Communication

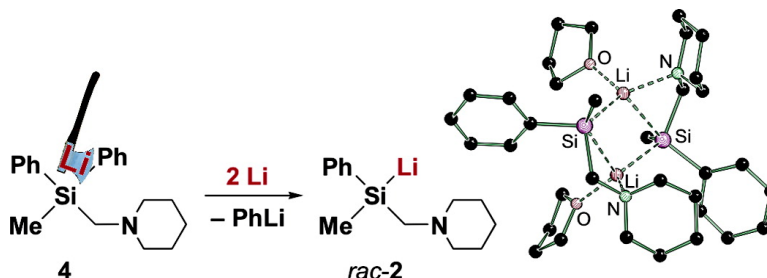# Selective Si–C Bond Cleavage as Synthetic Entry to a Functionalized Lithiosilane

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Selective Si−C Bond Cleavage as Synthetic Entry to a Functionalized Lithiosilane

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Functionalized lithiosilanes are versatile reagents in organic and organometallic chemistry.[1] They are used for the nucleophilic introduction of protecting groups and synthesis of silyl-substituted transition metal complexes[1] or silicon-based polymers.[2] Of all known functionalized lithiosilanes especially systems of type $R_2(R_2N)SiLi$ (developed by K. Tamao) are used for these purposes.[1a,3] In contrast to closely related alkyllithiums, methods of preparation for lithiosilanes such as Si−Si bond cleavage of disilanes or metal−metal exchange reactions are limited to specialized starting compounds and can result in the formation of byproducts. Our interest in this field concerns an alternative and simple access to functionalized or even highly enantiomerically enriched lithiosilanes, which are generally prepared by Si−Si bond cleavage of suitable disilanes such as highly enantiomerically enriched (R)-1 (cf. Scheme 1).[4] In comparison to disilanes, functionalized tetraorganosilanes are more readily accessible starting materials and easier to handle.
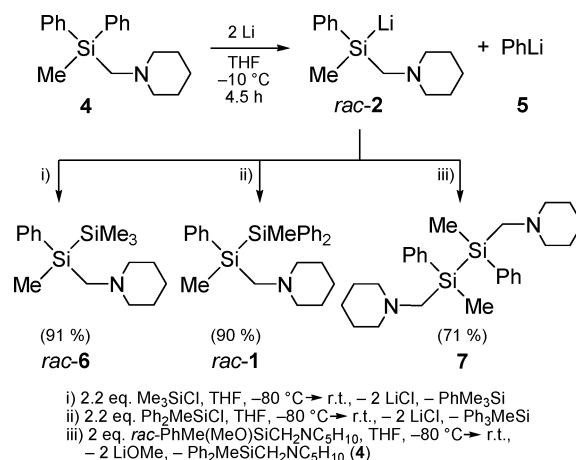
Scheme 1
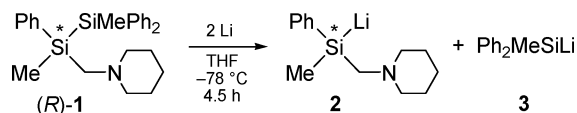
Herein we report a new example of reductive Si−C bond cleavage by lithium resulting in the selective formation of the lithiosilane rac-2, which should have synthetic potential similar to that of the systems of K. Tamao. This reaction type was hitherto only observed as an unwanted side reaction,[5] offering in some cases access to special compounds, which despite their low yields are of significant interest.[5c−e] Our focus rests on developing tetraorganosilane precursors for selective Si−C bond cleavage reactions with lithium metal. In prior work, the Si−CHPh₂ bond in (diphenylmethyl)-substituted tetraorganosilanes was successfully cleaved with lithium metal.[6] The steric demand of the (diphenylmethyl) group, however, prevented the preparation of starting material from which lithiosilane 2 could be accessed.

In our present work, treatment of the phenyl-substituted silane 4 with lithium metal afforded rac-2 by selective cleavage of one Si−C bond between silicon and a phenyl group (cf. Scheme 2). Moreover, the solid-state structure of the lithiosilane rac-2 was determined as the first example of a dimeric organyl-substituted lithiosilane in the presence of THF.[7] In addition, this analysis supplies vital structural information on the racemic form of the enantiomerically pure compound 2 (cf. Scheme 1).

The phenyl-substituted silane 4 is available in one step starting from (chloromethyl)methyldiphenylsilane by amination with piperidine.[8] When treating 4 with lithium metal in THF at room temperature after several minutes a significant change in color is observed, indicating the start of the Si−C cleavage reaction.[9] The reaction mixture is cooled to −10 °C and stirred for 4.5 h. Subsequent trapping reactions of the colored solution with chloro-

Scheme 2

i) 2.2 eq. Me₃SiCl, THF, −80 °C ➤ r.t., − 2 LiCl, − PhMe₃Si
ii) 2.2 eq. Ph₂MeSiCl, THF, −80 °C ➤ r.t., − 2 LiCl, − Ph₃MeSi
iii) 2 eq. rac-PhMe(MeO)SiCH₂NC₅H₁₀, THF, −80 °C ➤ r.t., − 2 LiOMe, − Ph₂MeSiCH₂NC₅H₁₀ (4)

rotrimethyl- or chloromethyldiphenylsilane at −80 °C result in the selective formation of disilanes rac-6 or rac-1 and trimethylphenylsilane or methyltriphenylsilane, respectively (cf. Scheme 2). No significant amounts of other compounds were detected by NMR and GC/MS analysis of the crude products, indicating a selective cleavage of the Si−C bond between silicon and one phenyl group. After workup, the disilanes rac-6 and rac-1 were isolated in yields of 91 and 90%, respectively. In contrast to the preparation of rac-2 by Si−Si bond cleavage of rac-1 (analogous to the reaction in Scheme 1), the new Si−C bond cleavage of 4 enables the removal of most of the byproduct phenyllithium from rac-2 by evaporation of THF and washing with n-hexane.

Although the Si−C bond cleavage of 4 affords synthetically utilizable solutions of rac-2, a precise NMR analysis of lithiosilane rac-2 required purer samples. This was achieved by reacting rac-2 with rac-methoxymethylphenyl(piperidinomethyl)silane[10] to give disilane 7 in good yield.[11] NMR analysis indicated that 7 was formed as a mixture of two diastereomers (d.r. = 57:43). As for other aryl-substituted disilanes, subsequent reaction of 7 with lithium metal results in Si−Si bond cleavage affording rac-2 in the absence of impurities.

When formed from 7, rac-2 can be isolated in the form of single crystals suitable for X-ray structural analysis by the removal of THF and recrystallization from Et₂O. Figure 1 shows the molecular structure of rac-2 in the solid state, which crystallized as the dimer (2·THF)₂ in the orthorhombic crystal system, space group $Pna2_1$.[12,13] The asymmetric unit contains two crystallographically independent dimers, which represent a pair of enantiomers. The central structural motif of each dimer is a four-membered ring formed by two lithium centers and one (R)- and one (S)-configured silicon center. This gives rise to one short [2.708(10)−2.734(12) Å] and one longer [2.855(11)−2.956(14) Å] Si−Li contact per lithium. The sum of Si−C bond angles at the Si centers indicates stronger pyramidalization on silicon compared to a tetrahedral arrangement, which is
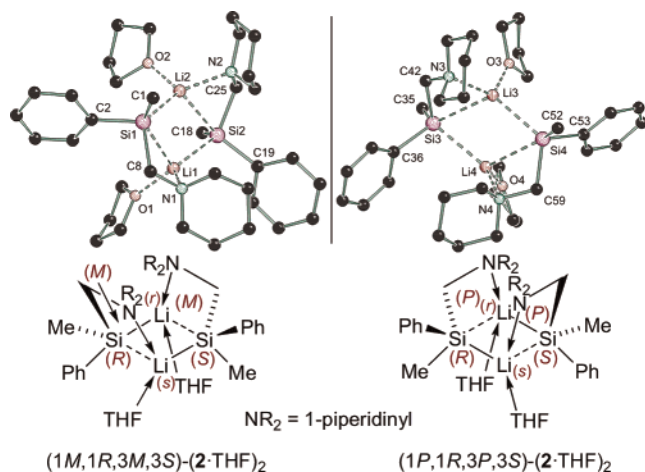
Figure 1. Molecular structure of *rac*-**2** in the crystal; the two crystallographic independent molecules (1*M*,1*R*,3*M*,3*S*)-(**2**·THF)$_2$ and (1*P*,1*R*,3*P*,3*S*)-(**2**·THF)$_2$ are shown (Schakal plots[15]). Selected bond lengths (Å) and angles (deg) of (1*M*,1*R*,3*M*,3*S*)-(**2**·THF)$_2$: Si(1)−C(1) 1.906(7), Si(1)−C(2) 1.925-(6), Si(1)−C(8) 1.940(9), Si(2)−C(18) 1.902(7), Si(2)−C(19) 1.912(7), Si-(2)−C(25) 1.958(6), Si(1)−Li(1) 2.933(11), Si(1)−Li(2) 2.711(11), Si(2)−Li(1) 2.734(12), Si(2)−Li(2) 2.864(11); C(1)−Si(1)−C(2) 102.3(3), C(1)−Si(1)−C(8) 103.0(3), C(2)−Si(1)−C(8) 101.0(3), C(18)−Si(2)−C(19) 103.8(3), C(18)−Si(2)−C(25) 99.6(3), C(19)−Si(2)−C(25) 106.2(3). (1*P*,1*R*,3*P*,3*S*)-(**2**·THF)2: Si(3)−C(35) 1.923(7), Si(3)−C(36) 1.960(6), Si-(3)−C(42) 1.947(6), Si(4)−C(52) 1.939(7), Si(4)−C(53) 1.924(7), Si(4)−C(59) 1.985(8), Si(3)−Li(3) 2.855(11), Si(3)−Li(4) 2.715(15), Si(4)−Li(3) 2.708(10), Si(4)−Li(4) 2.956(14), C(35)−Si(3)−C(36) 101.6(3), C(35)−Si(3)−C(42) 99.7(3), C(36)−Si(3)−C(42) 105.1(3), C(52)−Si(4)−C(53) 105.1(3), C(52)−Si(4)−C(59) 103.0(3), C(53)−Si(4)−C(59) 101.9(3).

a result of the hybridization defects[14] of Si in silyl anions or highly polar lithiosilanes [306.3° on Si(1), 309.6° on Si(2), 306.4° on Si-(3), and 308.3° on Si(4)].

Both lithium centers are coordinated by a nitrogen atom and one THF molecule, respectively. This leads to the formation of a ladder framework consisting of a central Si−Li−Si−Li and two Si−Li−N−C four-membered rings. The ligands on the Li centers in each dimer show formally C_2 symmetry (perpendicular to the central Si−Li−Si−Li ring), while the Si centers show formal inversion symmetry to each other. By this arrangement, in addition to the stereogenic silicon centers, two chiral planes are formed, resulting in four chiral elements per dimer.

In principle, when constructing dimeric aggregates from the monomeric lithiosilane *rac*-**2**, 16 different isomers are imaginable,[16] two enantiomers of which were found in the solid state. ^{1}H, ^{13}C, and ^{29}Si NMR analyses at −40 °C in toluene-d_8 (sample prepared by dissolving crystals of *rac*-**2**) indicate the existence of more than one isomer in solution. However, no further classification of these structures was possible. In THF-d_8, the situation is simplified as the observation of a [29]Si−[7]Li coupling at −70 °C (quartet; $^1J_{SiLi}$ = 48.9 Hz) in the ^{29}Si NMR spectrum clearly supports the existence of monomeric lithiosilane *rac*-**2**.

Although the solid-state structure concerns the racemic lithiosilane *rac*-**2**, one can also expect a dimeric molecular structure for the enantiomerically pure compound **2**. We further emphasize that this molecular structure has to be different from the structure found for the racemic lithiosilane *rac*-**2**, as each dimer observed in the crystal structure consists of one (*R*)- and one (*S*)-configured unit. To avoid possible stereochemical problems, all reactions involving the enantiomerically enriched lithiosilane **2** should be performed in THF solution.

Starting from simple compound **4**, an unanticipated and novel Si−C bond cleavage reaction permits preparation of the amino-

methyl-functionalized lithiosilane *rac*-**2**, which has major synthetic potential (e.g., for nucleophilic transfer of silicon moieties). Currently we are investigating related Si−C bond cleavage reactions as new synthetic entry to enantiomerically enriched lithiosilanes.

Supporting Information Available: Crystallographic (CIF) and experimental details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) This change of color is also known from the reaction of chlorosilanes under similar conditions. There it is evidence for the formation of the corresponding lithiosilane, although it is known that the color is not of the lithiosilane itself, but associated with traces of radical anions formed by side reactions. See ref 5a and references therein.

(10) The methoxysilane is available by one-pot reaction from chloro(chloromethyl)methylphenylsilane; cf. Supporting Information.

(11) Disilane **7** can also be prepared starting from disilane *rac*-**1**. But Si−Si cleavage of *rac*-**1** and reaction with *rac*-methoxymethylphenyl(piperidinomethyl)silane results in an inseparable product mixture of *rac*-**1** and **7**.

(12) Crystallographic data for (**2**·THF)$_2$: C$_{34}$H$_{56}$Li$_2$N$_2$O$_2$Si$_2$, M = 594.87, orthorhombic, space group $Pna2_1$ (no. 33), a = 19.777(4), b = 10.400-(2), c = 35.503(7) Å, V = 7302(3) Å^3, Z = 8, D_c = 1.082 Mg/m^3, μ = 0.127 mm^{-1}. 42 344 reflections, 11 040 unique reflections; 7687 with $I > 2\sigma(I)$; R1 = 0.0801 [$I > 2\sigma(I)$], wR2(F_o^2) = 0.1829 (all data), absolute structure parameter 0.05(19). X-ray crystallography data for (**2**·THF)$_2$ has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 260574.

(13) The crystal was mounted at −60 °C (N$_2$ stream), using the X-TEMP 2 device (Kottke, T.; Stalke, D. *J. Appl. Crystallogr.* **1993**, *26*, 615).

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(16) These isomers include seven pairs of enantiomers and two meso compounds (for a detailed representation of all isomers cf. Supporting Information). A thorough discussion of the occurring structural motifs was given, for example, for 2-lithiobenzylamines, where similar dimeric aggregates are found. See: (a) Reich, H. J.; Goldenberg, W. S.; Gudmundsson, B. O.; Sanders, A. W.; Kulicke, K. J.; Simon, K.; Guzei, I. A. *J. Am. Chem. Soc.* **2001**, *123*, 8067 and references therein. (b) Arink, A. M.; Kronenburg, C. M. P.; Jastrzebski, J. T. B. H.; Lutz, M.; Spek, A. L.; Gossage, R. A.; Van Koten, G. *J. Am. Chem. Soc.* **2004**, *126*, 16249 and references therein.

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