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Synthesis and Structural Characterization of Neutral Higher-Coordinate Silicon(IV) Complexes with Tridentate Dianionic Chelate Ligands

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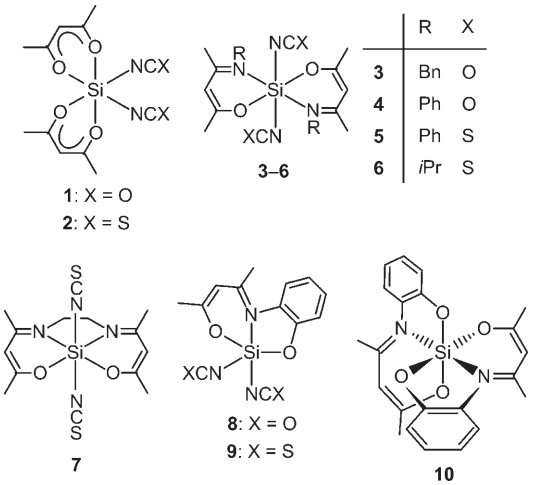
Abstract: The neutral pentacoordinate silicon(IV) complexes **8** and **9** with an SiO_2N_3 skeleton and the neutral hexacoordinate silicon(IV) complex **10**·1/2 CH_3CN with an SiO_4N_2 skeleton were synthesized, starting from tetra(cyanato-*N*)silane or tetra(thiocyanato-*N*)silane. Compounds **8** and **9** contain one tridentate dianionic ligand derived from 4-[(2-hydroxyphenyl)amino]pent-3-en-2-one and two monodentate singly charged cyanato-*N* or thiocyanato-*N* ligands bound to the silicon(IV) coordination center, whereas the silicon(IV) center of **10** is coordinated by two of these tridentate dianionic ligands. All compounds were characterized by single-crystal X-ray diffraction and solid-state and solution NMR spectroscopy. To get more information about the stereochemistry of the compounds studied, the experimental investigations were complemented by computational studies.

Keywords: coordination chemistry · cyanato-*N* ligands · silicon · thiocyanato-*N* ligands · tridentate ligands

Introduction

In our recent studies on higher-coordinate silicon compounds, we have demonstrated that the silanes tetra(cyanato-*N*)silane ($Si(NCO)_4$) and tetra(thiocyanato-*N*)silane ($Si(NCS)_4$) are very useful precursors in the synthesis of neutral hexacoordinate silicon(IV) complexes, such as compounds **1**–**7**.[1–3] These silicon(IV) complexes contain two monodentate NCX^- (X = O, S) ligands each and two bidentate monoanionic chelate ligands (**1**–**6**) or one tetradentate dianionic chelate ligand (**7**). We have now succeeded in synthesizing the pentacoordinate silicon compounds **8** and **9** and the hexacoordinate silicon compound **10**·1/2 CH_3CN, starting from $Si(NCO)_4$ or $Si(NCS)_4$. These silicon(IV) complexes contain one or two tridentate dianionic chelate ligands derived from 4-[(2-hydroxyphenyl)amino]pent-3-en-2-one by twofold deprotonation. We report here on the synthesis of compounds **8**, **9**, and **10**·1/2 CH_3CN and their structural characterization in the solid state and in solution.

The above-mentioned tridentate ligand has already been used in transition-metal coordination chemistry[4] and in silicon coordination chemistry as well,[5] including the synthesis of **10** (starting from $Si(OAc)_4$). However, to the best of our knowledge, compounds **8**, **9**, and **10**·1/2 CH_3CN are the first complexes with this ligand type whose crystal structures were established. These experimental investigations were complemented by computational studies (RI-MP2 geometry optimizations of **9** (C_1 symmetry) and **10** (C_2 symmetry) and their stereoisomers **9′** (C_S symmetry) and **10′** (C_2 symmetry); calculations of the ^{29}Si NMR chemical shifts using the optimized structures). The studies presented here are part of our systematic investigations on higher-coordinate silicon compounds (for recent publications, see reference [6]; for reviews dealing with higher-coordinate silicon compounds,



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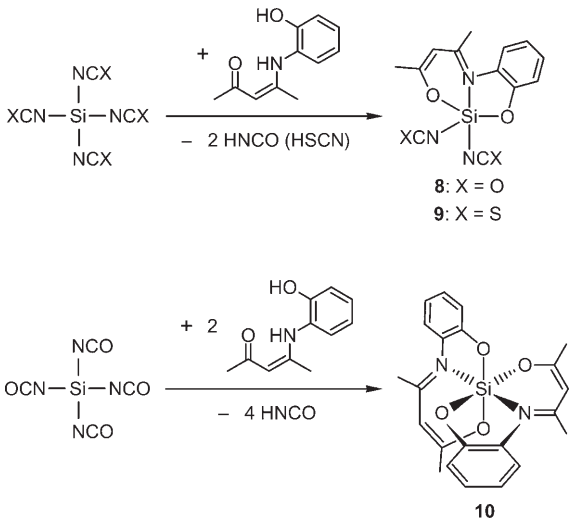
see reference [7]). Preliminary results of the studies reported here have already been presented elsewhere.[8]

Results and Discussion

Syntheses: Compound **8** was synthesized according to Scheme 1 by treatment of $Si(NCO)_4$ with one molar equivalent of 4-[(2-hydroxyphenyl)amino]pent-3-en-2-one at −20 °C in acetonitrile.[9] Compound **9** was prepared analogously at 20 °C, starting from $Si(NCS)_4$.[9] Treatment of $Si(NCO)_4$ with two molar equivalents of 4-[(2-hydroxyphenyl)amino]pent-3-en-2-one in acetonitrile at 20 °C yielded **10**·1/2 CH_3CN (Scheme 1). Compounds **8**, **9**, and **10**·1/2 CH_3CN were isolated as crystalline solids (yield: **8**, 55 %; **9**, 51 %; **10**·1/2 CH_3CN, 71 %). Their identities were established by elemental analyses (C, H, N, S), crystal structure analyses, and solution (^1H, ^{13}C, ^{29}Si) and solid-state (^{13}C, ^{15}N, ^{29}Si) NMR studies.



Scheme 1. Syntheses of compounds **8**, **9**, and **10**.

Crystal structure analyses: The crystal data and the experimental parameters used for the single-crystal X-ray diffraction studies of **8**, **9**, and **10**·1/2 CH_3CN are given in Table 1. The molecular structures of **8**–**10** in the crystal are shown in Figures 1–3; selected bond lengths and angles are given in the respective figure legends.

Table 1. Crystallographic data for compounds **8**, **9**, and **10**·1/2CH_3CN.

	8	**9**	**10**·1/2CH_3CN
empirical formula	$C_{13}H_{11}N_3O_4Si$	$C_{13}H_{11}N_3O_2S_2Si$	$C_{23}H_{23.5}N_{2.5}O_4Si$
formula mass [g mol^{-1}]	301.34	333.46	427.03
T [K]	173(2)	173(2)	173(2)
$\lambda(Mo_{K\alpha})$ [Å]	0.71073	0.71073	0.71073
crystal system	monoclinic	monoclinic	triclinic
space group (no.)	$P2_1/c$ (14)	$P2_1/c$ (14)	$P\bar{1}$ (2)
a [Å]	11.5110(14)	11.775(2)	9.8503(14)
b [Å]	8.5264(8)	8.8428(18)	10.9272(16)
c [Å]	13.9036(17)	14.322(3)	11.4690(16)
α [°]	90	90	87.469(17)
β [°]	98.670(15)	91.91(3)	65.413(16)
γ [°]	90	90	70.426(16)
V [Å^3]	1349.0(3)	1490.4(5)	1051.1(3)
Z	4	4	2
ρ_{calcd} [g cm^{-3}]	1.484	1.486	1.349
μ [mm^{-1}]	0.194	0.444	0.146
F_{000}	624	688	450
crystal dimensions [mm]	0.5 × 0.4 × 0.3	0.6 × 0.4 × 0.3	0.5 × 0.4 × 0.3
2θ range [°]	5.92–53.62	5.42–53.90	5.90–52.74
index ranges	$-14 \le h \le 14$, $-10 \le k \le 10$, $-17 \le l \le 16$	$-14 \le h \le 14$, $-11 \le k \le 11$, $-18 \le l \le 18$	$-12 \le h \le 12$, $-13 \le k \le 13$, $-14 \le l \le 14$
no. of collected reflns	10144	20910	15681
no. of independent reflns	2856	3199	4001
R_{int}	0.0284	0.0447	0.0600
no. of reflns used	2856	3199	4001
no. of parameters	192	192	294
S[a]	1.112	1.058	1.042
weight parameters a/b[b]	0.0746/0.6164	0.0465/0.5142	0.0731/0.0557
$R1$[c] [$I > 2\sigma(I)$]	0.0466	0.0310	0.0397
$wR2$[d] (all data)	0.1324	0.0860	0.1110
max./min. residual electron density [e Å^{-3}]	+0.423/−0.327	+0.252/−0.298	+0.388/−0.350

[a] $S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)\}^{0.5}$; n = no. of reflections; p = no. of parameters. [b] $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, with $P = [\max(F_o^2, 0) + 2F_c^2]/3$. [c] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [d] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{0.5}$.

The Si-coordination polyhedra of the pentacoordinate silicon(IV) complexes **8** and **9** are distorted trigonal bipyramids, with the two oxygen atoms of the tridentate ligand and a nitrogen atom of one of the two NCX^- ligands (X = O, S) occupying the equatorial positions. The Si–O distances of **8** and **9** are very similar, ranging from 1.6657(11) to 1.6891(14) Å. The Si–N (chelate ligand) bond lengths (**8**, 1.9668(16); **9**, 1.9218(12) Å) are very similar to those observed for the Si–N distances in the chelate rings of **3**–**6**.[3] The Si–N distances of the Si–NCX moieties of **8** (1.7330(18) and 1.7847(18) Å) and **9** (1.7375(13) and 1.7985(13) Å) are significantly shorter, the equatorial Si–NCX bonds being shorter than the axial ones. The Si-N-C angles of the Si–NCX groups are in the range 149.47(18)–167.97(17)°, and the N-C-X angles amount to 177.3(3)–178.68(13)°. Similar Si-N-C and N-C-X angles have also been reported for the Si-NCX moieties of **1**–**7**.[1–3]

To the best of our knowledge, compound **8** is the first pentacoordinate silicon compound with cyanato-*N* ligands

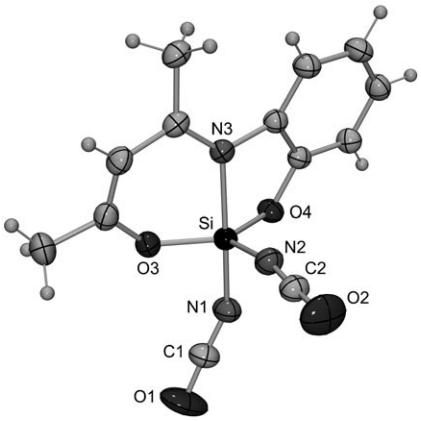


Figure 1. Molecular structure of **8** in the crystal (probability level of displacement ellipsoids 50%). Selected bond lengths [Å] and angles [°]: Si–O3 1.6779(14), Si–O4 1.6891(14), Si–N1 1.7847(18), Si–N2 1.7330(18), Si–N3 1.9668(16), N1–C1 1.170(3), N2–C2 1.176(3), C1–O1 1.174(3), C2–O2 1.178(3); O3-Si-O4 133.64(7), O3-Si-N1 89.94(8), O3-Si-N2 114.51(8), O3-Si-N3 90.05(7), O4-Si-N1 89.15(7), O4-Si-N2 111.58(8), O4-Si-N3 84.86(6), N1-Si-N2 97.13(9), N1-Si-N3 171.69(8), N2-Si-N3 90.43(8), Si-N1-C1 149.47(18), Si-N2-C2 167.97(17), N1-C1-O1 177.3(3), N2-C2-O2 177.4(2).

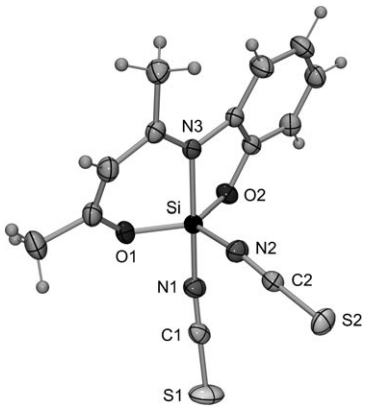


Figure 2. Molecular structure of **9** in the crystal (probability level of displacement ellipsoids 50%). Selected bond lengths [Å] and angles [°]: Si–O1 1.6657(11), Si–O2 1.6716(11), Si–N1 1.7985(13), Si–N2 1.7375(13), Si–N3 1.9218(12), N1–C1 1.166(2), N2–C2 1.183(2), C1–S1 1.5887(16), C2–S2 1.5746(15); O1-Si-O2 131.93(6), O1-Si-N1 89.06(6), O1-Si-N2 114.48(6), O1-Si-N3 91.83(5), O2-Si-N1 89.44(6), O2-Si-N2, 113.56(6), O2-Si-N3 86.33(6), N1-Si-N2 93.90(6), N1-Si-N3 175.03(6), N2-Si-N3 90.18(6), Si-N1-C1 162.01(12), Si-N2-C2 160.68(12), N1-C1-S1 178.59(15), N2-C2-S2 178.68(13).

to be reported in the literature, and so far 1-(thiocyanato-*N*)silatrane is the only pentacoordinate silicon compound with a thiocyanato-*N* ligand that has been structurally characterized by single-crystal X-ray diffraction. The Si–NCS bond length in 1-(thiocyanato-*N*)silatrane[10] (1.800(3) Å) is similar to that of the axial Si–NCS distance in **9** (1.7985(13) Å). However, in contrast to compound **9**, where Si-N-C angles of 162.01(12)° (axial) and 160.72(12)° (equatorial) are observed, the Si–NCS moiety of 1-(thiocyanato-*N*)silatrane is reported to be almost linear (Si-N-C 174.7(3)°)[10] (for computational studies of 1-(thiocyanato-*N*)silatrane, see reference [11]).

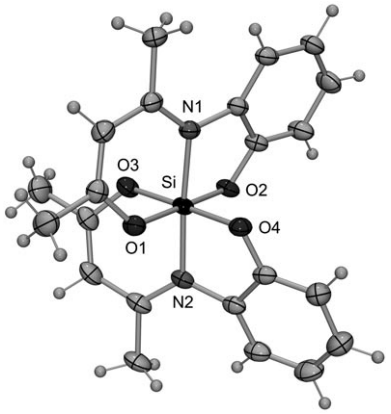


Figure 3. Molecular structure of **10**·1/2 CH_3CN in the crystal of **10**·1/2 CH_3CN (probability level of displacement ellipsoids 50%). Selected bond lengths [Å] and angles [°]: Si–O1 1.7593(12), Si–O2 1.7558(12), Si–O3 1.7763(12), Si–O4 1.7587(11), Si–N1 1.9024(13), Si–N2 1.8966(14); O1-Si-O2 178.77(5), O1-Si-O3 89.58(6), O1-Si-O4 89.48(5), O1-Si-N1 93.78(6), O1-Si-N2 89.55(6), O2-Si-O3 89.37(6), O2-Si-O4 91.56(6), O2-Si-N1 86.85(6), O2-Si-N2 89.87(6), O3-Si-O4 178.84(5), O3-Si-N1 89.95(6), O3-Si-N2 92.61(6), O4-Si-N1 90.79(5), O4-Si-N2 86.70(6), N1-Si-N2 175.82(6).

The Si-coordination polyhedron of the hexacoordinate silicon(IV) complex **10**·1/2CH_3CN is best described as a distorted octahedron, with O-Si-O angles in the ranges 89.37(6)–91.56(6)° and 178.77(5)–178.84(5)°, with O-Si-N angles in the range 86.70(6)–93.78(6)°, and with an N-Si-N angle of 175.82(6)°. The Si–O distances lie between 1.7558(12) and 1.7763(12) Å, and the Si–N distances range from 1.8966(14) to 1.9024(13) Å. As expected for the change of the Si-coordination number from five to six, the Si–O bonds of **10**·1/2 CH_3CN are longer than those observed for **8** and **9**; however, the Si–N (chelate ligand) distances of **10**·1/2 CH_3CN are shorter than those of **8** and **9**.

Figure 4 shows the different conformations of the tridentate ligands of **8**, **9**, and **10**·1/2 CH_3CN. In all cases, the chelate ligands are not planar, instead a torsion of the O–C=C–C=N moiety with respect to the plane spanned by the phenyl ring is observed. The conformations of the tridentate ligands of **8** and **9** are very similar but differ significantly from those of **10**·1/2 CH_3CN: the C=C–C=N torsion angles in the six-membered chelate rings of **8** and **9** amount to −13.7(3) and −15.2(2)°, respectively, whereas C=C–C=N torsion angles of 8.3(2) and 11.2(3)° are observed for **10**·1/2 CH_3CN. These different torsions allow the ligand to span totally different O-Si-O angles in the Si-coordination polyhedra of the pentacoordinate silicon(IV) complexes **8** (133.64(7)°) and **9** (131.93(6)°) and the hexacoordinate silicon(IV) complex **10**·1/2 CH_3CN (178.77(5) and 178.84(5)°).

The free non-deprotonated 4-[(2-hydroxyphenyl)amino]-pent-3-en-2-one[12,13] ligand is known to exist as the keto-enamine tautomer in the crystal, whereas the deprotonated ligand in the crystal structures of **8**, **9**, and **10**·1/2 CH_3CN is best described as a ligand of the imino-enolato type,[14] as can be seen from the calculated values for the imino-enol

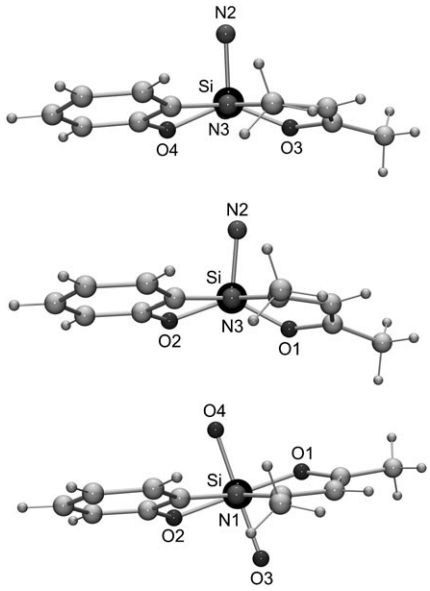


Figure 4. Conformations of the tridentate ligands of **8**, **9**, and **10**·1/2 CH_3CN in the crystal: view along the Si–N3 bond of **8** (top), along the Si–N3 bond of **9** (middle), and along the Si–N1 bond of **10**·1/2 CH_3CN (bottom). For reasons of clarity, the two monodentate ligands of **8** and **9** and the second chelate ligand of **10**·1/2 CH_3CN are only represented by their coordinating atoms, one of which is hidden behind the silicon atom.

tautomer 4-[(2-hydroxyphenyl)imino]pent-2-en-2-ol.[12] The bidentate ligands of **3**–**6** and the tetradentate ligand of **7** were also found to act as ligands of the imino-enolato type.[3]

NMR studies: Compounds **8**, **9**, and **10**·1/2 CH_3CN were characterized by solid-state VACP/MAS NMR spectroscopy (^{13}C, ^{15}N, ^{29}Si) and solution NMR spectroscopy (^{1}H, ^{13}C, ^{29}Si) using CD_2Cl_2 (**8**, **9**), $C_2D_2Cl_4$ (**10**), or [D_6]DMSO (**10**) as the solvent. The isotropic ^{29}Si chemical shifts obtained in the VACP/MAS NMR studies (**8**, $\delta = -140.6$ ppm; **9**, $\delta = -146.4$ ppm; **10**·1/2 CH_3CN, $\delta = -165.6$ ppm) clearly indicate the existence of higher-coordinate silicon atoms and match with the ^{29}Si chemical shifts obtained in solution (**8**, $\delta = -138.1$ ppm; **9**, $\delta = -146.1$ ppm; **10**, $\delta = -164.7$ ppm). The experimentally established ^{29}Si chemical shifts for **9** and **10** in solution and in the solid state are in reasonable agreement with the computed values for the structures obtained by geometry optimizations (**9**, $\delta = -144$ ppm; **10**, $\delta = -160$ ppm; see Computational Studies).

The ^{1}H and ^{13}C solution NMR spectra of **8** and **9** show only one set of resonance signals for the chelate ligands and are compatible with the structures determined by single-crystal X-ray diffraction. At low temperature (−90 °C), there is no indication for the existence of other stereoisomers of **8** and **9** (see Computational Studies) in solution; however, an isomerization process that is fast on the NMR time scale even at this temperature cannot be totally ruled out. In the ^{1}H and ^{13}C solution NMR spectra of **10**, there is also only one set of resonance signals for the two chelate ligands, indicating the presence of one single stereoisomer (see Computational Studies).

Upon addition of one molar equivalent of the optically active solvating agent (−)-2,2,2-trifluoro-1-(9-anthryl)ethanol to a solution of the racemic chiral silicon(IV) complex **10** in $C_2D_2Cl_4$, a splitting of the resonance signals in the ^{1}H NMR spectrum is observed (Figure 5), indicating that the enantiomers of **10** are configurationally stable (no change of absolute configuration) on the NMR time scale.

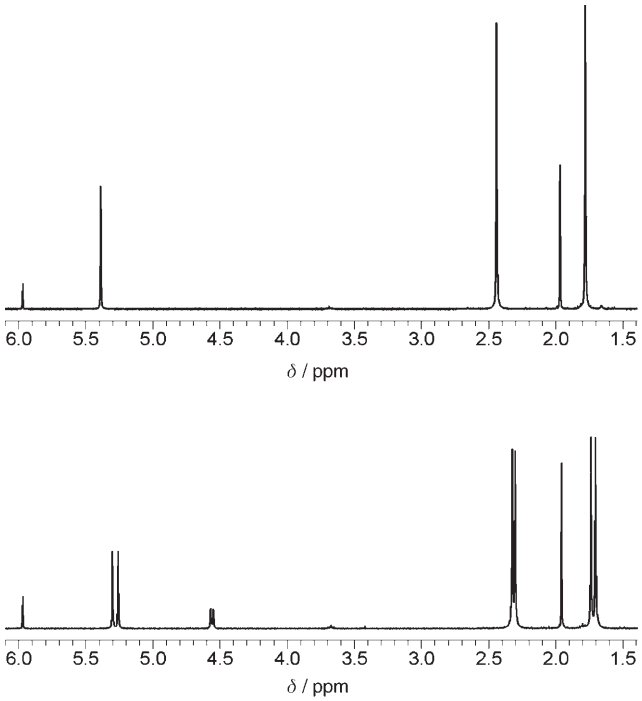


Figure 5. Effect of the chiral solvating agent (−)-2,2,2-trifluoro-1-(9-anthryl)ethanol (TFAE) on the ^{1}H NMR spectrum of **10** in $C_2D_2Cl_4$ (300.1 MHz, 22 °C): ^{1}H NMR spectrum of a 50 mM solution of **10** in $C_2D_2Cl_4$ in the absence of TFAE (top); ^{1}H NMR spectrum of a 50 mM solution of **10** in $C_2D_2Cl_4$ in the presence of TFAE (molar ratio **10**:TFAE = 1:1) (bottom).

Computational studies: Geometry optimizations for **9** (C_1 symmetry) and its stereoisomer **9′** (C_S symmetry) as well as for **10** (C_2 symmetry) and its stereoisomer **10′** (C_2 symmetry) were performed at the RI-MP2[15] level using a TZP basis set[16] and a TZVP auxiliary basis for the fit of the charge density.[17] The calculations were performed by using the TURBOMOLE program system.[18] The structures of the respective calculated minima are shown in Figures 6–9, with selected calculated bond lengths and angles in the respective figure legends. As can be seen from Figure 2 and Figure 6 and from Figure 3 and Figure 8, respectively, the calculated and experimentally established structures of **9** and **10** are in reasonable agreement.[19]

From a formal point of view, the stereoisomer **9′**, with its three nitrogen atoms in the equatorial positions of a trigonal-bipyramidal Si-coordination polyhedron, could be regarded as the product of a Berry-type pseudorotation of **9**,

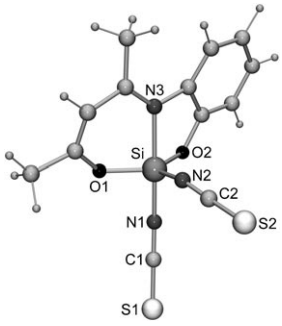


Figure 6. Calculated structure of **9** (C_1 symmetry); selected bond lengths [Å] and angles [°]: Si–O1 1.709, Si–O2 1.699, Si–N1 1.768, Si–N2 1.744, Si–N3 1.985, N1–C1 1.196, N2–C2 1.204, C1–S1 1.587, C2–S2 1.577; O1-Si-O2 128.7, O1-Si-N1 90.6, O1-Si-N2 111.6, O1-Si-N3 89.6, O2-Si-N1 90.8, O2-Si-N2 118.9, O2-Si-N3 84.1, N1-Si-N2 98.3, N1-Si-N3 173.6, N2-Si-N3 87.5, Si-N1-C1 162.6, Si-N2-C2 158.8, N1-C1-S1 178.5, N2-C2-S2 177.6. Calculated ^{29}Si NMR shift for this structure: $\delta = -144$ ppm.

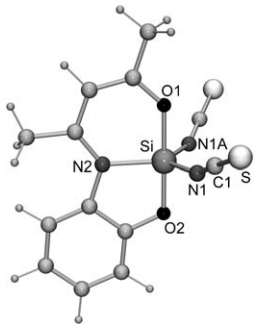


Figure 7. Calculated structure of **9′** (C_s symmetry); selected bond lengths [Å] and angles [°]: Si–O1 1.795, Si–O2 1.718, Si–N1 1.751, Si–N2 1.903, N1–C1 1.202, C1–S 1.581; O1-Si-O2 179.5, O1-Si-N1 87.5, O1-Si-N2 92.1, O2-Si-N1 92.7, O2-Si-N2 87.5, N1-Si-N1A 118.4, N1-Si-N2 120.8, Si-N1-C1 154.7, N1-C1-S 178.0. Calculated ^{29}Si NMR shift for this structure: $\delta = -140$ ppm.

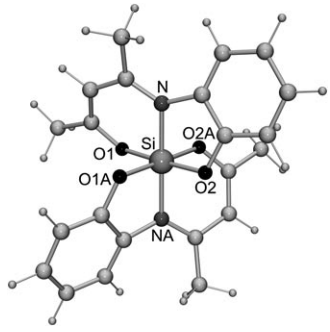


Figure 8. Calculated structure of **10** (C_2 symmetry); selected bond lengths [Å] and angles [°]: Si–O1 1.804, Si–O2 1.772, Si–N 1.883; O1-Si-O1A 86.4, O1-Si-O2 176.2, O1-Si-O2A 90.4, O1-Si-N 91.5, O1-Si-NA 89.9, O2-Si-O2A 92.8, O2-Si-N 86.4, O2-Si-NA 92.3, N-Si-NA 178.2. Calculated ^{29}Si NMR shift for this structure: $\delta = -160$ ppm.

with the equatorial thiocyanato-*N* ligand as the pivot ligand. The calculated energies of the two stereoisomers **9** and **9′** differ only by 35.7 kJ mol^{-1}, the stereoisomer **9** (which corresponds to the experimentally established crystal structure) being energetically more stable than **9′** (Figure 10). This result again reflects the high flexibility of the tridentate ligand, which is able to span O-Si-O angles between 130 and 180° (in this context, see also the crystal structures of **8**, **9**, and **10**·1/2 CH_3CN).

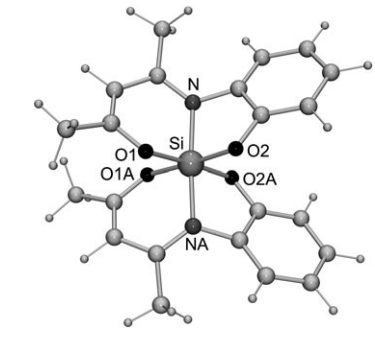


Figure 9. Calculated structure of **10′** (C_2 symmetry); selected bond lengths [Å] and angles [°]: Si–O1 1.802, Si–O2 1.782, Si–N 1.872; O1-Si-O1A 88.4, O1-Si-O2 90.6, O1-Si-O2A 177.1, O1-Si-N 90.8, O1-Si-NA 92.0, O2-Si-O2A 90.6, O2-Si-N 85.3, O2-Si-NA 92.0, N-Si-NA 176.1. Calculated ^{29}Si NMR shift for this structure: $\delta = -170$ ppm.

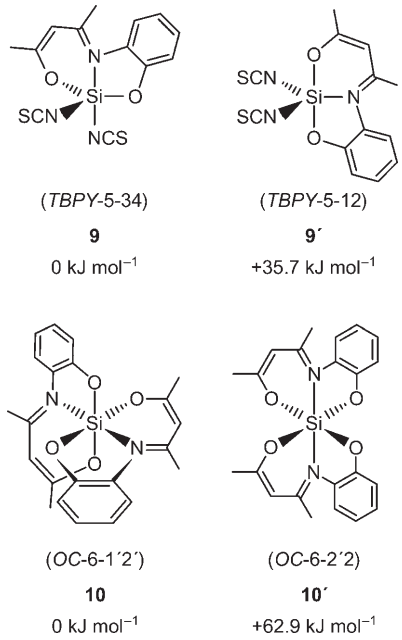


Figure 10. Top: Configurations and calculated relative energies for the stereoisomers **9** (C_1 symmetry) and **9′** (C_S symmetry). Bottom: Configurations and calculated relative energies for the stereoisomers **10** (C_2 symmetry) and **10′** (C_2 symmetry).

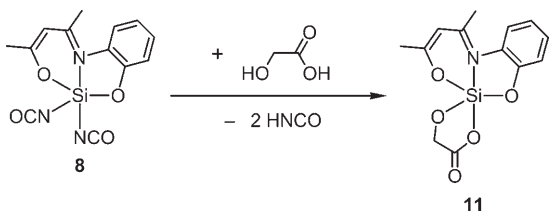
In addition to the (*OC*-6–22′)-stereoisomer **10** found in the crystal of **10**·1/2CH_3CN, with each tridentate ligand occupying three meridional positions in the octahedral Si-coordination polyhedron, five other diastereomers have to be considered, in which the tridentate ligands span three facial sites of the Si-coordination polyhedron, resulting in O-Si-O

angles close to 90°. The stereoisomer **10′** ((*OC*-6–2′2)-configuration) represents one of these isomers. The calculated energies of **10** and **10′** differ by 62.9 kJ mol^{-1} (Figure 10), indicating that O-Si-O angles close to 90° afford an energetically unfavored geometry of the ligand.

The isotropic ^{29}Si chemical shifts for **9**, **9′**, **10**, and **10′** were calculated at the HF/TZP level (see legends of Figure 6–9). The data obtained for **9** and **10** are in good agreement with the respective isotropic ^{29}Si chemical shifts obtained experimentally.

Conclusion

With the synthesis of the neutral pentacoordinate silicon(IV) complexes **8** and **9** and the hexacoordinate silicon(IV) complex **10**·1/2 CH_3CN, tetra(cyanato-*N*)silane and tetra(thiocyanato-*N*)silane again have been demonstrated to be very useful precursors for the synthesis of higher-coordinate silicon compounds. Compounds **8**, **9**, and **10**·1/2 CH_3CN are the first higher-coordinate silicon(IV) complexes with tridentate dianionic chelate ligands derived from 4-[(2-hydroxyphenyl)amino]pent-3-en-2-one that were structurally characterized by single-crystal X-ray diffraction. Based on the experimentally established bond lengths in the chelate rings, the tridentate ligand is best described as an imino-enolato rather than a keto-enamino type ligand. This ligand is able to span O-Si-O angles between approximately 130 (**8**, **9**) and 180° (**10**·1/2 CH_3CN), this high flexibility being mainly achieved by different C=C−C=N torsion angles in the six-membered chelate rings. To the best of our knowledge, compound **8** is the first pentacoordinate silicon(IV) complex containing cyanato-*N* ligands, and compound **9** is the first pentacoordinate silicon(IV) complex with two thiocyanato-*N* ligands, whereas a pentacoordinate silicon compound containing one thiocyanato-*N* ligand, 1-(thiocyanato-*N*)silatrane, has been reported in the literature. With the synthesis of compounds **8** and **9**, members of a new class of neutral pentacoordinate silicon(IV) complexes have been made available. Such compounds, with their two reactive Si−NCX (X = O, S) groups, may serve as precursors for the synthesis of other novel higher-coordinate silicon compounds. The successful synthesis of the heteroleptic neutral pentacoordinate silicon(IV) complex **11** gives an indication of the synthetic potential of these compounds (Scheme 2). Compound **11** contains an *Si*O_4N skeleton, and its Si-coordination polyhedron is a distorted trigonal bipyramid, with the nitrogen atom in an axial position.[20]



Scheme 2. Synthesis of compound **11**.

Experimental Section

General procedures: All syntheses were carried out under dry nitrogen. The organic solvents used were dried and purified according to standard procedures and stored under nitrogen. Melting points were determined with a Büchi Melting Point B-540 apparatus using samples in sealed capillaries. The ^{1}H, ^{13}C, and ^{29}Si solution NMR spectra were recorded at 22 °C on a Bruker DRX-300 NMR spectrometer (^{1}H, 300.1 MHz; ^{13}C, 75.5 MHz; ^{29}Si, 59.6 MHz) using CD_2Cl_2, $C_2D_2Cl_4$, or [D_6]DMSO as the solvent. Chemical shifts (ppm) were determined relative to internal $CHDCl_2$ (^{1}H, $\delta = 5.32$ ppm; CD_2Cl_2), C_2HDCl_4 (^{1}H, $\delta = 5.91$ ppm; $C_2D_2Cl_4$), [D_5]DMSO (^{1}H, $\delta = 2.49$ ppm; [D_6]DMSO), CD_2Cl_2 (^{13}C, $\delta = 53.8$ ppm; CD_2Cl_2), $C_2D_2Cl_4$ (^{13}C, $\delta = 74.2$ ppm; $C_2D_2Cl_4$), [D_6]DMSO (^{13}C, $\delta = 39.5$ ppm; [D_6]DMSO), or external TMS (^{29}Si, $\delta = 0$ ppm; CD_2Cl_2, $C_2D_2Cl_4$, [D_6]DMSO). Assignment of the ^{13}C NMR data was supported by DEPT 135 experiments. Solid-state ^{13}C, ^{15}N, and ^{29}Si VACP/MAS NMR spectra were recorded at 22 °C on a Bruker DSX-400 NMR spectrometer with bottom layer rotors of ZrO_2 (diameter, 7 mm) containing about 300 mg of sample (^{13}C, 100.6 MHz; ^{15}N, 40.6 MHz; ^{29}Si, 79.5 MHz; external standard, TMS (^{13}C, ^{29}Si; $\delta = 0$ ppm) or glycine (^{15}N, $\delta = -342.0$ ppm); spinning rate, 5–6 kHz; contact time, 1 ms (^{13}C), 3 ms (^{15}N), or 5 ms (^{29}Si); 90° ^{1}H transmitter pulse length, 3.6 μs; repetition time, 4 s). The precursors tetra(cyanato-*N*)silane and tetra(thiocyanato-*N*)silane were synthesized according to reference [21] (for the synthesis of tetra(thiocyanato-*N*)silane, toluene instead of benzene was used as the solvent[1]). 4-[(2-Hydroxyphenyl)amino]pent-3-en-2-one was synthesized according to reference [5].

Di(cyanato-*N*)-[4-{(2-hydroxyphenyl)imino}pent-2-en-2-olato(2−)-*N*,*O*,*O′*]-silicon(IV) (8): Tetra(cyanato-*N*)silane (500 mg, 2.55 mmol) was added at −30 °C to a stirred suspension of 4-[(2-hydroxyphenyl)amino]pent-3-en-2-one (488 mg, 2.55 mmol) in acetonitrile (10 mL). The reaction mixture was warmed to −20 °C over a period of 1 h and then kept undisturbed at −20 °C for three days. The resulting precipitate was isolated by filtration, washed with cold (0 °C) *n*-pentane (10 mL), and dried in vacuo (0.01 Torr, 20 °C, 2 h) to give **8** in 55 % yield (422 mg, 1.40 mmol) as a yellowish crystalline solid; m.p. 128 °C (decomp). ^{1}H NMR (CD_2Cl_2): $\delta =$ 2.23 (d, ^4J(H,H) = 0.5 Hz, 3H; CH_3), 2.59 (s, 3H; CH_3), 5.86 (q, ^4J-(H,H) = 0.5 Hz, 1H; C=CH−C), 7.01–7.43 ppm (m, 4H; C_6H_4); ^{13}C NMR (CD_2Cl_2): $\delta = 24.1$ (CH_3), 25.3 (CH_3), 108.8 (C=*C*H−C), 115.8, 120.7, 121.5, 129.1, 131.6, and 150.0 (C_6H_4), 122.3 (NCO), 169.4 (CO or CN), 171.4 ppm (CO or CN); ^{29}Si NMR (CD_2Cl_2): $\delta = -138.1$ ppm; ^{13}C VACP/MAS NMR: $\delta = 24.1$ (CH_3), 25.2 (CH_3), 109.0 (C=*C*H−C), 114.5, 122.1 (2C), 129.1, 131.5, and 149.1 (C_6H_4), 170.4 (CO or CN), 171.9 ppm (CO or CN);[22] ^{15}N VACP/MAS NMR: $\delta = -336.0$ (NCO), −323.1 (NCO), −173.4 ppm (CN); ^{29}Si VACP/MAS NMR: $\delta = -140.6$ ppm; elemental analysis calcd (%) for $C_{13}H_{11}N_3O_4Si$ (301.3): C 51.82, H 3.68, N 13.94; found: C 51.9, H 3.9, N 13.6.

[4-{(2-Hydroxyphenyl)imino}pent-2-en-2-olato(2−)-*N*,*O*,*O′*]di(thiocyanato-*N*)silicon(IV) (9): Tetra(thiocyanato-*N*)silane (664 mg, 2.55 mmol) was added at 20 °C to a stirred suspension of 4-[(2-hydroxyphenyl)amino]pent-3-en-2-one (488 mg, 2.55 mmol) in acetonitrile (20 mL). The reaction mixture was stirred at 20 °C for 30 min, the remaining solid was filtered off and discarded, the filtrate was stored at −20 °C for three days, and the resulting precipitate was isolated by filtration, washed with *n*-pentane (10 mL), and dried in vacuo (0.01 Torr, 20 °C, 2 h) to give **9** in 51 % yield (437 mg, 1.31 mmol) as a yellow crystalline solid; m.p. 93 °C (decomp). ^{1}H NMR (CD_2Cl_2): $\delta = 2.28$ (d, ^4J(H,H) = 0.5 Hz, 3H; CH_3), 2.65 (s, 3H; CH_3), 5.94 (q, ^4J(H,H) = 0.5 Hz, 1H; C=CH−C), 7.01–7.30 ppm (m, 4H; C_6H_4); ^{13}C NMR (CD_2Cl_2): $\delta = 24.0$ (CH_3), 25.5 (CH_3), 107.5 (C=*C*H−C), 116.0, 120.7, 122.2, 129.6, 131.3, and 149.2 (C_6H_4), 138.2 (NCS), 170.4 (CO or CN), 171.6 ppm (CO or CN); ^{29}Si NMR (CD_2Cl_2): $\delta = -146.1$ ppm; ^{13}C VACP/MAS NMR: $\delta = 21.7$ (CH_3), 25.4 (CH_3), 109.6 (C=*C*H−C), 113.2, 120.3, 122.4, 128.8, 129.8, and 147.4 (C_6H_4), 135.1 (NCS), 140.8 (NCS), 169.0 (CO or CN), 173.0 ppm (CO or CN); ^{15}N VACP/MAS NMR: $\delta = -255.2$ (NCS), −239.4 (NCS), −180.9 ppm (CN); ^{29}Si VACP/MAS NMR: $\delta = -146.4$ ppm; elemental analysis calcd (%) for $C_{13}H_{11}N_3O_2S_2Si$ (333.46): C 46.82, H 3.32, N 12.60, S 19.23; found: C 46.8, H 3.6, N 13.0, S 19.0.

Bis[4-{(2-hydroxyphenyl)imino}pent-2-en-2-olato(2−)-*N,O,O′*]silicon(IV)-hemiacetonitrile (10·1/2 CH_3CN): Tetra(cyanato-*N*)silane (250 mg, 1.27 mmol) was added at 20 °C to a stirred suspension of 4-[(2-hydroxyphenyl)amino]pent-3-en-2-one (488 mg, 2.55 mmol) in acetonitrile (20 mL). The mixture was stirred at 20 °C for 5 min and then kept undisturbed at −20 °C for three days, and the resulting precipitate was isolated by filtration, washed with *n*-pentane (10 mL), and dried in vacuo (0.01 Torr, 20 °C, 2 h) to give **10**·1/2 CH_3CN in 71 % yield (387 mg, 906 μmol) as a yellow crystalline solid; m.p. 259 °C (decomp). ^{1}H NMR ($C_2D_2Cl_4$): δ = 1.71 (s, 6H; CH_3), 1.91 (s, 1.5H; CH_3CN), 2.38 (s, 6H; CH_3), 5.33 (s, 2H; C=CH−C), 6.50–7.10 ppm (m, 8H; C_6H_4); ^{1}H NMR ([D_6]DMSO): δ = 1.71 (s, 6H; CH_3), 2.06 (s, 1.5H; CH_3CN), 2.48 (s, 6H; CH_3), 5.54 (s, 2H; C=CH−C), 6.47–7.37 ppm (m, 8H; C_6H_4); ^{13}C NMR ($C_2D_2Cl_4$): δ = 2.3 (*C*H_3CN), 24.2 (CH_3), 24.6 (CH_3), 102.6 (C=*C*H−C), 114.9, 117.1, 120.8, 127.5, 132.7, and 154.8 (C_6H_4), 168.6 (CO or CN), 177.2 ppm (CO or CN); ^{13}C NMR ([D_6]DMSO): δ = 1.13 (*C*H_3CN), 23.6 (CH_3), 23.9 (CH_3), 102.0 (C=*C*H−C), 113.8, 116.6, 120.7, 127.0, 131.8, and 153.9 (C_6H_4), 168.7 (CO or CN), 175.9 ppm (CO or CN); ^{29}Si NMR ($C_2D_2Cl_4$): δ = −163.7 ppm; ^{29}Si NMR ([D_6]DMSO): δ = −164.7 ppm; ^{13}C VACP/MAS NMR: δ = 23.1 (CH_3), 23.7 (CH_3), 26.1 (CH_3), 27.0 (CH_3), 103.4 (C=*C*H−C), 104.8 (C=*C*H−C), 113.5–133.5, 154.5, and 155.5 (C_6H_4), 168.6 (CO or CN), 170.8 (CO or CN), 173.6 (CO or CN), 176.7 ppm (CO or CN); ^{15}N VACP/MAS NMR: δ = −186.5 (CN), −182.2 (CN), −128.2 ppm (CH_3CN); ^{29}Si VACP/MAS NMR: δ = −165.6 ppm; elemental analysis calcd (%) for $C_{23}H_{23.5}N_{2.5}O_4Si$ (427.04): C 64.69, H 5.55, N 8.20; found: C 64.7, H 5.7, N 8.3.

Crystal structure analyses: Suitable single crystals of **8**, **9**, and **10**·1/2 CH_3CN were isolated directly from the respective reaction mixtures. The crystals were mounted in inert oil (perfluoroalkyl ether, ABCR) on a glass fiber and then transferred to the cold nitrogen gas stream of the diffractometer (Stoe IPDS diffractometer; graphite-monochromated $Mo_{K\alpha}$ radiation, λ = 0.71073 Å). All structures were solved by direct methods.[23] The non-hydrogen atoms were refined anisotropically.[24] A riding model was employed in the refinement of the C*H* hydrogen atoms. CCDC-266233 (**8**), CCDC-266234 (**9**), and CCDC-266235 (**10**·1/2 CH_3CN) 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.

Computational studies: RI-MP2[15] geometry optimizations of **9**, **9′**, **10**, and **10′** were carried out at the TZP level (with a TZVP auxiliary basis for the fit of the charge density)[16,17] using the TURBOMOLE program system.[18] The optimized structures were characterized as minima on the potential energy surfaces by harmonic vibrational frequency analysis. The ^{29}Si NMR chemical shift calculations for the optimized structures were carried out at the HF/TZP level using the module mpshift implemented in TURBOMOLE. Computed absolute shieldings (σ) were converted to relative shifts (δ) using the shielding of TMS (399.4 ppm), computed at the same theoretical level. The reported energy differences include the MP2 energies and the zero-point vibrational energies obtained by HF calculations.

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