

From monomeric iminosilane to a monomeric aminoalane: synthesis and crystal structures

Jörg Niesmann,^a Uwe Klingebiel,^{*a} Mathias Noltemeyer^a and Roland Boese^b

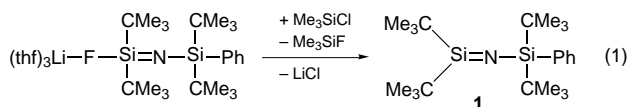
^a Institut für Anorganische Chemie der Universität, Tammannstr. 4, D-37077 Göttingen, Germany

^b Institut für Anorganische Chemie, Universität-GH Essen, Universitätsstr. 5-7, D-45117 Essen, Germany

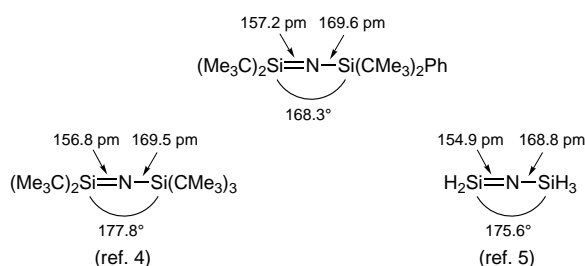
The reaction between the iminosilane $R_2Si=NR'$ [$R = CMe_3$, $R' = Si(CMe_3)_2Ph$] **1 and $AlMe_3$ in *n*-hexane at $-78^\circ C$ affords the first monomeric aminodimethylalane $Me_2Al=N-(R')R''$ [$R'' = Si(CMe_3)_2Me$] **2**; the crystal structure of **2** is presented.**

Compounds of multiple bond systems involving heavier main group elements were long considered to be unstable and synthetically inaccessible.^{1–3} The first silaethenes and disilenes were synthesised at the beginning of the 1980s, and the first iminosilanes were reported in the mid-1980s.^{1–3}

The uncoordinated and thermally stable iminosilane $R_2Si=NR'$ [$R = CMe_3$, $R' = Si(CMe_3)_2Ph$] **1** is formed in quantitative yield in the reaction between the lithiated fluoro-silylamine compound and $SiClMe_3$.¹ It is based on a fluorine/chlorine exchange with subsequent thermal $LiCl$ elimination [eqn. (1)].¹



The crystal structure of **1** shows a trigonal arrangement of the $C_2Si=N$ unit around the silicon atom. In solid state the iminosilane is monomeric and the $Si=N-Si$ skeleton is nearly linear (168.3°). The $Si-N$ bond lengths are drastically different. The $Si-N$ single bond is 169.6 pm, and the $Si=N$ double bond is 157.2 pm. The results are consistent with Wiberg's experimental⁴ and von Rague Schleyer's calculated⁵ results.



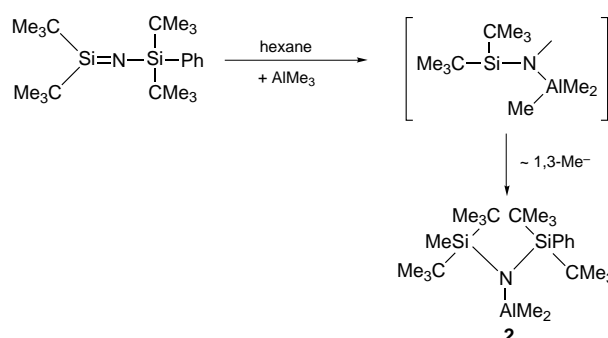
Iminosilanes react with Lewis bases, for example, with ethers or tertiary amines with formation of adducts. The adducts are often thermally stable and can be distilled without decomposition.^{1,6} Reactions of iminosilanes with Lewis acids are not described so far. We found that di-*tert*-butyl(di-*tert*-butylphenylsilyl)iminosilane **1** reacts with trimethylalane, $AlMe_3$, to give the monomeric aminoalane, $Me_2AlN[Si(CMe_3)_2Me]Si[Si(CMe_3)_2Ph]$ **2** (Scheme 1).^{†‡}

Unassociated compounds of the form $R_2M-NR'_2$ ($M = B, Al$, e.g. **2**) have the potential for π bonding between the main group 3 element (M) and nitrogen through overlap of the lone pair on nitrogen with the empty p orbital on boron or aluminium. Such π bonding is well established in molecules containing boron–nitrogen bonds.

The chemistry of the heavier group 3 elements, e.g. Al , is dominated by the tendency to form dimers or more highly

associated structures. However, three-coordination is achieved by the use of bulky substituents.⁷

For the first time a monomeric aminodimethylalane is obtained by a nucleophilic methanide-ion migration from aluminium to silicon. The methanide-ion migration can be explained by the strong Lewis acidity of the three-coordinate silicon, which must be stronger than the Lewis acidity of the three-coordinate aluminium.



Scheme 1

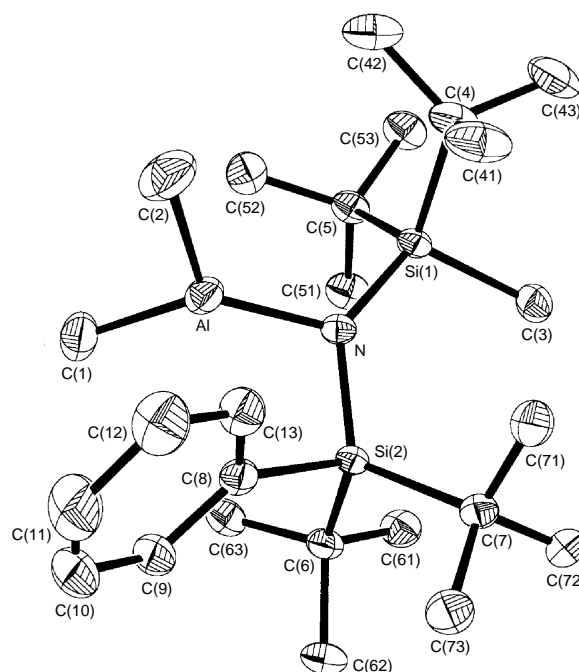


Fig. 1 Molecular structure of **2** (ORTEP, thermal ellipsoids at the 50% probability level). Principal distances (pm) and angles ($^\circ$): $Al-N$ 186.9(2), $Al-C(2)$ 195.4(2), $Al-C(1)$ 196.4(2), $Al-C(8)$ 256.4(3), $Al-Si(2)$ 284.43(8), $Si(1)-N$ 175.2(2), $Si(2)-N$ 175.0(2); $C(2)-Al-C(1)$ 108.03(11), $C(1)-Al-N$ 125.66(9), $C(2)-Al-N(1)$ 124.09(10), $\Sigma \angle Al(1) = 357.8^\circ$, $Si(2)-N-Si(1)$ 133.88(9), $Al-N-Si(2)$ 103.56(7), $Al-N-Si(1)$ 122.53(8), $\Sigma \angle N(1) = 360.0^\circ$. Torsion angle $C(1)-Al-N-Si(1) = -57.5^\circ$.

The structure of **2**[§] which is depicted in Fig. 1 consists of well separated Me₂AlN(R')R monomers. The Al–N bond length is 186.9 pm. The geometry of the Al atom is nearly planar (sum of angles = 357.8°). The C–Al–C angle is 108.03°. The geometry of the nitrogen centre is also planar (sum of angles = 360.0°) with the widest angle, 133.9°, between the silyl groups. The torsion angle of the C(2)–Al–N–Si(1) axis is –57.5°. There is a weak intramolecular interaction of the electron deficient aluminium atom with the C(8) atom of the phenyl ring facing the metal, Al–C(8) 256.4 pm. This decreases the Al–N–Si(2) angle (103.6°) and brings the Al and Si(2) atoms into close proximity [Al–Si(2) 284.4 pm]. The Al–N bond length is short in comparison to the simple sum of the aluminium and nitrogen covalent radii, *i.e.* 200 pm, which suggests the presence of Al–N p_π–p_π bonding. However, the dihedral angle C(1)–Al–N–Si(1) of –57.5° makes this very limited. Therefore most of the shortening of the Al–N bond should be attributed to the difference of the electronegativity. The Al–N bond length is comparable the Al–N distances of Bu₂AlN compounds.⁷

This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

Footnotes

† *Preparative details.* Starting materials: **1**,⁸ yellow oil, bp 108 °C (0.01 Torr), trimethylaluminium, 2.0 m solution in toluene. Reaction under dry argon. To 4.31 g (11.5 mmol) of di-*tert*-butyl(di-*tert*-butylphenylsilyl)iminosilane **1**,⁸ which was freshly distilled into a Schlenk bulb, was added 60 ml of degassed dry hexane. Then 5.74 ml (11.5 mmol, 2.0 m solution in toluene) trimethylaluminium were added at –78 °C. The solution was stirred at –78 °C for 2 h and at 25 °C for 1 day. After removal of the solvent *in vacuo* (10^{–2} Torr) and recrystallisation of the residue from toluene crystalline compound **2** was obtained in 74% yield; mp 121 °C; MS (EI): *m/z* (%) = 432(30) [M – CH₃]⁺, 390(100) [M – C₄H₉]⁺.

‡ *NMR data:* **2** (C₆D₆–toluene): ¹H, δ –0.63 (s, 6H, AlMe₂), 0.40 (s, 3H, SiMe), 1.21 (s, 18H, CMe₃), 1.23 (s, 18H, CMe₃), 6.97–8.06 (m, 5H, Ar-

H); ¹³C, δ –0.13 (s, SiMe), 1.82 (br s, AlMe₂), 22.83/23.56 (s, CMe₃), 30.97/31.54 (s, CMe₃), 129.29 [s, Ph (C-3, C-5)], 132.56 [s, Ph (C-4)], 137.60 [s, Ph (C-2, C-6)], 137.65 [s, Ph (C-1)]; ²⁹Si, δ –3.37 (s, SiPh), 7.13 (s, SiMe).

§ *Crystal data for 2:* a crystal of size 0.4 × 0.6 × 0.8 mm³ was measured on a STOE/Siemens AED2 four circle diffractometer with Mo-Kα radiation at 153 K. The space group is monoclinic, *P*2₁/*n*, with unit-cell dimensions *a* = 11.1930(10), *b* = 15.601(2), *c* = 16.622(3) Å, β = 105.750(10)°, *U* = 2793.6(7) Å³, *Z* = 4, refined from 30 reflections centred at positive and negative 2θ positions; μ = 0.170 mm^{–1} and *F*(000) = 992. 3401 reflections up to 2θ = 45° were collected, of which 3396 were independent (*R*_{int} = 0.014). The structure was solved using direct methods (SHELXS) and refined on *F*² (SHELXL93) with no disorder indicated: *R*₁[*I* > 2σ(*I*)] = 0.0347, *wR*₂ = 0.0852; for all 3391 data *R*₁ = 0.0391, *wR*₂ = 0.092, GOF = 1.071.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/311.

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Received, 22nd August 1996; Com. 6/05842F