

( $^{37}\text{Cl}/^{35}\text{Cl}$ ) numbers will be ubiquitous at these spectrometer frequencies.

Finally, it is clear that longitudinal and, particularly, transverse relaxation times of the protons in these molecules are long enough to attain the small line widths displayed in the spectra. Scalar relaxation of the second kind<sup>9</sup> by the rapidly flipping  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$  nuclei causes only a small broadening. At 300 MHz the line widths of the shifted peaks appear to be equal, perhaps a consequence of the very similar magnetic properties<sup>9</sup> of the two chlorine isotopes. However, from the reported  $T_2$  of 1.5 s for the proton<sup>10</sup> in  $\text{SiHCl}_3$ , it follows that isotope shifts in chlorosilanes will be observed only at the highest available frequencies.

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### A Silicon-Nitrogen Analogue of the $[\text{PPN}]^+$ Cation: Synthesis and Structural Characterization of the $[\text{Ph}_3\text{SiNSiPh}_3]^-$ Ion

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Alkali metal derivatives of silylamides have attracted considerable attention due to interest in their unusual structures, their utility as amide transfer agents, their strong nucleophilic character, and also the apparent multiple nature of their Si-N bonds.<sup>2</sup> Usually silicon-nitrogen bonds are about 1.73 Å in length, but this value is thought to be short because it is significantly less than the predicted sum of the radii of Si and N, which is approximately 1.84 Å.<sup>2</sup> The shortening may be accounted for in terms of delocalization of the nitrogen lone pair into silicon d-orbitals although other explanations are possible.<sup>2</sup> A number of structures of alkali metal silylamides have been reported.<sup>3-8</sup> However, these invariably involve a metal-nitrogen interaction and, unless a chelating ligand is used, the compounds are generally associated. Noting the isoelectronic nature of the  $[\text{PNP}]^+$  and  $[\text{SiNSi}]^-$  arrays we hoped to synthesize a compound involving an unassociated ion of the type  $[\text{R}_3\text{SiNSiR}_3]^-$  which should also have, by comparison with the  $[\text{PPN}]^+$  (i.e., bistrisphenylphosphiniminium) cation,<sup>9</sup> a significant degree of multiple bonding between Si and N. We now report that sequential treatment of the crowded hexaphenyldisilylamine  $\text{HN}(\text{SiPh}_3)_2$  (**1**) with *n*-BuLi and 12-crown-4

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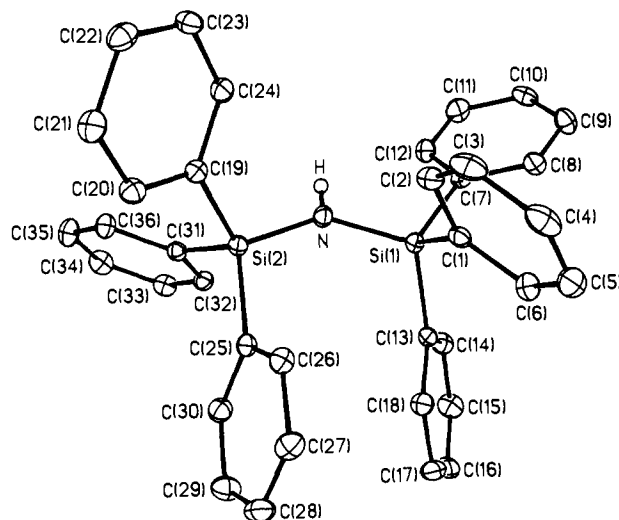
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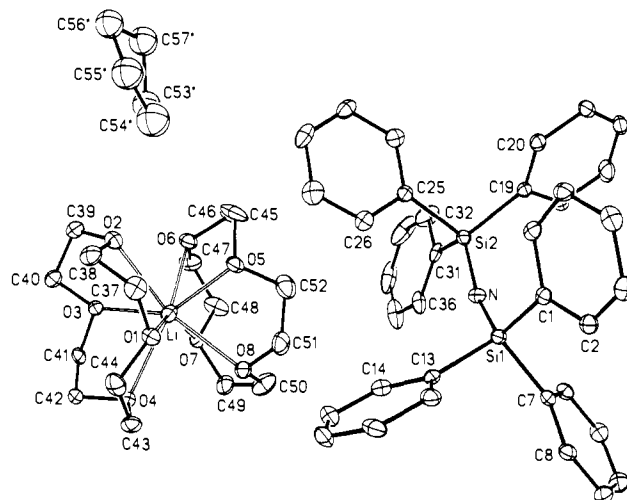
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**Figure 1.** Computer-generated plot of **1** (thermal ellipsoids at 30% probably level, arbitrary fixed radius circle used for H). Important bond distances (Å) and angles (deg) are the following:  $\text{NSi}(1) = 1.718$  (3),  $\text{NSi}(2) = 1.726$  (3),  $\text{NH} = 0.69$  (4),  $\text{Si}(1)\text{C}(1) = 1.871$  (4),  $\text{Si}(1)\text{C}(7) = 1.880$  (3),  $\text{Si}(1)\text{C}(13) = 1.877$  (3),  $\text{Si}(2)\text{C}(19) = 1.871$  (4),  $\text{Si}(2)\text{C}(25) = 1.872$  (4),  $\text{Si}(2)\text{C}(31) = 1.874$  (4),  $\text{Si}(1)\text{NSi}(2) = 136.1$  (2),  $\text{Si}(1)\text{NH} = 109$  (4),  $\text{Si}(2)\text{NH} = 115$  (4).



**Figure 2.** Computer-generated plot of **2** (30% probability level). THF molecule was symmetry generated from the refined THF position to show closest approach of C(54) (refined as an oxygen) to anion and cation (3.4 Å). Important bond distances (Å) and angles (deg) are the following:  $\text{Si}(1)\text{N} = 1.633$  (4),  $\text{Si}(2)\text{N} = 1.634$  (4),  $\text{Si}(1)\text{C}(1) = 1.909$  (5),  $\text{Si}(1)\text{C}(7) = 1.900$  (5),  $\text{Si}(1)\text{C}(13) = 1.920$  (5), similar SiC distances for  $\text{Si}(2)$ ,  $\text{SiNSi} = 154.9$  (3).

in THF results in the isolation of crystals of the complex  $[\text{Li}(12\text{-crown-4})_2][\text{N}(\text{SiPh}_3)_2] \cdot \text{THF}$ , (**2**), which has the novel ion  $[\text{Ph}_3\text{SiNSiPh}_3]^-$  as part of its crystal lattice.

The precursor disilylamine  $\text{HN}(\text{SiPh}_3)_2$ <sup>10</sup> (**1**) was synthesized by the treatment of  $\text{H}_2\text{NSiPh}_3$ <sup>11</sup> with *n*-BuLi and then  $\text{Ph}_3\text{SiCl}$  in THF. Its structure<sup>12</sup> (Figure 1) has a number of interesting features. The most notable is the wide Si-N-Si bond angle of  $136.1$  (2)° which suggested that a significantly wider angle might be obtained on deprotonation. The Si-N distances in **1** are normal, having an average value  $1.722$  (3) Å, and the  $\text{HNSi}(1)\text{Si}(2)$  array is planar. The structure may be contrasted to that of  $\text{HN}-$

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(SiMe<sub>3</sub>)<sub>2</sub>,<sup>13</sup> which has the corresponding structural parameters of 125.5 (1.8)° and 1.735 (12) Å.

Treatment of **1** (1.06 g, 2 mmol) in THF (20 mL) with *n*-BuLi (1.3 mL of a 1.6 M solution in hexane) afforded, after 30 min of stirring, a THF solution of LiN(SiPh<sub>3</sub>)<sub>2</sub>. Then 12-crown-4 (0.7 mL, ~4 mmol) was added by syringe and the resultant solution was stirred for 10 min. Filtration, followed by a reduction in volume under reduced pressure to incipient crystallization and overnight cooling in a -20 °C freezer, gave **2** as colorless crystals. Yield 1.1 g, 58%; mp 178–182 °C. The crystal structure of **2**<sup>12</sup> (Figure 2) shows that separation of the cation and anion is achieved to give the first example of a well-characterized free disubstituted amide (NR<sub>2</sub>)<sup>-</sup> ion. This occurrence is interesting since 12-crown-4 failed in this respect with both LiN(SiMe<sub>3</sub>)<sub>2</sub><sup>15</sup> and LiNPh<sub>2</sub><sup>16</sup> giving instead the adduct [12-crown-4-LiNR<sub>2</sub>] (R = SiMe<sub>3</sub> or Ph). Success in the case of **2** is probably due to the larger size of the SiPh<sub>3</sub> substituent and the more electron withdrawing effect of the SiPh<sub>3</sub> (in comparison with SiMe<sub>3</sub>), which reduces the strength of the Li-N bond. More subtle considerations probably involve a better size match between cation and anion, which affords a greater lattice energy and heat of formation for **2** over the corresponding species with either a [N(SiMe<sub>3</sub>)<sub>2</sub>]<sup>-</sup> or [NPh<sub>2</sub>]<sup>-</sup> anion.

The most interesting structural parameters for the anion of **2** involve the Si-N-Si angle, 154.9 (3)°, and the Si-N distances, 1.633 (4) and 1.634 (4) Å. The angle is considerably (~19°) wider and the bonds considerably (~0.09 Å) shorter than those of the precursor. These changes are in accord with a greater availability of both nitrogen lone pairs in the absence of the Li<sup>+</sup> ion. The increasing angle at N also implies more p-like orbitals for the lone pairs and a greater p-d (N-Si) interaction, which in turn gives a shorter Si-N bond. As already mentioned [Ph<sub>3</sub>SiNSiPh<sub>3</sub>]<sup>-</sup> is isoelectronic with [Ph<sub>3</sub>PNPPh<sub>3</sub>]<sup>+</sup>.<sup>17</sup> It is notable that since the latter species may adopt a large range (ca. 135–180°)<sup>18</sup> of angles at N it is quite probable that the corresponding angle in **2** will be equally variable and may, with the appropriate cation, afford a linear [Ph<sub>3</sub>Si-N-SiPh<sub>3</sub>]<sup>-</sup> array as seen in the isoelectronic species Ph<sub>3</sub>SiOSiPh<sub>3</sub>.<sup>19</sup> This should result in a further decrease in the Si-N bond length probably nearer to the value of 1.568 (3) Å seen for the SiN double bond in the compound *t*-Bu<sub>2</sub>Si=N-Si-*t*-Bu<sub>3</sub> (**3**).<sup>20</sup> The almost linear structure of this compound also suggests a considerable amount of nitrogen lone pair involvement indicated by *t*-Bu<sub>2</sub>Si=N-Si-*t*-Bu<sub>3</sub>. This N-Si distance is also shortened having a value of 1.695 (3) Å. Thus the average N-Si length in **2** is almost exactly equal to the mean of the N-Si bond lengths, 1.632 (3) Å, observed in **3**.

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**Supplementary Material Available:** Tables of data collection and refinement, atom coordinates, thermal parameters, bond distances and angles, and hydrogen coordinates (19 pages). Ordering information is given on any current masthead page.

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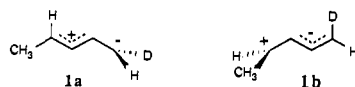
## Regioselective Photoisomerization of Fluoro Aryl Dienes. Role of Dipolar Intermediates of Excited Dienes<sup>†</sup>

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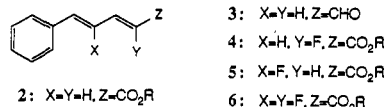
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Recently, Squillacote and Semple<sup>1</sup> reported regioselective isomerization of 1-deuterio-*trans*-1,3-pentadiene at the less substituted 1,2-center. The result was attributed to preferential formation of the orthogonal allyl (cation)-methylene (anion) (**1a**) intermediate. This suggestion was thought to be consistent with



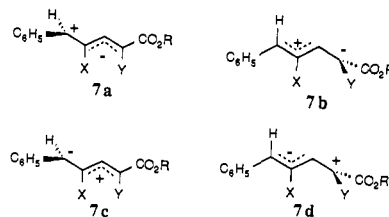
the calculated results<sup>2</sup> of such a dipolar structure being more stable than the oppositely polarized structure (**1b**), the latter first postulated by Dauben following the observation of a stereoselective cyclization of ethylenecyclooctene.<sup>3</sup> However, the result is also consistent with the reaction being directed by differences in mass or in reaction volume.<sup>4</sup> Now we report cases of regioselective isomerization of substituted dienes where the results are more likely to be dominated by the polar substituents and are consistent with selective formation of the Dauben intermediate.

Compounds prepared for this study are aryl diene esters (**2**, **4**, **5**, and **6**) and aldehyde (**3**) with or without fluorine substituents.



In most cases the all-*trans* and the monocis geometric isomers were isolated from synthetic mixtures or photomixtures, and the *dicis* isomer was isolated from reaction of C<sub>2</sub>-fluorophosphonate<sup>5</sup> with *cis*-cinnamaldehyde. The structures of the isomers were deduced from their <sup>1</sup>H and <sup>19</sup>F NMR spectra (data presented in the supplementary material). The all-*trans* isomers were then irradiated, with the progress of the reaction followed by HPLC or F NMR. With the exception of compound **2**, all isomerization reactions are highly regioselective, favoring formation of the 4-*cis* isomer. Selected data are listed in Table I. We might add that because of the minute amount of the minor product for compounds **3–6**, it was necessary to reach close to 20% conversion before it was possible to measure the product distribution.

Of the four possible zwitterionic intermediates (**7a–d**) it is clear that only structures **7a** and **7c** could lead to selective isomerization at the 4,5-bond. However, the nature of the substituents in these



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