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Tetrakis[lithium-*tert*-butyl(di-*tert*-butylfluorosilyl)amide]-dilithium oxide, $({}^{t}Bu_2SiF{-}NLi{}^{t}Bu)_4Li_2O$—a Li_6O^{4+}-cluster

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Abstract

Di-*tert*-butylfluorosilyl-*tert*-butylamine is converted into the lithium derivative $({}^{t}Bu_2SiFLiN{}^{t}Bu)_2$ (**1**) by *n*-BuLi. Compound **1** forms a dimer via the Li–N bond in non-polar solvents like *n*-hexane. In the reaction of **1** and Et_2O the ether adduct $({}^{t}Bu_2SiFLiN{}^{t}Bu)_2OEt_2$ (**2**) is formed. Compound **2** crystallised as a bicyclic compound with four-coordinate lithium in a $F_2Li(OEt_2)N$ unit and two-coordinate lithium in a NLiN unit. In the presence of trace quantities of water, which can account for its central oxo anion, or in the presence of atmospheric moisture the title compound tetrakis(lithium-di-*tert*-butylfluorosilylamide)-dilithium oxide, $({}^{t}Bu_2SiF{-}NLi{}^{t}Bu)_4Li_2O$, (**3**) is formed. The heteroatom core of **3** consists of four (OLiNLi) four-membered and four (OLiFSiNLi) six-membered rings. This presents a new mode for fluorosilylamide coordination to lithium. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Lithium-(fluorosilyl)amide; Hydrolysis; $\mu6{-}OLi_6$ coordination; Crystal structures

1. Introduction

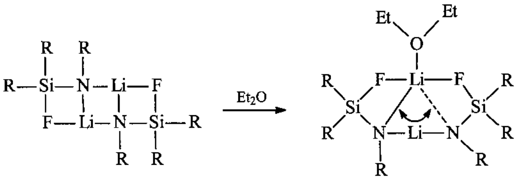
Lithiated aminofluorosilanes $(R_2SiFLiNR)_n$ [R=alkyl, aryl, silyl] are key reagents for many syntheses. They are commonly used under dry inert-atmosphere conditions to prevent their hydrolyses. Crystal structure determinations prove that lithiated aminofluorosilanes can, depending on the solvent and the substituents, be regarded as amides or LiF adducts of iminosilanes [1–4]. Lithium-*tert*-butyl-(di-*tert*-butylfluorosilyl)amide has been the first compound prepared and characterised by X-ray crystallography. It crystallises from *n*-hexane forming a tricyclic amide [3] and from THF forming a bicyclic amide [4]. According to these results it was found that it reacts like a silylamide as well as like an iminosilane, e.g. with aldehydes (SiNCO)-four-membered rings [5] were isolated or with $AlCl_3$ ${}^{t}Bu_2Si{=}N{}^{t}Bu{-}AlCl_3$ was obtained [6].

Here we describe the synthesis and structure of a diethylether adduct of lithium-*tert*-butyl-(di-*tert*-butylfluorosilyl)amide. We show also how such a system can be deliberately partially hydrolysed by addition of water to give, in reasonable yield, an aggregate incorporating Li_2O.

2. Results and discussion

2.1. Synthesis and structure of Bis[lithium-tert-butyl-(di-tert-butylfluorosilyl)amide-diethylether adduct

Starting from ${}^{t}Bu_2SiFNH{}^{t}Bu$ and BuLi we isolated the tricyclic amide **1** [3]. Compound **1** adds one molecule of Et_2O when crystallised from Et_2O to give **2**.



(1)

1 [3]

2

R = CMe₃

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In the solid state the bicyclic compound **2** has four-coordinate lithium in the $F_2Li(OEt_2)N$ unit and two-coordinate lithium in the NLiN unit (Fig. 1).

Compound **2** is made up of two different moieties, a nearly planar (±2.5 pm) six-membered ring [N(2)Li(1)F(1)Si(1)N(1)Li(2)] and a four-membered ring (±11 pm) [N(2)Li(1)F(2)Si(2)]. The dihedral angle between the six- and four-membered ring is 76°. The Si(1)–N(1) bond length (164.0 pm) is in the range of a double bond [2]. The Si(2)–N(2) bond (167.8 pm) of the four-membered ring is 3.8 pm longer and can be interpreted as a short single bond. N(2) is coordinated to two lithium atoms while N(1) is only coordinated to Li(2). Hence the negative charge at N(2) has to be distributed to two electropositive metals, elongating (while lowering electrostatic bond shortening) the Si(2)–N(2) bond. This explains the shift of Li(2) towards N(1):N(2) is already coordinated to a metal and not as attractive. The differences in bond length account for charge redistribution. Li(1) has a tetrahedral environment. Li(2) is two-coordinate and has a nearly linear environment. The N(1)–Li(2)–N(2) angle is measured with 167.7°. The Li(2)–N(1) bond is 11.9 pm shorter than the Li(2)–N(2) bond. The difference of the Li(1)–F(1) bond length (189.3 pm) and the Li(1)–F(2) bond length (202.7 pm) amounts 13.4 pm. Unusually short Li–C contacts of Li(2) to C(28) (276) and C(23) (270.2 pm) are found. However, NMR-spectra in solution show at room temperature equivalent H-, C-, F- and Si-atoms, a feature which is consistent with fluctuation of Li(1)–N(1) and Li(1)–N(2) bonds [4]. A NMR study at low temperatures could not be carried out.

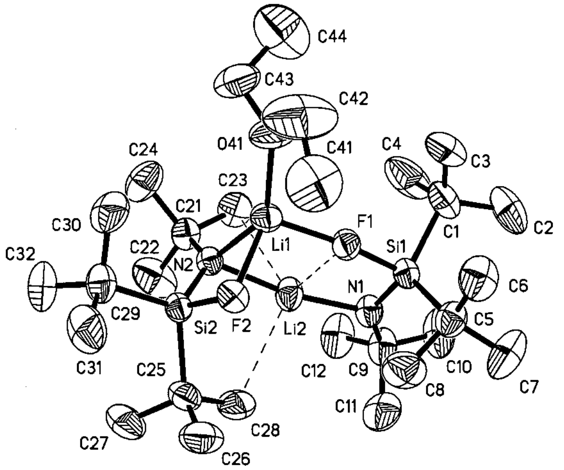


Fig. 1. Molecular structure of **2** (30% anisotropic probability ellipsoids); selected bond lengths (pm) and angles (°): Si(1)–N(1) 164.0(2), Si(1)–F(1) 169.17(13), Si(2)–F(2) 166.16(14), Si(2)–N(2) 167.8(2), F(1)–Li(1) 189.3(4), F(1)–Li(2) 224.8(4), F(2)–Li(1) 202.7(4), Li(1)–O(41) 193.9(4), Li(1)–N(2) 207.0(4), Li(2)–N(1) 192.8(4), Li(2)–N(2) 204.7(4), Li(2)–C(23) 270.2; C(9)–N(1)–Si(1) 137.9(2), N(1)–Si(1)–F(1) 99.13(8), Si(1)–F(1)–Li(1) 166.48(14), C(21)–N(2)–Si(2) 132.65(15), N(1)–Li(2)–N(2) 167.7(3).

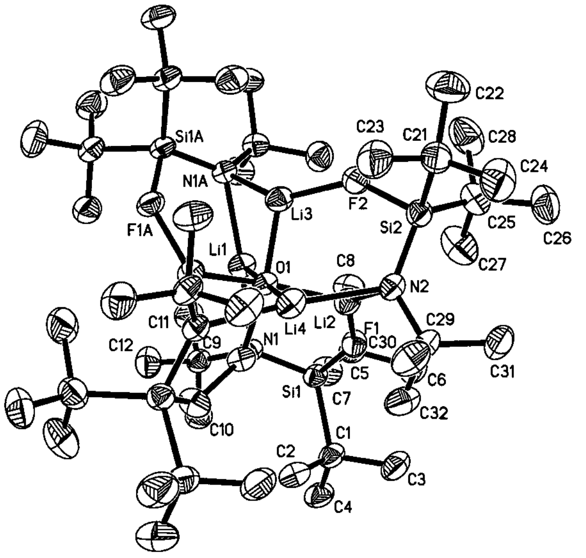
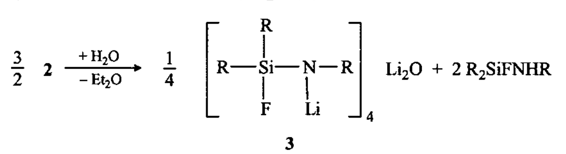


Fig. 2. Molecular structure of **3**; selected bond lengths (pm) and angles (°): Si(1)–F(1) 167.28(13), Si(1)–N(1) 167.8(2), F(1)–Li(2) 190.4(4), N(1)–Li(1) 218.4(2), N(1)–Li(3A) 206.0(4), Si(2)–F(2) 167.37(13), Si(2)–N(2) 167.7(2), F(2)–Li(3) 191.5(4), N(2)–Li(2) 204.9(4), N(2)–Li(4) 220.5(2), O(1)–Li(1) 194.0(5), O(1)–Li(2) 188.8(4), O(1)–Li(3) 189.4(3), O(1)–Li(4) 194.0(5), Li(1)–Li(2) 298.2(5), Li(1)–Li(3) 239.9(5), Li(2)–Li(3) 272.9(5), Li(2)–Li(4) 240.1(5), Li(3)–Li(4) 299.1(5); F(1)–Si(1)–N(1) 100.24(7), Si(1)–F(1)–Li(1) 141.77(13), C(9)–N(1)–Si(1) 128.58(13), Si(1)–N(1)–Li(3A) 101.10(13), Si(1)–N(1)–Li(1) 118.99(10), Li(3A)–N(1)–Li(1) 68.8(2), Si(2)–N(2)–Li(2) 103.16(13), Si(2)–N(2)–Li(4) 119.83(10), O(1)–Li(1)–N(1) 99.42(13), N(1)–Li(1)–N(1A) 161.2(3), O(1)–Li(2)–F(1) 108.5(2), O(1)–Li(2)–N(2) 106.5(2), F(1)–Li(2)–N(2) 141.7(2), O(1)F(2) 107.9(2), O(1)–Li(3)–N(1A) 105.6(2), N(2)–Li(4)–N(2A) 162.0(3), Li(2)–O(1)–Li(2A) 155.3(2), Li(2)–O(1)–Li(3) 92.37(15), Li(3)–O(1)–Li(3A) 154.9(2), Li(2)–O(1)–Li(1) 102.34(12), Li(3)–O(1)–Li(1) 77.46(12), Li(2)–O(1)–Li(4) 77.66(12), Li(3)–O(1)–Li(4) 102.54(12), Li(1)–O(1)–Li(4) 180.0.

Compound **2** crystallised and is very hygroscopic. The reaction of **2** with water in a molar ratio 1:1 leads quantitatively to the formation of the aminofluorosilane, ${}^tBu_2SiFNH{}^tBu$ (Eq. (2)).

$$\mathbf{2} + H_2O \rightarrow \mathbf{2}R_2SiFNHR + Li_2O \qquad (2)$$

Accidentally it was found that traces of water e.g. wet aminofluorosilane in the synthesis of **2** leads to the formation of tetrakis(lithium-*tert*-butyl(di-*tert*-butylfluorosilyl)amide-dilithium oxide (**3**). Significantly, the synthesis of **3** is reproducible under not completely anhydrous conditions (Eq. (3)).



$$\frac{3}{2}\,\mathbf{2} \xrightarrow[-\mathrm{Et_2O}]{+\mathrm{H_2O}} \frac{1}{4}\left[\begin{array}{ccccc} & & \mathrm{R} & & \\ & & | & & \\ \mathrm{R} & - & \mathrm{Si} & - & \mathrm{N}-\mathrm{R} \\ & & | & & | \\ & & \mathrm{F} & & \mathrm{Li} \end{array}\right]_4 \mathrm{Li_2O} + 2\,\mathrm{R_2SiFNHR} \qquad (3)$$

3

When the lithium fluorosilylamide **2** is stirred in hexane–Et_2O in the presence of atmospheric moisture or by adding small amounts of water partial hydrolysis occurs. Slow cooling of the warm solution at ambient temperature affords colourless crystals of the sparingly soluble cluster **3**, $[(^tBu_2SiFNLi^tBu)_4 \cdot Li_2O$. The structure of **3** is shown in Fig. 2, while Fig. 3 highlights the $(NSiF)_4Li_6O$ heteroatom core. It consists of four (OLiNLi) four-membered and four (OLiFSiNLi) six-membered rings. This presents a new mode for fluorosilylamide coordination to lithium. Regarding the Cambridge Structural Database (http://www.ccdc.cam.ac.uk) besides organic compounds with alkoxy-, amide-, or imide groups a related μ_6-OLi_6 coordination was reported only in a dilithiomethane–Li_2O-cluster, a lithium–barium-oxid-cluster, a dilithium–silylphosphandiide and arsandiide-cluster [7–17].

The six Li^+ cations surround the central oxo anion octahedrally. All the Li^+ cations in **3** have three-coordinate, pseudo-trigonal planar geometries. Two of them Li(1) and Li(4) are coordinated to two nitrogen anions and the oxo anion. The N–Li–N angles are 161.2 and 162.0°, about 20° larger than the N–Li–F angles. The other Li cations are coordinated to the oxo anion, a fluorine atom, and nitrogen anion of different fluorosilylamides. In terms of coordination environment the four N anions are all equivalent. The angle Li(1)–O(1)–Li(4) is 180°. The Li–O distances of the $[Li_6O]^{4+}$ cluster are in the range 188.8–194.0 pm. The Li–O distance in the Li_2O molecule (194.0) is significantly longer than that in the other Li–O bonds [12], clearly shorter than the Li–O bonds in solid Li_2O (198 pm).

3. Experimental

Compound **2**: Lithium-*tert*-butyl-(di-*tert*-butylfluorosilyl)amide (0.01 mol, 2.4 g) in 50 ml *n*-hexane was dissolved in 10 ml diethyl ether and heated to reflux for 1 h. After cooling the solution to −20 °C **2** crys-tallised. Yield 95%. **2** is analytically pure, stable in Ar, but moisture-sensitive. NMR (C_6D_6): ^1H δ 0.93 (t, CH_3, $^3J_{HH}$=7.1 Hz, 6H), 1.24 ($SiCMe_3$, 36H), 1.46 ($NCMe_3$, 18H), 3.21 (q, CH_2, $^3J_{HH}$=7.1 Hz, 4H); ^{13}C δ 14.49 (CH_3), 22.50 (d, $SiCMe_3$), $^2J_{CF}$=21.8 Hz, 29.52 ($SiC\mathit{Me}_3$), 38.62 ($NC\mathit{Me}_3$), 49.63 (d, $NCMe_3$, $^3J_{CF}$=11.4 Hz), 65.36 (CH_2); ^{19}F δ 4.98; ^{29}Si δ 0.72 (d, $^1J_{SiF}$=236.5 Hz).

Table 1
Crystal data and structure refinement parameters for **2** and **3**

	2	**3**
Empirical formula	$C_{28}H_{64}F_2Li_2N_2OSi_2$	$C_{48}H_{108}F_4Li_6N_4OSi_4$
Formula weight	552.87	987.38
Temperature (K)	203(2)	203(2)
Wavelength (pm)	71.073	71.073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$C2/c$
Unit cell dimensions		
a (pm)	1507.4(3)	2477.2(7)
b (pm)	1124.89(15)	1197.5(3)
c (pm)	2143.3(6)	2305.7(6)
α (°)	90	90
β (°)	92.39(2)	117.561(13)
γ (°)	90	90
V (Å^3)	3631.2(12)	6063.6(27)
Z	4	4
D_{calc} (mg m^{-3})	1.011	1.082
Absorption coefficient (mm^{-1})	0.128	0.144
$F(000)$	1224	2168
Crystal size (mm)	0.70 × 0.60 × 0.50	0.80 × 0.60 × 0.40
Theta range for data collection (°)	3.60–25.14	3.53–22.63
Index ranges	$-17 \leq h \leq 17$ $-12 \leq k \leq 13$ $-24 \leq l \leq 25$	$-26 \leq h \leq 26$ $-12 \leq k \leq 3$ $-24 \leq l \leq 21$
Reflections collected	8285	4047
Independent reflections	6469 [$R_{int} = 0.0232$]	4006 [$R_{int} = 0.0663$]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	6461/9/374	4001/0/322
Goodness-of-fit on F^2	1.036	1.040
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0549$, $wR_2 = 0.1513$	$R_1 = 0.0387$, $wR_2 = 0.0977$
R indices (all data)	$R_1 = 0.0640$, $wR_2 = 0.1690$	$R_1 = 0.0453$, $wR_2 = 0.1065$
Largest difference peak and hole (e Å^{-3})	0.465 and −0.509	0.179 and −0.253

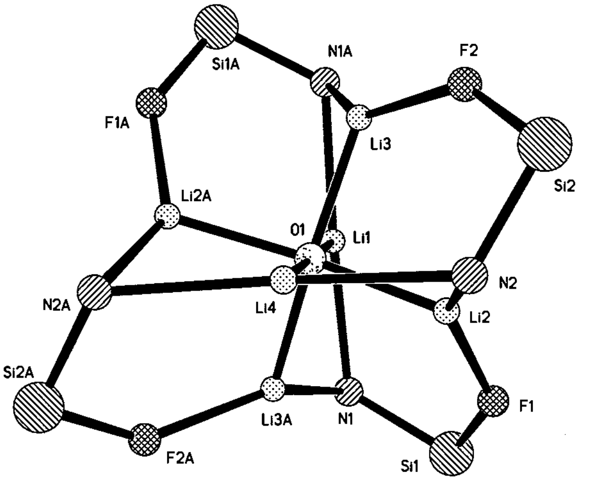


Fig. 3. Structure of **3** without ^{t}Bu groups.

Compound **3**: A solution of **2** (0.005 mol, 2.7 g) in *n*-hexane–diethyl ether (50 ml) was stirred in the presence of atmospheric moisture for 5 h. After cooling the solution to −20 °C **3** crystallised. Yield 5%. **3** is analytically pure, air stable, but moisture-sensitive.

$C_{48}H_{108}F_4Li_6N_4OSi_4$ (987.60). Anal. Calc. C, 58.38; H, 11.02; N, 5.67. Found: C, 58.63; H, 11.47; N, 5.37%.

3.1. *X-ray structure determinations of* **2** *and* **3**

The structures were solved by direct methods [18] and refined by full-matrix least-squares on F^2. Crystal data for compounds **2** and **3** are listed in Table 1. They were collected on a STOE AED 2 four circle diffractometer with Mo–K_α radiation.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 152449 for compound **2** and 152450 for compound **3**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax. +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk.

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References

[1] S. Walter, U. Klingebiel, Coord. Chem. Rev. 130 (1994) 481.
[2] I. Hemme, U. Klingebiel, Adv. Organomet. Chem. 39 (1996) 159.
[3] D. Stalke, N. Keweloh, U. Klingebiel, M. Noltemeyer, G.M. Sheldrick, Z. Naturforsch. 42b (1987) 1237.
[4] D. Stalke, U. Klingebiel, G.M. Sheldrick, J. Organomet. Chem. 344 (1988) 37.
[5] S. Vollbrecht, U. Klingebiel, D. Schmidt-Bäse, Z. Naturforsch. 46b (1991) 709.
[6] U. Klingebiel, M. Noltemeyer, H.-G. Schmidt, D. Schmidt-Bäse, Chem. Ber. Recu. 130 (1997) 753.
[7] F.M. Mackenzie, R.E. Mulvey, W. Clegg, L. Horsburgh, Polyhedron 17 (1998) 993.
[8] J.F.K. Müller, M. Neuburger, B. Spingler, Angew. Chem. Int. Ed. Engl. 38 (1999) 3549.
[9] C. Hilf, F. Bosold, K. Harms, J.C.W. Lohrenz, M. Marsch, M. Schimeczek, G. Boche, Chem. Ber. 130 (1997) 1201.
[10] N. Kuhn, U. Abram, C. Maichle-Mossmer, J. Wiethoff, Z. Anorg. Allg. Chem. 623 (1997) 1121.
[11] J.F.K. Müller, M. Neuburger, M. Zehnder, Helv. Chim. Acta 80 (1997) 2182.
[12] T. Chivers, A. Downard, G.P.A. Yap, J. Chem. Soc. Dalton Trans. (1998) 2603.
[13] W. Clegg, L. Horsburgh, P.R. Dennison, F.M. Mackenzie, R.E. Mulvey, J. Chem. Soc. Chem. Commun. (1996) 1065.
[14] S.C. Ball, J. Cragg-Hine, M.G. Davidson, R.P. Davies, M.J. Lopez-Solera, P.R. Raithley, D. Reed, R. Snaith, E.M. Vogl, J. Chem. Soc. Chem. Commun. (1995) 2147.
[15] H.-G. Gais, J. Vollhardt, H. Günther, D. Moskau, H.J. Linder, S. Braun, J. Am. Chem. Soc. 110 (1988) 978.
[16] H. Bock, T. Hauck, C. Näther, N. Rösch, M. Staufer, O.D. Häberlen, Angew. Chem. 107 (1995) 1438; Angew. Chem. Int. Ed. Engl. 34 (1995) 1353.
[17] M. Driess, H. Pritzkow, S. Martin, S. Rell, D. Fenske, G. Baum, Angew. Chem. 108 (1996) 1064; Angew. Chem. Int. Ed. Engl. 35 (1996) 986.
[18] G.M. Sheldrick, SHELXL-97, The SHELX-97 Manual, Göttingen, Germany, 1997.