

Oxidation of monomeric *N,N'*-dilithium *N,N'*-bis(di-*tert*-butylmethylsilyl)hydrazide to the diazene

Henning Witte-Abel, Uwe Klingebiel* and Mathias Noltemeyer

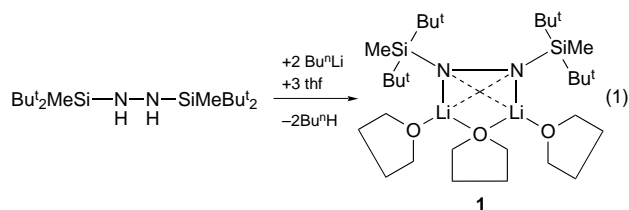
Institut für Anorganische Chemie der Universität, Tammannstr. 4, D-37077 Göttingen, Germany

The reaction between the bis(silyl)hydrazine RNHNHR and butyllithium in thf affords the first monomeric dilithium bis(silyl)hydrazide RNLiNLiR·3thf **1** (R = SiBu^t₂Me) and the crystal structure of **1** is presented; the thermally stable bis(silyl)diazene RN=NR **2** (R = SiBu^t₂Me) is formed in the reaction between **1** and Br₂.

The syntheses of the first silyl hydrazines were described by Aylett¹ and Wannagat and Liehr² in the 1950s. They developed essentially two methods of preparation;³ the reaction of halogenosilanes (X = Cl, Br, I) with (a) hydrazines and (b) lithium hydrazides. Especially lithium derivatives of silyl hydrazines showed a large variety in substitution and oxidation reactions. In 1964 Bailey and West discovered the migration of silyl groups from one nitrogen atom to the other and opened up a new era in organometallic chemistry.^{4,5} In 1968 Wiberg *et al.* prepared the first bis(silyl)diazene, Me₃SiN=NSiMe₃ in the reaction of lithium tris(trimethylsilyl)hydrazide with tosylazide, a very reactive, thermally unstable compound.^{6,7}

In spite of the successful use of the lithium hydrazides in preparative chemistry, the first crystal structure analyses were carried out only about 30 years later.^{3,8} Since then, the crystal structures of seven hydrazides, all of which are only silyl substituted, have been published. The results were often unexpected. Hexameric, tetrameric and dimeric hydrazides have been described.^{3,8–12} The lithium ions in these oligomers are differently 'side-on' and 'end-on' coordinated to the N–N unit. The degree of oligomerisation decreases with increasing bulkiness of the silyl substituents. We present the first crystal structure analysis of a monomeric dilithium derivative of an *N,N'*-bis(silyl)hydrazine and its oxidation to the bis(silyl)diazene.

Dilithiated *N,N'*-bis(di-*tert*-butylmethylsilyl)hydrazine **1** is formed in the reaction of the bis(silyl)hydrazine with 2 equiv. of *n*-butyllithium in thf [eqn. (1)].^{†‡}



The crystal structure of **1**§ which is depicted in Fig. 1 consists of well separated monomers. The lithium ions are 'side-on' coordinated to the N–N bond. They are *cis*-positioned to the hydrazine unit. The coordination sphere of the lithium ions is saturated with three thf molecules. One thf molecule bridges two lithium cations. In this case, Li–O contacts [Li(1)–O(2) 219.3 pm] are longer (19 pm) than the other [Li(1)–O(1) 200.0 pm]. The Li–N distances differ by about 10 pm [Li(1)–N(1a) 196.1; Li(1)–N(1) 185.7 pm]. The structural analysis confirms the *ab initio* calculations,¹³ according to which lithium cations in hydrazides can be coordinated equally by both N atoms of the hydrazine.

Silyl derivatives of diazenes can be prepared with different oxidation methods of lithium hydrazides.⁷ We used as oxidation

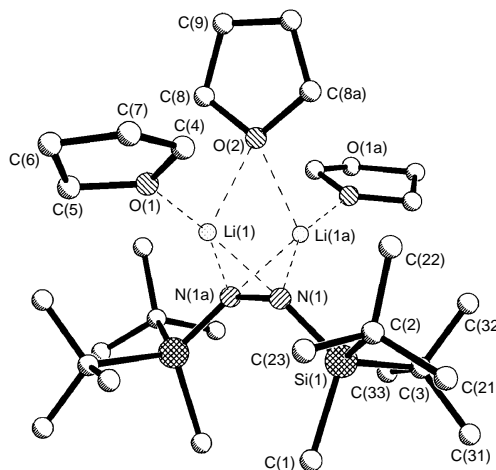
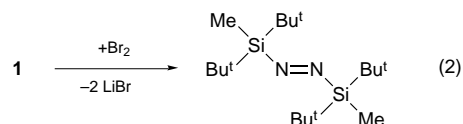


Fig. 1 Molecular structure of **1**; selected bond lengths (pm) and angles (°): Si(1)–N(1) 168.2(4), Si(1)–C(1) 189.4(6), Si(1)–C(2) 192.6(5), Si(1)–C(3) 194.1(5), N(1)–N(1a) 153.1(6), N(1)–Li(1) 185.7(8), N(1)–Li(1a) 196.1(9), Li(1)–N(1a) 196.1(9), Li(1)–O(1) 200.0(9), Li(1)–O(2) 219.3(9); N(1a)–N(1)–Si(1) 131.7(2), N(1a)–N(1)–Li(1) 70.0(3), N(1a)–N(1)–Li(1a) 62.8(3), Si(1)–N(1)–Li(1a) 121.6(3), Li(1)–N(1)–Li(1a) 80.8(5), N(1)–Li(1)–N(1a) 47.2(3), N(1)–Li(1)–O(1) 139.2(5), N(1a)–Li(1)–O(1) 158.2(5), N(1)–Li(1)–O(2) 101.4(4), N(1a)–Li(1)–O(2) 98.1(4), O(1)–Li(1)–O(2) 99.7(4), Li(1)–O(2)–Li(1a) 68.7(4); atoms labelled a, –z related to unlabelled equivalents by the symmetry operation $-x + 1, y, -z + \frac{1}{2}$

reagent of **1** elemental bromine in thf and isolated the diazene **2** in about 50% yield [eqn. (2)].



Compound **2** is light green and thermostable in contrast to other known bis(silyl)diazenes,⁷ which are thermally unstable, slowly decomposing above -35°C and extremely air sensitive (inflammable in oxygen). **2** can be distilled at 90°C (0.01 mbar) without decomposition and handled in the presence of air. Only one X-ray structural determination has been carried out of a bis(silyl)diazene, the bis(trimethylsilyl)diazene by Veith and Bärmighausen,¹⁴ which shows that the diazene is *trans*-configured with a planar SiNNSi framework. NMR measurements of **2** prove that it is only obtained as one stereoisomer.

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

Footnotes

* E-mail: uklinge@gwdg.de

† Preparative details: **1**: *N,N'*-bis(di-*tert*-butylmethylsilyl)hydrazine (0.01 mol, 3.4 g) in *n*-hexane (20 ml) and thf (10 ml) was metallated with 2 equiv.

of *n*-butyllithium (23% in *n*-hexane). The mixture was heated to reflux for 4 h and **1** was obtained in crystalline form by slow cooling to $-100\text{ }^{\circ}\text{C}$. Yield 95%.

2: **1** (0.03 mol, 10.3 g) was dissolved in 300 ml of thf. After cooling to $-70\text{ }^{\circ}\text{C}$, a solution of bromine (0.025 mol, 4.00 g) in 100 ml thf was added slowly. The mixture was warmed to room temp. within 6 h and heated to reflux for 1 h. The crude product was purified by distillation. Yield 50%, bp $90\text{ }^{\circ}\text{C}$ (0.01 mbar); FIMS: m/z (%) = 342 (100) [M]⁺.

‡ NMR data: **1**: ¹H NMR (C₆D₆, 250 MHz, SiMe₄), δ 0.28 (SiMe, 6 H), 1.15 (SiCMe₃, 36 H); ¹³C NMR (C₆D₆, 250 MHz, SiMe₄), δ -6.8 (SiC), 21.6 (SiCC₃), 29.9 (SiCC₃); ⁷Li NMR (C₆D₆, 250 MHz, LiCl), δ 0.67. **2**: ¹H NMR (C₆D₆, 250 MHz, SiMe₄), δ -0.23 (SiMe, 6 H), 1.11 (SiCMe₃, 36 H); ¹³C NMR (C₆D₆, 250 MHz, SiMe₄), δ -11.89 (SiC), 20.29 (SiCC₃), 28.90 (SiCC₃); ²⁹Si NMR (C₆D₆, 250 MHz, SiMe₄), δ 2.14.

§ Crystal data for **1**: a crystal of size $0.60 \times 0.40 \times 0.40$ mm placed on a STOE/Siemens AED 2 four-circle diffractometer equipped with Mo-K α radiation at 153 K. The space group is monoclinic, *C*2/*c*, with unit-cell dimensions $a = 18.840(6)$, $b = 12.104(7)$, $c = 18.170(7)$ Å, $\beta = 117.48(2)^{\circ}$, $U = 3676.3$ Å³, $Z = 4$; $\mu = 0.125\text{ mm}^{-1}$, $F(000) = 1272$. 2548 Reflections up to $2\theta = 45^{\circ}$ were collected, of which 2396 were independent ($R_{\text{int}} = 0.05222$). The structure was solved using direct methods (SHELXS) and refined on F^2 (SHELX-93) with no disorder indicated: $R_1[I > 2\sigma(I)] = 0.0767$, $wR_2 = 0.1878$; for all 2548 data $R_1 = 0.1104$, $wR_2 = 0.2203$, GOF = 1.024. 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 182/402.

References

- 1 B. J. Aylett, *J. Inorg. Nucl. Chem.*, 1956, **2**, 325.
- 2 U. Wannagat and W. Liehr, *Angew. Chem.*, 1957, **69**, 783.
- 3 K. Bode and U. Klingebiel, *Adv. Organomet. Chem.*, 1996, **40**, 1.
- 4 R. E. Bailey and R. West, *J. Am. Chem. Soc.*, 1964, **86**, 5369.
- 5 R. West, *Adv. Organomet. Chem.*, 1977, **16**, 1.
- 6 N. Wiberg, W.-Ch. Joo and W. Uhlenbrock, *Angew. Chem., Int. Ed. Engl.*, 1968, **7**, 640.
- 7 N. Wiberg, *Adv. Organomet. Chem.*, 1984, **23**, 131.
- 8 S. Dielkus, C. Drost, R. Herbst-Irmer and U. Klingebiel, *Angew. Chem.*, 1993, **105**, 1689; *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1625.
- 9 N. Metzler, H. Nöth and H. Sachdev, *Angew. Chem.*, 1994, **106**, 1837; *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1746.
- 10 H. Nöth, H. Sachdev, M. Schmidt and H. Schwenk, *Chem. Ber.*, 1995, **128**, 105.
- 11 K. Bode, U. Klingebiel, H. Witte-Abel, M. Gluth, M. Noltemeyer, R. Herbst-Irmer, M. Schäfer and W. Shomaly, *Phosphorus, Sulfur, Silicon*, 1996, **108**, 121.
- 12 K. Bode, C. Drost, C. Jäger, U. Klingebiel, M. Noltemeyer and Z. Zak, *J. Organomet. Chem.*, 1994, **482**, 285.
- 13 J. R. Dilworth, A. Rodriguez, G. R. Leigh and J. R. Murrell, *J. Chem. Soc., Dalton Trans.*, 1983, **2**, 455.
- 14 M. Veith and H. Bärnighausen, *Acta Crystallogr., Sect. B*, 1974, **30**, 1806.

Received in Cambridge, UK, 10th February 1997; Com. 7/00926G