

## Crystal Structures of the Chiral Lithiosilanes [(Lis)-PhMe<sub>2</sub>SiLi·THF·(-)-Sparteine] and [Ph<sub>2</sub>(NEt<sub>2</sub>)SiLi·(-)-Sparteine]

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For the synthesis of enantiomerically enriched lithium alkyls (with the stereogenic center at the metalated carbon), certain adducts between alkyllithium bases and (-)-sparteine have become highly important chiral reagents.<sup>1,2</sup> Known solid-state structures of lithium alkyls with coordinating (-)-sparteine exhibit monomeric or dimeric aggregates (Figure 1), whereas **3** is the first crystallized monomeric butyllithium derivative.<sup>3</sup> Here, we present our structural studies on (-)-sparteine-coordinated lithiosilanes to establish a proper basis for subsequent applications of these reagents. We present here (to the best of our knowledge) the first crystal structures of enantiomerically pure lithiosilanes.<sup>4</sup>

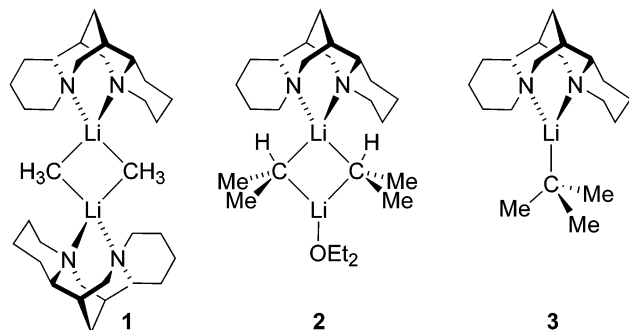


Figure 1. Structures of lithium alkyls with coordinating (-)-sparteine.

In contrast to a broad variety of oligomeric donor base free lithioalkyls,<sup>5</sup> lithiosilanes are almost exclusively accessible in donor solvents, and thus monomeric donor base stabilized contact ion pair structures are their dominating structural motif.<sup>6</sup>

Solvent separated structures are seldom observed, with only two examples described so far.<sup>7</sup> Dimeric, or more highly aggregated, lithiosilanes are generally prepared and crystallized in the absence of coordinating solvents.<sup>8</sup> However, if the lithiosilane itself contains coordinating substituents, formation of dimers is observed even in the presence of THF.<sup>9</sup>

Figure 2 shows the molecular structures of **4** and **5** (prepared by Si–Si bond cleavage of the corresponding disilanes and addition of (-)-sparteine) in the crystal. The first, **4**, crystallized from Et<sub>2</sub>O<sup>10</sup> in the monoclinic crystal system, space group *P*2<sub>1</sub>.<sup>11</sup> The central structural motif is a tetrahedral four-coordinate lithium with a Si–Li contact of 2.675(4) Å. The sum of the C–Si–C angles is 303.0°, and thus in the range of other contact ion pairs.<sup>6</sup> As a result of coordinating the lithium atom, both nitrogen centers are configurationally fixed, and the sparteine ligand thus possesses six stereogenic centers (cf. Figure 2).<sup>12</sup> The presence of an additional THF molecule causes the lithium center in **4** to also become a stereogenic center with *S*-configuration, rendering (Lis)-**4** one of two possible diastereomers. Formation of only one diastereomer can be explained by thermodynamic equilibrium between both stereoisomers (regulated by the energy difference between the two) or by effects relating to crystallization.

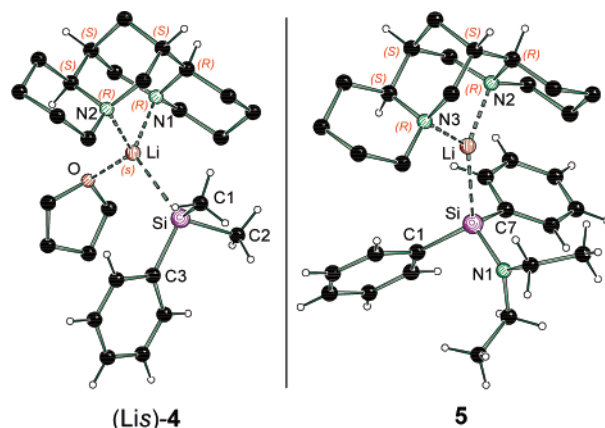


Figure 2. Molecular structures of PhMe<sub>2</sub>SiLi·THF·(-)-sparteine [(Lis)-**4**] and Ph<sub>2</sub>(NEt<sub>2</sub>)SiLi·(-)-sparteine (**5**) in the crystal [selected hydrogens on THF and on all nonchiral centers in (-)-sparteine were omitted for reasons of clarity; Schakal plots<sup>13</sup>]. Selected bond lengths (Å) and angles (°) of (Lis)-**4**: Si–C(1) 1.948(3), Si–C(2) 1.932(3), Si–C(3) 1.934(3), Si–Li 2.675(4), Li–N(1) 2.113(4), Li–N(2) 2.098(4), C(1)–Si–C(2) 100.1(1), C(1)–Si–C(3) 101.1(1), C(2)–Si–C(3) 101.8(1); **5**: Si–C(1) 1.923(4), Si–C(7) 1.922(4), Si–N(1) 1.763(3), Si–Li 2.600(5), Li–N(2) 2.001(6), Li–N(3) 2.011(7), C(7)–Si–N(1) 106.1(2), C(1)–Si–C(7) 100.6(2), C(1)–Si–N(1) 103.6(2).

Lithiosilane **5** was crystallized from Et<sub>2</sub>O<sup>10</sup> in the orthorhombic crystal system, space group *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub> (Figure 2).<sup>11</sup> Here, the central structural motif is (in contrast to **4**) a three-coordinate lithium center with a rather short Si–Li contact of 2.600(5) Å, which is among the smallest silicon–lithium distances observed in monomeric compounds so far. The sum of the C–Si–C and C–Si–N angles at Si, 310.3°, is rather high for lithiosilanes. The sum of bond angles on nitrogen N1 is 359.8°, indicating an almost planar environment. The solid-state structure of **5** represents the only possible enantiomer. Here, the lithium center has two diastereotopic coordination sites.

As chirality in systems **4** and **5** is induced at the silicon center by the sparteine ligand, for the silicon to successfully transfer stereogenic information to electrophiles (i.e., to act as a chiral nucleophile), the Si–Li contact has to remain intact in solution. In this context, it is important to know that an increase in steric demand at the silicon center in **4** primarily results in a decreased coordination number at the lithium site, and not in formation of solvent separated ion pairs (which carry no further stereochemical information). Strictly speaking, it is the simultaneous presence of sterically demanding substituents/ligands at both silicon and lithium centers that is responsible for the three-coordinate lithium center in **5**. This is additionally supported by the fact that exchange of (-)-sparteine for the smaller TMEDA ligand results in lithiosilane **6** (crystallized from Et<sub>2</sub>O<sup>10</sup> in space group *P*2<sub>1</sub>/c; for molecular structure cf. Figure 3), which again has a four-coordinate lithium center.

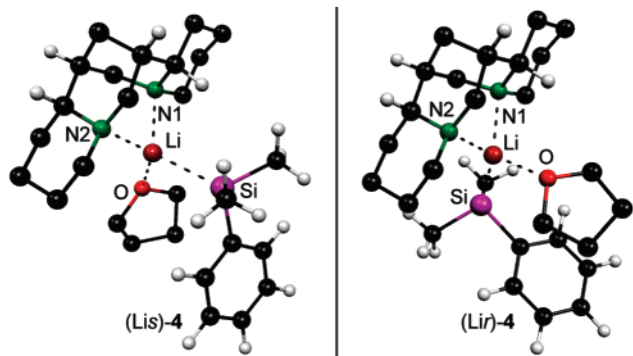


**Figure 3.** Molecular structures of  $\text{Ph}_2(\text{NEt}_2)\text{SiLi}\cdot\text{TMEDA}$  (**6**) in the crystal [hydrogens on THF and TMEDA were omitted for reasons of clarity; Schakal plot<sup>13</sup>]. Selected bond lengths (Å) and angles (°) of **6**: Si–C(1) 1.949(2), Si–C(7) 1.929(2), Si–N(1) 1.7849(17), Si–Li 2.737(3), Li–N(2) 2.175(4), Li–N(3) 2.173(4), C(7)–Si–N(1) 103.65(9), C(1)–Si–C(7) 101.69(9), C(1)–Si–N(1) 101.67(8).

To clarify the situation in solution, NMR studies of **4** and **5** in toluene- $d_8$  were conducted, indicating the presence of only one diastereomer of **4** in solution at  $-50^\circ\text{C}$ . The observation of a  $^{29}\text{Si}$ – $^7\text{Li}$  coupling ( $J_{\text{SiLi}} = 47.9$  Hz) and two  $^{13}\text{C}$  NMR signals for the diastereotopic methyl groups at silicon indicates a distinct Si–Li contact on the NMR time scale at  $-50^\circ\text{C}$ . At room temperature, no coupling in the  $^{29}\text{Si}$  NMR was observed; however, the methyl groups still emit two  $^{13}\text{C}$  NMR signals, showing the strength of the chiralizing influence of the (–)-sparteine ligand.

Further NMR analyses of **5** in toluene- $d_8$  also indicate one species in solution, which exhibits a  $^{29}\text{Si}$ – $^7\text{Li}$  coupling of 65.3 Hz at room temperature and two sets of signals for the diastereotopic phenyl groups on silicon. Both observations indicate a (–)-sparteine–Li–Si contact at room temperature, and that the lithium center is fixed at silicon on the NMR time scale. Upon cooling of the sample, the signal in the  $^{29}\text{Si}$  NMR broadens as a result of the quadrupole moment of  $^7\text{Li}$ . At  $-90^\circ\text{C}$ , the coupling is again well resolved ( $J_{\text{SiLi}} = 53.3$  Hz) as a result of slower relaxation at lower temperatures.<sup>14</sup>

To determine the relative energy ratios between the two relevant diastereomers of **4**, DFT calculations were performed on the B3LYP/6-31+G(d) level.<sup>15</sup> Starting from the structural parameters of the solid-state structure, six different isomers were proposed<sup>16</sup> and optimized in energy, resulting in the favored isomers (Lis)-**4** and (Lir)-**4**. The energy difference between them is 2.9 kJ/mol, with (Lis)-**4** as the most stable diastereomer (cf. Figure 4).



**Figure 4.** Energy optimized structures [B3LYP/6-31+G(d)] of (Lis)-**4** and (Lir)-**4** (selected hydrogens were omitted for clarity; Molekel plot<sup>17</sup>).

Although the small energy difference between both diastereomers has to be interpreted with caution, the most stable structure

corresponds to the isomer found in the crystal (Lis)-**4**. The prevalence of this isomer—as shown by it being the only one found in the crystal—could therefore be the result of a thermodynamically controlled epimerization in solution.

To the best of our knowledge, the title compounds represent the first crystal structures of enantiomerically pure lithiosilanes. In future reactions, parameters, such as the coordination number at the lithium center, the reaction solvent, the reaction temperature, and the concentration, can be varied. Currently, we are searching for suitable electrophiles to permit the transfer of stereoinformation by selective formation of a new stereogenic center.

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**Supporting Information Available:** Crystallographic (CIF), experimental, and computational data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (11) All crystals of (Lis)-**4**, **5**, and **6** were mounted at  $-60^\circ\text{C}$  ( $\text{N}_2$  stream), using the X-TEMP 2 device (Kottke, T.; Stalke, D. *J. Appl. Crystallogr.* **1993**, *26*, 615). Furthermore, X-ray crystallography data for (Lis)-**4**, **5**, and **6** have been deposited with the Cambridge Crystallographic Data Center as supplementary publication Nos. CCDC 287268 [(Lis)-**4**], CCDC 287269 (**5**), and CCDC 287270 (**6**), respectively.
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