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

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Abstract

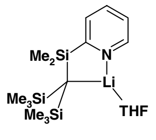
The lithium derivative $\overline{Li(THF)C(SiMe_3)_2(SiMe_2C_5H_4N}$-2) (**1**) reacted with $AlCl_3$ or Me_2AlCl to give, respectively, the monomeric compounds $\overline{AlCl_2C(SiMe_3)_2(SiMe_2C_5H_4N}$-2) (**2a**) and $\overline{AlMe_2C(SiMe_3)_2(SiMe_2C_5H_4N}$-2) (**2b**). The product from reaction 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 $[\overline{InCl(\mu\text{-}X)C(SiMe_3)_2(SiMe_2C_5H_4N}\text{-}2)]_2$ (**4**) with X = Cl (59%) or OH (41%). The X-ray crystal structures of **2a**, **3**, and **4** have been determined.

Keywords: Aluminium; Gallium; Indium; Organosilicon; Metallacycles

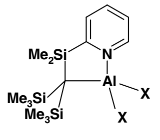
1. Introduction

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 $C(SiMe_3)_2(SiMe_2C_5H_4N\text{-}2)$ (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.

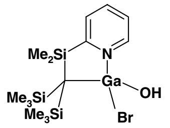
Our aim was to obtain dihalides RMX_2, were M is a Group 13 element, as potential precursors for syntheses



1



2a X = Cl **2b** X = Me



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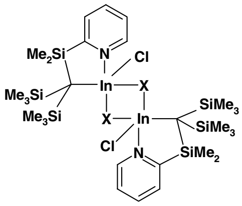

4 X = Cl or OH

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of organometallic compounds $(RM)_n$, in which the metal is in a formal oxidation state 1. It has been shown that reduction of compounds $RMCl_2$ [$R = C(SiMe_3)_3$] gives tetrameric compounds $(RM)_4$ [7]. When $R = C(SiMe_3)_2(SiMe_2C_5H_4N\text{-}2)$, 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 $(AlAr)_2$ [$Ar = C_6H_3\{C_6H_3{}^iPr_2\text{-}2,6\}_2\text{-}2,6$, 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 $GaBr_3$ and $InCl_3$ 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 C_6D_6 were recorded at 300.13 (^1H), 125.8 (^{13}C), 130.4 (^{27}Al) and 99.4 (^{29}Si) MHz. EI mass spectra were obtained at 70 eV and data are given for species containing ^{28}Si, ^{35}Cl and ^{69}Ga; in assignments $R = C(SiMe_3)_2(SiMe_2C_5H_4N)$.

2.1. $\overline{\mathrm{AlCl_2C(SiMe_3)_2(SiMe_2C_5H_4N}}\mathrm{\text{-}2)}$ (**2a**)

A solution of **1** (5.0 mmol) in THF (30 cm^3) was added slowly to a solution of $AlCl_3$ (0.67 g, 5.0 mmol) in THF (25 cm^3) at −78 °C. Solvents were removed and the residue was extracted with hexane (50 cm^3). The extract was filtered and the volume of the solution was reduced to 10 cm^3 to give colourless crystals of **2a** (1.10 g, 56%). Anal. Calc. for $C_{14}H_{28}AlCl_2NSi_3$: C, 42.84; H, 7.19; N, 3.57. Found: C, 41.66; H, 6.94; N, 3.41%. ^1H NMR: δ 0.33 ($SiMe_3$), 0.37 ($SiMe_2$), 6.33 (1H, m, 4-H), 6.77–6.85 (2H, m, 3- and 5-H), 8.30 (1H, d, 6-H). ^{13}C NMR: δ 3.4 ($SiMe_2$), 5.9 ($SiMe_3$), 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. ^{27}Al NMR: δ 126.6, $\Delta\nu_{1/2} = 1.2$ kHz. ^{29}Si NMR: δ −1.7 ($SiMe_3$), −0.4 ($SiMe_2$). MS: *m*/*z*: 376 (70, M − Me), 356 (20, M − Cl), 294 (10, R), 280 (30, RH − Me), 264 (100, $Me_2Si{=}C(SiMe_2C_5H_4N)SiMe_2$), 136 (15, $C_5H_4NSiMe_2$), 125 (50), 73.

2.2. $\overline{\mathrm{AlMe_2C(SiMe_3)_2(SiMe_2C_5H_4N}}\mathrm{\text{-}2)}$ (**2b**)

A solution of $AlMe_2Cl$ (3.5 mmol) in hexane (3.5 cm^3) was added to a solution of **1** (3.5 mmol) in THF (30 cm^3) 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 cm^3). The extract was filtered and the volume of the solution was reduced to 10 cm^3 to give colourless crystals of **2b** (0.87 g, 70%). Anal. Calc. for $C_{16}H_{34}AlNSi_3$: 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, $AlMe_2$), 0.28 (18H, s, $SiMe_3$), 0.40 (6H, s, $SiMe_2$), 6.34 (1H, t, 4-H), 6.79 (1H, t, 5-H), 6.91 (1H, d, 3-H), 7.92 (d, 1H, 6-H). ^{13}C NMR: δ −3.5 (b, $AlMe_2$), −0.3 (CSi_3), 3.9 ($SiMe_2$), 6.2 ($SiMe_3$), 124.0 (4-C), 128.8 (5-C), 138.0 (3-C), 145.5 (6-C), 173.6 (*i*-C). ^{27}Al NMR: δ 174 ($\Delta\nu_{1/2} = 2.6$ kHz). ^{29}Si NMR: δ −2.8 ($SiMe_3$), −0.6 ($SiMe_2$). 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. $\overline{\mathrm{GaBr(OH)C(SiMe_3)_2(SiMe_2C_5H_4N}}\mathrm{\text{-}2)}$ (**3**)

A solution of **1** (2.46 mmol) in THF (20 cm^3) was added slowly to a solution of $GaBr_3$ (1.00 g) in THF (20 cm^3) at −78 °C. Solvents were removed and the residue was extracted with hexane (50 cm^3). The extract was filtered and the volume of the solution was reduced to 10 cm^3 to give yellow crystals of **3** (0.96 g, 85%), m.p. 266 °C (softens 140 °C). Anal. Calc for $C_{14}H_{29}GaBrNOSi_3$: 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, $SiMe_3$), 0.31 and 0.55 (3H, s, $SiMe_2$), 6.41 (1H, m, 4-H), 6.80-6.89 (2H, m, 3- and 5-H), 8.06 (1H, d, 6-H). ^{13}C NMR: δ 2.9 and 4.2 ($SiMe_2$), 5.3 and 6.2 ($SiMe_3$), 124.7 (4-C), 129.1 (5-C), 138.5 (3-C), 145.5 (6-C), 172.2 (*i*-C). ^{29}Si NMR: δ: −1.7 and −0.4 ($SiMe_3$), 4.4 ($SiMe_2$). MS: *m*/*z*: 444 (20, M − OH), 380 (30, M − Br),