

# Carbon–fluorine bond activation in perfluorobenzonitrile by $\text{LiN}(\text{SiMe}_3)_2$ . Synthesis of $(\text{Me}_3\text{Si})_2\text{NC}_6\text{F}_4\text{CN}$ -4 and crystal structure of $\text{LiN}(\text{C}_6\text{F}_4\text{CN}-4)_2 \cdot 2\text{C}_4\text{H}_8\text{O}$

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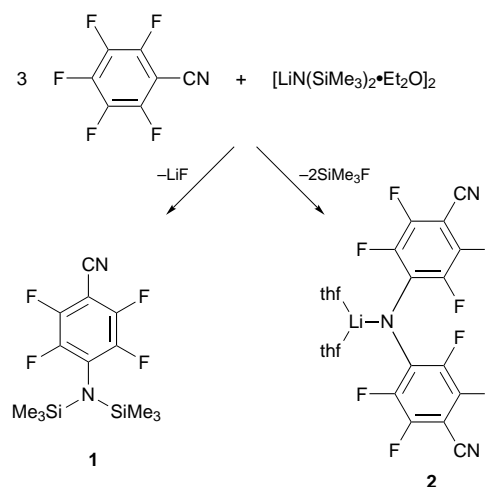
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The reaction of  $\text{C}_6\text{F}_5\text{CN}$  with the dimeric lithium salt  $[\text{Li}(\text{NSiMe}_3) \cdot \text{Et}_2\text{O}]_2$  yielded a 11:9 mixture of  $(\text{Me}_3\text{Si})_2\text{NC}_6\text{F}_4\text{CN}$ -4 **1** and  $\text{LiN}(\text{C}_6\text{F}_4\text{CN}-4)_2 \cdot 2\text{thf}$ , respectively (thf = tetrahydrofuran). The compounds were characterized spectroscopically and complex **2** by crystal structure determination. The central lithium forms a distorted trigonal bipyramid the apical position of which is filled by a nitrile nitrogen of an adjacent molecule, inducing chains running parallel to the *b*-direction of the crystal. The driving force for the production of **1** and **2** is the elimination of LiF and  $\text{SiMe}_3\text{F}$ , respectively. The calculated enthalpy for formation of **2** is more favourable compared to that for formation of **1**, although the similar yields indicate that similar enthalpies of activation apply to both systems.

The chemistry of lithium is spreading within organic chemistry.<sup>1,2</sup> However, the co-ordination chemistry of organolithium amido compounds and the mechanisms of organolithium–base reactions are uncommonly complex and poorly understood.<sup>3–6</sup> This complexity stems from the high tendency of N-lithiated compounds to self-assemble into higher aggregates, which is considerably dependent on the choice of solvent and the actual preparation conditions. It is enhanced by the rapid solvent exchanges as well as the extreme oxygen and moisture sensitivity of most organolithium derivatives. Thus, many organolithium reagents are prepared *in situ*, and there is no direct spectroscopic evidence of their solution- and solid-state structure. N-Lithiated species constitute a very important class of organolithium reagents. They are the preferred bases for the formation of ketone enolates,<sup>7</sup> generating low steady-state concentrations of some relatively unstable carbanions,<sup>8</sup> for the preparation of heterocyclic thiazenes incorporating a RCN moiety using lithium amidinates.<sup>9</sup> For the latter, these strong bases are used normally as halogen abstractors in the synthesis of transition-metal amidine and amido-complexes.<sup>10–12</sup>

The stability of fluorocarbons relative to their hydrocarbon counterparts is evidenced by the larger dissociation energies for C–F compared to C–H bonds.<sup>13</sup> The ability of the fluorine atom to function as both a  $\sigma$  acceptor and a  $\pi$  donor is what imparts the C–F bond its great strength. This  $\pi$ -donor ability of fluorine arises from the donation from its lone-pair orbitals into the  $\pi$  orbitals of the adjacent carbon atom.<sup>14</sup> It is widely recognized that fluorinated alkenes and arenes are more reactive than are their saturated counterparts since  $\pi$  frameworks are normally subject to nucleophilic attack and fluoride is a good leaving group.<sup>15</sup> Thus, some examples of C–F bond cleavage in fluoroarenes  $\text{C}_6\text{F}_5\text{X}$ , especially those containing electron-withdrawing substituents X such as CN and  $\text{NO}_2$ , have been reported.<sup>16–21</sup> This cleavage always occurs following attack on the arene by a strong nucleophile, eliminating  $\text{HF}$ ,<sup>21</sup> alkali-metal fluoride<sup>19</sup> or  $\text{SiMe}_3\text{F}$  for a N-silylated compound such as  $\text{Me}_3\text{SiN}=\text{PPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2$ .<sup>20</sup> Most of these activation reactions require energetic conditions and give *para*-substituted products. Here we report the first example of an easy C–F bond cleavage of perfluorobenzonitrile by a N-silylated lithium salt  $\text{LiN}(\text{SiMe}_3)_2$  at  $-78^\circ\text{C}$ . The compound  $\text{C}_6\text{F}_5\text{CN}$  undergoes competitive substitution either as a double metathesis with the  $\text{SiMe}_3$  group of

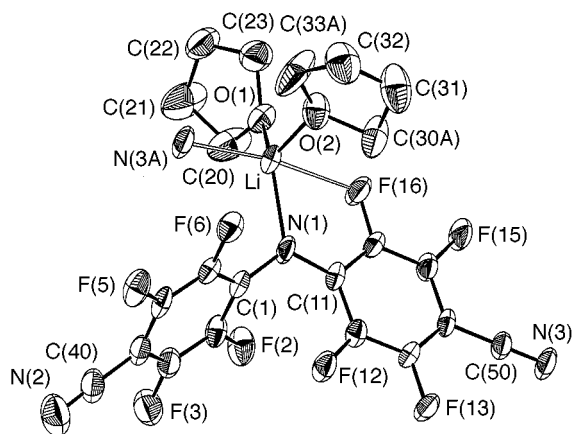


Scheme 1

the lithium amido salt, with the *p*-fluoro atom of the arene exclusively eliminating two molecules of  $\text{SiMe}_3\text{F}$ , or by nucleophilic attack of the nitrogen atom on the *p*-fluoro atom of the arene and concomitant elimination of LiF. The synthesis, isolation and characterization of both compounds obtained including the crystal structure of the perfluorobenzonitrile lithium amido salt are described.

## Results and Discussion

The reaction of  $\text{C}_6\text{F}_5\text{CN}$  with  $\text{LiN}(\text{SiMe}_3)_2$  [ $-78^\circ\text{C}$ , tetrahydrofuran (thf), 80%] produces a 11:9 mixture of the compounds  $(\text{Me}_3\text{Si})_2\text{NC}_6\text{F}_4\text{CN}$ -4 **1** and  $\text{LiN}(\text{C}_6\text{F}_4\text{CN}-4)_2 \cdot 2\text{thf}$  **2**, and the corresponding LiF and  $\text{SiMe}_3\text{F}$  elimination products, respectively (Scheme 1). Performing the reactions at higher temperatures ( $0$ – $25^\circ\text{C}$ ) or by changing the solvent (diethyl ether, benzene, hexane) does not change the product ratio dramatically ( $\approx 2$ – $5\%$ ). Interestingly, the formation of the mono-substituted lithium amido complex  $\text{LiN}(\text{SiMe}_3)(\text{C}_6\text{F}_4\text{CN}-4) \cdot 2\text{thf}$  **3** was not observed implying that the second metathesis reaction is faster than the first  $\text{Me}_3\text{Si}$  replacement. The synthesis of **1** involves cleavage of C–F and Li–N bonds and for-



**Fig. 1** A ZORTEP<sup>29</sup> drawing of the molecular structure of  $\text{LiN}(\text{C}_6\text{F}_4\text{CN-4})_2 \cdot 2\text{thf}$  **2**. Thermal ellipsoids are shown at the 40% probability level

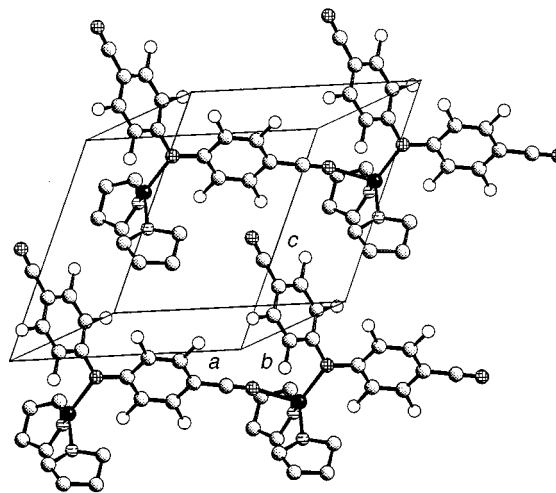
mation of Li–F and one C–N bond. The enthalpy change for this reaction can be estimated<sup>22,23</sup> as  $\Delta H = \Delta H(\text{Li-F}) + \Delta H(\text{N-C}) - \Delta H(\text{Li-N}) - \Delta H(\text{C-F}) = (-498 - 447 + 451 + 474) \text{ kJ mol}^{-1} = -20 \text{ kJ mol}^{-1}$ . In the formation of product **1** the formation of LiF seems to be the driving force. Similarly, the synthesis of **2** involves the cascade cleavage of two C–F and two  $\text{Me}_3\text{Si-N}$  bonds, and formation of two  $\text{Me}_3\text{Si-F}$  and C–N bonds. The enthalpy change for the first metathesis product can be estimated as  $\Delta H = \Delta H(\text{Si-F}) + \Delta H(\text{N-C}) - \Delta H(\text{Si-N}) - \Delta H(\text{C-F}) = (-601 - 447 + 468 + 474) \text{ kJ mol}^{-1} = -106 \text{ kJ mol}^{-1}$ . The second  $\text{Me}_3\text{Si}$  metathesis product will give theoretically another  $106 \text{ kJ mol}^{-1}$ . Therefore, formation of  $\text{SiMe}_3\text{F}$  seems to be the strong driving force for the formation of complex **2**, impeding the formation of the intermediate complex **3**.

Whereas the activation of the *ortho* position of the corresponding perfluorobenzonitrile compounds has been achieved as a result of intramolecular heteroatom (Pt<sup>24,25</sup> or Ni<sup>26</sup>) and intermolecular assisted processes,<sup>27</sup> our attempts to activate the *ortho* position by treating *para*-H tetrafluorobenzonitrile with  $\text{LiN}(\text{SiMe}_3)_2$  resulted in the precipitation of a black polymer insoluble in polar and non-polar solvents. Interestingly, the corresponding perfluorobenzamidinate products were not observed indicating the low anionic character of the nitrile carbon due to the nitrogen lone pair of electrons under the influence of the fluorine atoms of the ring.<sup>28</sup>

### Crystal structure of $\text{LiN}(\text{C}_6\text{F}_4\text{CN-4})_2 \cdot 2\text{thf}$

Suitable crystals of complex **2** were obtained from a thf–hexane solution cooled slowly to 0 °C. At –80 °C a phase transition occurs in the solid causing the disappearance of the reflections. At even lower temperatures no indexing of the unit cell was possible. To avoid phase transitions, the measurement was made at –50 °C.

The low-temperature crystal structure (Fig. 1, Table 1) consists of a five-fold, distorted trigonal-bipyramidally coordinated lithium atom with the nitrogen and two thf solvent oxygens forming the trigonal plane (sum of the angles = 347.6°), and a fluorine atom *ortho* to the amido nitrogen and a nitrogen from a nitrile moiety of an adjacent molecule occupying the apical positions. Thus, the molecules form chains running parallel to the *b* direction (Fig. 2). The Li–F close contact [2.610(7) Å] is responsible for the rotation of the corresponding  $\text{C}_6\text{F}_4\text{CN}$  ring out of the trigonal plane formed by the amido nitrogen (sum of angles = 359.7°) by 19.6°, whereas the second  $\text{C}_6\text{F}_4\text{CN}$  ring, with no interactions, is out of the planar plane by 57.6° arguing that the delocalization of the electron density affects mainly the attached ring. This effect is clearly shown by the N(1)–C(11) bond distance [1.355(5) Å] which is, as expected, somewhat shorter than the N(1)–C(1) bond [1.383(5) Å]. In a



**Fig. 2** Unit cell of complex **2** showing the chains running parallel to the *b* direction

similar fashion, due to the same close contact, the Li–O(2) bond [1.923(8) Å] is shorter than the corresponding Li–O(1) bond [1.955(8) Å]. Furthermore, our efforts to resolve different fluorine signals in solution were not successful arguing that the Li–F contact, if present, is very weak as compared with  $[\text{Li}(\text{thf})_2]^+[\text{C}_6\text{F}_5\text{NSiFR}_2]^-$  for which coalescence was found among the *ortho* Li–F bond [2.386(10) Å] and the Si–F–Li bond [2.273(10) Å] at –90 °C.<sup>30</sup> The Li–N (amido) bond [2.078(8) Å] is larger than the Li–N bond [2.026(12) Å] in the starting complex  $[\text{LiN}(\text{SiMe}_3)_2 \cdot \text{Et}_2\text{O}]_2$ ,<sup>31</sup> and the Li–N(3A) (nitrile) bond [2.128(8) Å], which is responsible for the chains running parallel to the *b* direction, is somewhat longer than in a similar lithium complex in which the benzonitrile moiety  $[\text{Li-N}\equiv\text{C} 2.098(8) \text{ Å}]$  is co-ordinated.<sup>28</sup>

The IR spectra of the new compounds **1** and **2** show a band assignable to  $\nu(\text{CN})$  at 2244 and 2235  $\text{cm}^{-1}$  as compared with 2249  $\text{cm}^{-1}$  for the starting  $\text{C}_6\text{F}_5\text{CN}$ . The large shift to lower wavenumber for **2** (14  $\text{cm}^{-1}$ ) with respect to the starting substrate can be explained by the interaction of the nitrile nitrogen with the lithium atom of an adjacent molecule in the solid state, forming the intermolecular chains as observed in the low-temperature crystal structure. The  $^{19}\text{F}$  NMR spectrum of complex **2** is shifted to higher field with respect to that of **1** caused by the preferred resonance structure involving the lone pair electrons of the amido nitrogen and the rings in **2**. The  $^{19}\text{F}$  NMR spectrum of **1** exhibits two multiplets centred at  $\delta -8.86$  and  $-17.76$  for the  $\alpha$ - (*ortho* to  $\text{C}\equiv\text{N}$ ) and  $\beta$ -fluorine atoms, respectively, corresponding to the expected AA'BB' system. For complex **2** a similar AA'BB' pattern is obtained at  $\delta -11.96$  and  $-26.35$  for the corresponding  $\alpha$ - and  $\beta$ -fluorine atoms, respectively. The  $^1\text{H}$  NMR spectrum for **1** shows the  $\text{Me}_3\text{Si}$  signal at  $\delta -0.07$  and for **2** only the attached thf ( $\delta 1.74, 3.60$ ) is observed.

This study shows that competitive elimination pathways are feasible for  $\text{SiMe}_3\text{F}$  and LiF in systems allowing their formation in almost equal amounts, despite the more favourable enthalpy for the elimination of  $\text{SiMe}_3\text{F}$ . This result argues for both elimination pathways and similar enthalpies of activation and is also corroborated by the unchanged product distribution ratio as a function of temperature. Furthermore, no benzamidinate formation is obtained for the fluorobenzonitrile systems due to the electronic effect of the fluorine atoms on the nitrile. The use of this perfluorobenzonitrile amidolithium salt as a potential ancillary ligand is under investigation.

### Experimental

All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flamed

**Table 1** Selected bond lengths (Å) and angles (°) for compound **2**

N(1)–C(11)	1.355(5)	C(5)–C(6)	1.371(6)	C(15)–F(15)	1.343(5)	C(21)–C(22)	1.450(8)
N(1)–C(1)	1.383(5)	C(6)–F(6)	1.342(5)	C(15)–C(16)	1.375(6)	C(22)–C(23)	1.470(7)
N(1)–Li	2.078(8)	C(40)–N(2)	1.139(6)	C(16)–F(16)	1.334(5)	O(2)–C(33B)	1.360(9)
C(1)–C(2)	1.389(6)	C(11)–C(16)	1.403(6)	F(16)–Li	2.610(7)	O(2)–C(30B)	1.390(2)
C(1)–C(6)	1.400(6)	C(11)–C(12)	1.418(6)	C(50)–N(3)	1.148(5)	O(2)–C(33A)	1.430(5)
C(2)–F(2)	1.349(5)	C(12)–F(12)	1.342(4)	Li–N(3A)	2.128(8)	O(2)–C(30A)	1.504(10)
C(2)–C(3)	1.360(6)	C(12)–C(13)	1.368(5)	Li–O(2)	1.923(8)	C(30A)–C(31)	1.563(11)
C(3)–F(3)	1.344(5)	C(13)–F(13)	1.341(4)	Li–O(1)	1.955(8)	C(30B)–C(31)	1.520(2)
C(3)–C(4)	1.385(6)	C(13)–C(14)	1.390(6)	O(1)–C(23)	1.402(6)	C(31)–C(32)	1.475(8)
C(4)–C(5)	1.384(6)	C(14)–C(15)	1.387(6)	O(1)–C(20)	1.411(6)	C(32)–C(33B)	1.420(9)
C(4)–C(40)	1.424(7)	C(14)–C(50)	1.426(6)	C(20)–C(21)	1.473(8)	C(32)–C(33A)	1.450(5)
C(5)–F(5)	1.338(5)						
C(11)–N(1)–C(1)	119.4(3)	F(6)–C(6)–C(1)	118.6(4)	F(16)–C(16)–C(11)	117.8(3)	O(1)–C(20)–C(21)	106.5(4)
C(11)–N(1)–Li	123.6(3)	C(5)–C(6)–C(1)	122.6(4)	C(15)–C(16)–C(11)	123.3(4)	C(22)–C(21)–C(20)	106.5(5)
C(1)–N(1)–Li	116.7(3)	N(2)–C(40)–C(4)	177.9(6)	C(16)–F(16)–Li	106.7(3)	C(21)–C(22)–C(23)	105.6(4)
N(1)–C(1)–C(2)	123.9(4)	N(1)–C(11)–C(16)	119.2(4)	N(3)–C(50)–C(14)	179.4(5)	O(1)–C(23)–C(22)	108.1(4)
N(1)–C(1)–C(6)	121.2(4)	N(1)–C(11)–C(12)	126.8(4)	C(50)–N(3)–Li <sup>I</sup>	169.4(4)	C(33B)–O(2)–C(30B)	101.0(4)
C(1)–C(1)–C(6)	114.7(4)	C(16)–C(11)–C(12)	113.8(3)	O(2)–Li–O(1)	110.2(4)	C(33A)–O(2)–C(30A)	111.0(2)
F(2)–C(2)–C(3)	118.4(4)	F(12)–C(12)–C(13)	117.9(4)	O(2)–Li–N(1)	115.0(4)	C(33B)–O(2)–Li	125.0(4)
F(2)–C(2)–C(1)	118.7(4)	F(12)–C(12)–C(11)	119.5(3)	O(1)–Li–N(1)	122.4(4)	C(30B)–O(2)–Li	133.6(7)
C(3)–C(2)–C(1)	122.9(4)	C(13)–C(12)–C(11)	122.5(4)	O(2)–Li–N(3 <sup>II</sup> )	103.6(3)	C(33A)–O(2)–Li	128.0(2)
F(3)–C(3)–C(2)	119.8(4)	F(13)–C(13)–C(12)	119.0(4)	O(1)–Li–N(3 <sup>II</sup> )	93.3(3)	C(30A)–O(2)–Li	114.1(5)
F(3)–C(3)–C(4)	118.2(4)	F(13)–C(13)–C(14)	118.6(3)	N(1)–Li–N(3 <sup>II</sup> )	108.2(3)	O(2)–C(30A)–C(31)	99.0(7)
C(2)–C(3)–C(4)	122.0(4)	C(12)–C(13)–C(14)	122.4(4)	O(2)–Li–F(16)	95.6(3)	O(2)–C(30B)–C(31)	106.5(12)
C(5)–C(4)–C(3)	116.3(4)	C(15)–C(14)–C(13)	116.1(3)	O(1)–Li–F(16)	73.1(2)	C(32)–C(31)–C(30B)	95.0(7)
C(5)–C(4)–C(40)	122.2(4)	C(15)–C(14)–C(50)	121.9(4)	N(1)–Li–F(16)	68.9(2)	C(32)–C(31)–C(30A)	106.9(5)
C(3)–C(4)–C(40)	121.4(4)	C(13)–C(14)–C(50)	122.0(4)	N(3 <sup>II</sup> )–Li–F(16)	159.5(4)	C(33B)–C(32)–C(31)	100.0(3)
F(5)–C(5)–C(6)	118.9(4)	F(15)–C(15)–C(16)	119.2(4)	C(23)–O(1)–C(20)	107.4(4)	C(33A)–C(32)–C(31)	107.0(2)
F(5)–C(5)–C(4)	119.5(4)	F(15)–C(15)–C(14)	119.0(3)	C(23)–O(1)–Li	123.3(4)	O(2)–C(33A)–C(32)	108.0(3)
C(6)–C(5)–C(4)	121.5(4)	C(16)–C(15)–C(14)	121.8(4)	C(20)–O(1)–Li	120.9(4)	O(2)–C(33B)–C(32)	114.0(7)
F(6)–C(6)–C(5)	118.8(4)	F(16)–C(16)–C(15)	118.8(4)				

Symmetry transformations used to generate equivalent atoms: I  $x - 1, y, z$ ; II  $x + 1, y, z$ .

Schlenk-type glassware on a dual-manifold Schlenk line, or interfaced to a high-vacuum ( $10^{-5}$  Torr, *ca.*  $1.33 \times 10^{-3}$  Pa) line, or in a nitrogen-filled Vacuum Atmospheres glove-box with a medium-capacity recirculator (1–2 ppm O<sub>2</sub>). Argon and nitrogen gases were purified by passage through a MnO oxygen-removal column and a Davison 4 Å molecular-sieve column. Ether solvents ([<sup>2</sup>H<sub>5</sub>]thf) were distilled under argon from sodium–benzophenone. Hydrocarbon solvents (C<sub>6</sub>D<sub>6</sub>) were distilled under nitrogen from Na/K alloy. All solvents for vacuum-line manipulations were stored *in vacuo* over Na/K alloy in resealable bulbs. The NMR spectra were recorded on Bruker AM 200 spectrometer. Chemical shifts for <sup>1</sup>H and <sup>13</sup>C were referenced to internal solvent resonances and are reported relative to tetramethylsilane. The <sup>19</sup>F NMR spectra were recorded on a Bruker AM 200 spectrometer and referenced to trifluoromethylbenzene CF<sub>3</sub>C<sub>6</sub>H<sub>5</sub>. The NMR experiments were conducted in Teflon valve-sealed tubes (J-Young) after vacuum transfer of the liquids in a high-vacuum line. The IR spectrum was recorded in the range 300–4000 cm<sup>−1</sup> on a Nicolet 400 FTIR spectrometer with Na/K dried Nujol in an air-tight container, electron-impact (EI); mass spectra on a Varian MAT 711 instrument (70 eV, *ca.*  $1.17 \times 10^{-17}$  J; variable source temperature). *n*-Butyllithium (solution in hexane) was obtained from Aldrich and [LiN(SiMe<sub>3</sub>)<sub>2</sub>·Et<sub>2</sub>O]<sub>2</sub> was prepared by published procedures.<sup>32</sup>

### Syntheses of (Me<sub>3</sub>Si)<sub>2</sub>NC<sub>6</sub>F<sub>4</sub>CN-4 and LiNI

To a magnetically stirred suspension of [LiN(SiMe<sub>3</sub>)<sub>2</sub>·Et<sub>2</sub>O]<sub>2</sub> (7.23 g, 0.015 mol) in dry thf (20 cm<sup>3</sup>) at −78 °C was added perfluorobenzonitrile (5.79 g, 0.030 mol) with dry thf (200 cm<sup>3</sup>). The mixture was stirred for 12 h at low temperature and slowly warmed to room temperature. All the volatiles were pumped out in a high-vacuum line to obtain an oily mixture. Hexane was added and a light brown precipitate separated. This was filtered through a frit, washed with hexane and dried in vacuum, yielding 3.28 g (45%) of complex **2**. The filtered solution

was evaporated in vacuum to an oil which was liquid–liquid extracted again with hexane and vacuum dried to obtain 2.64 g (55%) of compound **1**.

(Me<sub>3</sub>Si)<sub>2</sub>NC<sub>6</sub>F<sub>4</sub>CN-4 **1**: IR 2244 cm<sup>−1</sup> [ν(CN)]; <sup>1</sup>H NMR (200 MHz, C<sub>6</sub>D<sub>6</sub>) δ −0.07 (s, 18 H, Me<sub>3</sub>Si); <sup>13</sup>C-{F, H} NMR (50.288 MHz, C<sub>6</sub>D<sub>6</sub>) δ 150.4, 148.3, 143.6, 127.0 and 1.8; <sup>19</sup>F-{H} NMR (198.154 MHz, C<sub>6</sub>D<sub>6</sub>) δ −8.86 (m, 2F, Si–N–C=C–F) and −17.76 (m, 2F, N≡C–C=C–F); high-resolution mass spectrum *m/z* 334.0945 (Calc. for C<sub>13</sub>H<sub>18</sub>F<sub>4</sub>N<sub>2</sub>Si<sub>2</sub>) (Found: C, 46.35; H, 5.7; N, 8.55. Calc. for C<sub>13</sub>H<sub>18</sub>F<sub>4</sub>N<sub>2</sub>Si<sub>2</sub>: C, 46.7; H, 5.4; N, 8.4%).

LiN(C<sub>6</sub>F<sub>4</sub>CN-4)<sub>2</sub>·2thf **2**: IR 2235 cm<sup>−1</sup> [ν(CN)]; <sup>1</sup>H NMR (200 MHz, C<sub>6</sub>D<sub>6</sub>) δ 1.74 (m, 4 H, OCH<sub>2</sub>CH<sub>2</sub>) and 3.60 (m, 4 H, OCH<sub>2</sub>CH<sub>2</sub>); <sup>13</sup>C-{F, H} NMR (50.288 MHz, C<sub>6</sub>D<sub>6</sub>) δ 152.9, 148.0, 145.2, 140.3, 69.6 and 27.6; <sup>19</sup>F-{H} NMR (198.154 MHz, C<sub>6</sub>D<sub>6</sub>) δ −11.96 (m, 2F, Li–N–C=C–F) and −26.35 (m, 2F, N≡C–C=C–F) (Found: C, 51.35; H, 3.6; N, 8.45. Calc. for C<sub>22</sub>H<sub>16</sub>F<sub>8</sub>LiN<sub>3</sub>O<sub>3</sub>: C, 51.5; H, 3.15; N, 8.2%).

### Crystallography

Owing to the extreme sensitivity of compound **2** toward moisture and oxygen, a suitable crystal for X-ray analysis was mounted on the Enraf-Nonius CAD4 diffractometer where it was held in a cold stream of nitrogen at 223(2) K. Reflections were collected with graphite-monochromatized Mo-Kα radiation (λ = 0.710 73 Å). Cell data were based upon setting angles of 25 reflections with 6 < θ < 17°.

Structure solution was accomplished with the SHELXS 86<sup>33</sup> program by direct methods. Refinement was completed with the SHELXL 93<sup>34</sup> program. Hydrogen atoms were fixed at idealized positions. The atoms C(30A) and C(33A) are disordered, the occupancy of the two sites being 1 : 2. For the graphic representation the programs ZORTEP<sup>29</sup> and SCHAKAL<sup>35</sup> were used. Crystal data, measurement conditions and details of the structure refinement are shown in Table 2.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallo-

**Table 2** Crystal data and structure refinement for compound **2**\*

Empirical formula	C <sub>22</sub> H <sub>16</sub> F <sub>8</sub> LiN <sub>3</sub> O <sub>2</sub>
<i>M</i>	513.32
Crystal system	Triclinic
Space group	<i>P</i> $\bar{1}$
<i>a</i> /Å	10.010(4)
<i>b</i> /Å	10.190(2)
<i>c</i> /Å	10.010(4)
$\alpha$ /°	70.39(2)
$\beta$ /°	70.94(3)
$\gamma$ /°	68.34(3)
<i>U</i> /Å <sup>3</sup>	1141.5(6)
<i>Z</i>	2
<i>D<sub>c</sub></i> /Mg m <sup>-3</sup>	1.493
$\mu$ /mm <sup>-1</sup>	0.140
<i>F</i> (000)	520
Crystal size/mm	2.75 × 3.75 × 1.88
Scan mode	$\omega$
Scan width/°	1.40 + 0.63 tan $\theta$
$\theta$ Range for data collection/°	2.22–26.25
<i>hkl</i> Ranges	–10 to 2, –12 to 10, –13 to 13
Reflections collected	3858
Observed reflections [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	1998
Independent reflections	2884 ( <i>R</i> <sub>int</sub> = 0.0455)
Refinement method	Full-matrix least squares on <i>F</i> <sup>2</sup>
Data, restraints, parameters	2594, 0, 333
Goodness of fit on <i>F</i> <sup>2</sup>	1.061
<i>R</i> 1 [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0668
<i>wR</i> 2 (all data)	0.1831
Largest difference peak and hole/e Å <sup>-3</sup>	0.422, –0.333

\* Weighting scheme  $w = 1/\sigma^2 F_o^2 + (0.1072P)^2 + 0.3021P$  where  $P = (F_o^2 + 2F_c^2)/3$ .

graphic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/517.

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