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Si–C bond cleavage in the reaction of gallium chloride with lithium bis(trimethylsilyl)amide and thermolysis of base adducts of dichloro(trimethylsilyl)amido gallium compounds

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Abstract

The known cyclic dimer, $(Me_3SiNSiMe_2)_2$ (**1**), was isolated in the reaction of $GaCl_3$ with one equivalent of $Li[N(SiMe_3)_2]$ at room temperature as the result of cleavage of a Si–C bond from the $N(SiMe_3)_2$ anion. Although the gallium product was not isolated from the $GaCl_3$ reaction, pyrolysis of the new base-stabilized dichloro(silyl)amido gallium compounds, $Cl_2Ga[N(SiMe_3)_2](quin)$ (**2**) (quin = quinuclidine), $Cl_2Ga[N(SiMe_3)_2](NMe_3)$ (**3**), $Cl_2Ga[N(SiMe_3)(^tBu)](quin)$ (**4**) and $Cl_2Ga[N(SiMe_3)(2,6\text{-}^iPrC_6H_3)](quin)$ (**5**), afforded $MeGaCl_2(quin)$ and $MeGaCl_2(NMe_3)$ in 27–61% yields confirming a methyl migration from Si to Ga. The Si–C bond cleavage and methyl migration were proposed to occur through transition states containing a $\overline{\mathrm{Ga{-}N{-}Si{-}Me}}$ ring. No unusual Ga···C interaction was found in the solid-state structure of **2** that was monomeric with the gallium atom adopting a distorted tetrahedral geometry. Improved structural data for **1** are also reported. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Si–C bond cleavage; Chlorogallium compounds; Amidogallium compounds; X-ray structures

1. Introduction

A substantial portion of Group 13 chemistry has focused on the study of new molecular precursors to Group 13–15 materials. Several of the precursors including $[Cl_2AlN(H)SiMe_3]_2$ [1,2], $[X_2GaP(SiMe_3)_2]_2$ [3,4], $X_3GaP(SiMe_3)_3$ [5] (X = Cl, Br, I) and mixtures of X_3Ga (X = Cl, Br) and $As(SiMe_3)_3$ [6] produced AlN powders, nanocrystalline GaP or GaAs by elimination of Me_3SiX. This method has not been successfully applied to gallium nitride synthesis. The reaction of $GaCl_3$ with $HN(SiMe_3)_2$ was reported to eliminate 1 mol of Me_3SiCl to yield $[Cl_2GaN(H)SiMe_3]_2$ [7,8]. Further, heating beyond 150° C caused partial Me_3SiCl elimination and the formation of an unidentified solid [8]. Barry and Richeson [9] reported that $[Li(THF)_2][GaN(SiMe_3)_2(OSiMe_3)_2Cl]$ and $Ga[N(SiMe_3)_2](OSiMe_3)_2(pyridine)$ were synthesized from the reactions involving $Cl_2Ga[N(SiMe_3)_2](THF)$ that was generated from the reaction of $GaCl_3$ with one equivalent of $Li[N(SiMe_3)_2](THF)_n$ in hexane, however, details regarding the isolation and characterization of $Cl_2Ga[N(SiMe_3)_2](THF)$ are not presented.

In our study, the reaction of $GaCl_3$ with one equivalent of $Li[N(SiMe_3)_2]$ in benzene did not afford $Cl_2Ga[N(SiMe_3)_2]$, but surprisingly a small amount of $(Me_3SiNSiMe_2)_2$ (**1**) and other uncharacterized products. To understand the reaction, a series of new base-stabilized dichloro(trimethylsilyl)amidogallium compounds, $Cl_2GaN[(SiMe_3)R](quin)$ [quin = quinuclidine, R = $SiMe_3$ (**2**), ^tBu (**4**), $2,6\text{-}^iPr_2C_6H_3$ (**5**)] and $Cl_2GaN(SiMe_3)_2(NMe_3)$ (**3**) were synthesized, characterized and reacted at elevated temperatures. In this paper we report the results of these studies.

2. Experimental

2.1. Materials and general procedures

Gallium chloride and quinuclidine were purchased from Strem and other chemicals were obtained from

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Aldrich. Gallium chloride, anhydrous trimethylamine, quinuclidine and *n*-butyllithium were used as received. Lithium bis(trimethylsilyl)amide was recrystallized from hexanes. 2,6-Diisopropylaniline was distilled over CaH_2 under reduced nitrogen pressure. *N*-*t*-Butyltrimethylsilylamine, $HN(SiMe_3)(^tBu)$, and chlorotrimethylsilane were distilled under nitrogen over NaOH and P_2O_5, respectively. The quinuclidine adduct of gallium chloride, $GaCl_3$(quin), was prepared as previously described [10]. The trimethylamine adduct of gallium chloride, $GaCl_3(NMe_3)$, was prepared as a white powder by condensing one equivalent of NMe_3 onto $GaCl_3$. Lithium N-*t*-butyltrimethylsilylamide, $LiN(SiMe_3)(^tBu)$, was prepared as a colorless crystalline solid (64% yield) from the reaction of $HN(SiMe_3)(^tBu)$ with one equivalent of ^nBuLi followed by recrystallization in pentane. $MeGaCl_2$ was prepared from the reaction of Me_3Ga with two equivalents of $GaCl_3$ [11]. Diethyl ether, pentane, hexanes, benzene and toluene were predried over CaH_2 and freshly distilled over sodium–benzophenone under nitrogen. Benzene-d_6 was distilled over CaH_2 hydride under nitrogen. All experiments were conducted under an oxygen-free, dry-nitrogen atmosphere using standard Schlenk and glovebox techniques.

Proton NMR spectra were obtained in benzene-d_6 solutions at room temperature (r.t.) in a Varian INOVA 300 spectrometer, and the residual proton (7.15 ppm) in C_6D_6 was used as the internal standard. In the cases that the resonance of the residual proton was not distinguishable from the aromatic hydrogen atoms of the samples, the sharp singlet (0.29 ppm) from silicone grease was used as the internal standard. The IR spectra of KBr pellets were recorded in a Nicolet MAGNA-IR 560 spectrometer. Chemical ionization mass spectra were acquired in a Finnigan Mat 95 spectrometer using a direct insertion probe. The samples were evaporated at temperatures ranging from 25 to 340° C, and except for compound **1** for which isobutane was used, the ionization gas was methane containing 4% NH_3. The electron ionization mass spectra were collected on the same spectrometer using a 70 eV electron flow. Melting points were obtained in sealed, nitrogen filled capillaries and were uncorrected. Elemental analyses were obtained from Schwarzkopf Microanalytical Laboratories, Woodside, NY or Desert Analytics, Tucson, AZ.

2.2. Reaction of $GaCl_3$ with one equivalent of $Li[N(SiMe_3)_2]$; isolation of $(Me_3SiNSiMe_2)_2$ (1)

In a typical experiment, a solution of $Li[N(SiMe_3)_2]$ (2.85 g, 17.0 mmol) in 50 ml of benzene was added dropwise to a solution of $GaCl_3$ (3.00 g, 17.0 mmol) in 90 ml of benzene at r.t. The mixture was stirred for 20 h and filtered to separate a white precipitate and a pale yellow filtrate. The weight of the precipitate (1.58 g) was much higher than the expected weight of LiCl (0.72 g). Benzene was removed from the filtrate under vacuum affording a yellow sticky solid. The ^{1}H-NMR spectrum of the solid showed more than ten singlets in the 0.03–0.50 ppm region with the highest peaks at 0.29, 0.27 and 0.09 ppm. Sublimation of the solid at r.t. to a cold finger at 0° C afforded colorless plates of $(Me_3SiNSiMe_2)_2$ (**1**) (0.12 g, 5% yield based on silicon). M.p.: 42.0–43.5° C. ^{1}H-NMR: δ 0.09 (18H, s, $SiMe_3$), 0.29 (12H, s, $SiMe_2$). EI MS [assignment, % relative intensity]: 291 $[[M+H]^+$, 18], 275 $[[M-Me]^+$, 100], 130 $[(0.5M-Me)^+$, 20], 73 $[Me_3Si^+$, 14]. Other products were not characterized.

2.3. Synthesis of $Cl_2Ga[N(SiMe_3)_2]$(quin) (2)

To a stirred solution of $GaCl_3$(quin) (1.50 g, 5.22 mmol) in 50 ml of toluene was added a solution of $Li[N(SiMe_3)_2]$ (0.874 g, 5.22 mmol) in 50 ml of toluene at r.t. A white precipitate (LiCl) was formed immediately and the mixture was stirred for 3 h and filtered. After the colorless filtrate was concentrated to ca. 50 ml and stored at −20° C overnight, colorless plates were collected (1.83 g, 85% yield). M.p.: 175° C, decomposed without melting. ^{1}H-NMR: δ 0.46 (18H, s, $SiMe_3$), 0.81 (6H, m, CH_2), 1.01 (1H, m, CH), 2.88 (6H, t, NCH_2). CIMS [assignment, % relative intensity]: 413 $[[M+H]^+$, 2.3], 397 $[[M-Me]^+$, 25], 377 $[[M-Cl]^+$, 36], 302 $[[M-\text{quin}+H]^+$, 3.0], 286 $[[M-\text{quin}-Me]^+$, 19], 266 $[[M-\text{quin}-Cl]^+$, 52], 252 $[[M-N(SiMe_3)_2]^+$, 67], 230 $[\{Ga+HN(SiMe_3)_2\}^+$, 24], 162 $[H_2N(SiMe_3)_2^+$, 19], 146 $[(HNSi_2Me_5)^+$, 89], 112 $[(\text{quin}+H)^+$, 100]. Anal. Calc. for $C_{13}H_{31}Cl_2GaN_2Si_2$: C, 37.88; H, 7.58; N, 6.80. Found: C, 37.51; H, 7.96; N, 6.73%.

2.4. Synthesis of $Cl_2Ga[N(SiMe_3)_2](NMe_3)$ (3)

To a stirred solution of $GaCl_3(NMe_3)$ (1.50 g, 6.38 mmol) in 30 ml of benzene was added a solution of $Li[N(SiMe_3)_2]$ (1.07 g, 6.38 mmol) in 20 ml of benzene at r.t. A white precipitate (LiCl) was formed immediately after the addition of $Li[N(SiMe_3)_2]$. After the mixture was stirred for 14 h, all the volatiles were removed under vacuum leaving a white solid. Toluene (10 ml) and hexanes (20 ml) were added and the mixture was filtered. The colorless filtrate was stored at −20° C overnight and colorless plates were collected (1.83 g, 80% yield). M.p.: 124–130° C. ^{1}H-NMR: δ 0.39 (18H, s, $SiMe_3$), 1.85 (9H, s, NMe_3). CIMS [assignment, % relative intensity]: 361 $[[M+H]^+$, 0.3], 319 $[[M-NMe_3+NH_4]^+$, 0.8], 217 $[[M-N(SiMe_3)_2+NH_3]^+$, 13], 162 $[((Me_3Si)_2NH_2)^+$, 100], 90 $[(Me_3SiNH_3)^+$, 9.2]. The sample decomposed upon sealing in a glass vial under vacuum when prepared for elemental analysis.

2.5. Synthesis of $Cl_2Ga[N(SiMe_3)(^tBu)](quin)$ (**4**)

To a stirred solution of $GaCl_3$(quin) (2.00 g, 6.96 mmol) in 40 ml of benzene was added a solution of $Li[N(SiMe_3)(^tBu)]$ (1.05 g, 6.96 mmol) in 50 ml of benzene at r.t. A white precipitate (LiCl) was formed immediately after the addition of $Li[N(SiMe_3)(^tBu)]$. The mixture was stirred for 5 h and filtered to obtain a pale yellow filtrate. After the filtrate was concentrated to ca. 15 ml and stored at 0° C overnight, colorless plates were collected (2.04 g, 74% yield). M.p.: 169–171° C. ^{1}H-NMR: δ 0.50 (9H, s, $SiMe_3$), 0.86 (6H, m, CH_2), 1.05 (1H, m, CH), 1.56 (9H, s, ^{t}Bu), 2.94 (6H, m, NCH_2). CIMS [assignment, % relative intensity]: CIMS: 397 [$[M+H]^+$, 1.7], 361 [$[M-Cl]^+$, 1.9], 303 [$[M-quin+NH_4]^+$, 1.5], 286 [$[M-quin+H]^+$, 0.4], 267 [$[M-quin-Cl+NH_3]^+$, 1.5], 249 [$[M-quin-Cl]^+$, 1.5], 146 [$\{H_2N(SiMe_3)(^tBu)\}^+$, 18], 112 [$(quin+H)^+$, 100]. Anal. Calc. for $C_{14}H_{34}Cl_2GaN_2Si$: C, 42.45; H, 7.89; N, 7.07. Found: C, 41.40; H, 7.99; N, 6.66%.

2.6. Synthesis of $Li[N(SiMe_3)(2,6\text{-}^iPr_2C_6H_3)]$

To a precooled toluene solution (200 ml) of 2,6-$^iPr_2C_6H_3NH_2$ (8.68 g, 48.9 mmol) at −78° C was added a hexane solution (19.6 ml) of ^{n}BuLi (48.9 mmol). After the mixture was allowed to warm to r.t. and stirred for 2 h, a white slurry was obtained. Me_3SiCl (5.32 g, 48.9 mmol) was added to the above slurry at r.t. The mixture was stirred for 1 h and filtered to obtain a pale yellow filtrate. The filtrate was cooled to −78° C and a hexane solution (19.6 ml) of ^{n}BuLi (48.9 mmol) was added once more. After the mixture was allowed to warm to r.t. and stirred for 1 h, a yellow solution was obtained. The solution was stored at −20° C and a colorless crystalline solid was isolated. The remaining solution was further concentrated and stored at −20° C to afford additional product. This process was repeated several times to yield 9.48 g (76% yield) of $Li[N(SiMe_3)(2,6\text{-}^iPr_2C_6H_3)]$. ^{1}H-NMR: δ 0.12 (9H, s, $SiMe_3$), 0.89 and 1.19 (total 12H, d, $CH(CH_3)_2$), 3.49 (2H, m, $CH(CH_3)_2$), 6.87 and 6.99 (3H, m, C_6H_3).

2.7. Synthesis of $Cl_2Ga[N(SiMe_3)(2,6\text{-}^iPr_2C_6H_3)](quin)$ (**5**)

To a stirred solution of $GaCl_3$(quin) (1.50 g, 5.22 mmol) in 40 ml of Et_2O was added a solution of $Li[N(SiMe_3)(2,6\text{-}^iPr_2C_6H_3)]$ (1.33 g, 5.22 mmol) in 40 ml of Et_2O at r.t. A white precipitate (LiCl) was formed immediately and the mixture was stirred for 3 h and filtered. Toluene (10 ml) was used to wash the filter cake. After the yellow filtrate was concentrated to ca. 5 ml and stored at −20° C overnight, colorless plates were collected (1.72 g, 66% yield). M.p.: 138–148° C. ^{1}H-NMR: δ 0.39 (9H, s, $SiMe_3$), 0.80 (6H, m, CH_2), 0.95 (1H, m, CH in quinuclidine), 1.31 and 1.39 (total 12H, d, $CH(CH_3)_2$), 2.91 (6H, m, NCH_2), 3.98 (2H, m, $CH(CH_3)_2$, 7.10 (3H, s, C_6H_3). CIMS [assignment, % relative intensity]: 518 [$[M+NH_4]^+$, 2.6], 501 [$[M+H]^+$, 4.7], 465 [$[M-Cl]^+$, 0.8], 407 [$[M-quin+NH_4]^+$, 7.1], 269 [$\{Cl_2Ga(quin)(NH_3)\}^+$, 18], 250 [$\{H_2N(SiMe_3)(2,6\text{-}^iPr_2C_6H_3)\}^+$, 58], 178 [$\{H_3N(2,6\text{-}^iPr_2C_6H_3)\}^+$, 35], 112 [$(quin+H)^+$, 100], 90 [$(H_3NSiMe_3)^+$, 5.2]. Anal. Calc. for $C_{22}H_{39}Cl_2GaN_2Si$: C, 52.82; H, 7.86; N, 5.60. Found: C, 52.79; H, 7.98; N, 5.53%.

2.8. Synthesis of $Cl_2GaMe(quin)$ (**6**)

To a stirred solution of $MeGaCl_2$ (0.500 g, 3.21 mmol) in 35 ml of Et_2O was added a solution of quinuclidine (0.357 g, 3.21 mmol) in 35 ml of Et_2O at r.t. A small amount of white precipitate was formed after the addition of quinuclidine. Then the mixture was stirred for 4 h and filtered. The insoluble compound was not characterized. After the colorless filtrate was concentrated to ca. 40 ml and stored at −20° C overnight, colorless plates were collected (0.51 g, 59% yield). M.p.: 165–167° C. ^{1}H-NMR: δ 0.06 (3H, s, Me), 0.78 (6H, m, CH_2), 1.01 (1H, m, CH), 2.57 (6H, t, NCH_2). CIMS [assignment, % relative intensity]: 379 [$[M+quin+H]^+$, 8.1], 305 [$\{Cl_3Ga(quin)(NH_4)\}^+$, 7.9], 285 [$[M+NH_4]^+$, 100], 269 [$[M+NH_3-Me]^+$, 13], 247 [$[M+NH_3-Cl]^+$, 18], 230 [$[M-Cl]^+$, 4.1], 112 [$(quin+H)^+$, 45], 69 [Ga^+, 1.4]. Anal. Calc. for $C_8H_{16}Cl_2GaN$: C, 36.01; H, 6.04; N, 5.25. Found: C, 35.83; H, 6.34; N, 5.26%.

2.9. Synthesis of $Cl_2GaMe(NMe_3)$ (**7**)

NMe_3 (3 ml) was condensed onto Cl_2GaMe (0.300 g, 1.93 mmol) at −78° C. Then the mixture was allowed to warm to r.t. and the excess NMe_3 was evaporated leaving a white crystalline solid (0.38 g, 91% yield). M.p.: 135–137° C. ^{1}H-NMR: δ −0.02 (3H, s, GaMe), 1.67 (9H, s, NMe_3). CIMS [assignment, % relative intensity]: 285 [$[M+NH_4]^+$, 100], 217 [$\{Cl_2Ga(NMe_3)(NH_3)\}^+$, 4.9], 191 [$\{Cl_2Me(NH_3)(NH_4)\}^+$, 37], 178 [$\{ClGaMe(NMe_3)\}^+$, 2.1], 153 [$\{ClGaMe(NH_3)_2\}^+$, 17], 69 [$Ga^+$, 1.5], 60 [$Me_3NH^+$, 6.6].

2.10. Pyrolysis of compound **2**

Compound **2** (0.800 g, 1.94 mmol) in a Schlenk flask (diameter, 2 cm; length, 15 cm) was heated to 210° C in an oil bath. After heating for 1 h, the system was connected to the vacuum source. A white crystalline solid was sublimed to the unheated top of the flask and a glassy, yellow solid remained on the bottom. Toluene (15 ml) was added carefully to dissolve the residue on the bottom and transferred to another flask. The crystalline solid on the wall was dissolved in toluene (4 ml) affording a colorless solution. After the solution was stored at −20° C overnight, colorless plates of $MeGaCl_2(quin)$ were collected (0.32 g, 61% yield). Its ^1H-NMR and IR spectra were identical with those of the authentic sample. The glassy yellow solid was isolated after evaporation of the toluene solvent and its ^1H-NMR spectrum showed a complex pattern and was attributed to as yet unidentified products.

*2.11. Pyrolysis of compound **3***

The procedure was similar to the pyrolysis of **2**. A sample of **3** (1.00 g, 2.78 mmol) was heated at 200° C for 0.5 h. Crystals of $MeGaCl_2(NMe_3)$ (0.33 g, 55% yield) were obtained after the crude product was recrystallized from a mixture of toluene (5 ml) and hexanes (10 ml). ^1H-NMR and IR spectra of the product were identical with those of the authentic sample.

*2.12. Pyrolysis of compound **4***

The procedure was similar to the pyrolysis of **2**. A sample of **4** (0.800 g, 2.02 mmol) was heated at 220° C for 1 h. Crystals of $MeGaCl_2(quin)$ (0.13 g, 27% yield) were obtained after the crude product was recrytallized from toluene (4 ml). ^1H-NMR and IR spectra of the product were identical with those of the authentic sample.

*2.13. Pyrolysis of compound **5***

The procedure was similar to the pyrolysis of **2**. A sample of **5** (1.00 g, 2.00 mmol) was heated at 230° C for 3 h. Crystals of $MeGaCl_2(quin)$ (0.20 g, 37% yield) were obtained after the crude product was crystallized from toluene (3 ml). ^1H-NMR and IR spectra of the product were identical with those of the authentic sample.

2.14. X-ray data collection, structure solution and refinement

Suitable crystals of compounds **1** and **2** were mounted on glass fibers under N_2 atmosphere. The data collections were conducted in a Siemens SMART system. In each experiment, an initial set of cell constants was calculated from reflections harvested from three sets of 20 frames. These sets of frames were oriented so that orthogonal wedges of reciprocal space were surveyed. A randomly oriented region of reciprocal space was surveyed to the extent of 1.3 hemispheres to a resolution of 0.84 Å. Three major swaths of frames were collected with 0.30° steps in ω. The data collection technique was generally known as a hemisphere collection. The final cell constants were calculated from 3557 strong reflections for **1** and 5927 for **2**.

The space groups $P2_1/n$ for **1** and $P2_1$ for **2** were determined based on systematic absences and intensity statistics. Successful direct-methods solutions were applied to both structures that provided most non-hydrogen atoms from the E-maps. Several full-matrix, least-squares/difference Fourier cycles were performed which located the remainder of the non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters.

All calculations were performed using SGI INDY R4400-SC or Pentium computers and the SHELXTL V5.0 suite of programs. The experimental conditions and unit cell information are summarized in Table 1.

3. Results

*3.1. Reaction of $GaCl_3$ with one equivalent of $Li[N(SiMe_3)_2]$; isolation of compound **1***

The reaction of $GaCl_3$ with one equivalent of $Li[N(SiMe_3)_2]$ in benzene afforded a white precipitate and a yellow sticky solid after filtration and removal of the solvent. The precipitate included LiCl but its weight was much larger than the calculated value assuming that one equivalent of LiCl was formed in the reaction. The ^1H-NMR spectrum of the sticky solid obtained from the filtrate exhibited more than ten singlets in the region of 0.03–0.50 ppm with the highest peaks at 0.29, 0.27 and 0.09 ppm. A small amount of $(Me_3SiNSiMe_2)_2$ (**1**) (5% yield based on silicon) was isolated via sublimation of the raw product. Extensive attempts to isolate and characterize other products failed. The isolation of **1** was reproducible and its identity was unambiguously confirmed by single crystal XRD, ^1H-NMR and mass spectroscopy.

Compound **1** had been previously synthesized via several methods [12–15] and its structure was determined in 1962 [16]. The structure possessed a Si_2N_2 ring with each nitrogen atom bonded to two silicon atoms and a terminal $SiMe_3$ group and each silicon atom to two nitrogen atoms and two methyls (Scheme 1). The structure obtained in our experiment was essentially the same as that previously reported. The unit cell volume was found to be 942.26(9) Å^3, 24 Å^3 lower than the previously reported value. The Si–N bond lengths were 1.718(3) (terminal), 1.750(2) (bridging) and 1.752(2) Å (bridging), comparable to the previously reported values, 1.71(4), 1.72(4) and 1.72(4) Å. Selected bond lengths and angles of **1** are given in Table 2.

Table 1
Crystal data and structure refinement parameters for compounds **1** and **2**

Empirical formula	$C_{10}H_{30}N_2Si_4$ (**1**)	$C_{13}H_{31}Cl_2Ga_2Si_2$ (**2**)	
Formula weight	290.72	412.20	
Temperature (°C)			−100
Color	Colorless	Colorless	
Habit	Block	Plate	
Size (mm^3)	0.30 × 0.25 × 0.25	0.90 × 0.60 × 0.40	
Space group	$P2_1/n$	$P2_1$	
Unit cell dimensions			
a (Å)	6.6553(4)	6.7764(2)	
b (Å)	13.1345(7)	13.3672(4)	
c (Å)	11.1129(6)	11.3334(3)	
β (°	104.076(1)	105.6180(10)	
V ($Å^3$)	942.26(9)	988.69(5)	
Z			2
λ (Å)			0.71073
μ (cm^{-1})	3.00	17.77	
Total reflections	4718	7070	
Independent reflections	1648 [$R_{int} = 0.0773$]	3393 [$R_{int} = 0.0273$]	
Parameters	74	181	
R_1 [$I > 2\sigma(I)$], wR_2 (all data)[a]	0.0583, 0.1522	0.0230, 0.0519	

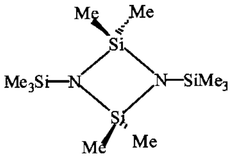
[a] $R_1 = \Sigma||F_o| - |F_c||\Sigma|F_o|$ and $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + (bP)]$, $P = (F_o^2 + 2F_c^2)/3$ and a, b are constants.

*3.2. Synthesis and characterization of compounds **2**–**5** and the structure of **2***

Compounds **2**–**5** were isolated as colorless crystalline solids in good yields (74–85%) from the reactions of $GaCl_3$(quin) or $GaCl_3(NMe_3)$ with the corresponding lithium amide compounds (Scheme 2), and were characterized by elemental analysis and spectroscopic methods. The structure of **2** was determined by single crystal XRD. The new reactant, $Li[N(SiMe_3)(2,6\text{-}^iPr_2C_6H_3)]$, was obtained as a colorless solid in 76% yield from the reactions described in Section 2.

The C–H–N analysis results for compounds **2**, **4** and **5** were satisfactory. In our repeated efforts to prepare a sample of **3** for elemental analysis the crystals of **3** turned into a glassy solid within several hours in a glass vial that had been sealed under vacuum. Repeated analytical data from these samples were inconsistent with each other suggesting decomposition had occurred. The molecular ions (+1) were found with the intensities ranging from 0.5 to 4.7% of the base peaks in the chemical ionization mass spectra of all the four compounds. The ^{1}H-NMR spectra of **2**–**5** were consistent with their formulas. It was noteworthy that the two doublets at 1.31 and 1.39 ppm in the spectrum of **5** were due to the magnetic inequivalency of the two methyls in each $-CHMe_2$ group.

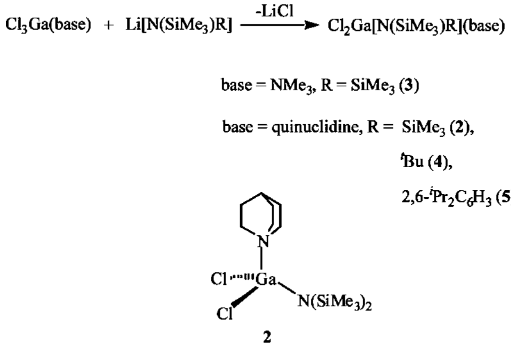
Selected bond lengths and angles for **2** are given in Table 3. In the structure of **2** (Fig. 1), the gallium atom adopted a distorted tetrahedral geometry with the bond angles N(2)–Ga(1)–N(1) [113.56(7)°], N(2)–Ga(1)–Cl(1) [115.13(11)°] and N(2)–Ga(1)–Cl(2) [118.46(10)°] being significantly larger than other angles on gallium [100.57(9)–104.67(2)°]. The sum of the angles around the three-coordinate N(2) was 357.0(5)° and the two Si atoms were slightly non-planar with Ga(1) and N(2) in a manner such that the two $SiMe_3$ groups bent away from the quinuclidine ligand. The Ga(1)–N(2)–Si(1) and Ga(1)–N(2)–Si(2) bond angles were 116.64(16) and 121.43(18)°, respectively. The distortion from a perfect planar geometry on N(2) and the different Si–N–Ga bond angles were attributed to the ligand steric interactions as indicated by the short distances of C(3)···C(9) (3.680 Å), C(5)···C(13) (3.530 Å) and C(10)···C(12) (3.264 Å). This crowdedness was also reflected in the shorter van der Waal's contacts of Ga(1)···C(13) (3.534



Scheme 1.

Table 2
Selected bond lengths (Å) and bond angles (°) for $(Me_3SiNSiMe_2)_2$ (**1**)

Bond lengths			
Si(1)–N(1)	1.752(2)	Si(1)–C(1)	1.864(3)
Si(1)–N(1A)	1.750(2)	Si(1)–C(2)	1.865(3)
Si(2)–N(1)	1.718(3)		
Bond angles			
N(1)–Si(1)–N(1A)	89.45(12)	C(1)–Si(1)–C(2)	108.5(2)
N(1)–Si(1)–C(1)	115.23(13)	Si(1)–N(1)–Si(1A)	90.55(12)
N(1)–Si(1)–C(2)	114.02(13)	Si(1)–N(1)–Si(2)	134.53(13)
N(1A)–Si(1)–C(1)	113.76(13)	Si(2)–N(1)–Si(1A)	133.88(13)
N(1A)–Si(1)–C(2)	115.13(14)		



Scheme 2.

Table 3
Selected bond lengths (Å) and angles (°) for $Cl_2Ga[N(SiMe_3)_2](quin)$ (**2**)

Bond lengths			
Ga(1)–N(1)	2.0293(18)	Ga(1)–Cl(2)	2.1952(8)
Ga(1)–N(2)	1.8658(17)	N(2)–Si(1)	1.757(3)
Ga(1)–Cl(1)	2.2011(8)	N(2)–Si(2)	1.747(3)
Bond angles			
N(1)–Ga(1)–N(2)	113.56(7)	Cl(1)–Ga(1)–Cl(2)	104.67(2)
N(1)–Ga(1)–Cl(1)	100.57(9)	Ga(1)–N(2)–Si(1)	116.64(16)
N(1)–Ga(1)–Cl(2)	102.19(9)	Ga(1)–N(2)–Si(2)	121.43(18)
N(2)–Ga(1)–Cl(1)	115.13(11)	Si(1)–N(2)–Si(2)	118.95(10)
N(2)–Ga(1)–Cl(2)	118.46(10)		

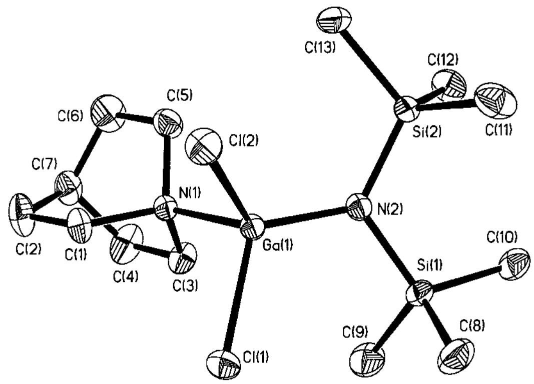


Fig. 1. Molecular structure and atom labeling scheme for $Cl_2Ga[N(SiMe_3)_2](quin)$ (**2**). Atoms are shown at the 50% probability level. All hydrogen atoms are omitted for clarity.

Å) and Ga(1)···C(8) (3.752 Å), whereas the regular van der Waals radii of Ga and a methyl were 1.9 [17] and 2.0 Å [18], respectively. The dative Ga(1)–N(1) bond length [2.0293(18) Å] was longer than that in $Cl_2GaH(quin)$ [2.017(3) Å] [10] due to the larger steric repulsion in **2**, but shorter than the corresponding Ga–N bond in $H_2Ga[N(SiMe_3)_2](quin)$ [2.108(2) Å] [19] reflecting the higher Lewis acidity on gallium for the $Cl_2Ga[N(SiMe_3)_2]$ species. The Ga(1)–N(2) bond length [1.8658(17) Å] was typical for the terminal Ga–N bonds (1.82–1.94 Å) [20].

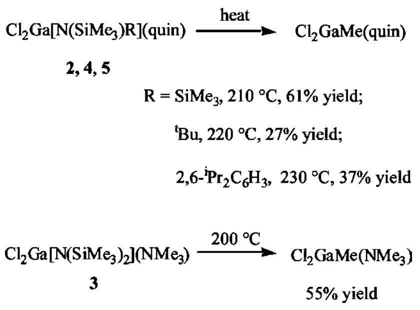
*3.3. Isolation of compounds **6** and **7** from thermolysis of compounds **2**–**5***

When compounds **2**–**5** were heated to 200–230° C for a period of 0.5–3 h, methyl abstraction yielded **6** or **7** in 27–61% yields based on gallium (Scheme 3). These products were purified by sublimation and recrystallization from toluene or a mixture of toluene and hexanes. By-products from the thermal decomposition of **2**–**5** were glassy, yellow or brown solids whose ^1H-NMR spectra exhibited unresolved, complicated patterns. Attempts to isolate and characterize these materials were unsuccessful. Compounds **6** and **7** were also prepared independently from the reactions of $MeGaCl_2$ with quinuclidine and NMe_3, respectively.

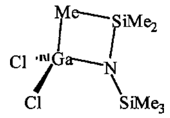
4. Discussion

4.1. Proposed mechanisms for the Si–C bond cleavage and methyl migration from Si to Ga

As previously mentioned, [9] $[Li(THF)_2][GaN(SiMe_3)_2(OSiMe_3)_2Cl]$ was synthesized from the reaction of $GaCl_3$ with one equivalent of $Li[N(SiMe_3)_2](THF)_n$ followed by addition of two equivalents of $LiOSiMe_3$ in THF. $Ga[N(SiMe_3)_2](OSiMe_3)_2(pyridine)$ was obtained if hexane was used as the solvent in the second step and pyridine was added [9]. These results indicated that $Cl_2Ga[N(SiMe_3)_2](THF)$ formed in the first step was stable for at least a period of time allowing its reaction with $LiOSiMe_3$. With the use of benzene in this work, $Cl_2Ga[N(SiMe_3)_2]$, if formed, was unstable at room temperature. The isolation of **1**, which possessed $SiMe_2$ moieties, clearly indicated the cleavage of a Si–C bond presumably from a gallium-coordinated $N(SiMe_3)_2$ ligand. The loss of a β-methyl from $N(SiMe_3)_2$ could lead to a reactive intermediate, '$Me_3SiN{=}SiMe_2$', dimerization of which would afford compound **1**. '$Me_3SiN{=}SiMe_2$' had been previously proposed to be the intermediate in several reactions leading to **1** [15,16]. Because of the complexity with the presence of Cl, Li and Ga in the reaction system



Scheme 3.



Scheme 4.

and the reactive nature of the Si=N compound, [21] dimerization would not be expected to be the only reaction, perhaps explaining the low yield of **1** and formation of other uncharacterized products.

Strong bases, quinuclidine and NMe$_3$, stabilized the species Cl$_2$Ga[N(SiMe$_3$)$_2$], implying that the coordinative unsaturation of gallium was responsible for the Si–C bond cleavage in the reaction of GaCl$_3$ with Li[N(SiMe$_3$)$_2$]. The isolation of good yields of **6** (61%) and **7** (55%) from the thermolysis of **2** and **3** indicated that at higher temperatures a β-methyl migrates from a SiMe$_3$ group to Ga. The pyrolysis of **4** and **5** indicated that this type of methyl migration was general.

Because of the electronegativity difference between Si and C, the methyls in the SiMe$_3$ groups were partially negatively charged. The delocalization of the lone pair electrons of the N to Si through the pπ–dπ interaction in N(SiMe$_3$)$_2$ enhanced the negative charges on C atoms. Although an intermolecular process could not be ruled out, the Si–C bond cleavage in the reaction of GaCl$_3$ and Li[N(SiMe$_3$)$_2$] possibly occurred via an intermediate with bridging Me and N between Ga and Si as shown in Scheme 4. The higher reaction temperatures needed to promote the β-methyl elimination in **2**–**5** were consistent with a required quinuclidine or trimethylamine dissociation to form an open coordination site on gallium. Compared with the quinuclidine adducts (**2**, **4** and **5**), the decomposition of compound **3** took place at a lower temperature, consistent with the lower basicity, and thus, the lower stabilizing power, of NMe$_3$ over quinuclidine. This observation supports the above mechanism, however, more quantitative studies would be required to clarify the nature of the β-methyl elimination step. Finally, a methyl migration from silicon to gallium was previously found in the reaction of GaCl$_3$ with SiMe$_4$ for which an intermediate with bridging Cl and Me between Si and Ga was suggested by Schmidbaur and Findeiss [22].

4.2. Comparisons with related compounds and reactions in Group 13 chemistry

The amido-bridging ligands in [Cl$_2$GaN(H)SiMe$_3$]$_2$ and [Cl$_2$GaN(Me)SiMe$_3$]$_2$ were stable at room temperature, and partial elimination of Me$_3$SiCl rather than a methyl migration occurred for [Cl$_2$GaN(H)SiMe$_3$]$_2$ at elevated temperatures [8]. The enhanced stability of NHSiMe$_3$ and N(Me)SiMe$_3$ containing complexes compared to those bearing a N(SiMe$_3$)$_2$ ligand is probably due to their smaller size which promotes the stability of the dimeric structures. The reactions of GaCl$_3$ with two and three equivalents of LiN(SiMe$_3$)$_2$ in ether afforded stable ClGa[N(SiMe$_3$)$_2$]$_2$ [23] and Ga[N(SiMe$_3$)$_2$]$_3$, [23,24], respectively. Both are monomeric with trigonal planar gallium and nitrogen atoms [23]. Apparently, the reduced Lewis acidities in these complexes compared with that in the suggested dichlorogallium intermediate (Scheme 4) is insufficient to induce methyl migration.

Monomeric Cl$_2$BN(SiMe$_3$)$_2$ was prepared from the reaction of BCl$_3$(OEt$_2$) with LiN(SiMe$_3$)$_2$ [25] or the reaction of BCl$_3$(NEt$_3$) with HN(SiMe$_3$)$_2$ [26]. Me$_3$SiCl elimination took place from Cl$_2$BN(SiMe$_3$)$_2$ at higher temperatures affording trimeric (ClBNSiMe$_3$)$_3$ [25]. The stability of Cl$_2$BN(SiMe$_3$)$_2$ was largely attributed to the reduced Lewis acidity on B because of the pπ–pπ interaction between N and B. However, compound **1** and R$_2$N(Me)BN(SiMe$_3$)$_2$, where R = Et and ^{i}Pr, formed when R$_2$N(Cl)BN(SiMe$_3$)$_2$ reacted with one equivalent of Na[N(SiMe$_3$)$_2$] in refluxing xylene [25]. Finally, the reactions of AlCl$_3$ and InCl$_3$ with one equivalent of Li[N(SiMe$_3$)$_2$] afforded ClAl[N(SiMe$_3$)$_2$]$_2$ (30% yield) [27] and Me(Cl)In[N(SiMe$_3$)$_2$] (no exact yield but a statement that the yield was lower than 65% was given), [28] respectively.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 170545 and 170546 for compounds **1** and **2**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB12 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

6. Note added in proof

A report has appeared describing the formation of [MeGaCl$_2$]$_2$ from the reaction of GaCl$_3$ with N(SiMe$_3$)$_3$. See C.J. Carmalt, J.D. Mileham, A.J.P. White, D.J. Williams, J.W. Steed, Inorg. Chem. 40 (2001) 6035

Acknowledgements

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