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# Synthesis and structures of $M(Me_3SiNCHNSiMe_3)_3$ (M = Al, Ga) via reactions of M-hydrides with $Me_3SiNCNSiMe_3$

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**Reactions of $LiAlH_4$ and $LiGaH_4$ with $Me_3SiNCNSiMe_3$ yield, respectively, the monomeric hexacoordinate $Al(Me_3SiNCHNSiMe_3)_3$ (1) and $Ga(Me_3SiNCHNSiMe_3)_3$, (2) metal amidinate compounds. A unique feature of the work is the creation of the previously unknown bidentate $[Me_3SiNCHNSiMe_3]$ anion ligand which shows the propensity to fully encapsulate the Al and Ga metal centers despite potential steric crowding associated with the six-fold coordination. Compound 1 was also obtained by the reaction of $(Me_3N)AlH_3$ with $Me_3SiNCNSiMe_3$ via displacement of $NMe_3$ followed by reduction of the carbodiimide group. The structural properties of 1 and 2 derived from single crystal X-ray diffraction are elucidated and compared with various coordination analogs.**


**KEYWORDS:** amidinates; cyanamide; hexacoordinate aluminum and gallium

## INTRODUCTION

There is considerable interest in the synthesis of high-performance ceramics containing large concentrations of light elements such as carbon and nitrogen.[1] A highly desirable class of materials that fulfils this requirement is based on group III cyanamides with stoichiometry $LiM(NCN)_2$ (M = B, Al, Ga). The structure of the target systems can be viewed as a $[M(NCN)_2]^{1-}$ anion framework with $SiO_2$ crystobalite structure in which the $O^{2-}$ is replaced by the linear carbodiimide moiety $(-N{=}C{=}N-)^{2-}$.[2] The lithium counterions are presumed to occupy the interstitial tetrahedral sites and provide a charge balance in the crosslinked polymeric solid. The anticipated structure is analogous to filled crystoballite and an excellent example of this is $LiPN_2$ in which the Li atoms are situated in the tetrahedral holes of the framework of $PN_4$ tetrahedra.[3]

One strategy toward the synthesis of such compounds including $LiB(NCN)_2$, $LiAl(NCN)_2$ and $LiGa(NCN)_2$ involves reactions of 1,3-bis-(trimethylsilyl)carbiimide $Me_3SiNCNSiMe_3$ (Me = $CH_3$) with $LiMX_4$ (X = F,Cl). However, our attempts using this route resulted in disproportionation of LiX leading to lithium-deficient amorphous powders containing –M–NCN–M– functionalities as evidenced by spectroscopic characterizations. We therefore adopted an alternative approach based on the reaction of $LiMH_4$ with $Me_3SiNCNSiMe_3$ as described by equation (1):

$$LiMH_4 + 2Me_3SiNCNSiMe_3 \longrightarrow LiM(NCN)_2 + 4\,Me_3SiH\ (M = B,Al,Ga) \qquad (1)$$

This was envisaged to yield trimethylsilane and a ternary cyanamide via desilylation of the $Me_3SiNCNSiMe_3$ source. However, initial attempts toward this synthesis resulted in an unexpected but intriguing result. We found that the reaction involving Al, Ga yielded the monomeric hexacoordinate $Al(Me_3SiNCHNSiMe_3)_3$ (**1**) and $Ga(Me_3SiNCHNSiMe_3)_3$ (**2**) species, respectively, which incorporate the $[Me_3SiNCHNSiMe_3]^{1-}$ bidentate anion instead of the $(-N{=}C{=}N-)^{2-}$ linear unit (see Fig. 1). A polycrystalline precipitate was also isolated and identified by its spectroscopic properties to be the previously reported $LiNCNSiMe_3$ salt.[4] While this approach did not yield the hypothetical $LiM(NCN)_2$ extended frameworks, it did produce the new molecular compounds **1** and **2** possessing

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interesting structural properties that are of fundamental interest. This work also establishes a potentially useful synthetic pathway to producing coordination complexes in the general amidinate class of compounds. Amidimate moieties of the general formula –(R1)N–C(R2)–N(R1)–[where (R1, R2) = Me, Ph, Et] have been utilized in prior studies to produce partially substituted compounds of Ga and Al.[5] In this regard a unique feature of the work is the creation of the $[Me_3SiNCHNSiMe_3]^{1-}$ anion, which shows the propensity to fully encapsulate the Al and Ga metal centers despite the potential for steric crowding associated with the six-fold coordination.

We note that, since the reaction of $Me_3SiNCNSiMe_3$ with $Al(CH_3)_3$, proceeds via methylation of the central C of (–N═C═N–) to form the monomeric $Me_2Al[Me_3SiNC(CH_3)NSiMe_3]$[6], analogous reactions with Al and Ga molecular hydrides might produce partially coordinated alanes and gallanes such as $MH_{3-x}(Me_3SiNCHNSiMe_3)_x$ with potential uses in materials science. Accordingly, we briefly explore this concept in this study (as discussed below) using reactions of the well-known $(Me_3N)AlH_3$ with $Me_3SiNCNSiMe_3$ to produce coordinated Al systems via displacement of $NMe_3$ and subsequent reduction of the carbodiimide group. In this paper we describe in detail the above syntheses and elucidate the structural properties of the new compounds **1** and **2**.

## RESULTS AND DISCUSSION

The reaction of $Me_3SiNCNSiMe_3$ with $LiAlH_4$ in 3 : 1 molar ratio produced $LiNCNSiMe_3$, $Me_3SiH$ and $Al(Me_3SiN\text{-}CH\text{-}NSiMe_3)_3$ (**1**). Minor byproducts of partially substituted alanes were also detected in the reaction mixture. A plausible reaction mechanism leading to the formation of these compounds is summarized by equations (2) and (3).

$$LiAlH_4 + Me_3SiNCNSiMe_3 \longrightarrow LiNCNSiMe_3 + {}'AlH_3' + Me_3SiH \quad (2)$$

$${}'AlH_3' + (3-x)Me_3SiNCNSiMe_3 \longrightarrow H_{3-x}Al(Me_3SiNCHNSiMe_3)_x \ (x = 1\text{–}3) \quad (3)$$

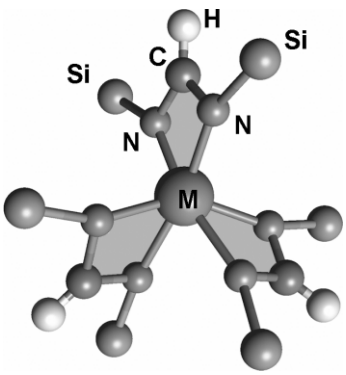


**Figure 1.** Structural representation of compound **1** and **2** showing the six-fold coordinated structure. Note that the Si, N, C and H atoms are co-oplanar. The methyl groups of the $-SiMe_3$ ligand are not shown for clarity.

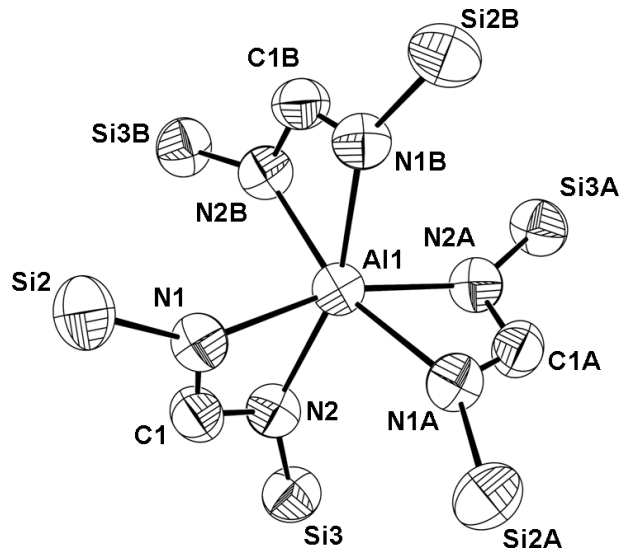


**Figure 2.** Molecular core of compound **1** showing the central Al metal and the three chelating ligands including the Si atoms. In each 'propeller' the Al–N–C–N ring and the two corresponding Si atoms reside on the same plane.

According to this reaction pathway the $LiNCNSiMe_3$ salt is initially formed along with a transient '$AlH_3$' species. This in turn combines with $Me_3SiNCNSiMe_3$ to generate $H_xAl[Me_3SiNCHNSiMe_3]_{3-x}$ ($x = 1, 2$) intermediates via hydrogen reduction of the carbodiimide group. Successive reductions of the ligands eventually yield the fully hexacoordinated compound **1**. The lithium salt was readily isolated in substantial yields and identified by its IR spectrum which matched exactly previously published data.[4] Furthermore, its combustion analysis for C, H, and N as well as the $^7Li$ NMR spectrum was consistent with the $LiNCNSiMe_3$ formula.

Compound **1** was isolated as slightly air-sensitive colorless crystals that do not melt but decompose upon heating at $T > 250\,^{\circ}C$. Single-crystal X-ray diffraction revealed a molecular structure in which a single Al(III) center is coordinated by three $[Me_3SiNCHNSiMe_3]^{1-}$ bidentate ligands as shown in Fig. 2. These 'aminidate' groups form three Al–N–C–N 'propeller paddles' terminated by six $-SiMe_3$ groups, surrounding the central metal atom. The Al–N–C–N ring and the two corresponding Si atoms lie virtually on the same plane within each 'propeller paddle'. A detailed account of the structural properties is presented below where comparison is made with the closely related structure of the Ga analog.



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The identity of **1** was further corroborated by elemental analysis and spectroscopic methods including NMR, IR and mass spectrometry. Combustion analysis results for C, H and N were found to be consistent with the $C_{21}H_{57}AlN_6Si_6$ composition of the molecule. In spite of its large molecular weight, the compound is significantly volatile in the mass spectrometer. The highest mass peak appeared at 588 amu and the observed isotopic pattern matched the one calculated for the parent ion ($M^+$). The IR spectra showed strong adsorptions at 1542 and 1518 $cm^{-1}$ corresponding to Al–N–CH–N ring vibrations. The presence of the Al atom in the structure was verified by $^{27}Al$ NMR, which revealed a single sharp resonance at 21.52 ppm. The expected $^1H$- and $^{13}C$-NMR peaks of the $Si(CH_3)_3$ groups were observed to be at 0.22 and 0.77 ppm, respectively. In addition, the $^1H$- and $^{13}C$ NMR spectra showed peaks at 7.98 and 169.92 ppm, respectively, which are consistent with a 'C–H' component within the 'propeller' ring structure. The two-dimensional HMQC (heteronuclear multiple quantum coherence) spectrum indicates that this proton (7.98 ppm) is directly bonded to the ring carbon (169.92 ppm), confirming the presence of a conjugated bonding configuration within the planar core of the chelating ligand.

The above results prompted us to pursue stoichiometric reactions of the well-known trimethylamine alane, $(Me_3N)AlH_3$, with $Me_3SiNCNSiMe_3$ as an alternative synthesis route of **1.** In addition, these reactions were explored as a potential pathway to partially substituted alane derivatives. An objective was to systematically produce such compounds in high-purity yield for possible applications in materials synthesis. The initial experiments involved a 1 : 3 molar ratio of $(Me_3N)AlH_3$ and $Me_3SiNCNSiMe_3$ as shown by equation (4).

$$(Me_3N)AlH_3 + 3\ Me_3SiNCNSiMe_3 \longrightarrow Al(Me_3SiNCHNSiMe_3)_3 + Me_3N \quad (4)$$

This reaction produced a viscous liquid which was crystallized in hexane to form large transparent crystals of compound **1** as evidenced by their NMR, IR and mass spectra. A colorless liquid was also obtained from the hexane solution and was extensively analyzed by IR and NMR (including $^{27}Al$, $^{13}C$ and $^1H$). Collectively, the data suggested a mixture of the $H_2Al(Me_3SiNCHNSiMe_3)$ and $HAl(Me_3SiNCHNSiMe_3)_2$ indicating that proposed mechanism shown by equations (2) and (3) is consistent with the formation of partially substituted intermediates en route to the fully coordinated species. A similar reaction mechanism has been observed in the formation of related amidinate metal compounds. Our observation of such intermediates prompted us to explore stoichiometric reactions of $(Me_3N)AlH_3$ with $Me_3SiNCNSiMe_3$ in 1 : 1 and 1 : 2 molar ratios to promote the formation of $H_2Al(Me_3SiNCHNSiMe_3)$ and $HAl(Me_3SiNCHNSiMe_3)_2$, respectively, as the primary product. These experiments invariably produced mixtures of the compounds which could not be fully separated by simple distillation techniques without significant decomposition. Because of this fundamental limitation, this approach was not pursued any further in the present study.

The successful preparation of **1** using $LiAlH_4$ prompted us to pursue analogous reactions with $LiGaH_4$ to explore the synthesis of the gallium analog, $Ga(Me_3SiNCHNSiMe_3)_3$ (**2**). For reactant ratios less than 4 : 1, according to equation (5), we obtained mixtures of compound **2** and partially substituted gallanes.

$$LiGaH_4 + 4Me_3SiNCNSiMe_3 \longrightarrow LiNCNSiMe_3 + Me_3SiH + Ga(Me_3SiNCHNSiMe_3)_3 \quad (5)$$

We therefore employed an excess of $Me_3SiNCNSiMe_3$ with $LiGaH_4$ in *n*-butyl ether to ensure full substitution of the Ga center. A single crystal structural determination showed that **2** is isostructural to **1**. Compound **2** was also characterized by spectroscopic methods, and by C,H,N combustion analysis, which is consistent with the $C_{21}H_{57}GaN_6Si_6$ formula. The IR spectrum showed two closely spaced and very intense bands at 1586 and 1555 $cm^{-1}$ assigned to $\nu_{as}$N–CH–N. Strong Si–Me bonds were also observed at 1255 and 842 $cm^{-1}$. The highest mass peak (615 amu) corresponds to the expected isotopic pattern for ($M^+ - Me$) while the strongest peak centered at 444 amu is associated with $[M^+ - (Me_3SiNCHNSiMe_3)]$. The NMR analyses again confirm the presence of aromatic 'C–H' units (7.79 ppm) within the ring structures.

## Structural analyses of 1 and 2

The crystallographic analyses of **1** and **2** revealed that the compounds are monomeric in the solid state. In both cases

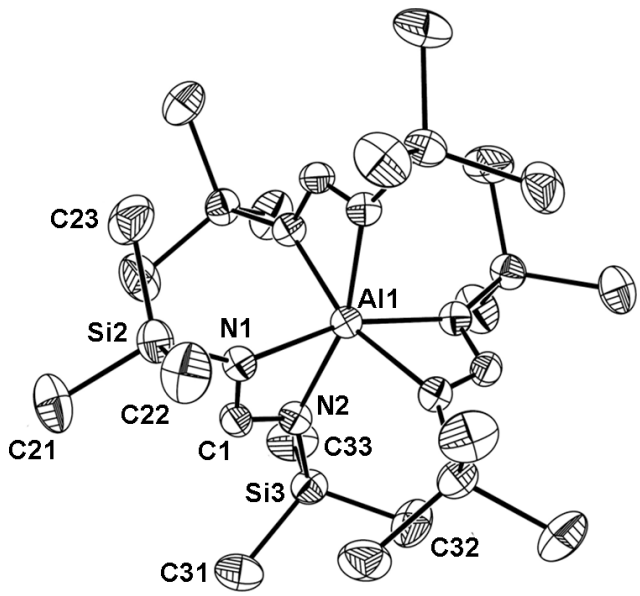


**Figure 3.** Molecular structure of $Al(Me_3SiNCHNSiMe_3)_3$ (**1**) showing all constituent atoms except the hydrogens. The Ga analog **2** has a virtually identical structure.



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**Table 1.** Selected bond distances (Å) and bond angles (degrees) for **1** and **2**

| | | | |
|---|---|---|---|
| Bond distances | | | |
| Al1–N1 | 2.0166(17) | Ga1–N1 | 2.0862(17) |
| Al1–N1 | 2.0282(18) | Ga1–N2 | 2.0911(17) |
| Al1–C1 | 2.364(2) | Ga1–C1 | 2.437(2) |
| Si2–N1 | 1.7386(18) | Si2–N1 | 1.7345(18) |
| Si2–C22 | 1.860(3) | Si2–C21 | 1.857(3) |
| N1–C1 | 1.322(3) | N1–C1 | 1.314(3) |
| Bond angles | | | |
| N1–Al–N1 | 99.95(7) | N1–Ga1–N1 | 101.03(6) |
| N1–Al–N2 | 67.82(7) | N1–Ga1–N2 | 65.51(6) |
| N1–A1–N2 | 162.98(7) | N1–Ga1–N2 | 161.02(6) |
| N2–Al–N2 | 100.28(7) | N2–Ga1–N2 | 101.06(6) |
| C1–Al–C1 | 120.000 | C1–Ga1–C1 | 119.999(1) |
| N1–Si2–C23 | 108.17(11) | N1–Si2–C23 | 108.23(11) |
| C1–N1–Si2 | 125.67(15) | C1–N1–Si2 | 126.71(16) |
| C1–N1–Al | 87.55(13) | C1–N1–Ga | 88.55(13) |
| Si2–N1–Al | 145.69(11) | Si2–N1–Ga | 143.65(11) |
| N2–C1–N1 | 117.45(19) | N2–C1–N1 | 117.86(19) |

the central metal is uniquely bonded to six nitrogen atoms. In compound **1** the Al–N1 and Al–N2 bond lengths are 2.0166(17) and 2.0282 (18) Å respectively (Fig. 3, Table 1). As expected these are longer than the typical Al–N bonds [1.928(2), 1.929(2) Å] found in the lower coordination analogs such as $Me_2Al[Me_3SiNC(CH_3)NSiMe_3]$ compound and the four-membered ring structure of $[Br(CH_3)AlN_3]_4$ in which Al–N is ~1.92 Å.[7] In compound **2** the Ga–N1 and Ga–N2 bond lengths [2.0862(17), 2.0911(17) Å] are slightly elongated relative to those in **1** and substantially longer than the four coordinate Ga–N (1.96 Å) bonds found in the $[Cl(CH_3)GaN_3]_4$[8] compound. This is consistent with a simple bond valence estimate which predicts a bond length difference of 0.15 Å between four-coordinate and six-coordinate Ga-nitrogen compounds and indicates that the observed Ga–N bond length distribution is not significantly affected by steric crowding.[9] The 'propeller paddle' structures in both compounds are nearly identical in terms of bond distances.

The three aromatic 'C–H' units and the central metal atom define the equatorial plane of the propeller structure. Accordingly the C1–M–C1 (see Fig. 2 for labeling) angles is exactly 120° within experimental error for M = Al, Ga. We denote the nitrogens in the 'propeller paddles' according to their position (top and bottom) relative to this equatorial plane. The angles between an adjacent pair of top or bottom nitrogens and the central metal atom [N1–M–N1 and N2–M–N2], respectively span a very narrow range of 100°–101°.

Besides the metal nitrogens bonds, the internal ring structure of the 'paddles' also involves two equivalent nitrogen–carbon bonds of the amidinate ligand such as N1–C1 and N2–C1. These range from 1.314 to 1.322 Å and are typical of $sp^2$ hybridized C–N cyclic structures.[10] The internal ring bond angles for **1** are very similar to the corresponding angles for **2** (see Table 1).

**Table 2.** Structure determination summary for **1** and **2**

| Formula | $C_{21}H_{57}AlN_6Si_6$ | $C_{21}H_{57}GaN_6Si_6$ |
|---|---|---|
| a (Å) | 17.1836(8) | 17.1899(7) |
| c (Å) | 11.1924(8) | 11.2471(7) |
| V ($Å^3$) | 2862.1(3) | 2878.2(2) |
| FW | 589.25 | 631.99 |
| Z | 3 | 3 |
| space group | *R3* | *R3* |
| $\rho_{calc}$ ($gcm^{-3}$) | 1.026 | 1.094 |
| μ ($mm^{-1}$) | 0.260 | 0.923 |
| No. obs. reflns | 1995 | 2882 |
| R (obs. data %) | R = 3.20, wR = 7.18 | R = 3.48, wR = 6.79 |
| R (all data %) | R = 3.62, wR = 7.32 | R = 4.45, wR = 7.02 |
| a (weight/scheme) | 0.0429 | 0.0357 |

Each 'paddle' is terminated by two $-Si(CH_3)_3$ ligands whose connecting Si–N bonds are coplanar with ring structure of the 'paddle'. The Si–C and Si–N bond lengths in both molecules are in the ranges 1.85–1.88 and 1.73–1.74 Å, respectively which are close to the normal values found in Si–C and Si–N compounds.[11] The angle between the metal, the nitrogen of the paddle and the Si atom is also the same in both compounds with a typical value of ~145°. The orientation and packing of the terminal methyl groups in the outer coordination sphere is very symmetric and occurs in a manner that minimizes repulsions. In summary we note that the structural data overall do not suggest that the compounds are sterically hindered. Details of the crystallographic analysis for **1** and **2** are presented in the Experimental section and Table 2.

## EXPERIMENTAL

### General methods

Reactions were performed under purified nitrogen using standard Schlenk and drybox techniques. Solvents were dried over benzophenone ketyl and distilled under nitrogen prior to use. The NMR spectra were recorded on Gemini 300, Inova 400 and Inova 500 Varian spectrometers. NMR spectra for $^{13}C$, $^{27}Al$ and $^{7}Li$ were referenced to TMS, $AlCl_3$ and LiCl (in $D_2O/H_2O$), respectively. FTIR spectra were recorded on Nicolet Magna-IR 550 spectrometer. Elemental analyses were performed by Desert Analytics (Tucson, AZ, USA). Electron impact mass spectra were obtained on a Finnigan-MAT model 312 mass spectrometer (IE = 70 eV) in the Arizona State University departmental mass spectrometry facility. $GaCl_3$ and LiH (Aldrich) were used as received, and $LiAlH_4$ (Aldrich) was purified by extraction with ether. The $Me_3SiNCNSiMe_3$ species was prepared according literature methods[12] and its purity was checked by NMR and



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FTIR spectroscopy. $(Me_3N)AlH_3$ was prepared according to literature methods.[13] The toluene-$d_8$ and THF-$d_4$ NMR solvents were dried over Na/K alloy and vacuum-distilled prior to use.

### Preparation of $Al(Me_3SiNCHNSiMe_3)_3$ (1) via reactions of $LiAlH_4$

A *n*-dibutyl ether solution (150 ml) of $Me_3SiNCNSiMe_3$ (18.61 g, 100 mmol) was added slowly to a suspension of $LiAlH_4$ (0.947 g, 25 mmol) in 20 ml *n*-dibutyl ether. The mixture was stirred at room temperature for 3h to form a clear solution which was then heated at 140 °C for 18 h. During this time a colorless precipitate was formed. The solid was filtered and dried in vacuum and was identified by $^7$Li NMR, IR and elemental analysis to be $LiNCNSiMe_3$. The clear filtrate was cooled to −25 °C and, within a week, colorless blocky crystals were obtained (3.06 g, 21% yield). Anal. calcd for $C_{21}H_{57}AlN_6Si_6$: C, 42.80; H, 9.75; N, 14.26. Found: C, 42.67; H, 9.72; N, 14.29. IR (Nujol, $cm^{-1}$) 1542 (s), 1518 (s), 1289 (s), 1242 (s), 1025 (s), 845 (vs), 685 (w), 513 (m), 435 (w); $^1$H NMR (400 MHz, toluene-$d_8$) $\delta$ 7.98 and $\delta$ 0.22. $^{13}$C NMR (106 MHz, toluene-$d_8$) $\delta$ 169.92 and $\delta$ 0.77; $^{27}$Al NMR (104.2 MHz, toluene-$d_8$) $\delta$ 21.52. EIMS (*m*/*e*): isotopic envelopes centered at 588 for $M^+$ [$M = Al(Me_3SiNCHNSiMe_3)_3$], 573 ($M^+ - Me$), 401 [$M^+ - (Me_3SiNCHNSiMe_3)$] the strongest peak, 329 ($M^+ - Me_3SiNCHNSiMe_3 - SiMe_3$), 215 [$M^+ - 2(Me_3SiNCHN - SiMe_3)$], 171 ($Me_2SiNCHNSiMe_3 - Me$) and 147 ($Me_3SiSiMe_3$).

*$LiNCNSiMe_3$* (1.60 g, 50.9% yield): anal. calcd for $C_4H_9LiN_2Si$: C, 39.98; H, 7.50; N, 23.31. Found: C, 38.70; H, 7.34; N, 21.60. IR (Nujol, $cm^{-1}$) 3429 (w), 2117 (vs,b), 1338 (s), 1251 (s), 845 (vs,b), 766 (m), 755 (m), 745 (ms), 692 (s), 641 (m), 625 (m), 571 (m), 431 (ms,b), and 381 (ms,b). $^1$H NMR (THF) $\delta$ − 0.04; $^7$Li NMR (THF) $\delta$ 0.61.

### Preparation of $Al(Me_3SiNCHNSiMe_3)_3$ (1) using $(Me_3N)AlH_3$

A toluene solution (40 ml) of $Me_3SiNCNSiMe_3$ (4.014 g, 21.6 mmol) was added slowly at −78 °C, to a solution (20 ml in toluene) of $(Me_3N)AlH_3$ (0.64 g, 7.2 mmol). The mixture was stirred at 22 °C for 2 h and then refluxed for an additional 4 h after which the volatiles were removed in vacuum to yield a colorless solid. This was dissolved in hexane and cooled to −25 °C to form single crystals of compound **1** (1.49 g, 35% yield).

### Preparation of $Ga(Me_3SiNCHNSiMe_3)_3$ (2)

A *n*-dibutyl ether solution (40 ml) of $Me_3SiNCNSiMe_3$ (9.24 g, 49.6 mmol) was added at −78 °C, to a solution of $LiGaH_4$ (1.00 g, 12.4 mmol) in 40 ml of *n*-dibutyl ether. This was warmed slowly to 25 °C and then heated at 100 °C for 18 h. During this time a grey-white solid was formed which was extracted with dry THF to remove any possible Ga metal impurities (due to decomposition of $LiGaH_4$) and recrystallized at −25 °C to yield pure $LiNCNSiMe_3$ (0.614 g, 41.2% yield). The volatiles were removed from the filtrate to yield a colorless solid which was recrystallized in hexane at (−25 °C) to form large crystals of compound **2**, (0.9 g, 12% yield). Anal. calcd for $C_{21}H_{57}GaN_6Si_6$: C, 38.90; H, 9.03; N, 13.30. Found: C, 38.90; H, 8.98; N, 12.34: IR (Nujol, $cm^{-1}$) 1545 (s), 1520 (s), 1286 (s), 1255 (ms), 1242 (s), 1015 (s), 1001 (w), 687 (w), 842 (vs, b), 424 (ms); $^1$H NMR (500.6 MHz, toluene-$d_8$) $\delta$ 7.79, and $\delta$ 0.23; $^{13}$C NMR (125 MHz, toluene-$d_8$) $\delta$ 166.98 and $\delta$ 1.22; EIMS (*m*/*e*): isotopic envelopes centered at 615 ($M^+ - Me$, where $M^+$ is the parent ion), 444 [$M^+ - (Me_3SiNCHNSiMe_3)$], the strongest peak], 257 [$M^+$ $2(Me_3SiNCHNSiMe_3)$], 187 $[Me_3SiNCHNSiMe_3]^+$, 146 $[Me_3SiSiMe_3]^+$, 131 $[Me_2SiSiMe_3]^+$ and 73 $(Me_3Si)^+$.

### Structural determination of (1) and (2)

Colorless polyhedral crystals of **1** (0.15 × 0.20 × 0.30) mm and **2** (0.22 × 0.22 × 0.25) mm were each mounted under $N_2$ in 0.5 mm X-ray capillary tubes using Apiezon grease. All measurements were made at room temperature on a Bruker Smart APEX area detector with graphite-monochromated Mo $K_\alpha$ radiation. Refinement was on $F^2$ with anisotropic displacement parameters, H atoms in calculated positions and a weighting scheme of the form $w = 1/[\sigma^2(Fo^2) + (aP)^2]$ where $P = (Fo^2 + 2Fc^2)/3$. The structure for $Ga(Me_3SiNCHNSiMe_3)_3$ is twinned according to the twin law (−1,−1,−1) with the major component comprising 71.8(8)% of the crystal used for the determination. Crystallographic data are given in Table 2. All structure solutions and refinements were performed using the SHELX-S-97 program[14].

## CONCLUSION

We report the synthesis of the hexacoordinate compounds $Al(Me_3SiNCHNSiMe_3)_3$ (**1**) and $Ga(Me_3SiNCHNSiMe_3)_3$ (**2**), which incorporate the $[Me_3SiNCHNSiMe_3]^{1-}$ bidentate anion are synthesized. En route to **1** and **2** we produce in good yields the $LiNCNSiMe_3$ species which may be a convenient source of the $[NCNSiMe_3]^{1-}$ anion. The X-ray crystal structures of 1 and 2 indicate that the compounds are perfectly isostructural.

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