Zeitschrift für Anorganische und
Allgemeine Chemie

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Journal:	<i>Zeitschrift für Anorganische und Allgemeine Chemie</i>
Manuscript ID:	zaac.200900080
Wiley - Manuscript type:	Article
Date Submitted by the Author:	02-Feb-2009
Complete List of Authors:	Wagler, Jörg; TU Bergakademie Freiberg, Inst. für Anorganische Chemie Roewer, Gerhard; TU Bergakademie Freiberg, Fak. Chemie und Physik Gerlach, Daniela; TU Bergakademie Freiberg, Inst. für Anorganische Chemie
Keywords:	Chelate, Hypercoordination, Rearangement, Schiff Base, Tin

Full Paper

DOI: 10.1002/zaac.200((please insert the last 6 DOI digits))

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 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 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

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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}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}Si NMR shifts (δ in ppm relative to SiMe_4) detected in the product mixture after irradiation of compounds **2-9**, **11** and **13**.

	$\delta(^{29}\text{Si})_1$ ^[a]	$\delta(^{29}\text{Si})_2$ ^[b]		$\delta(^{29}\text{Si})_1$ ^[a]	$\delta(^{29}\text{Si})_2$ ^[b]
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 8
5	-113.9		11	-114.3	-117.3
6	-101.8	-103.1	13	-129.5 d	

^{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_4) of the (Ph,Aryl,N,R)-substituted carbon atoms detected in the product mixture after irradiation of the hexacoordinate diorganosilicon compounds **2-9**, **11** and **16**.

	$\delta(^{13}\text{C})_1$ ^[a]	$\delta(^{13}\text{C})_2$ ^[b]		$\delta(^{13}\text{C})_1$ ^[a]	$\delta(^{13}\text{C})_2$ ^[b]
2	65.5 ^[c]		7	65.5	64.3, 70.5
3	69.6 ^[c]		8	70.2	68.2-73.1 ^[c]
4	72.6	69.2 ^[d]	9	69.2 ^[d]	Other signals as for 8
5	73.1		11	70.1	69.2 ^[d] , 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.

Figure 1. Molecular structure of **4a** in the crystal. (Thermal ellipsoids at the 20% probability level, H-atoms omitted, selected atoms labeled). Selected bond lengths [Å] and angles [deg.]: Si1–O1 1.706(1), Si1–O2 1.716(1), Si1–N1 1.989(1), Si1–N2 1.738(1), Si1–C31 1.886(2), N1–C7 1.295(2), N2–C22 1.496(2), O1–Si1–N2 126.3(1), O1–Si1–C31 108.9(1), N2–Si1–C31 123.5(1), O2–Si1–N1 171.5(1). For comparison the corresponding bond lengths and angles in molecule **5a** in an isostructural crystal lattice: Si1–O1 1.711(1), Si1–O2 1.719(1), Si1–N1 1.987(1), Si1–N2 1.740(1), Si1–C31 1.889(2), N1–C7 1.295(2), N2–C22 1.495(2), O1–Si1–N2 126.1(1), O1–Si1–C31 109.6(1), N2–Si1–C31 123.0(1), O2–Si1–N1 171.7(1).

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** ($\delta^{29}\text{Si}$ = -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}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'PhArylN-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_2ArylN -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.

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 eA^{-3}). MO #102 represents the HOMO.

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 of a 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.

Scheme 3.

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 ^1H and ^{13}C NMR spectroscopically [17].

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)₂ (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 175.5(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), Si1–C37–C38 122.6(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 synthesized 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 ¹J_{SiF} = 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 ²⁹Si NMR spectrum, δ = -129.5 ppm, ¹J_{SiF} = 188 Hz), but from the presence of an intense triplet signal (δ = -187.0 ppm, ¹J_{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.

Scheme 5.

Figure 4. Molecular structures of **15** in a crystal of **15**.(CHCl₃)₂ (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 1.916(1), Si1–N2 1.926(1), Si1–F1 1.658(1), Si1–F2 1.678(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–Cl1 2.267(1), Si1–Cl2 2.226(1), N1–C7 1.303(2), N2–C22 1.307(2), O1–Si1–N2 1.783(1), O2–Si1–N1 1.770(1), Cl1–Si1–Cl2 174.1(1).

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 SiMe_3 substituted salen-type ligands proposed by Singh et al. [18], **12** comprises SiMe_3 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 Ph_2ECl_2 (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–C7 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 *mer-mer* coordination mode, as concluded from ¹³C and ¹H NMR spectroscopic data, which render the two CH₂ and CH₃ groups and the methylene protons of each CH₂ 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 emerging of a signal indicative of a Ph₂ArylN-substituted quaternary 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–N2 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 **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 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 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).

Scheme 6. Relative energies (kcal/mol) with respect to **SI**, **GE** and **SN**, respectively, which were set 0: **SIa** –21.0; **GEa** –13.9; **SN'** +4.8, **SNa** –8.3.

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 sp^2 -C-substituent was successful for the $SiPh_2$ -substitution pattern only, whereas competing rearrangements were encountered for a (ONNO)SiPhVi 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 leads to further 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 ¹H, ¹³C and ²⁹Si spectra. X-ray diffraction data were recorded on a BRUKER NONIUS X8 diffractometer with APEX II CCD detector using Mo K α radiation. The structures were solved by direct methods (SHELXS) and refined with full-matrix least-squares on F^2 . 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**.(CHCl₃)₂), CCDC-718480 (**12**), CCDC-718479 (**14**.toluene), CCDC-718484 (**15**.(CHCl₃)₂), CCDC-718487 (**15.o-C₆H₄(OH)₂**), 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 (λ_{max} = 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. 5 h (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 anaerobic 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 presumably do both suppress solvolysis noticeably and 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**: C₄₂H₄₂N₂O₄Si, M_r =666.87, T =296(2) K, monoclinic, space group $P2_1/n$, a =14.5474(5), b =15.0231(5), c =17.2716(6) Å, β =113.388(2)°, V =3464.5(2) Å³, Z =4, ρ_{calcd} =1.279 Mg m⁻³, μ (Mo K α)=0.114 mm⁻¹, $F(000)$ =1416, $2\theta_{\text{max}}$ =54.0°, 27597 collected reflections, 7547 unique reflections (R_{int} =0.0385), 444 parameters, S =1.052, R_1 =0.0431 ($I>2\sigma(I)$), wR_2 (all data)=0.1107, max./min. residual electron density +0.256/–0.342 eÅ⁻³. Crystal structure analysis of **5a**: C₄₂H₃₆N₂O₄Si, M_r =660.82, T =296(2) K, monoclinic, space group $P2_1/n$, a =14.3526(6), b =15.0411(5), c =17.1985(7) Å, β =112.836(1)°, V =3421.8(2) Å³, Z =4, ρ_{calcd} =1.283 Mg m⁻³, μ (Mo K α)=0.115 mm⁻¹, $F(000)$ =1392, $2\theta_{\text{max}}$ =56.0°, 33530 collected reflections, 8244 unique reflections (R_{int} =0.0347), 442 parameters, S =1.052, R_1 =0.0434 ($I>2\sigma(I)$), wR_2 (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 phenyldichlorosilane (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 PhCl₂Si-CH₂-CH₂-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): 0.03 (s, 9 H, Si-CH₃), 0.6 (m, 2 H, Me₃Si-CH₂), 1.2 (m, 2 H, PhCl₂Si-CH₂), 7.40–7.55 (m, 3 H), 7.65–7.75 (m, 2 H). ¹³C NMR (δ /ppm, CDCl₃): –2.3 (Si-CH₃), 7.6 (Me₃Si-CH₂), 13.7 (PhCl₂Si-CH₂), 128.3, 133.5 (Ph *o/m*), 131.5 (Ph *p*), 132.4 (Ph *i*). ²⁹Si NMR (δ /ppm, CDCl₃): 3.8 (CH₂-SiMe₃), 19.8 (CH₂-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 **10** (2.95 g, 10.7 mmol) was added dropwise, whereupon [Et₃NH]⁺Cl[–] precipitated. The resulting 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 dissolved in chloroform (35 mL). This solution was then heated to reflux and hexane (40 mL) was slowly added. This clear yellow solution was stored at 8°C for 5 days to yield **11**.(CHCl₃)₂ as yellow crystals, which were filtered, washed with a mixture of chloroform (2 mL) and hexane (4 mL) and were briefly dried in vacuo. Yield 4.50 g (4.87 mmol, 47 %) of compound **11**.(CHCl₃)₂ as yellow solid. C/H/N analysis found (%): C 56.02, H 4.91, N 3.19. Calcd. for C₄₃H₄₆N₂O₄Si₂Cl₆ (923.70) (%): C 55.89, H 5.02, N 3.03. ¹H NMR (δ /ppm, CDCl₃): –0.21 (s, 9 H, Si-CH₃), 0.6 (m, 2 H, Me₃Si-CH₂), 0.9 (m, 2 H, Ph(ONNO)Si-CH₂), 3.14 (m, 4 H, N-CH₂), 3.78 (s, 6 H, O-CH₃), 6.07 (dd, 2 H, 2.4 Hz, 8.8 Hz), 6.48 (d, 2 H, 2.4 Hz), 6.52 (d, 2 H, 8.8 Hz), 6.90–7.15 (mm, 7 H), 7.25–7.45 (m, 6 H), 7.65–7.70 (m, 2 H). ¹³C NMR (δ /ppm, CDCl₃): –1.9 (Si-CH₃), 14.8, 23.5 (Si-CH₂-CH₂-Si), 48.3 (N-CH₂-CH₂-N), 55.3 (OCH₃), 104.3, 106.1, 114.7, 124.7, 126.1, 126.3, 126.4, 128.9, 129.1, 129.2, 133.1, 134.5, 135.6, 163.9, 165.7, 166.0, 170.1. ²⁹Si NMR (δ /ppm, CDCl₃): 1.5, –169.3. Crystal structure analysis of **11**.(CHCl₃)₂: C₄₃H₄₆N₂O₄Si₂Cl₆, M_r =923.70, T =93(2) K, triclinic, space group $P-1$, a =12.9235(4), b =13.2011(4), c =30.1001(9) Å, α =83.339(2)°, β =80.573(2)°, γ =62.851(1)°, V =4502.7(2) Å³, Z =4, ρ_{calcd} =1.363 Mg m⁻³, μ (Mo K α)=0.478 mm⁻¹, $F(000)$ =1920, $2\theta_{\text{max}}$ =60.0°, 102690 collected reflections, 26200 unique reflections (R_{int} =0.0343), 1085 parameters, S =1.146, R_1 =0.0490 ($I>2\sigma(I)$), wR_2 (all data)=0.1630, max./min. residual electron density +1.144/–0.743 eÅ⁻³.

Synthesis of compound 12: In contrast to our previously reported method, [2a] this attempt allowed for the isolation of **12** as a crystalline solid: Ligand **1** (5.00 g, 10.4 mmol) and hexamethyldisilazane (2.52 g, 15.7 mmol) were placed in a 100 mL Schlenk flask and were stirred at 125 °C for 3 h to yield a clear yellowish solution (as expected the evolution of gas, NH₃, was observed). Within 2 days at ambient temperature compound **12** crystallized from this mixture. The solid was then stirred with a mixture of hexane (5 mL) and hexamethyldisilazane (5 mL), filtered off, washed with hexane (10 mL) and dried in vacuo to yield 5.80 g (9.28 mmol, 89 %) of compound **12** as colorless solid. Mp 135 °C, C/H/N analysis found (%): C 69.15, H 7.03, N 4.67. Calcd. for C₃₆H₄₄N₂O₄Si₂ (624.91) (%): C 69.19, H 7.10, N 4.48. ¹H NMR (δ /ppm, CDCl₃): 0.04 (s, 18 H, Si-CH₃), 3.76 (m, 4 H, N-CH₂), 3.82 (s, 6 H, O-CH₃), 6.42 (d, 2 H, 2.4 Hz), 6.5–6.6 (m, 2 H), 6.96 (d, 2 H, 8.4 Hz), 7.2–7.35 (m, 6 H), 7.56 (d, 4 H, 6.8 Hz). ¹³C NMR (δ /ppm, CDCl₃): 0.3 (Si-CH₃), 55.3 (OCH₃), 55.5 (N-CH₂), 105.7, 106.1, 121.0, 127.8, 128.0, 129.3, 130.3, 130.4, 140.7, 153.6, 160.3, 160.7, 166.1. ²⁹Si NMR (δ /ppm, CDCl₃): 19.8. Crystal structure analysis of **12**: Single crystals were obtained by recrystallization from hexane. C₃₆H₄₄N₂O₄Si₂, M_r =624.91, T =90(2) K,

monoclinic, space group $P2_1/c$, $a = 17.8374(6)$, $b = 16.3345(6)$, $c = 12.0348(4)$ Å, $\beta = 98.524(2)^\circ$, $V = 3467.8(2)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 1.197$ Mg m⁻³, $\mu(\text{Mo K}\alpha) = 0.142$ mm⁻¹, $F(000) = 1336$, $2\theta_{\text{max}} = 60.0^\circ$, 63330 collected reflections, 10104 unique reflections ($R_{\text{int}} = 0.0369$), 448 parameters, $S = 1.063$, $R_1 = 0.0785$ ($I > 2\sigma(I)$), wR_2 (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), 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 Me₃SiF nor precipitation of product), the solution was cooled to room temperature, some crystals (ca. 20 mg) of tetrabutylammonium fluoride were added and the solution was again heated to 60 °C, whereupon evolution of Me₃SiF 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, 88 %). C/H/N analysis found (%): C 71.78, H 5.21, N 4.89. Calcd. for C₃₆H₃₁N₂O₄SiF (602.73) (%): C 71.74, H 5.18, N 4.65. ¹H NMR (δ/ppm, CDCl₃): 3.1 – 3.4 (m, 4 H, N-CH₂), 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 (δ/ppm, CDCl₃): 47.7 (N-CH₂), 55.4 (OCH₃), 104.1, 107.3, 113.6, 125.8, 126.3, 126.5, 126.9, 128.9, 129.2, 129.3, 133.0, 134.3, 135.0, 159.0, 165.3, 165.9, 171.9. ²⁹Si NMR (δ/ppm, CDCl₃): -180.3 (d, ¹J_{SiF} 166 Hz).

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 (1.77 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 (9.86 mmol, 95 %). C/H/N analysis found (%): C 66.33, H 5.38, N 4.23. Calcd. for C₃₇H₃₄N₂O₄SiCl₂ (669.65) (%): C 66.36, H 5.12, N 4.18. ¹H NMR (δ/ppm, CDCl₃): 3.70 (s, 4 H, N-CH₂), 3.84 (s, 6 H, O-CH₃), 6.27 (dd, 2 H, 2.4 Hz, 9.2 Hz), 6.64 (d, 2 H, 9.2 Hz), 6.70 (d, 2 H, 2.4 Hz), 7.25–7.30 (m, 4 H), 7.45–7.55 (m, 6 H). ¹³C NMR (δ/ppm, CDCl₃): 47.8 (N-CH₂), 55.7 (OCH₃), 104.0, 109.3, 112.2, 126.2, 129.2, 129.8, 134.2, 134.6, 163.4, 167.1, 171.8. ²⁹Si NMR (δ/ppm, CDCl₃): -183.7. Crystal structure analysis of **14.toluene**: Single crystals were obtained from the reaction mixture. C₃₇H₃₄N₂O₄SiCl₂, $M_r = 669.65$, $T = 183(2)$ K, triclinic, space group $P-1$, $a = 9.8583(3)$, $b = 12.9594(4)$, $c = 14.0537(5)$ Å, $\alpha = 94.948(2)^\circ$, $\beta = 105.219(2)^\circ$, $\gamma = 102.616(2)^\circ$, $V = 1670.90(10)$ Å³, $Z = 2$, $\rho_{\text{calcd}} = 1.331$ Mg m⁻³, $\mu(\text{Mo K}\alpha) = 0.273$ mm⁻¹, $F(000) = 700$, $2\theta_{\text{max}} = 54.0^\circ$, 27801 collected reflections, 7292 unique reflections ($R_{\text{int}} = 0.0316$), 478 parameters, $S = 1.028$, $R_1 = 0.0335$ ($I > 2\sigma(I)$), wR_2 (all data) = 0.0892, max./min. residual electron density +0.274/−0.276 eÅ⁻³.

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 solid thus 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)₂** crystallized, which was isolated by decantation and briefly dried in vacuo. Yield: 0.47 g (0.60 mmol, 38 %) of colorless crystals. C/H/N analysis found (%): C 48.76, H 3.75, N 3.60. Calcd. for C₃₂H₂₈N₂O₄SiF₂Cl₆ (783.35) (%): C 49.06, H 3.60, N 3.58. ¹H NMR (δ/ppm, CDCl₃): 3.57 (s, 4 H, N-CH₂), 3.85 (s, 6 H, O-CH₃), 6.20 (dd, 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 (m, 4 H), 7.4 – 7.5 (m, 6 H). ¹³C NMR (δ/ppm, CDCl₃): 48.7 (N-CH₂), 55.5 (OCH₃), 104.1, 107.7, 113.0, 126.8, 129.1, 129.5, 134.2, 134.5, 164.6, 166.0, 171.7. ²⁹Si NMR (δ/ppm, CDCl₃): -187.0 (t, ¹J_{SiF} 174 Hz). Crystal structure analysis of **15.(CHCl₃)₂**: C₃₂H₂₈N₂O₄SiF₂Cl₆, $M_r = 783.35$, $T = 90(2)$ K, triclinic, space group $P-1$, $a = 10.1109(3)$, $b = 12.7146(4)$, $c = 14.6322(5)$ Å, $\alpha = 112.640(2)^\circ$, $\beta = 100.292(2)^\circ$, $\gamma = 91.155(2)^\circ$, $V = 1699.96(10)$ Å³, $Z = 2$, $\rho_{\text{calcd}} = 1.530$ Mg m⁻³, $\mu(\text{Mo K}\alpha) = 0.592$ mm⁻¹, $F(000) = 800$, $2\theta_{\text{max}} = 92.0^\circ$, 134572 collected reflections, 29432 unique reflections ($R_{\text{int}} = 0.0372$), 454 parameters, $S = 1.066$, $R_1 = 0.0361$ ($I > 2\sigma(I)$), wR_2 (all data) = 0.1079, max./min. residual electron density +0.710/−0.662 eÅ⁻³. Compound **15** proved stable towards catechol! From a 1:1-stoichiometric solution of **15.(CHCl₃)₂** and catechol (0.59 mmol each) in chloroform (3 mL) the “solvate” **15.o-C₆H₄(OH)₂** crystallized. Even upon heating this mixture to reflux for 15 min the ¹H and ²⁹Si NMR reveal the undisturbed co-existence of these two compounds without any sign of decomposition reactions. C/H/N analysis found (%): C 65.60, H 4.91, N 4.30. Calcd. for C₃₆H₃₂N₂O₆SiF₂ (654.73) (%): C 66.04, H 4.93, N 4.28. Crystal structure analysis of **15.o-C₆H₄(OH)₂**: C₃₆H₃₂N₂O₆SiF₂, $M_r = 654.73$, $T =$

90(2) K, triclinic, space group $P-1$, $a = 9.9652(2)$, $b = 12.9318(4)$, $c = 13.1290(3)$ Å, $\alpha = 97.778(2)^\circ$, $\beta = 111.920(2)^\circ$, $\gamma = 102.560(2)^\circ$, $V = 1487.59(7)$ Å³, $Z = 2$, $\rho_{\text{calcd}} = 1.462$ Mg m⁻³, $\mu(\text{Mo K}\alpha) = 0.145$ mm⁻¹, $F(000) = 684$, $2\theta_{\text{max}} = 50.0^\circ$, 14687 collected reflections, 5209 unique reflections ($R_{\text{int}} = 0.0593$), 432 parameters, $S = 0.978$, $R_1 = 0.0478$ ($I > 2\sigma(I)$), wR_2 (all data) = 0.1032, max./min. residual electron density +0.249/−0.342 eÅ⁻³.

Synthesis of compound 16: Diphenyldichlorogermane (3.50 g, 11.7 mmol) was added dropwise to a suspension of **1** (5.60 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 resulting solution, after removal of ca. 40 mL of the solvent under reduced pressure, was stored at 8 °C overnight, followed by filtration. 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** thus obtained were 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 %). C/H/N analysis found (%): C 62.44, H 4.52, N 3.35. Calcd. for C₄₃H₃₇N₂O₄GeCl₃ (%): C 62.62, H 4.52, N 3.40. ¹H NMR (δ/ppm, CDCl₃): 3.26 (s, 4 H, N-CH₂), 3.71 (s, 6 H, O-CH₃), 5.87 (dd, 2 H, 2.4 Hz, 9.2 Hz), 6.40 (m, 4 H), 7.0 – 7.8 (mm, 20 H). ¹³C NMR (δ/ppm, CDCl₃): 49.1 (N-CH₂), 55.1 (OCH₃), 105.3, 105.4, 114.9, 126.1, 126.2, 126.8, 128.9, 129.0, 133.2, 135.4, 136.3, 156.7, 165.3, 168.8, 173.1. From the filtrate (upon storage at 8 °C) some crystals of **16** had formed which were suitable for X-ray diffraction analysis. Crystal structure analysis of **16**: C₄₂H₃₆N₂O₄Ge, $M_r = 705.32$, $T = 93(2)$ K, monoclinic, space group $P2_1$, $a = 12.7812(10)$, $b = 7.1041(5)$, $c = 19.1238(16)$ Å, $\beta = 99.810(4)^\circ$, $V = 1711.0(2)$ Å³, $Z = 2$, $\rho_{\text{calcd}} = 1.369$ Mg m⁻³, $\mu(\text{Mo K}\alpha) = 0.941$ mm⁻¹, $F(000) = 732$, $2\theta_{\text{max}} = 50.8^\circ$, 24464 collected reflections, 6227 unique reflections ($R_{\text{int}} = 0.0517$), 442 parameters, $S = 1.017$, $R_1 = 0.0330$ ($I > 2\sigma(I)$), wR_2 (all data) = 0.0605, max./min. residual electron density +0.380/−0.408 eÅ⁻³.

Synthesis of compound 17: A solution of diphenyldichlorotin (4.50 g, 13.1 mmol) in THF (50 mL) was added dropwise to a suspension of **1** (6.15 g, 12.8 mmol) and triethylamine (3.0 g, 30 mmol) in THF (100 mL), which was stirred at ambient temperature. After 3 h the [Et₃NH]⁺Cl[−] precipitate was filtered off and washed with THF (15 mL). From the combined filtrate and washings the solvent was removed under reduced pressure. The yellow solid residue was recrystallized from chloroform (25 mL) to yield **17** as a yellow crystalline powder, which was filtered off, washed with chloroform (10 mL) and dried in vacuo. Yield: 6.70 g (8.92 mmol, 70 %). C/H/N analysis found (%): C 67.05, H 4.97, N 3.74. Calcd. for C₄₂H₃₆N₂O₄Sn (%): C 67.13, H 4.83, N 3.73. ¹H NMR (δ/ppm, CDCl₃): 3.22 (s, 4 H, N-CH₂), 3.69 (s, 6 H, O-CH₃), 5.8 – 7.9 (mm, 26 H). ¹³C NMR (δ/ppm, CDCl₃): 51.6 (N-CH₂), 55.1 (OCH₃), 104.9, 105.4, 115.4, 126.4, 127.5, 127.7, 128.8, 128.9, 135.0, 136.2, 137.0, 151.0, 165.1, 171.5, 176.8. ¹¹⁹Sn NMR (δ/ppm, CDCl₃): -555.0. Crystal structure analysis of **17**: C₄₂H₃₆N₂O₄Sn, $M_r = 751.42$, $T = 93(2)$ K, triclinic, space group $P-1$, $a = 11.677(4)$, $b = 12.902(6)$, $c = 14.066(11)$ Å, $\alpha = 100.820(17)^\circ$, $\beta = 105.03(2)^\circ$, $\gamma = 116.520(13)^\circ$, $V = 1714.7(17)$ Å³, $Z = 2$, $\rho_{\text{calcd}} = 1.455$ Mg m⁻³, $\mu(\text{Mo K}\alpha) = 0.791$ mm⁻¹, $F(000) = 768$, $2\theta_{\text{max}} = 54.0^\circ$, 15393 collected reflections, 7194 unique reflections ($R_{\text{int}} = 0.0286$), 442 parameters, $S = 1.036$, $R_1 = 0.0296$ ($I > 2\sigma(I)$), wR_2 (all data) = 0.0698, max./min. residual electron density +0.679/−0.401 eÅ⁻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 **SI**, **GE**, **SN**, **SN'**, **SIa**, **GEa**, **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/SDD for **SI**, **GE**, **SN**, **SN'**, **SIa**, **GEa** and **SNa**.

Acknowledgements: This work was supported by Deutsche Forschungsgemeinschaft (DFG).

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