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Photo-Driven Si-C Bond Cleavage in Hexacoordinate Silicon Complexes

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Received (will be filled in by the editorial staff)

Dedicated to Prof. Robert J. P. Corriu on the Occasion of his 75th Birthday

Abstract. Hexacoordinate diorganosilicon complexes of the type (ONNO)SiR'R", with (ONNO) being a di-anionic salen-type Schiff base ligand, were shown to undergo Si–C bond cleavage and intramolecular rearrangement (1,3-shift of R" to a former imine carbon atom) upon irradiation with UV. The course of this reaction depends on the nature of Si-bound substituents: Whereas complexes (ONNO)SiMe₂ and (ONNO)SiPh₂ give rise to the rearrangement of a methyl and a phenyl group, respectively, complexes of the type (ONNO)Si(aryl)(alkyl) were found to undergo Si–C(alkyl) bond cleavage exclusively. Furthermore, such alkyl groups bearing β-H atoms may lead to β-H transfer to the imine carbon atom accompanied by olefin elimination. Irradiation of compounds (ONNO)SiRX, with X being a non-carbon sacrificial ligand, was shown to give rise to further side reactions: In case of X=F the unexpected formation of (ONNO)SiF₂ was observed. In analogy to the photo-induced rearrangement of (ONNO)SiPh₂, the heavier congenor (ONNO)GePh₂ exhibits similar reactivity, whereas the related tin compound (ONNO)SnPh₂ proved inert under these reaction conditions applied.

Keywords: Chelate; Hypercoordination; Rearrangement; Schiff Base; Tin

Introduction

One of the most intriguing aspects of silicon coordination chemistry is the activation of various Si–X bonds upon “hypercoordination” of the Si-atom. In particular, one or two additional donor atoms brought into closer proximity of a silicon atom, hence giving rise to silicon penta- and hypercoordination, respectively, may provoke Si–X bond splitting, i.e. a lowering of the silicon coordination number down to tetra- or pentacoordination, respectively. A great variety of reactions following this fundamental scheme can be found in the literature, e.g., the formation of tetracoordinate siliconium cations from N-methylimidazole and trimethylsilylbromide [1] and Si–Cl bond dissociation to yield pentacoordinate siliconium cations [2]. Furthermore, the release of initially Si-bound halides may provoke reactions at the ligand backbone [3]. As soon as Si–X bonds other than Si-Halide are getting activated by Si-hypercoordination, the groups X may exhibit reactivities of camouflaged nucleophiles, i.e., group X may attack electrophilic centres in the ligand backbone such as carbonyl and imine carbon atoms. Such reactivity was shown for hexacoordinate silacyclobutanes [4], allylsilanes [5], disilanes [6], cyanosilanes [7] and H-silanes [8]. Even an unexpected alkyl group shift towards an imine ligand was reported recently [9]. Furthermore, coordination to silicon as central atom may induce rearrangements of isomeric ligand moieties one into another [10] or even give rise to the Si-templated formation of novel ligands [11].

Our recent research on hypercoordinate diorganosilanes [12] revealed remarkably activated Si–C bonds, which, upon irradiation, are cleaved to yield a novel ligand moiety coordinated to the silicon atom (Scheme 1) [13]. Hexacoordination of the silicon atom was shown to be one of the keys to this reactivity pattern since pentacoordinate silicon compounds comprising related ligand backbones proved inert under similar reaction conditions [14]. Furthermore, the approach to the ligand within this 1,3-shift reaction proved to proceed towards the sterically less crowded imine carbon atom, as demonstrated with an asymmetric ONN′O′ ligand [15]. In our herein presented study we elucidate further parameters which may control the direction of the reactions following photo-induced Si–C bond cleavage.

Scheme 1. 1,3-Shift of an initially Si-bound ethyl group upon UV irradiation.

Results and Discussion

As reported earlier, a variety of hexacoordinate diorganosilanes (2-8) was accessible via reaction between the tetradeinate Schiff base ligand 1 and the respective diorganodichlorosilanes (Scheme 2) [12]. In accord with the exclusive 1,3-shift of the Si-bound alkyl group of 2 and 3 upon UV irradiation under formation of 2a and 3a, respectively [13], in compound 4, which comprises a sterically more
demanding alkyl substituent (i.e., a cyclohexyl group) the 1,3-alkyl shift is still favored.

![Scheme 2](https://example.com/scheme2.png)

Scheme 2. Synthesis of hexacoordinate diorganosilanes 2-8 and their photo-assisted rearrangement into pentacoordinate silicon complexes 2a-8a. For 2a-8a (not applicable for 5a) the diastereomer with swapped positions R’ vs. Ph was observed. For 2a and 8a spectroscopically as a minor component (< 10 %) of the reaction mixture. For 3a and 4a the product of β-hydride transfer (R’ = H) was also observed NMR spectroscopically as a minor component (< 10%) [13].

Table 1. \(^{29}\)Si NMR shifts (δ in ppm relative to SiMe\(_3\)) detected in the product mixture after irradiation of compounds 2-9, 11 and 13.

<table>
<thead>
<tr>
<th>δ(Si)</th>
<th>2a</th>
<th>3a</th>
<th>4a</th>
<th>5a</th>
<th>6a</th>
<th>7a</th>
</tr>
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<tbody>
<tr>
<td>2</td>
<td>-113.3</td>
<td>-111.8</td>
<td>7</td>
<td>115.5</td>
<td>-116.7</td>
<td>-101.5</td>
</tr>
<tr>
<td>3</td>
<td>-114.5</td>
<td>-114.8</td>
<td>-117.4</td>
<td>8</td>
<td>-116.3</td>
<td>-113.3, -113.6, -114.6, -117.9</td>
</tr>
<tr>
<td>4</td>
<td>-112.7</td>
<td>-114.8</td>
<td>-118.2</td>
<td>9</td>
<td>-114.8</td>
<td>Other signals as for 8</td>
</tr>
<tr>
<td>5</td>
<td>-113.9</td>
<td>11</td>
<td>-114.3</td>
<td>11</td>
<td>-117.3</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>-101.8</td>
<td>-101.1</td>
<td>13</td>
<td>-129.5 d</td>
<td></td>
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</table>

\( ^{a}\) Predominant signal \( ^{b}\) Additional signal(s) \( ^{c}\) corresponds to the β-H transfer product.

Table 2. \(^{13}\)C NMR shifts (δ in ppm relative to SiMe\(_3\)) of the (Ph, Aryl,N,R)-substituted carbon atom detected in the product mixture after irradiation of the hexacoordinate diorganosilanes compounds 2-9, 11 and 16.

<table>
<thead>
<tr>
<th>δ(C)</th>
<th>2a</th>
<th>3a</th>
<th>4a</th>
<th>5a</th>
<th>6a</th>
<th>7a</th>
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<tr>
<td>2</td>
<td>65.5</td>
<td>65.5</td>
<td>64.3, 70.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>69.6</td>
<td>70.2</td>
<td>68.2, 72.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>72.6</td>
<td>69.2</td>
<td>69.2, 68.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>73.1</td>
<td>73.1</td>
<td>69.2, 68.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>65.4</td>
<td>64.1</td>
<td>64.1</td>
<td></td>
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\( ^{a}\) Predominant signal \( ^{b}\) Significant additional signal(s) in the spectra of the crude product \( ^{c}\) The isolated major isomer \( ^{d}\) corresponds to the β-H transfer product \( ^{e}\) Additional signals were observed from 68.2 to 73.1 ppm, thus indicating the formation of a great variety of products.

Even β-hydride transfer to the imine carbon atom, which was found as a minor side reaction when 3 was irradiated, did not play any pronounced role. Table 1 reveals the formation of pentacoordinate silicon complexes upon UV irradiation of 2, 3, 4 and 5. The very narrow \(^{29}\)Si NMR shift range underlines the formation of silicon compounds bearing very similar Si-bound moieties, i.e., compounds comprising the (ONN’O’)Si-Ph pattern. On the formation of a minor diastereomeric product in case of 2 and 3 as well as the β-hydride transfer product in case of 3 (δ\(^{29}\)Si = -114.8 ppm) we have reported earlier [13]. These features can also be found for compound 4, whereas the rearrangement product of 5 reveals only one \(^{29}\)Si NMR signal, as expected. From the crude reaction products \(^{13}\)C NMR spectra were recorded in order to gather information to the \(^{13}\)C chemical shift of the altered former imine carbon atom (Table 2). In addition to the distinct signals of the characteristic R’PhArN-substituted quarternary C-atoms, a resonance peak emerges at 69.2 ppm for the β-H transfer product in case of the product mixtures resulting from 4, 9 and 11, vide infra, not recorded for 3).

We succeeded in crystallizing 4a from the reaction mixture (Fig. 1). As in 3a [13], the silicon atom in 4a is housed in a distorted trigonal bipyramidal coordination sphere. The bonding parameters about the Si-atom are similar to those found for 3a. The ultimate reactivity of the Si–C(alkyl) bond in 2, 3, 4 and 4 gave rise to the question whether Si–C(aryl) might prove capable of rearranging in a similar manner. Hence, compound 5 was also irradiated, with success. The exclusive presence of Si–C(aryl) bonds rendered an Si-bound phenyl group suitable to rearrange. The molecular structure of the rearrangement product 5a (determined crystallographically) is similar to 4a, thus not further discussed. Selected bonding parameters of 5a are provided in caption of Figure 1.

The next essential question addressed was the role of the phenyl group in the rearrangement reactions of 2-5. One could consider the phenyl moiety as an antenna for electromagnetic power input into the molecules, thus activating the Si–C bond trans-disposed to Si–C(phenyl). Successful rearrangement of one of the Si-bound methyl groups in 6 proved this hypothesis wrong and, furthermore, provided insights into the stability of the reaction product 6a. So far,
we only knew that the Si–C(aryl) bonds in compounds such as 2a-5a are not susceptible to any further UV-assisted rearrangement. In conclusion, this applies to Si–Me as well. The formation of the proposed rearrangement product 6a and a diastereomer thereof is indicated in the $^{29}$Si NMR spectrum by significantly down-field shifted signals (i.e., −101.8 and −103.1 ppm) with respect to the Si–Ph substituted pentacoordinate Si-complexes.

Vinyl substituted complexes 7 and 8 (Scheme 2, Table 1) deliver further information. The Si-bound vinyl group in compound 7 adopts the role of the phenyl group in 2, thus rendering the Si-bound methyl group most susceptible to photo-assisted 1,3-rearrangement to yield 7a. A minor product comprising a pentacoordinate Si-atom with an Si-bound methyl group (as indicated by a signal at −101.5 ppm) proves the vinyl group less resistant towards rearrangement than the phenyl group. In addition, a $^{13}$C NMR signal of a quaternary carbon atom at 70.5 ppm (Table 2), which is in closer proximity to the signals of the Ph/ArylN-substituted quaternary C-atoms (see 73.1 ppm for 5a), underlines the 1,3-shift of this sp$^2$-carbon substituent in a competing reaction. Upon irradiation of compound 8, however, a product mixture results which can be explained by alternative rearrangement of vinyl and phenyl group. This is, the two sp$^2$-carbon substituents Ph and Vi compete with each other. Hence, the sp$^3$ vs sp$^2$ hybrid character of the Si-bound-C-substituent proved to dominate the course of the reaction. Therefore, we considered the molecular orbital situation along the C–Si–C 3-centre bond axis as a fundamental factor which determines the way an Si–C bond in complexes such as 2–8 is cleaved.

A computational study of model compound 2' (Figure 2) revealed an interesting feature of the orbital situation along the C–Si–C axis (Figure 2). We were able to identify four orbitals (two bonding, i.e., #94, #98, and two anti-bonding ones, i.e., #130, #131) which exhibit noticeable contributions on the C–Si–C 3-centre bonding situation. Whereas the contributions of the Si–C bonds to these orbitals are nearly equal, the HOMO (#102) exhibits remarkable contributions from the Si–C(methyl) bond to an MO which is predominantly created by π-interactions within the ligand system. One can assume that UV excitation of the HOMO would thus result in pronounced weakening of the Si–C(Me) bond, whereas the Si–C(Ph) bond would probably be less influenced. This is merely a little hint to the origin of the different 1,3-shift behavior of the methyl and phenyl group. Further studies will have to address the investigation of the role of the tetradeutate ligand as an antenna for the energy input.

In a previous publication we have reported on the synthesis of a di-nuclear diorganosilane 9 comprising two hexacoordinate silicon atoms (Scheme 3) [16]. This tempted us to explore photo-induced rearrangement of this di-nuclear phenyl-alkyl-silane. In sharp contrast to our expectations, there was no indication for the formation of a dinuclear complex such as 9a. Instead, $^{29}$Si NMR spectroscopy of the product mixture thus obtained exhibited the same signal pattern as the $^{29}$Si NMR spectrum of the products obtained upon irradiation of vinyl-phenyl-silane 8. Additionally, an intense peak at −114.8 ppm indicated the simultaneous formation of the equivalent amount of complex 9b, which was previously found to be a side product in the rearrangement reaction of 3 and 4, i.e. resulting from β-hydride transfer. This conclusion was supported $^1$H and $^{13}$C NMR spectroscopically [17].
the structural features of the molecules of 11 (Figure 3) are related to those found for 3 [13]. Indeed, photo-induced rearrangement of 11 predominantly led to the undisturbed rearrangement of the 2,3-trimethylsilylyethyl group to yield 11a whereas β-hydride transfer was found to play the role of a minor side reaction as in the analogous reactions of 3 and 4.

In all above rearrangement reactions a phenyl group (alternatively, a vinyl or methyl group) acts as a sacrificial ligand which does not undergo any 1,3-shift reaction. Whereas the Si–C bond is only kinetically inert, an Si–F bond is thermodynamically more stable and might therefore prove a suitable sacrificial ligand as well. Thus, compound 13 was synthesized according to Scheme 5. Its identity (as the F-trans-phenyl isomer) was confirmed by $^1$H, $^13$C and $^{29}$Si NMR spectroscopy. Whereas the $^1$H and $^{13}$C spectra exhibit only one set of NMR signals characteristic of half a tetradeutate ligand, the $^{29}$Si NMR spectrum ($\delta = -180.3$ ppm, dublett $^{1}J_{SF} = 166$ Hz) reveals hexacoordination of the silicon atom and the presence of one fluorine atom in its coordination sphere. Upon UV-irradiation of 13 the expected rearrangement product 13a had formed (indicated by a dublet in the $^{29}$Si NMR spectrum, $\delta = -129.5$ ppm, $^{1}J_{SF} = 188$ Hz), but from the presence of an intense triplet signal ($\delta = -187.0$ ppm, $^{1}J_{SF} = 174$ Hz) the formation of an SiF$_2$-substituted hexacoordinate silicon compound became instantly obvious. Deliberate synthesis and characterization of complex 15 (Scheme 5, bottom) proved identity with the side product formed upon UV-irradiation of 13. So far, the fate of the originally Si-bound phenyl group is not clear. At least, due to the absence of a $^{29}$Si NMR signal at $\approx 113.9$ ppm, we can exclude formation of 5a in a combined photolysis + ligand-scrambling reaction, in addition to having shown that an Si-bound phenyl group would be the dummy ligand of choice for such photo-driven rearrangement reactions.

Compounds 12, 14 and 15 were obtained as crystalline solids, thus allowing for X-ray diffraction analyses thereof. Compound 12
does not exhibit any unusual structural features. In sharp contrast to molecular structures of SiMe₃ substituted salen-type ligands proposed by Singh et al. [18], 12 comprises SiMe₃ groups with tetracoordinate silicon atoms. Both compounds 14 and 15 represent hexacoordinate silicon complexes with significantly longer Si–N and Si–O bonds in the fluoro silicon compound 15. In previous studies we have also recognized this coordinative behavior of bond lengthening upon Cl vs. F substitution [19]. It can be interpreted as enhanced O and N donor action in chlorosilicon complexes owing to the longer Si–Cl bond with pronounced ionic contributions [20].

In addition to Si-substituent effects, the influence of the group 14 element on this kind of rearrangement was to be considered. Therefore, two Ge- and Sn-compounds (16 and 17, respectively) were synthesized starting from ligand 1, triethylamine and the desired diphenyldichlorometallane Phe₂ECl₂ (E = Ge, Sn, respectively). The molecular structures of these compounds were determined X-ray crystallographically. The molecular shape of the germanium complex 16 (Figure 5) is related to its silicon analogue 5 [12]. This is a hexacoordinate Ge-complex comprising trans-disposed Ge–C bonds.

Figure 5. Molecular structure of 16 in the crystal. (Thermal ellipsoids at the 50% probability level, H-atoms omitted, selected atoms labeled). Selected bond lengths [Å] and angles [deg.]: Ge1–O1 1.928(2), Ge1–O2 1.936(2), Ge1–N1 2.057(2), Ge1–N2 2.086(2), Ge1–C31 2.005(3), Ge1–C37 1.995(3), N1–C31 1.289(3), N2–C22 1.285(3), O1–Ge1–N2 170.6(1), O2–Ge1–N1 170.2(1), C31–Ge1–C37 177.0(1).

The molecular structure of Sn-complex 17 (Figure 6) was entirely different. Surprisingly, compound 17 exhibits the tetradentate (ONNO) ligand in a mer-fac coordination mode. In a previous report [21] we had demonstrated that a complex of the type (ONNO)SnPhCl with a related salen-type ligand might exhibit this unexpected coordination pattern whereas in other salen-Sn complexes (ONNO)SnR₂ (comprising two identical substituents R) the Sn-bound monodentate groups R are trans-disposed to one another [22]. Now complex 17 clearly shows that even complexes of the general pattern (ONNO)SnR₂ may also comprise a salen-type ligand in mer-fac coordination mode. (In solution, however, the tetradentate ligand backbone of compound 17 may also engage the Sn-bound monodentate groups R.) In addition to the structural differences between 16 and 17 in the solid state, their reactivity upon UV-irradiation proved different. Whereas complex 16 gives rise to UV-induced Ge-C bond cleavage and migration of a phenyl group to the ligand backbone (as described for above hexacoordinate silicon complexes such as 5), unaltered compound 17 was recovered from the UV reactor, and there was no indication for the formation of another tin compound other than 17. The identity of the rearrangement product resulting from compound 16 was established by comparison of its ¹³C NMR data with the corresponding data of the related silicon compound 5a. This is: In addition to the emergence of a signal indicative of a Phe₂ArN₃ substituted quarternary C-atom at 74.2 ppm (Table 2) two sets of two signals arise for the two chemically inequivalent OMe groups and the N-CH₂CH₂-N unit of the ligand backbone (55.7, 55.0 and 49.9, 46.3 ppm for 5a; 55.6, 55.0 and 49.1, 46.2 ppm for its analogue 16a).

In order to elucidate the differences between 16 and 17 in both reactivity and structural patterns, computational analyses were performed at the MP2/SDD level of theory, in which the gas phase geometries of the hexacoordinate group 14 compounds Si, Ge and Sn as well as SN⁺ (the cis-C-Sn-C isomer) and their potential rearrangement products Sia, GEA and SNa were optimized. Their relative energies (Scheme 6) hint to the general trend of decreasing thermodynamic driving force (by means of enthalpy) for the C-M bond cleavage and phenyl shift reaction, although above data still renders the rearrangement of SN into SNa a slightly exothermic reaction. Furthermore, the difference in energy between SN and SN⁺ (4.8 kcal/mol) proves the structure of 17 an unexpected case, less favorable than its trans-C-Sn-C isomer. This finding is well in accord with a computational study by Tacke et al., which proved a mer-mer coordinated silicon complex within a tetradentate ONNO ligand system more stable than its mer-fac isomer [23]. The rather small difference in energy, however, shows that the special ligand arrangement in 17 in the solid state may arise for reasons such as crystal packing effects and revert into the more favorable arrangement upon dissolution (as found in NMR spectra).
In Conclusion, the Si-bound phenyl group of hexacoordinate diorganosilanes was shown to be a suitable sacrificial ligand in UV-induced 1,3-shift reactions of one Si-bound organyl group to an imine carbon atom of an imine ligand. Whereas an Si-bound vinyl group proved to compete with alkyl groups, the Si-bound phenyl substituent behaves innocent. The selective 1,3-shift of an sp2-C-substituent was successful for the SiPh2-substitution pattern only, whereas competing rearrangements were encountered for a (ONNO)SiPh2 system. Although thermodynamically tight bound to the silicon atom, a fluorine substituent cannot adopt the role of a sacrificial ligand for such cases to overcome competing reactions: The Si-F group further leads to side reactions (rearrangement reactions), the mechanisms of which are not clear yet. Furthermore, β-H bearing alkyl substituents were shown to contribute to the range of side reactions by β-H transfer to the imine group to variable extent. As to the role of the group 14 element, a related (ONNO)GePh2 system was shown to undergo a similar UV-induced 1,3-rearrangement of a Ge-bound phenyl group whereas a (ONNO)SnPh2 system proved inert under the reaction conditions applied.

Experimental Section

Syntheses, NMR spectroscopy and X-ray crystallography

Syntheses were performed under an inert atmosphere of dry argon using Schlenk line techniques and anhydrous solvents. NMR spectra (of CDCl3 solutions) were recorded on a BRUKER DPX 400 spectrometer (10 mm probe) using SiMe4 as internal standard for ²⁹Si and ¹³C spectra. X-ray diffraction data were recorded on a BRUKER NONIUS X8 diffractometer with APEX II CCD detector using Mo Kα radiation. The structures were solved by direct methods (SHELXS) and refined with full-matrix least-squares on F². All non-hydrogen atoms were refined anisotropically. H-atoms were refined isotropically in idealized positions (riding model). Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre, CCDC-718481 (4a), CCDC-718483 (5a), CCDC-718486 (11(CH3)2), CCDC-718488 (12), CCDC-718479 (14-toluen), CCDC-718484 (15-(CH3)2), CCDC-718487 (15-(CH3)2(OH)), CCDC-718482 (16) and CCDC-718485 (17). Copies of the data can be obtained free of charge online via www.ccdc.cam.ac.uk/data_request/cif.

The syntheses of compounds 2–8 [12, 13] and 9 [16] were reported earlier. Irradiation of the compounds 2–9, 11 and 13 with UV followed the protocol as reported for 2 and 3 in our preliminary communication [13]. This is, a 150 mL reactor equipped with a magnetic stirring bar and a medium pressure Hg lamp (λmax = 365 – 436 nm) was charged with 130 mL of tetrahydrofuran (THF) and ca. 5 mmol of the respective hexacoordinate silicon complex. The solution or suspension was then exposed to UV for ca. 5h (at 15°C), whereupon the resulting solution was transferred into a Schlenk flask, the solvent was removed under reduced pressure and the residue was dissolved in CDCl3 for NMR analyses. As to further purification of the rearrangement products, our attempts to recrystallize the crude products under anarobic conditions failed (except compounds 2a and 3a, which were characterized as pure solids). As shown previously [13] compounds such as 2a and 3a undergo solvolysis in chloroform/methanol mixture. However, in case of the rearrangement products 4a and 5a some single crystals suitable for X-ray diffraction analyses were obtained by immediate addition of anhydrous methanol (2 mL) to a solution of the respective crude product in chloroform (1 mL). Although this is not the method of choice, the Cy- and Ph-substituted ligands with suspension points as low as 10°C allowed for rapid crystallization. The solid state structures of 4a and 5a confirm cyclohexyl- and phenyl-1,3-migration to the tetradentate ligand, respectively. Crystal structure analysis of 4a: C8H16N2O2Si, M=666.87, T= 296(2) K, monoclinic, space group P2₁/a, a = 14.5474(5), b = 15.0231(5), c = 17.2176(6) Å, β = 113.388(2°), V = 3464.52(1) Å³, Z = 4, ρ(calcd) = 1.279 Mgm⁻³, µ(Mo Kα) = 0.114 mm⁻¹, F(000) = 1416, 2θ(max) = 54.0°, 27597 collected reflections, 7547 unique reflections (R(int)=0.0385), 444 parameters, S=1.052, R=0.0431 (I>2σ(I)), wR= (all data)=0.1107, max./min. residual electron density =0.256–0.342 eÅ⁻³. Crystal structure analysis of 5a: C10H18N2O2Si, M=666.82, T= 296(2) K, monoclinic, space group P2₁/a, a = 14.5326(6), b = 15.0411(5), c = 17.1985(7) Å, β = 112.836(4)°, V = 3421.82(2) Å³, Z = 4, ρ(calcd) = 1.283 Mgm⁻³, µ(Mo Kα) = 0.115 mm⁻¹, F(000) = 1392, 2θ(max) = 66.0°, 3353 collected reflections, 8244 unique reflections (R(int)=0.0347), 442 parameters, S=1.052, R=0.0434 (I>2σ(I)), wR= (all data)=0.1168, max./min. residual electron density =0.263–0.320 eÅ⁻³.

Synthesis of compound 10: The hydroisolation of vinyltrimethylsilane (4.0 g, 40 mmol) with phenylidichlorosilane (6.60 g, 37.3 mmol) was carried out in chlorotrimethylsilane (5 mL) as a solvent using a Pt catalyst as described for the related synthesis of PhClSi(CH3)2(ONNOSiPh3Pt) [16]. After removal of the solvent and excess vinyltrimethylsilane the Pt catalyst was allowed to precipitate and compound 10 was obtained as colorless liquid (quantitative yield) and used for the synthesis of 11 without further purification. ¹H NMR (δ/ppm, CDCl3): 0.03 (s, 9 H, Si-CH₃), 0.6 (m, 2 H, Me-Si-CH₂), 1.2 (m, 2 H, Me-Si-CH₂), 6.70–7.55 (m, 15 H) (1C NMR (δ/ppm, CDCl3): -2.3 (Si-CH₂), 7.6 (Me-Si-CH₃), 13.7 (3H-Si(CH₃)), 128.3, 133.5 (Ph on m), 131.5 (Ph p), 132.4 (Ph q). ³²Si NMR (δ/ppm, CDCl3): 3.8 (CH₂-SiMe₃), 19.8 (CH₃-SiPh₂Cl).
monoclinic, space group P2₁/c, α = 17.8374(6), β = 16.3345(6), c = 12.0348(4) Å, β = 98.9824(2)°, V = 3467.2(3) Å³, Z = 4, $\rho_{\text{calcd}}$ = 1.197 Mgm⁻³, $\mu$(Mo Kα) = 0.142 mm⁻¹, F(000) = 1336, 2θ$_{\text{max}}$ = 60.0°, 6330 collected reflections, 10104 unique reflections (Rint = 0.0369), 448 parameters, S = 1.063, R = 0.0785 (I/2σ(I)), wR2 (all data) = 0.2174, max./min. residual electron density = +0.986~-0.598 eÅ⁻³.

Synthesis of compound 13: To a solution of 12 (9.10 g, 14.5 mmol) in toluene (75 ml), was stirred at ambient temperature, phenyltrifluorosilane (2.40 g, 14.8 mmol) was added dropwise followed by heating to 60 °C. Since there was no indication for a reaction between 12 and PhSiF₃ (neither evolution of gaseous Me₂SiF nor precipitation of product), the solution was cooled to room temperature, some crystals (ca. 20 mg) of target compound were added and the mixture was stirred for 2 h to 60 °C, whereupon a fine yellow precipitate formed within some minutes. Within 4 weeks storage at ambient temperatures this precipitate re-crystallized to yield 13. The solution was filtered off and washed with THF (15 mL). From the filtrate the solvent was removed in vacuo and the mixture was stored at 8°C for 7 d. The yellow solid residue was recrystallized from chloroform (25 mL) to yield 13 as a yellow crystalline powder, which was isolated by decantation and briefly filtered off and washed with THF (15 mL) and hexane (5 mL) and briefly dried in vacuo. Yield: 2.20 g (2.67 mmol, 23 %). CHN analysis found (%): C 66.4, H 4.52, N 3.35. Calcd. for C₂₅H₂₈N₄O₄SiCl, (%): C 65.74, H 4.91, N 4.30. Calcd. for C₂₅H₂₈N₄O₄SiCl, (%) 64.57, T = 90.2(3) K, triclinic, space group P1, a = 9.6526(2), b = 12.9318(4), c = 13.1290(3) Å, α = 97.778(2), β = 111.920(2), γ = 102.56(2)°, V = 1487.597(14) Å³, Z = 2, $\rho_{\text{calcd}}$ = 1.462 Mgm⁻³, $\mu$(Mo Kα) = 0.145 mm⁻¹, F(000) = 684, 2θ$_{\text{max}}$ = 50.0°, 14687 collected reflections, 5209 unique reflections (Rint = 0.0593), 432 parameters, S = 0.978, R = 0.0478 (I/2σ(I)), wR2 (all data) = 0.1032, max./min. residual electron density +0.249~-0.342 eÅ⁻³.

Synthesis of compound 16: Diphenyldichlorogeranamine (3.50 g, 11.7 mmol) and triethylamine (3.0 g, 30 mmol) in THF (200 ml), which was stirred at ambient temperature. After 20 min the solid precipitate was filtered off and extracted with THF from the filtrate. The solution was stored, after removal of 40 ml of the solvent under reduced pressure, was stored at 8°C overnight. From the filtrate the solvent was removed in vacuo and the yellow solid residue was recrystallized from chloroform (15 mL) and hexane (15 mL). The crystals of 16-CHCl₃ were observed until filtered off, washed with a mixture of chloroform (5 mL) and hexane (5 mL) and briefly dried in vacuo. Yield: 2.20 g (2.67 mmol, 23 %). CHN analysis found (%): C 66.4, H 4.52, N 3.35. Calcd. for C₂₅H₂₈N₄O₄Cl, (%): C 65.74, H 4.91, N 4.30. Calcd. for C₂₅H₂₈N₄O₄Cl, (%) 64.57, T = 90.2(3) K, triclinic, space group P1, a = 9.6526(2), b = 12.9318(4), c = 13.1290(3) Å, α = 97.778(2), β = 111.920(2), γ = 102.56(2)°, V = 1487.597(14) Å³, Z = 2, $\rho_{\text{calcd}}$ = 1.462 Mgm⁻³, $\mu$(Mo Kα) = 0.145 mm⁻¹, F(000) = 684, 2θ$_{\text{max}}$ = 50.0°, 14687 collected reflections, 5209 unique reflections (Rint = 0.0593), 432 parameters, S = 0.978, R = 0.0478 (I/2σ(I)), wR2 (all data) = 0.1032, max./min. residual electron density +0.249~-0.342 eÅ⁻³.

References


Quantum chemical calculations

All computational analyses using density functional theory (DFT) calculations were performed with the GAUSSIAN 03 program suite [24]. The cartesian coordinates of atomic positions obtained by X-ray diffraction analyses of 5, 5a, 16 and 17 were used as initial input data and the desired molecules Si, Ge, Sn, Sn', Sla, GeS, Sna were generated therefrom by replacement of Si vs Ge vs Sn and replacement of ligand-bound Ph- and OMe-groups by hydrogen atoms. In the same manner, the input coordinates for 2' were generated from crystallographic data of 2. The optimization of the molecular structures and further analyses of the model compounds were performed using B3LYP/6-311G(d,p) for 2' and MP2/5D2 for SI, GE, SN, Sla, GeS, GEa and Sna.

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