

## Complexes between Fluorobenzenes and Lithium Hexamethyldisilazide Dimer

Paul G. Williard\* and Qi-Yong Liu

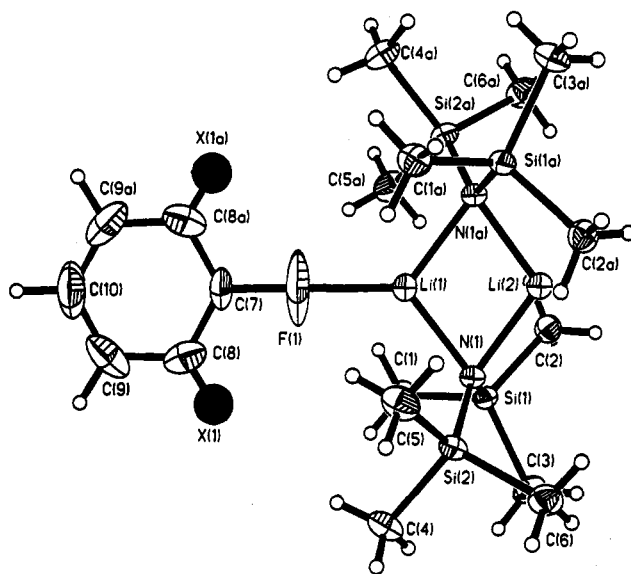
Department of Chemistry, Brown University, Providence, Rhode Island 02912

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**Summary:** New complexes of lithium hexamethyldisilazide (LiHMDS) and three different fluorobenzenes were prepared, isolated, and characterized by X-ray diffraction analysis.

Among almost all the simple dimeric alkali amide base crystal structures reported to date, coordination to the metal cations (Li, Na, K) occurs to either nitrogen or oxygen atoms.<sup>1</sup> An alternative second-row element capable of coordination to these metal cations is fluorine. Indeed, fluorine is known to coordinate to lithium via an internal chelate ring in some fluorosilyl amides.<sup>2</sup> During the course of our structural investigations of amide bases,<sup>3</sup> we isolated and characterized several complexes between lithium hexamethyldisilazide (LiHMDS) and fluorinated benzenes. We now report the structures of three such complexes, (LiHMDS)<sub>2</sub>-C<sub>6</sub>H<sub>5</sub>F (1),<sup>4</sup> (LiHMDS)<sub>2</sub>-o-C<sub>6</sub>H<sub>4</sub>F<sub>2</sub> (2),<sup>5</sup> and [(LiHMDS)<sub>2</sub>-p-C<sub>6</sub>H<sub>4</sub>F<sub>2</sub>]<sub>n</sub> (3).<sup>6</sup> In these three complexes fluorinated benzenes solvate the lithium cations of dimeric LiHMDS exclusively through direct Li-F complexation.

A unique feature of complexes 1 and 2 is monosolvation. The representative plot of these two cyclic dimers is depicted in Figure 1. Complex 3 is a linear polymer with each *p*-difluorobenzene bridging the dimeric units as shown in Figure 2. The dimeric units in all three complexes are similar to each other and resemble the oxy- and aza-donor



**Figure 1.** Computer-generated thermal ellipsoid of 1 (shaded atoms = H) and 2 (shaded atoms = 1/2 H and 1/2 F) at 30% probability. Selected bond lengths (Å) and angles (deg) (data in brackets are corresponding parameters in 2): (Si-N)av = 1.704(2) [1.705(3)]; Si(1)-N(1)-Si(2) = 122.76(12) [122.5(2)]; N(1)-Li(1) = 1.995(4) [2.002(6)]; N(1)-Li(2) = 1.980(4) [1.981(6)]; N(1)-Li(1)-N(1a) = 106.4(3) [105.8(6)]; N(1)-Li(2)-N(1a) = 107.6(3) [107.4(5)]; F(1)-Li(1) = 1.866(7) [1.894(10)]. The shortest Li-C and Li-H distances (Å) for Li(1) and Li(2): Li(1)-C(5) = 3.007 [2.996]; Li(1)-H(5A) = 2.629 [2.612]; Li(2)-C(2) = 2.711 [2.715]; Li(2)-H(2A) = 2.495 [2.504].

solvated LiHMDS dimers. The central (Li-N)<sub>2</sub> cores are planar, and the silylamido groups are skewed relative to such cores.<sup>3e</sup> The tricoordinate Li atoms are trigonal planar. Fluorobenzenes approach the LiHMDS dimers from the planes defined by the (Li-N)<sub>2</sub> cores. It is noteworthy that this is exactly the same plane occupied by both ethereal solvents and carbonyl donors complexed to LiHMDS dimers.<sup>3d</sup> In fact, the two-dimensional solvent molecules and the (Li-N)<sub>2</sub> plane are almost coplanar in the monosolvated dimers 1 and 2. The dihedral angle between the plane of the benzene ring and the (Li-N)<sub>2</sub> core-defined plane is 7.0° in 1, 3.5° in 2, and 0° in 3. The C<sub>aryl</sub>-F-Li bond angles are linear in all three complexes.<sup>7</sup>

Structural parameters such as the Si-N bond lengths and Si-N-Si bond angles are very similar in all three complexes and lie within the limit found in the oxy- and aza-donor solvated dimeric LiHMDS complexes.<sup>1,3</sup> Besides the obvious differences due to coordination number, the geometry around the tricoordinated Li atoms and around the dicoordinate Li atoms is nearly identical in 1 and 2. However, differences are noted in the nonbonding Li-C and Li-H distances for the differently solvated

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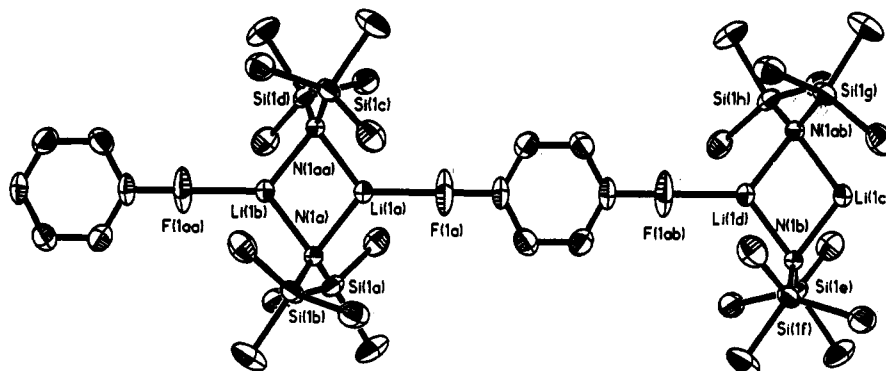
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(4) Full matrix structure refinements on F<sub>2</sub> using SHELXL-93 (Sheldrick, G. J. *Appl. Crystallogr.* 1993, in press) were performed for all three structures. Crystal parameters for 1: monoclinic space group, C2/c; a = 10.953(3) Å, b = 23.044(6) Å, c = 11.507(2) Å, β = 110.49(0)°; V = 2720.6(11) Å<sup>3</sup>; z = 8; d<sub>calc</sub> = 1.05 g cm<sup>-3</sup>; μ(Mo Kα) = 0.231 mm<sup>-1</sup>; F(000) = 936; intensity data 0 ≤ h ≤ 12, 0 ≤ k ≤ 25, -12 ≤ l ≤ 12; 2θ<sub>max</sub> = 47.1°; R(1) = 0.040 for 1674 F<sub>o</sub> > 4σ(F<sub>o</sub>) and 0.053 for all 2022 data, wR(2) = 0.124, GOF = 1.042.

(5) Crystal parameters for 2: monoclinic space group, C2/c; a = 11.008(1) Å, b = 23.119(3) Å, c = 11.521(2) Å, β = 111.19(0)°; V = 2733.8(6) Å<sup>3</sup>; z = 8; d<sub>calc</sub> = 1.090 g cm<sup>-3</sup>; μ(Mo Kα) = 0.237 mm<sup>-1</sup>; F(000) = 968; intensity data 0 ≤ h ≤ 12, 0 ≤ k ≤ 25, -12 ≤ l ≤ 12; 2θ<sub>max</sub> = 47.0°; R(1) = 0.061 for 1610 F<sub>o</sub> > 4σ(F<sub>o</sub>) and 0.077 for all 2013 data, wR(2) = 0.171, GOF = 1.069.

(6) Crystal parameters for 3: orthorhombic space group, Ccca, a = 12.785(10) Å, b = 18.594(3) Å, c = 11.743(2) Å; V = 2791.6(7) Å<sup>3</sup>; z = 16; d<sub>calc</sub> = 1.07 g cm<sup>-3</sup>; μ(Mo Kα) = 0.232 mm<sup>-1</sup>; F(000) = 968; intensity data 0 ≤ h ≤ 14, 0 ≤ k ≤ 20, 0 ≤ l ≤ 13; 2θ<sub>max</sub> = 47.0°; R(1) = 0.054 for 752 F<sub>o</sub> > 4σ(F<sub>o</sub>) and 0.082 for all 1044 data, wR(2) = 0.149, GOF = 1.052.

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**Figure 2.** Computer-generated thermal ellipsoid of **3** at 30% probability. Hydrogens are omitted for clarity. Selected bond lengths (Å) and angles (deg): Si–N = 1.700(2); Si–N–Si = 123.0(2); N–Li = 1.991(5); N–Li–N = 106.3(3); F(1)–Li(1) = 1.999(8).

lithiums. The shortest H...Li and C...Li distances for the dicoordinate Li atoms are much shorter than those for the tricoordinate Li atoms (Figure 1). This reflects the coordinative unsaturation and the less crowded nature of the dicoordinate Li atoms.

LiHMDS complexes 1–3 represent rare examples of lithium amide base solvation by fluorinated aromatic solvents. They also illustrate the ability of lithium and fluorine to form a weak intermolecular interaction. Formation of monosolvated LiHMDS dimers is unexpected. Dimeric LiHMDS is the most aggregated state of this base in both the solid state and in solution.<sup>8</sup> We are unaware of any previous structural evidence for a monosolvated dimer, although both the completely unsolvated trimeric LiHMDS and a related but somewhat more sterically hindered, unsolvated dimer are known.<sup>9</sup> It is noteworthy that no chelation is observed in the *o*-difluorobenzene complex **2** despite the ability of *o*-difluorobenzene to form a chelate ring. Perhaps monosolvated dimers such as **1** and **2** are prototypical intermediates for ligand–ligand or ligand–substrate exchange<sup>10</sup> not involving fragmentation of the cyclic (Li–N)<sub>2</sub> core.<sup>11</sup>

Schleyer has recently calculated the relative stability of geometrically different complexes between lithium hydride and fluorobenzene.<sup>12</sup> These calculations indicate that  $\eta^6$ -coordination of lithium by the aryl ring is preferable to

direct Li–F coordination by a small amount (0.4 kcal mol<sup>-1</sup>). Our previous characterization of potassium hexamethyldisilazide (KHMDS) dimer solvated by toluene<sup>3h</sup> did not clearly identify the  $\eta^6$ -coordination in this KHMDS dimer.<sup>13</sup> This KHMDS structure clearly illustrates that  $\eta^6$ -aryl coordination is observable with an amide base dimer. Although there are several additional structural examples of  $\eta^6$ -aryl–Li complexation,<sup>1c,d</sup> we were unable to isolate a LiHMDS/ $\eta^6$ -aryl complex similar to that found for KHMDS. Hence, we believe that the steric bulk of the trimethylsilyl groups in LiHMDS impedes  $\eta^6$ -complexation of LiHMDS dimers. Thus, the only choice for solvation of LiHMDS dimer by fluorobenzene is direct coordination to the fluorine leading to the formation of **1**–**3**. We are unable to explain the preference for monosolvation in **1** and **2**.

In conclusion, the first structures between a lithium amide base and fluorinated solvents were characterized using X-ray diffraction analysis.<sup>14</sup> The monosolvated cyclic dimers **1** and **2** represent a new solvation pattern of LiHMDS complexes. Attempts to observe the interaction between LiHMDS and fluorobenzenes in solution and extension of the study to the sodium and potassium analogues of LiHMDS are in progress.

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(14) The author has deposited atomic coordinates for **1**–**3** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.