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

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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)SiRR', 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 hexacoordination, 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 silaclobutanes [4], allylsilanes [5], disilanes [6], cyano silanes [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-template formation of novel ligands [11].

Our recent research on hypercoordinate diorgansilanes [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 ONNO’ 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.

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

Results and Discussion

As reported earlier, a variety of hexacoordinate diorganosilanes (2-8) was accessible via reaction between the tetradentate 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. 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 \(^{29}\text{Si}\) NMR 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. \(^{29}\text{Si}\) NMR shifts (δ in ppm relative to SiMe\(_4\)) detected in the product mixture after irradiation of compounds 2-9, 11 and 13.

| 2  | -113.3 | -115.8 | 7  | -115.5 | -116.7 | -101.5 |
| 3  | -114.5 | -114.8\(^{[c]}\), -117.4 | 8  | -116.3 | -113.3 | -113.6, -114.6, -117.9 |
| 4  | -112.7 | -114.8\(^{[c]}\), -118.2 | 9  | -114.8\(^{[c]}\) | Other signals as for 3 |
| 5  | -113.9 | 11 | -114.3 | -117.3 |
| 6  | -101.8 | -101.1 | 13 | -129.5 d |

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

Table 2. \(^{13}\text{C}\) NMR shifts (δ in ppm relative to SiMe\(_4\)) of the (Ph,Ar\(_1\),N,R)-substituted carbon atom detected in the product mixture after irradiation of the hexacoordinate diorganosilanes 2-9, 11 and 16.

| 2  | 65.5\(^{[b]}\) |  | 7  | 65.5 | 64.3, 70.5  |
| 3  | 69.6\(^{[b]}\) |  | 8  | 70.2 | 68.2, 72.7\(^{[b]}\) |
| 4  | 72.6 | 69.2\(^{[b]}\) | 9  | 69.2\(^{[b]}\) | Other signals as for 3 |
| 5  | 73.1 | 11 | 70.1 | 69.2\(^{[b]}\), 68.2 |
| 6  | 65.4 | 64.1 | 16 | 74.2 |

\(^{[a]}\) 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 \(^{[e]}\) 9 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 \(^{29}\text{Si}\) 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\(^{29}\text{Si} = -114.8\) ppm) we have reported earlier [13]. These features can also be found for compound 4, whereas the rearrangement product of 5 reveals only one \(^{29}\text{Si}\) NMR signal, as expected. From the crude reaction products \(^{13}\text{C}\) NMR spectra were recorded in order to gather information to the \(^{13}\text{C}\) chemical shift of the altered former imine carbon atom (Table 2). In addition to the distinct signals of the characteristic \(\text{R'PhAr}_1\text{N}-\text{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 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 quarternary carbon atom at 70.5 ppm (Table 2), which is in closer proximity to the signals of the Ph/ArylN-substituted quarternary 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 tetradentate ligand as an antenna for the energy input.

![Figure 2](image-url)

Figure 2. Molecular orbitals of 2’ (from left) #94, #98 (bottom), #102 = HOMO (middle), #130, #131 (top), which exhibit significant contributions on the C–Si–C bond axis (limiting isosurface: 0.05 eÅ$^3$). MO #102 represents the HOMO.

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].

![Scheme 3](image-url)

Scheme 3.

![Scheme 4](image-url)

Scheme 4.

At least two parameters can be considered to drive the rearrangement reaction of 9 into this unexpected direction: 1) The β-silyl substituted alkyl group might exhibit an activating influence on the β-hydrogen atoms; 2) The steric bulk about the ethylene bridge might render the formation of two mono-nuclear complexes more likely. In order to rule out the first option, complex 11 was synthesized according to Scheme 4. Except the β-silyl substituent...
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-trimethylsilylethyl 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.

Figure 3. Molecular structure of one of the two crystallographically independent molecules of 11 in a crystal of 11(CHCl₃). (Thermal ellipsoids at the 50% probability level, H-atoms and chloroform molecules omitted, selected atoms labeled). Selected bond lengths [Å] and angles [deg.]: Si1−O1 1.769(1), Si1−O2 1.770(1), Si1−N1 1.959(1), Si1−N2 1.960(1), Si1−C31 1.960(1), Si1−C37 1.970(1), N1−C7 1.299(2), N2−C22 1.298(2), N1−Si1−O2 175.3(1), N2−Si1−O1 176.8(1), C31−Si1−C37 176.4(1), Si1−C37−C38 122.6(1), Si2−C38−C37 115.1(1), Si2−C38−C37 115.1(1).

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 synthesis according to Scheme 5. Its identity (as the F-trans-phenyl isomer) was confirmed by ¹H, ¹³C and ²⁹Si NMR spectroscopy. Whereas the ¹H and ¹³C spectra exhibit only one set of NMR signals characteristic of half a tetradentate ligand, the ²⁹Si NMR spectrum (δ = −180.3 ppm, doublet J_{SiF} = 166 Hz) reveals hexacoordination of the silicon atom and the presence of one fluoride atom in its coordination sphere. Upon UV-irradiation of 13 the expected rearrangement product 13a had formed (indicated by a doublet in the ²⁹Si NMR spectrum, δ = −129.5 ppm, J_{SiF} = 188 Hz), but from the presence of an intense triplet signal (δ = −187.0 ppm, J_{SiF} = 174 Hz) the formation of an SiF₂-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 ²⁹Si NMR signal at −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

Scheme 5.

Figure 4. Molecular structures of 15 in a crystal of 15(CHCl₃) (top) and 14 in a crystal of 14 (toluene) (bottom). (Thermal ellipsoids at the 50% probability level, H-atoms and solvent molecules omitted, selected atoms labeled). Selected bond lengths [Å] and angles [deg.]: 15: Si1−O1 1.736(1), Si1−O2 1.728(1), Si1−N1 1.91(1), Si1−N2 1.926(1), Si1−N2 1.986(1), Si1−N3 1.705(1), N1−C7 1.300(1), N2−C22 1.297(1), O1−Si1−N2 176.8(1), O2−Si1−N1 175.9(1), F1−Si1−F2 174.2(1). 14: Si1−O1 1.705(1), Si1−O2 1.709(1), Si1−N1 1.901(1), Si1−N2 1.900(1), Si1−C7 1.267(1), Si1−C12 1.226(1), N1−C7 1.302(1), N2−C12 1.307(2), O1−Si1−N2 1.783(1), O2−Si1−N1 1.770(1), Cl1−Si1−Cl2 174.1(1).
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 SiMe₅ 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 fluorosilicon 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 Ph₂ECl₂ (E = Ge, Sn, respectively). The molecular structures of these compounds were determined X-ray crystallographically. The molecular shape of the germanium complex (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–C7 1.285(3), N2–C22 1.285(3), O1–Ge1–N1 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 tetradeinate (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 tetradeinate ligand backbone of compound 17 may also engage the mer–mer coordination mode, as concluded from ¹³C and ¹⁹H NMR spectroscopic data, which render the two CH₂ and CH₃ groups and the methylene protons of each CH₃ group chemically equivalent.) 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 Ph₂ArylN-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).

Figure 6. Molecular structure of 17 in the crystal. (Thermal ellipsoids at the 50% probability level, H-atoms omitted, selected atoms labeled). Selected bond lengths [Å] and angles [deg.]: Sn1–O1 2.049(2), Sn1–O2 2.127(2), Sn1–N1 2.303(2), Sn1–N2 2.205(2), Sn1–C31 2.177(3), Sn1–C37 2.156(3), N1–C7 1.296(3), N2–C22 1.321(3), O1–Sn1–N1 152.6(1), O2–Sn1–C31 171.5(1), N1–Sn1–C37 169.0(1), C31–Sn1–C37 100.7(1).

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 Sn, Ge and Sn as well as SN' (the cis-C-Sn-C isomer) and their potential rearrangement products Sn₁a, 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 M-C 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 tetradeinate 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).
the data can be obtained free of charge online via [15]. Irradiation of the compounds (squares on diffraction data were recorded on a BRUKER NONIUS X8 diffractometer (10 mm solutions) were recorded on a BRUKER DPX 400 spectrometer (10 mm conditions failed (except compounds 3a 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-containing ligands with suprasymmetric substituents allow 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: C32H48N2O2Si, M=666.87, T=296(2) K, monoclinic, space group P21/n, a = 14.5474(4), b = 15.0231(5), c = 17.2176(4) Å, β = 113.385(2), V = 3464.82(2) Å3, Z = 4, ρcalcd = 1.279 Mgm⁻³, μ(Mo Kα) = 0.114 mm⁻¹, F(000) = 1416, 2θmax = 54.0°, 27597 collected reflections, 7547 unique reflections (Rint=0.0385), 444 parameters, S=1.052, Rs=0.043 (I>2σ(I)), wR2 (all data)=0.1107, max./min. residual electron density =0.256–0.342 eÅ⁻³. Crystal structure analysis of 5a: C26H38N2O2Si, M=666.82, T=296(2) K, monoclinic, space group P21/n, a = 14.5426(6), b = 15.0411(5), c = 17.1985(7) Å, β = 112.836(12)°, V = 3421.82(2) Å³, Z = 4, ρcalcd = 1.283 Mgm⁻³, μ(Mo Kα) = 0.115 mm⁻¹, F(000) = 1392, 2θmax = 56.0°, 3350 collected reflections, 8244 unique reflections (Rint=0.0347), 442 parameters, S=1.052, R=0.0434 (I>2σ(I)), wR2 (all data)=0.1168, max./min. residual electron density =0.263–0.320 eÅ⁻³.

Synthesis of compound 10: The hydrosilylation of vinyltrimethylsilane (4.0 g, 40 mmol) with phenylidichlorosilane (6.6 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 PhCl(Si(CH₂)₃)₂(SiCl₂Ph) [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): 0.09 (s, 9 H, Si-CH₃), 0.08 (m, 1 H, Me-Si-CH₂), 1.2 (m, 2 H, Me-Si-CH₂), 4.16 (t, 2 H, 2.4 Hz, 8.8 Hz), 4.18 (d, 2 H, 2.4 Hz), 4.20 (d, 2 H, 2.4 Hz), 4.47 (t, 2 H, 2.4 Hz, 8.8 Hz), 4.65 (t, 2 H, 2.4 Hz, 8.8 Hz), 4.67 (d, 2 H, 2.4 Hz). 13C NMR (δ/ppm, CDCl₃): -2.3 (Si-C), 7.6 (Me-Si-CH₂), 13.7 (CH₂-SiCl₂Ph), 128.3, 133.5 (Ph) (m), 131.5 (Ph p), 132.4 (Ph). 29Si NMR (δ/ppm, CDCl₃): 3.8 (CH₂-SiMe₃), 19.8 (CH₃-SiPhCl₂).

Synthesis of compound 11: To a stirred suspension of ligand 1 (5.00 g, 10.4 mmol) and triethylamine (3.0 g, 30 mmol) in THF (150 mL) silane (5.00 g, 10.4 mmol) and hexamethyldisilazane (2.52 g, 15.7 mmol) were applied. After removal of the solvent and excess vinyltrimethylsilane the Pt catalyst was allowed to precipitate. The mixture was stirred at room temperature for 5 min. Then the hydrochloride precipitate was filtered off and washed with THF (20 mL). From the combined filtrate and washings the solvent was removed in vacuo and the yellow residue was then exposed to UV for ca. 5h (at 15°C), was charged with 130 mL of tetrahydrofuran (6 H, O-CH₂), 6.90- 7.15 (mm, 7 H), 7.25-7.45 (m, 6 H), 7.65-7.70 (m, 2 H).

In Conclusion

3. All non-hydrogen atoms were refined anisotropically. H-atoms were placed in calculated positions (C–H 0.98, 1.00 Å).

4. Si-F group leads to further side reactions (rearrangement products, which were set 0: 

Scheme 6. Relative energies (kcal/mol) with respect to SI, GE and SN, respectively, which were set to -21.0, -13.9, SN*: 4.8, SNa - 8.3. Wiley-VCH
monochromatic, space group P2_1/c, a = 17.837(6) Å, b = 16.3345(6) Å, c = 12.0348(4) Å, β = 98.524(2)°, V = 3467.8(3) Å³, Z = 4, ρ_{calcd} = 1.197 Mg/m³, μ(Mo Kα) = 0.142 mm⁻¹, F(000) = 1336, 2θ_{max} = 60.0°, 6333 collected reflections, 10104 unique reflections (R(int) = 0.0369), 448 parameters, S = 1.063, R = 0.0785 (I/σ(I)), wR² (all data) = 0.2174, max/min. residual electron density ±0.986–0.598 e Å⁻³.

Synthesis of compound 13: To a solution of 12 (9.10 g, 14.5 mmol) in toluene (75 mL), which 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 toluene-SiF₃ were added and filtration was then performed to wash the precipitate to 60°C, whereupon evolution of Me₂SiF and precipitation of complex 13 commenced. The mixture was then heated to reflux and kept under reflux for 2 h. Then the suspension was cooled to room temperature and the solid white product was filtered off, washed with toluene (40 mL) and dried in vacuo. Yield: 7.70 g (12.7 mmol, 89%), CHN analysis found (%): C 71.7, H 4.8, N 4.89. Calcd. for C₇₁H₉₄N₄SiF₁₈O₆ (602.73) %: C 71.74, H 5.18, N 4.65. H NMR (600 ppm, CDCl₃): 3.1 – 3.4 (m, 4 H, N–CH₃), 3.81 (s, 6 H, O–CH₃), 6.18 (dd, 2 H, 2.4 Hz, 9.2 Hz), 6.64 (d, 2 H, 9.2 Hz, 6.66 (d, 2 H, 2.4 Hz, 7.0 – 7.6 (mm, 15 H)). ¹³C NMR (600 ppm, CDCl₃): 47.7 (N–CH₃, 55.4 (OCH₃), 104.1, 107.3, 113.6, 125.8 (6 H), 126.5, 126.9, 129.2, 129.3, 133.0, 134.3, 135.0, 163.5, 165.9, 171.9. ⁷⁷Se NMR (600 ppm, CDCl₃), -180.3 (δ, 171.6 ppm).

Synthesis of compound 14: To a solution of 12 (6.50 g, 10.4 mmol) in toluene (40 mL), which was stirred at ambient temperature, a solution of SiCl₄ (7.7 g, 10.4 mmol) in toluene (20 mL) was added dropwise, whereupon a fine yellow precipitate formed within some minutes. Within 4 weeks storage at ambient temperatures this precipitate re-crystallized to yield the solvate 14-toluene as a beige crystalline solid, which was separated from the solution by decantation, washed with toluene (10 mL) and dried in vacuo. Yield: 6.60 g (86 mmol, 95%), CHN analysis found (%): C 69.3, H 5.38, N 4.23. Calcd. for C₇₀H₈₂N₄SiF₁₈Cl₂O₆ (669.65) %: C 66.36, H 5.12, ¹³C NMR (600 ppm, CDCl₃), 7.0 – 7.6 (mm, 15 H). ¹¹B NMR (600 ppm, CDCl₃): 7.01 (s, 6 H, O–CH₃), 6.27 (dd, 2 H, 2.4 Hz, 9.2 Hz), 6.64 (2 H, 9.2 Hz), 7.0. ⁷⁷Se NMR (600 ppm, CDCl₃), 54.7 (OCH₃), 104.0, 109.3, 112.2, 126.2, 129.2, 129.8, 133.2, 134.3, 135.0, 163.5, 165.9, 171.9. ⁷⁷Se NMR (600 ppm, CDCl₃), -183.7. Crystal structure analysis of 14-toluene.

Synthesis of compound 15: A suspension of 14-toluene (1.05 g, 1.57 mmol) and ZnF₂ (0.30 g, 2.9 mmol) in THF (40 mL) was stirred at ambient temperature for 12 d. Then the volume was diminished to ca. 15 mL by removal of volatiles in vacuo and the mixture was stored at 8°C for 7 d. The solvate obtained was filtered off, washed with THF (2 mL) and extracted with chloroform (4 mL). Upon storage of the extract at 8°C the product 15.(CHCl₃), which was crystallized, which is isolated by decantation and briefly dried in vacuo. Yield: 0.47 g (0.60 mmol, 38%) of colorless crystals. CHN analysis found (%): C 48.76, H 3.75, N 3.60. Calcd. for C₇₁H₈₃N₄SiF₁₈Cl₄O₆ (735.30) %: C 3.45 (6 H, O–CH₃), 3.96 (6 H, O–CH₃), 6.06, N 5.58. ¹³C NMR (600 ppm, CDCl₃), 3.7 (s, 4 H, N–CH₃), 3.85 (s, 6 H, O–CH₃), 6.20 (2 H, 2.4 Hz, 8.8 Hz), 6.61 (d, 2 H, 8.8 Hz), 6.72 (d, 2 H, 2.4 Hz, 7.2 – 7.3 (mm, 4 H), 7.4 – 7.5 (mm, 6 H)). ¹¹B NMR (600 ppm, CDCl₃): 48.7 (N–CH₃, 55.5 (OCH₃), 104.1, 107.4, 113.0, 126.8, 129.1, 129.5, 134.2, 154.6, 166.0, 167.9. ⁷⁷Se NMR (600 ppm, CDCl₃): 139.4 (all H, 55.1 (OCH₃), 104.9, 105.4, 115.4, 126.5, 127.7, 128.8, 128.9, 135.0, 136.2, 137.0, 151.0, 165.1, 171.5, 176.8. ⁷⁷Se NMR (600 ppm, CDCl₃): 51.6 (N–CH₃, 551.1 (OCH₃), 104.9, 105.4, 115.4, 126.5, 127.7, 128.8, 128.9, 135.0, 136.2, 137.0, 151.0, 165.1, 171.5, 176.8. The crystals were used as initial input data and the desired structure solution was obtained with the software APEX2 and SHELXL-2018/5. The calculated parameters were checked and the reflections were checked and the unique reflections (R(int) = 0.0316, 442 parameters, S = 1.036, R = 0.0296 (I/σ(I)), wR² (all data) = 0.0698, max/min. residual electron density ±0.679–0.401 e Å⁻³.

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 Si₉, Ge₉, Sn₉, Sn₉, Ge₉ and Sn₉ 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 2b were generated from crystallographic data of 2. The optimization of the molecular structures and further calculations of the model compounds were performed using B3LYP/6-311G(d,p) for 2b and MP2/SDD for Si₉, Ge₉, Sn₉, Sn₉, Ge₉ and Sn₉.

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References

As pointed out in ref. [15], the β-H-transfer product 9b which was encountered in the reaction mixtures upon irradiation of 3, 4, 9 and 11, was deliberately synthesized by reaction of ligand 1 with phenyldichlorosilane in order to establish its identity. However, from this hydrosilylation approach a mixture of two diastereomers arises, whereas the β-H-transfer product 9b is diastereomerically pure, i.e., the transferred H-atom is trans to the Si-bound Ph-group with respect to the (ONNO) ligand plane.


