Syntheses of Allyl- and 3-Silylpropyl-substituted Salen-like Tetradentate Ligands *via* Hypercoordinate Silicon Complexes

Jörg Wagler and Gerhard Roewer

Institut für Anorganische Chemie, Technische Universität Bergakademie Freiberg, Leipziger Str. 29, D-09596 Freiberg, Germany

Reprint requests to Dr. Jörg Wagler. Fax: (+49) 3731 39 4058.
E-mail: joerg.wagler@chemie.tu-freiberg.de

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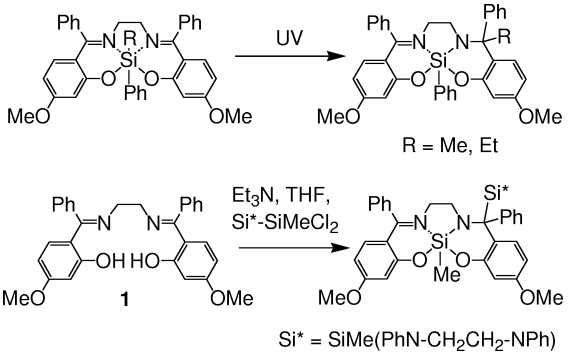
The reaction of allylchlorosilanes ($AllSiCl_3$, $AllSiPhCl_2$) with the tetradentate salen-like ligand **1**, *o*-HO-*p*-MeO-C_6H_3-C(Ph)=N-$(CH_2)_2$-N=C(Ph)-C_6H_3-*p*-OMe-*o*-OH, yields pentacoordinate silicon complexes of an allyl-substituted ligand system (*o*-O-*p*-MeO-C_6H_3-C(Ph)=N-$(CH_2)_2$-N-C(Ph,All)-C_6H_3-*p*-OMe-*o*-O)SiR (**2a**: R = Ph, **3**: R = Cl). The allyl shift step involved in the formation of **2a** and **3** probably occurs *via* an intermediate hexacoordinate silicon complex. This reaction is diastereoselective. The missing diastereomer of **2** (**2b**) was prepared using an alternative synthesis route, which starts from the trimethylsilyl derivative of ligand **1** *o*-Me_3SiO-*p*-MeO-C_6H_3-C(Ph)=N-$(CH_2)_2$-N=C(Ph)-C_6H_3-*p*-OMe-*o*-$OSiMe_3$. The diastereomers of **2** obtained from modified reaction pathways give rise to suggestions about the mechanism of formation of these complexes.

Further functionalization of the allyl-substituted ligand system of **3** was carried out by hydrosilylation with $HSiCl_3$ to yield complex **4** (*o*-O-*p*-MeO-C_6H_3-C(Ph)=N-$(CH_2)_2$-N-C(Ph)[$(CH_2)_3$-$SiCl_3$]-C_6H_3-*p*-OMe-*o*-O)SiCl.

Key words: Allyl, Chelate, Hypercoordination, Rearrangement, Silicon

Introduction

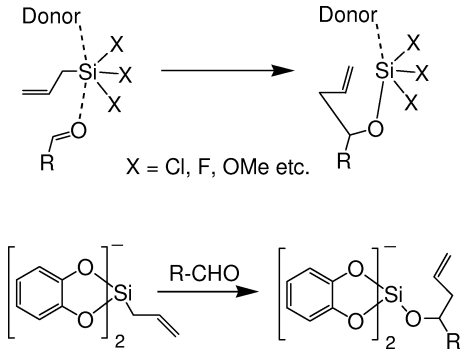
Recently we reported the syntheses of hexacoordinate diorganosilanes with salen-type ligands [1]. Some of these complexes were irradiated with UV light to undergo a 1,3-shift reaction of one organic substituent from the Si atom to an imine carbon atom to yield pentacoordinate Si complexes with a modified tetradentate ligand system (Scheme 1, top) [1a]. Surprisingly, a Si-Si bond was cleaved much easier than a Si-C bond and a similar 1,3-shift reaction of a silyl substituent took place without irradiation (Scheme 1, bottom) [2].



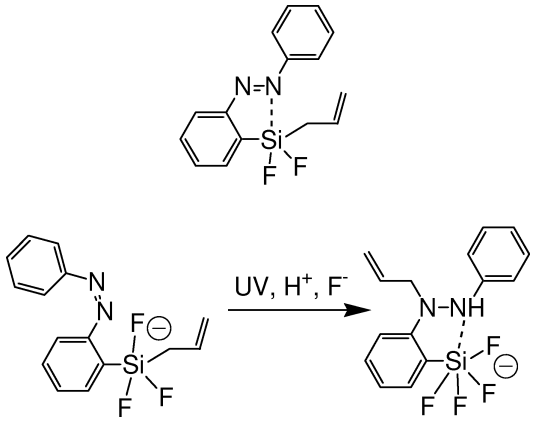
Scheme 1.

This behavior tempted us to investigate more Si-E (herein: E = C) cleavage and rearrangement reactions in the coordination sphere of salen-type ligands. It is known that Si-C bonds to allyl substituents may be cleaved to transfer the allyl moiety onto carbonyl compounds (Scheme 2). In such reactions the Si-C bond gets activated by hypercoordination of the Si atom. Many efforts have been made to employ this "Sakurai reaction" in organic syntheses. Thus, various allylsilanes with tetracoordinate Si-atoms (*e. g.* allyltrimethoxy-, allyltrichloro-, allyltrifluorosilanes) as well as pentacoordinate Si complexes proved to be suitable reagents [3]. Intermediate hypercoordination of their Si atom is usually achieved either by interaction with additional donors (Scheme 2, top) or by the preorganized hypercoordinate Si-environment (Scheme 2, bottom). The O atom of the carbonyl moiety is also one donor at the Si atom.

The organic target molecules – allylated methanols – were isolated, and also the structures of some intermediate hypercoordinate silicon complexes, products of the allyl shift, have been characterized [3]. Nevertheless, the question arises whether hexacoor-



Scheme 2.



Scheme 3.

dination of the Si atom is essential to induce such allyl rearrangement reactions or not. Till now, there are only two crystal structures of hypercoordinate allylsilanes. One of them represents the allylsilatrane molecule which can not undergo any intramolecular rearrangement reactions due to the lack of unsaturated C=X moieties [4]. The other one is a pentacoordinate allyldifluorosilane with an azobenzene ligand which generally offers the possibility for allyl rearrangement (Scheme 3, top). Recently, the photochemically shifted hexacoordination of an allylfluorosilane and the subsequent allylation of the azobenzene moiety were reported by Kano *et al.* (Scheme 3, bottom) [4]. Photochemical activation, however, may contribute to the ease of organyl shift reactions as we have recently shown [1a]. Thus, N-donor ligands might still provide access to hypercoordinate allylsilanes which do not undergo rearrangement reactions unless activated otherwise (*e. g.* by UV irradiation). Does the C=N moiety offer some possibility to create penta- or even hexacoordinate allylsilanes without any rearrangement reaction?

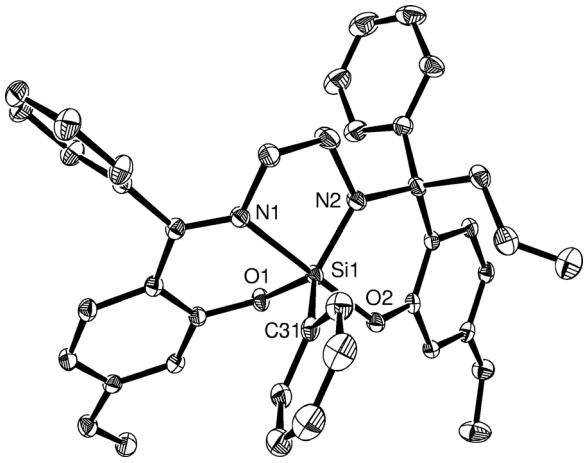
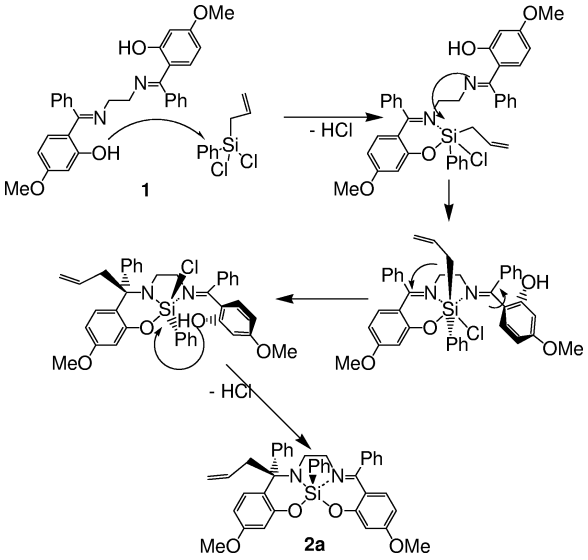


Fig. 1. Molecular structure of **2a** (ORTEP plot with 30% probability ellipsoids, hydrogen atoms omitted).



Scheme 4.

Results and Discussion

The route which led to various hexacoordinate diorganosilanes (Scheme 1, top) was applied to ligand **1** and allylphenyldichlorosilane. The rearrangement of the allyl group to an imine carbon atom took place without further activation. Surprisingly, the reaction product consisted of only one diastereomer – complex **2a**. Its molecular structure is given in Fig. 1.

The allyl group as well as the Si-bonded phenyl group are situated on the same side of the tetradentate ligand. This diastereoselectivity is assumed to originate from a mechanism depicted in Scheme 4. A sim-

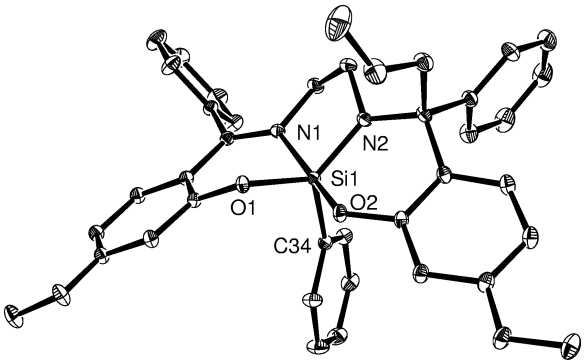


Fig. 2. Molecular structure of **2b** in a crystal of **2b** · $2CHCl_3$ in space group $P2_1$ (ORTEP plot with 50% probability ellipsoids, hydrogen atoms and chloroform molecules omitted).

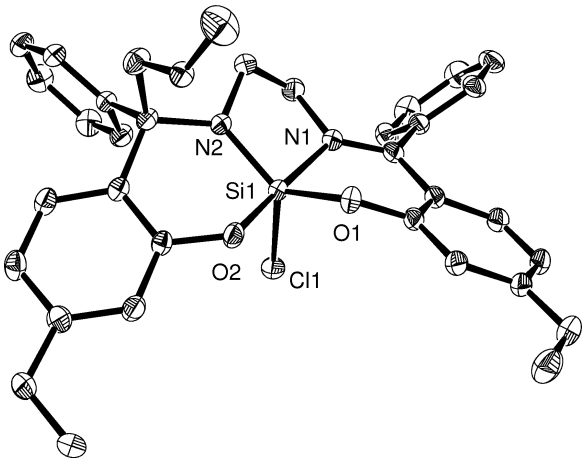


Fig. 3. Molecular structure of **3** (ORTEP plot with 30% probability ellipsoids, hydrogen atoms omitted). The allyl group is disordered over three sites (7 : 2 : 1 ratio), the dominating position is depicted only.

ilar pathway was suggested for the 1,3-silyl-shift in Scheme 1, bottom [2a]. After initial substitution of one of the silane's two chlorine atoms for an oxygen atom, a stepwise chelation with the salen-like ligand leads to a hexacoordinate silicon atom. In this way, the Si-C(allyl) bond appears to be sufficiently activated for the rearrangement. After the 1,3-allyl-shift a rear attack of the ligand's second oxygen atom diastereoselectively produces **2a**.

Changes of the ligand educt used should lend support to this hypothesis. Trimethylsilyl derivatives of various chelating ligands proved to be suitable starting materials for the syntheses of hypercoordinate silicon complexes [6]. Thus, **1** was silylated to yield **1-(TMS)$_2$** [6a] and this compound was also reacted with allylphenyldichlorosilane. After initial substitution of one chlorine atom, the next few steps should take place according to Scheme 4. The rear attack of the second O atom, however, should not be preferred in this case. Indeed, both diastereomers of the product, **2a** and **2b**, are formed in a ratio of about 2 : 3 under the conditions given in the experimental section. X-ray structure analyses of crystals of **2b** · $2CHCl_3$ revealed the formation of two polymorphous modifications. Despite the different space groups ($P2_1$ and $P2_1/n$), both molecular structures of **2b** differ scarcely from each other. Therefore, only the molecular structure of **2b** which was found in the space group $P2_1$ is discussed and depicted in Fig. 2.

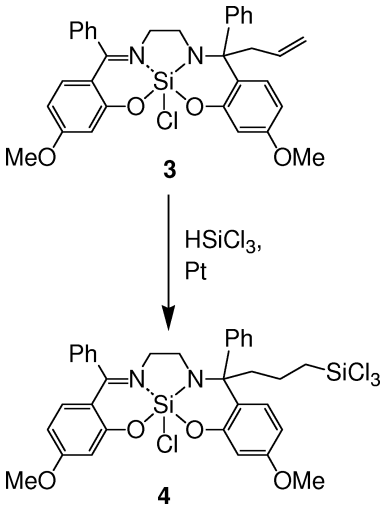
A similar reaction of **1-(TMS)$_2$** with allyltrichlorosilane diastereoselectively yielded **3**. Its molecular structure is given in Fig. 3.

The origin of the diastereoselective formation of **3** is difficult to grasp. As known from other experiments, halide exchange and configurational inversion are generally possible [7].

In complexes **2a**, **2b** and **3** the Si atoms have a more or less distorted trigonal bipyramidal coordination (**2a**: 93.5% TBP; **2b**: 64.8% TBP; **3**: 70.6% TBP). In the chlorosilicon complex **3** the axial Si-N and Si-O bonds [1.947(2) and 1.692(1) Å] are significantly shorter than those in the phenylsilicon complexes **2a** [2.009(1) and 1.715(1) Å] and **2b** [1.994(1), 1.732(1) Å]. The electron withdrawal by the Cl atom is expected to be responsible for these bond contractions in **3**. The equatorial Si-N and Si-O bonds, however, are not so much influenced: **3** [1.717(2) and 1.688(1) Å] as compared to **2a** [1.728(1) and 1.697(1) Å] and **2b** [1.739(1), 1.709(1) Å]. Referring to **2a**, the slightly longer equatorial Si-N and Si-O bonds in **2b** should be a result of the equatorial N-Si-O bond angle widening.

As shown in a related study [8], reaction between the tridentate ligand *o*-HO-*p*-MeO-C_6H_3-C(Ph)=N-(*o*-C_6H_4)-OH and allylphenyldichlorosilane yielded the pentacoordinate silicon complex (Ph)(All)Si[*o*-O-*p*-MeO-C_6H_3-C(Ph)=N-(*o*-C_6H_4)-O] still featuring an allyl substituted Si-atom. Thus, one can conclude that the hexacoordination of the Si-atom, which can be realized with a tetradentate salen-like ligand such as **1**, should be essential for the allyl shifts to the C=N moieties in the cases given above.

Hydrosilylation of the allyl moiety's C=C bond should be generally possible in complexes **2** and **3**. Only **3** as a representative example was reacted with trichlorosilane in the presence of a platinum cata-



Scheme 5.

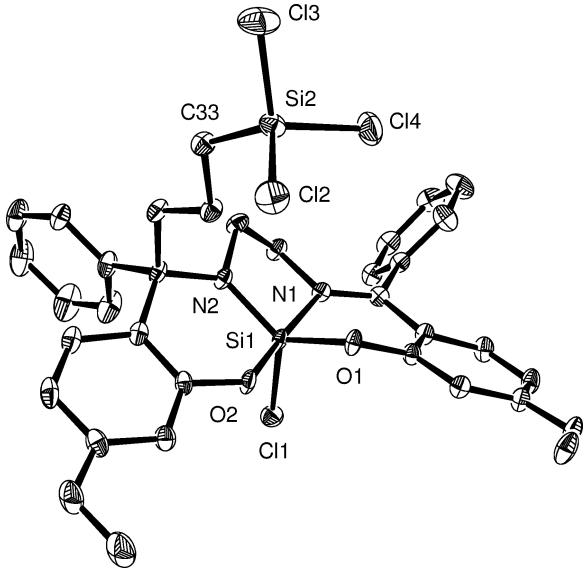
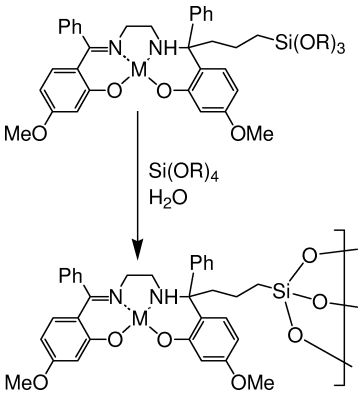


Fig. 4. Molecular structure of **4** in a crystal of **4** · 1.5$CHCl_3$ (ORTEP plot with 50% probability ellipsoids, hydrogen atoms and chloroform molecules omitted).

lyst to yield **4** (Scheme 5). Crystals of **4** suitable for X-ray analysis were obtained from chloroform/hexane (Fig. 4).

The arrangement of the salen-like ligand around the Si atom is hardly changed in consequence of the transformation from **3** into **4**. The Si atom is still situated in a distorted trigonal bipyramidal coordination sphere, only the extent of distortion is slightly changed (**3**: 70.6% TBP, **4**: 74.9% TBP). The C_3Si-chain of the trichlorosilylpropyl moiety has a staggered conformation and there is no discernible disorder of the molecule.



Scheme 6.

This crystal structure, however, is complex because it involves chloroform molecules (**4** · 1.5 $CHCl_3$), one of them being fourfold disordered and the other one (0.5 $CHCl_3$) twofold in positions close to a centre of symmetry.

Complex **4** is expected to yield trimethoxysilyl-substituted salen-derived ligands upon solvolysis with methanol [1a]. Modified routes to hydrosilylation products (*e. g.* addition of trimethoxysilane, methyldichlorosilane *etc.*) of complexes such as **2** or **3** can provide a variety of silyl-substituted tetradentate ligand systems which offer the possibility to be fixed in silica gels *via* the sol-gel route (Scheme 6). Therefore, the allyl rearrangement reactions presented herein represent more than a basic study of reactivities of hypercoordinate allylsilanes. They open a convenient route to 3-silylpropyl substituted tetradentate ligand systems which may be useful tools to fix metal ions in silica gels for various purposes such as heterogeneous catalysis.

Conclusions

Hypercoordinate allylsilanes have been shown to undergo 1,3-allyl-shift reactions in the coordination sphere of salen-type ligands without additional activation. This rearrangement reaction gives access to silicon complexes of mono-allyl substituted $\langle ONN'O' \rangle$ tetradentate ligands. Their allyl moieties can be further modified *via* hydrosilylation. Analogously to a previously published procedure [1a], subsequent alcoholysis of the hydrosilylation products should give rise to 3-alkoxysilylpropyl functionalized tetradentate ligands which may be linked to silica gel *via* sol-gel processes. Investigations of the coordination behavior of those ligands towards other metal ions are currently under way.

Experimental Section

All manipulations were carried out under an inert atmosphere of dry argon. Triethylamine was distilled from calcium hydride and stored over molecular sieve 3 Å. Chloroform (stabilized with amylene) was dried over molecular sieve 3 Å. Hexane, THF and toluene were distilled from sodium/benzophenone and stored over sodium wire. NMR spectra were recorded on a BRUKER DPX 400 instrument ($CDCl_3$ solutions with TMS as internal standard). Elemental analyses were carried out on a Foss Heraeus CHN-O-Rapid.

***1**:* Ligand **1** was prepared according to standard procedures for preparation of salen-type ligands. In brief: Reaction of 2-hydroxy-4-methoxybenzophenone (70.0 g, 306 mmol) and ethylenediamine (9.21 g, 153 mmol) in refluxing isopropanol for 6 h afforded **1** as a pale yellow powder. The solution was cooled to r. t., the solid product was filtered off with suction, washed with isopropanol and dried in air. Yield: 67.0 g (140 mmol, 92%).

***2a**:* In thf (120 mL) ligand **1** (7.00 g, 14.6 mmol) and triethylamine (4.00 g, 39.6 mmol) were stirred at r. t. and allylphenyldichlorosilane (3.30 g, 15.2 mmol) was added dropwise. The resulting mixture was stored at 7 °C over night. Then the precipitated hydrochloride was filtered off and washed with thf (30 mL). The volatiles were removed from the filtrate under vacuum to yield a solid residue which was dissolved in chloroform (8 mL). A ^{29}Si NMR spectrum of the crude product revealed the formation of one silicon complex only. Upon addition of *n*-hexane (22 mL) to this solution small amounts of a yellow solid precipitated which were filtered off. More hexane (9 mL) was added to the filtrate, whereupon a pale yellow crystalline solid precipitated which was filtered off after 1 h, washed with a chloroform/hexane mixture 1 : 4 (10 mL) as well as with hexane (5 mL) and dried in vacuum. Yield: 6.55 g (10.5 mmol, 72%). Crystals for X-ray analysis were grown from a mixture of chloroform and hexane. – ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.20-3.50$ (m, 6H, N-CH_2CH_2-N, CH_2-CH=CH_2), 3.73, 3.84 (2s, 6H, O-CH_3), 5.10 (m, 2H, CH=CH_2), 6.04 (m, 1H, CH=CH_2), 6.20 – 7.75 (m, 21H, ar). – ^{13}C NMR (101 MHz, $CDCl_3$): $\delta = 42.7$, 43.6, 48.0 (N-CH_2CH_2-N, CH_2-CH=CH_2), 55.1, 55.7 (O-CH_3), 67.9 (*C*-Ar,Ph,All,N), 103.9, 105.2, 105.7, 108.8, 113.9, 116.6, 124.7, 126.0, 127.2, 127.3, 127.9 (2×), 128.0, 128.3, 128.7, 128.8, 129.7, 130.0, 133.0 (2×), 133.1, 136.2, 143.9, 148.5 (ar), 157.1, 159.1, 162.1, 165.2, 168.0 (ar C-O, C=N). – ^{29}Si NMR (79 MHz, $CDCl_3$): $\delta = -116.9$. – $C_{39}H_{36}N_2O_4Si$ (624.81): calcd. C 74.97, H 5.81, N 4.48; found C 74.85, H 5.97, N 4.75.

***2b**:* The trimethylsilyl derivative of **1** [6a] (6.50 g, 10.4 mmol) was dissolved in toluene (75 mL) and allylphenyldichlorosilane (2.40 g, 11.1 mmol) was added at r. t. The solution was stirred under reflux for 2 h, cooled to r. t. and filtered. The volatiles of the filtrate were removed under vacuum and the solid product was dissolved in chloroform (8 mL). A ^{29}Si NMR spectrum of the crude product revealed the formation of two silicon complexes, **2a** and **2b** in 2 : 3 ratio. After addition of hexane (13 mL) and a seed crystal of **2a**, compound **2a** crystallized (1.20 g, *ca.* 1.9 mmol, 18%), together with a few crystals of **2b** · $2CHCl_3$ ($P2_1/n$). Further addition of chloroform (1.5 mL) and hexane (1.5 mL) to the filtrate and storage at 7 °C yielded a fraction of crystals which consisted of almost pure **2b** · $2CHCl_3$ and were suitable for NMR and X-ray analysis ($P2_1$). Yield: 1.25 g (*ca.* 1.5 mmol, 14%). – ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.45-3.50$ (m, 6H, N-CH_2CH_2-N, C-CH_2-CH=CH_2), 3.67, 3.86 (2s, 6H, O-CH_3), 5.08 (m, 2H, CH=CH_2), 6.20 – 7.70 (m, 22H, ar, CH=CH_2). – ^{13}C NMR (101 MHz, $CDCl_3$): $\delta = 43.2$, 43.8, 51.6 (N-CH_2CH_2-N, CH_2-CH=CH_2), 55.0, 55.8 (O-CH_3), 68.8 (*C*-Ar,Ph,All,N), 104.0, 104.7, 105.9, 109.0, 114.0, 116.7, 124.6, 126.2, 127.1, 127.2, 127.7, 127.8, 128.2, 128.3, 128.7, 128.8, 130.0, 130.1, 132.8, 133.7, 134.0, 135.3, 142.8, 150.1 (ar), 156.8, 158.9, 162.5, 165.5, 170.0 (ar C-O, C=N). – ^{29}Si NMR (79 MHz, $CDCl_3$): $\delta = -114.9$. – $C_{41}H_{38}N_2O_4SiCl_6$ (863.57): calcd. C 57.03, H 4.44, N 3.24; found C 58.36, H 4.47, N 3.61. The slightly higher C/H/N contents result from a loss of chloroform from the crystals.

***3**:* The trimethylsilyl derivative of **1** [6a] (13.0 g, 20.8 mmol) was dissolved in toluene (150 mL). Allyltrichlorosilane (3.80 g, 21.6 mmol) was added at 45 °C and the solution was heated ro reflux for 15 min. The solution was cooled to r. t., hexane (60 mL) was added, and the solution was stored at 7 °C for 2 weeks. The solid product was then filtered off, washed with hexane (20 mL) and dried in vacuum. Yield: 9.75 g (16.7 mmol, 80.5%), beige crystalline powder. – ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.40-3.55$ (m, 6H, N-CH_2CH_2-N, C-CH_2-CH=CH_2), 3.71, 3.88 (2s, 6H, O-CH_3), 5.12 (m, 2H, CH=CH_2), 6.00 (m, 1H, CH=CH_2), 6.20 – 7.70 (mm, 16H, ar). – ^{13}C NMR (101 MHz, $CDCl_3$): $\delta = 42.8$, 43.9, 50.1 (N-CH_2CH_2-N, CH_2-CH=CH_2), 55.1, 55.9 (O-CH_3), 69.3 (*C*-Ar,Ph,All,N), 103.4, 104.6, 107.2, 110.2, 113.1, 117.3, 123.1, 126.5, 127.4, 127.7, 128.1, 128.2, 128.8, 129.0, 129.5, 130.1, 130.5, 133.2, 133.4, 134.5, 149.7 (ar), 155.1, 159.0, 161.6, 166.0, 170.2 (ar C-O, C=N). – ^{29}Si NMR (79 MHz, $CDCl_3$): $\delta = -122.8$, (79 MHz, CP/MAS) $\delta_{iso} = -118.9$. – $C_{33}H_{31}N_2O_4SiCl$ (583.16): calcd. C 67.97, H 5.36, N 4.80; found C 67.17, H 5.55, N 4.74.

***4**:* $H_2PtCl_6 \cdot 6H_2O$ (60 mg) was dissolved in 5 drops of isopropanol plus THF (1 mL) and Zn powder (40 mg) was added. After shaking for 5 min, this catalyst was added to a stirred mixture of **3** (3.40 g, 5.84 mmol) with trimethylchlorosilane (10 mL) at r. t. After 5 min trichlorosilane (2.1 g, 15.5 mmol) was added. After addition of chloroform (20 mL) **3** began to dissolve. The reaction mix-

Table 1. Data of crystal structure determination and refinement of **2a**, **2b**, **3** and **4**.

Compound	**2a**	**2b** · 2 $CHCl_3$	**3**	**4** · 1.5 $CHCl_3$
Empirical formula	$C_{39}H_{36}N_2O_4Si$	$C_{41}H_{38}Cl_6N_2O_4Si$	$C_{33}H_{31}ClN_2O_4Si$	$C_{34.5}H_{33.5}Cl_{8.5}N_2O_4Si$
T [K]	203(2)	93(2)	203(2)	93(2)
Crystal system	monoclinic	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$	$P2_1$	$P2_1/n$	$P\bar{1}$
a [Å]	12.8764(2)	10.2052(4)	12.2879(2)	9.7664(10)
b [Å]	12.8109(2)	19.4949(7)	16.0017(3)	11.6844(14)
c [Å]	19.9637(3)	11.0631(4)	15.9484(3)	18.734(2)
α [°]	90	90	90	73.836(3)
β [°]	101.618(1)	109.267(2)	109.309(1)	83.007(3)
γ [°]	90	90	90	81.702(3)
Z, V [Å^3]	4, 3225.71(9)	2, 2077.72(13)	4, 2959.49(9)	2, 2024.3(4)
ρ_{calc} [g cm^{-3}]	1.287	1.380	1.309	1.473
μ [mm^{-1}]	0.118	0.485	0.210	0.689
$F(000)$	1320	892	1224	918
Crystal size [mm^3]	0.33×0.30×0.25	0.60×0.40×0.20	0.45×0.25×0.17	0.40×0.20×0.03
$2\theta_{max}$ [°]	50	80	50	53
Index ranges	$-15 \le h \le 15$, $-15 \le k \le 13$, $-23 \le l \le 23$	$-18 \le h \le 18$, $-35 \le k \le 35$, $-19 \le l \le 14$	$-13 \le h \le 14$, $-17 \le k \le 19$, $-18 \le l \le 16$	$-12 \le h \le 12$, $-14 \le k \le 14$, $-23 \le l \le 23$
Reflections collected, R_{int}	33515, 0.0305	86061, 0.0205	30091, 0.0316	31986, 0.0296
Independent reflections	5688	25563	5205	8363
Parameters	416	488	395	538
R Indices [$I \ge 2\sigma(I)$]	$R_1 = 0.0333$, $wR_2 = 0.0905$	$R_1 = 0.0299$, $wR_2 = 0.0806$	$R_1 = 0.0371$, $wR_2 = 0.1007$	$R_1 = 0.0497$, $wR_2 = 0.1462$
R Indices (all data)	$R_1 = 0.0431$, $wR_2 = 0.0939$	$R_1 = 0.0337$, $wR_2 = 0.0826$	$R_1 = 0.0516$, $wR_2 = 0.1057$	$R_1 = 0.0660$, $wR_2 = 0.1553$
Largest diff. peak and hole [e Å^{-3}]	0.264, −0.292	0.941, −0.623	0.289, −0.255	0.663, −0.883

ture was stirred for 3 d, then the catalyst was filtered off and the volatiles were removed from the filtrate under reduced pressure. The solid product was dissolved in chloroform (5.5 mL) and heated to 45 °C. When hexane (7.5 mL) was added, small amounts of oily drops separated out of the solution. The drops were allowed to settle down at r. t. and the clear solution was transferred into another Schlenk flask. Upon storage at −20 °C white crystals of **4** · 1.5$CHCl_3$ formed the mother liquor of which was decanted off after 1 d. The crystals were dried in vacuum. Yield: 3.30 g (3.67 mmol, 63%), beige crystalline powder. (Prior to separation from the mother liquor some crystals were picked out for X-ray analysis). – ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.30-3.55$ (m, 10H, N-CH_2CH_2-N, C-$(CH_2)_3$-$SiCl_3$), 3.73, 3.88 (2s, 6H, O-CH_3), 6.20 – 7.70 (m, 16H, ar). – ^{13}C NMR (101 MHz, $CDCl_3$): $\delta = 17.0$ (CH_2-$SiCl_3$), 24.5 (CH_2-CH_2-$SiCl_3$), 40.6, 42.9, 50.0 (N-CH_2CH_2-N, CH_2-$(CH_2)_2SiCl_3$), 55.1, 55.9 (O-CH_3), 69.4 (*C*-Ar,Ph,$(CH_2)_3SiCl_3$,N), 103.5, 104.6, 107.2, 110.2, 113.0, 122.7, 126.5, 127.4, 127.5, 128.1, 128.3, 128.8, 129.0, 129.9, 130.6, 133.2 (2×), 149.8 (ar), 155.2, 159.0, 161.5, 166.1, 170.1 (ar C-O, C=N). – ^{29}Si NMR (79 MHz, $CDCl_3$): $\delta =$ 13.3, −122.7. – $C_{34.5}H_{33.5}N_2O_4Si_2Cl_{8.5}$ (897.68): calcd. C 46.16, H 3.76, N 3.12; found C 50.22, H 4.23, N 3.58. The crystals readily loose chloroform: **4** · 0.75 $CHCl_3$: $C_{33.75}H_{32.75}N_2O_4Si_2Cl_{6.25}$ (808.14): calcd. C 50.16, H 4.08, N 3.47; found C 50.22, H 4.23, N 3.58.

X-ray structure analyses

X-ray structure data were recorded on a Bruker-Nonius-X8-APEX2-CCD diffractometer with MoK_α-radiation ($\lambda =$ 0.71073 nm) and semi-empirical absorption correction (SADABS). The structures were solved with Direct Methods (SHELXS-97) and refined by full-matrix least-squares methods (refinement on F^2 against all reflections with SHELXL-97). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in idealized positions and refined isotropically. Selected data of structure determination and refinement are presented in Table 1. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-611915 (**2a**), CCDC-611914 (**2b** · 2$CHCl_3$ in $P2_1$), CCDC-611913 (**3**), and CCDC-611916 (**4** · 1.5$CHCl_3$). The crystal structure of **2b** · 2$CHCl_3$ in $P2_1/n$, which is not further discussed, has also been deposited (CCDC-611917). Copies of the data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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