

## Synthesis and Structural Characterisation of Compounds with Gallium–Silicon and Indium–Silicon Bonds

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The compounds  $\{[(\text{Me}_3\text{Si})_3\text{Si}]_2\text{M}(\mu\text{-Cl})_2\text{Li}(\text{thf})_2\}$  ( $\text{M} = \text{Ga}$  or  $\text{In}$ ;  $\text{thf} = \text{tetrahydrofuran}$ ) have been prepared and the structures of both compounds have been determined by X-ray crystallography.

The use of indium and gallium compounds in the electronics industry has stimulated interest in the chemistry of these elements. In this context, the recent reports of novel tris(trimethylsilyl)methyl indium compounds by Eaborn, Smith *et al.*<sup>1</sup> prompt us to report comparable developments with the analogous tris(trimethylsilyl)silyl ligand. Previous examples of gallium–silicon and indium–silicon compounds appear to be confined to  $(\text{Me}_3\text{Si})_3\text{M}$ ,  $\text{M} = \text{Ga}$ <sup>2</sup> or  $\text{In}$ ,<sup>3</sup> and  $\text{Li}[\text{Ga}(\text{SiMe}_3)_4]$ .<sup>2</sup> However, no structural data are available for these heat-, light-, and oxygen-sensitive compounds.† Recognising the kinetic stabilisation afforded by bulky groups, it seemed reasonable to explore the implications of replacing the  $\text{Me}_3\text{Si}$  by the  $(\text{Me}_3\text{Si})_3\text{Si}$  ligand. In passing, we note that organometallic complexes featuring the latter ligand are rather rare.<sup>4</sup>

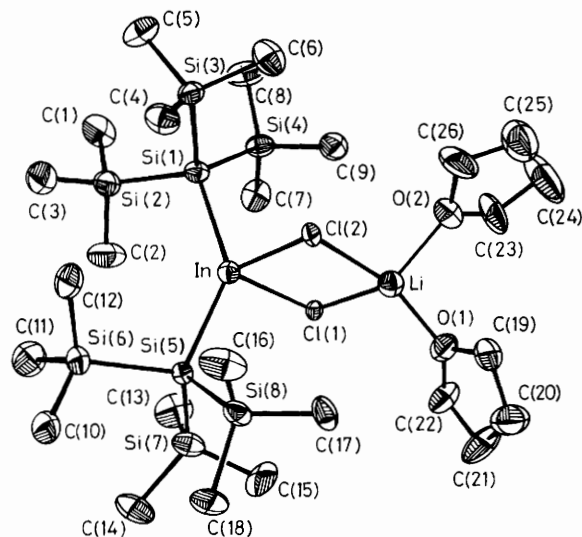
Treatment of  $\text{MCl}_3$  ( $\text{M} = \text{Ga}$  or  $\text{In}$ ) with three equivalents of  $\text{Li}[\text{Si}(\text{SiMe}_3)_3] \cdot 3\text{thf}^\ddagger$  ( $\text{thf} = \text{tetrahydrofuran}$ ) in  $\text{Et}_2\text{O}$  solution at  $-78^\circ\text{C}$ , followed by slow warming to room temperature, resulted in cream coloured solutions and a white precipitate. Evaporation of the  $\text{Et}_2\text{O}$ , re-dissolution of the residues in *n*-hexane, and filtration produced pale yellow solutions. X-Ray-quality crystals of  $\{[(\text{Me}_3\text{Si})_3\text{Si}]_2\text{M}(\mu\text{-Cl})_2\text{Li}(\text{thf})_2\}$ ,  $\text{M} = \text{Ga}$ , (1);  $\text{M} = \text{In}$ , (2), formed upon cooling saturated *n*-hexane solutions to  $-20^\circ\text{C}$ . Both compounds are thermally stable but somewhat air-sensitive.

Compounds (1) and (2) can be regarded as a double-chloride bridged complex of  $[(\text{Me}_3\text{Si})_3\text{Si}]_2\text{MCl}$  and solvated

$\text{LiCl}$  (Figure 1).‡ The Si, Li, and M atoms adopt tetrahedral geometries, albeit with varying degrees of distortion. Thus, the  $\text{Si}(1)\text{-M-Si}(5)$  angles of  $138.0(2)^\circ$  ( $\text{M} = \text{Ga}$ ) and  $139.9(2)^\circ$  ( $\text{M} = \text{In}$ ) are unusually wide, presumably owing to steric interactions. Likewise, the average  $\text{Si-Si-Si}$  angle is  $\sim 2^\circ$  less than the average  $\text{M-Si-Si}$  angle in both molecules. To the best of our knowledge, gallium–silicon and indium–silicon bond lengths have not been reported previously. However, our average  $\text{Ga-Si}$  and  $\text{In-Si}$  bond lengths of  $2.439(5)$  and  $2.591(7)$  Å, respectively, are somewhat larger than the sums of covalent radii ( $\text{Ga-Si} = 2.37$ ;  $\text{In-Si} = 2.55$  Å). Mention

‡ *Crystal data* for (1):  $\text{C}_{26}\text{H}_{70}\text{Cl}_2\text{GaLiO}_2\text{Si}_8$ ,  $M = 787.10$ , monoclinic, space group  $P2_1/c$  (No. 14),  $a = 13.754(3)$ ,  $b = 17.180(3)$ ,  $c = 20.813(4)$  Å,  $\beta = 104.25(2)^\circ$ ,  $U = 4767$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.097$  g cm<sup>-3</sup>,  $\mu(\text{Mo-K}_\alpha) = 9.05$  cm<sup>-1</sup>; *crystal data* for (2):  $\text{C}_{26}\text{H}_{70}\text{Cl}_2\text{InLiO}_2\text{Si}_8$ ,  $M = 832.21$ , monoclinic, space group  $P2_1/c$  (No. 14),  $a = 13.817(3)$ ,  $b = 17.315(3)$ ,  $c = 20.953(3)$  Å,  $\beta = 105.12(1)^\circ$ ,  $U = 4839$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.203$  g cm<sup>-3</sup>,  $\mu(\text{Mo-K}_\alpha) = 15.68$  cm<sup>-1</sup>. Totals of 7686 and 6713 unique reflections were measured on an Enraf-Nonius CAD-4 diffractometer over the range  $3.0 \leq 2\theta \leq 46^\circ$  ( $\theta/2\theta$  scan mode) for (1) and (2) respectively. The data were corrected for Lorentz, polarisation, and decay effects. Empirical absorption corrections were also applied to (1) and (2). Both structures were solved by direct methods and refined (difference Fourier, full-matrix, least-squares) using 1625 and 2542 reflections with  $I > 3.0\sigma(I)$  for (1) and (2) respectively. The final residuals were  $R = 0.0830$  and  $R_w = 0.0930$  for (1) and  $R = 0.0738$  and  $R_w = 0.0820$  for (2). Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1986.

†  $(\text{Me}_3\text{Si})_3\text{In}$  is also light-sensitive.<sup>3</sup>



**Figure 1.** View (ORTEP) of  $[(\text{Me}_3\text{Si})_3\text{Si}]_2\text{In}(\mu\text{-Cl})_2\text{Li}(\text{thf})_2$  (**2**), showing the atom numbering scheme. Important bond lengths (Å) and angles ( $^\circ$ ) are as follows [the corresponding values for (**1**) are given in brackets]: In–Si(1) 2.591(7) [2.443(5)], In–Si(5) 2.605(7) [2.435(5)], Si(1)–Si(2) 2.353(11) [2.334(8)], Si(1)–Si(3) 2.365(10) [2.389(7)], Si(1)–Si(4) 2.346(10) [2.338(7)], Si(5)–Si(6) 2.334(9) [2.360(7)], Si(5)–Si(7) 2.360(10) [2.356(8)], Si(5)–Si(8) 2.337(10) [2.334(7)], Si(1)–In–Si(5) 139.9(2) [138.0(2)], Cl(1)–In–Cl(2) 90.6(1) [93.75(9)].

should be made of the fact that the chlorine atom positions of both molecules are disordered owing to the presence of  $\sim 17\%$  of bromine. In turn, the incorporation of bromine into (**1**) and (**2**) stems from the use of a MeLi–LiBr complex in the

preparation of  $\text{Li}[\text{Si}(\text{SiMe}_3)_3] \cdot 3\text{thf}$ .<sup>5a</sup> The presence of bromine was corroborated by the 70 eV electron impact mass spectra of (**1**) and (**2**) which exhibit peaks corresponding to Me loss from  $[(\text{Me}_3\text{Si})_3\text{Si}]_2\text{MCl}$  and  $[(\text{Me}_3\text{Si})_3\text{Si}]_2\text{MBr}$ .

Finally, attempts were made to prepare  $(\text{Me}_3\text{Si})_3\text{SiIn}$  by treatment of  $\text{InCl}$  with  $\text{Li}[\text{Si}(\text{SiMe}_3)_3] \cdot 3\text{thf}$ . However, only (**2**) was isolated owing presumably to the disproportionation  $3\text{InCl} \rightarrow 2\text{In} + \text{InCl}_3$ .

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