

Research Article

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Lithium fluoroarylsilylamides and their structural features

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Abstract: In order to probe the role of $\text{Li}\cdots\text{F}$ interactions toward the stabilisation of low-coordinate lithium complexes, the four fluoroarylsilylamides $[\text{LiN}(\text{SiMe}_3)(2\text{-C}_6\text{H}_4\text{F})]$ (**1-Li**), $[\text{LiN}(\text{SiMe}_3)(2,6\text{-C}_6\text{H}_3\text{F}_2)]$ (**2-Li**), $[\text{LiN}(\text{SiMe}_3)(\text{C}_6\text{F}_5)]$ (**3-Li**), and $[\text{LiN}(\text{SiMe}_2\text{H})(2\text{-C}_6\text{H}_4\text{F})]$ (**4-Li**) have been synthesised in high yields by deprotonation of the parent amines with $n\text{BuLi}$. They have been comprehensively characterised by multinuclear NMR spectroscopy, and complete assignments were achieved with the help of 2D NMR data. The molecular solid-state structures of $[(\text{2-Li})_2]_\infty$, $[\text{3-Li-Et}_2\text{O}]_2$, and $[\text{4-Li}]_8$ were determined by single-crystal X-ray diffraction. They feature unusual coordination patterns, notably for the formation of the polymeric $[(\text{2-Li})_2]_\infty$ and a unique octagonal, crown-like $[\text{4-Li}]_8$. In both structures, the role of $\text{Li}\cdots\text{F}$ non-covalent interactions was the key toward the building of the final architecture. It is shown that Li-F and C-F interatomic distances, along with $|^1J_{\text{C,F}}|$ coupling constants, can be used as qualitative tools for the evaluation of the presence and relative strength of $\text{Li}\cdots\text{F}$ contacts.

Keywords: lithium, fluoroarylsilylamides, $\text{Li}\cdots\text{F}$ interaction, X-ray structures, NMR spectroscopy

1 Introduction

Fluorine-containing substituents and molecules are attracting much interest, in particular on account of the remarkable chemical properties of C-F bonds. They have become a

common motif in agrochemical, pharmaceutical, and bioactive compounds. The incorporation of fluorine allows for the modulation of ligand binding affinities by establishing electrostatic or hydrogen-bonding effects that are not found in the nonfluorinated congeners (Fujiwara and O'Hagan, 2014; Meanwell, 2018; Purser et al., 2008).

The organometallic chemistry of early main group alkali and large alkaline-earth metals is gaining momentum, in particular because they represent affordable, widespread, and non-toxic alternatives to transition metals in homogeneous catalysis. These elements have been used to great effect for the production of molecular catalysts that display high reactivity and selectivity in a broadening range of metal-catalysed organic transformations, e.g. for hydrofunctionalisation, dehydrocoupling, and polymerisation reactions (Harder, 2020). Low-coordinate, highly electrophilic complexes of the large alkaline earths (Ca, Sr, Ba) have been shown to be extremely versatile and effective catalysts. Among the most prominent features, the need for a coordinatively unsaturated metal centre, that is, with a low coordination number, appears to be essential to achieve unique reactivity (Rösch et al., 2021; Rösch and Harder, 2021; Wilson et al., 2017). As established earlier for rare-earth compounds, the syntheses of stable alkaline-earth complexes with coordination numbers as low as two or three have been made possible through the implementation of reliable synthetic strategies, relying either on the kinetic stabilisation imparted by bulky and specifically designed ancillary ligands, or via the deliberate inclusion of secondary interactions that bring additional thermodynamic stability (Le Coz et al., 2018; Chapple and Sarazin, 2020). Among these non-covalent interactions, agostic (Brookhart et al., 2007), $\pi\text{-}\pi$ (Salonen et al., 2011), cation- π (Dougherty, 2013), and dispersion force interactions (Liptrot and Power, 2017) are the most salient and well-known ones. A review article in 2010 highlighted the importance of weak interactions in alkaline-earth chemistry (Buchanan et al., 2010), and they have certainly been essential to many of the breakthroughs that the field has witnessed since. Interactions between a metal and fluorine atoms, for instance in fluoroalkoxides, are also very effective at stabilising electron-deficient complexes

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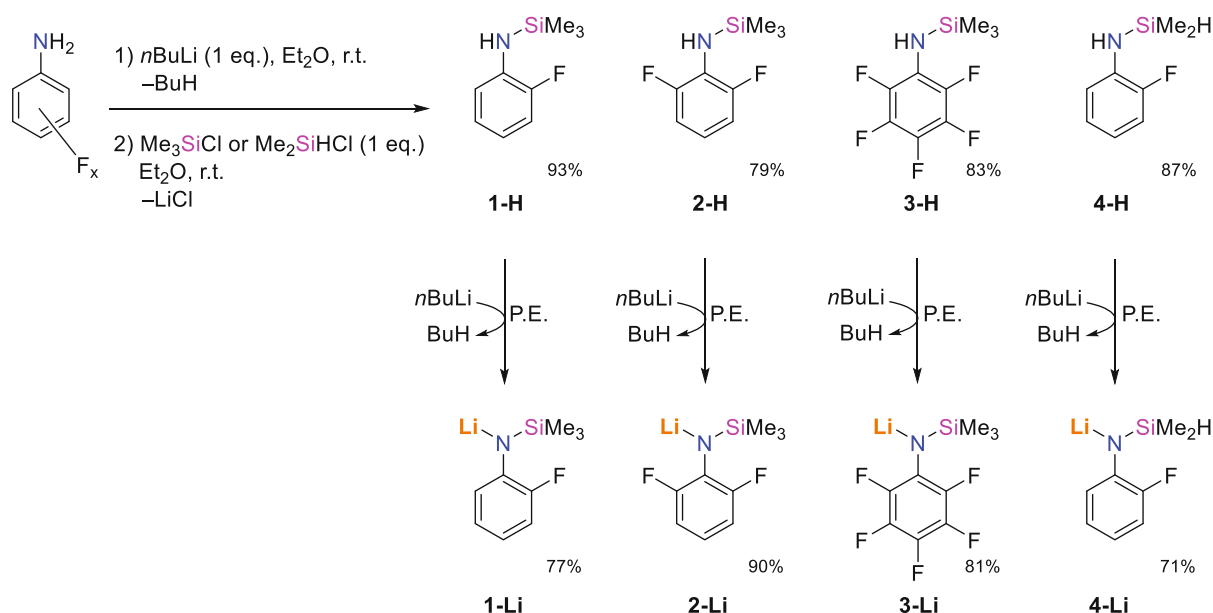
(Roşca et al., 2014; Sarazin et al., 2011). Our group and that of Harder have recently demonstrated how low coordinate, stable, and yet highly reactive alkaline-earth amides [(ligand)MN(C₆F₅)₂] could be generated by exploitation of M...F interactions for M = Ca, Sr, Ba (Fischer et al., 2019; Roueindeji et al., 2019).

Organolithium compounds are remarkably useful and versatile reagents with synthetic applications in organic and organometallic chemistry that populate every synthetic chemistry laboratory (Hevia et al., 2022; Luisi and Capriati, 2014; Luisi et al., 2022; Wakefield, 1988). Despite being known for a century, these seemingly simple species are still attracting sustained attention, notably because the fascinating and often unpredictable structure–reactivity relationships they display are far from being fully comprehended (Barozzino-Consiglio et al., 2017; Hédouin et al., 2023). A recent article from the Arnold group elegantly described how NMR data, and most prominently ¹J_{C,F} couplings, could be used to gauge the strength of Li...F interactions in a lithiated *m*-terphenyl ligand bearing fluorine atoms at the *ortho* positions (Skeel et al., 2020). As part of our interest in low-coordinate *s*-block metals stabilised by secondary interactions, we report here on the utilisation of fluoroarylsilylamines to prepare non-solvated lithiated fluoroarylsilylamides. The solid-state structures of several of these complexes, which display varying patterns of intramolecular and intermolecular Li...F interactions, as well as their NMR data, are discussed.

2 Results and discussion

N-(2-Fluorophenyl)-trimethylsilylamine (**1-H**), *N*-(2,6-difluorophenyl)-trimethylsilylamine (**2-H**), *N*-(pentafluorophenyl)-trimethylsilylamine (**3-H**), and *N*-(2-Fluorophenyl)-1,1-dimethylsilylamine (**4-H**) were isolated in 79–93% yields as colourless liquids upon deprotonation of the appropriate fluoroaniline with *n*BuLi, followed by quenching with Me₃SiCl or, for **4-H**, with Me₂SiHCl (Scheme 1). After initial work-up, the compounds were obtained as analytically pure samples following trap-to-trap transfer. Note that **1-H** (Yin et al., 2016) and **3-H** (Oliver and Graham, 1969) have already been described; we propose here adapted procedures and full characterisations.

The identity of the fluoroarylsilylamines was established by NMR spectroscopy in benzene-*d*₆ (¹H, ¹³C, ¹⁹F, and 2D spectra) and mass spectrometry. In the ¹⁹F NMR spectra, the amines were characterised by single, well-defined resonances at δ_F –135.2 ppm for **1-H**, –135.0 ppm for **2-H**, and –135.4 ppm for **4-H**, with corresponding integrations of 1F, 2F, and 1F. The pertaining |¹J_{C,F}| coupling constants, determined from the ¹³C{¹H} NMR spectra, are 236.5, 238.5, and 241.5 Hz, respectively. These latter values are typically in the range found for other C_{arene}–F bonds (Skeel et al., 2020). The ¹⁹F NMR spectrum for **3-H** exhibits the expected resonances at –159.0 (*o*-F), –165.4 (*m*-F), and –173.7 (*p*-F) ppm. The NMR data for **2-H** were also recorded in thf-*d*₈; they confirmed that the coupling constants, most notably the J_{C,F} ones, are, within the limits of the detection



Scheme 1: Synthesis of the fluoroarylamines **1-H** – **4-H** and their lithiated derivatives **1-Li** – **4-Li** (isolated yields).

method, not affected by the nature of the solvent, and that the ^{19}F NMR spectrum is identical to that in benzene- d_6 .

The equimolar reaction between the fluoroarylamines and $n\text{BuLi}$ in petroleum ether at room temperature afforded the corresponding solvent-free lithiated *N*-(2-fluorophenyl)-trimethylsilylamide [$\text{LiN}(\text{SiMe}_3)(2\text{-C}_6\text{H}_4\text{F})$] (**1-Li**), *N*-(2,6-difluorophenyl)-trimethylsilylamide [$\text{LiN}(\text{SiMe}_3)(2,6\text{-C}_6\text{H}_3\text{F}_2)$] (**2-Li**), *N*-(pentafluorophenyl)-trimethylsilylamide [$\text{LiN}(\text{SiMe}_3)(\text{C}_6\text{F}_5)$] (**3-Li**), and *N*-(2-fluorophenyl)-1,1-dimethylsilylamide [$\text{LiN}(\text{SiMe}_2\text{H})(2\text{-C}_6\text{H}_4\text{F})$] (**4-Li**) in good to high isolated yields (71–90%). The four lithiated amides were obtained as colourless powders. They are sparingly soluble in hydrocarbons, but they dissolve readily in Et_2O and in thf at room temperature; they decompose rapidly in chlorinated solvents. Due to the limited solubility of all four complexes in aromatic hydrocarbons, their NMR data were recorded in thf- d_8 . Full assignment of all resonances in the ^1H and $^{13}\text{C}\{^1\text{H}\}$ spectra was achieved using standard combinations of ^1H , $^{13}\text{C}\{^1\text{H}\}$, and 2D (COSY ^1H – ^1H , HSQC, and HMBC ^1H – ^{13}C) data. Note that **4-Li** is not stable in solution. For instance, an initially colourless solution of the complex in thf- d_8 will gradually turn red over the course of 12 h, with the release of a non-identified compound; in its ^{19}F NMR spectrum, this is concomitant with

the appearance of a (yet unidentified) resonance of growing intensity at δ_{F} –140.8 ppm, whereas the resonance for the complex itself is found at –145.2 ppm. The ^7Li NMR spectra for **1-Li**, **2-Li**, and **4-Li** were characterised by a singlet resonance in the range δ_{Li} 1.18–1.27 ppm; by comparison, the resonance for **3-Li** at 0.90 ppm was slightly more shielded. The use of thf- d_8 as the NMR solvent instead of non-coordinating alternatives precluded useful DOSY NMR analysis regarding the actual aggregation of these species.

The representative $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **2-Li** recorded in thf- d_8 is displayed in Figure 1. It shows in particular a doublet of doublets at δ_{C} 159.9–158.0 ppm ($|^1J_{\text{C,F}}| = 226.4$ Hz and $|^3J_{\text{C,F}}| = 13.8$ Hz) diagnostic of the two *ortho*-CF carbon atoms (aka C_2), along with two 1:2:1 triplets centred on δ_{C} 139.1 and 104.2 ppm for the *ipso* (aka C_1 ; $|^2J_{\text{C,F}}| = 17.6$ Hz) and *para* (aka C_4 ; $|^3J_{\text{C,F}}| = 10.7$ Hz) C-atoms, respectively. In addition, the spectrum also features a multiplet centred on δ_{C} 110.3 ppm for carbon atoms in *meta* position of the aromatic ring (aka C_3), and a 1:2:1 triplet at 3.3 ppm with a scalar coupling constant $|^5J_{\text{C,F}}| = 3.8$ Hz for the CH_3 atoms coupled to the fluorine atoms in *ortho* positions. Similar scalar couplings with *ortho* fluorines, with comparable intensities, were observed in several cases, both for the fluoroarylamines and for the corresponding

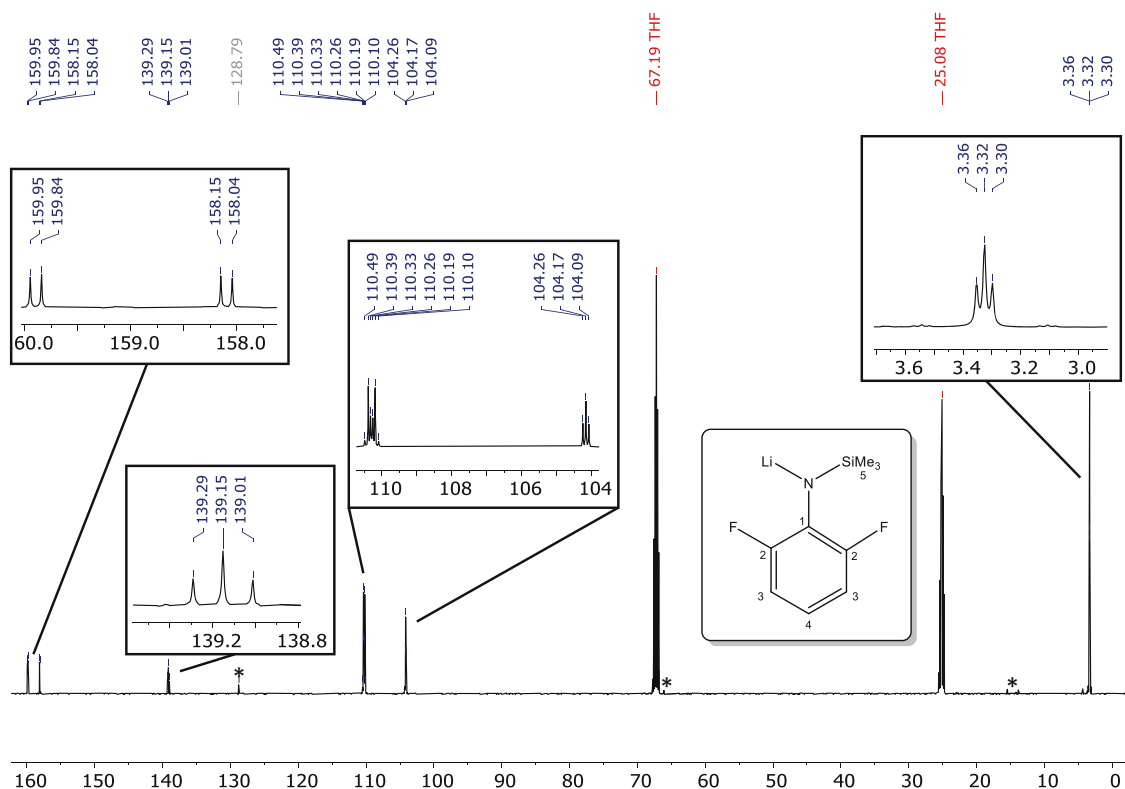


Figure 1: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (thf- d_8 , 125.77 MHz, 27°C) of [$\text{LiN}(\text{SiMe}_3)(2,6\text{-C}_6\text{H}_3\text{F}_2)$] (**2-Li**). * = residual solvent (petroleum ether, Et_2O , and benzene).

lithiated complexes. In these instances, the $^5J_{C,F}$ scalar nature of the coupling, instead of a through-space dipolar one, was unambiguously demonstrated by a ^{19}F - ^{13}C HMBC experiment (Figure S17 in the Supplementary material).

The unsolvated **2-Li** is crystallised from a concentrated solution in petroleum ether. Due to the presence of multiple $Li\cdots F$ interactions, it forms the solid-state infinite zigzag monodimensional chains of coordination polymer. The repetitive motif is a centro-symmetric dimer formed by two molecules of **2-Li** with bridging N atoms forming a planar Li_2N_2 core, and the crystalline solid-state structure of the compound is hence best depicted as $[(2-Li)_2]_\infty$ (Figures 2 and 3). With two $Li\cdots F$ interactions per metal, the geometry about each lithium atom forms a distorted tetrahedron with $\tau_4 = 0.75$ (Yang *et al.*, 2007). The $Li1-N1$ and $Li1-N1^{#2}$ interatomic distances of 2.068(9) and 2.047(8) Å are unexceptional. They compare well with those found in similar lithium amides, for instance in the trimeric, solvent-free $[LiN(SiMe_3)_2]_3$ (2.00(2) Å) or in the Et_2O -solvated dimer $[LiN(SiMe_3)_2Et_2O]_2$ (2.06(1) Å) (Lapport *et al.*, 1983). The intramolecular $Li1-F2$ interatomic distance of 1.985(8) Å is at the low end of values reported for similar interactions and is substantially shorter than the intermolecular one ($Li^{#1}-F1 = 2.107(9)$ Å). For comparison, $Li-F$ distances were in the range 1.972(8)–2.000(9) Å in the

heterobimetallic complex $C\{SiMe_2N(2-C_6H_4F)\}_3Sn(Li)$ (Lutz *et al.*, 2003). The $Li-F$ distances in the known tmeda adduct $[2-Li.tmeda]$ (2.082(5) Å) is also longer (Aharonovich *et al.*, 2009) than the $Li1-F2$ one, but both distances in $[(2-Li)_2]_\infty$ are in the range of those measured in the dimeric $[LiN(C_6F_5)_2]_2 \cdot (o-C_6H_3F_2)]$ solvated by a single molecule of difluorobenzene (1.986(3)–2.139(3) Å; Schorpp *et al.*, 2020). By contrast, $Li-F$ interatomic distances were shorter (1.925(4)–1.945(5) Å) in $[Terph^F-Li]_2$, where $Terph^F$ is 2,6-bis(2,6-difluoro-4-trimethylsilylphenyl)-4-*tert*-butylphenyl (Skeel *et al.*, 2020). The $C5-F1$ and $C9-F2$ bond lengths of 1.389(5) and 1.384(5) Å in $[(2-Li)_2]_\infty$ are conventional and match those in the three aforementioned reported lithium complexes.

The creation of coordination polymers through the formation of intermolecular $Li\cdots F$ interactions, as encountered in $[(2-Li)_2]_\infty$, is already documented. A number of patterns in organometallic and inorganic examples have been described, e.g. as in $[Li(diglyme)][BF_4]$ (Andreev *et al.*, 2005) and in $[Li(Et_2O)][B(C_6F_5)_4]$ (Kuprat *et al.*, 2010) or, more relevantly to our work, in the monodimensional $[LiN(SiMe_3)_2p-C_6H_4F_2]_\infty$ which presents short $Li-F$ interatomic distances (1.999(8) Å; Williard and Liu, 1994). Non-covalent interactions, such as $Li\cdots F$ ones in our case, are now an established synthetic tool frequently used to synthesise highly electrophilic complexes with low coordination numbers and devoid of coordinated Lewis base. With s-block oxophilic metals, the $M\cdots F$ interaction has been shown to be essentially ionic, although it also possesses a non-negligible covalent character (Roueindeji *et al.*, 2019). It can be safely assumed that it is because of the absence of additional donor onto the lithium centres that $[(2-Li)_2]_\infty$ forms a polymer in the solid state. Coordination of, for instance, Et_2O molecules, would be expected to disrupt many if not all of the $Li\cdots F$ contacts.

Single crystals of **1-Li** and **3-Li** suitable for X-ray diffraction could not be obtained despite repeated attempts. However, X-ray quality crystals of **[3-Li- Et_2O]** were grown from a solution of **3-Li** in Et_2O . The solvated complex exists as a centro-symmetric dimer with four-coordinated metal centres as a result of coordination by two N-atoms and one O-atom along with a single $Li\cdots F$ interaction (Figure 4). The bridging positions are occupied by the nitrogen atoms, and as a result the dimer exhibits a planar Li_2N_2 core. The geometry about the metal atoms forms a distorted tetrahedra ($\tau_4 = 0.31$). The $Li-N$ interatomic distances, in the range 2.061(3)–2.075(3) Å, are unremarkable; they match those found in $[(2-Li)_2]_\infty$. Despite the presence of a coordinated Et_2O molecule in **[3-Li- Et_2O]**, the complex still shows one $Li\cdots F$ interaction

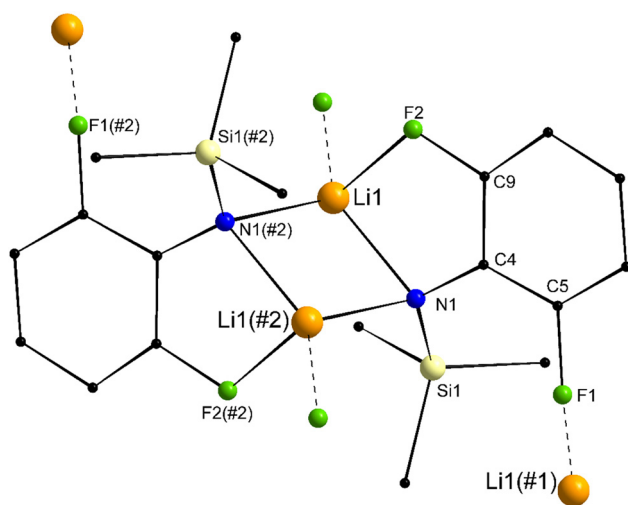


Figure 2: Representation of the molecular solid-state structure of the dimeric $[LiN(SiMe_3)(2,6-C_6H_3F_2)]_2[(2-Li)_2]$. H atoms are omitted for clarity. $Li\cdots F$ intermolecular interactions within the 1D-coordination network shown in dotted lines. Selected bond lengths (Å) and angles ($^\circ$): $Li1-N1 = 2.068(9)$, $Li1-N1^{#2} = 2.047(8)$, $Li1-F2 = 1.985(8)$, $Li^{#1}-F1 = 2.107(9)$, $C5-F1 = 1.389(5)$, $C9-F2 = 1.384(5)$; $N1-Li1-N1^{#2} = 104.2(4)$, $Li1-N1-Li1^{#2} = 75.8(4)$. Symmetry transformations: #1: $x, y, z, T = [0, -1, 0]$; #2: $-x, -y, -z, T = [0, 2, 0]$. Colour code: C, black; F, green; Li, orange; N, blue; Si, beige.

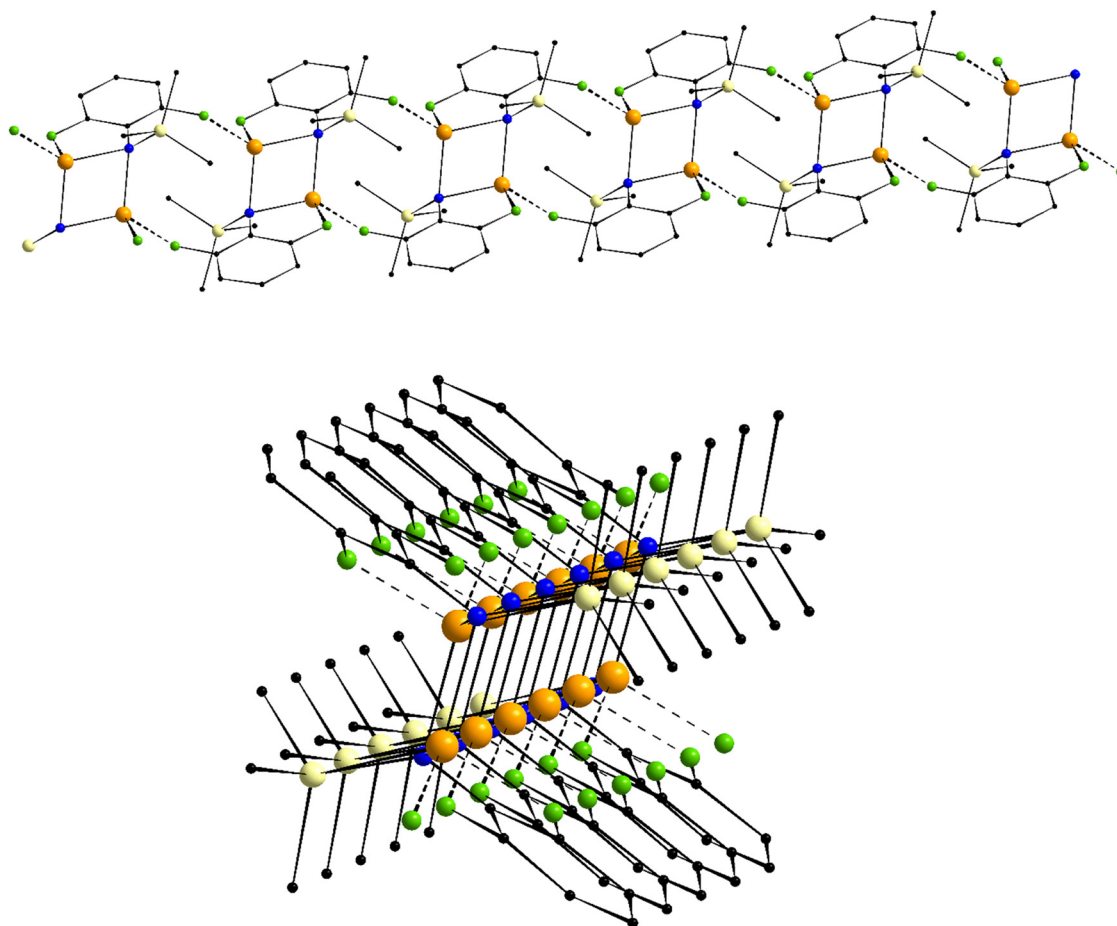


Figure 3: Representation of the molecular solid-state structure of $[\text{LiN}(\text{SiMe}_3)(2,6\text{-C}_6\text{H}_3\text{F}_2)]_2 \cdot [(\text{2-Li})_2]_\infty$, showing the one-dimensional zigzag arrangement through the presence of intermolecular $\text{Li} \cdots \text{F}$ interactions. H atoms are omitted for clarity. $\text{Li} \cdots \text{F}$ interactions within the coordination network are shown in dotted lines. Colour code: C, black; F, green; Li, orange; N, blue; Si, beige.

per metal, albeit the pertaining $\text{Li1-F1} = 2.106(3) \text{ \AA}$ distance suggests its intensity is lesser than those in $[(\text{2-Li})_2]_\infty$. There is no significant elongation of the C–F bond length as a result of the (weak) interaction of the fluorine (aka F1) with the metal (aka Li1), as indicated by the very similar C2–F1 and C6–F5 interatomic distances of $1.3643(18)$ and $1.3541(19) \text{ \AA}$, respectively.

The molecular structure of the octamer $[\text{4-Li}]_8$ is depicted in Figure 5. The crystals were obtained by recrystallisation from a concentrated toluene solution, in the hope that both C–F and Si–H motifs found in **4-Li** would induce an unusual structural arrangement in the molecular solid state through the presence of $\text{Li} \cdots \text{F}$ or $\text{Li} \cdots \text{H-Si}$ non-covalent interactions (Roşca et al., 2016). The unit cell contains two identical molecules of $[\text{4-Li}]_8$, one of which only is shown in Figure 5, and two non-interacting toluene molecules. The octamer adopts a unique crown-like arrangement. It features four inequivalent pairs of lithium ions and a crystallographic C_4 -symmetry

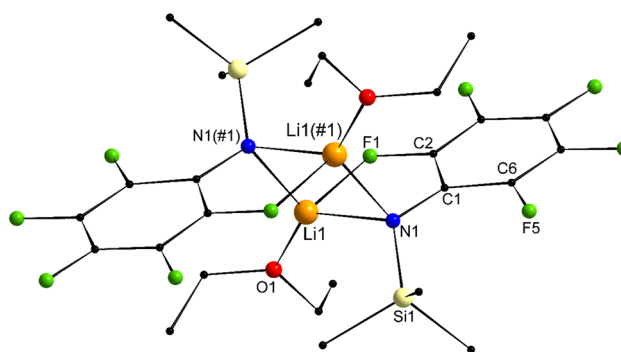


Figure 4: Representation of the molecular solid-state structure of the dimer $[\text{LiN}(\text{SiMe}_3)(\text{C}_6\text{F}_5) \cdot \text{Et}_2\text{O}]_2 \cdot [3\text{-Li-Et}_2\text{O}]_2$. H atoms omitted for clarity. Selected bond lengths ($\text{\AA}$) and angles ($^\circ$): $\text{Li1-F1} = 2.106(3)$, $\text{Li1-N1} = 2.061(3)$, $\text{Li1-N1}^{\#1} = 2.075(3)$, $\text{Li1-O1} = 1.910(3)$, $\text{C2-F1} = 1.3643(18)$, $\text{C6-F5} = 1.3541(19)$; $\text{N1-Li1-F1} = 81.81(11)$, $\text{N1}^{\#1}\text{-Li1-F1} = 108.69(12)$, $\text{N1-Li1-N1}^{\#1} = 103.33(12)$, $\text{N1-Li1-O1} = 128.96(14)$, $\text{N1}^{\#1}\text{-Li1-O1} = 125.20(14)$, $\text{O1-Li1-F1} = 95.29(12)$, $\text{Li1-N1-Li1}^{\#1} = 76.67(12)$. Symmetry operations: $-x, -y, -z, T = [1, 1, 1]$. Colour code: C, black; F, green; Li, orange; N, blue; O, red; Si, beige.

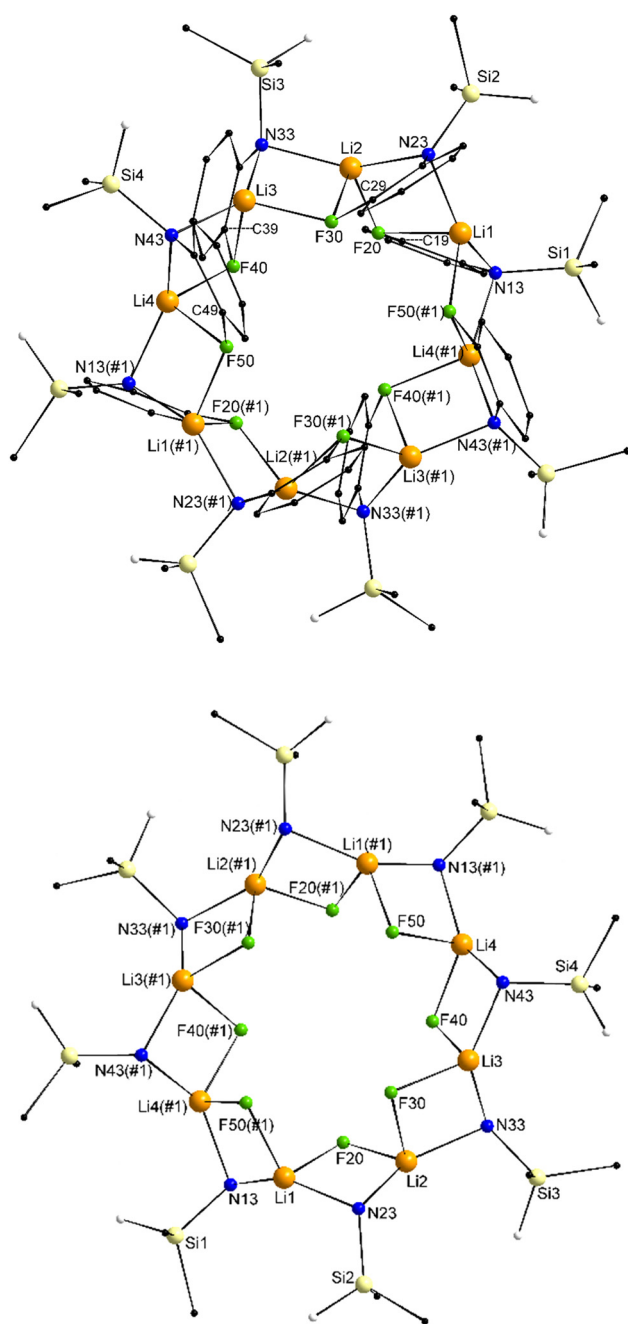


Figure 5: (top) Representation of the molecular solid-state structure of $[\text{LiN}(\text{SiMe}_2\text{H})(2\text{-C}_6\text{H}_4\text{F})]_8$ ($[4\text{-Li}]_8$). Non-interacting toluene molecules and H atoms except those of Si atoms omitted for clarity. Only one of the two independent and identical molecules in the unit cell is depicted. Selected bond lengths (Å): $\text{Li1-F50}^{\#1} = 2.044(6)$, $\text{Li1-F20} = 2.301(6)$, $\text{Li1-N13} = 1.981(6)$, $\text{Li1-N23} = 2.011(6)$, $\text{Li2-F20} = 1.975(5)$, $\text{Li2-F30} = 2.259(5)$, $\text{Li2-N23} = 1.984(6)$, $\text{Li2-N33} = 2.009(6)$, $\text{Li3-F30} = 2.022(5)$, $\text{Li3-F40} = 2.240(5)$, $\text{Li3-N33} = 1.965(5)$, $\text{Li3-N43} = 1.977(5)$, $\text{Li4-F40} = 2.044(5)$, $\text{Li4-F50} = 2.227(5)$, $\text{Li4-N13}^{\#1} = 2.021(6)$, $\text{Li4-N43} = 1.993(6)$, $\text{C19-F20} = 1.400(3)$, $\text{C29-F30} = 1.403(3)$, $\text{C39-F40} = 1.410(3)$, $\text{C49-F50} = 1.407(3)$. Symmetry operations: $-x + 1/2, -y, -z + 1/2, T = [1, 0, 0]$. (bottom) Top view of the crown-like molecular solid-state structure of $[\text{LiN}(\text{SiMe}_2\text{H})(2\text{-C}_6\text{H}_4\text{F})]_8$ ($[4\text{-Li}]_8$). Non-interacting toluene molecules, aromatic N-bound rings, and H atoms except those of Si atoms omitted for clarity. Colour code: C, black; F, green; H, white; Li, orange; N, blue; Si, beige.

axis orthogonal through its centre to the ring delineated by the eight metal centres (yet, the structure was solved in the monoclinic $P2_1/n$ space group of lower symmetry due to the presence of lattice toluene molecules). Each lithium is in a highly distorted tetrahedral environment, with two Li–N bonds and two very different Li $\cdots$ F interactions; there is no anagostic contact between the metal ions and the Si–H moieties. In fact, the SiMe_2H groups are pushed away from the Li_8 ring, with Li $\cdots$ H–Si distances well over 3 Å.

The Li_8 octagon is held together by bridging N- and F-atoms. The Li–N interatomic distances to the bridging N-atoms, in the range 1.965(5)–2.021(6), are all within the same narrow range. They are noticeably shorter than those measured in the polymeric $[(2\text{-Li})_2]_\infty$ (2.047(8)–2.068(9) Å) and in the dimer $[\mathbf{3-Li-Et}_2\text{O}]_2$ (2.061(3)–2.075(3) Å). For each Li centre, one Li $\cdots$ F interaction is very much stronger than the other, as indicated by the largely different Li–F interatomic distances: $\text{Li1-F50}^{\#1} = 2.044(6)$ vs $\text{Li1-F20} = 2.301(6)$ Å, $\text{Li2-F20} = 1.975(5)$ vs $\text{Li2-F30} = 2.259(5)$ Å, $\text{Li3-F30} = 2.022(5)$ vs $\text{Li3-F40} = 2.240(5)$ Å, and $\text{Li4-F40} = 2.044(5)$ vs $\text{Li4-F50} = 2.227(5)$ Å. In fact, one may question whether the set of weak Li $\cdots$ F contacts are truly significant, even if they are much shorter than the sum of van der Waals radii for Li and F (1.82 and 1.47 Å, respectively); note however that, perhaps more relevantly, the tabulated ionic radius of the tetra-coordinated Li^+ ion is 0.59 Å (Shannon, 1976). The shorter set of Li–F distances, in the range 1.975(5)–2.044(5) Å, compare well with those in the already discussed complexes $[(2\text{-Li})_2]_\infty$ (1.985(8)–2.107(9) Å) and $\text{C}[\text{SiMe}_2\text{N}(2\text{-C}_6\text{H}_4\text{F})]_3\text{Sn}(\text{Li})$ (1.972(8)–2.000(9) Å; Lutz *et al.*, 2003). We note that the C–F bonds in $[\mathbf{4-Li}]_8$, with interatomic distances in the range 1.400(3)–1.410(3) Å, are slightly stretched compared to those in $[(2\text{-Li})_2]_\infty$ (1.389(5)–1.384(5) Å) and $[\mathbf{3-Li-Et}_2\text{O}]_2$ (1.3541(19)–1.3643(18) Å). By comparison, the C–F bond lengths are also shorter (1.371(5) Å) in the titanium(III) triamidotriamine complex bearing the 1,4,7- $\{\text{N}(2\text{-C}_6\text{H}_4\text{F})\text{SiMe}_2\}_3$ -1,4,7-triazacyclononane ligand and where no Ti $\cdots$ F interaction was detected (Martins *et al.*, 2005). Overall, we interpret the increase of the C–F bond lengths in crystalline $[(2\text{-Li})_2]_\infty$ as a consequence (and an evidence) of the Li $\cdots$ F interactions and resulting slight weakening of the pertaining C–F bonds. This hypothesis also agrees with the NMR data for $\mathbf{4-Li}$, which witnesses a very tangible reduction of the $|^1J_{\text{C,F}}|$ coupling constant on moving from $\mathbf{4-H}$ (241.5 Hz) to the lithiated complex (217.3 Hz). Similar decreases were also observed for $\mathbf{2-Li}$ ($|^1J_{\text{C,F}}| = 226.4$ vs 238.5 Hz in $\mathbf{2-H}$) and $\mathbf{3-Li}$ ($|^1J_{\text{C,F}}| = 221.3$ vs 243.5 Hz in $\mathbf{3-H}$). Although there is no direct correlation between the C–F interatomic distances and corresponding values of the $|^1J_{\text{C,F}}|$ couplings, it seems legitimate to see both types of physical data only as

valuable qualitative tools to evaluate the presence of $\text{Li}\cdots\text{F}$ interactions in the lithium fluoroarylsilylamides. On the other hand, variations of NMR chemical shifts from amine to amide are of little relevance, as these will mostly be affected by the developing negative charge on the nitrogen atom as a result of the deprotonation of the amine. A more thorough interpretation of these data and structural analysis for the complexes would require in-depth analysis of NMR data in a non-coordinating solvent (including DOSY NMR analysis to probe whether the crystalline structures are retained in solution and ^6Li NMR), but such studies were unfortunately prohibited by the poor solubility in the compounds in aromatic hydrocarbons and their instability in chlorinated solvents. A summary of the most salient properties for complexes **2-Li**, **3-Li**, and **4-Li** is collated in Table 1.

3 Conclusion

A set of lithium fluoroarylsilylamides have been prepared in high yields upon deprotonation of the parent amines with $n\text{BuLi}$ in petroleum ether. The complexes have been comprehensively characterised by all available analytical tools, and detailed NMR data are provided. Three of the complexes, namely $[\text{LiN}(\text{SiMe}_3)(2,6\text{-C}_6\text{H}_3\text{F}_2)]$ (**2-Li**), $[\text{LiN}(\text{SiMe}_3)(\text{C}_6\text{F}_5)]$ (**3-Li**), and $[\text{LiN}(\text{SiMe}_2\text{H})(2\text{-C}_6\text{H}_4\text{F})]$ (**4-Li**) were crystallised under different experimental conditions, and the molecular solid-state structures of the corresponding $[(\mathbf{2-Li})_2]_\infty$, $[\mathbf{3-Li-Et_2O}]_2$, and $[\mathbf{4-Li}]_8$ were solved. In all cases, medium to very strong $\text{Li}\cdots\text{F}$ interactions were detected. These secondary interactions are the key toward the construction of unusual arrangements, such as the coordination polymer $[(\mathbf{2-Li})_2]_\infty$ or the octagonal $[\mathbf{4-Li}]_8$. The presence of $\text{Li}\cdots\text{F}$ interactions could be related to the elongation of the pertaining C–F bond along with a decrease of the

corresponding $|^1J_{\text{C,F}}|$ coupling constants in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of the complexes, although no direct relationship between $d(\text{Li-F})$, $d(\text{C-F})$, and $\Delta(|^1J_{\text{C,F}}|)$ could be drawn. The results presented herein constitute another evidence that $\text{M}\cdots\text{F}$ interactions can be used to obtain unorthodox molecular structure for low-coordinate oxophilic elements, and we will endeavour to further exploit this feature in our ongoing research program.

Experimental section

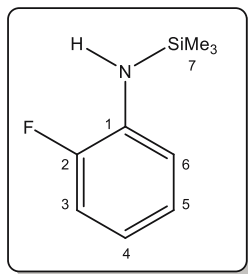
General procedures

All manipulations were performed under an inert atmosphere by using standard Schlenk techniques or in a dry, solvent-free glovebox (Jacomex; $\text{O}_2 < 1$ ppm, $\text{H}_2\text{O} < 3$ ppm). Petroleum ether, toluene, and diethyl ether were collected from MBraun SPS-800 purification alumina columns and thoroughly degassed with argon before being stored on 4 Å molecular sieves; thf was distilled under argon from Na/benzophenone prior to use. Deuterated solvents (Eurisotop, Saclay, France) were stored in sealed ampoules over activated 4 Å molecular sieves or a potassium mirror and degassed by a minimum of three freeze–thaw cycles. NMR spectra were recorded with Bruker AM-300, AM-400, or AM-500 spectrometers. All chemical shifts (δ) [ppm] were determined relative to the residual signal of the deuterated solvent in benzene- d_6 or thf- d_8 or to FCCL_3 for ^{19}F NMR. Assignments of signals were carried out using 1D and 2D NMR experiments. Reliable and reproducible elemental analyses for the compounds could not be obtained, most probably on account of their high hydrolytic sensitivity.

Table 1: Representative NMR and single-crystal XRD data for complexes 1-Li–4-Li

		1-Li [LiN(SiMe ₃)(2-F-C ₆ H ₄)]	2-Li [LiN(SiMe ₃)(2,6-F ₂ -C ₆ H ₃)]	3-Li [LiN(SiMe ₃)(C ₆ F ₅)]	4-Li [LiN(SiMe ₂ H)(2-F-C ₆ H ₄)]
NMR	$ ^1J_{\text{C,F}} $ (Hz)				
	Parent amine	236.5	238.5	243.5	241.5
	Complex	216.3	226.4	221.3	217.3
	$\Delta(^1J_{\text{C,F}})$ (Hz)	20.2	12.1	22.2	24.2
	δ_{Li} (ppm)	1.27	1.20	0.90	1.18
XRD	Structure	n/a	$[(\mathbf{2-Li})_2]_\infty$	$[\mathbf{3-Li-Et_2O}]_2$	$[\mathbf{4-Li}]_8$
	$d(\text{Li-F})$ (Å)	n/a	1.985(8)–2.107(9)	2.106(3)	1.975(5)–2.044(5) 2.227(5)–2.301(6)
	$d(\text{C-F})$ (Å)	n/a	1.389(5)–1.384(5)	1.354(2)–1.364(2)	1.400(3)–1.410(3)

Synthesis of *N*-(2-fluorophenyl)-trimethylsilylamine (1-H)



The synthesis of **1** was adapted from a known protocol (Yin *et al.*, 2016). In a round-bottom flask, *n*BuLi (18.6 mL of a 1.57 M solution in hexanes, 29.2 mmol) was added dropwise (ca. 30 min) at -78°C to a solution of *o*-F-C₆H₄-NH₂ (2.8 mL, 3.2 g, 28.8 mmol) in diethyl ether (50 mL). The clear and colourless solution was then allowed to warm to room temperature. A solution of Me₃SiCl (3.8 mL, 3.2 g, 29.9 mmol) in diethyl ether (50 mL) was added in two portions. The resulting slurry was stirred overnight at room temperature. The precipitate was then eliminated by filtration. The volatiles were pumped off under dynamic vacuum to give the title compound as an analytically pure colourless liquid. Isolated yield: 4.9 g (93%). MS ASAP for [M + H]⁺, calcd *m/z* 184.09523. Found 184.0950 (1 ppm).

¹H NMR (400.16 MHz, 27°C, benzene-*d*₆): δ 6.93–6.88 (ddd, $|^1J_{\text{H,H}}| = 12.0$ Hz, $|^2J_{\text{H,H}}| = 8.0$ Hz, $|^3J_{\text{H,H}}| = 1.6$, 1H, C₃H), 6.83–6.79 (m, 1H, C₅H), 6.76–6.72 (m, 1H, C₆H), 6.53–6.47 (m, 1H, C₄H), 3.59 (br s, 1H, NH), 0.07 (s, 9H, CH₃) ppm.

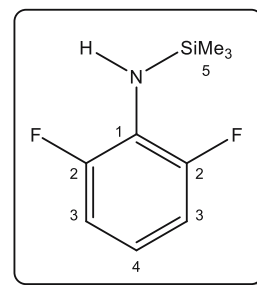
¹³C{¹H} NMR (100.63 MHz, 27°C, benzene-*d*₆): δ 154.4–152.1 (d, $|^1J_{\text{C,F}}| = 236.5$ Hz, C₂), 136.2–136.1 (d, $|^2J_{\text{C,F}}| = 12.1$ Hz, C₁), 124.7 (d, $|^4J_{\text{C,F}}| = 3.0$ Hz, C₅), 117.8 (d, $|^3J_{\text{C,F}}| = 7.0$ Hz, C₄), 116.9 (d, $|^3J_{\text{C,F}}| = 3.0$ Hz, C₆), 115.5–115.3 (d, $|^2J_{\text{C,F}}| = 19.1$ Hz, C₃), -0.2 (t, $|^1J_{\text{Si,Cl}}| = 57.3$ Hz, CH₃) ppm.

¹⁹F NMR (376.47 MHz, 25°C, benzene-*d*₆): δ -135.1 (s, 1F) ppm.

¹H NMR (400.16 MHz, 25°C, thf-*d*₈): δ 6.93–6.80 (m, 3H, arom-CH), 6.59–6.54 (m, 1H, arom-CH), 6.53–6.48 (m, 1H, arom-CH), 4.21 (br s, 1H, NH), 0.26 (s, 9H, CH₃) ppm.

¹⁹F NMR (376.47 MHz, 25°C, thf-*d*₈): δ -135.2 (s, 1F) ppm.

Synthesis of *N*-(2,6-difluorophenyl)-trimethylsilylamine (2-H)



In a protocol identical to that described for **1**, the title compound was obtained by reaction of 2,6-difluoroaniline (2.2 mL, 2.6 g, 20 mmol), *n*BuLi (12.6 mL of a 1.57 M solution in hexanes, 19.8 mmol), and Me₃SiCl (2.6 mL, 2.2 g, 20.0 mmol). Compound **2** was isolated as a colourless liquid. Isolated yield: 3.2 g (79%). MS ASAP for [M + H]⁺, calcd *m/z* 202.08581. Found 202.0856 (1 ppm).

¹H NMR (400.13 MHz, 24°C, benzene-*d*₆): δ 6.62–6.58 (m, 2H, C₃H), 6.23–6.18 (m, 1H, C₄H), 3.44 (br s, 1H, NH), 0.15 (t, $|^5J_{\text{H,F}}| = 1.4$ Hz, 9H, CH₃) ppm.

¹³C{¹H} NMR (100.62 MHz, 26°C, benzene-*d*₆): δ 154.8–152.4 (dd, $|^1J_{\text{C,F}}| = 238.5$ Hz, $|^3J_{\text{C,F}}| = 8.0$ Hz, C₂), 116.4 (t, $|^3J_{\text{C,F}}| = 9.0$ Hz, C₄), 111.6–111.2 (dd, $|^2J_{\text{C,F}}| = 27.2$ Hz, $|^4J_{\text{C,F}}| = 4.0$ Hz, C₃), 111.5 (m, C₁), 0.07 (t, $|^1J_{\text{Si,Cl}}| = 58.4$ Hz, $|^5J_{\text{C,F}}| = 3.0$ Hz, CH₃) ppm.

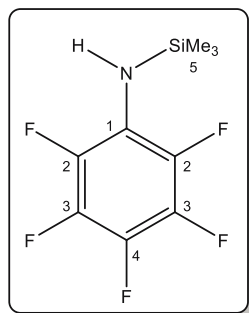
¹⁹F NMR (282.36 MHz, 25°C, benzene-*d*₆): δ -128.5 (s, 2F) ppm.

¹H NMR (400.16 MHz, 27°C, thf-*d*₈): δ 6.84–6.77 (m, 2H, C₃H), 6.60–6.53 (m, 1H, C₄H), 4.01 (br s, 1H, NH), 0.24 (s, 9H, CH₃) ppm.

¹³C{¹H} NMR (100.63 MHz, 27°C, thf-*d*₈): δ 155.3–152.9 (dd, $|^1J_{\text{C,F}}| = 238.5$ Hz, $|^3J_{\text{C,F}}| = 8.2$ Hz, C₂), 125.9 (t, $|^2J_{\text{C,F}}| = 16.3$ Hz, C₁), 116.7 (t, $|^3J_{\text{C,F}}| = 9.4$ Hz, C₄), 111.8–111.4 (m, C₃), 0.70 (t, $|^1J_{\text{Si,Cl}}| = 58.3$ Hz, $|^5J_{\text{C,F}}| = 3.4$ Hz, CH₃) ppm.

¹⁹F NMR (376.47 MHz, 27°C, thf-*d*₈): δ -128.8 (s, 2F) ppm.

Synthesis of *N*-(pentafluorophenyl)-trimethylsilylamine (3-H)



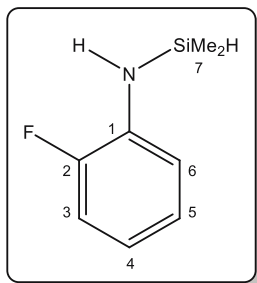
In a protocol identical to that described for **1**, the title compound was obtained by reaction of pentafluoroaniline (3.0 g, 16.5 mmol), *n*BuLi (10.5 mL of a 1.57 M solution in hexanes, 16.5 mmol), and Me₃SiCl (2.1 mL, 1.8 g, 16.5 mmol). Compound **3** was isolated as a colourless liquid. Isolated yield: 3.5 g (83%). Anal. found: C, 42.4; H, 4.1; N, 5.8. Calcd for C₉H₁₀F₅NSi (255.26 g·mol⁻¹): C, 42.35; H, 3.95; N, 5.49. MS ASAP for [M + H]⁺, calcd *m/z* 256.05754. Found 256.0573 (1 ppm).

¹H NMR (400.16 MHz, 27°C, benzene-*d*₆): δ 3.04 (br s, 1H, NH), 0.05 (t, ⁵*J*_{H,F} = 1.4 Hz, 9H, CH₃) ppm.

¹³C{¹H} NMR (100.62 MHz, 26°C, benzene-*d*₆): δ 139.9–139.4 and 137.5–137.2 (overlapping dm, C₂ and C₃) 134.8–132.0 (dt, ¹*J*_{C,F} = 243.5 Hz, ²*J*_{C,F} = 14.1 Hz, ³*J*_{C,F} = 5.0 Hz, C₄), 123.5–123.2 (t, ²*J*_{C,F} = 13.1 Hz, C₁), 0.30 (t, ¹*J*_{Si,Cl} = 58.4 Hz, ⁵*J*_{C,F} = 3.1 Hz, CH₃) ppm.

¹⁹F NMR (376.47 MHz, 25°C, benzene-*d*₆): δ -159.0 (d, ³*J*_{F,F} = 18.8 Hz, 2F, *o*-F), -165.4 (m, ³*J*_{F,F} = 18.8 Hz, 2F, *m*-F), -173.7 (m, ³*J*_{F,F} = 18.8 Hz, 1F, *p*-F) ppm.

N-(2-fluorophenyl)-1,1-dimethylsilylamine (4-H)



A solution of 2-fluoroaniline (4.4 mL, 5.0 g, 45.4 mmol) in diethyl ether (100 mL) was cooled down to 0°C, and *n*BuLi (29.3 mL of a 1.55 M solution in hexanes, 45.4 mmol) was then added dropwise over 30 min. The reaction mixture was then left to gently warm up to room temperature for

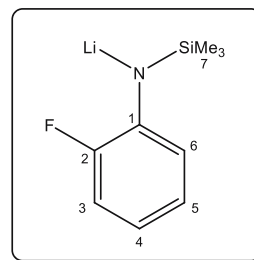
1 h. A solution of chlorodimethylsilane (5.1 mL, 4.3 g, 45.8 mmol) in Et₂O (70 mL) was then added dropwise, and the milky suspension was stirred at room temperature for 16 h. The solution was then filtered to eliminate the precipitate, and the volatiles were removed under vacuum. The amine was isolated as analytically pure colourless oil by trap-to-trap transfer. Isolated yield: 6.7 g (87%). MS ASAP for [M + H]⁺, calcd *m/z* 170.07958. Found 170.0795 (0 ppm).

¹H NMR (400.16 MHz, 27°C, benzene-*d*₆): δ 6.93–6.83 (m, 1H, C₃H), 6.81–6.78 (m, 2H, C₅H, and C₆H), 6.53–6.47 (m, 1H, C₄H), 4.77 (m, with ¹*J*_{Si,H} = 204.0 Hz and ¹*J*_{H,H} = 1.6 Hz, 1H, SiH), 3.51 (1H, NH), 0.02 (d, ³*J*_{H,H} = 3.2 Hz, 6H, CH₃) ppm.

¹³C{¹H} NMR (100.62 MHz, 26°C, benzene-*d*₆): δ 154.4–152.0 (d, ¹*J*_{C,F} = 241.5 Hz, C₂), 135.9 (d, ²*J*_{C,F} = 13.1 Hz, C₁), 124.9 (d, ⁴*J*_{C,F} = 4.0 Hz, C₅), 118.3 (d, ³*J*_{C,F} = 7.0 Hz, C₄), 116.7 (d, ³*J*_{C,F} = 4.0 Hz, C₆), 115.4–115.2 (d, ²*J*_{C,F} = 20.1 Hz, C₃), -2.4 (s, ¹*J*_{Si,Cl} = 57.3 Hz, CH₃) ppm.

¹⁹F NMR (376.44 MHz, 24°C, benzene-*d*₆): δ -135.4 (s, 1F) ppm. The presence of an impurity (ca. 1 mol%) was detected at -136.0 ppm.

Synthesis of lithium *N*-(2-fluorophenyl)-trimethylsilylamide (1-Li)



At -78°C, *n*BuLi (3.5 mL of a 1.57 M solution in hexanes, 5.5 mmol) was added dropwise (ca. 30 min) to a solution of **1-H** (1.0 g, 5.5 mmol) in petroleum ether (50 mL). The mixture was allowed to warm to room temperature and was stirred for 4 h, leading to the formation of a white precipitate. The supernatant was removed by filtration, and the title complex was obtained as a white powder after drying the precipitate to constant weight under vacuum. Isolated yield: 0.8 g (77%).

¹H NMR (500.13 MHz, 27°C, thf-*d*₈): δ 6.63–6.50 (overlapping m, 3H, arom-H), 5.86–5.82 (m, 1H, arom-H), 0.04 (s, 9H, CH₃) ppm.

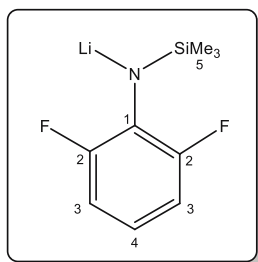
¹³C{¹H} NMR (125.77 MHz, 27°C, thf-*d*₈): δ 160.6–158.9 (d, ¹*J*_{C,F} = 216.3 Hz, C₂), 150.8 (d, ²*J*_{C,F} = 10.1 Hz, C₁),

125.3 (d, $|^4J_{C,F}| = 2.5$ Hz, C₅), 121.0 ppm (d, $|^3J_{C,F}| = 6.3$ Hz, C₄), 112.8 (d, $|^2J_{C,F}| = 23.4$ Hz, C₃), 107.0 (d, $|^3J_{C,F}| = 8.8$ Hz, C₆), 1.8 (s, $|^1J_{Si,Cl}| = 53.6$ Hz, CH₃) ppm.

^{19}F NMR (470.52 MHz, 27°C, thf-*d*₈): δ -145.2 (s, 1F) ppm.

^7Li NMR (thf-*d*₈, 194.37 MHz, 27°C): δ 1.27 (s) ppm.

Synthesis of lithium *N*-(2,6-difluorophenyl)-trimethylsilylamide (2-Li)



Following the same protocol as that described for **1-Li**, amine **2-H** (1.0 g, 5.0 mmol) was reacted with *n*BuLi (3.2 mL of a 1.57 M solution in hexanes, 5.0 mmol) to afford the title compound as a colourless solid. Isolated yield: 0.9 g (90%). X-ray quality crystals of [2-Li]_∞ were grown from a concentrated solution in petroleum ether stored at -30°C.

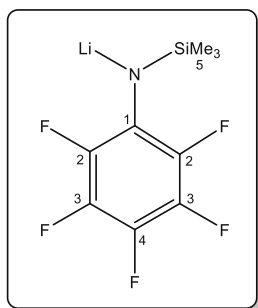
^1H NMR (500.13 MHz, 27°C, thf-*d*₈): δ 6.51–6.47 (overlapping m, 2H, C₃H), 5.79–5.73 (m, 1H, C₄H), 0.02 (s, 9H, CH₃) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (125.77 MHz, 27°C, thf-*d*₈): δ 159.9–158.0 (dd, $|^1J_{C,F}| = 226.4$ Hz, $|^3J_{C,F}| = 13.8$ Hz, C₂), 139.1 (t, $|^2J_{C,F}| = 17.6$ Hz, C₁), 110.3 (m, C₃), 104.2 (t, $|^3J_{C,F}| = 10.7$ Hz, C₄), 3.3 (t, $|^5J_{C,F}| = 3.8$ Hz, CH₃) ppm.

^{19}F NMR (470.52 MHz, 27°C, thf-*d*₈): δ -135.0 (s, 2F) ppm.

^7Li NMR (thf-*d*₈, 194.37 MHz, 27 °C): δ 1.20 (s) ppm.

Synthesis of lithium *N*-(pentafluorophenyl)-trimethylsilylamide (3-Li)



In a similar procedure to that described for **1-Li**, the title compound was isolated as a colourless solid by reaction of **3-H** (1.0 g, 3.9 mmol) and *n*BuLi (2.5 mL of a 1.57 M

solution in hexanes, 3.9 mmol). Isolated yield: 0.85 g (81%). The NMR data repeatedly showed the presence (ca. 4 mol%) of an unknown unidentified side-product, possibly (C₆F₅)SiMe₃ or (Me₃Si)(C₆F₅)N-N(C₆F₅)(SiMe₃). Single crystals of [3-Li-Et₂O] suitable for XRD analysis were grown from a solution in Et₂O.

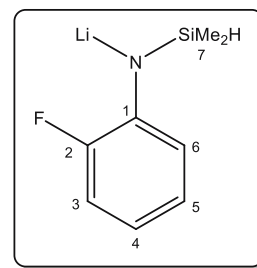
^1H NMR (500.13 MHz, 27°C, thf-*d*₈): δ 0.04 (s, 9H, CH₃) ppm. The presence of an unknown product was detected (v. small singlet at 0.06 ppm).

$^{13}\text{C}\{^1\text{H}\}$ NMR (125.77 MHz, 27°C, thf-*d*₈): δ 143.7–142.0 (dt, $|^1J_{C,F}| = 221.3$ Hz, $|^2J_{C,F}| = 9.5$ Hz, C₄), 140.3–138.4 (dm, $|^1J_{C,F}| = 247.7$ Hz, C₂ or C₃), 137.3 (t, $|^2J_{C,F}| = 14.8$ Hz, C₁), 128.1–126.2 (dm, $|^1J_{C,F}| = 229.9$ Hz, C₂ or C₃), 2.8 (t, $|^1J_{Si,Cl}| = 55.3$ Hz, $|^5J_{C,F}| = 3.1$ Hz, CH₃) ppm. The presence of an unknown product was detected by a singlet resonance at δ -0.7 ppm.

^{19}F NMR (470.52 MHz, 27°C, thf-*d*₈): δ -163.7 (br s, 2F, *o*-F), -172.0 (t, $|^3J_{F,F}| = 21.2$ Hz, 2F, *m*-F), -192.5 (br s, 1F, *p*-F) ppm. The resonances for an unidentified product were detected at δ -147.9, -163.7, and -166.2 ppm.

^7Li NMR (thf-*d*₈, 155.51 MHz, 25°C): δ 0.90 ppm.

Synthesis of lithium *N*-(2-fluorophenyl)-1,1-dimethylsilylamide (4-Li)



Compound **4-H** (0.4 g, 2.4 mmol) was diluted in petroleum ether (15 mL). *n*BuLi (1.5 mL of a 1.57 M solution in hexanes, 2.4 mmol) was added dropwise at 0°C. The reaction mixture was stirred for 1 h at room temperature; formation of a white precipitate was observed. The solid was isolated by filtration, and dried to constant weight under vacuum. We found that the various samples we prepared always contained residual petroleum ether that could not be easily removed under vacuum. A crop of colourless X-ray quality single crystals of [4-Li]₈ was obtained by recrystallisation from a saturated toluene solution. Isolated yield: 0.3 g (71%).

^1H NMR (400.13 MHz, 25°C, thf-*d*₈): δ 6.68–6.56 (m, 3H, C₃H + C₄H + C₅H), 5.92 (m, 1H, C₆H), δ 4.84 (hept, 1H, $|^3J_{H,H}| = 2.9$ Hz, $|^1J_{Si,H}| = 176.0$ Hz, SiH), 0.08 (d, $|^3J_{H,H}| = 2.9$ Hz, 6H, CH₃) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (100.62 MHz, 26°C, $\text{thf-}d_8$): δ 160.6–158.4 (d, $|^1J_{\text{C,F}}| = 217.3$ Hz, C_2), 150.7 (d, $|^2J_{\text{C,F}}| = 10.1$ Hz, C_1), 125.3 (d, $|^4J_{\text{C,F}}| = 2.0$ Hz, C_5), 120.6 (d, $|^3J_{\text{C,F}}| = 4.0$ Hz, C_4), 112.8 (d, $|^2J_{\text{C,F}}| = 23.1$ Hz, C_3), 108.0 (d, $|^3J_{\text{C,F}}| = 9.0$ Hz, C_6), 0.24 (s, $|^1J_{\text{Si,C}}| = 54.3$ Hz, CH_3) ppm.

^{19}F NMR (376.44 MHz, 24°C, $\text{thf-}d_8$): δ –145.2 (s) ppm. Gradual decomposition in solution was visible by a resonance of growing intensity at –140.8 ppm.

^7Li NMR (155.51 MHz, 24°C, $\text{thf-}d_8$): δ 1.18 (s) ppm.

X-ray diffraction crystallography

For $[\mathbf{2-Li}]_\infty$ ($\text{C}_9\text{H}_{12}\text{F}_2\text{LiNSi}$, $M = 207.23$ g·mol $^{-1}$), CCDC 2238385. A suitable crystal for X-ray diffraction single crystal experiment (colourless stick, dimensions = 0.300 mm $\times$ 0.120 mm $\times$ 0.110 mm) was selected and mounted on the goniometer head of a APEXII Kappa-CCD (Bruker-AXS) diffractometer equipped with a CCD plate detector, using Mo-K α radiation ($\lambda = 0.71073$ Å, graphite monochromator) at $T = 150(2)$ K. The crystal structure has been described in monoclinic symmetry and $P2_1/n$ (I.T.#14) centric space group. Cell parameters have been refined as follows: $a = 10.760(2)$, $b = 6.5810(16)$, $c = 14.522(3)$ Å, $\beta = 91.476(11)^\circ$, $V = 1,028.0(4)$ Å 3 . Number of formula unit Z is equal to 4 and calculated density d and absorption coefficient μ values are 1.339 g·cm $^{-3}$ and 0.212 mm $^{-1}$, respectively. The crystal structure was solved by dual-space algorithm using SHELXT (Sheldrick, 2015a), and then refined with full-matrix least-squares methods based on F^2 (SHELXL; Sheldrick, 2015b). All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions and treated as riding on their parent atom with constrained thermal parameters. A final refinement on F^2 with 2,289 unique intensities and 130 parameters converged at $\omega R_{F2} = 0.1968$ ($R_F = 0.0834$) for 1,344 observed reflections with $I > 2\sigma(I)$.

For $[\mathbf{3-Li-Et_2O}]_2$ ($\text{C}_{26}\text{H}_{38}\text{F}_{10}\text{Li}_2\text{N}_2\text{O}_2\text{Si}_2$, $M = 670.64$ g·mol $^{-1}$), CCDC 2238384. A suitable crystal for X-ray diffraction single crystal experiment (colourless prism, dimensions = 0.600 mm $\times$ 0.490 mm $\times$ 0.250 mm) was selected and mounted on the goniometer head of a APEXII Kappa-CCD (Bruker-AXS) diffractometer equipped with a CCD plate detector, using Mo-K α radiation ($\lambda = 0.71073$ Å, graphite monochromator) at $T = 150(2)$ K. The crystal structure has been described in triclinic symmetry and $P-1$ (I.T.#2) centric space group. Cell parameters have been refined as follows: $a = 9.0873(7)$, $b = 10.5228(8)$, $c = 10.6719(9)$ Å, $\alpha = 116.451(2)$, $\beta = 99.726(3)$, $\gamma = 106.944(2)^\circ$, $V = 819.10(11)$ Å 3 . Number of formula unit Z is equal to 1 and calculated density d and absorption

coefficient μ values are 1.360 g·cm $^{-3}$ and 0.191 mm $^{-1}$, respectively. The crystal structure was solved by dual-space algorithm using SHELXT (Sheldrick, 2015a), and then refined with full-matrix least-squares methods based on F^2 (SHELXL; Sheldrick, 2015b). All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions and treated as riding on their parent atom with constrained thermal parameters. A final refinement on F^2 with 3,713 unique intensities and 204 parameters converged at $\omega R_{F2} = 0.1094$ ($R_F = 0.0389$) for 3,151 observed reflections with $I > 2\sigma(I)$.

For $[\mathbf{4-Li}]_8$ ($\text{C}_{64}\text{H}_{88}\text{F}_8\text{Li}_8\text{N}_8\text{Si}_8\text{C}_7\text{H}_8$, $M = 1,493.79$ g·mol $^{-1}$), CCDC 2238386. D8 VENTURE Bruker AXS diffractometer equipped with a (CMOS) PHOTON 100 detector, Mo-K α radiation ($\lambda = 0.71073$ Å, multilayer monochromator), $T = 150$ K; monoclinic $P2_1/n$ (I.T.#13), $a = 16.620(3)$, $b = 12.903(2)$, $c = 19.799(4)$ Å, $\beta = 89.952(7)^\circ$, $V = 4,245.6(13)$ Å 3 . $Z = 2$, $d = 1.168$ g·cm $^{-3}$, $\mu = 0.186$ mm $^{-1}$. The structure was solved by dual-space algorithm using the SHELXT program (Sheldrick, 2015a), and then refined with full-matrix least-squares methods based on F^2 (SHELXL; Sheldrick, 2015b). All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. Except hydrogen atoms linked to silicon atoms that were introduced in the structural model through Fourier difference maps analysis, H atoms were finally included in their calculated positions and treated as riding on their parent atom with constrained thermal parameters. A final refinement on F^2 with 9,756 unique intensities and 479 parameters converged at $\omega R_{F2} = 0.1227$ ($R_F = 0.0527$) for 8,734 observed reflections with $I > 2\sigma(I)$.

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