Synthesis of a Highly Enantiomerically Enriched Silagermane and Selective Cleavage of the Si−Ge Bond with Lithium

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Received August 23, 2007

(R)-PhMe($CH_2NC_5H_{10}$)$SiGeMe_3$, the first enantiomerically pure silagermane with stereoinformation at the silicon, was synthesized via a lithiosilane with retention of configuration. Further reaction with lithium resulted in unanticipated silicon−germanium bond cleavage to form PhMe($CH_2NC_5H_{10}$)SiLi, although the disilane (R)-PhMe($CH_2NC_5H_{10}$)$SiSiMe_3$ undergoes silicon−phenyl bond cleavage. A trapping reaction with pentamethylchlorodisilane occurred with retention of configuration. DFT calculations on the model systems PhH_2SiSiH_3 and PhH_2SiGeH_3 indicate a stepwise, dissociative electron transfer mechanism for the silicon−element bond cleavage.

Introduction

Functionalized lithiosilanes are versatile reagents in organic and organometallic chemistry for the nucleophilic introduction of protecting groups and synthesis of silyl-substituted transition metal complexes or silicon-based polymers, for example.[1–3] In particular, highly enantiomerically enriched lithiosilanes have attracted much interest, as they are configurationally stable at the lithiated silicon center.[4] Their inversion process has been described in review articles and textbooks[1c,5] as the inversion of a free silyl anion, which should be significantly more stable than the corresponding carbanion.[6] Further investigation by our research group showed that there is another possible mechanism involving a second solvated lithium cation.[7] As the synthetic pathways to highly enantiomerically enriched lithiosilanes are extremely limited, only a few authors have reported the synthesis of such compounds so far (see Figure 1).

All synthetic routes start with enantiomerically enriched compounds. Enantiomerically enriched lithiosilanes may be synthesized from chlorosilanes (Figure 1, compound **5**),[8] by a cobalt−lithium exchange reaction (see Figure 1, compound **2**),[2c,d] from stannylsilanes (see Figure 1, compound **3**),[3a] or by silicon−silicon bond cleavage with lithium metal (see Figure 1, compounds **1** and **4**),[2a,b,3c,l] with the latter in particular proving a very reliable and convenient method. A general prerequisite for these Si−Si bond cleavages is the presence of at least one aromatic substituent on the silicon atom. It is hypothesized that the lowest unoccupied molecular orbital (LUMO) of the disilane is otherwise too high in energy to accept an electron.[9] By adapting the method by which an optically active silyllithium was first synthesized by Sommer et al.,[2a,b] our own research group has achieved synthesis of the highly enantiomerically enriched lithiosilane **4** by selective Si−Si cleavage of the disilane (R)-**7**.[3c] Bond cleavage of the lithiosilane **4** and a subsequent trapping reaction with chlorosilanes occurred with retention of configuration over the whole reaction sequence (see Scheme 1).

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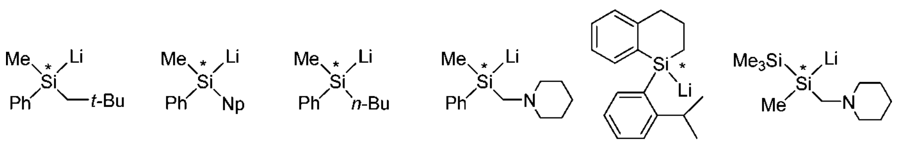


1 Sommer (1965)
2 Corriu (1976)
3 Kawakami (2000)
4 Strohmann (2002)
5 Oestreich (2005)
6 Strohmann (2007)

Figure 1. Synthesized highly enantiomerically enriched lithiosilanes.

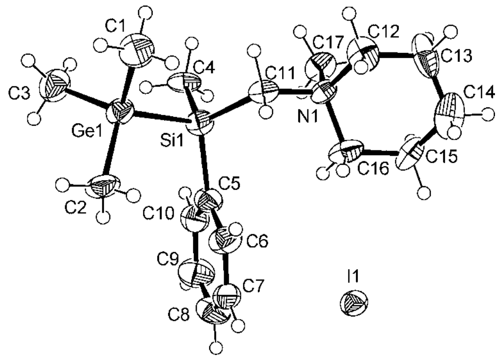
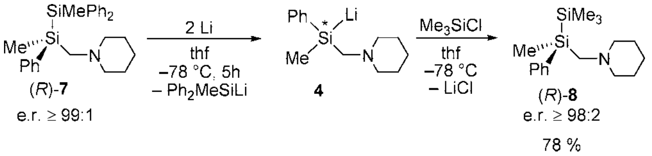
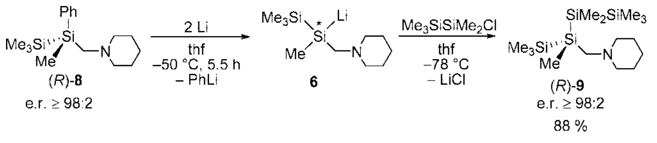


Figure 2. Molecular structure and numbering scheme of (*R*)-**10**·MeI in the solid state (ORTEP plot at 50% probability level, molecule 1 of 4). Selected bond lengths [Å] and angles [deg]: Si(1)–Ge(1) 2.391(3), C(1)–Ge(1)–Si(1) 111.0(4), C(11)–Si(1)–Ge(1) 102.8(3), N(1)–C(11)–Si(1) 123.7(6).

Scheme 1. Selective Cleavage of the Si–Si Bond in the Disilane (*R*)-7 as a Selective Synthetic Route to the Functionalized Lithiosilane 4



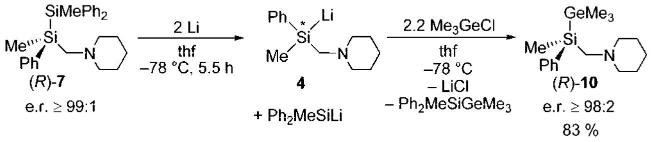
Scheme 2. Selective Cleavage of the Si–Ph Bond in the Disilane (*R*)-8 as a Selective Synthetic Route to the Functionalized Lithiosilane 6



Most recently, our group reported the synthesis of the highly enantiomerically enriched lithiosilane **6** by the novel means of selective Si–C bond cleavage of a phenyl group from silicon in the disilane (*R*)-**8** with lithium metal in thf (see Scheme 2).[31] A trapping reaction of the resulting lithiosilane **6** with pentamethylchlorodisilane resulted in the first highly enantiomerically enriched (er ≥ 98:2) tetrasilane, (*R*)-**9**, with stereoinformation located on the silicon atom (see Scheme 2). In all cases, we determined the absolute configuration at the stereogenic silicon center of the compounds involved by X-ray diffraction analysis. Si–C cleavage and trapping of the lithiosilane **6** occurred with full retention of stereochemical information (see Scheme 1 and Scheme 2).

As part of our studies on highly enantiomerically enriched lithiosilanes, we present here the synthesis of the first highly enantiomerically enriched silagermane with silicon as the stereogenic center, (*R*)-**10**. In contrast to the corresponding disilane (*R*)-**8**, where treatment with elemental lithium causes silicon–phenyl bond cleavage, we observed in the case of the silagermane (*R*)-**10** an unanticipated, selective cleavage of the silicon–germanium bond on reaction with lithium. Quantum chemical studies were used to understand the process of the involved silicon–element bond cleavage.

Scheme 3. Synthesis of the Silagermane (*R*)-10 via the Highly Enantiomerically Enriched Lithiosilane 4



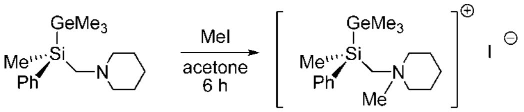
Results and Discussion

Synthesis of the Silagermane (*R*)-10. The starting compound for our synthesis was the disilane (*R*)-**7**. *rac*-**7** can be obtained from dichloro(chloromethyl)methylsilane by a three-step method.[3c] The enantiomerically pure disilane (*R*)-**7** (see Scheme 1) was obtained by resolution of the enantiomers with mandelic acid. (*R*)-**7** crystallized with (*R*)-mandelic acid from Et_2O, while (*S*)-**7**·(*R*)-mandelic acid remained as a yellow resin. After five crystallization cycles (*R*)-**7** could be obtained with an enantiomeric ratio ≥99:1.[3c]

Treatment of (*R*)-**7** with lithium metal in thf resulted in the formation of the dark brown solution of the highly enantiomerically enriched lithiosilane **4** (see Scheme 3). Due to racemization in solution within hours above 0 °C, the whole reaction sequence was carried out at −78 °C, as full cleavage of the silicon–silicon bond and preservation of the stereoinformation are guaranteed at this temperature.[3c,7] Because the reaction is heterogeneous, the reaction time for full cleavage of the Si–Si bond varies between 4 and 6 h, and the concentration of disilane in the thf solution becomes very important: on one hand a higher concentration of (*R*)-**7** increases the reaction time, but on the other hand the high viscosity of the solution makes it impossible to increase the concentration too high (the reaction mixture is almost solid at −78 °C). To track the progress of the reaction, a small amount of the brown solution was treated with trimethylchlorosilane (as a trapping reagent) and examined by ^1H NMR spectroscopy. After a reaction time of 5.5 h, full cleavage of the Si–Si bond could be observed, and an excess of 2.2 equiv of trimethylchlorgermane was added to the dark brown solution at −78 °C. After aqueous workup and final distillation, the highly enantiomerically enriched silagermane (*R*)-**10** was obtained in 83% yield (see Scheme 3). The determination of the er of the silagermane (*R*)-**10** was performed with the common method[3c] in the presence of 3 equiv of (*R*)-mandelic acid in C_6D_6 (for details, see the Supporting Information).

In the synthesis of *rac*-**10**, silicon–silicon bond cleavage of *rac*-**7** could be carried out at 0 °C, as preservation of stereoinformation was not necessary in this case (although reaction with trimethylchlorogermane was still carried out at −78 °C). As a consequence of the higher reaction temperature, a reaction time of 3.5 h was allowed and *rac*-**10** was isolated in 78% yield.

Scheme 4. Synthesis of (*R*)-10·MeI



(*R*)-**10**
e.r. ≥ 98:2

(*R*)-**10**·MeI
e.r. ≥ 98:2

Stereochemical Pathway of the Reaction Sequence of Si−Si Bond Formation and Si−Ge Bond Cleavage. Although lithiosilanes are expected to react with electrophiles with retention of the absolute configuration at the stereogenic silicon center, there are some examples where inversion has been observed.[3d] It was therefore important to determine the absolute configuration of the synthesized silagermane.

The absolute configuration of (*R*)-**10** could be determined as the *R*-configuration by X-ray structural analysis of (*R*)-**10**·MeI (see Scheme 4). Measurements were taken on three different single crystals of the silagermane (er ≥ 98:2), all of which showed an *R*-configuration. Hence, the whole reaction sequence from (*R*)-**7** to (*R*)-**10** took place with retention of the absolute configuration at the stereogenic silicon center.

(*R*)-**10**·MeI crystallized from *i*-PrOH/Et_2O in the monoclinic crystal system, space group $P2_1$ (see Figure 2; see Table 1 in the Supporting Information for additional crystal data and structural refinement details) as colorless needles. The asymmetric unit contains four molecules of the silagermane. With an average value of 2.39 Å, the Si−Ge bond lengths are only slightly shorter than the sum of the covalent radii of silicon and germanium (2.40 Å)[10] and in the range typically displayed by other achiral silagermanes.[11] On close examination, one can see that all four molecules in the asymmetric unit have different conformations, arising from rotation around the silicon−germanium and Si−C(11) bonds. Furthermore, the vibrational ellipsoids at the trimethylgermyl groups indicate that rotation around the Si−Ge bond is a low-energy process.

Unanticipated Silicon−Germanium Bond Cleavage in (*R*)-10. On closer examination of the two highly enantiomerically enriched compounds (*R*)-**8** and (*R*)-**10**, it is apparent that both compounds are analogues, apart from the fact that the trimethyl-substituted silicon atom of (*R*)-**8** is replaced by a trimethylgermyl group in (*R*)-**10**. The silicon−germanium bond in (*R*)-**10** has a similar bond length (2.39 Å) to the silicon−silicon bond in (*R*)-**8** (2.35 Å),[31] and the silicon−germanium bond (≈200 kJ·mol^{-1}) is almost as stable as the silicon−silicon bond (≈220 kJ·mol^{-1}).[5d,e] However, this does not necessarily imply that (*R*)-**10** and (*R*)-**8** are nearly identical in terms of stability and reactivity. This may be illustrated by the reactions of the two compounds with lithium metal. The potential products of treating **10** with lithium are the lithiosilanes **4** (see *Path 2* in Scheme 5) and **11** (see *Path 1* in Scheme 5) or a mixture of the two; **8** is known to undergo Si−C bond cleavage under these conditions (Scheme 2).

We carried out the reaction by treating *rac*-**10** with lithium metal in thf at a temperature of 0 °C. In the event, we observed *only* selective cleavage of the silicon−germanium bond, to form the lithiosilane **4**. Treatment of **4** with pentamethylchlorodisilane resulted in the formation of the racemic trisilane *rac*-**12** at 82% yield after aqueous workup. We found no trace in the NMR spectra of the trapping product of **11**, which would have resulted from silicon−carbon bond cleavage. The compounds **8** and **10** thus show significantly different reactivity toward lithium metal, in spite of their similarities.

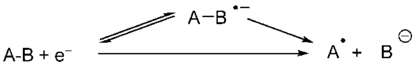


Figure 3. Suggested mechanisms for ET-induced bond cleavage.

Treatment of the highly enantiomerically enriched compound (*R*)-**10** with lithium in thf at −78 °C and trapping the resultant lithiosilane **4** with pentamethylchlorodisilane resulted in the formation of (*R*)-**12** with a yield of 78%. (*R*)-**12** is the second highly enantiomerically enriched trisilane reported.[31] We assume that the synthesis of (*R*)-**12** (shown in Scheme 6) follows the same stereochemical pathway as the syntheses of **8** and **9** (Schemes 1 and 2, respectively).[3c,l] The determination of the er of the silagermane (*R*)-**10** was performed with the common method[3c] in the presence of 3 equiv of (*R*)-mandelic acid in C_6D_6 (for details, see the Supporting Information).

Element−Element Bond Cleavage with Metals: Reaction Behavior of (*R*)-8 and (*R*)-10. As described above, the nearly identical compounds (*R*)-**8** and (*R*)-**10** show different reaction behavior with lithium. In the disilane (*R*)-**8** the Si−C bond is cleaved, while in the silagermane (*R*)-**10** the Si−Ge bond reacts instead. *Why does this difference arise?* The cleavage of Si−C, Si−Si, and Si−Ge bonds with lithium should be strongly exothermic due to the formation of ionic compounds. For a rate-determing step characterized by a reactant-like transition state, one expects ease of cleavage to vary as Si−Ge > Si−Si > Si−C. However, the element−element bond cleavages here are occurring via electron transfer (ET) processes, which can effect significant structural and electronic changes in the species involved and reorganization of the surrounding solvent molecules.[12] Two possible reaction mechanisms have been discussed for bond cleavage arising from ET from a metal. For some molecular systems, electron uptake by the acceptor species (AB) and σ-bond-breaking to yield a radical (A*) and an anion (B^-) occur together in a concerted, one-step process. More often, the dissociative mechanism is stepwise, involving the radical anion (AB^{*-}) as a discrete intermediate in a two-step process (see Figure 3).[13,14]

According to F. Maran et al., cleavage of sulfur−sulfur bonds in disulfanes follows the stepwise pathway, of which they described two limiting cases: (i) a more concerted pathway, where the SOMO of the radical anion intermediate looks almost the same as the σ*-orbital of the bond to be cleaved (in this case, the bond length is significantly elongated by the ET); (ii)

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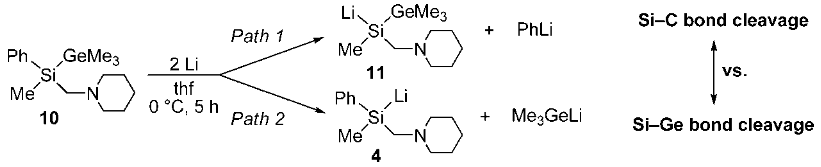
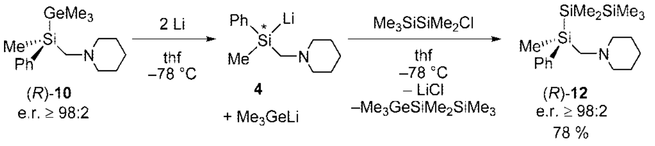
Scheme 5. Reactivity Studies of *rac*-10: Treatment with Lithium Metal in thf at 0 °C Leads to Selective Cleavage of the Silicon−Gemanium Bond



Scheme 6. Synthesis of the Highly Enantiomerically Enriched Trisilane (*R*)-12 by a Trapping Reaction of the Highly Enantiomerically Enriched Lithiosilane 4 with Pentamethylchlorodisilane



a more stepwise pathway, where the SOMO (single occupied molecular orbital) and σ^*-orbital are quite different and the bond to be cleaved is only slightly elongated after ET. To the best of our knowledge, no studies have been performed on these processes in disilanes. To understand the reaction mechanism of (*R*)-**8** and (*R*)-**10** with lithium, and the reasons for the different products in each case, two model systems were studied using DFT methods [B3LYP/6-31+G(d)]. The chosen model compounds [PhH_2SiSiH_3 (**C**) for (*R*)-**8** and PhH_2SiGeH_3 (**D**) for (*R*)-**10**] were geometry-optimized both as neutral species and as the radical anions $PhH_2SiXH_3^{\bullet-}$ (X = Si or Ge, respectively). The ET causes slightly elongated Si−X bonds (**C** to $\mathbf{C}^{\bullet-}$: Si−Si 2.358 to 2.481 Å; **D** to $\mathbf{D}^{\bullet-}$: Si−Ge: 2.364 to 2.487 Å). Furthermore, the Si−Ph bond length in the disilane slightly increases from a value of 1.886 Å (**A**) to 1.902 Å ($\mathbf{C}^{\bullet-}$), but is shortened from 1.880 Å (**D**) to 1.862 Å ($\mathbf{D}^{\bullet-}$) in the silagermane. This can be explained both in molecular orbital terms (the SOMO has more Si−C bonding character in $\mathbf{D}^{\bullet-}$ than in $\mathbf{C}^{\bullet-}$, as can be seen by inspection of Figure 4)[15] and in terms of ionic bonding: the product of NBO charges on Si (+ve) and C (−ve) increases on reduction for **D** (**D**: −0.350, $\mathbf{D}^{\bullet-}$: −0.364), indicating stronger electrostatic interactions; for **C**, on the other hand, the charge product decreases on reduction (**C**: −0.338, $\mathbf{C}^{\bullet-}$: −0.270), indicating a weakening of ionic bonding.

The HOMO and the LUMO of the neutral systems and the SOMO of the radical anions were then visualized (Figure 4). The shape of the SOMO shows the location of the unpaired electron and possible regions where it is stabilized after ET.

Both the HOMO and LUMO differ little between the two neutral compounds. Even the SOMOs of the radical anion are similar for the disilane $\mathbf{C}^{\bullet-}$ and the silagermane $\mathbf{D}^{\bullet-}$. Crucially, in both cases the SOMOs differ significantly from the LUMO of the neutral compound, and therefore the bond cleavage reaction should follow the more stepwise pathway (ii). This statement is supported by the only slightly increased Si−X (X = Ge or Si) distances. The SOMO is a combination of Si−Ph and Si−X σ-antibonding orbitals; hence, there are two possible reactive bonds present, and a balance of different effects determines which of the two will break, and thus which product will result. The important conclusions we can draw from the model systems are that (i) especially Si−Ge and Si−Si bonds are significantly elongated and (ii) the Si−Ph bond in $\mathbf{D}^{\bullet-}$ is shorter and stronger than the Si−Ph bond in $\mathbf{C}^{\bullet-}$. Nevertheless, these investigations do not include the effects and possible location of the nearby lithium cation or the influence of the solvent. Either of these considerations could conceivably have significant effects on the reactivities of the different bonds. In our current investigations, we are attempting to improve our understanding of the reaction mechanism.

Conclusions

The first highly enantiomerically enriched silagermane [(*R*)-**10**] with stereoinformation located at the silicon center has been synthesized with an er of ≥98:2. X-ray structural analysis of the methylated compound (*R*)-**10**·MeI proved that the whole reaction sequence proceeds with retention of the stereoinformation at −50 °C. Subsequent treatment of (*R*)-**10** with lithium resulted in the selective cleavage of the silicon−germanium bond, yielding the highly enantiomerically enriched trisilane (*R*)-**11** after trapping reaction (er ≥98:2). DFT calculations at the b3lyp/6-31+g(d) level support a stepwise, dissociative electron transfer mechanism for the silicon−element bond cleavage.

All hitherto conducted experiments concerning silicon−element bond cleavages (element = carbon, silicon, and germanium) proceed under retention of configuration, enabling us to obtain highly enantiomerically pure compounds by means of this synthetic route. At the moment we are trying to get a deeper insight into the single steps of these silicon−element cleavages.

Experimental Section

General Procedures. All reactions were carried out under an argon atmosphere using Schlenk tubes. All solvents, including the NMR solvents, were dried according to standard procedures. NMR spectra were measured on a Bruker DRX-300 NMR spectrometer and on a Bruker-Avance-500 NMR spectrometer with an external standard of tetramethylsilane (δ = 0.0). Signal assignments were supported by DEPT-135 and C,H-COSY experiments and the relative intensities of the resonance signals. Crystal structure determination of (*R*)-**10**·MeI was accomplished on a Bruker APEX diffractometer (D8 three-circle goniometer) (Bruker AXS); data collection, cell determination, and refinement: Smart version 5.622 (Bruker AXS, 2001); integration: SaintPlus version 6.02 (Bruker AXS, 1999); empirical absorption correction: SADABS version 2.01 (Bruker AXS, 1999). The structure was solved by applying direct and Fourier methods, using SHELXS-90[17] and SHELXL-97.[18] The non-hydrogen atoms were refined anisotropically. All of the H atoms were placed in geometrically calculated positions, and each was assigned a fixed isotropic displacement parameter based on a riding model. CCDC 658253 contains the detailed crystallographic data for this publication. This data may be obtained free of charge from the Cambridge Crystallographic Data Center through www.ccdc.

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(15) The SOMO is mostly antibonding between Si and C. Looking at Figure 4, on the underside of the bond, the interaction between the red and blue areas is antibonding, whereas on the top, some π-bonding interactions are taking place.

(16) *Gaussian 03* (Revision B.04): M. J. Frisch et al., for details see the Supporting information.

(17) Sheldrick, G. M. *SHELXS-90*, *A Program for the Solution of Crystal Structures*; Universität Göttingen, 1990.

(18) Sheldrick, G. M. *SHELXL-97*, *A Program for Crystal Structure Refinement*; Universität Göttingen, 1997.

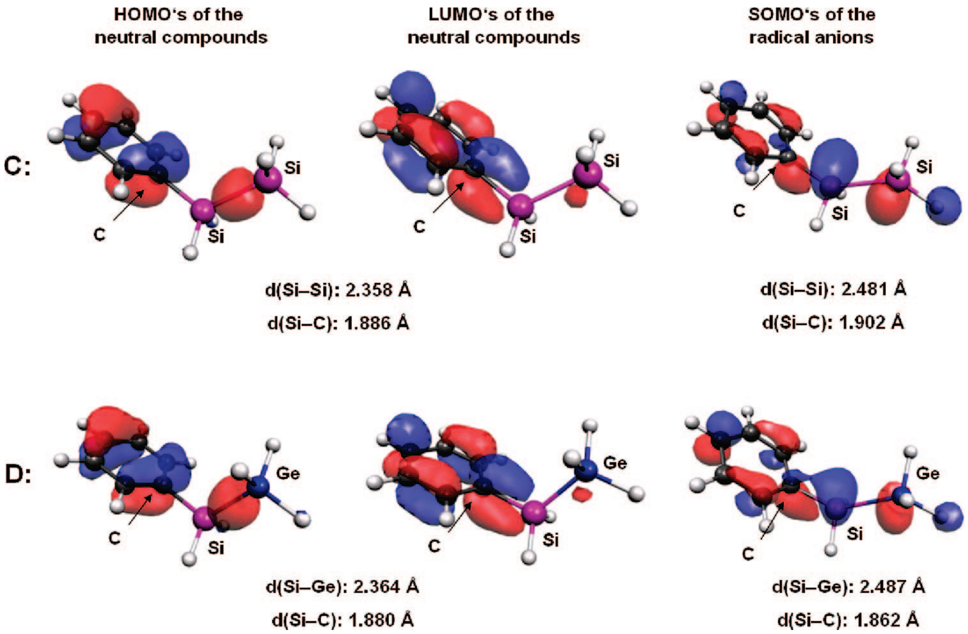

Figure 4. HOMOs (left) and LUMOs (middle) of the two neutral model systems PhH_2SiSiH_3 and PhH_2SiGeH_3 and SOMOs of the corresponding radical anions (right).

cam.ac.uk/data_request/cif. Elemental C, H, N analysis was performed on a Leco CHNS 932 elemental analyzer. GC/MS analyses were performed on a ThermoQuest TRIO-1000 (EI = 70 eV); column; Zebron, capillary GC column, ZB-1. Determination of the optical rotation was performed on a Jasco P-1030 polarimeter.

Synthesis of (*R*)-10. At a temperature of 0 °C, 1.24 g (2.98 mmol) of (*R*)-1,2-dimethyl-1,2,2-triphenyl-1-(piperidinomethyl)disilane, (*R*)-**7**, was added to 45.5 mg (6.56 mmol) of lithium in 5 mL of thf. At the first sign of color change, the mixture was cooled to −78 °C and stirred for 5.5 h at this temperature. Afterward the now-black solution was separated from leftover lithium and added at −78 °C to a solution of 1.00 g (6.55 mmol) of trimethylchlorogermane in 5 mL of thf, which caused immediate decoloration of the solution. Afterward the solution was slowly warmed to room temperature and all volatile compounds were removed under vacuum. The residue was suspended in 35 mL of 2 M NaOH and extracted five times with 10 mL of diethyl ether. The combined organic layers were extracted five times with 10 mL of 2 M HCl and afterward set to pH 12 with NaOH. Finally the aqueous layer was extracted five times with 10 mL of diethyl ether, and the combined organic layers were dried over Na_2SO_4. After removal of all volatile compounds under vacuum the crude product was purified by "Kugelrohr distillation" [oven temperature: 149 °C, pressure: 1.6×10^{-5} mbar; $[\alpha]_D^{20} = -7.0$ (*c* 0.16 in cyclohexane)]. Yield: 830 mg (2.47 mmol, 83%). Anal. Calcd: C 57.18, H 8.69, N 4.17. Found: C 57.83, H 8.51, N 4.38. GC/EI-MS: $t_R = 8.12$ min [80 °C (2 min)−10 °C·min^{-1}−280 °C (5 min)]; *m*/*z* [%] 336 (0.8) $[(M - H)^+]$, 322 (5) $[(M - CH_3)^+]$, 218 (80) $\{[M - Ge(CH_3)_3]^+\}$, 98 (100) $[H_2C{=}N(C_5H_{10})^+]$. ^1H NMR (500.1 MHz, C_6D_6): δ 0.44 [s, 9H; $SiGe(CH_3)_3$], 0.59 (s, 3H; $SiCH_3$), 1.33−1.40 (m, 2H; $NCCCH_2$), 1.55−1.62 (m, 4H; $NCCH_2$), 2.38, 2.48 (AB system, $^2J_{AB} = 14.4$ Hz, 2H; $SiCH_2N$), 2.39−2.47 (s [br], 4H; NCH_2C), 7.32−7.37 (m, 3H; aromat. H), 7.68−7.72 (m, 2H; aromat. H). $\{^1H\}^{13}C$ NMR (125.76 MHz, C_6D_6): δ −4.8 (1C) ($SiCH_3$), −2.3 (3C) $[Ge(CH_3)_3]$, 24.2 (1C) ($NCCCH_2$), 26.7 (2C) ($NCCH_2C$), 49.8 (1C) ($SiCH_2N$), 58.8 (2C) (NCH_2C), 128.5 (2C) (*C-m*), 129.0 (2C) (*C-p*), 134.3 (2C) (*C-o*), 138.5 (1C) (*C-i*). $\{^1H\}^{29}Si$ NMR (99.4 MHz, C_6D_6): δ −16.3 (NC*Si*Ge). $[\alpha]_D^{20} = -7.0$ (*c* 0.16 in cyclohexane).

Synthesis of *rac*-10. At a temperature of 0 °C, 1.49 g (3.58 mmol) of (*R*)-1,2-dimethyl-1,2,2-triphenyl-1-(piperidinomethyl)disilane, (*R*)-**7**, was added to 54.7 mg (7.88 mmol) of lithium in 5 mL of thf and stirred for 5.0 h at this temperature. Afterward the now-black solution was separated from leftover lithium and added at −78 °C to a solution of 1.21 g (7.88 mmol) of trimethylchlorogermane in 5 mL of thf, which caused immediate decoloration of the solution. Afterward all volatile compounds were removed under vacuum. The residue was suspended in 35 mL of 2 M NaOH and extracted five times with 10 mL of diethyl ether. The combined organic layers were extracted five times with 10 mL of 2 M HCl and afterward set to pH 12 with NaOH. Finally the aqueous layer was extracted five times with 10 mL of diethyl ether, and the combined organic layers were dried over Na_2SO_4. After removal of all volatile compounds under vacuum the crude product was purified by "Kugelrohr distillation" [oven temperature: 138 °C, pressure: 1.7×10^{-5} mbar; yield: 940 mg (2.80 mmol, 78%)]. The analytical data comply with the those for (*R*)-**10**.

(*R*)-10·MeI. To a solution of 50.0 mg (0.15 mmol) of (*R*)-**10** in 2 mL of acetone was added 21.2 mg (0.15 mmol) of methyl iodide, and the mixture was stirred for 4.5 h at room temperature. After removal of all volatile compounds under vacuum, the residue was dissolved again in 3 mL of 2-propanol. After this, a few drops of Et_2O were added to the reaction mixture until the first signs of precipitation, and the mixture then was stored at −30 °C. After 24 h, a white, crystalline solid was obtained, filtered from the solvent, and finally washed with a small amount of ice cold 2-propanol/Et_2O. Yield: 64.0 mg (0.13 mmol, 90%). Anal. Calcd: C 42.71, H 6.75, N 2.93. Found: C 42.90, H 6.65, N 3.13. ^1H NMR (500.1 MHz, $CDCl_3$): δ 0.03 (s, 3H; NCH_3), 0.3 [s, 9H; $SiGe(CH_3)_3$], 0.75 (s, 3H; $SiCH_3$), 1.62−1.68, 1.69−1.74 (m, 1H each; $NCCCH_2$), 1.69−1.74, 1.77−1.82 (m, 2H each; $NCCH_2$), 3.72, 3.73 (s, 1H each; $SiCH_2N$), 3.40−3.35 (m, 1H; NCH_2C), 3.57−3.62 (m, 2H; NCH_2C), 3.65−3.70 (m, 1H; NCH_2C), 7.35−7.40 (m, 3H; H-*m* and H-*p*), 7.55−7.62 (m, 2H; H-*o*). $\{^1H\}^{13}C$ NMR (125.76 MHz, $CDCl_3$): δ −4.1 ($SiCH_3$), −2.3 (3C) $[Ge(CH_3)_3]$, 0.96 (NCH_3), 20.3 ($NCCCH_2$), 20.6, 20.7 (1C each) ($NCCH_2C$), 55.8 ($SiCH_2N$), 64.45, 64.32 (1C each) (NCH_2C), 128.9 (2C) (*C-m*), 130.5 (2C) (*C-p*), 134.4 (2C) (*C-o*), 134.6 (1C) (*C-i*). $\{^1H\}^{29}Si$ NMR (99.4 MHz, $CDCl_3$): δ −18.9 (Ge*Si*CH_3).

***rac*-12.** At a temperature of 0 °C, 1.15 g (3.42 mmol) of (*rac*)-**10** was added to 52.3 mg (7.53 mmol) of lithium in 5 mL of thf and stirred for 5.0 h at this temperature. Afterward the now-black solution was separated from leftover lithium and added at −78 °C to a solution of 1.26 g (7.53 mmol) of pentamethylchlorodisilane in 5 mL of thf, which caused immediate decoloration of the solution. Afterward all volatile compounds were removed under vacuum. The residue was suspended in 35 mL of 2 M NaOH and extracted five times with 10 mL of diethyl ether. The combined organic layers were extracted five times with 10 mL of 2 M HCl and afterward set to pH 12 with NaOH. Finally the aqueous layer was extracted five times with 10 mL of diethyl ether, and the combined organic layers were dried over Na_2SO_4. After removal of all volatile compounds under vacuum the crude product was purified by "Kugelrohr distillation" [oven temperature: 190 °C, pressure: 1.0×10^{-2} mbar; yield: 981 mg (2.81 mmol, 82%)]. Anal. Calcd: C 61.8, H 10.1, N 4.0. Found: C 61.7, H 9.9, N 3.9. GC/EI-MS: t_R = 9.30 min [80 °C (2 min)−10 $°C \cdot min^{-1}$−280 °C (5 min)]; *m/z* [%] 334 (1) $[(M - CH_3)^+]$, 276 (12) $\{[M - Si(CH_3)_3]^+\}$, 218 (27) $\{[M - Si(CH_3)_2Si(CH_3)_3]^+\}$, 98 (100) $[(H_2C{=}NC_5H_{10})^+]$, 73 (12) $[(CH_3)_3Si^+]$. ^1H NMR (300.1 MHz, $CDCl_3$): δ 0.03 [s, 9H; $Si(CH_3)_3$], 0.09 [s, 6H; $Si(CH_3)_2$], 0.43 (s, 3H; $SiCH_3$), 1.25−1.40 (m, 2H; $NCCCH_2$), 1.40−1.55 (m, 4H; $NCCH_2C$), 2.15−2.40 (m, 4H, NCH_2C), 2.23, 2.31 (AB system, $^2J_{AB}$ = 14.4 Hz, 2H; $SiCH_2$), 7.25−7.35 (m, 2H; aromat. H), 7.40−7.55 (m, 3H; aromat. H). $\{^1H\}^{13}C$ NMR (75.5 MHz, $CDCl_3$): δ −6.3 (2C) $[Si(CH_3)_2]$, −5.0 ($SiCH_3$), −1.5 (3C) $[Si(CH_3)_3]$, 23.8 ($NCCCH_2$), 26.3 (2C) ($NCCH_2C$), 49.5 ($SiCH_2$), 58.6 (2C) (NCH_2C), 127.6 (2C) (*C-m*), 128.3 (*C-p*), 134.0 (2C) (*C-o*), 139.1 (*C-i*). $\{^1H\}^{29}Si$ NMR (59.6 MHz, $CDCl_3$): δ −47.8 (SiSiSi), −20.3 ($SiCH_3$), −15.4 $[Si(CH_3)_3]$.

(*R*)-12. At a temperature of 0 °C, 0.89 g (2.65 mmol) of (*rac*)-**10** was added to 40.4 mg (5.83 mmol) of lithium in 3 mL of thf. At the first sign of color change, the mixture was cooled to −78 °C and stirred for 5.5 h at this temperature. Afterward the now-black solution was separated from leftover lithium and added at −78 °C to a solution of 972 mg (5.83 mmol) of pentamethylchlorodisilane in 2 mL of thf, which caused immediate decoloration of the solution. Afterward all volatile compounds were removed under vacuum. The residue was suspended in 25 mL of 2 M NaOH and extracted five times with 5 mL of diethyl ether. The combined organic layers were extracted five times with 10 mL of 2 M HCl and afterward set to pH 12 with NaOH. Finally the aqueous layer was extracted five times with 8 mL of diethyl ether, and the combined organic layers were dried over Na_2SO_4. After removal of all volatile compounds under vacuum the crude product was purified by "Kugelrohr distillation" [oven temperature: 190 °C, pressure: 1.0×10^{-2} mbar; yield: 722 mg (2.07 mmol, 78%)]. The analytical data comply with those of *rac*-**11**. $[\alpha]_D^{20}$ = 12.2 (*c* 2.40 in cyclohexane).

Acknowledgment. We are grateful to the Institut für Anorganische Chemie Würzburg, the Fonds der Chemischen Industrie, and the DFG for financial support. Furthermore we acknowledge the Wacker Chemie AG for providing us with special chemicals. C.D. thanks the Studienstiftung des Deutschen Volkes for a doctoral scholarship. Finally, we are grateful to Dr. James Asher for technical assistance.

Supporting Information Available: NMR studies, X-ray (cif), and computational data. This material is available free of charge via the Internet at http://pubs.acs.org.

OM700848Z