

# Synthesis and Structure of a New Lithium Amide Ligand Precursor: A Tridentate Nitrogen-Based Donor Set of the Formula $N(\text{SiMe}_2\text{CH}_2\text{NMe}_2)_2$ . Synthesis and Structure of the Group 4 Amides $\text{MCl}_3[\text{N}(\text{SiMe}_2\text{CH}_2\text{NMe}_2)_2]$ ( $\text{M} = \text{Ti}, \text{Zr}, \text{Hf}$ )

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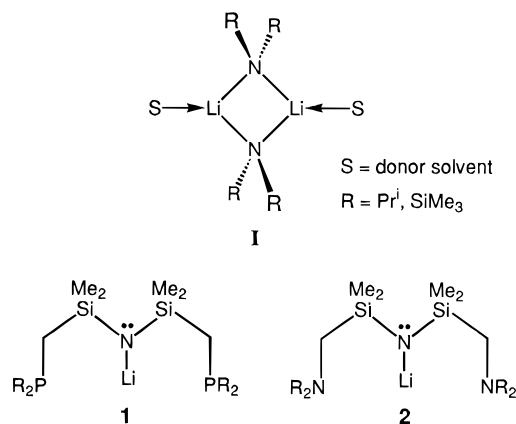
Received February 12, 1997<sup>⊗</sup>

The new lithium amide  $\text{LiN}(\text{SiMe}_2\text{CH}_2\text{NMe}_2)_2$  was prepared by reaction of  $\text{NH}_3$  with the corresponding silylamine  $\text{Me}_2\text{NSiMe}_2\text{CH}_2\text{NMe}_2$  followed by addition of butyllithium. This lithium derivative exists as a dimer in the solid state wherein the two lithium ions are bridged by the two amido units with the amine arms of each unit bonded to opposite lithium centers in an overall pseudo  $D_2$  structure; however, in solution, a fluxional process serves to interconvert the enantiomeric forms of the dimer unit. The coordination chemistry of the lithium amide dimer has been investigated; reaction with a series of group 4 starting halides,  $\text{MCl}_4$ , leads to the corresponding complexes  $\text{MCl}_3[\text{N}(\text{SiMe}_2\text{CH}_2\text{NMe}_2)_2]$ , where  $\text{M} = \text{Ti}, \text{Zr},$  and  $\text{Hf}$ . The structures of these starting trihalides in solution and in the solid state are presented.

Lithium amide bases constitute one of the most common classes of reagents in organic chemistry due to their ability to deprotonate a variety of compounds under mild conditions. Because of their synthetic utility, many studies have been undertaken to unravel their solid- and solution-state structures.<sup>1–8</sup> Reagents such as lithium diisopropyl amide (LDA)<sup>6,7,9–12</sup> and lithium hexamethyldisilazide ( $\text{LiHMDS}$ )<sup>3–5,13,14</sup> are often written as monomeric species, but in fact their structures in solution are more complicated, being dimeric (**1**) or oligomeric with solvents playing a major role in determining dynamics and aggregation.

Lithiated amides have also been found to be useful in coordination chemistry in the preparation of early and late metal amide complexes.<sup>15,16</sup> Efforts from our group for example have shown the lithium amido diphosphine  $\text{LiN}(\text{SiMe}_2\text{CH}_2\text{PR}_2)_2$  (**1**)

Chart 1



serves as a convenient starting material for the preparation of a wide variety of metal amide complexes.<sup>17–22</sup> Our success with this ligand system provided the impetus to examine the related all nitrogen-donor ligand precursor  $\text{LiN}(\text{SiMe}_2\text{CH}_2\text{NR}_2)_2$  (**2**). In this paper we describe the synthesis and structure of the lithium amido diamine  $\text{LiN}(\text{SiMe}_2\text{CH}_2\text{NMe}_2)_2$  and its coordination chemistry with the group 4 elements, Ti, Zr, and Hf.

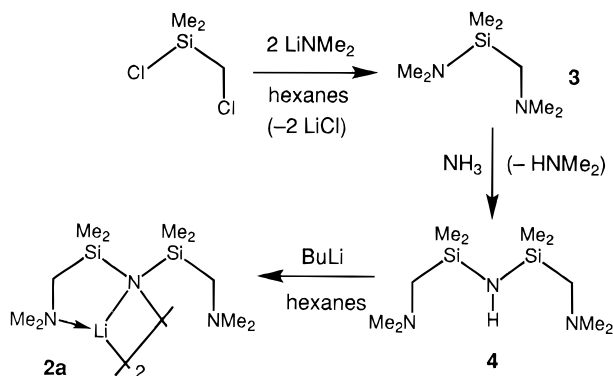
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⊗ Abstract published in *Advance ACS Abstracts*, July 15, 1997.

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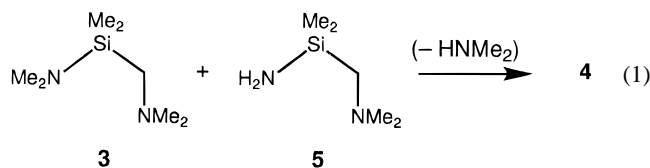
## Scheme 1



## Results and Discussion

The preparation of the amido diphosphine ligand precursor **1** relies on the nucleophilic/radical displacement<sup>23</sup> of chloride from the bis((chloromethyl)dimethylsilyl)amine starting material  $\text{HN}(\text{SiMe}_2\text{CH}_2\text{Cl})_2$  by lithiated phosphide anions,  $\text{LiPR}_2$ . However, the analogous reaction of  $\text{HN}(\text{SiMe}_2\text{CH}_2\text{Cl})_2$  with lithium amides, for example with  $\text{LiNMe}_2$  or LDA, generates a mixture of products, none of which correspond to the amido diamine **2**. Although we have not made a detailed analysis of this reaction, strong amide bases might promote the formation of silaziridine type products or engage in nucleophilic attack directly at Si. Fortunately, a large-scale preparation of **2a** could be effected starting from  $\text{ClSiMe}_2\text{CH}_2\text{Cl}$ , the precursor to  $\text{HN}(\text{SiMe}_2\text{CH}_2\text{Cl})_2$ , by first converting it to  $\text{Me}_2\text{NSiMe}_2\text{CH}_2\text{NMe}_2$  (**3**). This is outlined in Scheme 1.

The reaction of  $\text{Me}_2\text{NSiMe}_2\text{CH}_2\text{NMe}_2$ <sup>24,25</sup> with  $\text{NH}_3$  (generated in situ by  $\text{NH}_4\text{Cl}$  and  $\text{NET}_3$ ) at 100 °C in toluene produces the disilyltriamine  $\text{HN}(\text{SiMe}_2\text{CH}_2\text{NMe}_2)_2$  (**4**) as shown in Scheme 1. Presumably, the first step is amine exchange at Si to produce  $\text{H}_2\text{NSiMe}_2\text{CH}_2\text{NMe}_2$  (**5**) and  $\text{HNMe}_2$  in equilibrium with starting material **3**. Subsequently, the monosilylamine **5** reacts with the starting material **3** to generate the product **4** (eq 1).



The disilylamine **4** can be deprotonated by  $\text{BuLi}$  in hexanes to give the corresponding lithium amide **2a** as colorless crystals (Scheme 1). In the solid state, the structure of **2a** is dimeric with pseudo  $D_2$  symmetry as shown in Figure 1; the molecule has two lithium ions bridged by the two disilylamido units with the amine arms of each one of these units coordinated to opposite lithium centers. In the almost planar, diamond-shaped  $\text{Li}_2\text{N}_2$  core, each lithium is four-coordinate due to the chelating amine donors; in other dimeric disilylamide structures, the lithium ions are generally three coordinate.<sup>1,2,26</sup> However, four coordination has been observed in dimeric aryllithium structures that contain amine substituents.<sup>27,28</sup> The two planes defined by

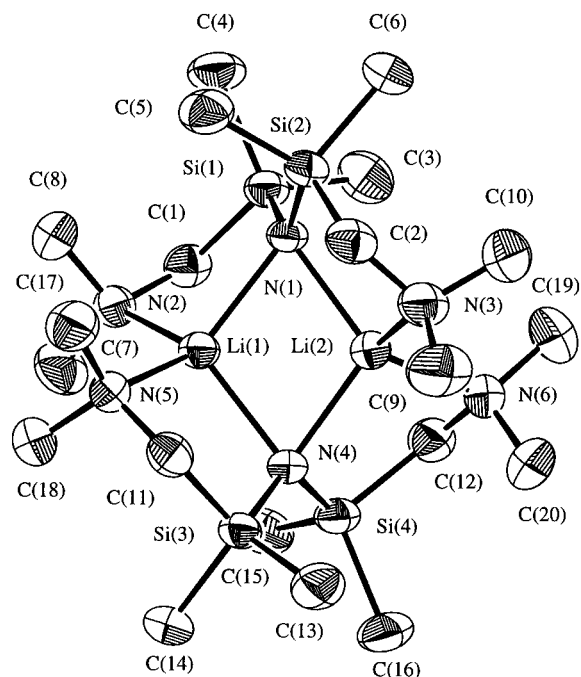


Figure 1. Perspective view of  $\{\text{LiN}(\text{SiMe}_2\text{CH}_2\text{NMe}_2)_2\}_2$ , **2a**, with 33% probability thermal ellipsoids shown.

the Si–N–Si moieties are rotated by approximately 72° with respect to the  $\text{Li}_2\text{N}_2$  plane; in addition, the planes defined by the amine donors and the lithium ions are rotated by about 62° with respect to the above  $\text{Li}_2\text{N}_2$  plane. There are two types of Li–N distances; the average amido–lithium bond length is 2.153(11) Å while the average amine–lithium distance is 2.186(14) Å. The lithium amide distances are longer than that normally found for dimeric amide derivatives; typically, other similar Li–N bond lengths are in the 1.936–2.055 Å range.<sup>1</sup> Presumably, with the fact that each lithium center is four-coordinate in **2a**, steric crowding can be relieved by lengthening the various Li–N bonds.

At room temperature in toluene solution, NMR spectral studies indicate that **2a** retains its dimeric structure since the  $^{15}\text{N}\{^1\text{H}\}$  NMR spectrum of the doubly labeled  $[\text{Li}^{15}\text{N}(\text{SiMe}_2\text{CH}_2\text{NMe}_2)_2]_2$  shows a single binomial quintet at 14.5 ppm due to coupling from two equivalent  $^6\text{Li}$  nuclei ( $^1J_{^{15}\text{N},^6\text{Li}} = 2.7$  Hz,  $I = 1$ , 96% enriched). At temperatures > 30 °C in the  $^1\text{H}$  NMR spectrum, the dimeric molecule is fluxional by amine arm dissociation and recoordination thereby rendering all of the silyl methyls ( $\text{SiMe}_2$ ) equivalent and all of the amine methyls ( $\text{NMe}_2$ ) equivalent. As the temperature is lowered decoalescence occurs to generate a spectrum consistent with the dimeric solid-state structure; at –50 °C in  $\text{C}_7\text{D}_8$ , one observes two silyl methyl peaks (singlets at 0.2 and 0.5 ppm), two methylene resonances as an AB quartet (doublets at 1.4 and 2.25 ppm,  $^2J_{\text{HH}} = 15$  Hz), and two amine methyl peaks (singlets at 2.01 and 2.14 ppm), all due to the diastereotopicity intrinsic to the  $D_2$  structure in the low-temperature limit;<sup>29</sup> DNMR simulation studies provide activation parameters for this process:  $\Delta H^\ddagger = 14.8$  kcal  $\text{mol}^{-1}$ ,  $\Delta S^\ddagger = 8 \pm 5$  cal  $\text{mol}^{-1} \text{K}^{-1}$ , and  $\Delta G^\ddagger = 12.7$  kcal  $\text{mol}^{-1}$  at  $T_c = -10.2$  °C. The small value of  $\Delta S^\ddagger$  precludes dissociation into monomeric  $\text{LiN}(\text{SiMe}_2\text{CH}_2\text{NMe}_2)_2$  units in hydrocarbon solvents. One possible exchange process is shown in Scheme 2 whereby the two enantiomeric forms **2a** and **2a'**

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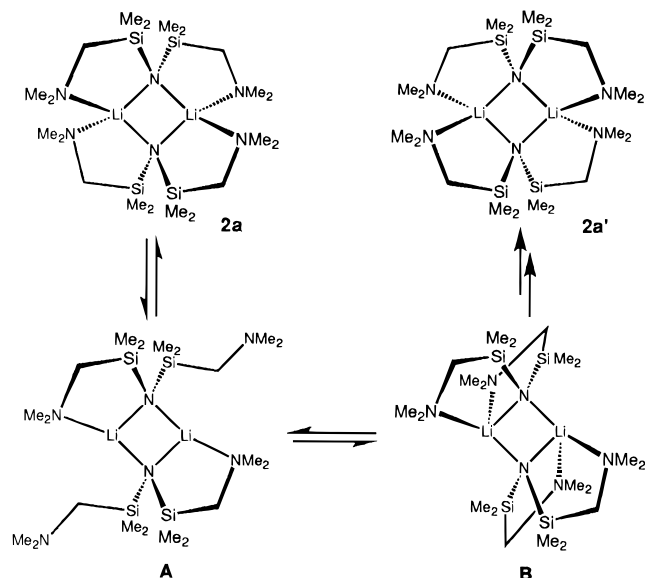
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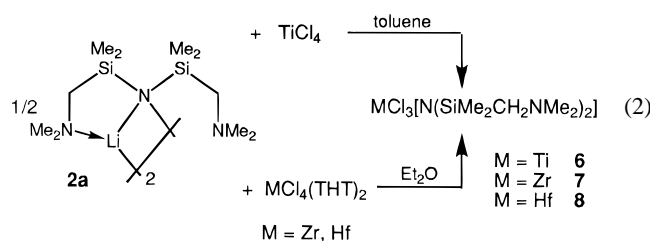
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## Scheme 2



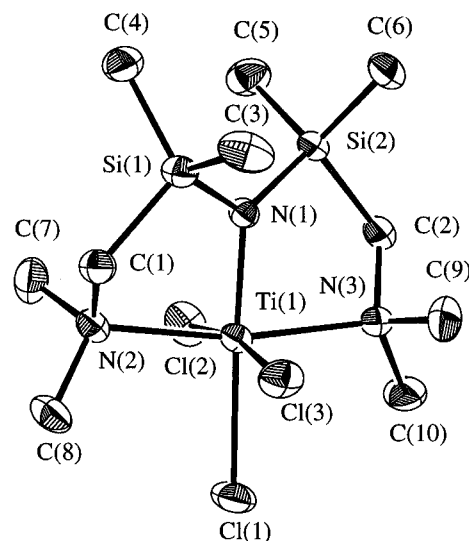
exchange via amine arm dissociation to **A** and then reassociation to the symmetric  $C_{2h}$  isomer **B**; subsequent dissociation of the amine arms from **B** via the enantiomer of **A** followed by reassociation results in **2a'**, in other words, racemization.

The lithium amide dimer reacts cleanly with a variety of group 4 metal halides to transfer this amidodiamine ancillary ligand system to the metal center. For example, reaction of 0.5 equiv of dimer **2a** with 1 equiv of  $TiCl_4$  in toluene at  $-78^\circ C$ , followed by warming to room temperature overnight, results in the metathesis of one of the  $Ti-Cl$  bonds to form  $TiCl_3[N(SiMe_2CH_2NMe_2)_2]$  (**6**) as a red-orange, microcrystalline powder. The  $^1H$  and  $^{13}C\{^1H\}$  NMR spectra of **6** both exhibit three narrow resonances for the  $SiMe_2$ ,  $NCH_2Si$ , and  $NMe_2$  groups at room temperature suggesting a symmetric structure in solution. A similar reaction ensues for the heavier congeners of group 4 by the use of the soluble precursors  $MCl_4(THT)_2$  ( $THT = \text{tetrahydrothiophene}$ ) (eq 2).



The NMR spectral features of the Zr and Hf analogues,  $MCl_3[N(SiMe_2CH_2NMe_2)_2]$  ( $M = Zr$  (**7**),  $Hf$  (**8**)), are virtually identical to the Ti derivative in that very symmetric environments for the amido diamine ligand are observed; thus, both the Zr and Hf complexes show only one type of silylmethyl resonance, one type of methyl attached to nitrogen, and one type of methylene environment in both the  $^1H$  NMR and  $^{13}C\{^1H\}$  NMR spectra.

Crystals of the titanium complex **6** suitable for X-ray analysis were isolated from cold ( $-30^\circ C$ ) toluene; Figure 2 shows the molecular structure and numbering scheme, and selected bond distances and angles are given in Table 3. The complex adopts a distorted octahedral geometry, with the ligand binding to the metal in a *meridional* fashion. While the amide nitrogen is close to being trans to  $Cl(1)$ , i.e.,  $Cl(1)-Ti(1)-N(1)$  is  $174.48(9)^\circ$ , the remaining two *trans* bond angles,  $N(2)-Ti(1)-N(3)$  and  $Cl(2)-Ti(1)-Cl(3)$ , are bent back from  $180^\circ$  to  $169.08(10)$  and



**Figure 2.** Perspective view of  $TiCl_3[N(SiMe_2CH_2NMe_2)_2]$ , **6**, with 33% probability thermal ellipsoids shown.

$169.84(4)^\circ$ , respectively. The backbone of the amidodiamine ligand is twisted with respect to the plane defined by the three nitrogen donors and the titanium; this imparts a chairlike conformation to the two fused five-membered rings of the ancillary ligand. The  $Ti(1)-N(1)$  distance of  $1.896(3) \text{ \AA}$  is comparable to other titanium amides.<sup>15</sup> The titanium chloride bond lengths show some variation ranging in value from  $2.326(1) \text{ \AA}$  for  $Ti-Cl(2)$  to  $2.389(1) \text{ \AA}$  for  $Ti-Cl(1)$ , this latter chloride being trans to the amido nitrogen of the tridentate ligand. The remaining bond distances and angles (see Table 3) are not unusual.

In the solid state, the zirconium and hafnium complexes **7** and **8** are isomorphous and isostructural to each other; the Hf analogue is shown in Figure 3 with selected bond lengths and bond angles listed in Table 3, respectively. What becomes immediately obvious is that the heavier members of group 4 display the isomeric facial geometry (i.e., relative to the titanium analogue) in the crystalline state. Thus the tridentate ligand in complexes **7** and **8** binds with *cis* amine donors with the  $N(2)-Hf-N(3)$  bond angle at  $117.4(2)^\circ$ ; the overall geometry is perhaps best described as distorted bicapped tetrahedral.<sup>30</sup> Diagnostic of this descriptor for the geometry rather than distorted octahedral is the observation that there is no chloride ligand trans to the amide nitrogen; thus the  $Cl(1)-Hf-N(1)$  angle of  $143.8(1)^\circ$  is much smaller than expected for a *trans* relationship. In such a geometry, the four formally anionic ligands, the three  $Cl^-$ 's, and the amide, generate the tetrahedral motif with the two amine donors capping two faces of the distorted tetrahedron. Table 3 lists the bond lengths and bond angles in a way that allows facile comparison of the differences between the Ti complex and the heavier members of group 4 as well as being able to see the isostructural similarities of the Zr and Hf derivatives. We have no explanation for the difference in coordination geometries in the solid state as a function of the metal in group 4. The greater size of the heavier members, Zr and Hf, as compared to Ti must play a role.

As mentioned above, in solution, the NMR data of the titanium complex **6** is consistent with the observed solid-state structure. However, this is not the case for the Zr and Hf complexes **7** and **8** since their NMR spectra closely resemble the titanium data. Because the solid-state structures of both **7** and **8** have *cis* amine donors in a bicapped tetrahedral geometry,

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**Table 1.** Crystallographic Data<sup>a</sup>

|                                       | compound   |   |   |  |
|---------------------------------------|--|---|---|--|
|                                       | 2a   | 6   | 7   | 8  |
| formula                               | C <sub>20</sub> H <sub>56</sub> Li <sub>2</sub> N <sub>6</sub> Si <sub>4</sub> | C <sub>10</sub> H <sub>28</sub> Cl <sub>3</sub> N <sub>3</sub> Si <sub>2</sub> Ti | C <sub>10</sub> H <sub>28</sub> Cl <sub>3</sub> N <sub>3</sub> Si <sub>2</sub> Zr | C <sub>10</sub> H <sub>28</sub> Cl <sub>3</sub> HfN <sub>3</sub> Si <sub>2</sub> |
| fw                                    | 506.93   | 400.78  | 444.10  | 531.37   |
| cryst system                          | monoclinic   | monoclinic  | monoclinic  | monoclinic   |
| space group                           | P2 <sub>1</sub> /n (No. 14)  | P2 <sub>1</sub> /n (No. 14)   | P2 <sub>1</sub> /n (No. 14)   | P2 <sub>1</sub> /n (No. 14)  |
| a, Å                                  | 9.235(2)   | 10.180(2)   | 7.860(2)  | 7.867(2)   |
| b, Å                                  | 22.904(1)  | 12.597(1)   | 20.791(1)   | 20.845(1)  |
| c, Å                                  | 15.941(1)  | 15.386(1)   | 12.721(1)   | 12.636(1)  |
| β, deg                                | 97.54(1)   | 98.463(9)   | 94.33(1)  | 94.00(1)   |
| V, Å <sup>3</sup>                     | 3342.5(7)  | 1951.4(4)   | 2073.0(6)   | 2067.0(5)  |
| Z                                     | 4  | 4   | 4   | 4  |
| ρ <sub>calc</sub> , g/cm <sup>3</sup> | 1.007  | 1.364   | 1.423   | 1.707  |
| ρ <sub>meas</sub> , g/cm <sup>3</sup> | not measd  | not measd   | not measd   | not measd  |
| T, °C                                 | 21   | 21  | 21  | 21   |
| radiation                             | Cu   | Mo  | Mo  | Mo   |
| λ, Å                                  | 1.541 78   | 0.710 69  | 0.710 69  | 0.710 69   |
| μ, cm <sup>-1</sup>                   | 17.67  | 9.62  | 10.25   | 55.02  |
| R(F)                                  | 0.042  | 0.034   | 0.035   | 0.029  |
| R <sub>w</sub> (F)                    | 0.042  | 0.031   | 0.030   | 0.027  |

$$^a R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, R_w = \left( \frac{\sum w(|F_o| - |F_c|)^2}{\sum w|F_o|^2} \right)^{1/2}.$$

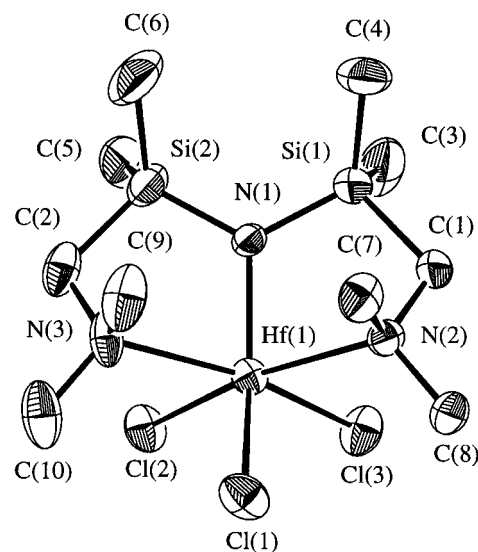
**Table 2.** Selected Bond Lengths (Å) and Angles (deg) for 2a

|                  |          |                  |          |
|------------------|----------|------------------|----------|
| Si(1)–N(1)       | 1.691(2) | Si(2)–N(1)       | 1.691(2) |
| Si(3)–N(4)       | 1.688(2) | Si(4)–N(4)       | 1.690(2) |
| N(1)–Li(1)       | 2.148(5) | N(1)–Li(2)       | 2.142(5) |
| N(2)–Li(1)       | 2.179(5) | N(3)–Li(2)       | 2.211(6) |
| N(4)–Li(1)       | 2.171(5) | N(4)–Li(2)       | 2.151(5) |
| N(5)–Li(1)       | 2.181(5) | N(6)–Li(2)       | 2.174(6) |
| Li(1)–Li(2)      | 2.581(7) |                  |          |
| Li(1)–N(1)–Li(2) | 74.0(2)  | Li(1)–N(4)–Li(2) | 73.3(2)  |
| N(1)–Li(1)–N(2)  | 96.5(2)  | N(1)–Li(1)–N(4)  | 105.1(2) |
| N(1)–Li(1)–N(5)  | 126.4(2) | N(2)–Li(1)–N(4)  | 127.1(2) |
| N(2)–Li(1)–N(5)  | 107.4(2) | N(4)–Li(1)–N(5)  | 97.4(2)  |
| N(1)–Li(2)–N(3)  | 97.1(2)  | N(1)–Li(2)–N(4)  | 106.0(2) |
| N(1)–Li(2)–N(6)  | 126.9(3) | N(3)–Li(2)–N(4)  | 126.0(3) |
| N(3)–Li(2)–N(6)  | 107.8(2) | N(4)–Li(2)–N(6)  | 96.1(2)  |

**Table 3.** Selected Bond Lengths (Å) and Angles (deg) for 6–8

|                  | M          |            |           |
|------------------|------------|------------|-----------|
|                  | Ti         | Zr         | Hf        |
| M(1)–Cl(1)       | 2.389(1)   | 2.422(1)   | 2.409(2)  |
| M(1)–Cl(2)       | 2.326(1)   | 2.427(1)   | 2.429(1)  |
| M(1)–Cl(3)       | 2.337(1)   | 2.441(1)   | 2.416(2)  |
| M(1)–N(1)        | 1.896(3)   | 2.056(3)   | 2.048(4)  |
| M(1)–N(2)        | 2.275(3)   | 2.447(4)   | 2.426(4)  |
| M(1)–N(3)        | 2.263(3)   | 2.437(4)   | 2.431(5)  |
| Cl(1)–M(1)–Cl(2) | 86.29(4)   | 102.20(6)  | 102.37(6) |
| Cl(1)–M(1)–Cl(3) | 83.76(4)   | 103.08(5)  | 102.00(7) |
| Cl(1)–M(1)–N(1)  | 176.48(9)  | 142.7(1)   | 143.8(1)  |
| Cl(1)–M(1)–N(2)  | 96.59(7)   | 81.7(1)    | 82.5(1)   |
| Cl(1)–M(1)–N(3)  | 93.64(7)   | 82.2(1)    | 81.7(1)   |
| Cl(2)–M(1)–Cl(3) | 169.84(4)  | 83.22(5)   | 83.09(6)  |
| Cl(2)–M(1)–N(1)  | 96.90(8)   | 105.8(1)   | 103.9(1)  |
| Cl(2)–M(1)–N(2)  | 90.42(8)   | 162.3(1)   | 163.1(1)  |
| Cl(2)–M(1)–N(3)  | 86.42(8)   | 79.63(10)  | 79.5(1)   |
| Cl(3)–M(1)–N(1)  | 93.10(8)   | 104.3(1)   | 105.4(1)  |
| Cl(3)–M(1)–N(2)  | 88.68(8)   | 79.1(1)    | 80.0(1)   |
| Cl(3)–M(1)–N(3)  | 96.23(8)   | 162.79(10) | 162.6(1)  |
| N(1)–M(1)–N(2)   | 84.9(1)    | 79.2(2)    | 79.6(2)   |
| N(1)–M(1)–N(3)   | 85.1(1)    | 79.1(1)    | 79.2(2)   |
| N(2)–M(1)–N(3)   | 169.08(10) | 118.1(1)   | 117.4(2)  |

one generates a molecule with C<sub>s</sub> symmetry and this is not consistent with the observed data. To rationalize the solution structure of **7** and **8**, either the complexes isomerize upon dissolution to give the more symmetric meridional geometry or the bicapped tetrahedral geometry is maintained in solution but undergoes a fast fluxional process whereby each amine donor moves from one tetrahedral face to the other thereby equilibrating all of the pairs of methyls and hydrogens on the

**Figure 3.** Perspective view of HfCl<sub>3</sub>[N(SiMe<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>], **8**, with 33% probability thermal ellipsoids shown. (Compound **7** is isomorphous and isostructural.)

backbone of the ligand.<sup>30</sup> By examining the low-temperature <sup>1</sup>H NMR spectra of the zirconium derivative **7**, we find evidence for the latter process since as the temperature is lowered, decoalescence is observed to give two types of silylmethyls, two amine methyls, and inequivalent methylene protons. In the low temperature limit, the solution- and solid-state structures of the heavier member complexes **7** and **8** are therefore identical and different from the titanium congener **6**.

## Conclusions

In this work we have developed a high-yield preparation of a new amido ligand that incorporates two amine donors into a potentially tridentate array of nitrogen donors. The lithiated form of the amido diamine ligand exists as a dimer in solution and in the solid state. In addition, the lithium amide derivative serves as a useful precursor for transferring this new tridentate ligand system onto the group 4 elements.

## Experimental Section

**Procedures.** Unless otherwise stated all manipulations were performed under an atmosphere of dry, oxygen-free nitrogen using a Vacuum Atmospheres HE-553-2 model glovebox equipped with a MO-

40–2H purification system and a  $-40\text{ }^{\circ}\text{C}$  freezer or using standard Schlenk-type glassware on a dual vacuum/nitrogen line.  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were recorded on a Varian XL-300 instrument operating at 299.9 and 75.429 MHz, respectively, or on a Bruker AC200 instrument operating at 200.132 and 50.323 MHz, respectively.  $^1\text{H}$  NMR spectra were referenced to internal  $\text{C}_6\text{D}_5\text{H}$  (7.15 ppm) or  $\text{C}_6\text{D}_5\text{-CD}_2\text{H}$  (2.09 ppm), and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were referenced to  $\text{C}_6\text{D}_6$  (128.0 ppm) or  $\text{C}_6\text{D}_5\text{CD}_3$  (20.4 ppm). Microanalyses (C, H, N) were performed by Mr. P. Borda of this department.

The variable-temperature  $^1\text{H}$  NMR spectra of  $\{\text{LiN}(\text{SiMe}_2\text{CH}_2\text{NMe}_2)_2\}_2$  were run on the Varian XL-300. DNMR simulations on the silylmethyl hydrogen resonances were performed using the WINNMR software and the resulting  $k$ 's plotted using the standard Eyring equation.

**Materials.**  $\text{LiNMe}_2$ ,  $n\text{-BuLi}$  (1.6M in hexanes),  $\text{TiCl}_4$  (1.0 M in toluene), and  $\text{MeLi}$  (1.4 M in  $\text{Et}_2\text{O}$ ) were purchased from the Aldrich Chemical Co. and used without further purification. Anhydrous  $\text{ZrCl}_4$  and  $\text{HfCl}_4$  were purchased from Aldrich and sublimed prior to use;  $\text{ZrCl}_4(\text{THT})_2$  and  $\text{HfCl}_4(\text{THT})_2$  were prepared by the addition of 2 equiv of tetrahydrothiophene (THT) to the corresponding metal halide suspended in dry  $\text{CH}_2\text{Cl}_2$ ; after 1–2 h, removal of all the volatiles produces the precursor derivatives as white powders in quantitative yield.  $\text{ClSiMe}_2\text{CH}_2\text{Cl}$  was purchased from PCR Research Chemicals and vacuum transferred prior to use.  $\text{NH}_4\text{Cl}$  was sublimed under vacuum prior to use, and  $\text{Et}_3\text{N}$  was predried over  $\text{NaOH}$ , distilled from  $\text{CaH}_2$ , and freeze–pump–thawed three times.

Toluene, hexanes, and THF were refluxed over  $\text{CaH}_2$  and  $\text{Et}_2\text{O}$  was predried over 4 Å molecular sieves prior to a final distillation under Ar from either sodium or sodium benzophenone ketyl. Methylene chloride was dried by refluxing over  $\text{CaH}_2$  for at least 48 h followed by vacuum transfer. Deuterated solvents were dried by heating under vacuum over Na or Na/K alloy and then vacuum transferred.

**$\text{HN}(\text{SiMe}_2\text{CH}_2\text{NMe}_2)_2$ .**  $\text{NH}_4\text{Cl}$  (2.478 g, 46.3 mmol),  $\text{Me}_2\text{NSiMe}_2\text{-CH}_2\text{NMe}_2$ <sup>24,25</sup> (12.103 g, 75.5 mmol), and toluene (200 mL) were added to a 400 mL thick-walled glass reactor equipped with a Kontes needle valve.  $\text{Et}_3\text{N}$  (6.35 mL, 45.5 mmol) was syringed into the solution, and the reactor was quickly sealed, cooled to 77 K, evacuated, and resealed. The mixture was then heated in a 100 °C oil bath for 2 days during which time a white precipitate ( $\text{Et}_3\text{NHCl}$ ) developed. The flask was cooled to room temperature and evacuated to remove unreacted  $\text{NH}_3$  and  $\text{HNMe}_2$  byproduct. The toluene solution was filtered through Celite and evaporated yielding a colorless liquid which was sufficiently pure for use in the next step of the synthesis. Yield: 8.255 g (88%).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , ppm):  $\delta$  2.18 (s, 12H,  $\text{CH}_2\text{NMe}_2$ ); 1.78 (s, 4H,  $\text{CH}_2$ ); 0.19 (s, 12H,  $\text{SiMe}_2$ ); N–H (not observed).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , ppm):  $\delta$  53.3 ( $\text{CH}_2$ ); 49.7 ( $\text{CH}_2\text{NMe}_2$ ); 1.5 ( $\text{SiMe}_2$ ).

**$\{\text{LiN}(\text{SiMe}_2\text{CH}_2\text{NMe}_2)_2\}_2$ .**  $\text{HN}(\text{SiMe}_2\text{CH}_2\text{NMe}_2)_2$  (1.003 g, 4.05 mmol) was dissolved in 10 mL of hexanes, and  $n\text{-BuLi}$  (2.5 mL, 4.0 mmol) was syringed into the solution. The solution was swirled, and some bubbling was observed. It was cooled to  $-30\text{ }^{\circ}\text{C}$  overnight during which time crystals of  $\{\text{LiN}(\text{SiMe}_2\text{CH}_2\text{NMe}_2)_2\}_2$  were formed. Successive recrystallizations from hexanes yielded 0.803 g of the crystalline product (79%).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , ppm):  $\delta$  2.11 (s, 12H,  $\text{NMe}_2$ ); 1.84 (s br, 4H,  $\text{CH}_2$ ), 0.30 (s, 12H,  $\text{SiMe}_2$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , ppm):  $\delta$  57.0 ( $\text{CH}_2$ ); 50.3 ( $\text{NMe}_2$ ); 6.4 ( $\text{SiMe}_2$ ). Anal. Calcd for  $\text{C}_{10}\text{H}_{28}\text{N}_3\text{Si}_2\text{-Li}$ : C, 47.39; H, 11.13; N, 16.58. Found: C, 47.01; H, 10.87; N, 16.40. Mass spectrum (EI, g mol<sup>-1</sup>):  $\text{M}^+ = 253$  [ $\text{LiN}(\text{SiMe}_2\text{CH}_2\text{NMe}_2)_2$ ].

**$\text{TiCl}_3[\text{N}(\text{SiMe}_2\text{CH}_2\text{NMe}_2)_2]$ .**  $\{\text{LiN}(\text{SiMe}_2\text{CH}_2\text{NMe}_2)_2\}_2$  (1.006 g, 1.98 mmol) was dissolved in toluene (25 mL) and added dropwise to a solution of  $\text{TiCl}_4$  at  $-78\text{ }^{\circ}\text{C}$  (prepared by diluting 4.2 mL of 1.0 M  $\text{TiCl}_4$  to 100 mL, 4.2 mmol). The solution was warmed to room temperature and stirred overnight. The orange solution was filtered through Celite, and the toluene was evaporated *in vacuo* until a solid began to precipitate. The solution was cooled to  $-30\text{ }^{\circ}\text{C}$  to give a red-orange microcrystalline material. Yield: 1.43 g (91%).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , ppm):  $\delta$  2.52 (s, 12H,  $\text{NMe}_2$ ), 2.41 (s, 4H,  $\text{CH}_2$ ), 0.15 (s, 12H,  $\text{SiMe}_2$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , ppm): 61.8 ( $\text{CH}_2$ ), 58.6 ( $\text{NMe}_2$ ), 0.8 ( $\text{SiMe}_2$ ). Anal. Calcd for  $\text{C}_{10}\text{H}_{28}\text{N}_3\text{Si}_2\text{Cl}_3\text{Ti}\cdot 0.15\text{toluene}$ : C, 32.02; H, 7.06; N, 10.14. Found: C, 31.73; H, 7.39; N, 10.32.

**$\text{ZrCl}_3[\text{N}(\text{SiMe}_2\text{CH}_2\text{NMe}_2)_2]$ .** An intimate mixture of  $\text{ZrCl}_4(\text{THT})_2$  (2.604 g, 6.36 mmol) and  $\{\text{LiN}(\text{SiMe}_2\text{CH}_2\text{NMe}_2)_2\}_2$  (1.527 g, 3.01 mmol) was suspended in  $\text{Et}_2\text{O}$  (120 mL) at  $-78\text{ }^{\circ}\text{C}$ . The solution was warmed to room temperature and stirred overnight, and the  $\text{Et}_2\text{O}$  was

evaporated. The white residue was extracted into toluene (50 mL) and filtered through Celite, and the toluene was reduced *in vacuo* until a solid began to appear. The flask was cooled to  $-40\text{ }^{\circ}\text{C}$  overnight. The toluene was decanted off and the product washed with cold hexanes. After the product was dried *in vacuo*, a white powder was isolated. Yield: 2.203 g (82%).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , ppm): 2.40 (s, 12H,  $\text{NMe}_2$ ), 2.20 (s, 4H,  $\text{CH}_2$ ), 0.11 (s, 12H,  $\text{SiMe}_2$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , ppm): 56.9 ( $\text{CH}_2$ ), 53.2 ( $\text{NMe}_2$ ), 2.3 ( $\text{SiMe}_2$ ). Anal. Calcd for  $\text{C}_{10}\text{H}_{28}\text{N}_3\text{Si}_2\text{Cl}_3\text{Zr}$ : C, 27.05; H, 6.35; N, 9.46. Found: C, 27.43; H, 6.66; N, 9.40. Mass spectrum (EI, g mol<sup>-1</sup>):  $\text{M}^+ = 443$  ( $\text{ZrCl}_3[\text{N}(\text{SiMe}_2\text{CH}_2\text{NMe}_2)_2]$ ); 408,  $\text{M}^+ - \text{Cl}$ ; 385,  $\text{M}^+ - \text{CH}_2\text{NMe}_2$ .

**$\text{HfCl}_3[\text{N}(\text{SiMe}_2\text{CH}_2\text{NMe}_2)_2]$ .** An intimate mixture of  $\text{HfCl}_4(\text{THT})_2$  (1.839 g, 3.70 mmol) and  $\{\text{LiN}(\text{SiMe}_2\text{CH}_2\text{NMe}_2)_2\}_2$  (0.896 g, 1.77 mmol) was suspended in  $\text{Et}_2\text{O}$  (90 mL) at  $-78\text{ }^{\circ}\text{C}$ . The solution was warmed to room temperature and stirred overnight, and the  $\text{Et}_2\text{O}$  was evaporated. The white residue was extracted into toluene (50 mL) and filtered through Celite, and the toluene was removed *in vacuo*. The product was washed with cold hexanes, and after it was dried *in vacuo*, a white powder was isolated. Yield: 1.670 g (89%).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , ppm): 2.46 (s, 12H,  $\text{NMe}_2$ ), 2.19 (s, 4H,  $\text{CH}_2$ ), 0.12 (s, 12H,  $\text{SiMe}_2$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , ppm): 58.1 ( $\text{CH}_2$ ), 54.6 ( $\text{NMe}_2$ ), 2.2 ( $\text{SiMe}_2$ ). Anal. Calcd:  $\text{C}_{10}\text{H}_{28}\text{N}_3\text{Si}_2\text{Cl}_3\text{Hf}$ : C, 22.60; H, 5.31; N, 7.91. Found: C, 23.23; H, 5.43; N, 7.70.

**X-ray Crystallographic Analyses of  $\{\text{LiN}(\text{SiMe}_2\text{CH}_2\text{NMe}_2)_2\}_2$ , **2a**, and  $\text{MCl}_3[\text{N}(\text{SiMe}_2\text{CH}_2\text{NMe}_2)_2]$  ( $\text{M} = \text{Ti}$  (**6**),  $\text{Zr}$  (**7**),  $\text{Hf}$  (**8**)).** Crystallographic data appear in Table 1. The final unit-cell parameters were obtained by least-squares on the setting angles for 25 reflections with  $2\theta = 61.8\text{--}69.7^\circ$  for **2a**,  $26.2\text{--}32.0^\circ$  for **6**,  $21.9\text{--}28.3^\circ$  for **7**, and  $23.4\text{--}28.3^\circ$  for **8**. The intensities of three standard reflections, measured every 200 reflections, decayed linearly by 6.6% for **2a**, by 1.9% for **6**, and by 2.0% for **8** and showed only small random fluctuations for **7**. The data were processed,<sup>31</sup> corrected for Lorentz and polarization effects, decay (**2a**, **6**, **8**), and absorption (empirical: based on azimuthal scans).

The structures were solved by direct (**2a**) or Patterson (**6–8**) methods. Complexes **7** and **8** are isomorphous and isostructural. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were fixed in idealized positions (staggered methyl groups,  $\text{C–H} = 0.98\text{ \AA}$ ,  $B_{\text{H}} = 1.2B_{\text{bonded atom}}$ ). Secondary extinction corrections (Zachariasen type, isotropic) were applied, the final values of the extinction coefficients being  $3.61(9) \times 10^{-6}$  for **2a**,  $1.2(3) \times 10^{-7}$  for **6**,  $2.60(15) \times 10^{-7}$  for **7**, and  $1.05(6) \times 10^{-7}$  for **8**. Neutral atom scattering factors and anomalous dispersion corrections were taken from ref 32. Selected bond lengths and angles for **2a** and **6–8** appear in Tables 2 and 3. Full crystallographic data, final atomic coordinates, and equivalent isotropic thermal parameters, complete tables of bond lengths and angles, hydrogen atom parameters, anisotropic thermal parameters, torsion angles, intermolecular contacts, and least-squares planes are included as Supporting Information.

**Acknowledgment.** This work was supported by the NSERC of Canada in the form of Research Grants and a Collaborative Grant (M.D.F. and S.G.).

**Supporting Information Available:** For **2a** and **6–8**, complete crystallographic data, atomic coordinates and equivalent isotropic thermal parameters, anisotropic thermal parameters, complete bond lengths and angles, torsion angles, intermolecular contacts, and least-squares planes (90 pages). Ordering information is given on any current masthead page.

IC970168U

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