Neutral Pentacoordinate Silicon(IV) Complexes with Silicon–Chalcogen (S, Se, Te) Bonds

Bastian Theis, Stefan Metz, Christian Burschka, Rüdiger Bertermann, Stefan Maisch, and Reinhold Tacke*^[a]

Dedicated to Professor Helmut Werner on the occasion of his 75th birthday

Abstract: The neutral pentacoordinate silicon(IV) complexes 1 (SiS₂ONC skeleton), 2 (SiSeSONC), 3 (SiTeSONC), 6/9 (SiSe₂O₂C), 7 (SiSe₂S₂C), and 8/10 (SiSe₄C) were synthesized and structurally characterized by using single-crystal X-ray diffraction and multinuclear solid-state and solution-state (except for 6–9) NMR spectroscopy. With the synthesis of compounds 1–3 and 6–10, it has been demonstrated that pentacoordinate silicon compounds with soft chalcogen ligand atoms (S, Se, Te) can be stable in the solid state and in solution.

Introduction

Small, strongly electronegative (hard) ligand atoms, such as fluorine, oxygen, nitrogen, and carbon, are generally regarded to be ideal candidates for pentacoordination of the hard silicon(IV) coordination center.^[1] However, pentacoordinate silicon compounds with chloro or bromo ligands have also been described in the literature (see for example, ref. [2]), and recently, we have even succeeded in synthesizing a pentacoordinate silicon(IV) complex that contains a soft iodo ligand.^[2d] In addition, there are also a few reports on pentacoordinate silicon compounds with Si-P^[3] or Si-S bonds.^[2d,4] Obviously, contrary to the widely held view, the hard silicon(IV) coordination center also tolerates soft ligand atoms. We have now succeeded in synthesizing a further series of novel pentacoordinate silicon(IV) complexes with soft ligand atoms, compounds 1 (two Si-S bonds), 2 (one Si-S and one Si-Se bond), and 3 (one Si-S and one Si-Te bond), showing that even soft selenium and tellurium ligand atoms are tolerated. Pentacoordinate silicon compounds with Si-Se and Si-Te bonds have not previously been reported.^[5] Compounds 2 (SiSeSONC skeleton) and 3 (SiTeSONC skeleton) contain five different ligand atoms in the silicon coor-

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dination sphere. Most surprisingly, the oxygen analogue of 2 (Se/O exchange) and 3 (Te/O exchange), compound 4, could not be synthesized. Although 4 contains a hard oxygen ligand atom instead of the soft selenium (2) or tellurium ligand atom (3), we were not able to prepare the pentacoordinate silicon complex 4; instead, we obtained the isomeric tetracoordinate silicon compound 5.



In our search for novel Si coordination polyhedra with soft ligand atoms, we have also succeeded in synthesizing the zwitterionic λ^5 Si-silicon(IV) complexes 6 and 9 (SiSe₂O₂C skeletons), 7 (SiSe₂S₂C skeleton), and 8 and 10 (SiSe₄C skeletons). The synthesis of these compounds was realized by using the "zwitterion trick" (in this context, see ref. [4c]). Compounds 8 and 10 are especially remarkable as they contain one carbon ligand atom and four soft selenium



ligand atoms bound to the hard silicon(IV) coordination center, and **10** is even stable in solution.

Results and Discussion

Syntheses: Compounds **1** and **2** were synthesized according to Scheme 1 by treating the pentacoordinate chlorosili-



Scheme 1. Syntheses of compounds 1-3.

con(IV) complex $11^{[2d]}$ with one molar equivalent of benzenethiol or benzeneselenol, respectively, and one molar equivalent of triethylamine to give the crystalline solids $1 \cdot CH_3CN$ (74% yield) and $2 \cdot CH_3CN$ (77% yield). Alternatively, compound $1 \cdot CH_3CN$ could also be prepared by treating 11 with *S*-(trimethylsilyl)benzenethiol (60% yield; Scheme 1).

Compound **3** was synthesized analogously by treatment of **1** with phenyl trimethylsilyl telluride (Scheme 1) and was isolated as the extremely air- and moisture-sensitive solvate **3**·CH₃CN (55% yield). In addition, solvent-free **3** (which is somewhat more stable) was also prepared by using a modified crystallization method (69% yield; for details, see the Experimental Section).

Surprisingly, compound **11** did not react with trimethyl-(phenoxy)silane under the same conditions used for the synthesis of **1** and **3**, and could be reisolated almost quantitatively (Scheme 2). Treatment of **11** with one molar equiva-

 $\begin{array}{c} + PhOSiMe_{3} \\ PhOSi-S \\ PhOSi-S \\ Cl \\ 11 \\ - [HNEt_{3}]Cl \end{array} \begin{array}{c} PhOSi-N \\ PhOSi-N \\ PhOSi-S \\ - [HNEt_{3}]Cl \end{array}$

Scheme 2. Synthesis of compound 5.

lent each of phenol (instead of benzenethiol or benzeneselenol) and triethylamine afforded **5** (54% yield). The crystalline bulk material was a mixture of two diastereomers, one of which was characterized by single-crystal X-ray diffraction.

The identities of 1·CH₃CN, 2·CH₃CN, 3, and 5 were established by elemental analyses, solid- and solution-state NMR spectroscopy, and crystal structure analyses.

Compounds 6–10 were synthesized according to Scheme 3 by treatment of the corresponding trihydridosilanes $12^{[6a]}$ and $13^{[6b]}$ with two molar equivalents of 2-selenylphenol



Scheme 3. Syntheses of compounds 6-10.

(14), 2-selenylbenzenethiol (15), and benzene-1,2-diselenol (16), respectively, as the ligands. The syntheses were performed at 20 °C by using dichloromethane (9) or acetonitrile (6-8 and 10) as the solvent. Compounds 6-10 were isolated as crystalline solids (yields: 6 68%, 7 65%, 8 79%, 9 65%, 10 80%), and their identities were established by elemental analyses, solid-state NMR spectroscopy, solution-state NMR spectroscopy (10 only), and crystal structure analyses. Compounds 6-10 are sensitive to moisture and air (oxygen) but can be stored at 20°C under glovebox conditions for a period of several months.

Ligand **14** was synthesized for the first time, to the best of our knowledge, and was isolated as an oily liquid (49% yield; Scheme 4). The syntheses of the known ligands **15** and



Scheme 4. Syntheses of compounds 14-16.

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16 were carried out according to Scheme 4 by using the procedure outlined in ref. [7]. Based on this report, we have developed a detailed and reliable synthetic protocol for the synthesis of 15 and 16 (yields: 15 65 %, 16 54 %). The identities of 14–16 were established by elemental analyses and solution-state NMR spectroscopy. All these ligands are sensitive to air (oxygen) but can be stored at -20 °C under an argon atmosphere over a period of at least 6 months.

Crystal structure analyses: Compounds **1**·CH₃CN, **2**·CH₃CN, **3**, and **5–10** were structurally characterized by single-crystal X-ray diffraction. The crystal data and experimental parameters used for the crystal structure analyses are given in Tables 1 and 2. The molecular structures of **1–3** and **5–10** in the crystal are shown in Figures 1–4; selected bond lengths and angles are given in the respective legends.

The Si coordination polyhedra of the pentacoordinate silicon(IV) complexes 1-3 are distorted trigonal bipyramids, with the oxygen and sulfur atoms of the tridentate S,N,O ligand in the axial positions (see Figure 1). The S-Si-O angles range from 167.90(4) to 170.23(4)°, and the sum of the equatorial bond angles amounts to between 359.3 and 359.7°. The coordination mode of the tridentate ligand of 1-3 is totally different from that observed for the related

chlorosilicon(IV) complex **11** and its iodo and trifluoromethanesulfonato derivatives (Cl/I and Cl/OSO₂CF₃ exchange, respectively) in which the oxygen and sulfur atoms of the S,N,O ligand occupy equatorial sites of the trigonal-bipyramidal Si coordination polyhedron.^[2d] It is reasonable to assume that this change in stereochemistry, which was also observed in solution (see below), is mainly based on electronic effects because the steric demand of the XPh (X=S, Se, Te) groups is similar to that of the Cl, I, and OSO₂CF₃ ligands.

The Si–XPh bond lengths for 1·CH₃CN (X=S), 2·CH₃CN (X=Se), and 3 (X=Te) are 2.1881(6), 2.3201(3), and 2.5184(4) Å, respectively. These bond lengths are very similar to the respective sums of the covalent radii (Si–S 2.21, Si–Se 2.34, Si–Te 2.54 Å).^[8] The Si–Se bond length of 2·CH₃CN (2.3201(3) Å) is similar to the equatorial Si–Se bond lengths observed for compounds 6 and 8–10 (2.2846(4)–2.3439(8) Å; see below). Pentacoordinate silicon compounds with Si–Se and Si–Te bonds have not yet been described in the literature. As can be seen from Table 3, exchange of the XPh (X=S, Se, Te) group of 1·CH₃CN, 2·CH₃CN, and 3 only slightly affects the analogous Si–S, Si–O, Si–N, and Si–C bond lengths of these compounds. In contrast, replacement of the chloro ligand of 11 by an iodo or

Table 1. Crystallographic data for compounds 1-CH₃CN, 2-CH₃CN, 3, and 5-8.

| | 1-CH ₃ CN | 2-CH ₃ CN | 3 | 5 | 6 | 7 | 8 |
|--------------------------------------------------------|-------------------------------------------------------------------|--------------------------------|-----------------------------------|-----------------------------------------------------|-----------------------------|------------------------------|--------------------------------|
| formula | C ₂₅ H ₂₄ N ₂ OS ₂ Si | C25H24N2OSSeSi | C23H21NOSSiTe | C ₂₃ H ₂₁ NO ₂ SSi | C20H19NO2Se2Si | C20H19NS2Se2Si | C20H19NSe4Si |
| $M_{\rm r} [{ m gmol}^{-1}]$ | 460.67 | 507.57 | 515.16 | 403.56 | 491.37 | 523.49 | 617.29 |
| $T[\mathbf{K}]$ | 193(2) | 98(2) | 101(2) | 193(2) | 193(2) | 193(2) | 193(2) |
| $\lambda(Mo_{K\alpha})$ [Å] | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| crystal system | monoclinic | monoclinic | monoclinic | monoclinic | monoclinic | monoclinic | orthorhombic |
| space group (no.) | $P2_{1}/c$ (14) | $P2_{1}/c$ (14) | $P2_1/n$ (14) | C2/c (15) | $P2_{1}/c$ (14) | $P2_1/c$ (14) | $P2_{1}2_{1}2_{1}$ (19) |
| <i>a</i> [Å] | 7.2119(8) | 7.1535(2) | 7.3408(2) | 19.813(3) | 9.938(2) | 10.240(2) | 6.5504(13) |
| <i>b</i> [Å] | 24.155(3) | 23.9810(6) | 16.8311(4) | 12.2057(11) | 12.996(3) | 13.637(3) | 16.095(3) |
| <i>c</i> [Å] | 14.1455(14) | 14.1167(3) | 17.9108(4) | 19.693(4) | 15.330(3) | 15.604(3) | 20.240(4) |
| β[°] | 98.370(12) | 98.3670(10) | 94.3530(10) | 119.008(18) | 95.67(3) | 106.08(3) | 90 |
| V [Å ³] | 2438.0(5) | 2395.92(10) | 2206.56(9) | 4165.0(11) | 1970.2(7) | 2093.6(7) | 2133.9(7) |
| Z | 4 | 4 | 4 | 8 | 4 | 4 | 4 |
| $ ho_{ m calcd} [m gcm^{-3}]$ | 1.255 | 1.407 | 1.551 | 1.287 | 1.657 | 1.661 | 1.921 |
| $\mu [{\rm mm}^{-1}]$ | 0.287 | 1.724 | 1.510 | 0.231 | 3.828 | 3.793 | 6.938 |
| F_{000} | 968 | 1040 | 1024 | 1696 | 976 | 1040 | 1184 |
| crystal dimensions [mm] | $0.5 \times 0.3 \times 0.3$ | $0.30 \times 0.10 \times 0.09$ | $0.204 \times 0.176 \times 0.096$ | $0.5 \times 0.4 \times 0.4$ | $0.5 \times 0.5 \times 0.4$ | $0.6 \times 0.2 \times 0.08$ | $0.40 \times 0.25 \times 0.25$ |
| 2θ range [°] | 5.70-58.18 | 3.38-72.56 | 3.32-66.2 | 5.26-58.14 | 5.34-58.26 | 5.10-58.28 | 4.76-58.10 |
| index ranges | $-9 \le h \le 9$ | $-11 \le h \le 11$ | $-11 \le h \le 11$ | $-26 \le h \le 26$ | $-13 \le h \le 13$ | $-13 \le h \le 13$ | $-8 \le h \le 8$ |
| - | $-32 \leq k \leq 33$ | $-39 \leq k \leq 39$ | $-25 \leq k \leq 25$ | $-16 \leq k \leq 16$ | $-17 \le k \le 17$ | $-18 \le k \le 18$ | $-21 \leq k \leq 21$ |
| | $-19 \le l \le 19$ | $-22 \leq l \leq 23$ | $-27 \leq l \leq 27$ | $-26 \leq l \leq 26$ | $-20 \le l \le 20$ | $-21 \le l \le 21$ | $-27 \le l \le 27$ |
| reflns collected | 30843 | 63367 | 97838 | 26049 | 32768 | 29679 | 30820 |
| independent reflns | 6404 | 11551 | 8362 | 5514 | 5250 | 5143 | 5584 |
| R _{int} | 0.0382 | 0.0527 | 0.0636 | 0.0463 | 0.0798 | 0.0585 | 0.0404 |
| restraints | 43 | 151 | 0 | 0 | 0 | 114 | 0 |
| parameters | 315 | 363 | 255 | 255 | 240 | 230 | 240 |
| $S^{[a]}$ | 1.054 | 1.031 | 1.080 | 1.033 | 1.037 | 1.058 | 1.075 |
| weight parameters $a/b^{[b]}$ | 0.0399/1.0736 | 0.0409/0.6952 | 0.0232/1.5920 | 0.0719/0.6613 | 0.0563/0.0000 | 0.0386/2.0312 | 0.0319/0.2462 |
| $R_1^{[c]}[I > 2\sigma(I)]$ | 0.0396 | 0.0348 | 0.0255 | 0.0427 | 0.0337 | 0.0405 | 0.0238 |
| $wR_2^{[d]}$ (all data) | 0.0957 | 0.0873 | 0.0628 | 0.1231 | 0.0919 | 0.0956 | 0.0564 |
| absolute structur | | | | | | | -0.008(9) |
| parameter | | | | | | | |
| max/min residual electron density [e Å ⁻³] | 0.336/-0.235 | 0.985/-0.346 | 1.916/-0.563 | 0.492/-0.251 | 0.876/-1.002 | 0.665/-0.403 | 0.527/-0.425 |
| | 0.5 | | | 1 0 | 2 2 | 2 | 2 |

[a] $S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)\}^{0.5}$; n = number of reflections, p = number of parameters. [b] $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$; $P = [\max(F_o^2, 0) + 2F_c^2]/3$. [c] $R_1 = \Sigma ||F_o| - |F_c||/\Sigma |F_o|$. [d] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{0.5}$.

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| Table 2. | Crystallographic | data for comp | pounds 9 and 10. |
|----------|------------------|---------------|------------------|
|----------|------------------|---------------|------------------|

| | 9 | 10 |
|--------------------------------------------------------|--------------------------------------------------------------------|------------------------------------------------------|
| formula | C ₁₇ H ₁₉ NO ₃ Se ₂ Si | C ₁₇ H ₁₉ NOSe ₄ Si |
| $M_{\rm r} [{\rm gmol}^{-1}]$ | 471.34 | 597.26 |
| <i>T</i> [K] | 100(2) | 193(2) |
| $\lambda(Mo_{K\alpha})$ [Å] | 0.71073 | 0.71073 |
| crystal system | orthorhombic | monoclinic |
| space group (no.) | Pbca (61) | $P2_1/c$ (14) |
| a [Å] | 19.255(4) | 13.8787(18) |
| b [Å] | 9.2112(18) | 11.6100(12) |
| <i>c</i> [Å] | 20.130(4) | 13.0991(17) |
| β [°] | 90 | 103.679(15) |
| V [Å ³] | 3570.3(12) | 2050.8(4) |
| Ζ | 8 | 4 |
| $ ho_{ m calcd} [m gcm^{-3}]$ | 1.754 | 1.934 |
| $\mu \text{ [mm^{-1}]}$ | 4.225 | 7.218 |
| F ₀₀₀ | 1872 | 1144 |
| crystal dimensions [mm] | $0.2 \times 0.15 \times 0.08$ | $0.5 \times 0.4 \times 0.3$ |
| 2θ range [°] | 4.04-66.66 | 4.62-58.24 |
| index ranges | $-29 \le h \le 29$ | $-18 \leq h \leq 18$ |
| | $-14 \leq k \leq 14$ | $-15 \leq k \leq 15$ |
| | $-30 \le l \le 30$ | $-17 \le l \le 17$ |
| reflns collected | 216549 | 27916 |
| independent reflns | 6860 | 5447 |
| R _{int} | 0.0541 | 0.0418 |
| restraints | 0 | 0 |
| parameters | 220 | 228 |
| $S^{[a]}$ | 1.073 | 1.013 |
| weight parameters $a/b^{[b]}$ | 0.0225/1.9603 | 0.0320/0.0525 |
| $R_1^{[c]}[I > 2\sigma(I)]$ | 0.0185 | 0.0253 |
| $wR_2^{[d]}$ (all data) | 0.0494 | 0.0574 |
| max/min residual electron density $[e \text{ Å}^{-3}]$ | 0.585/-0.300 | 0.482/-0.552 |

[a] $S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)\}^{0.5}$; n = number of reflections, p = number of parameters. [b] $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$; $P = [\max(F_o^2, 0) + 2F_c^2]/3$. [c] $R_1 = \Sigma ||F_o| - |F_c||/\Sigma |F_o|$. [d] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{0.5}$.

trifluoromethanesulfonato ligand significantly affects these bond lengths. $^{\left[2d\right] }$

Compound **5** has a slightly distorted tetrahedral Si coordination polyhedron, with X-Si-X (X=C, N, O) angles in the range of 104.05(7) to 114.34(7)° and Si-X bond lengths shorter than those in the pentacoordinate compounds **1**·CH₃CN, **2**·CH₃CN, and **3** (see Figure 2).

The Si coordination polyhedra of the zwitterionic pentacoordinate silicon(IV) complexes 6 and 8–10 are distorted trigonal bipyramids (trigonal bipyramid—square pyramid transition: 6 24.2% (pivot atom: C1), 8 10.8% (pivot atom: Se3), 9 8.5% (pivot atom: C1), 10 16.9% (pivot atom: C1)),^[9] in which each bidentate ligand spans one axial and one equatorial site (see Figure 3 and Table 4). The Si coordination polyhedron of 7 is a somewhat distorted square pyramid, with the carbon ligand in the apical position (see Figure 4a).

In the case of **6** (SiSe₂O₂C skeleton), the oxygen atoms O1 and O2 occupy the axial positions, in accordance with the VSEPR concept. In contrast, compound **9** (SiSe₂O₂C skeleton), which differs from **1** only in the (ammonio)organyl group, shows a non-VSEPR structure, with the selenium atom Se2 and the oxygen atom O1 in the axial positions (in this context, see ref. [4c]).



Figure 1. Molecular structures of a) 1 in the crystal of 1-CH₃CN, b) 2 in the crystal of 2·CH₃CN, and c) 3; displacement ellipsoids drawn at the 50% probability level. Selected bond lengths [Å] and angles [°] for 1: Si-S1 2.2935(6), Si-S2 2.1881(6), Si-O 1.7676(10), Si-N 1.8592(12), Si-C1 1.8782(16); S1-Si-S2 81.89(2), S1-Si-O 167.90(4), S1-Si-N 84.85(4), S1-Si-C1 98.87(5), S2-Si-O 92.85(4), S2-Si-N 127.66(4), S2-Si-C1 121.65(5), O-Si-N 89.86(5), O-Si-C1 93.17(6), N-Si-C1 110.33(6). Selected bond lengths [Å] and angles [°] for 2: Si-Se 2.3201(3), Si-S 2.2893(4), Si-O 1.7644(8), Si-N 1.8545(10), Si-C1 1.8757(12); Se-Si-S 81.793(13), Se-Si-O 92.76(3), Se-Si-N 125.76(3), Se-Si-C1 122.29(4), S-Si-O 168.68(3), S-Si-N 85.09(3), S-Si-C1 98.48(4), O-Si-N 90.15(4), O-Si-C1 92.82(5), N-Si-C1 111.61(5). Selected bond lengths [Å] and angles [°] for 3: Si-Te 2.5184(4), Si-S 2.3248(5), Si-O 1.7774(11), Si-N 1.8431(13), Si-C1 1.8757(14); Te-Si-S 82.424(15), Te-Si-O 93.77(4), Te-Si-N 125.14(4), Te-Si-C1 126.01(5), S-Si-O 170.23(4), S-Si-N 84.51(4), S-Si-C1 95.47(5), O-Si-N 90.42(5), O-Si-C1 94.04(6), N-Si-C1 108.13(6).

As can be seen from Table 4, the equatorial Si–Se bond lengths of **6** and **8–10** are in the range of 2.2846(4) to 2.3439(8) Å. These bond lengths are very similar to the sum of the covalent radii of silicon and selenium (2.34 Å),^[8] whereas the axial Si–Se bond lengths are significantly longer (2.4585(9)-2.5797(4) Å). The longest axial Si–Se

Table 3. Comparison of the Si–X (X=S, O, N, C) bond lengths [Å] of $1-CH_3CN$, $2-CH_3CN$, and 3.

| Si–X | 1-CH ₃ CN | 2-CH ₃ CN | 3 |
|---------------------|----------------------|----------------------|------------|
| Si-S ^[a] | 2.2935(6) | 2.2893(4) | 2.3248(5) |
| Si-O | 1.7676(10) | 1.7644(8) | 1.7774(11) |
| Si–N | 1.8592(12) | 1.8545(10) | 1.8431(13) |
| Si-C1 | 1.8782(16) | 1.8757(12) | 1.8757(14) |

[a] Si-S1 for 1-CH₃CN.



Figure 2. Molecular structure of **5** (displacement ellipsoids drawn at the 50% probability level). Selected bond lengths [Å] and angles [°]: Si–O1 1.6375(13), Si–O2 1.6327(12), Si–N 1.7159(13), Si–C1 1.8437(18); O1-Si-O2 108.25(7), O1-Si-N 104.05(7), O1-Si-C1 113.33(7), O2-Si-N 114.34(7), O2-Si-C1 105.68(7), N-Si-C1 111.38(7).

Table 4. Selected bond lengths [Å] and angles [°] of compounds 6 and 8–10.

| 6 | 8 | 9 | 10 |
|--------------------------|---------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| | 2.4585(9), | 2.5797(4) | 2.4715(7), |
| | 2.5049(9) | | 2.5088(7) |
| 2.3221(8), | 2.2957(9), | 2.2846(4) | 2.2935(7), |
| 2.3439(8) | 2.3051(10) | | 2.2988(7) |
| 1.7669(17), | | 1.7419(8) | |
| 1.7874(16) | | | |
| | | 1.6798(8) | |
| 1.919(2) | 1.917(3) | 1.9183(11) | 1.928(2) |
| 171.92(9) ^[a] | 175.43(4) ^[b] | 176.60(3) ^[c] | 173.84(3) ^[b] |
| | 6 2.3221(8), 2.3439(8) 1.7669(17), 1.7874(16) 1.919(2) 171.92(9) ^[a] | 6 8 2.4585(9), 2.5049(9) 2.3221(8), 2.2957(9), 2.3439(8) 2.3051(10) 1.7669(17), 1.7874(16) 1.919(2) 1.917(3) 171.92(9) ^[a] 175.43(4) ^[b] | 6 8 9 2.4585(9), 2.5797(4) 2.5049(9) 2.3221(8), 2.3221(8), 2.2957(9), 2.2846(4) 2.3439(8) 2.3051(10) 1.7419(8) 1.7669(17), 1.7419(8) 1.7874(16) 1.7874(16) 1.6798(8) 1.919(2) 1.917(3) 1.9183(11) 171.92(9) ^[a] 175.43(4) ^[b] 176.60(3) ^[c] |

[a] X, Y=O. [b] X, Y=Se. [c] X=Se, Y=O.

bond lengths were observed for **9** (2.5797(4) Å) and **10** (2.5088(7) Å), which can be explained by the intramolecular N–H···Se hydrogen bonds (see Figures 3c and 3d). In the case of **6**, an intramolecular N–H···O hydrogen bond also leads to a strong differentiation between the two axial Si–O bond lengths (1.7669(17) vs. 1.7874(16) Å; see Figure 3a).

The four basal ligand atoms of the slightly distorted square-pyramidal Si coordination polyhedron of **7** are disordered in the crystal. Due to the similar covalent radii and electronegativities of sulfur and selenium, these ligand atoms can replace each other leading to different isomers. The major isomer (occupancy about 70%) is depicted in Figure 4a; the possible minor isomers (total occupancy about 30%) are shown in Figure 4b. As expected, the two



Figure 3. Molecular structures of a) **6**, b) **8**, c) **9**, and d) **10**; displacement ellipsoids drawn at the 50% probability level. Selected bond lengths [Å] and angles [°] for **6**: Si–Sel 2.3439(8), Si–Sel 2.3221(8), Si–O1 1.7669(17), Si–O2 1.7874(16), Si–C1 1.919(2); Sel-Si-Sel 2128.00(3), Sel-Si-O1 89.40(6), Sel-Si-O2 88.10(6), Sel-Si-C1 113.35(7), Sel-Si-O1 85.82(6), Sel-Si-O2 89.68(6), Sel-Si-C1 118.63(7), O1-Si-O2 171.92(9), O1-Si-C1 93.75(9), O2-Si-C1 94.30(9). Intramolecular N–H···O2 hydrogen bond: N–H 0.86(4), H···O2 1.96(3), N···O2 2.713(3), N–H···O2 146(3). Selected bond lengths [Å] and angles [°] for **8**: Si–Sel 2.5049(9), Si–Sel 2.3051(10), Si–Sel 2.2957(9), Si–Sel 2.4585(9), Si–C1 1.917(3); Sel-Si-Sel 2.949(3), Sel-Si-Sel 39.244(3), Sel-Si-Sel 175.43(4), Sel-Si-C1 88.13(9), Sel-Si-Sel 3120.73(4), Sel-Si-Sel 486.64(3), Sel-Si-C1 123.16(11), Sel-Si-Sel 91.62(3), Sel-Si-Sel 39.244(3), Sel-Si-C1 91.95(10). Intramolecular bifurcated N–H···Sel/Sel hydrogen bond: N–H 0.84(5), H···Sel 2.76(5), N···Sel 3.364(3), H···Sel 2.85(5), N···Sel 3.595(3), N–H···Sel 130(4), N–H···Sel 149(4), Sel-···H···Sel 74.3(12). Selected bond lengths [Å] and angles [°] for **9**: Si–Sel 2.2846(4), Si–Sel 2.5797(4), Si–O1 1.7419(8), Si–O2 1.6798(8), Si–C1 1.9183(11); Sel-Si-Sel 2.308(17), Sel-Si-C1 91.25(3), Sel-Si-C1 121.78(3), Sel-Si-C1 121.88(4), Sel-Si-Sel 2.2986(7), Si–Sel 2.2051(7), Si–Sel 2.3.1404(10), N–H···Sel 137.8(15). Selected bond lengths [Å] and angles [°] for **10**: Si–Sel 2.5088(7), Si–Sel 2.2988(7), Si–Sel 2.2935(7), Si–Sel 2.4715(7), Si–C1 1.928(2); Sel-Si-Sel 91.61(2), Sel-Si-Sel 83.67(2), Sel-Si-C1 89.88(7). Intramolecular N–H···Sel hydrogen bond: N–H 0.87(4), H···Sel 2.491(4), Ne-Sel 3.209(2); Sel-Si-Sel 91.61(2), Sel-Si-C1 118.09(8), Sel-Si-C1 89.88(7). Intramolecular N–H···Sel hydrogen bond: N–H 0.87(4), H···Sel 2.49(4), N···Sel 3.209(2), N–H···Sel 140(3).

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Figure 4. a) Molecular structure of the major isomer of **7** (displacement ellipsoids drawn at the 50% probability level). Selected bond lengths [Å] and angles [°]: Si–Sel 2.378(3), Si–Se2 2.381(2), Si–Sl 2.208(8), Si–S2 2.245(9), Si–C31 1.916(3); Sel-Si-Se2 83.09(7), Sel-Si-S1 89.7(3), Sel-Si-S2 154.0(3), Sel-Si-C31 103.65(12), Se2-Si-S1 147.5(4), Se2-Si-S2 89.1(3), Se2-Si-C31 104.22(11), S1-Si-S2 83.7(4), S1-Si-C31 108.3(4), S2-Si-C31 102.3(3). Intramolecular bifurcated N–H··S1/S2 hydrogen bond: N–H 0.96(6), H···S1 2.45(6), N···S1 3.307(12), H···S2 2.61(6), N···S2 3.319(12), N–H··S1 148(4), N–H··S2 131(4), S1···H··S2 71.8(16). b) Coordination polyhedra of the three possible minor isomers of **7** in the crystal.

Si-Se bond lengths of the major isomer of 7 (2.378(3) and 2.381(2) Å) are somewhat longer in the equatorial case and shorter in the axial case than the Si-Se bond lengths of 6 and 8-10.

Solid- and solution-state NMR spectroscopic studies: Compounds 1-CH₃CN, 2-CH₃CN, and 3 were characterized by solid-state ¹³C, ¹⁵N, ²⁹Si, ⁷⁷Se (2·CH₃CN only), and ¹²⁵Te (3 only) NMR spectroscopy (see the Experimental Section). The isotropic ²⁹Si chemical shifts obtained in the solid-state VACP/MAS NMR measurements reflect the presence of pentacoordinate silicon atoms (1·CH₃CN $\delta = -79.3$, 2·CH₃CN -82.6, 3 -90.6 ppm). These ²⁹Si chemical shifts are very similar to those obtained in solution (solvent CD_2Cl_2 ; 1 $\delta = -79.7$, 2 -82.7, 3 -93.3 ppm) indicating similar structures in the solid state and in solution. The ²⁹Si NMR spectra of 2·CH₃CN show ⁷⁷Se satellites with ${}^{1}J({}^{29}\text{Si}, {}^{77}\text{Se})$ coupling constants of 121 (solid state) and 132 Hz (solution), thus confirming the existence of an Si-Se bond.^[10] Likewise, the ²⁹Si VACP/MAS NMR spectrum of 3 shows ¹²⁵Te satellites with a ${}^{1}J({}^{29}\text{Si},{}^{125}\text{Te})$ coupling constant of 397 Hz; however, these satellites could not be detected in solution.[11]

Solution-state NMR spectroscopic studies (solvent CD_2Cl_2) of **1** (Si–SPh) and **2** (Si–SePh) revealed the existence of a dynamic equilibrium between the pentacoordinate species **A** and the tetracoordinate species **B** (Scheme 5, Table 5). In the case of **3** (Si–TePh), only the pentacoordinate species **A** could be detected in the ²⁹Si NMR spectrum



Scheme 5. Equilibrium reactions of compounds 1–3 and 5 in solution (A: pentacoordination; B: tetracoordination).

Table 5. Solution-state ²⁹Si NMR spectroscopic data [ppm] of compounds 1-3 and 5.^[a]

| | δ^{29} Si (A) | δ^{29} Si (B) ^[b] | A/B ratio ^[c] |
|---|----------------------|----------------------------------------------|--------------------------|
| 1 | -79.7 | -23.8, -22.2 | 75:25 |
| 2 | -82.7 | -20.5, -18.4 | 93:7 |
| 3 | -93.3 | _ | traces of B |
| 5 | - | -56.4, -56.2 | 0:100 |

[a] Solvent CD₂Cl₂, T=23 °C. [b] Two diastereomers. [c] Ratios determined by ¹H NMR spectroscopy.

within the experimental detection limits; however, ¹H NMR spectroscopy experiments indicate that traces of the tetracoordinate species exist. On the other hand, when compound **5** (Si–OPh) was dissolved, only the tetracoordinate species **B** could be detected. These results indicate that the chalcogen atoms stabilize the pentacoordination in the following order: Te > Se > S > O; that is, the softer the chalcogen ligand atom, the more favored the pentacoordinate species **A** is. This is in sharp contrast to what one would expect if it is assumed that hard ligand atoms should favor pentacoordination of the hard silicon(IV) coordination center (O > S > Se > Te).

The ratio of \mathbf{A}/\mathbf{B} also depends on the solvent. Less polar solvents (such as C_6D_6) favor the tetracoordinate species \mathbf{B} (e.g., compound $\mathbf{1}$, \mathbf{A}/\mathbf{B} ca. 35:65), whereas more polar solvents (such as CD_3CN) favor the pentacoordinate species \mathbf{A} . However, the NMR spectrum of $\mathbf{5}$ in CD_3CN did not indicate the existence of a pentacoordinate species.

Compounds **6–10** were also characterized by solid-state ¹³C, ¹⁵N, ²⁹Si, and ⁷⁷Se NMR spectroscopy (see Table 6 and the Experimental Section). The NMR spectra obtained are in agreement with the crystal structures of **6–10**. The solid-state ²⁹Si NMR spectrum of **7** (Figure 5, left) does not reflect the four different isomeric structures found in the crystal. Probably because of the similar isotropic chemical shifts of

Table 6. Solid-state ²⁹Si and ⁷⁷Se NMR spectroscopic data [ppm] of compounds **6–10**.

| | δ^{29} Si | δ^{77} Se |
|-------------------------|------------------|----------------------------|
| 6 | -68.2 | -31.4, -17.2 |
| 7 ^[a] | -66.6 | 224.6, 255.8 |
| 7 ^[b] | -70.7 | 199.1, 234.7 |
| 8 | -107.9 | 249.1, 285.1, 367.5, 411.1 |
| 9 | -72.1 | 28.3, 60.7 |
| 10 | -99.6 | 204.9, 264.8, 275.6, 299.9 |

[a] Relative intensity 92%. [b] Relative intensity 8%.



Figure 5. ^{29}Si NMR spectra of compounds 7 (left; solid state) and 10 (right; in solution, solvent CD_2Cl_2).

these isomers (with shift differences similar to the linewidth of the resonance signals detected), only two signals at $\delta = -66.6$ and -70.7 ppm could be observed (estimated ratio, 92:8).

All attempts to characterize compounds 6-9 by solutionstate NMR spectroscopy failed owing to their poor solubility in common organic solvents, but compound 10 was suitable for solution-state studies (solvent CD₂Cl₂) by ¹H, ¹³C, ²⁹Si, and ⁷⁷Se NMR spectroscopy. The isotropic ²⁹Si chemical shift of 10 ($\delta = -98.1$ ppm; Figure 5, right) is very similar to that obtained in the ²⁹Si VACP/MAS NMR experiment ($\delta =$ -99.6 ppm), indicating that **10** exists in solution as well. The A_2X spin system observed for the SiC(H_A)₂NH_X protons of 10 in the temperature range of 23 to -95 °C indicates that the Λ and Δ enantiomers are not configurationally stable on the NMR time scale. The ²⁹Si NMR spectra of 10 show selenium satellites in the solid state and in solution, which clearly indicates the presence of covalent Si–Se bonds. The 77Se chemical shift of **10** in solution ($\delta = 243.3$ ppm) is very similar to the average of the four isotropic ⁷⁷Se chemical shifts measured in the solid state ($\delta = 204.9$, 264.8, 275.6, 299.9 ppm; average $\delta = 261.3$ ppm). In this context, it should be mentioned that the ⁷⁷Se nucleus is a very sensitive probe; as can be seen from Table 6, the isotropic ⁷⁷Se chemical shifts of the structurally related compounds 6-10 range from $\delta = -31.4$ (6, SiSe₂O₂C skeleton) to 411.1 ppm (8, SiSe₄C skeleton).

Conclusion

With the synthesis of the pentacoordinate silicon(IV) complexes 1 (SiS₂ONC skeleton), 2 (SiSeSONC), and 3 (SiTeSONC), we have demonstrated that pentacoordination of silicon with soft chalcogen ligand atoms (S, Se, Te) is possible. These compounds exist in the solid state and in solution. Quite surprisingly, the corresponding oxygen analogue 4 (SiSO₂NC skeleton) could not be synthesized, and the tetracoordinate silicon compound **5** was obtained instead. In

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this series of compounds, pentacoordination with chalcogen ligand atoms is favored in the following order: Te > Se > S > O; that is, the softer the chalcogen ligand atom, the more favored pentacoordination is. This contrasts sharply with the widely held view that pentacoordination of the hard silicon(IV) coordination center is favored by hard ligand atoms. Obviously, this classical concept is too simple to explain the trend found for this particular series of compounds.

The high potential of soft ligand atoms to form stable pentacoordinate silicon(IV) complexes is further supported by the synthesis of compounds 6–10, which have $SiSe_2O_2C$ (6, 9), $SiSe_2S_2C$ (7), or $SiSe_4C$ skeletons (8, 10). Based on the approach reported here, the synthesis of further siliconselenium compounds of this type, with other element combinations in the silicon coordination sphere, should be possible. These compounds can serve as a platform to extend our knowledge about the stereochemistry and bonding situation of pentacoordinate silicon(IV) complexes with soft ligand atoms.

The selenium compounds **14–16**, for which reliable synthetic protocols have been developed, are also very promising ligand systems for studying the coordination chemistry of other elements.

Experimental Section

General procedures: All syntheses were carried out under dry argon. The organic solvents used were dried and purified according to standard procedures and stored under nitrogen. Compound 11 was synthesized according to ref. [2d], and phenyl trimethylsilyl telluride was synthesized according to known procedures by treating tellurium powder with phenyllithium,^[12] followed by treatment with chlorotrimethylsilane.^[13] The solution-state 1H, 13C, 29Si, 77Se, and 125Te NMR spectra were recorded at 23°C by using a Bruker DRX-300 (1H 300.1 MHz, 13C 75.5 MHz, 29Si 59.6 MHz, ⁷⁷Se 57.2 MHz; 14-16) or a Bruker Avance 500 NMR spectrometer (1H 500.1 MHz, 13C 125.8 MHz, 29Si 99.4 MHz, 77Se 95.4 MHz, 125 Te 157.8 MHz; 1–3, 5, and 10), with CD₂Cl₂ as the solvent. Chemical shifts were determined relative to internal CDHCl₂ (¹H; $\delta = 5.32$ ppm), internal CD₂Cl₂ (¹³C; $\delta = 53.8$ ppm), external TMS (²⁹Si; $\delta = 0$ ppm), external Me₂Se with 5% C₆D₆ (⁷⁷Se; $\delta = 0$ ppm), or an external solution of Ph₂Te₂ (0.1 M) in CDCl₃ (¹²⁵Te; $\delta = 422$ ppm). Assignment of the ¹³C NMR spectroscopic data was supported by DEPT135 experiments. Solid-state ¹³C, ¹⁵N, ²⁹Si, and ⁷⁷Se VACP/MAS NMR spectra and ¹²⁵Te{¹H} HPDec/ MAS NMR spectra were recorded at 22 °C by using a Bruker DSX-400 NMR spectrometer with bottom layer rotors of ZrO₂ (diameter 7 mm) containing about 300 mg of sample (13C 100.6 MHz, 15N 40.6 MHz, 29Si 79.5 MHz, ⁷⁷Se 76.3 MHz, ¹²⁵Te 126.2 MHz; external standard TMS (¹³C, ²⁹Si; $\delta = 0$ ppm), glycine (¹⁵N; $\delta = -342.0$ ppm), Me₂Se (⁷⁷Se; $\delta = 0$ ppm), or Te(OH)₆ (125 Te; $\delta = 685.5$ and 692.2 ppm); contact time 1–2 ms (13 C), 3 ms (¹⁵N), 3–5 ms (²⁹Si), or 5 ms (⁷⁷Se); 90° ¹H transmitter pulse length 3.6 µs; repetition time 4 s).

Synthesis of 1-CH₃CN

Method A: Triethylamine (234 mg, 2.31 mmol) and benzenethiol (255 mg, 2.31 mmol) were sequentially added in single portions to a stirred solution of **11** (800 mg, 2.31 mmol) in tetrahydrofuran (20 mL) at 20 °C and the reaction mixture was stirred for 30 min at 20 °C. The resulting solid was filtered off, washed with tetrahydrofuran (5 mL), and discarded. The solvent of the filtrate (including the wash solution) was removed in vacuo, then acetonitrile (5 mL) was added to the solid residue, and the resulting solution was allowed to stand at -20 °C for 2 h. The precipitate

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was dissolved (heating at ca. 60°C), and the resulting solution was then allowed to stand at 20 °C for 3 h and then at -20 °C for a further 24 h. The yellow crystalline product was isolated by filtration, washed with npentane (6 mL), and dried in vacuo (0.01 mbar, 20 °C, 10 min; yield: 798 mg, 1.73 mmol, 75%).^[14] M.p. >110 °C (decomp.); ¹H NMR:^[15] $\delta =$ 1.32 (d, ${}^{4}J({}^{1}H,{}^{1}H) = 0.3$ Hz, 3H; C(O)CH₃), 1.97 (s, 3H; CH₃CN), 2.36 (s, 3H; C(N)CH₃), 5.84 (q, ⁴J(¹H, ¹H) = 0.3 Hz, 1H; CCHC), 6.93-7.38 and 7.74–7.76 ppm (m, 14H; SC₆H₄N, SC₆H₅, SiC₆H₅); ${}^{13}C$ NMR: $\delta = 2.0$ (CH₃CN), 22.9 (C(O)CH₃), 23.9 (C(N)CH₃), 104.4 (CCHC), 116.9 (CH₃CN), 123.0, 123.2, 127.0, 127.5 (2C), 128.0, 128.7 (2C), 129.2, 129.4, 129.6, 134.5 (2C), 135.1 (2C), 136.8, 139.6 and 140.2 (SC₆H₄N, SC₆H₅, SiC₆H₅), 172.4 (*C*(N)CH₃), 182.3 ppm (*C*(O)CH₃); ²⁹Si NMR: $\delta =$ -79.7 ppm; ¹³C VACP/MAS NMR: $\delta = 0.7 \text{ (CH}_3\text{CN})$, 23.0 (CCH₃), 24.3 (CCH₃), 102.9 (CCHC), 119.3 (CH₃CN), 123.1, 124.9, 127.1, 129.0, 130.4 134.2, 135.1, 136.3, 137.2, 138.3 and 138.9 (SC₆H₄N, SC₆H₅, SiC₆H₅), 172.1 $(C(N)CH_3)$, 181.2 ppm $(C(O)CH_3)$; ¹⁵N VACP/MAS NMR: $\delta = -190.3$ (SiNC), -126.5 ppm (CH₃CN); ²⁹Si VACP/MAS NMR: $\delta = -79.3$ ppm; elemental analysis calcd (%) for $C_{25}H_{24}N_2OS_2Si$ ($M_r = 460.70$): C 65.18, H 5.25, N 6.08, S 13.92; found: C 64.4, H 5.2, N 5.6, S 13.7.^[16]

Method B: *S*-(Trimethylsilyl)benzenethiol (329 mg, 1.80 mmol) was added in a single portion to a stirred suspension of **11** (500 mg, 1.45 mmol) in acetonitrile (9 mL) at 20 °C and the reaction mixture was stirred for 30 min at 20 °C. The undissolved residue was filtered off and discarded, and the filtrate was allowed to stand at -20 °C for 48 h. The yellow crystalline product was isolated by filtration, washed with *n*-pentane (7 mL), and dried in vacuo (0.01 mbar, 20 °C, 10 min; yield: 402 mg, 873 µmol, 60%). The analytical data of the product were identical to those obtained for the product synthesized via Method A.

Synthesis of 2-CH₃CN: Triethylamine (176 mg, 1.74 mmol) and benzeneselenol (272 mg, 1.73 mmol) were sequentially added in single portions to a stirred solution of 11 (600 mg, 1.73 mmol) in tetrahydrofuran (15 mL) at 20 °C and the reaction mixture was stirred for 30 min at 20 °C. The resulting solid was filtered off, washed with tetrahydrofuran (5 mL), and discarded. The solvent of the filtrate (including the wash solution) was removed in vacuo, then acetonitrile (3 mL) was added to the solid residue, and the resulting solution was allowed to stand at -20 °C for 2 h before addition of acetonitrile (5 mL). The precipitate was dissolved (heating of the mixture to ca. 60°C), and the resulting solution was allowed to stand at 20°C for 4 h and then at -20°C for a further 16 h. The yellow-orange crystalline product was isolated by filtration, washed with n-pentane (6 mL), and dried in vacuo (0.01 mbar, 20°C, 1 h; yield: 680 mg, 1.34 mmol, 77 %).^[14] M.p. >80 °C (decomp.); ¹H NMR:^[15] $\delta =$ 1.38 (d, ${}^{4}J({}^{1}H,{}^{1}H) = 0.3$ Hz, 3H; C(O)CH₃), 1.96 (s, 3H; CH₃CN), 2.35 (s, 3H; C(N)CH₃), 5.87 (q, ⁴*J*(¹H, ¹H) = 0.3 Hz, 1H; CCHC), 6.94–6.97, 7.03– 7.08, 7.13-7.16, 7.20-7.30, 7.50-7.52, and 7.74-7.76 ppm (m, 14H; SC_6H_4N , SeC_6H_5 , SiC_6H_5); ¹³C NMR: $\delta = 2.0$ (CH₃CN), 23.0 (C(O)CH₃), 24.0 (C(N)CH₃), 104.4 (CCHC), 116.9 (CH₃CN), 123.1, 123.3, 127.1, 127.5 (2 C), 128.1, 128.8 (2 C), 129.1, 129.4, 132.9, 134.5 (2 C), 136.3 (2 C), 137.9, 139.8, and 140.2 (SC₆H₄N, SeC₆H₅, SiC₆H₅), 172.7 (C(N)CH₃), 182.1 ppm (C(O)CH₃); ²⁹Si NMR: $\delta = -82.7$ ppm (⁷⁷Se satellites, ${}^{1}J({}^{29}\text{Si}, {}^{77}\text{Se}) = 132 \text{ Hz}); {}^{77}\text{Se NMR: } \delta = 161.6 \text{ ppm}; {}^{13}\text{C VACP/MAS NMR:}$ $\delta = 0.9$ (CH₃CN), 22.9 (CCH₃), 25.2 (CCH₃), 102.3 (CCHC), 117.4 $(CH_3CN),\ 124.9,\ 125.2,\ 126.4,\ 127.4,\ 128.6,\ 129.3,\ 130.0,\ 130.7,\ 134.1,$ 135.1, 136.8, 137.1, and 141.7 (SC6H4N, SeC6H5, SiC6H5), 173.6 $(C(N)CH_3)$, 179.5 ppm $(C(O)CH_3)$; ¹⁵N VACP/MAS NMR: $\delta = -186.4$ (SiNC), -128.7 ppm (CH₃CN); ²⁹Si VACP/MAS NMR: $\delta = -82.6$ ppm $(^{77}\text{Se satellites}, {}^{1}J({}^{29}\text{Si}, {}^{77}\text{Se}) = 121 \text{ Hz}); {}^{77}\text{Se VACP/MAS NMR}: \delta =$ 181.9 ppm; elemental analysis calcd (%) for $C_{25}H_{24}N_2OSSeSi$ ($M_r =$ 507.59): C 59.16, H 4.77, N 5.52, S 6.32; found: C 58.9, H 4.7, N 5.1, S 6.5.

Synthesis of 3-CH₃CN: Phenyl trimethylsilyl telluride (552 mg, 1.99 mmol) was added in a single portion to a stirred suspension of 11 (550 mg, 1.59 mmol) in acetonitrile (10 mL) at 20 °C and the reaction mixture was stirred for 30 min at 20 °C. The undissolved residue was filtered off and discarded, and the filtrate was then allowed to stand at -20 °C for 2 h (precipitation of a yellow solid). The resulting suspension was heated to 40 °C until a clear solution was obtained, which was then allowed to stand at 20 °C for 4 h and then at -20 °C for a further 16 h. The yellow–orange crystalline product was isolated by filtration, washed

with *n*-pentane (5 mL), and dried in vacuo (0.01 mbar, 20 °C, 30 min; yield: 489 mg, 879 μ mol, 55%). Except for additional CH₃CN resonance signals in the ¹H and ¹³C NMR spectra, the solution-state NMR spectroscopic data of the product were identical to those of compound **3**.

Synthesis of 3: Phenyl trimethylsilyl telluride (502 mg, 1.81 mmol) was added in a single portion to a stirred suspension of 11 (500 mg, 1.45 mmol) in acetonitrile (8 mL) at 20 °C and the reaction mixture was stirred for 30 min at 20°C. The undissolved residue was filtered off and discarded, a few crystals of 3-CH3CN were added to the filtrate (spontaneous crystallization), and then the mixture was allowed to stand at 20°C for 4 h and then at 4°C for a further 16 h. The orange crystalline product was isolated by filtration, washed with n-pentane (7 mL), and dried in vacuo (0.01 mbar, 20 °C, 2 h; yield: 512 mg, 994 µmol, 69 %). M.p. > 40 °C (decomp.); ¹H NMR: $\delta = 1.46$ (d, ⁴J(¹H, ¹H) = 0.3 Hz, 3H; C(O)CH₃), 2.36 (s, 3H; C(N)CH₃), 5.92 (q, ${}^{4}J({}^{1}H,{}^{1}H) = 0.3$ Hz, 1H; CCHC), 6.95–6.98, 7.05-7.11, 7.20-7.28, and 7.73-7.77 ppm (m, 14H; SC₆H₄N, TeC₆H₅, SiC_6H_5); ¹³C NMR: $\delta = 23.3$ (C(O)CH₃), 24.1 (C(N)CH₃), 104.4 (CCHC), 116.5, 123.28, 123.30, 127.4, 127.5 (2 C), 128.2, 128.8, 128.9 (2 C), 129.5, 134.5 (2C), 137.9, 140.5, 140.6 (2C), and 140.7 (SC₆H₄N, TeC₆H₅, SiC₆H₅), 173.0 (C(N)CH₃), 181.9 ppm (C(O)CH₃); ²⁹Si NMR: $\delta =$ -93.3 ppm (¹²⁵Te satellites not detected); ¹²⁵Te NMR: $\delta = 105.6$ ppm; ¹³C VACP/MAS NMR: δ = 21.3 (CCH₃), 24.4 (CCH₃), 104.0 (CCHC), 115.0, 125.4, 127.9, 129.5, 130.5, 131.4, 138.2, 139.4, and 141.8 (SC₆H₄N, TeC₆H₅, SiC₆H₅), 172.5 (*C*(N)CH₃), 182.2 ppm (*C*(O)CH₃); ²⁹Si VACP/MAS NMR: $\delta = -90.6 \text{ ppm} (^{125}\text{Te satellites}, ^{1}J(^{29}\text{Si},^{125}\text{Te}) = 397 \text{ Hz}); ^{125}\text{Te}\{^{1}\text{H}\}$ HPDec/MAS NMR: $\delta = 75 \text{ ppm}$; elemental analysis calcd (%) for C₂₃H₂₁NOSSiTe (*M*_r=515.18): C 53.62, H 4.11, N 2.72, S 6.22; found: C 53.1, H 4.1, N 2.8, S 6.3.

Synthesis of 5: A solution of phenol (272 mg, 2.89 mmol) in tetrahydrofuran (5 mL) was added dropwise over 5 min to a stirred suspension of 11 (1.00 g, 2.89 mmol) and triethylamine (293 mg, 2.90 mmol) in tetrahydrofuran (20 mL) at 20 °C and the reaction mixture was stirred for 30 min at 20 °C. The resulting solid was filtered off, washed with tetrahydrofuran (5 mL), and discarded. The solvent of the filtrate (including the wash solution) was removed in vacuo, the residue was dissolved in n-pentane (10 mL), the resulting mixture was stirred at 20 °C for 10 min, and the remaining residue was filtered off and discarded. The filtrate was allowed to stand at 4°C for 4 h, and then the clear solution was separated from the oily residue with a syringe and transferred into another flask. This solution was then allowed to stand at 20 °C for 4 h (formation of crystals) and then at -20 °C for a further 16 h. The colorless crystalline product (a mixture of two racemates) was isolated by filtration, washed with cold (-20°C) n-pentane (5 mL), and dried in vacuo (0.01 mbar, 20°C, 3 h; yield: 626 mg, 1.55 mmol, 54%). M.p. >85°C (decomp.); ¹H NMR (*: resonance signal of the major isomer): $\delta = 1.45^*$ (s, 1.8H; $C(N)CH_3$, 1.79 (s, 1.2H; $C(N)CH_3$), 1.85 (d, ${}^{4}J({}^{1}H,{}^{1}H) = 1.1$ Hz, 1.2H; $C(O)CH_3$, 1.90* (d, ${}^{4}J({}^{1}H,{}^{1}H) = 1.0$ Hz, 1.8H; $C(O)CH_3$), 5.04 (q, ${}^{4}J({}^{1}H,{}^{1}H) = 1.1 \text{ Hz}, 0.4 \text{ H}; \text{ CCHC}), 5.08^{*} (q, {}^{4}J({}^{1}H,{}^{1}H) = 1.0 \text{ Hz}, 0.6 \text{ H};$ CCHC), 6.69-6.71, 6.76-6.86, 6.95-6.99, 7.08-7.21, 7.31-7.37, 7.45-7.48, 7.53–7.56, 7.59–7.63, 7.70–7.73, and 7.96–7.98 ppm (m, 14 H; $SC_6H_4N,$ OC₆H₅, SiC₆H₅); ¹³C NMR (*: resonance signals of the major isomer):
$$\begin{split} &\delta\!=\!21.4 \quad (C(O)CH_3), \quad 21.6^* \quad (C(O)CH_3), \quad 34.0^* \quad (C(N)CH_3), \quad 34.6 \\ &(C(N)CH_3), \quad 77.5 \quad (NCS), \quad 78.2^* \quad (NCS), \quad 106.2^* \quad (CCHC), \quad 106.5 \quad (CCHC), \end{split}$$
113.3, 114.0*, 119.9 (2 C), 120.6* (2 C), 122.0, 122.1*, 122.6, 122.7*, 123.0, 123.5*, 125.2*, 125.3, 128.4*, 128.5* (2C), 128.8 (2C), 129.3, 129.68 (2C), 129.75*, 130.0* (2C), 130.3, 131.9*, 132.1, 135.3 (2C), 135.4* (2C), 143.7*, 143.8, 147.3, 147.5*, 153.1, and 153.4* ppm (SC₆H₄N, OC₆H₅, SiC_6H_5 , $C(O)CH_3$; ²⁹Si NMR (*: resonance signal of the major isomer): $\delta = -56.4^{*}$ and -56.2 ppm; ¹³C VACP/MAS NMR: $\delta = 18.1$ (C(O)CH₃), 32.1 (C(N)CH₃), 76.7 and 77.3 (NCS), 103.4 (CCHC), 113.6, 119.4, 120.6, 121.4, 123.5, 126.8, 127.7, 129.2, 134.3, 141.9, 142.3, 145.1, and 152.1 ppm $(SC_6H_4N, OC_6H_5, SiC_6H_5, C(O)CH_3)$; ¹⁵N VACP/MAS NMR: $\delta =$ -285.6 ppm; ²⁹Si VACP/MAS NMR: $\delta = -57.8$ and -57.4 ppm; elemental analysis calcd (%) for $C_{23}H_{21}NO_2SSi$ ($M_r = 403.58$): C 68.45, H 5.24, N 3.47, S 7.95; found: C 68.3, H 5.2, N 3.5, S 7.9.

Synthesis of 6: Compound 12^[6a] (173 mg, 1.14 mmol) was added in a single portion to a stirred solution of 14 (395 mg, 2.28 mmol) in acetonitrile (25 mL) at 20 °C and the reaction mixture was stirred for 20 min

(evolution of hydrogen) and then allowed to stand at 20 °C for 2 d in the absence of light. The resulting colorless crystalline solid was isolated by filtration, washed with *n*-pentane (10 mL), and dried in vacuo (0.01 mbar, 20 °C, 2 h; yield: 381 mg, 775 µmol, 68 %). M.p. >180 °C (decomp.); ¹³C VACP/MAS NMR: δ =44.6 (NCH₃), 47.2 (NCH₃), 112.8, 114.0, 118.2, 121.7, 122.3, 123.5, 126.5, 126.9, 128.5, 129.5 (2C), 130.3, 130.8, 136.6 (2C), 146.3, 155.6, and 155.9 ppm (SeC₆H₄O, SiC₆H₄N); ¹⁵N VACP/MAS NMR: δ = -326.9 ppm; ²⁹Si VACP/MAS NMR: δ = -68.2 ppm (with ⁷⁷Se satellites);^[17] ⁷⁷Se VACP/MAS NMR: δ = -31.4, -17.2 ppm; elemental analysis calcd (%) for C₂₀H₁₉NO₂Se₂Si (*M_r*=491.38): C 48.89, H 3.90, N 2.85; found: C 48.5, H 3.9, N 3.0.

Synthesis of 7: Compound 12^[6a] (174 mg, 1.15 mmol) was added in a single portion to a stirred solution of 15 (434 mg, 2.29 mmol) in acetonitrile (10 mL) at 20 °C and the reaction mixture was stirred for 40 min at 20°C (evolution of hydrogen) and then allowed to stand at 20°C for 1 d in the absence of light. Subsequently, the solution was covered with a layer of n-pentane (5 mL) and then allowed to stand at 20°C for two weeks in the absence of light. The resulting colorless crystalline solid was isolated by filtration, washed with n-pentane (3×5 mL), and dried in vacuo (0.01 mbar, 20°C, 3 h; yield: 392 mg, 749 µmol, 65%). M.p. >160 °C (decomp.); ¹³C VACP/MAS NMR: $\delta = 49.6$ (br, NCH₃) 120-146 ppm (not well resolved, SeC₆H₄S, SiC₆H₄N); ¹⁵N VACP/MAS NMR: $\delta = -324.9$ ppm; ²⁹Si VACP/MAS NMR: -70.7 (relative intensity 8%), -66.6 ppm (relative intensity 92%); ⁷⁷Se VACP/MAS NMR: $\delta = 199.1$ and 234.7 (relative intensity 8%), 224.6 and 255.8 ppm (relative intensity 92%); elemental analysis calcd (%) for $C_{20}H_{19}NS_2Se_2Si$ ($M_r = 523.52$): C 45.89, H 3.66, N 2.68, S 12.25; found: C 45.8, H 3.7, N 2.8, S 12.1.

Synthesis of 8: Compound **12**^[6a] (116 mg, 767 µmol) was added in a single portion to a stirred solution of **16** (362 mg, 1.53 mmol) in acetonitrile (5 mL) at 20 °C and the reaction mixture was stirred for 30 min at 20 °C (evolution of hydrogen) and then allowed to stand at 20 °C for 3 d in the absence of light. The resulting colorless crystalline solid was isolated by filtration, washed with *n*-pentane (3×5 mL), and dried in vacuo (0.01 mbar, 20 °C, 3 h; yield: 373 mg, 604 µmol, 79%). M.p. > 120 °C (decomp.); ¹³C VACP/MAS NMR: δ =47.0 (NCH₃), 47.6 (NCH₃), 119.6, 125.7, 126.6, 126.9, 127.3, 128.2, 129.4, 130.0, 131.6 (2C), 132.5, 139.5, 140.5 (2C), 141.5, 143.6, 145.8, and 146.0 ppm (SeC₆H₄Se, SiC₆H₄N); ¹⁵N VACP/MAS NMR: δ =-324.3 ppm; ²⁹Si VACP/MAS NMR: δ =249.1, 285.1, 367.5, and 411.1 ppm; elemental analysis calcd (%) for C₂₀H₁₉NSe₄Si (M_r =617.30): C 38.91, H 3.10, N 2.27; found: C 39.0, H 3.1, N 2.4.

Synthesis of 9: Compound 13^[6b] (138 mg, 1.05 mmol) was added in a single portion to a stirred solution of 14 (363 mg, 2.10 mmol) in dichloromethane (10 mL) at 20 °C and the reaction mixture was stirred for 15 min at 20 °C (evolution of hydrogen) and then allowed to stand at 4 °C for 3 d in the absence of light. The resulting colorless crystalline solid was isolated by filtration, washed with *n*-pentane (3×5 mL), and dried in vacuo (0.01 mbar, 20 °C, 1 h; yield: 321 mg, 681 µmol, 65%). M.p. > 140 °C (decomp.); ¹³C VACP/MAS NMR: δ =53.0, 55.0, and 55.7 (SiCH₂N, NCH₂C), 64.9 (2C) (OCH₂C), 111.0, 114.7, 120.5, 121.3, 125.3 (2C), 127.4, 129.3 (2C), 133.2, 154.4, and 155.4 ppm (SeC₆H₄O); ¹⁵N VACP/MAS NMR: δ =-72.1 ppm (with ⁷⁷Se satellites);^[17] ⁷⁷Se VACP/MAS NMR: δ =28.3, 60.7 ppm; elemental analysis calcd (%) for C₁₇H₁₉NO₃Se₂Si (*M_r*=471.35): C 43.32, H 4.06, N 2.97; found: C 43.3, H 4.0, N 3.1.

Synthesis of 10: Compound $13^{[6b]}$ (134 mg, 1.02 mmol) was added in a single portion to a stirred solution of 16 (482 mg, 2.04 mmol) in acetonitrile (15 mL) at 20 °C and the reaction mixture was stirred for 30 min at 20 °C (evolution of hydrogen and then allowed to stand at 20 °C for 4 d in the absence of light. The resulting colorless crystalline solid was isolated by filtration, washed with *n*-pentane (3×5 mL), and dried in vacuo (0.01 mbar, 20 °C, 3 h; yield: 487 mg, 815 µmol, 80 %). M.p. >120 °C (decomp.); ¹H NMR;^[18] δ =3.10–3.20 (m, 2H; NCH₂C), 3.29–3.36 (m, 2H; NCH₂C), 3.38 (d, ³*J*(¹H,¹H)=4.7 Hz, 2H; SiCH₂N), 3.54–3.64 (m, 2H; OCH₂C), 3.89–3.96 (m, 2H; OCH₂C), 6.88–6.92 (m, 4H; H-4/H-5, SeC₆H₄Se), 7.38–7.42 (m, 4H; H-3/H-6, SeC₆H₄Se), 9.0 ppm (brs, 1H; NH); ¹³C NMR: δ =55.7 (NCH₂C), 61.3 (SiCH₂N), 65.0 (OCH₂C), 126.0 (C-4/C-5, SeC₆H₄Se), 129.4 (C-3/C-6, SeC₆H₄Se), 141.3 ppm (C-1/C-2, SeC₆H₄Se); ²⁹Si NMR: $\delta = -98.1$ ppm (⁷⁷Se satellites, ¹J(²⁹Si,⁷⁷Se) = 109 Hz); ⁷⁷Se NMR: $\delta = 243.3$ ppm; ¹³C VACP/MAS NMR: $\delta = 54.3$ (NCH₂C), 56.2 (NCH₂C), 61.8 and 62.2 (2 C) (SiCH₂N, OCH₂C), 124.2, 125.4 (2 C), 126.4, 127.9, 130.2, 131.0, 132.1, 139.4, 144.5, 144.9, and 145.6 ppm (SeC₆H₄Se); ¹⁵N VACP/MAS NMR: $\delta = -308.5$ ppm; ²⁹Si VACP/MAS NMR: $\delta = -99.6$ ppm (with ⁷⁷Se satellites);^{117]} ⁷⁷Se VACP/MAS NMR: $\delta = 204.9$, 264.8, 275.6, 299.9 ppm; elemental analysis calcd (%) for C₁₇H₁₉NOSe₄Si ($M_r = 597.27$): C 34.19, H 3.21, N 2.35; found: C 33.8, H 3.2, N 2.5.

Synthesis of 14: 2-Bromophenol (4.33 g, 25.0 mmol) was added dropwise over 15 min to a stirred mixture of a solution of sec-butyllithium (1.3 M, 75.0 mmol) in cyclohexane/hexane (92:8; 57.7 mL), N,N,N',N'-tetramethylethane-1,2-diamine (5.81 g, 50.0 mmol), and n-hexane (30 mL) at -40 °C and the reaction mixture was stirred for a further 30 min at -40°C. Subsequently, the reaction mixture was allowed to warm to 20°C over a period of 2 h and then stirred at this temperature for a further 30 min. The reaction mixture was cooled to 0°C, then selenium powder (1.97 g, 24.9 mmol) was added at this temperature in a single portion, and the reaction mixture was allowed to warm to 20 °C over 30 min and then stirred at this temperature for a further 24 h. The reaction mixture was poured into cold (4°C) hydrochloric acid (3M, 100 mL), the organic layer was separated, the aqueous layer was extracted with *n*-pentane $(5 \times$ 50 mL), and the combined organic extracts were dried over anhydrous sodium sulfate. The solvents were removed by distillation under normal pressure, and the residue was purified by fractional distillation in vacuo to afford 14 as a colorless, oily liquid with an unpleasant odor (yield: 2.13 g, 12.3 mmol, 49 %). B.p. 78–80 °C, 4 mbar; ¹H NMR: $\delta = 1.23-1.27$ (m. ⁷⁷Se satellites, ${}^{1}J({}^{1}H, {}^{77}Se) = 48$ Hz, 1H; SeH), 6.06 (brs, 1H; OH), 6.79-6.87, 6.94-7.01, 7.21-7.30, and 7.53-7.60 ppm (m, 4H; SeC₆H₄O); ¹³C NMR: $\delta = 108.9$ (C-2, SeC₆H₄O), 115.1 (C-6, SeC₆H₄O), 121.5 (C-4, SeC₆H₄O), 131.1 (C-5, SeC₆H₄O), 137.4 (C-3, SeC₆H₄O), 156.6 ppm (C-1, SeC₆H₄O); ⁷⁷Se NMR: $\delta = -24.0$ ppm; elemental analysis calcd (%) for C₆H₆OSe (M_r=173.07): C 41.64, H 3.49; found: C 41.9, H 3.8.

Synthesis of 15: A solution of n-butyllithium (2.5 M, 122 mmol) in hexanes (48.9 mL) was added dropwise over 30 min to a stirred solution of benzenethiol (6.14 g, 55.7 mmol) and N,N,N',N'-tetramethylethane-1,2-diamine (7.12 g, 61.3 mmol) in n-hexane (100 mL) at 0 °C, and the resulting mixture was stirred for a further 1 h. The reaction mixture was then allowed to warm to 20°C over 2 h and stirred at 20°C for a further 3 d. Subsequently, the mixture was cooled to 0°C and selenium powder (4.40 g, 55.7 mmol) was added in a single portion, and then the reaction mixture was allowed to warm to 20 °C over 2 h and stirred for 2 d. The mixture was poured into cold (4°C) hydrochloric acid (3 M, 160 mL), the organic layer was separated, the aqueous layer was extracted with diethyl ether (3×50 mL), and the combined organic extracts were dried over anhydrous sodium sulfate. The solvents were removed by distillation, and the residue was purified by fractional distillation in vacuo to afford 15 as a colorless, oily liquid with an unpleasant odor (yield: 6.82 g, 36.1 mmol, 65%). B.p. 98–100°C, 5 mbar; ¹H NMR:^[18] δ =1.89–1.92 (m, ⁷⁷Se satellites, ${}^{1}J({}^{1}H, {}^{77}Se) = 55$ Hz, 1H; SeH), 3.89–3.91 (m, 1H; SH), 6.98–7.06, 7.09–7.17, 7.34–7.41, and 7.48–7.55 ppm (m, 4H; SeC_6H_4S); ¹³C NMR: $\delta = 127.2$ (C-4, SeC₆H₄S), 127.6 (C-2, SeC₆H₄S), 127.9 (C-5, SeC₆H₄S), 131.1 (C-6, SeC₆H₄S), 133.7 (C-1, SeC₆H₄S), 134.4 ppm (C-3, SeC₆H₄S); ⁷⁷Se NMR: $\delta = 134.8$ ppm; elemental analysis calcd (%) for C₆H₆SSe (M_r=189.14): C 38.10, H 3.20, S 16.95; found: C 38.5, H 3.3, S 16.8.

Synthesis of 16: A solution of *n*-butyllithium (2.5 M, 62.3 mmol) in hexanes (24.9 mL) was added dropwise within 20 min to a stirred solution of benzeneselenol (4.44 g, 28.3 mmol) and N,N,N',N'-tetramethylethane-1,2-diamine (3.61 g, 31.1 mmol) in *n*-hexane (50 mL) at 0 °C, and the resulting mixture was stirred for a further 1 h at 0 °C. The reaction mixture was then allowed to warm to 20 °C over 1 h and stirred for a further 20 h at 20 °C. The reaction mixture was cooled to 0 °C and selenium powder (2.23 g, 28.2 mmol) was added in a single portion, and then the reaction mixture for 4 d. The reaction mixture was poured into cold (4° C) hydrochloric acid (3 M, 80 mL), the organic layer was separated, the aqueous layer was extracted with diethyl ether ($3 \times 60 \text{ mL}$), and the combined or-

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ganic extracts were dried over anhydrous sodium sulfate. The solvents were removed by distillation at normal pressure, and the residue was purified by fractional distillation in vacuo to afford **16** as a colorless, oily liquid with an unpleasant odor (yield: 3.64 g, 15.4 mmol, 54%). B.p. 94–96°C, 3 mbar; ¹H NMR.^[18] δ =2.07–2.10 (m, ⁷⁷Se satellites ¹*J*(¹H,⁷⁷Se) = 54 Hz, 2H; SeH), 7.03–7.11 and 7.49–7.56 ppm (m, 4H; SeC₆H₄Se); ¹³C NMR: δ =128.0 (C-4/C-5, SeC₆H₄Se), 129.9 (C-1/C-2, SeC₆H₄Se), 134.3 ppm (C-3/C-6, SeC₆H₄Se); ⁷⁷Se NMR: δ =160.2 ppm; elemental analysis caled (%) for C₆H₆Se₂ (*M*_r=236.03): C 30.53, H 2.56; found: C 31.2, H 2.7.

Crystal structure analyses: Suitable single crystals of 1-CH₃CN, 2-CH₃CN, 3, and 5–10 were mounted in inert oil (perfluoropolyalkyl ether, ABCR) on a glass fiber and then transferred to the cold nitrogen gas stream of the diffractometer (Stoe IPDS (1-CH₃CN, 5–8, and 10; graphite-monochromated Mo_{Ka} radiation, λ =0.71073 Å) or Bruker Nonius KAPPA APEX II (2-CH₃CN, 3, and 9; Montel mirror, Mo_{Ka} radiation, λ = 0.71073 Å)). All structures were solved by direct methods (SHELXS-97^[19a]) and refined by full-matrix least-squares methods on F^2 for all unique reflections (SHELXL-97^[19b]). For the CH hydrogen atoms, a riding model was employed. CCDC-734846 (1-CH₃CN), -734847 (2-CH₃CN), -734848 (3), -734849 (5), -734850 (6), -734851 (7), -734852 (8), -734853 (9), and -734854 (10) contain the supplementary crystallographic data for this paper. These 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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- [14] Drying in vacuo over a longer period of time led to a partial loss of acetonitrile.
- [15] The reported ¹H, ¹³C, and ²⁹Si chemical shifts are those of the pentacoordinate species.
- [16] The accuracy of the elemental analysis is affected by the partial loss of acetonitrile (even at storage at standard temperature and pressure conditions).
- [17] The solid-state ²⁹Si NMR spectra of 6, 8, 9, and 10 show the existence of ¹J(²⁹Si,⁷⁷Se) satellites in the range between 60–150 Hz. However, owing to overlapping satellites and satellites close to the main ²⁹Si resonance signal, not all pairs of satellites expected from the respective structures could be found.
- [18] C1 is the atom bound to the XH group with the highest priority: OH > SH > SeH.
- [19] a) G. M. Sheldrick, SHELXS-97 Program for crystal structure solution, University of Göttingen, Göttingen, Germany, 1997; b) G. M. Sheldrick, SHELXL-97 Program for crystal structure refinement, University of Göttingen, Göttingen, Germany, 1997.

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