Schmidt, *Organometallics* 19 (2000) 3085.
- [23] G.S. Hair, S.L. Battle, A. Decken, A.H. Cowley, R.A. Jones, *Inorg. Chem.* 39 (2000) 27;
J.-D. Lee, C.-K. Baek, J. Ko, K. Park, S. Cho, S.-K. Min, S.O. Kang, *Organometallics* 18 (1999) 2189;
P. Jutzi, M. Bangel, B. Neumann, H.-G. Stammer, *Organometallics* 15 (1996) 4559.
- [24] A. Mar, S.J. Rettig, A. Storr, J. Trotter, *Can. J. Chem.* 66 (1988) 101;
D.A. Atwood, A.H. Cowley, P.R. Harris, R.A. Jones, S.U. Koschmieder, C.M. Nunn, J.L. Atwood, S.G. Bott, *Organometallics* 12 (1993) 24;
G.S. Smith, J.L. Hoard, *J. Am. Chem. Soc.* 81 (1959) 3907;
S.J. Rettig, M. Sandercock, A. Storr, J. Trotter, *Can. J. Chem.* 68 (1990) 59;
J. Storre, A. Klemp, H.W. Roesky, H.-G. Schmidt, M. Noltemeyer, R. Fleischer, D. Stalke, *J. Am. Chem. Soc.* 118 (1996) 1380;
C. Schnitter, H.W. Roesky, T. Albers, H.-G. Schmidt, C. Röpken, E. Parisini, G.M. Sheldrick, *Chem. Eur. J.* 3 (1997) 1783.
- [25] H. Schmidbaur, W. Bublak, B. Huber, G. Müller, *Organometallics* 5 (1986) 1647;
H. Schmidbaur, W. Bublak, B. Huber, G. Müller, *Helv. Chem. Acta* 69 (1986) 1742;
M. Uson-Finkenzeller, W. Bublak, B. Huber, G. Müller, H. Schmidbaur, *Z. Naturforsch. B* 41 (1986) 346;
H. Schmidbaur, W. Bublak, B. Huber, G. Müller, *Z. Naturforsch. B* 42 (1987) 147.
- [26] M. Häußlein, H.-D. Hausen, K.W. Klinkhammer, J. Weidlein, *Z. Anorg. Allg. Chem.* 625 (1999) 1608.
- [27] O.T. Beachley, E.F. Spiegel, J.P. Kopasz, R.D. Rogers, *Organometallics* 8 (1989) 1915;
K. Mertz, W. Schwarz, F. Zettler, H.-D. Hausen, *Z. Naturforsch. B* 30 (1975) 159.
- [28] S.S. Al-Juaid, N.H. Buttrus, C. Eaborn, P.B. Hitchcock, A.T.L. Roberts, J.D. Smith, A.C. Sullivan, *J. Chem. Soc., Chem. Commun.* (1986) 908;
N.W. Alcock, I.A. Degnan, S.M. Roe, M.G.H. Wallbridge, *J. Organomet. Chem.* 414 (1991) 285;
W. Uhl, R. Graupner, I. Hahn, *Z. Anorg. Allg. Chem.* 623 (1997) 565;
M.G. Walawalkar, *Organometallics* 22 (2003) 879;
M. Stender, P.P. Power, *Polyhedron* 21 (2002) 525.
- [29] J.T. Leman, J.W. Ziller, A.R. Barron, *Organometallics* 10 (1991) 1766;
M.F. Self, A.T. McPhail, L.J. Jones, R.L. Wells, J.C. Huffman, *Polyhedron* 13 (1994) 199.
- [30] G.H. Robinson, X.-W. Li, W.T. Pennington, *J. Organomet. Chem.* 501 (1995) 399.
- [31] S. Schulz, S. Pusch, E. Pohl, S. Dielkus, R. Herbst-Irmer, A. Meller, H.W. Roesky, *Inorg. Chem.* 32 (1993) 3343;
M.A. Petrie, P.P. Power, H.V. Rasika Dias, K. Ruhlandt-Senge, K.M. Waggoner, R.J. Wehmschulte, *Organometallics* 12 (1993) 1086.